Supporting Information

Lewis Base-Catalyzed Amino-Acylation of Arylallenes via C−N Bond Cleavage: Reaction Development and Mechanistic Studies

Zheng-Bing Zhang,[a,c] Yusheng Yang,[b] Zhi-Xiang Yu*,[b] and Ji-Bao Xia*,[a,c]

[a] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Center for Excellence in Molecular Synthesis, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), University of Chinese Academy of Sciences, Chinese Academy of Sciences, Lanzhou 730000, China

[b] Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

[c] University of Chinese Academy of Sciences, Beijing 100049, China

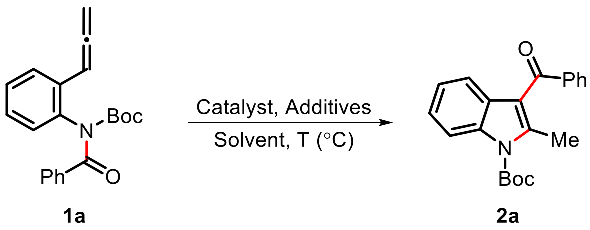
*Corresponding Author: yuzx@pku.edu.cn, jibaoxia@licp.cas.cn

1. General Information

All of the Lewis base-catalyzed amino-acylation of allenes were carried out in oven-dried Schlenk tube in dried solvent. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 ºC or 30-60 ºC). The High Resolution MS analyses were performed on Thermo Fisher Scientific LTQ FT Ultra with DART Positive Mode or Agilent 6530 Accurate-Mass Q-TOF LC/MS with ESI mode. NMR spectra were recorded on a 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, using tetramethylsilane as an internal reference and $CDCl_3$ as solvent. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to tetramethylsilane (δ 0). Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); m (multiplet); br (broad). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz. Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl_3$ (δ 77.0). Materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas, or other commercial suppliers and used as received unless otherwise noted.

2. Optimization of the Reaction Conditions

Table S1. Condition screening for intramolecular amino-acylation of allenes[a]

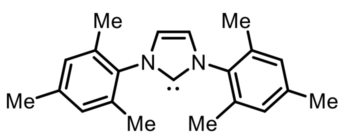


Entry	Catalyst (x mol %)	Solvent (mmol/mL)	*T* (°C)	Yield (%)[b]
1	(IMes)Ni(allyl)Cl (10)	THF (0.2)	80	trace
2	(IPr)Ni(allyl)Cl (10)	THF (0.2)	80	0
3	IPrCuCl (10)	THF (0.2)	80	0
4	$Pd_2(dba)_3$ (10) / I^{t}Bu (20)	THF (0.2)	80	0
5	$Rh(cod)_2SO_3CF_3$ (10) / I^{t}Bu (20)	THF (0.2)	80	12
6	$Rh(cod)_2SO_3CF_3$ (10) / IAd (20)	THF (0.2)	80	trace
7	$Rh(cod)_2SO_3CF_3$ (10) / IMes (20)	THF (0.2)	80	4
8	I^{t}Bu (20)	THF (0.2)	80	31
9	I^{t}Bu (20)	1,4-dioxane (0.2)	80	33
10	I^{t}Bu (20)	1,4-dioxane (0.2)	100	35
11[c]	NHC-Cat. (20)	1,4-dioxane (0.2)	100	10
12	PPh_3 (20)	1,4-dioxane (0.2)	100	trace
13	PCy_3 (20)	1,4-dioxane (0.2)	100	38
14	PBu_3 (20)	1,4-dioxane (0.2)	100	trace
15	$P(4\text{-}MeOC_6H_4)_3$ (20)	1,4-dioxane (0.2)	100	46
16	$P(3\text{-}MeOC_6H_4)_3$ (20)	1,4-dioxane (0.2)	100	7
17	$P[2,4,6\text{-}(MeO)_3C_6H_2]_3$ (20)	1,4-dioxane (0.2)	100	3
18	$P(NMe_2)_3$ (20)	1,4-dioxane (0.2)	100	trace
19	DMAP (20)	1,4-dioxane (0.2)	100	51
20	PPy (20)	1,4-dioxane (0.2)	100	48
21	4-MeOPy (20)	1,4-dioxane (0.2)	100	20
22	Et_3N (20)	1,4-dioxane (0.2)	100	trace
23	DMAP (20)	MeCN (0.2)	100	45

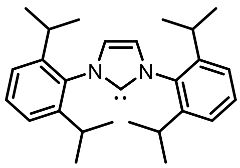
Continuing the Table S1

24	DMAP (20)	THF (0.2)	100	46
25	DMAP (20)	toluene (0.2)	100	45
26	DMAP (20)	MeOH (0.2)	100	0
27	DMAP (20)	DMF (0.2)	100	0
28[d]	DMAP (20)	1,4-dioxane (0.1)	100	37
29[d]	DMAP (20)	MeCN (0.1)	100	41
30[d]	DMAP (20)	THF (0.1)	100	61
31[d]	DMAP (20)	THF (0.05)	100	66 (63)[e]
32[d]	DMAP (10)	THF (0.05)	100	50
33[d,f]	-	THF (0.05)	100	0

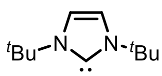
[a]All reactions were conducted with **1a** (0.1 mmol) for 20 h. [b]The yield was determined by GC with *n*-dodecane as an internal standard. [c]With $Na(OAc)_2$ (30 mol %). [d]48 h. [e]Isolated yield in the parenthesis. [f]Without catalyst.



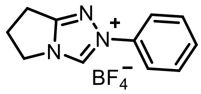
IMes



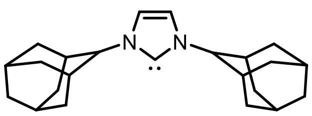
IPr



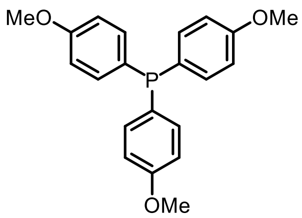
I^{t}Bu



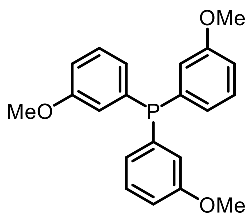
NHC-Cat.



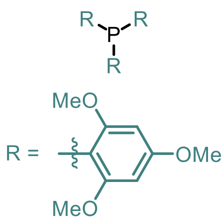
IAd



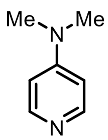
P(4-MeO-C_6H_4)$_3$



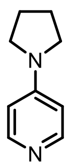
P(3-MeO-C_6H_4)$_3$



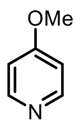
P[2,4,6-$(MeO)_3C_6H_2$]$_3$



DMAP

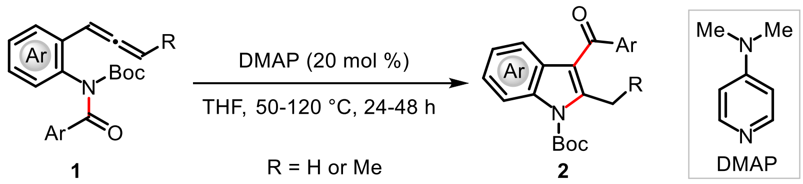


PPy

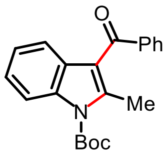


4-MeOPy

3. General Procedure and Characterization Data

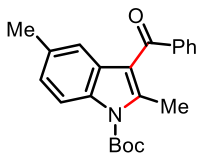


General Procedure: To a 25 mL oven-dried Schlenk tube was added substrate **1** (0.10 mmol), DMAP (0.02 mmol, 2.4 mg) and a stir bar. The Schlenk tube was transferred into a N_2-filled glovebox and freshly distilled anhydrous THF was added (2 mL). The tube was then removed out from the glovebox and stirred at 50 ~ 120 ℃ for 24 ~ 48 hours. The resulting mixture was concentrated under vacuum and purified by flash column chromatography on silica gel to give the desired product **2**.



2a

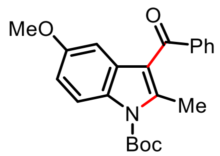
***N*-Boc-3-benzoyl-2-methylindole (2a)**. Synthesized according to the general procedure with substrate **1a** (0.10 mmol, 33.5 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give **2a** as a colorless oil (21.0 mg, 63% yield). With **1a** (1.0 mmol, 335.4 mg) as substrate, according to the general procedure (20 mol % DMAP, 20 mL THF, 100 ℃, 48 h), **2a** was obtained in 52% yield (174.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.46 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 7.6, 7.6 Hz, 1H), 2.63 (s, 3H), 1.72 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 150.2, 142.3, 139.5, 135.4, 132.7, 129.5, 128.5, 127.9, 124.1, 123.3, 120.4, 119.4, 115.2, 85.0, 28.2, 16.0. HRMS (ESI) Calcd for $[C_{21}H_{22}NO_3]^+$ $[M+H]^+$ 336.1594, Found 336.1602.



2b

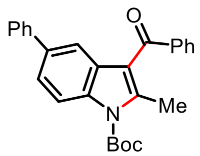
***N*-Boc-3-benzoyl-2,5-dimethylindole (2b).** Synthesized according to the general procedure with substrate **1b** (0.10 mmol, 34.9 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 40 : 1) to give **2b** as a colorless oil (20.5 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.46 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.18 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 2.58 (s, 3H), 2.34 (s, 3H), 1.70 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 150.3, 142.0, 139.7, 133.8, 132.9, 132.7, 129.6, 128.5, 128.2, 125.5, 120.3, 119.3, 114.9, 84.8, 28.2, 21.3, 16.1. HRMS (ESI) Calcd for

$[C_{22}H_{24}NO_3]^+$ $[M+H]^+$ 350.1751, Found 350.1744.



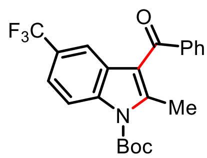
2c

***N*-Boc-3-benzoyl-5-methoxyl-2-methylindole (2c).** Synthesized according to the general procedure with substrate **1c** (0.10 mmol, 36.5 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give **2c** as a colorless oil (21.2 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 9.2 Hz, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 6.8 Hz, 1H), 7.47 (dd, J = 7.6, 7.6 Hz, 2H), 6.90 – 6.87 (m, 2H), 3.70 (s, 3H), 2.58 (s, 3H), 1.70 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 156.2, 150.1, 142.9, 139.6, 132.7, 130.1, 129.5, 128.8, 128.5, 119.2, 116.0, 113.1, 102.7, 84.9, 55.4, 28.2, 16.3. HRMS (ESI) Calcd for $[C_{22}H_{24}NO_4]^+$ $[M+H]^+$ 366.1700, Found 366.1709.



2d

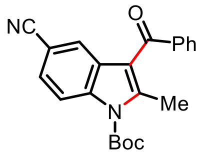
***N*-Boc-3-benzoyl-5-phenyl-2-methylindole (2d).** Synthesized according to the general procedure with substrate **1d** (0.10 mmol, 41.1 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **2d** as a colorless oil (30.4 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 7.6 Hz, 2H), 7.61 – 7.45 (m, 7H), 7.37 (dd, J = 7.6, 7.6 Hz, 2H), 7.28 (dd, J = 7.2, 7.2 Hz, 1H), 2.64 (s, 3H), 1.73 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 150.2, 142.8, 141.3, 139.6, 136.6, 135.0, 132.9, 129.6, 128.7, 128.5, 127.3, 126.9, 123.7, 119.6, 118.8, 115.5, 85.1, 28.2, 16.2. HRMS (ESI) Calcd for $[C_{27}H_{26}NO_3]^+$ $[M+H]^+$ 412.1907, Found 412.1911.



2e

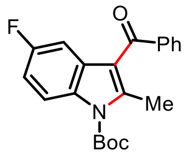
***N*-Boc-3-benzoyl-5-trifluoromethyl-2-methylindole (2e).** Synthesized according to the general procedure with substrate **1e** (0.10 mmol, 40.3 mg) at 70 ℃ for 36 h. Purified by flash column chromatography on silica gel (PE : EA = 40 : 1) to give **2e** as a colorless oil (34.8 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.70 (s, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.54 – 7.47 (m, 3H), 2.61 (s, 3H), 1.72 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 149.8, 143.6, 139.2, 137.1, 133.1, 129.5, 128.6, 127.8, 125.8 (q, J = 32.3 Hz), 124.5 (q, J =

270.0 Hz), 121.0 (q, J = 3.4 Hz), 119.4, 117.8 (q, J = 3.9 Hz), 115.6, 85.9, 28.2, 16.2. HRMS (ESI) Calcd for $[C_{22}H_{21}F_3NO_3]^+$ $[M+H]^+$ 404.1468, Found 404.1469.



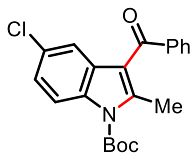
2f

***N*-Boc-3-benzoyl-5-cyano-2-methylindole (2f).** Synthesized according to the general procedure with substrate **1f** (0.10 mmol, 36.0 mg) at 50 ℃ for 24 h. Purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to give **2f** as a colorless oil (28.5 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.70 (s, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.54 – 7.48 (m, 3H), 2.63 (s, 3H), 1.73 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 149.4, 144.2, 138.9, 137.4, 133.3, 129.4, 128.7, 128.0, 127.3, 125.1, 119.4, 118.9, 116.1, 106.9, 86.3 28.1, 16.1. HRMS (ESI) Calcd for $[C_{22}H_{20}N_2O_3Na]^+$ $[M+Na]^+$ 383.1366, Found 383.1376.



2g

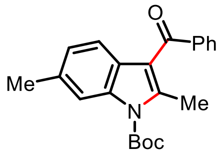
***N*-Boc-3-benzoyl-5-fluoro-2-methylindole (2g).** Synthesized according to the general procedure with substrate **1g** (0.10 mmol, 35.4 mg) at 60 ℃ for 36 h. Purified by flash column chromatography on silica gel (PE : EA = 40 : 1) to give **2g** as a colorless oil (32.4 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.07 (m, 1H), 7.81 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 7.2 Hz, 1H), 7.47 (dd, J = 7.2, 6.8 Hz, 2H), 7.00 (dd, J = 10.0, 9.2 Hz, 2H), 2.61 (s, 3H), 1.71 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 159.4 (d, J = 238.4 Hz), 149.9, 143.8, 139.3, 132.9, 131.8, 129.4, 129.9 (d, J = 10.0 Hz), 128.6, 119.1 (d, J = 3.9 Hz), 116.3 (d, J = 9.0 Hz), 111.9 (d, J = 24.8 Hz), 106.0 (d, J = 24.9), 85.3, 28.1, 16.2. HRMS (ESI) Calcd for $[C_{21}H_{20}FNO_3Na]^+$ $[M+Na]^+$ 376.1319, Found 376.1316.



2h

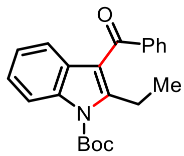
***N*-Boc-3-benzoyl-5-chloro-2-methylindole (2h).** Synthesized according to the general procedure with substrate **1h** (0.10 mmol, 37.0 mg) at 70 ℃ for 24 h. Purified by flash column chromatography on silica gel (PE : EA = 40 : 1) to give **2h** as a colorless oil (27.8 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 7.2 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.48 (dd, J = 7.6, 7.6 Hz, 2H), 7.35 (d, J = 2.0 Hz, 1H), 7.23 (dd, J = 9.2, 2.0 Hz, 1H), 2.59 (s, 3H), 1.71 (s, 9H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 192.9, 149.8, 143.3, 139.2, 133.9, 133.0, 129.5, 129.1, 128.6, 124.4, 119.9, 118.8, 116.3, 85.5, 28.1, 16.2. HRMS (ESI) Calcd for $[C_{21}H_{21}ClNO_3]^+$ $[M+H]^+$ 370.1204, Found 370.1210.



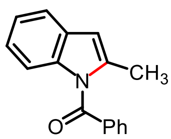
2i

***N*-Boc-3-benzoyl-2,6-methylindole (2i).** Synthesized according to the general procedure with substrate **1i** (0.10 mmol, 37.0 mg) at 120 ℃ for 36 h. Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **2i** as a colorless oil (16.3 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 6.8 Hz, 1H), 7.45 (dd, *J* = 6.8, 6.8 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 2.62 (s, 3H), 2.46 (s, 3H), 1.71 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 150.3, 141.6, 139.6, 135.9, 134.1, 132.7, 129.5, 128.4, 125.7, 124.7, 120.0, 119.4, 115.4, 84.8, 28.2, 21.9, 16.0. HRMS (ESI) Calcd for $[C_{22}H_{24}NO_3]^+$ $[M+H]^+$ 350.1751, Found 350.1748.



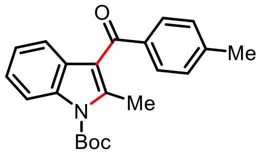
2k

***N*-Boc-3-benzoyl-2-ethynylindole (2k).** Synthesized according to the general procedure with substrate **1k** (0.10 mmol, 34.9 mg), DMAP (0.03 mmol, 3.7 mg) in THF (1 mL) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **2k** as a colorless oil (16.9 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.45 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.12 – 7.10 (m, 2H), 3.18 (q, *J* = 7.2 Hz, 2H), 1.73 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 150.0, 147.9, 139.6, 135.6, 132.7, 129.5, 128.4, 127.9, 124.1, 123.1, 120.4, 118.9, 115.4, 85.0, 28.1, 21.2, 15.0. HRMS (ESI) Calcd for $[C_{22}H_{24}NO_3]^+$ $[M+H]^+$ 350.1751, Found 350.1759.



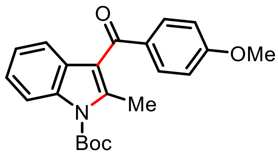
2l

***N*-Benzoyl-2-methylindole (2l).** Synthesized according to the general procedure with *N*-benzoyl-2-allenylaniline **1l** (0.10 mmol, 23.5 mg), DMAP (0.02 mmol, 2.4 mg) in THF (2 mL) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **2l** as a white solid(20.1 mg, 86% yield). The ^{1}H NMR spectra is the same as the reported data.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.16 – 7.12 (m, 1H), 7.04 – 6.98 (m, 2H), 6.43 (s, 1H), 2.41 (s, 3H).



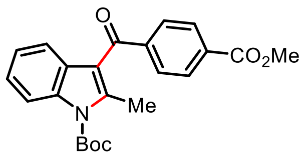
2m

***N*-Boc-3-(4-(methyl)benzoyl)-2-methylindole (2m).** Synthesized according to the general procedure with substrate **1m** (0.10 mmol, 34.9 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **2m** as a colorless oil (22.5 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.24 (m, 3H), 7.16 (dd, *J* = 7.6, 7.6 Hz, 1H), 2.63 (s, 3H), 2.43 (s, 3H), 1.71 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 150.2, 143.6, 141.7, 136.8, 135.4, 129.8, 129.1, 128.0, 124.0, 123.2, 120.3, 119.6, 115.2, 84.9, 28.2, 21.7, 16.0. HRMS (ESI) Calcd for $[C_{22}H_{23}NO_3Na]^+$ $[M+Na]^+$ 372.1570, Found 372.1569.



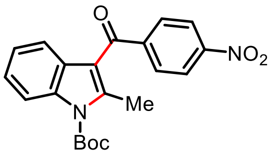
2n

***N*-Boc-3-(4-methoxylbenzoyl)-2-methylindole (2n).** Synthesized according to the general procedure with substrate **1n** (0.10 mmol, 36.5 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to give **2n** as a colorless oil (26.4 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 9.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.17 – 7.13 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 2.63 (s, 3H), 1.71 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 163.5, 150.3, 141.1, 135.5, 132.2, 132.0, 128.2, 124.0, 123.2, 120.3, 119.8, 115.2, 113.7, 84.8, 55.5, 28.2, 15.9. HRMS (ESI) Calcd for $[C_{22}H_{24}NO_4]^+$ $[M+H]^+$ 366.1700, Found 366.1707.



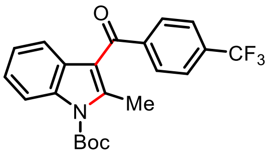
2o

***N*-Boc-3-(4-(methoxycarbonyl)benzoyl)-2-methylindole (2o).** Synthesized according to the general procedure with substrate **1o** (0.10 mmol, 39.3 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to give **2o** as a colorless oil (27.0 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.12 (m, 3H), 7.87 (d, *J* = 6.8 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.15 (dd, *J* = 7.2, 8.0 Hz, 1H), 3.96 (s, 3H), 2.64 (s, 3H), 1.72 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 166.3, 150.0, 143.3, 143.2, 135.4, 133.4, 129.7, 129.3, 127.6, 124.3, 123.4, 120.3, 118.9, 115.2, 85.2, 52.4, 28.2, 16.0. HRMS (ESI) Calcd for $[C_{23}H_{23}NO_5Na]^+$ $[M+Na]^+$ 416.1468, Found 416.1458.



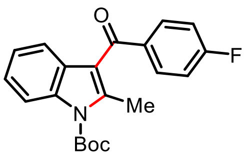
2p

***N*-Boc-3-(4-(nitro)benzoyl)-2-methylindole (2p).** Synthesized according to the general procedure with substrate **1p** (0.10 mmol, 38.0 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **2p** as a colorless oil (22.6 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.31 (dd, *J* = 8.0, 8.8 Hz, 1H), 7.22 – 7.15 (m, 2H), 2.68 (s, 3H), 1.73 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 150.0, 144.7, 143.9, 135.4, 130.3, 127.3, 124.5, 123.8, 123.6, 120.1, 118.4, 115.4, 85.5, 28.1, 16.0. HRMS (ESI) Calcd for $[C_{21}H_{20}N_2O_5Na]^+$ $[M+Na]^+$ 403.1264, Found 403.1264.



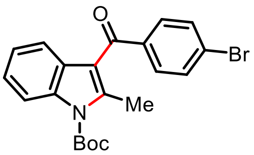
2q

***N*-Boc-3-(4-(trifluoromethyl)benzoyl)-2-methylindole (2q).** Synthesized according to the general procedure with substrate **1q** (0.10 mmol, 40.3 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **2q** as a colorless oil (17.7 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.19 – 7.17 (m, 1H), 2.65 (s, 3H), 1.72 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 150.1, 143.3, 142.7, 135.5, 134.0 (q, *J* = 32.6 Hz), 129.7, 127.6, 125.6 (q, *J* = 3.8 Hz), 124.4, 123.9 (q, *J* = 231.1 Hz), 123.6, 120.2, 118.8, 115.3, 85.3, 28.2, 16.0. HRMS (ESI) Calcd for $[C_{22}H_{21}F_3NO_3]^+$ $[M+H]^+$ 404.1468, Found 404.1476.



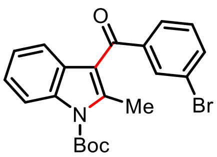
2r

***N*-Boc-3-(4-(fluoro)benzoyl)-2-methylindole (2r).** Synthesized according to the general procedure with substrate **1r** (0.10 mmol, 35.3 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 40 : 1) to give **2r** as a colorless oil (24.7 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.89 – 7.87 (m, 2H), 7.29 – 7.26 (m, 2H), 7.18 – 7.12 (m, 3H), 2.64 (s, 3H), 1.72 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 165.6 (d, *J* = 252.7 Hz), 150.1, 142.2, 135.8, 135.4, 132.2 (d, *J* = 9.1 Hz), 127.8, 124.2, 123.3, 120.2, 119.2, 115.6 (d, *J* = 21.8 Hz), 115.3, 85.1, 28.2, 15.9. HRMS (ESI) Calcd for $[C_{21}H_{21}FNO_3]^+$ $[M+H]^+$ 354.1500, Found 354.1508.



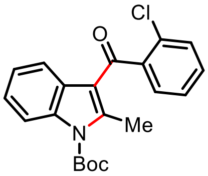
2s

***N*-Boc-3-(4-(bromo)benzoyl)-2-methylindole (2s).** Synthesized according to the general procedure with substrate **1s** (0.10 mmol, 41.4 mg), DMAP (0.02 mmol, 2.4 mg) in THF (2 mL) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 40 : 1) to give **2s** as a colorless oil (19.2 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.17 (dd, *J* = 7.6, 7.2 Hz, 1H), 2.64 (s, 3H), 1.72 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 150.1, 142.6, 138.3, 135.4, 131.8, 131.1, 127.8, 127.7, 124.3, 123.4, 120.2, 118.9, 115.3, 85.2, 28.2, 16.0. HRMS (ESI) Calcd for $[C_{21}H_{20}BrNO_3Na]^+$ $[M+Na]^+$ 436.0519, Found 436.0517.



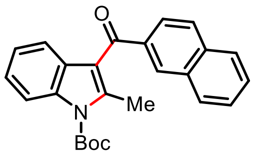
2t

***N*-Boc-3-(3-(bromo)benzoyl)-2-methylindole (2t).** Synthesized according to the general procedure with substrate **1t** (0.10 mmol, 41.4 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 40 : 1) to give **2t** as a colorless oil (23.5 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.72 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.35 – 7.26 (m, 3H), 7.18 (dd, *J* = 7.6, 7.6 Hz, 1H), 2.64 (s, 3H), 1.72 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 150.1, 142.9, 141.4, 135.5, 135.4, 132.3, 130.1, 128.1, 127.6, 124.3, 123.5, 122.7, 120.2, 118.8, 115.3, 85.2, 28.2, 16.0. HRMS (ESI) Calcd for $[C_{21}H_{20}BrNO_3Na]^+$ $[M+Na]^+$ 436.0519, Found 436.0510.



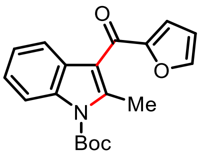
2u

***N*-Boc-3-(2-(chloro)benzoyl)-2-methylindole (2u).** Synthesized according to the general procedure with substrate **1u** (0.10 mmol, 37.0 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **2u** as a colorless oil (12.7 mg, 34% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.43 (m, 3H), 7.38 (d, *J* = 6.4 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.16 (dd, *J* = 7.6, 7.2 Hz, 1H), 2.67 (s, 3H), 1.71 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 149.9, 145.6, 141.1, 135.6, 131.3, 131.2, 130.4, 129.1, 127.3, 127.1, 124.3, 123.8, 120.3, 119.0, 114.9, 85.4, 28.1, 15.3. HRMS (ESI) Calcd for $[C_{21}H_{20}ClNO_3Na]^+$ $[M+Na]^+$ 392.1024, Found 392.1017.



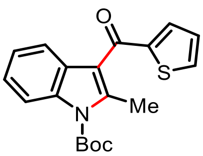
2v

***N*-Boc-3-(2-naphthoyl)-2-methylindole (2v).** Synthesized according to the general procedure with substrate **1v** (0.10 mmol, 38.5 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **2v** as a colorless oil (14.0 mg, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.98 – 7.87 (m, 4H), 7.61 (dd, *J* = 7.6, 6.4 Hz, 1H), 7.53 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.14 (dd, *J* = 8.0, 7.6 Hz, 1H), 2.66 (s, 3H), 1.73 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 150.2, 142.2, 136.8, 135.5, 132.5, 131.5, 129.5, 128.4, 128.3, 128.1, 127.8, 126.7, 125.2, 124.2, 123.4, 122.2, 120.4, 119.6, 115.2, 85.0, 28.2, 16.0. HRMS (ESI) Calcd for $[C_{25}H_{24}NO_3]^+$ $[M+H]^+$ 386.1751, Found 386.1757.



2w

***N*-Boc-3-(furan-2-carbonyl)-2-methylindole (2w).** Synthesized according to the general procedure with substrate **1w** (0.10 mmol, 32.5 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to give **2w** as a colorless oil (26.8 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.21 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.16 (d, *J* = 3.6 Hz, 1H), 6.58 (dd, *J* = 3.6, 1.2 Hz, 1H), 2.69 (s, 3H), 1.71 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 153.5, 150.1, 146.7, 141.6, 135.5, 127.5, 124.2, 123.3, 119.9, 119.6, 119.0, 115.3, 112.3, 85.0, 28.2, 15.8. HRMS (ESI) Calcd for $[C_{19}H_{19}NO_4Na]^+$ $[M+Na]^+$ 348.1206, Found 348.1201.

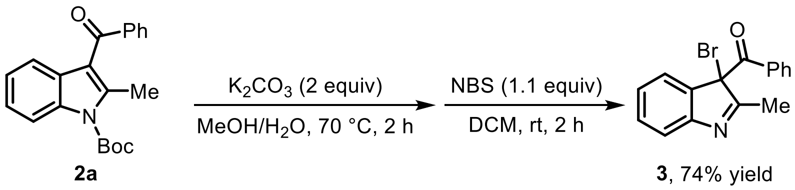


2x

***N*-Boc-3-(thiophene-2-carbonyl)-2-methylindole (2x).** Synthesized according to the general procedure with substrate **1x** (0.10 mmol, 34.1 mg) at 100 ℃ for 48 h. Purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give **2x** as a colorless oil (27.4mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 3.6 Hz, 1H), 7.58 (s, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.28 (dd, *J* = 9.6, 6.8 Hz, 1H), 7.20 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.11 – 7.11 (m, 1H), 2.69 (s, 3H), 1.71 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 150.2, 145.6, 140.8, 135.4, 134.6, 134.2, 128.0, 127.7, 124.2, 123.2, 120.0, 119.7, 115.3, 84.9, 28.2, 16.0. HRMS (ESI) Calcd for $[C_{19}H_{20}NO_3S]^+$ $[M+H]^+$ 342.1158, Found 342.1157.

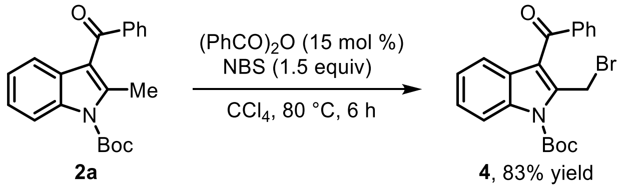
4. Synthetic Applications

Preparation of 3*H*-indole 3



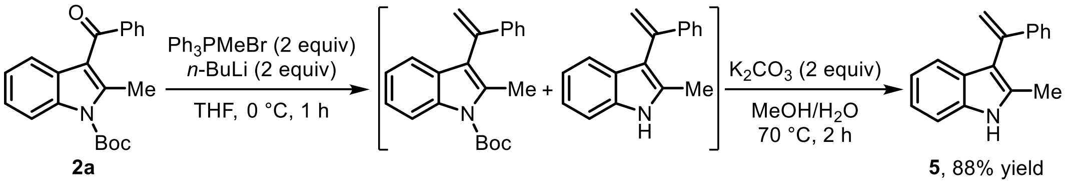
To a 25 mL Schlenk tube was added **2a** (0.1 mmol, 33.5 mg), K_2CO_3 (0.2 mmol, 27.6 mg) and MeOH/H_2O (3/1, 1 mL). The mixture was stirred at 70 ^{o}C for 5 h. The solution was cooled to room temperature and filtered. The filtrate was dried over Na_2SO_4 and concentrated under vacuum to give crude 3-benzoyl-2-methylindole as a solid without further purification. Then, crude 3-benzoyl-2-methylindole was dissolved in DCM (1 mL). To the above solution was added *N*-bromosuccinimide (0.11 mmol, 19.5 mg) and the resulting mixture was stirred at room temperature for 2 h. The mixture was evaporated to get the crude product, which was purified by flash silica gel chromatography with petroleum ether/ethyl acetate (5:1) to give 3*H*-indole **3** as a white solid (23.3 mg, 74% yield). Compound **3** is very difficult to be dissolved in various deuterated solvents. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 6.8 Hz, 3H), 7.57 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.48 – 7.45 (m, 3H), 7.27 – 7.26 (m, 1H), 7.26 – 7.25 (m, 1H), 2.54 (s, 3H). HRMS (ESI) Calcd for $[C_{16}H_{12}BrNONa]^+$ $[M+Na]^+$ 335.9994, Found 335.9986.

Preparation of benzilic bromide 4.



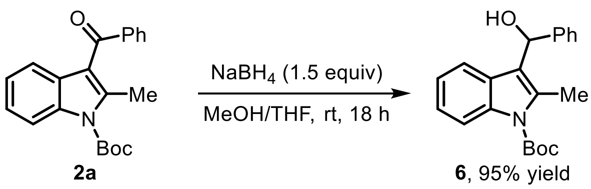
To a solution of **2a** (0.1 mmol, 33.5 mg) in CCl_4 (1 mL) was added *N*-bromosuccinimide (0.1 mmol, 17.8 mg) and benzoyl peroxide (0.01 mmol, 2.3 mg). The mixture was heated at 80 ^{o}C for 3 h. Then, an additional portion of *N*-bromosuccinimide (0.05 mmol, 8.9 mg) and benzoyl peroxide (0.005 mmol, 1.2 mg) was added. The mixture was stirred at 80 ^{o}C for another 3 h. After cooling to room temperature and filtered. The filtrate was evaporated to get the crude product, which was purified by flash silica gel chromatography with petroleum ether/ethyl acetate (50:1) to give benzilic bromide **4** as a colorless oil (43.2 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.61 (dd, *J* = 7.6, 6.8 Hz, 1H), 7.47 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.27 – 7.33 (m, 1H), 7.14 (d, *J* = 3.6 Hz, 2H), 5.12 (s, 2H), 1.76 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 149.3, 138.9, 138.8, 136.2, 133.3, 129.7, 128.6, 127.0, 125.8, 123.6, 121.5, 121.2, 115.6, 86.0, 28.0, 23.8. HRMS (ESI) Calcd for $[C_{21}H_{20}BrNO_3Na]^+$ $[M+Na]^+$ 436.0519, Found 436.0523.

Preparation of 3-alkenyl indole 5



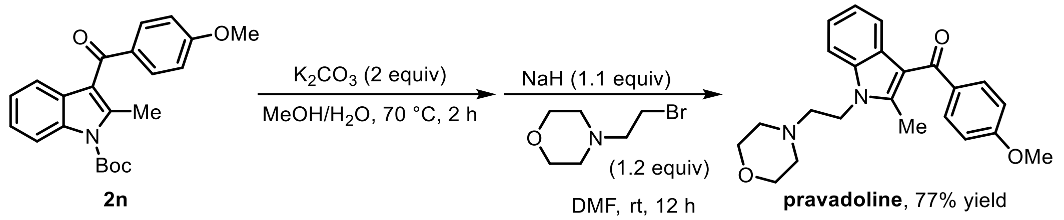
The *n*-BuLi (0.28 mmol, 1.3 M in THF, 215 uL) was added dropwise to a suspension of methyltriphenylphosphoniumbromide (0.28 mmol, 100 mg) in dry THF (4.4 mL) at 0 ºC and the reaction mixture was stirred for 20 min under nitrogen. To the ylide was added **2a** (0.14 mmol, 46.9 mg) and the reaction mixture was stirred under nitrogen at 0 ºC for 1 h. Aqueous HCl solution (1 mol/L) was added and the mixture was extracted with ethyl acetate. The combined organic phases were evaporated to get the crude mixture of olefin products without further purification. Then, to a solution of crude mixture of olefin products was added K_2CO_3 (0.28 mmol, 38.7 mg) in MeOH/H_2O (3:1, 2 mL). The reaction mixture was refluxed at 70 ºC for 2 h. The solution was cooled to room temperature and filtered. The filtrate was dried over Na_2SO_4 and evaporated to get the crude product, which was purified by flash silica gel chromatography with petroleum ether/ethyl acetate (10:1) to give 3-alkenyl **5**.as a colorless oil (28.8 mg, 88% yield). The ^{1}H NMR spectra is the same as the reported data.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.39 (d, *J* = 5.6 Hz, 2H), 7.30 – 7.27 (m, 3H), 7.22 – 7.20 (m, 1H), 7.10 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.98 (dd, *J* = 7.6, 7.2 Hz, 1H), 5.72 (s, 1H), 5.32 (s, 1H), 2.24 (s, 3H).

Preparation of indole 6



To a dry THF/MeOH solution (1 mL/1 mL) of **2a** (0.1 mmol, 33.5 mg) was added $NaBH_4$ (0.15 mmol, 5.7 mg) at 0 ℃. The reaction mixture was allowed warm to room temperature and was stirred for 18 h. the reaction was quenched with water and diluted with ethyl acetate. The organic layer was washed with water and brine, and then dried over dry Na_2SO_4. After concentration under reduced pressure, the residue was purified by flash silica gel chromatography with petroleum ether/ethyl acetate (10:1) to give **6** as a colorless oil (33.6 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.41 (m, 3H), 7.29 (dd, *J* = 7.6, 7.4 Hz, 2H), 7.23 – 7.17 (m, 2H), 7.07 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.16 (s, 1H), 2.62 (s, 3H), 1.67 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 142.8, 136.0, 134.7, 128.2, 127.7, 127.0, 125.8, 123.4, 122.5, 120.0, 119.7, 115.3, 83.9, 68.7, 28.2, 14.2. HRMS (ESI) Calcd for $[C_{21}H_{23}NO_3Na]^+$ $[M+Na]^+$ 360.1570, Found 360.1561.

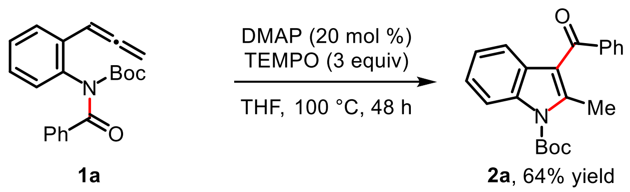
Preparation of pravadoline



To a 25 mL Schlenk tube was added **2n** (0.18 mmol, 67.1 mg), K_2CO_3 (0.54 mmol, 74.6 mg) and $MeOH/H_2O$ (3/1, 2 mL). The mixture was stirred at 70 °C for 5 h. The solution was cooled to room temperature and filtered. The filtrate was dried over Na_2SO_4 and concentrated under vacuum to give crude *N*-H 3-aroylindole without further purification. To an anhydrous DMF (2 mL) solution of the crude *N*-H 3-aroylindole was added NaH (0.2 mmol, 60% in mineral oil, 8.0 mg) slowly at 0 °C. The reaction mixture was stirred continuously at 0 °C for 30 min before 4-(2-bromoethyl)morpholine (0.22 mmol, 42.7 mg) was added. The mixture was stirred at room temperature for 12 h. The reaction mixture was quenched by a dropwise addition of water. The mixture was extracted with ethyl acetate and the combined organic phases were dried over Na_2SO_4 and evaporated to get the crude product, which was purified by flash silica gel chromatography with petroleum ether/ethyl acetate (10:1) to give pravadoline as a white solid (52.1 mg, 77% yield). The ^{1}H NMR spectra is the same as the reported data.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.19 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.07 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.25 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 3.72 – 3.71 (brs, 4H), 2.70 (t, *J* = 6.8 Hz, 2H), 2.60 (s, 3H), 2.53 – 2.51 (brs, 4H).

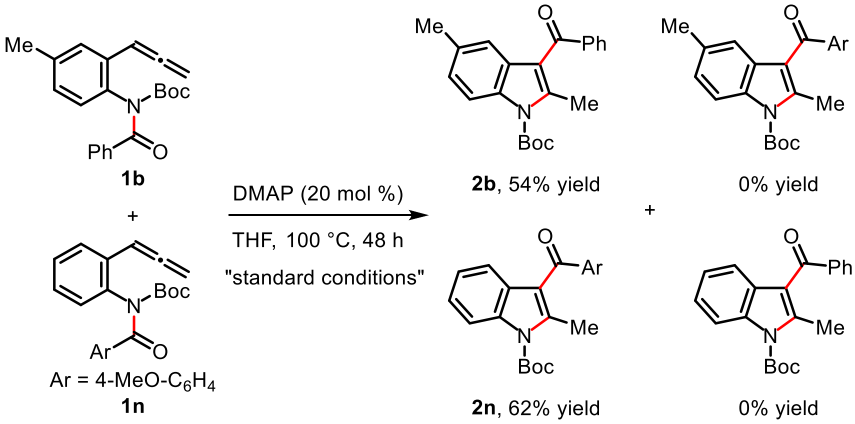
5. Control Experiments and Mechanistic Studies

Radical-trapping experiment



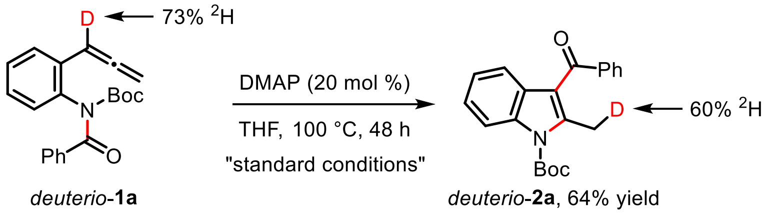
To a 25 mL oven-dried Schlenk tube was added **1a** (0.10 mmol, 33.5 mg), TEMPO (0.3 mmol, 47.9 mg), DMAP (0.02 mmol, 2.4 mg) and a stir bar. The Schlenk tube was transferred into a N_2-filled glovebox and added freshly distilled THF (2 mL). The tube was then removed out from the glovebox and stirred at 100 ℃ for 48 h. The resulting mixture was concentrated under vacuum and purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give the desired product **2a** as a colorless oil (20.9 mg, 64% yield).

Crossover reaction



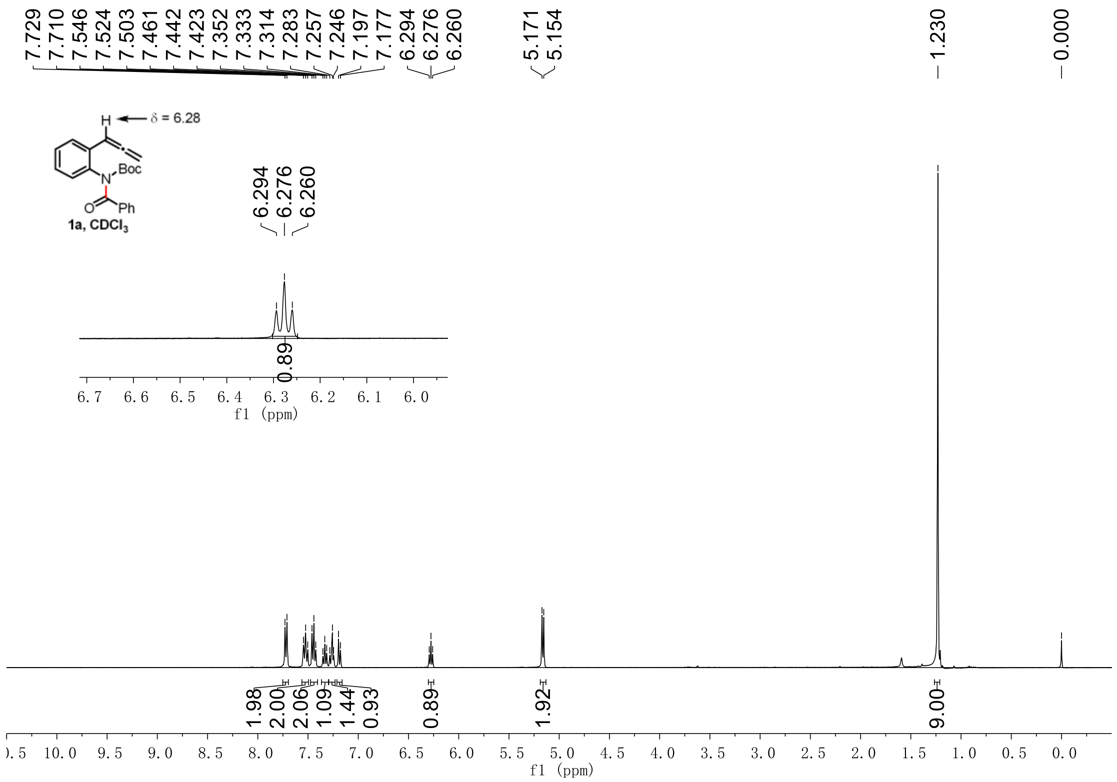
To a 25 mL oven-dried Schlenk tube was added **1b** (0.1 mmol, 34.9 mg) and **1n** (0.1 mmol, 36.5 mg), DMAP (0.02 mmol, 2.4 mg) and a stir bar. The Schlenk tube was transferred into a N_2-filled glovebox and added freshly distilled THF (2 mL). The tube was then removed out from the glovebox and stirred at 100 ℃ for 48 hours. The resulting mixture was concentrated under vacuum and purified by flash column chromatography on silica gel to give **2b** (18.9 mg, 54% yield) and **2n** (22.8 mg, 62% yield) and no corresponding crossover product was observed in this reaction.

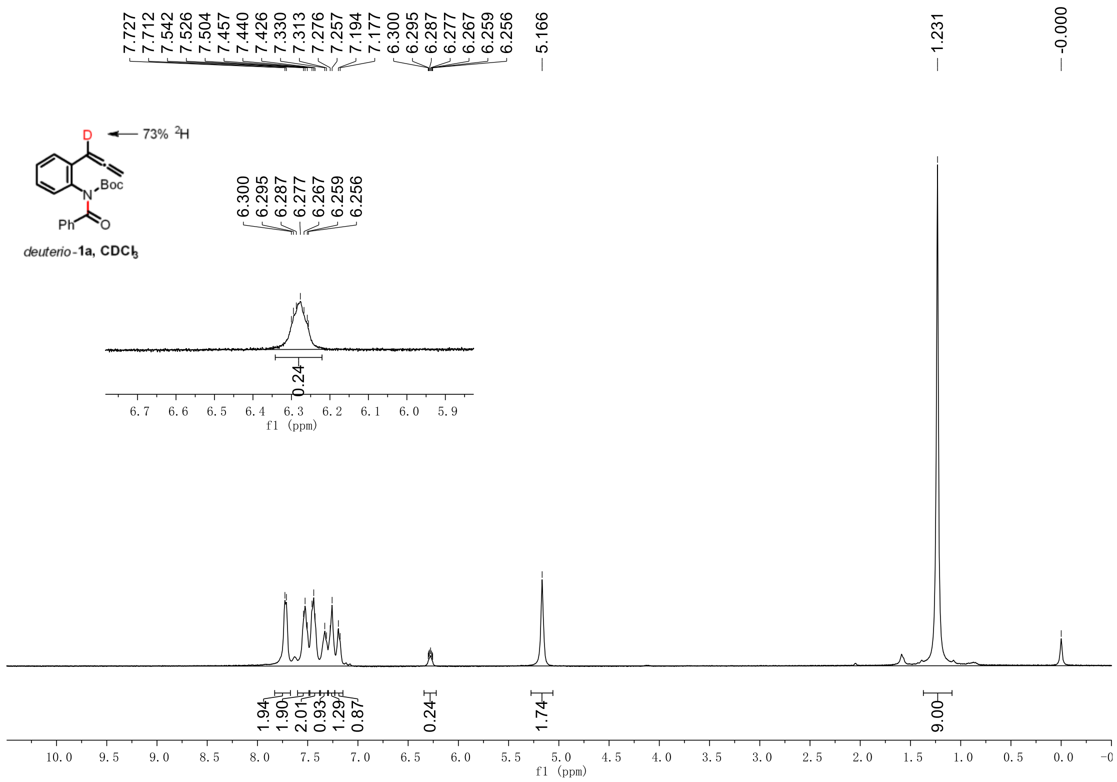
Deuterium labeling experiment



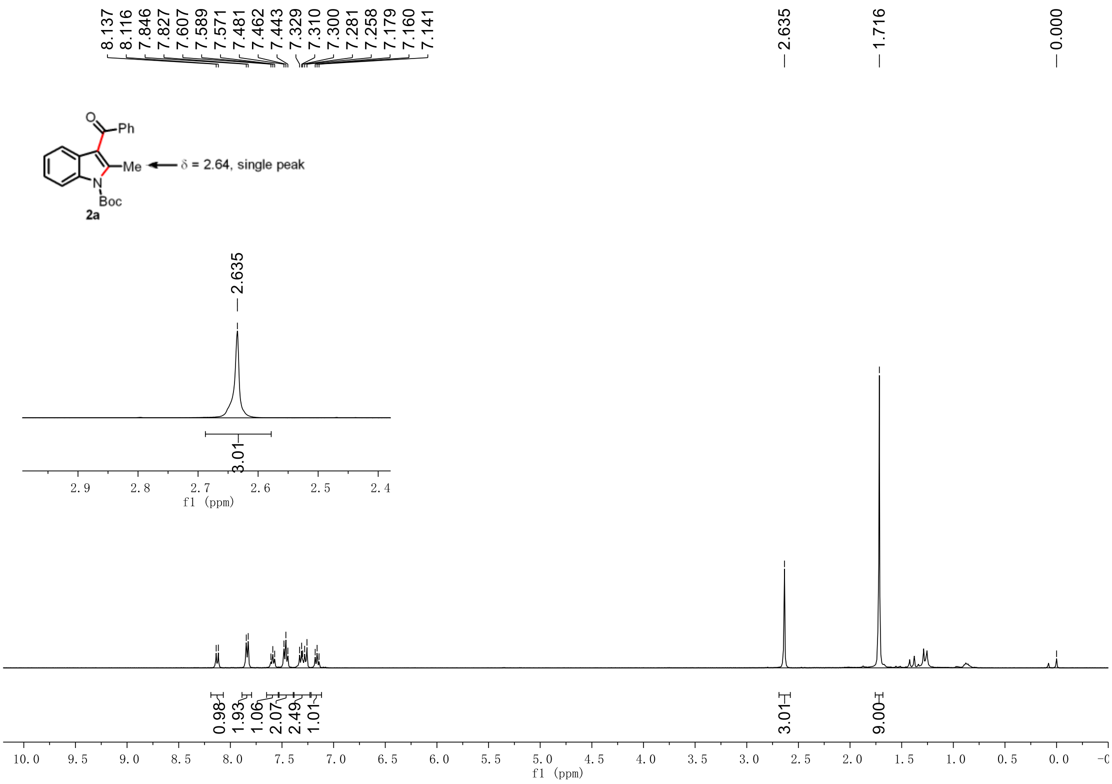
To a 25 mL oven-dried Schlenk tube was added *deuterio*-**1a** (0.10 mmol, 33.6 mg), DMAP (0.02 mmol, 2.4 mg) and a stir bar. The Schlenk tube was transferred into a N_2-filled glovebox and added freshly distilled THF (2 mL). The tube was then removed out from the glovebox and stirred at 100 ℃ for 48 hours. The resulting mixture was concentrated under vacuum and purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give the product *deuterio*-**2a** as a colorless oil (21.6 mg, 64% yield). The ^{1}H NMR spectra of *deuterio*-**1a** was compared with ^{1}H NMR spectra of **1a**, indicating that there was 70% ^{2}H at α-postion of allene in *deuterio*-**1a**. After the reaction, the ^{1}H NMR spectra of *deuterio*-**2a** was compared with ^{1}H NMR spectra of **2a**, a single deuterium atom (70% ^{2}H) was incorporated at the 2-methyl group of the 3-aroylindole product *deuterio*-**2a**.

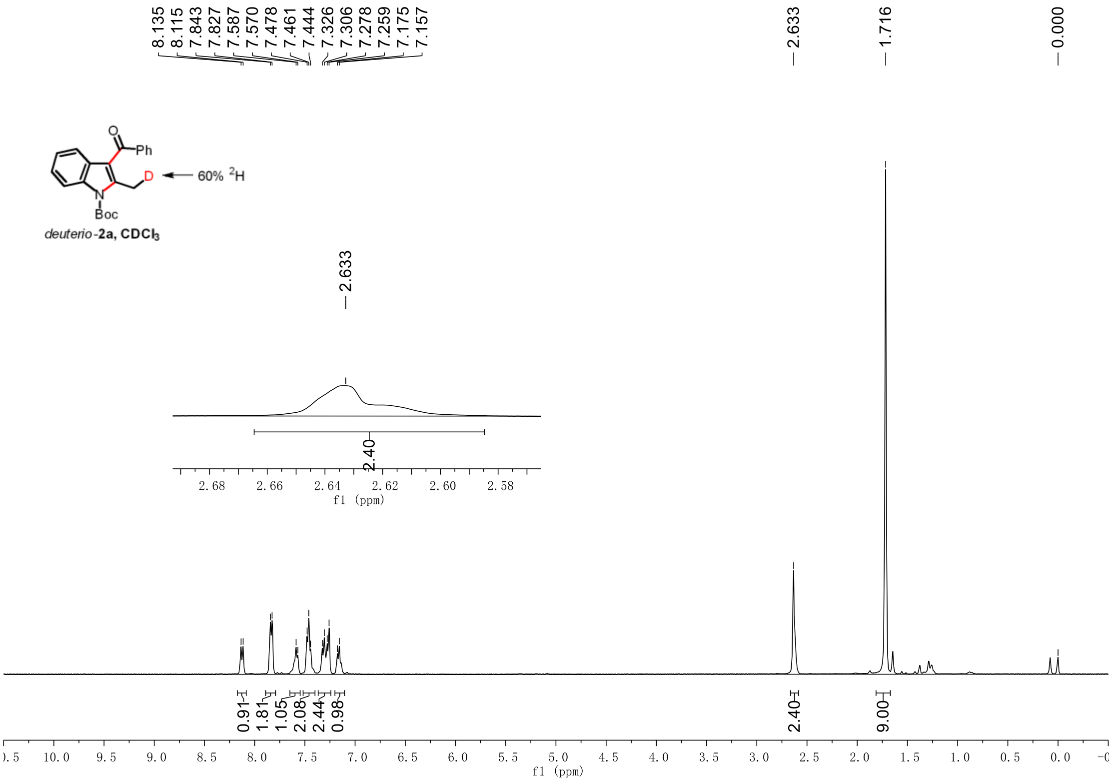
^{1}H NMR spectrum of **1a** and *deuterio*-**1a**



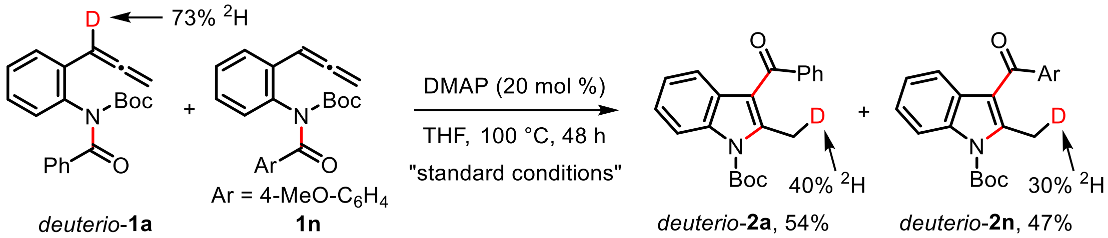


^{1}H NMR spectrum of **2a** and *deuterio*-**2a**



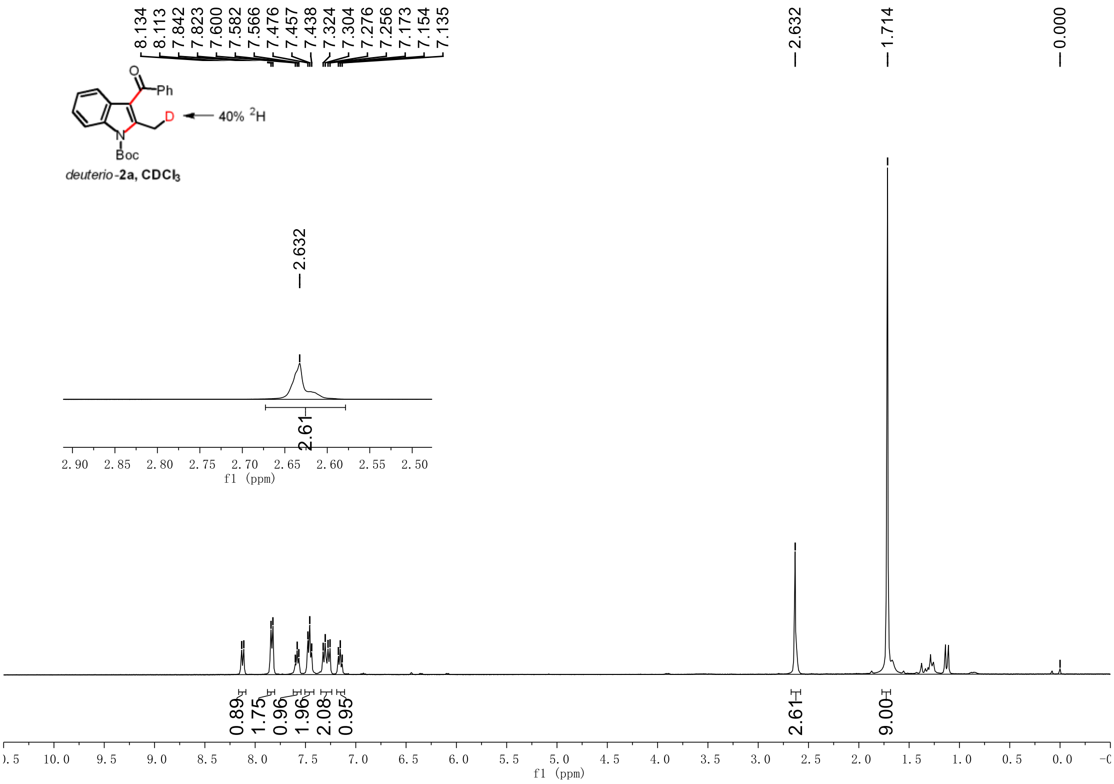


Deuterium scrambling experiment with substrate *deuterio*-1a and 1n

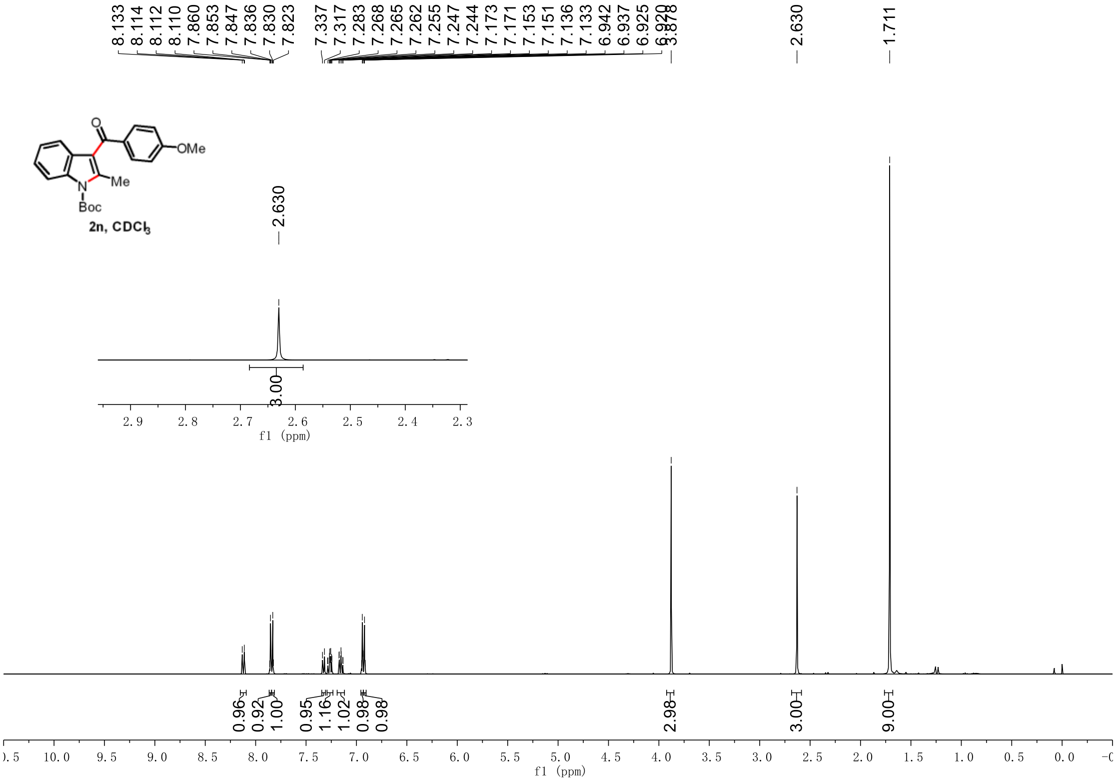


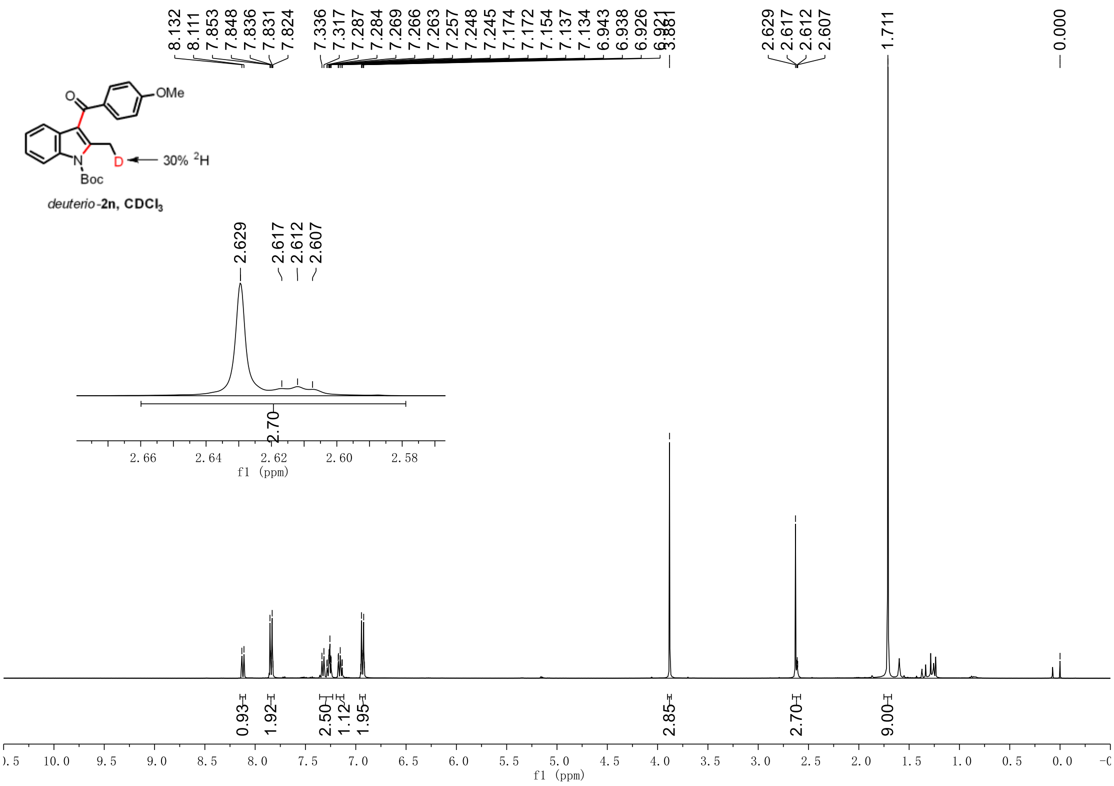
To a 25 mL oven-dried Schlenk tube was added *deuterio*-**1a** (0.10 mmol, 33.6 mg), **1n** (0.10 mmol, 36.5 mg), DMAP (0.02 mmol, 2.4 mg) and a stir bar. The Schlenk tube was transferred into a N_2-filled glovebox and added freshly distilled THF (2 mL). The tube was then removed out from the glovebox and stirred at 100 ℃ for 48 hours. The resulting mixture was concentrated under vacuum and purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give the product *deuterio*-**2a** (18.3 mg, 54% yield) and *deuterio*-**2n** (17.1 mg, 47% yield) as a colorless oil. The ^{1}H NMR spectra of *deuterio*-**2a** was compared with ^{1}H NMR spectra of **2a**, a single deuterium atom (40% ^{2}H) was incorporated at the 2-methyl group of the 3-aroylindole product *deuterio*-**2a**. The ^{1}H NMR spectra of *deuterio*-**2n** was compared with ^{1}H NMR spectra of **2n**, a single deuterium atom (30% ^{2}H) was incorporated at the 2-methyl group of the 3-aroylindole product *deuterio*-**2n**.

^{1}H NMR spectrum of *deuterio*-**2a**

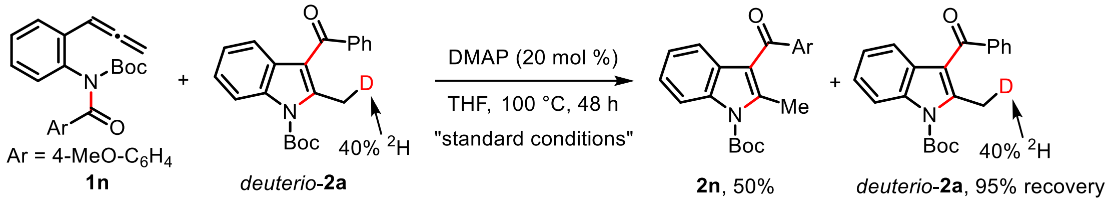


^{1}H NMR spectrum of **2n** and *deuterio*-**2n**



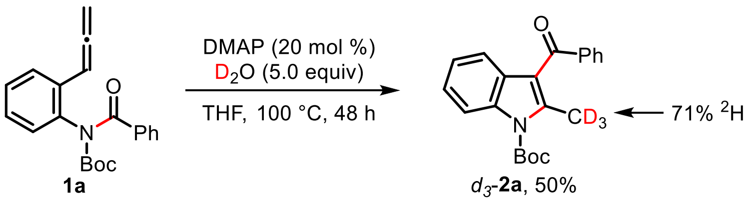


Deuterium scrambling experiment with substrate 1n and product *deuterio*-2a



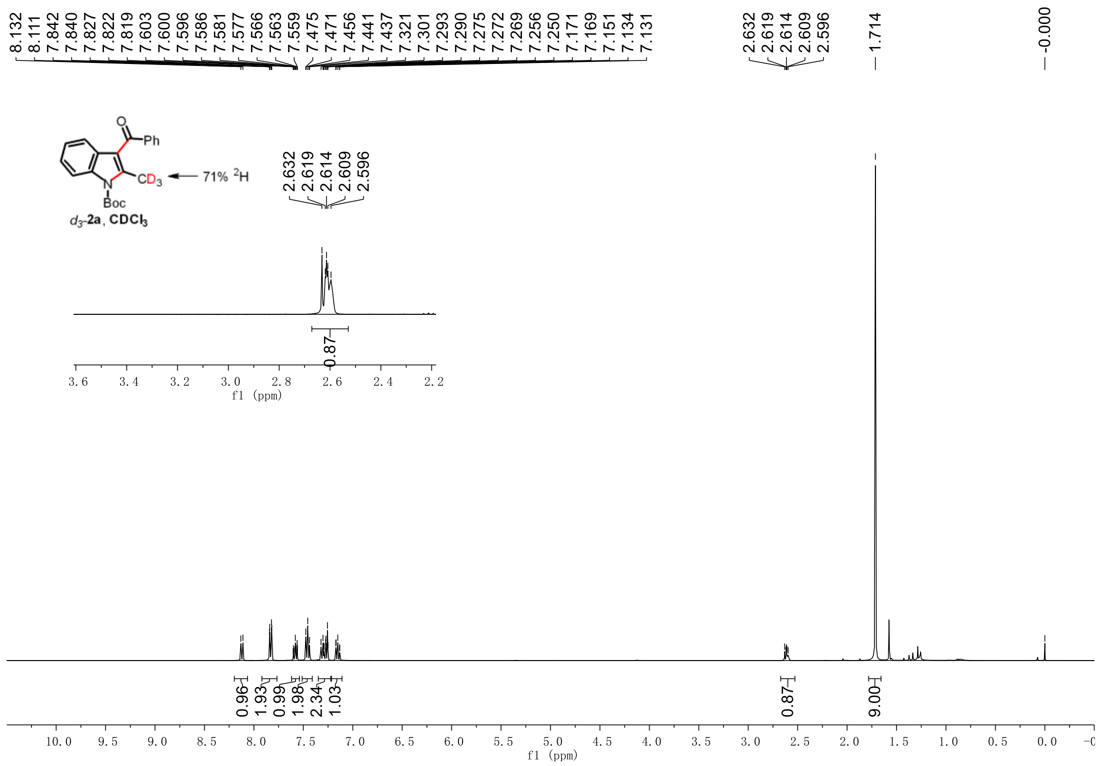
To a 25 mL oven-dried Schlenk tube was added *deuterio*-**2a** (0.05 mmol, 16.8 mg), **1n** (0.05 mmol, 18.2 mg), DMAP (0.01 mmol, 1.2 mg) and a stir bar. The Schlenk tube was transferred into a N_2-filled glovebox and added freshly distilled THF (1 mL). The tube was then removed out from the glovebox and stirred at 100 ℃ for 48 hours. The resulting mixture was concentrated under vacuum and purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give the product *deuterio*-**2a** (16.0 mg, 95% yield recovery) and **2n** (9.1 mg, 50% yield) as a colorless oil. The ^1H NMR spectra of *deuterio*-**2a** was compared with ^1H NMR spectra of **2a**, a single deuterium atom (40% ^2H) was incorporated at the 2-methyl group of the 3-aroylindole product *deuterio*-**2a**.

Deuterium scrambling experiment with 1a in the presence of D_2O



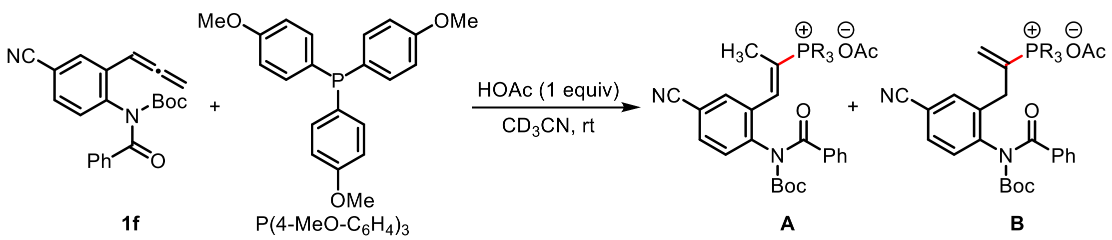
To a 25 mL oven-dried Schlenk tube was added **1a** (0.10 mmol, 33.5 mg), DMAP (0.02 mmol, 2.4 mg) and a stir bar. The Schlenk tube was transferred into a N_2-filled glovebox and added freshly distilled THF (2 mL). The tube was then removed out from the glovebox and was added D_2O (0.5 mmol, 10 uL) under N_2 atomosphere. The reaction mixture stirred at 100 ℃ for 48 h. The resulting mixture was concentrated under vacuum and purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give the product d_3-**2a** as a colorless oil (16.8 mg, 50% yield). The ^1H NMR spectra of d_3-**2a** was compared with ^1H NMR spectra of **2a**, three deuterium atom (71% ^2H) was incorporated at the 2-methyl group of the 3-aroylindole product d_3-**2a**.

^{1}H NMR spectrum of d_3-**2a**



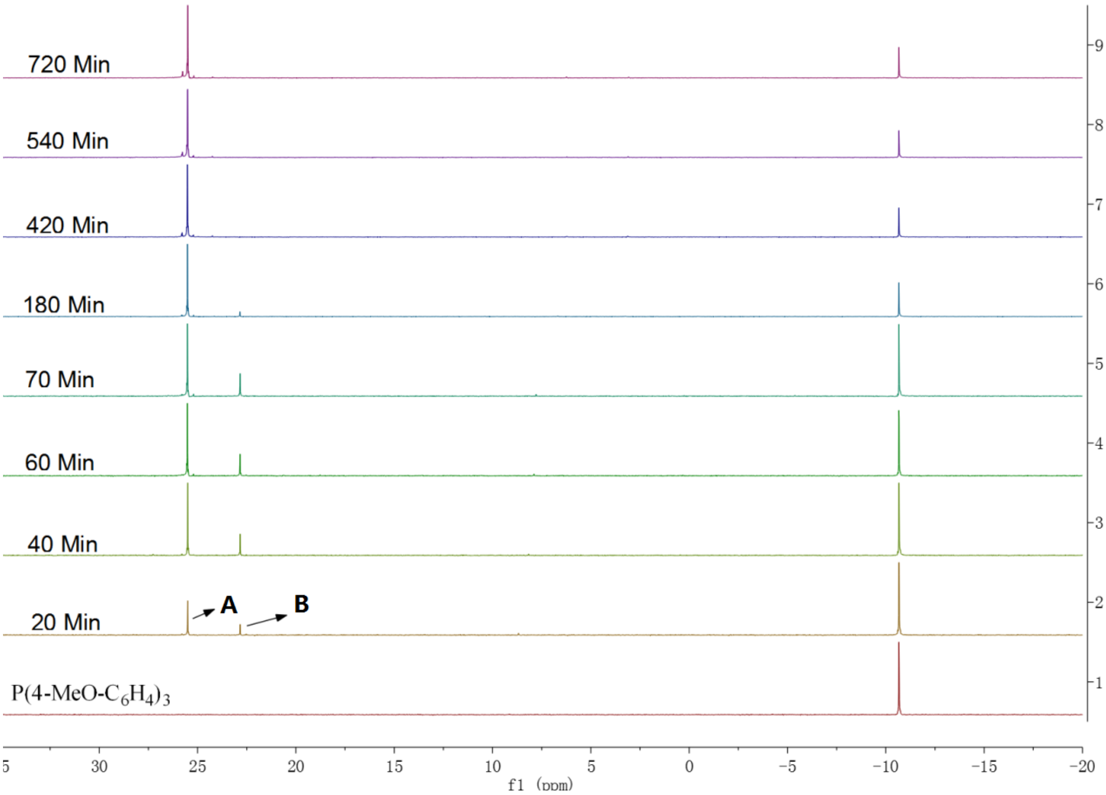
In situ ^{31}P and ^{1}H NMR monitoring experiments

We attempt to detect or isolate DMAP-incorporated reaction intemediate was unsuccessful. We used in situ ^{31}P NMR to detect the reaction intermediate with $P(4\text{-MeO-}C_6H_4)_3$, which showed moderate catalytic reactivity in condition screening (Table S1, entry 15). The reaction was run with **1f** as substrate in the presence of 1 equivalent of acetic acid in CD_3CN

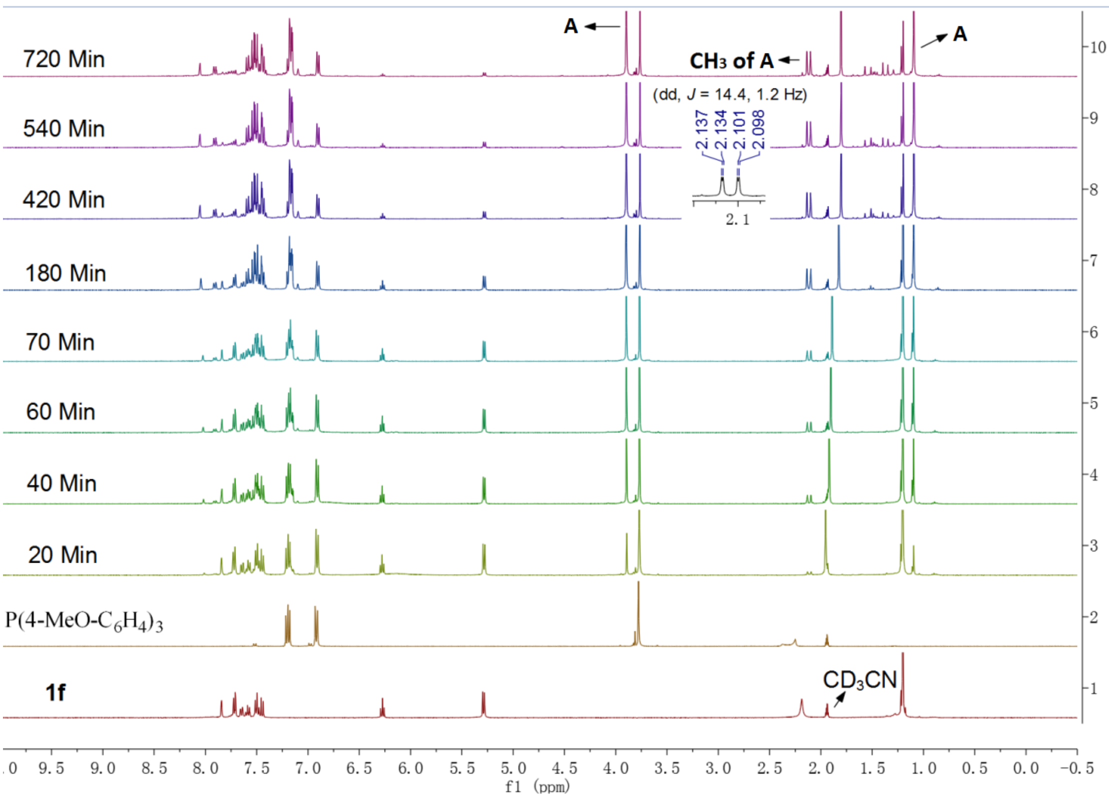


To an oven-dried NMR tube was added **1f** (0.05 mmol, 18.0 mg), $P(4\text{-MeO-}C_6H_4)_3$ (0.05 mmol, 17.6 mg), HOAc (0.05 mmol, 2.9 uL) and CD_3CN (0.5 mL) in a N_2-filled glovebox. The NMR tube was sealed and removed out from the glovebox. The mixture was monitored by ^{31}P and ^{1}H NMR. The mixture was analysed by High Resolution MS after 12 hours. HRMS (ESI) Calcd for **A** $[C_{43}H_{42}N_2O_6P]^+$ $[M\text{-}(OAc)^-]$ 713.2775, Found 713.2782.

^{31}P NMR monitoring experiment

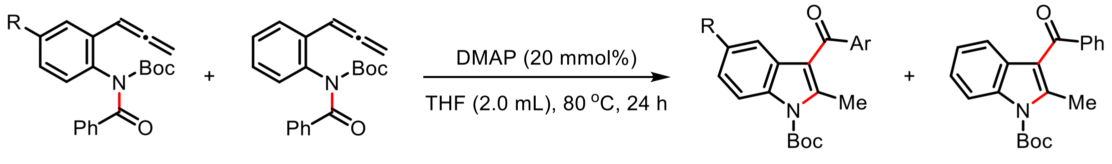


^{1}H NMR monitoring experiment



The NMR experiments clearly showed the addition of phosphine to central carbon atom of allene. After mixing **1f** and P(4-MeO-C_6H_4)$_3$ in a NMR tube, vinyl phosphonium salt **A** was detected shortly in the ^{31}P NMR monitoring experiment. The process was also monitored by ^{1}H NMR spectroscopy. The assigned structure of **A** was consistent with the ^{1}H NMR data, two doublets for methyl group (CH_3, δ 2.12 ppm, $J_{P\text{–}H}$ = 14.4). The vinyl phosphonium **A** was further confirmed by High Resolution MS analyses. We speculate that a resonance-stabilized zwitterionic phosphonium intermediate is formed, followed by protonation with acetic acid to generate **A** and **B**.

Hammett analysis through competition experiments



To a 25 mL oven-dried Schlenk tube was added **1a** (0.10 mmol, 33.5 mg), **1b** (0.1 mmol, 34.9 mg), DMAP (0.02 mmol, 2.4 mg) a stir bar. The Schlenk tube was transferred into a N_2-filled glovebox and added freshly distilled THF (2 mL). The tube was then removed out from the glovebox and stirred at 80 ℃ for 24 h. The mixture was concentrated under vacuum. The ratio **2b**/**2a** was determined by ^{1}H NMR. Similar procedure is used to determine ratios **2c**/**2a** and **2g**/**2a**. A plot of log(k_X/k_H) obtained in the formation of **2a**, **2b**, **2c**, **2g** versus the corresponding *para*-position of aniline σ_p or *meta*-position of allenes σ_m values resulted in two Hammett plots.

product	R	σ_p	σ_m	product ratio (k_X/k_H)	log(k_X/k_H)
2c	OMe	-0.27	0.11	1.39/1	0.14
2b	Me	-0.17	-0.07	1.23/1	0.09
2a	H	0	0	0	0
2g	F	0.06	0.34	3.1/1	0.49

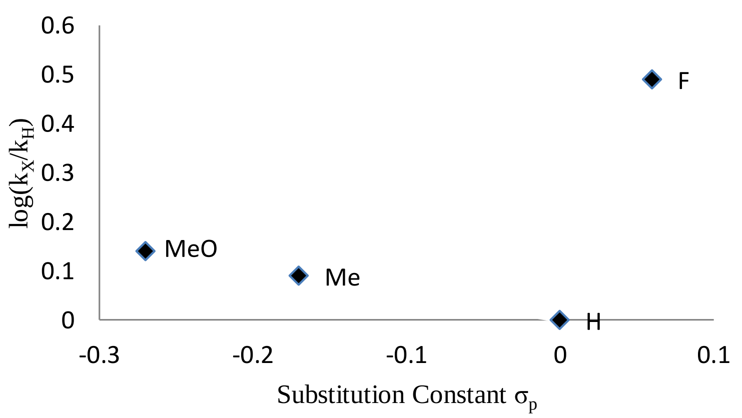


Figure S1. Hammet plot versus σ_p

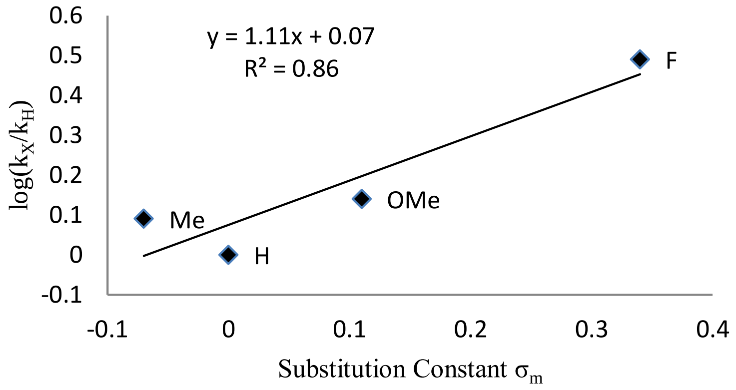
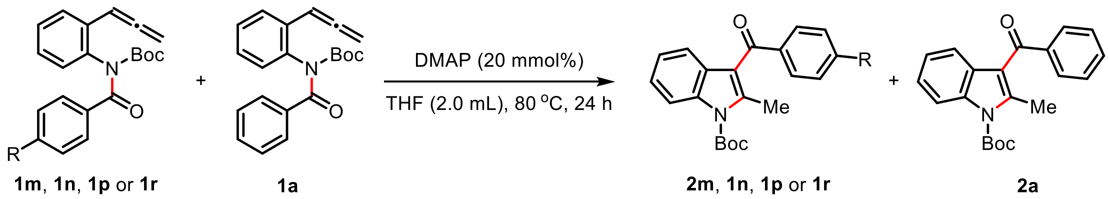


Figure S2. Hammet plot versus σ_m



To a 25 mL oven-dried Schlenk tube was added **1a** (0.10 mmol, 33.5 mg), **1m** (0.1 mmol, 34.9 mg), DMAP (0.02 mmol, 2.4 mg) a stir bar. The Schlenk tube was transferred into a N_2-filled glovebox and added freshly distilled THF (2 mL). The tube was then removed out from the glovebox and stirred at 80 ℃ for 24 h. The mixture was concentrated under vacuum. The ratio **2m/2a** was determined by ^{1}H NMR. Similar procedure is used to determine ratios **2n/2a**, **2p/2a** and **2r/2a**. A plot of $\log(k_X/k_H)$ obtained in the formation of **2a**, **2n**, **2m**, **2p**, **2r** versus the corresponding *para*-position of aroyl group σ_p resulted in one Hammett plots.

product	R	σ_p	product ratio (k_X/k_H)	$\log(k_X/k_H)$
2n	MeO	-0.27	0.76/1	-0.12
2m	Me	-0.17	0.89/1	-0.05
2a	H	0	0	0
2r	F	0.06	0.64/1	-0.19
2p	NO_2	0.78	1.61/1	0.21

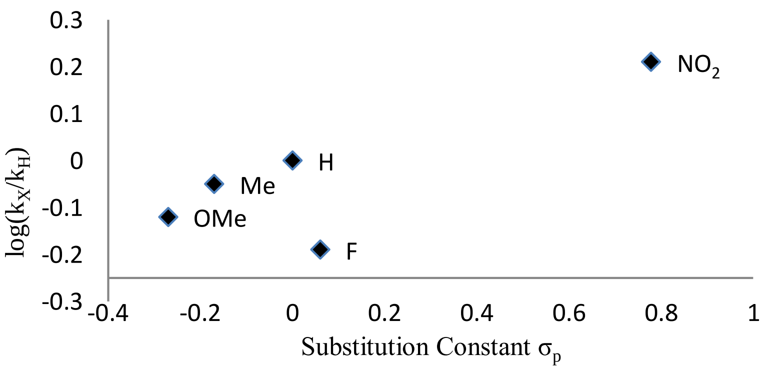
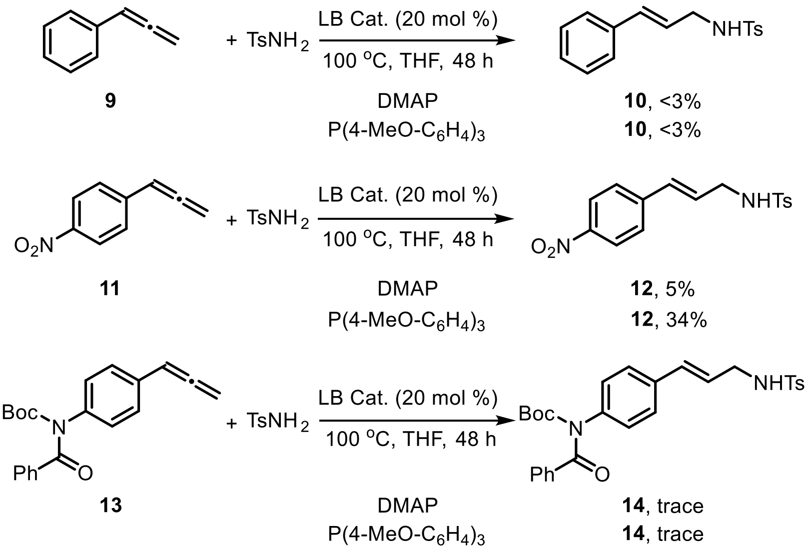


Figure S3. Hammet plot versus σ_p

As shown above, no linear relationship was observed when the plot is derived from the *para*-position of aniline moiety σ_p values or the *para*-position of aroyl group σ_p values (**Figure S1** and **Figure S3**). However, the plot that is derived from the *meta*-position of allenes σ_m values shows a good linear relationship (**Figure S2**). This positive relationship indicates that the electron-withdrawing group on the aryl ring of aniline is capable of stabilizing negative charge of the transition state in the rate determining step. Therefore, we think the rate determine step of this reaction may be the addition of the DMAP to allene moiety.

Lewis base-catalyzed γ-additions of sulfonamide with allenes

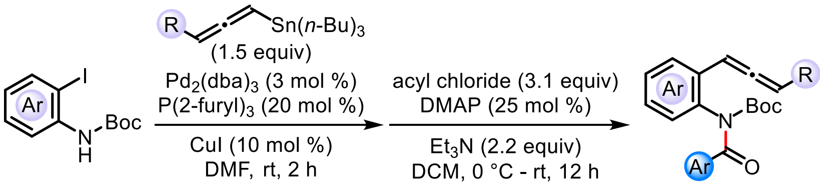
To gain insight into the inherent distinction between weakly activated allenes and activated allenes bearing an electron-withdrawing group in Lewis base catalysis, we performed experiments to compare the reactivity of different allenes though γ-addition reaction with sulfonamide ($TsNH_2$).



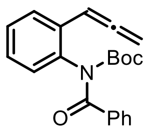
To a 25 mL oven-dried Schlenk tube was added allene (0.10 mmol), $TsNH_2$ (0.15 mmol) and a stir bar. The Schlenk tube was transferred into a N_2-filled glovebox and added Lewis base (0.02 mmol), freshly distilled THF (1 mL). The tube was then removed out from the glovebox and stirred at 100 ℃ for 48 h. The resulting mixture was concentrated under vacuum and purified by flash column chromatography on silica gel to give yellow solid **12** or was detected by GC-MS and crude ^{1}H NMR spectrum. The NMR data of the product **12**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.23 (m, 1H), 3.80 (t, *J* = 6.4 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 143.7, 142.6, 136.9, 130.5, 129.8, 129.4, 127.2, 126.9, 123.9, 45.0, 21.5. The data of compound **12** are consistent with the reported literature[4]

6. Substrate Preparation

All of *N*-Boc-2-iodoanilines was purchased commercially or prepared by reported literature method.[5]

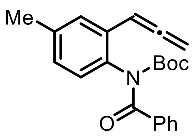


The solution of *N*-Boc-2-iodoanilines (1.0 equiv) and allenyltributyltin (1.5 equiv) in anhydrous DMF (0.125 M) was degassed and purged with nitrogen. $Pd_2(dba)_3$ (3 mol %), $P(2\text{-furyl})_3$ (20 mol %), and CuI (10 mol %) were added to the reaction mixture at room temperature (rt) under argon atmosphere. The reaction mixture was stirred at rt for 2 h, quenched by addition of 10% aqueous amonium solution and extracted with diethyl ether. The combined extractions were washed with water, brine, dried over anhydrous sodium sulfate and evaporated to get the residues without further purification. Then, to a solution of the crude material in DCM (0.4 M) was added Et_3N (2.2 equiv), DMAP (25 mol %), and acyl chloride (3.1 equiv) at 0 ^{o}C. The mixture was stirred at rt overnight. The mixture was evaporated to get the crude product, which was purified by flash silica gel chromatography with petroleum ether/ethyl acetate to give **1a** ~ **1k**.



1a

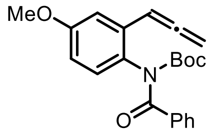
***N*-Boc-*N*-benzoyl-2-allenylaniline (1a)**. According to the general procedure, **1a** was synthesized with *N*-Boc-2-iodoaniline (3 mmol, 957.0 mg). Purified by flash column chromatography on silica gel (PE : EA = 40 : 1) to give **1a** as a light yellow solid (753.8 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.52 (dd, *J* = 8.8, 8.4 Hz, 2H), 7.44 (dd, *J* = 7.6, 7.6 Hz 2H), 7.33 (dd, *J* = 7.6, 7.6 Hz 1H), 7.28 – 7.25 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 6.28 (t, *J* = 6.8 Hz, 1H), 5.16 (d, *J* = 6.8 Hz, 2H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 172.1, 153.0, 136.6, 136.1, 132.2, 131.5, 129.1, 128.6, 128.2, 128.1, 128.0, 127.7, 89.1, 83.5, 78.8, 27.4. HRMS (ESI): Calcd for $[C_{21}H_{22}NO_3]^+$ $[M+H]^+$ 336.1594, Found 336.1603.



1b

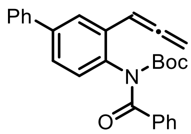
***N*-Boc-*N*-benzoyl-2-allenyl-4-methylaniline (1b)**. According to the general procedure, **1b** was synthesized with *N*-Boc-2-iodo-4-methylaniline (3.7 mmol, 1.2412 g). Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give

1b as a light yellow oil (996.5 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.42 (dd, *J* = 6.8, 7.2 Hz, 2H), 7.32 (s, 1H), 7.06 (brs, 2H), 6.24 (t, *J* = 6.6 Hz, 1H), 5.14 (d, *J* = 6.8 Hz, 1H), 2.34 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 172.2, 153.1, 138.4, 136.7, 133.5, 131.56, 131.4, 128.7, 128.7, 128.5, 128.1, 127.9, 89.0, 83.4, 78.8, 27.4, 21.1. HRMS (ESI): Calcd for $[C_{22}H_{24}NO_3]^+$ $[M+H]^+$ 350.1751, Found 350.1744.



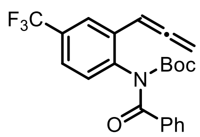
1c

***N*-Boc-*N*-benzoyl-2-allenyl-4-methoxyaniline (1c)**. According to the general procedure, **1c** was synthesized with *N*-Boc-2-iodo-4-methoxyaniline (3.2 mmol, 1.1242 g). Purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give **1c** as a yellow solid (742.6 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.69 (m, 2H), 7.51 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.43 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 2.6 Hz, 1H), 6.81 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.24 (dd, *J* = 6.8, 6.8 Hz, 1H), 5.17 (d, *J* = 6.8 Hz, 2H), 3.81 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 172.3, 159.3, 153.2, 136.7, 133.2, 131.4, 130.0, 129.0, 128.1, 127.9, 113.9, 112.3, 89.2, 83.4, 79.1, 55.4, 27.4. HRMS (ESI): Calcd for $[C_{22}H_{24}NO_4]^+$ $[M+H]^+$ 366.1700, Found 366.1699.



1d

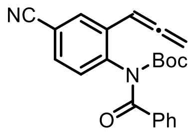
***N*-Boc-*N*-benzoyl-2-allenyl-4-phenylaniline (1d)**. According to the general procedure, **1d** was synthesized with *N*-Boc-2-iodo-4-phenylaniline (0.82 mmol, 325.9 mg). Purified by flash column chromatography on silica gel (PE : EA = 60 : 1) to give **1d** as a white solid (193.8 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 3H), 7.63 – 7.55 (m, 2H), 7.54 – 7.50 (m, 1H), 7.48 – 7.42 (m, 5H), 7.37 – 7.33 (m, 1H), 7.26 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.33 (td, *J* = 6.8, 2.6 Hz, 1H), 5.19 (d, *J* = 6.4 Hz, 2H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 172.1, 153.01, 141.6, 140.4, 136.7, 135.3, 132.4, 131.6, 129.4, 128.7, 128.2, 128.0, 127.5, 127.2, 126.9, 126.6, 89.2, 83.7, 79.0, 27.4. HRMS (ESI): Calcd for $[C_{27}H_{26}NO_3]^+$ $[M+H]^+$ 412.1907, Found 412.1915.



1e

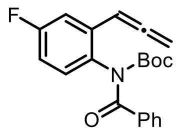
***N*-Boc-*N*-benzoyl-2-allenyl-4-(trifluoromethyl)aniline (1e)**. According to the general procedure, **1e** was synthesized with *N*-Boc-2-iodo-4-(trifluoromethyl)aniline (2.3 mmol, 883.3 mg). Purified by flash column chromatography on silica gel (PE :

EA = 20 : 1) to give **1e** as a white solid (717.2 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.63 – 7.43 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 1H), 6.28 (t, *J* = 6.4 Hz, 1H), 5.25 (d, *J* = 6.4 Hz, 2H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.8, 171.8, 152.50, 143.3, 138.9, 136.1, 133.5, 130.8 (q, *J* = 32.7 Hz), 130.5, 129.8, 129.0, 128.3, 128.1, 125.2 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.9 Hz), 124.3 (q, *J* = 3.5 Hz), 88.6, 84.2, 79.8, 27.4. HRMS (ESI): Calcd for $[C_{22}H_{21}F_3NO_3]^+$ $[M+H]^+$ 404.1468, Found 404.1467.



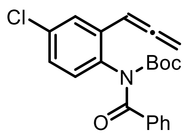
1f

***N*-Boc-*N*-benzoyl-2-allenyl-4-cyanideaniline (1f)**. According to the general procedure, **1f** was synthesized with *N*-Boc-2-iodo-4-cyanideaniline (1.6 mmol, 559.0 mg). Purified by flash column chromatography on silica gel (PE : EA = 10 : 1) to give **1f** as a white solid (362.4 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.59-7.53 (m, 2H), 7.47 (dd, *J* = 6.8, 6.8 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 6.24 (t, *J* = 6.8 Hz, 1H), 5.28 (d, *J* = 6.4 Hz, 2H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 171.6, 152.2, 139.9, 135.8, 134.3, 132.1, 130.7, 130.3, 128.3, 128.1, 118.1, 112.7, 88.1, 84.5, 80.0, 27.4. HRMS (ESI): Calcd for $[C_{22}H_{20}N_2O_3Na]^+$ $[M+Na]^+$ 383.1366, Found 383.1362.



1g

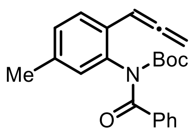
***N*-Boc-*N*-benzoyl-2-allenyl-4-fluoroaniline (1g)**. According to the general procedure, **1g** was synthesized with *N*-Boc-4-fluoro-2-iodoaniline (1.6 mmol, 559.0 mg). Purified by flash column chromatography on silica gel (PE : EA = 60 : 1) to give **1g** as a yellow oil (1.1106 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.70 (m, 2H), 7.53 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.44 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.23 (dd, *J* = 9.6, 2.8 Hz, 1H), 7.17 (dd, *J* = 8.8, 5.2 Hz, 1H), 6.96 (td, *J* = 8.4, 2.8 Hz, 1H), 6.23 (t, *J* = 6.8 Hz, 1H), 5.20 (d, *J* = 6.8 Hz, 2H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 172.1, 162.3 (d, *J* = 245.6 Hz), 152.8, 136.3, 134.6 (d, *J* = 8.7 Hz), 131.8 (d, *J* = 2.5 Hz), 131.7, 130.0 (d, *J* = 8.9 Hz), 128.2, 127.9, 114.8 (d, *J* = 23.1 Hz), 114.2 (d, *J* = 23.9 Hz), 88.7, 83.8, 79.5, 27.3. HRMS (ESI): Calcd for $[C_{21}H_{21}FNO_3]^+$ $[M+H]^+$ 354.1500, Found 354.1508.



1h

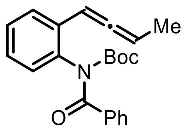
***N*-Boc-*N*-benzoyl-2-allenyl-4-chloroaniline (1h)**. According to the general procedure, **1h** was synthesized with *N*-Boc-4-chloro-2-iodoaniline (2.2 mmol, 762.8

mg). Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **1g** as a yellow oil (534.5 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.0 Hz, 2H), 7.53 – 7.45 (m, 4H), 7.24 (dd, *J* = 8.0, 6.8 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.21 (t, *J* = 5.2 Hz, 1H), 5.22 (d, *J* = 5.2 Hz, 2H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 172.0, 152.7, 136.2, 134.4, 134.1, 131.8, 130.4, 128.2, 128.0, 127.8, 127.8, 88.4, 83.9, 79.6, 27.4. HRMS (ESI): Calcd for $[C_{21}H_{20}ClNO_3Na]^+$ $[M+Na]^+$ 392.1024, Found 392.1017.



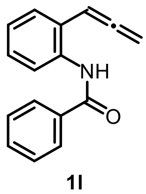
1i

***N*-Boc-*N*-benzoyl-2-allenyl-5-methylaniline (1i)**. According to the general procedure, **1i** was synthesized with *N*-Boc-2-iodo-5-methylaniline (4.1 mmol, 1.3801 g). Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **1i** as a yellow solid (991.2 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 2H), 7.53 – 7.49 (m, 1H), 7.45 – 7.40 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 6.23 (t, *J* = 6.8 Hz, 1H), 5.12 (d, *J* = 6.8 Hz, 2H), 2.33 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 172.1, 153.0, 137.8, 136.8, 135.9, 131.5, 129.6, 129.5, 129.1, 128.2, 128.0, 89.0, 83.4, 78.6, 27.4, 20.9. HRMS (ESI): Calcd for $[C_{22}H_{24}NO_3]^+$ $[M+H]^+$ 350.1751, Found 350.1760.



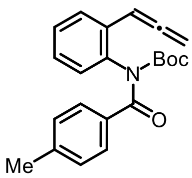
1k

***N*-Boc-*N*-benzoyl-2-(3’-methylallenyl)aniline (1k)**. According to the general procedure, **1k** was synthesized with *N*-Boc-2-iodoaniline (3.0 mmol, 957.3 mg). Purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give **1k** as a yellow solid (582.2 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.43 (dd, *J* = 7.6 , 7.2 Hz, 2H), 7.31 (ddd, *J* = 7.2, 7.6, 0.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.16 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.21 (dq, *J* = 6.0, 2.8 Hz, 1H), 5.58 – 5.51 (m, 1H), 1.77 (dd, *J* = 7.2, 3.2 Hz, 3H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 172.1, 153.0, 143.3, 136.7, 136.0, 133.1, 131.5, 129.0, 128.5, 128.1, 128.0, 127.5, 89.7, 89.1, 83.4, 27.4, 13.8. HRMS (ESI): Calcd for $[C_{22}H_{23}NO_3Na]^+$ $[M+Na]^+$ 372.1570, Found 372.1573.



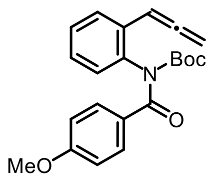
1l

***N*-benzoyl-2-allenylaniline (1l)**. According to the general procedure, **1l** was synthesized with *N*-benzoyl-2-iodoaniline (3.0 mmol, 969.3 mg). Purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give **1l** as a white solid (600.0 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.49 (dd, *J* = 6.8, 8.0 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.15 (dd, *J* = 7.2, 6.8 Hz, 1H), 6.34 (t, *J* = 6.8 Hz, 1H), 5.14 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 165.8, 135.4, 134.9, 131.8, 129.1, 128.6, 128.0, 127.2, 125.0, 124.0, 123.4, 91.2, 78.8. HRMS (ESI): Calcd for $[C_{16}H_{14}NO]^+$ $[M+H]^+$ 236.1070, Found 236.1075.



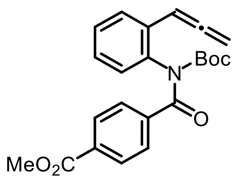
1m

***N*-Boc-*N*-(4-(methyl)benzoyl)-2-allenylaniline (1m)**. According to the general procedure, **1m** was synthesized with *N*-Boc-2-iodoaniline (3.0 mmol, 957.3 mg). Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **1m** as a yellow solid (650.2 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.23 – 7.22 (m, 3H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.28 (t, *J* = 6.8 Hz, 1H), 5.15 (d, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 172.0, 153.1, 142.2, 136.3, 133.5, 132.2, 129.0, 128.8, 128.4, 128.3, 128.0, 127.7, 89.1, 83.3, 78.7, 27.5, 21.6. HRMS (ESI): Calcd for $[C_{22}H_{23}NO_3Na]^+$ $[M+Na]^+$ 372.1570, Found 372.1565.



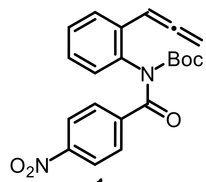
1n

***N*-Boc-*N*-(4-(methoxyl)benzoyl)-2-allenylaniline (1n)**. According to the general procedure, **1n** was synthesized with *N*-Boc-2-iodoaniline (1.5 mmol, 0.4787g). Purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to give **1n** as a white solid (383.5 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.30 (dd, *J* =7.6, 7.2 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.29 (t, *J* = 6.8 Hz, 1H), 5.15 (d, *J* = 6.8 Hz, 2H), 3.84 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 171.4, 162.5, 153.2, 136.4, 132.1, 130.6, 129.0, 128.3, 128.3, 128.0, 127.6, 113.4, 89.1, 83.1, 78.8, 55.4, 27.5. HRMS (ESI): Calcd for $[C_{22}H_{24}NO_4]^+$ $[M+H]^+$ 366.1700, Found 366.1701.



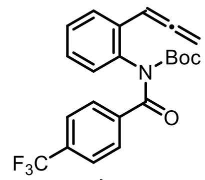
1o

***N*-Boc-*N*-(4-(methoxycarbonyl)benzoyl)-2-allenylaniline (1o)**. According to the general procedure, **1o** was synthesized with *N*-Boc-2-iodoaniline (3.0 mmol, 957.3 mg). Purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to give **1o** as a white solid (852.2 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.53 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.35 (dd, *J* = 8.0, 6.8 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 6.24 (t, *J* = 6.8 Hz, 1H), 5.17 (d, *J* = 6.8 Hz, 2H), 3.95 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 171.23, 166.1, 152.5, 140.6, 135.5, 132.3, 132.0, 129.4, 128.9, 128.7, 128.2, 127.8, 127.6, 88.9, 84.0, 78.9, 52.4, 27.4. HRMS (ESI): Calcd for $[C_{23}H_{23}NO_5Na]^+$ $[M+Na]^+$ 416.1468, Found 416.1465.



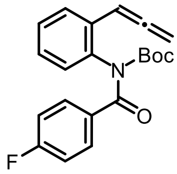
1p

***N*-Boc-*N*-(4-(nitro)benzoyl)-2-allenylaniline (1p)**. According to the general procedure, **1p** was synthesized with *N*-Boc-2-iodoaniline (3.0 mmol, 957.3 mg). Purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to give **1p** as a yellow solid (531.4 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.36 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.21 (t, *J* = 6.8 Hz, 1H), 5.18 (d, *J* = 6.8 Hz, 2H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 170.0, 152.3, 149.1, 142.4, 135.3, 132.1, 129.0, 128.9, 128.5, 128.4, 127.9, 123.4, 89.0, 84.4, 78.8, 27.5. HRMS (ESI): Calcd for $[C_{21}H_{20}N_2O_5Na]^+$ $[M+Na]^+$ 403.1264, Found 403.1273.



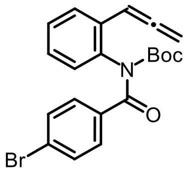
1q

***N*-Boc-*N*-(4-(trifluoromethyl)benzoyl)-2-allenylaniline (1q)**. According to the general procedure, **1q** was synthesized with *N*-Boc-2-iodoaniline (3.0 mmol, 957.3 mg). Purified by flash column chromatography on silica gel (PE : EA = 50 : 1) to give **1q** as a yellow oil (496.9 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.26 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 6.23 (t, *J* = 6.8 Hz, 1H), 5.16 (d, *J* = 6.8 Hz, 2H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 170.8, 152.5, 140.0, 135.6, 132.8 (q, *J* = 32.8 Hz), 132.1, 129.0, 128.8, 128.3, 128.0, 127.8, 125.2 (q, *J* = 3.2 Hz), 123.6 (q, *J* = 271 Hz), 89.0, 84.1, 78.8, 27.4. HRMS (ESI): Calcd for $[C_{22}H_{20}F_3NO_3Na]^+$ $[M+Na]^+$ 426.1287, Found 426.1267.



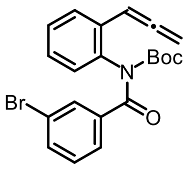
1r

***N*-Boc-*N*-(4-(fluoro)benzoyl)-2-allenylaniline (1r)**. According to the general procedure, **1r** was synthesized with *N*-Boc-2-iodoaniline (3.0 mmol, 957.3 mg). Purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give **1r** as a white solid (900.5 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.32 (ddd, *J* = 7.6, 8.0, 1.6 Hz, 1H), 7.24 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.16 – 7.07 (m, 3H), 6.25 (t, *J* = 6.8 Hz, 1H), 5.15 (d, *J* = 6.8 Hz, 2H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 170.8, 164.6 (d, *J* = 251,4), 152.9, 136.0, 132.5 (d, *J* = 2.5), 132.1, 130.5 (d, *J* = 8.9), 129.0, 128.6, 128.1, 127.7, 115.3 (d, *J* = 22.0), 89.0, 83.6, 78.8, 27.5. HRMS (ESI): Calcd for $[C_{21}H_{20}FNO_3Na]^+$ $[M+Na]^+$ 376.1319, Found 376.1318.



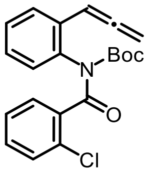
1s

***N*-Boc-*N*-(4-(bromo)benzoyl)-2-allenylaniline (1s)**. According to the general procedure, **1s** was synthesized with *N*-Boc-2-iodoaniline (3.0 mmol, 957.3 mg). Purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give **1s** as a yellow solid (548.3 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.23 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.23 (t, *J* = 6.8 Hz, 1H), 5.14 (d, *J* = 6.8 Hz, 2H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.52, 170.95, 152.66, 135.78, 135.20, 132.00, 131.33, 129.50, 128.88, 128.58, 128.09, 127.67, 126.04, 88.96, 83.70, 78.78, 27.40. HRMS (ESI): Calcd for $[C_{21}H_{20}BrNO_3Na]^+$ $[M+Na]^+$ 436.0519, Found 436.0515.



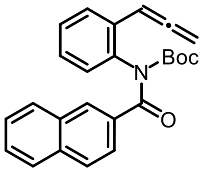
1t

***N*-Boc-*N*-(3-(bromo)benzoyl)-2-allenylaniline (1t).** According to the general procedure, **1t** was synthesized with *N*-Boc-2-iodoaniline (3.0 mmol, 957.3 mg). Purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give **1t** as a yellow solid (910.2 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.65 – 7.62 (m, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.30 – 7.28 (m, 1H), 7.19 – 7.17 (m, 1H), 6.24 – 6.20 (m, 1H), 5.17 (d, *J* = 6.8 Hz, 2H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 170.4, 152.6, 138.5, 135.8, 134.3, 132.2, 130.9, 129.8, 129.0, 128.8, 128.3, 127.8, 126.4, 122.1, 89.1, 84.0, 78.8, 27.5. HRMS (ESI): Calcd for [$C_{21}H_{20}BrNO_3Na$]$^+$ [M+Na]$^+$ 436.0519, Found 436.0529.



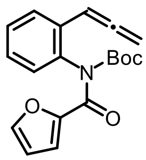
1u

***N*-Boc-*N*-(2-(chloro)benzoyl)-2-allenylaniline (1u)**. According to the general procedure, **1u** was synthesized with *N*-Boc-2-iodoaniline (3.0 mmol, 957.3 mg). Purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give **1u** as a yellow solid (814.7 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.46 (m, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.32 – 7.28 (m, 2H), 6.26 (t, *J* = 6.8 Hz, 1H), 5.16 (d, *J* = 6.8 Hz, 2H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 169.0, 151.5, 137.5, 135.4, 131.9, 130.6, 130.0, 129.3, 128.9, 128.7, 128.3, 128.1, 127.8, 126.9, 89.2, 83.8, 78.6, 27.3. HRMS (ESI): Calcd for [$C_{21}H_{21}ClNO_3$]$^+$ [M+H]$^+$ 370.1204, Found 370.1211.



1v

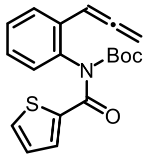
***N*-Boc-*N*-(2-naphthoyl)-2-allenylaniline (1v)**. According to the general procedure, **1v** was synthesized with *N*-Boc-2-iodoaniline (3.2 mmol, 1.0211g). Purified by flash column chromatography on silica gel (PE : EA = 30 : 1) to give **1v** as a yellow solid (742.2 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.96 – 7.83 (m, 3H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.52 (m, 3H), 7.33 – 7.32 (m, 1H), 7.29 – 7.24 (m, 2H), 6.34 (t, *J* = 6.4 Hz, 1H), 5.17 (d, *J* = 6.4 Hz, 2H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 172.0, 153.1, 136.2, 134.7, 133.7, 132.4, 132.3, 129.1, 128.9, 128.8, 128.6, 128.2, 127.9, 127.8, 127.8, 127.7, 126.8, 124.6, 89.2, 83.5, 78.8, 27.4. HRMS (ESI): Calcd for [$C_{25}H_{24}NO_3$]$^+$ [M+H]$^+$ 386.1751, Found 386.1761.



1w

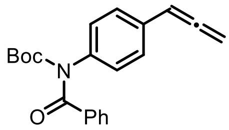
***N*-Boc-*N*-(furan-2-carbonyl)-2-allenylaniline (1w)**. According to the general procedure, **1w** was synthesized with *N*-Boc-2-iodoaniline (3.2 mmol, 1.0211g). Purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to give **1w** as a yellow solid (536.7 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.33 (dd, *J* = 7.2, 6.4 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.19 (d, *J* = 6.8 Hz, 1H), 6.97 (brs, 1H), 6.50 (brs, 1H), 6.31 (t, *J* = 5.6 Hz, 1H), 5.14 (d, *J* = 5.6 Hz, 2H), 1.37

(s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 160.7, 152.4, 148.0, 144.9, 135.4, 132.3, 129.3, 128.7, 127.9, 127.6, 117.8, 112.2, 88.9, 83.3, 78.8, 27.5. HRMS (ESI): Calcd for $[C_{19}H_{19}NO_4Na]^+$ $[M+Na]^+$ 348.1206, Found 348.1200.



1x

***N*-Boc-*N*-(thiophene-2-carbonyl)-2-allenylaniline (1x)**. According to the general procedure, **1x** was synthesized with *N*-Boc-2-iodoaniline (3.0 mmol, 957.3 mg). Purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to give **1x** as a yellow solid (773.0 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 2H), 7.44 (dd, *J* = 3.6, 0.8 Hz, 1H), δ 7.35 – 7.30 (m, 1H), 7.25 – 7.15 (m, 1H), 7.00 – 6.98 (m, 2H), 6.31 (t, *J* = 6.8 Hz, 1H), 5.14 (d, *J* = 6.8 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 164.2, 152. 8, 138.5, 136.2, 133.0, 132.6, 132.4, 129.4, 128.8, 128.1, 127.7, 127.1, 89.1, 83.5, 78.8, 27.7. HRMS (ESI): Calcd for $[C_{19}H_{20}NO_3S]^+$ $[M+H]^+$ 342.1158, Found 342.1153.



13

***N*-Boc-*N*-benzoyl-4-allenylaniline (13)** To a solution of *N*-Boc-4-iodoaniline (3.0 mmol, 957.3 mg) in dry THF (9 mL) was added sodium hydride (4.5 mmol, 60% in mineral iol, 180 mg) at 0 ℃ under N_2 atomosphere. After being stirred at the same temperature for 10 min, acyl chloride (3.6 mmol, 506.0 mg) was added at −78 °C. After being stirred at the same temperature for 1 h, the reaction mixture was quenched with 1 M aqueous HCl at 0 ℃. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous sodium sulfate and evaporated to get the residues without further purification. Then, to a solution of the crude material and allenyltributyltin (9.0 mmol, 1.4805 g) in anhydrous DMF (0.125 M) was degassed and purged with nitrogen. $Pd(PPh_3)_4$ (5 mol %, 173.3 mg), LiCl(9.0 mmol, 381.6 mg) were added to the reaction mixture at room temperature (rt) under N_2 atmosphere. The reaction mixture was stirred at 80 ºC for 2 h, added water and extracted with diethyl ether. The combined extractions were washed with brine, dried over anhydrous sodium sulfate and evaporated to get the residues, which was purified by flash silica gel chromatography on silica gel (PE : EA = 40 : 1) to give **13** as a white solid (654.0 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 2H), 7.51 (dd, *J* = 7.2 Hz, 1H), 7.43 (dd, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.17 (t, *J* = 6.8 Hz, 1H), 5.16 (d, *J* = 6.8 Hz, 2H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 172.7, 153.2, 137.6, 136.9, 133.6, 131.7, 128.2, 128.1, 128.0, 127.4, 93.4, 83.5, 78.9, 27.46. HRMS (ESI): Calcd for $[C_{21}H_{22}NO_3]^+$ $[M+H]^+$ 336.1594, Found 336.1599.

7. DFT Studies

Computational methods

DFT calculations were performed with Gaussian 09.[6] The hybrid-meta GGA functional M06-2X[7] with 6-31+G(d,p) was employed for optimizing the geometries of minima and transition states. The SMD[8] implicit solvation model was used to account for solvation effects of tetrahydrofuran (THF). Pruned integration grids with 99 radial shells and 590 angular points per shell were used. Unscaled harmonic frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298 K. Quasiharmonic corrections were applied during the entropy calculations by setting all positive frequencies that are less than 100 cm^{-1} to 100 cm^{-1}.[9] On the basis of the optimized structures, single-point energies were computed at the SMD(THF)-M06-2X/6-311+G(d,p) level. All discussed energy differences were based on Gibbs energies in THF at 298 K. Standard states for solutes in THF solution are the hypothetical states at 1 mol/L.

For [1,3]-proton transfer assisted by water, the activation energy is 19.3 kcal/mol, which is higher than intramolecular [1,4]-proton transfer to NBoc anion pathway (11.5 kcal/mol, **TS4**) and [1,4]-proton transfer pathway assisted by water (11.3 kcal/mol, **TS8**). From **INT3** to **INT5**, both a direct [1,3]-proton transfer and a [1,3]-proton transfer assisted by water are quite difficult (Figure S4).

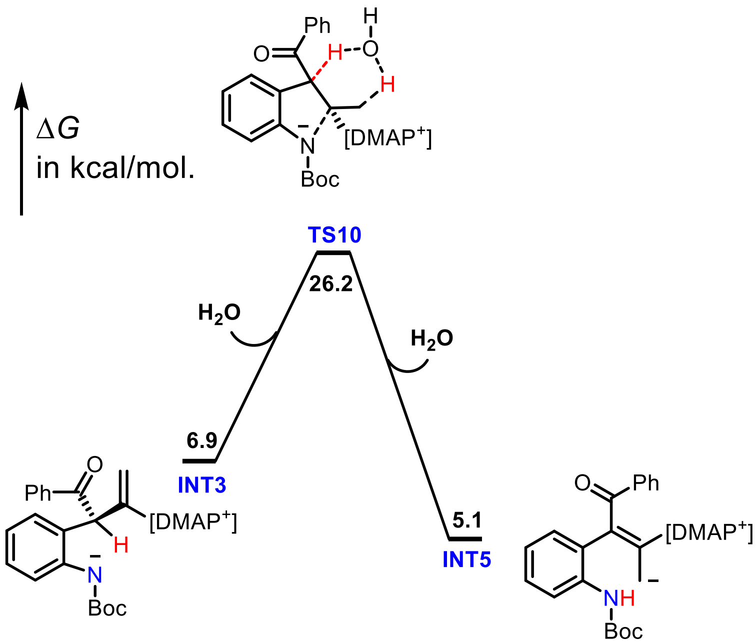


Figure S4 [1,3]-Proton transfer assisted by water. Computed at the SMD(THF)-M06-2X/6-311+G(d,p)//SMD(THF)-M06-2X/6-31+G(d,p) level.

For **INT3** and **INT4**, the protonations are thermodynamically disfavored. As a result, the proton transfer processes can't be stepwise assisted by a trace amount of water in THF.

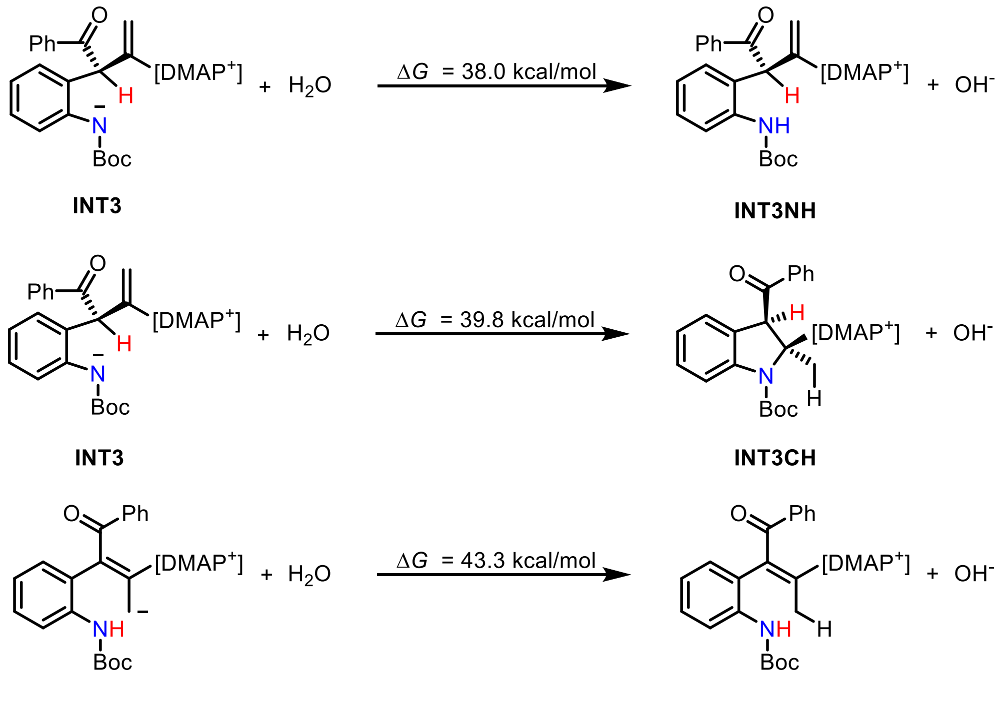


Figure S5 Direct protonations of INT3 and INT4 by water. Computed at the SMD(THF)-M06-2X/6-311+G(d,p)//SMD(THF)-M06-2X/6-31+G(d,p) level.

Computed Energies for the Stationary Points

Table S2. Thermal corrections to Gibbs energies (TCGs), single-point energies (SPEs) and Gibbs energies.

	TCGs	SPEs	Gibbs Energies
DMAP	0.130507	-382.2009522	-382.0704452
1a	0.325192	-1093.154545	-1092.829353
2a	0.33007	-1093.215651	-1092.885581
DMAP	0.130507	-382.2009522	-382.0704452
INT1	0.484128	-1475.356339	-1474.872211
INT2	0.487143	-1475.370419	-1474.883276
INT2p	0.487296	-1475.356876	-1474.86958
INT3	0.485928	-1475.371675	-1474.885747
INT4	0.485848	-1475.383244	-1474.897396
INT5	0.484584	-1475.373198	-1474.888614
INT6	0.487865	-1475.404116	-1474.916251
INT7	0.26319	-729.8538213	-729.5906313
INT8	0.18473	-498.8202191	-498.6354891
INT9	0.225583	-726.716443	-726.49086
INT3NH	0.499234	-1475.854563	-1475.355329

INT3CH	0.502465	-1475.854983	-1475.352518
INT4CH	0.499485	-1475.858081	-1475.358596
H2O	0.003691	-76.42793912	-76.42424812
OH-	-0.007476	-75.88655743	-75.89403343
9	0.106196	-347.6566987	-347.5505027
15	0.031385	-116.6313454	-116.5999604
16	0.06871	-344.4984305	-344.4297205
TS1	0.480242	-1475.331947	-1474.851705
TS2	0.484262	-1475.346403	-1474.862141
TS2p	0.484868	-1475.338961	-1474.854093
TS3p	0.486494	-1475.351214	-1474.86472
TS4	0.480876	-1475.348412	-1474.867536
TS5	0.480759	-1475.349087	-1474.868328
TS6	0.484597	-1475.350997	-1474.8664
TS7	0.486008	-1475.392964	-1474.906956
TS8	0.50438	-1551.793433	-1551.289053
TS9	0.502069	-1551.780224	-1551.278155
TS10	0.504952	-1551.779012	-1551.27406
TS11	0.260069	-729.8331294	-729.5730604
TS12	0.182419	-498.8007631	-498.6183441
TS13	0.222066	-726.6839372	-726.4618712
TS-1,3	0.481567	-1475.300561	-1474.818994
TS-L	0.480815	-1475.342155	-1474.86134

Cartesian coordinates for the stationary points

```
DMAP
 C          0.564421    1.200065   -0.008470
 C          1.948933    1.134147   -0.010763
 N          2.664204    0.000044   -0.001931
 C          1.948948   -1.134056    0.009062
 C          0.564440   -1.199939    0.011421
 C         -0.186863    0.000079    0.003400
 N         -1.546063   -0.000062    0.006841
 C         -2.270620   -1.258598   -0.020207
 C         -2.271159    1.258393    0.014802
 H          0.082842    2.169917   -0.019311
 H          2.520696    2.059863   -0.021335
 H          2.520735   -2.059783    0.016975
 H          0.082819   -2.169774    0.022671
 H         -2.062488   -1.860346    0.872994
 H         -3.339151   -1.049893   -0.053148
 H         -2.008598   -1.849932   -0.905851
 H         -2.004189    1.864804    0.888371
 H         -2.068942    1.844956   -0.890092
 H         -3.339315    1.049767    0.058886
1a
 C          4.937423   -0.649297   -0.667959
 C          4.113742   -1.434143   -1.474178
 C          2.730963   -1.348619   -1.329806
 C          2.179884   -0.503195   -0.373926
 C          2.991493    0.272222    0.467926
 C          4.378756    0.197667    0.285322
 N          0.746541   -0.411788   -0.285379
 C          0.069228   -1.425443    0.413243
 O          0.683840   -2.187284    1.134579
 C          2.463777    1.171073    1.517916
 C          1.343709    1.009606    2.188585
 C          0.250066    0.839404    2.881972
 O         -0.956752    1.052299   -0.077696
```

C	-1.802372	2.201839	-0.420097
C	-3.046075	1.945983	0.420828
C	-2.146273	2.187924	-1.904575
C	-1.096660	3.481647	0.008759
C	0.188615	0.818188	-0.695693
O	0.753268	1.545170	-1.481521
C	-1.394117	-1.606294	0.164046
C	-2.211713	-1.935080	1.246063
C	-3.572128	-2.159343	1.042931
C	-4.107079	-2.084355	-0.243636
C	-3.282266	-1.778254	-1.328197
C	-1.927494	-1.528689	-1.125173
H	6.016181	-0.695148	-0.781165
H	4.541589	-2.096263	-2.220063
H	2.064850	-1.929141	-1.962074
H	5.021975	0.806671	0.914862
H	3.101931	2.012699	1.786794
H	-0.696748	1.262782	2.552944
H	0.258482	0.249672	3.796362
H	-2.794146	1.922106	1.485797
H	-3.775667	2.743178	0.253380
H	-3.499470	0.987364	0.145950
H	-1.272424	2.389580	-2.525799
H	-2.895549	2.962009	-2.096219
H	-2.575994	1.220730	-2.185325
H	-1.783504	4.325763	-0.107046
H	-0.803915	3.417363	1.062142
H	-0.207663	3.667057	-0.597008
H	-1.779452	-2.002363	2.240255
H	-4.212325	-2.398611	1.886467
H	-5.165326	-2.268607	-0.402925
H	-3.695464	-1.730554	-2.331204
H	-1.284868	-1.282284	-1.967465

2a

C	1.658224	3.362189	-0.625151
C	0.349817	3.799384	-0.360254
C	-0.683520	2.898927	-0.127983
C	-0.366740	1.537352	-0.159901
C	0.940968	1.079812	-0.412425
C	1.963127	2.008653	-0.658286
N	-1.187378	0.403879	-0.017118
C	2.002625	-1.315341	-0.634448
O	1.839739	-2.348473	-1.271479
C	0.888532	-0.369314	-0.408878
C	-0.410960	-0.750912	-0.176794
C	-0.933961	-2.136848	0.008521
O	-3.184378	-0.628787	-0.106350
C	-4.621533	-0.821618	0.159668
C	-4.845104	-2.259277	-0.288651
C	-5.434347	0.146154	-0.690266
C	-4.895626	-0.669879	1.650410
C	-2.573282	0.496412	0.216927
O	-3.085518	1.509318	0.635094
C	3.347613	-0.998415	-0.057146
C	3.480846	-0.256269	1.121627
C	4.744832	-0.028410	1.662281
C	5.879020	-0.523526	1.018017
C	5.749853	-1.261629	-0.160585
C	4.486779	-1.508105	-0.690560
H	2.439852	4.092707	-0.809452
H	0.134933	4.863315	-0.338481
H	-1.689560	3.240307	0.072607
H	2.973618	1.676844	-0.874845
H	-1.558957	-2.443553	-0.834202
H	-1.538242	-2.207711	0.916018
H	-0.090416	-2.822359	0.079050
H	-4.234579	-2.947932	0.303196
H	-5.897582	-2.523386	-0.154528
H	-4.587459	-2.377051	-1.345390
H	-5.297855	1.178982	-0.366445
H	-6.493912	-0.111344	-0.598765
H	-5.150444	0.057722	-1.743506
H	-5.925058	-0.982136	1.849758
H	-4.225903	-1.314503	2.228909
H	-4.777372	0.362632	1.982450
H	2.598438	0.132962	1.621773
H	4.844166	0.537056	2.583634
H	6.864189	-0.336344	1.434981
H	6.632806	-1.646093	-0.661855
H	4.369265	-2.089759	-1.599923

INT1

C	1.741509	4.935759	-0.693528
C	2.977533	4.301130	-0.839418
C	3.029032	2.920827	-0.641284
C	1.891500	2.208787	-0.294234
C	0.617604	2.821518	-0.109006
C	0.601086	4.226463	-0.336517
N	2.036373	0.786546	-0.102956

C	2.632787	0.331172	1.086771
O	2.657094	1.030860	2.080766
C	-0.530304	2.040406	0.229224
C	-1.830097	2.509778	0.516299
C	-2.376895	3.716564	0.854982
C	-3.937066	-0.234891	-0.860988
C	-3.014365	0.768802	-0.733064
N	-2.827635	1.424337	0.435862
C	-3.563246	1.083921	1.518410
C	-4.498705	0.083980	1.473063
C	-4.724669	-0.626751	0.259356
N	-5.628219	-1.614312	0.175451
C	-6.425539	-1.978069	1.340926
C	-5.813881	-2.329738	-1.081498
O	1.129753	-1.232170	-0.495906
C	0.646849	-2.361293	-1.293760
C	0.746628	-3.520575	-0.310491
C	1.542943	-2.613492	-2.501584
C	-0.799345	-2.088022	-1.685850
C	1.429322	-0.058310	-1.045963
O	1.178511	0.289670	-2.177823
C	3.347935	-0.985651	1.056723
C	4.084339	-1.385621	-0.061438
C	4.800214	-2.580156	-0.029454
C	4.768936	-3.383408	1.111810
C	4.035249	-2.981170	2.229089
C	3.336226	-1.776350	2.207177
H	1.661480	6.007553	-0.858147
H	3.869980	4.857874	-1.104719
H	3.964113	2.376636	-0.755311
H	-0.334905	4.763323	-0.250990
H	-0.408878	0.963568	0.286227
H	-3.453388	3.827625	0.922142
H	-1.763202	4.573388	1.095005
H	-4.045314	-0.710342	-1.826732
H	-2.392025	1.098767	-1.557198
H	-3.352816	1.645017	2.421277
H	-5.040375	-0.151277	2.379211
H	-7.015222	-1.124606	1.691460
H	-7.107239	-2.779862	1.064017
H	-5.786581	-2.328909	2.158322
H	-6.154282	-1.652324	-1.871763
H	-4.880715	-2.807018	-1.399699
H	-6.566598	-3.102212	-0.937382
H	0.161020	-3.311857	0.589832
H	0.364766	-4.434268	-0.774816
H	1.790631	-3.682355	-0.019755
H	1.435485	-1.838924	-3.261435
H	1.266550	-3.576815	-2.941240
H	2.591181	-2.671460	-2.190905
H	-1.206131	-2.956980	-2.213299
H	-1.403096	-1.911489	-0.789904
H	-0.866840	-1.216332	-2.341793
H	4.106564	-0.760891	-0.951597
H	5.380713	-2.884466	-0.895241
H	5.320788	-4.318422	1.132266
H	4.012696	-3.603096	3.118765
H	2.771658	-1.446404	3.074075

INT2

C	1.973838	-2.512850	-2.454240
C	0.999502	-3.422971	-2.047265
C	-0.158691	-3.009138	-1.380553
C	-0.324378	-1.645284	-1.119073
C	0.653732	-0.723654	-1.532380
C	1.794503	-1.148610	-2.197573
N	-1.363841	-0.976635	-0.461492
C	-0.872576	0.443997	-0.008368
O	-0.353490	0.419533	1.190090
C	0.199376	0.666829	-1.191356
C	1.240798	1.689366	-0.835650
C	1.088413	2.997954	-1.036022
C	4.864065	1.217832	-0.237373
C	3.672031	1.654709	-0.740816
N	2.482039	1.217141	-0.251867
C	2.460361	0.303106	0.756536
C	3.620107	-0.176291	1.303031
C	4.886530	0.265937	0.825540
N	6.037010	-0.188599	1.337443
C	6.019961	-1.162049	2.424711
C	7.312906	0.297566	0.823535
O	-3.143624	-0.787780	0.864124
C	-4.481280	-1.127120	1.320678
C	-4.947431	0.175631	1.961168
C	-4.420560	-2.247411	2.353818
C	-5.376704	-1.480509	0.136229
C	-2.429862	-1.623246	0.102076
O	-2.708527	-2.800712	-0.087613
C	-2.009687	1.462413	-0.206069

C	-2.872752	1.440457	-1.307603
C	-3.855475	2.416780	-1.461315
C	-3.979166	3.443008	-0.519541
C	-3.114704	3.476579	0.573682
C	-2.138269	2.488535	0.727693
H	2.863362	-2.857899	-2.972237
H	1.135059	-4.481783	-2.249736
H	-0.909228	-3.723966	-1.073599
H	2.541689	-0.426856	-2.521350
H	-0.336213	1.071070	-2.058289
H	1.826604	3.722223	-0.706026
H	0.194344	3.364563	-1.529842
H	5.774557	1.601545	-0.676755
H	3.619755	2.353205	-1.567275
H	1.448305	0.041286	1.097386
H	3.539042	-0.895417	2.107145
H	5.510706	-2.080655	2.115851
H	7.045888	-1.405649	2.694007
H	5.513781	-0.753768	3.305586
H	7.408815	0.085388	-0.246117
H	7.413750	1.376269	0.984012
H	8.118553	-0.209208	1.350286
H	-4.954818	0.980477	1.217786
H	-5.957392	0.054925	2.364270
H	-4.273933	0.462722	2.774510
H	-4.092784	-3.183832	1.899434
H	-5.414574	-2.392979	2.789303
H	-3.728035	-1.979613	3.158241
H	-6.413320	-1.553201	0.480383
H	-5.322260	-0.691845	-0.622358
H	-5.090089	-2.431484	-0.315492
H	-2.788435	0.640206	-2.040715
H	-4.528178	2.377412	-2.314041
H	-4.743746	4.205386	-0.639319
H	-3.203364	4.269514	1.311765
H	-1.466677	2.480879	1.580791

INT2p

C	2.354466	-2.346738	-2.585516
C	1.679699	-3.254934	-1.769690
C	0.524295	-2.894502	-1.068863
C	0.045406	-1.586389	-1.200483
C	0.722275	-0.668390	-2.022072
C	1.868159	-1.040704	-2.709336
N	-1.057166	-0.969613	-0.595721
C	-1.426879	0.336757	-1.428090
O	-2.195606	0.066052	-2.433068
C	0.075077	0.686161	-1.952718
C	0.914011	1.728853	-1.240799
C	0.741918	3.043856	-1.371515
C	2.871452	-0.171382	1.283459
C	1.839274	0.307461	0.527257
N	2.017261	1.274201	-0.411095
C	3.265958	1.769801	-0.615893
C	4.345559	1.345016	0.105819
C	4.191754	0.334445	1.100558
N	5.227405	-0.119209	1.813938
C	6.563475	0.427297	1.598395
C	5.030313	-1.176227	2.801566
O	-3.078996	-0.954302	0.336994
C	-4.080355	-1.310191	1.327670
C	-5.066977	-0.151660	1.222897
C	-3.458521	-1.351949	2.720613
C	-4.752834	-2.627648	0.955692
C	-1.954502	-1.657311	0.178637
O	-1.744648	-2.754652	0.682248
C	-1.950551	1.421851	-0.467847
C	-1.556530	1.571432	0.866075
C	-2.037997	2.621770	1.645581
C	-2.924090	3.553668	1.099076
C	-3.328567	3.410471	-0.227277
C	-2.846188	2.349716	-0.998459
H	3.248135	-2.651128	-3.121636
H	2.053867	-4.270410	-1.672283
H	0.014137	-3.606543	-0.435077
H	2.383006	-0.316096	-3.336813
H	-0.125765	1.093849	-2.946437
H	1.340974	3.762447	-0.820731
H	-0.031735	3.420020	-2.032968
H	2.650112	-0.939231	2.012327
H	0.828337	-0.059745	0.651790
H	3.356953	2.510020	-1.401347
H	5.309626	1.780372	-0.119568
H	6.578811	1.504096	1.794485
H	7.255668	-0.059003	2.282490
H	6.898339	0.245097	0.571985
H	4.347655	-0.847892	3.592031
H	4.624704	-2.076655	2.329525
H	5.990978	-1.420707	3.249950

H	-5.478357	-0.093658	0.210697
H	-5.888743	-0.293179	1.931281
H	-4.563793	0.795649	1.445746
H	-2.755590	-2.181059	2.819904
H	-4.251923	-1.473926	3.464874
H	-2.938032	-0.410227	2.927051
H	-5.606927	-2.797648	1.619402
H	-5.120846	-2.582989	-0.074251
H	-4.059530	-3.465046	1.048842
H	-0.892060	0.842452	1.321686
H	-1.728398	2.708780	2.683976
H	-3.300406	4.373372	1.704519
H	-4.026288	4.121170	-0.662528
H	-3.166009	2.210193	-2.026596

INT3

C	-4.114387	1.811487	-1.835737
C	-3.507982	3.042722	-1.590266
C	-2.226268	3.128340	-1.047357
C	-1.490190	1.962276	-0.723110
C	-2.133329	0.711183	-0.971384
C	-3.409524	0.647327	-1.519450
N	-0.216958	1.877918	-0.205067
C	-2.179227	-1.772692	-0.356654
O	-2.091138	-2.773336	-1.047311
C	-1.334163	-0.531830	-0.643511
C	-0.293587	-0.829944	-1.698431
C	-0.399721	-0.619335	-3.003803
C	2.844077	-1.299587	0.189561
C	1.693844	-0.758486	-0.312694
N	0.911238	-1.453031	-1.183776
C	1.263583	-2.704819	-1.569164
C	2.401188	-3.304183	-1.104185
C	3.248719	-2.614841	-0.186783
N	4.363784	-3.173808	0.297673
C	4.744141	-4.523289	-0.106266
C	5.207588	-2.437013	1.233425
O	1.745992	2.558566	0.539341
C	2.760012	3.514202	0.913840
C	3.933918	2.627695	1.325155
C	2.306992	4.357609	2.105116
C	3.166530	4.384516	-0.275260
C	0.505414	2.966611	0.078953
O	0.234311	4.169691	-0.009142
C	-3.094034	-1.742943	0.831723
C	-3.973128	-2.817247	1.015587
C	-4.836302	-2.839933	2.106644
C	-4.823275	-1.789745	3.026695
C	-3.947561	-0.718335	2.851136
C	-3.087429	-0.690199	1.755571
H	-5.111505	1.753808	-2.260617
H	-4.039460	3.961652	-1.826519
H	-1.773480	4.094039	-0.867931
H	-3.867959	-0.323148	-1.704787
H	-0.790403	-0.313715	0.284730
H	0.407837	-0.872023	-3.684022
H	-1.302612	-0.176025	-3.410607
H	3.431565	-0.698321	0.870243
H	1.346885	0.248576	-0.071880
H	0.580974	-3.196118	-2.252604
H	2.625940	-4.306082	-1.443695
H	4.914341	-4.574305	-1.186694
H	5.665972	-4.794268	0.404456
H	3.967808	-5.244877	0.168197
H	5.592479	-1.521124	0.773146
H	4.648444	-2.174355	2.137260
H	6.049573	-3.066170	1.514394
H	4.254974	2.006787	0.482112
H	4.780211	3.242960	1.645652
H	3.645383	1.973328	2.154384
H	1.485957	5.019456	1.826923
H	3.145528	4.962212	2.467160
H	1.977189	3.705939	2.921570
H	4.052546	4.972424	-0.012436
H	3.418183	3.751480	-1.133231
H	2.361768	5.062640	-0.560851
H	-3.971059	-3.627511	0.293166
H	-5.519239	-3.673229	2.240370
H	-5.496574	-1.805626	3.878696
H	-3.936293	0.100302	3.563835
H	-2.420148	0.157085	1.628558

INT4

C	-4.508883	-0.052794	-1.730077
C	-4.680081	1.231267	-1.213202
C	-3.637077	1.846837	-0.524165
C	-2.419541	1.183629	-0.362490
C	-2.211970	-0.109698	-0.892793
C	-3.286225	-0.702191	-1.573786
N	-1.380120	1.758100	0.398836

C	-0.818213	-2.151209	-0.298881
O	0.162537	-2.912379	-0.488298
C	-0.908144	-0.807505	-0.759919
C	0.227400	-0.164001	-1.384070
C	0.232140	0.864891	-2.258367
C	3.081764	-1.128172	0.787082
C	1.854924	-0.711036	0.351635
N	1.550283	-0.624809	-0.963129
C	2.470360	-0.993290	-1.882445
C	3.717568	-1.431483	-1.526966
C	4.079158	-1.517434	-0.152678
N	5.287173	-1.949483	0.236914
C	6.269579	-2.369830	-0.755422
C	5.599814	-2.067561	1.656662
O	0.235583	3.173275	0.916297
C	0.966315	4.438153	0.907903
C	2.181944	4.130330	1.773903
C	0.126235	5.541203	1.543522
C	1.399090	4.782639	-0.513441
C	-0.920761	3.038201	0.239922
O	-1.481315	3.914698	-0.390904
C	-1.959482	-2.722109	0.518637
C	-2.297280	-4.067119	0.335593
C	-3.313768	-4.655107	1.086657
C	-3.989415	-3.908607	2.053271
C	-3.641736	-2.573119	2.261734
C	-2.638154	-1.983017	1.494727
H	-5.318111	-0.541925	-2.264167
H	-5.624808	1.752641	-1.335119
H	-3.762051	2.835786	-0.097435
H	-3.143598	-1.693857	-1.996030
H	-0.694107	1.096135	0.746333
H	1.157074	1.351413	-2.549375
H	-0.699310	1.245796	-2.662357
H	3.260720	-1.163758	1.853054
H	1.063265	-0.430328	1.036738
H	2.150913	-0.937477	-2.915795
H	4.398907	-1.723963	-2.314154
H	6.492682	-1.554821	-1.451065
H	7.188666	-2.646934	-0.242737
H	5.909195	-3.234850	-1.322965
H	5.531552	-1.094370	2.153470
H	4.917891	-2.768063	2.150526
H	6.617098	-2.439313	1.760998
H	2.762218	3.309234	1.341684
H	2.822828	5.014107	1.839068
H	1.872186	3.848100	2.784729
H	-0.728373	5.804009	0.918861
H	0.749552	6.430667	1.678892
H	-0.233212	5.222676	2.527409
H	2.068050	5.648439	-0.484621
H	1.944640	3.942346	-0.955261
H	0.542703	5.023101	-1.145072
H	-1.752213	-4.644659	-0.405480
H	-3.575967	-5.696434	0.922112
H	-4.777756	-4.365729	2.644278
H	-4.153333	-1.989456	3.021708
H	-2.376438	-0.941131	1.661407

INT5

C	-2.464529	-3.571632	-2.204050
C	-3.639427	-2.913916	-1.822526
C	-3.597188	-1.685108	-1.178153
C	-2.368886	-1.042359	-0.873597
C	-1.183298	-1.707716	-1.305632
C	-1.246472	-2.958445	-1.933838
N	-2.234750	0.096169	-0.116797
C	1.176750	-1.990285	-0.379877
O	2.228266	-2.265794	-0.935492
C	0.154758	-1.111952	-1.067684
C	0.497604	0.121065	-1.464536
C	-0.315409	1.099532	-2.243231
C	3.237914	1.402131	0.674173
C	2.020948	0.952577	0.243328
N	1.798516	0.630195	-1.056145
C	2.795553	0.766355	-1.965157
C	4.036446	1.212270	-1.609130
C	4.314038	1.549592	-0.250218
N	5.518481	1.983968	0.134447
C	6.591998	2.135855	-0.843275
C	5.766257	2.311774	1.535248
O	-2.940795	1.964762	0.850162
C	-3.780124	3.127122	1.004172
C	-3.107402	3.890149	2.143672
C	-5.199949	2.738027	1.416327
C	-3.773263	3.983706	-0.262166
C	-3.206539	1.013242	-0.113757
O	-4.206476	1.117631	-0.839035
C	0.849838	-2.516114	0.978163

C	1.637595	-3.542790	1.513114
C	1.375438	-4.025875	2.790516
C	0.331863	-3.477838	3.541393
C	-0.449067	-2.449624	3.013137
C	-0.197837	-1.968615	1.728946
H	-2.499919	-4.535523	-2.701480
H	-4.604657	-3.372700	-2.023098
H	-4.517002	-1.195142	-0.882550
H	-0.319119	-3.446419	-2.229449
H	0.279729	1.510303	-3.067170
H	-1.209426	0.624980	-2.648233
H	3.351503	1.642598	1.722483
H	1.173240	0.832887	0.909993
H	2.552504	0.481006	-2.982500
H	4.793266	1.285691	-2.378190
H	6.310990	2.853493	-1.620944
H	7.479421	2.504512	-0.333363
H	6.830480	1.175447	-1.311555
H	5.116599	3.129142	1.864707
H	5.596482	1.439192	2.173874
H	6.802357	2.625714	1.643207
H	-2.080027	4.153976	1.872504
H	-3.658161	4.810194	2.362304
H	-3.079677	3.276011	3.049414
H	-5.718921	2.227634	0.604500
H	-5.761509	3.637427	1.691574
H	-5.167078	2.075702	2.288357
H	-4.276699	4.936302	-0.064621
H	-2.741440	4.198971	-0.561947
H	-4.281615	3.475825	-1.082534
H	2.446004	-3.954257	0.916359
H	1.979709	-4.828195	3.202680
H	0.127357	-3.855343	4.539069
H	-1.259084	-2.023905	3.597240
H	-0.812001	-1.166975	1.318200
H	-0.622650	1.929560	-1.596636

INT6

C	3.233108	-2.601837	2.105020
C	2.156748	-3.459116	2.313295
C	0.943077	-3.247682	1.639279
C	0.859494	-2.178587	0.760498
C	1.947682	-1.303946	0.508594
C	3.138553	-1.526429	1.214831
N	-0.260065	-1.738653	0.000699
C	2.167661	0.819648	-0.984844
O	1.580243	1.687148	-1.692948
C	1.530476	-0.304842	-0.451264
C	0.087611	-0.563519	-0.817870
C	-0.110147	-0.830683	-2.309921
C	-2.089552	2.545245	-0.787216
C	-1.346312	1.474154	-1.214391
N	-0.780858	0.605959	-0.353750
C	-0.913125	0.815053	0.975353
C	-1.641702	1.854863	1.484035
C	-2.278105	2.776280	0.602361
N	-3.007465	3.804928	1.060109
C	-3.170386	4.008120	2.495001
C	-3.614527	4.742762	0.123463
O	-2.390824	-1.589092	-0.644070
C	-3.795676	-1.985223	-0.744683
C	-4.389792	-0.863372	-1.587540
C	-4.438050	-2.008727	0.637828
C	-3.908709	-3.322833	-1.466183
C	-1.507938	-2.314490	0.053902
O	-1.762778	-3.330832	0.674022
C	3.638604	1.024980	-0.721839
C	4.587566	0.148454	-1.256458
C	5.949328	0.370972	-1.052360
C	6.373058	1.466729	-0.298895
C	5.430225	2.346962	0.235163
C	4.069906	2.132200	0.014314
H	4.165447	-2.764506	2.638739
H	2.243729	-4.294064	3.001535
H	0.095745	-3.899232	1.800569
H	3.990544	-0.870050	1.078889
H	-1.160289	-0.925881	-2.592750
H	0.396622	-1.774919	-2.522017
H	0.371322	-0.042918	-2.891445
H	-2.512493	3.201868	-1.535323
H	-1.184230	1.296037	-2.267302
H	-0.411500	0.107416	1.626093
H	-1.708232	1.955672	2.558828
H	-2.204923	4.195035	2.977474
H	-3.812766	4.871799	2.655530
H	-3.637909	3.134772	2.961510
H	-4.322641	4.231905	-0.537798
H	-4.151579	5.502927	0.687215
H	-2.850289	5.235318	-0.487219

H	-3.887589	-0.803563	-2.558427
H	-5.453950	-1.050261	-1.756550
H	-4.279816	0.097922	-1.074872
H	-4.063245	-2.835659	1.242078
H	-5.520971	-2.118561	0.523624
H	-4.242812	-1.065689	1.159770
H	-4.964098	-3.533913	-1.664254
H	-3.381446	-3.281251	-2.424883
H	-3.496595	-4.135785	-0.866292
H	4.254587	-0.715326	-1.827468
H	6.678986	-0.312970	-1.476548
H	7.432738	1.636233	-0.131480
H	5.755528	3.202253	0.820684
H	3.333264	2.821153	0.419802

INT7

C	-2.164777	-2.060099	-0.982016
C	-3.360854	-2.577799	-0.481847
C	-4.189700	-1.720129	0.253637
C	-3.821053	-0.405431	0.495796
C	-2.597762	0.147583	0.017485
C	-1.791784	-0.737605	-0.753993
C	-2.294676	1.519486	0.317817
C	-1.091640	2.226954	0.115458
C	-0.875727	3.572154	-0.010185
C	1.514679	-0.219942	1.154628
C	0.383331	0.547660	1.114376
N	0.144084	1.421426	0.108191
C	1.042105	1.540531	-0.896889
C	2.194434	0.801407	-0.932434
C	2.482182	-0.123422	0.112562
N	3.599083	-0.864168	0.113049
C	4.557228	-0.742804	-0.979606
C	3.855614	-1.804688	1.198216
H	-1.512020	-2.691548	-1.580883
H	-3.646821	-3.607822	-0.669516
H	-5.135893	-2.085589	0.646146
H	-0.876041	-0.380049	-1.214967
H	-3.120017	2.122163	0.687433
H	0.117912	3.995262	0.091091
H	-1.718655	4.245996	-0.113996
H	1.644514	-0.894129	1.990294
H	-0.382989	0.500959	1.879662
H	0.778125	2.244304	-1.677189
H	2.862392	0.934418	-1.772814
H	4.946193	0.278515	-1.046275
H	5.388653	-1.419360	-0.793069
H	4.095356	-1.011744	-1.935516
H	3.912140	-1.284324	2.159962
H	3.069795	-2.565559	1.250192
H	4.807313	-2.299773	1.015271
H	-4.481727	0.234337	1.077472

INT8

C	-3.509475	0.929804	0.869551
C	-2.963920	0.000004	0.000013
C	-3.509504	-0.929793	-0.869510
C	0.568056	1.184108	-0.246424
C	-0.801665	1.143476	-0.235223
N	-1.483634	-0.000001	-0.000008
C	-0.801667	-1.143480	0.235202
C	0.568054	-1.184121	0.246374
C	1.319058	-0.000012	-0.000049
N	2.661408	-0.000018	-0.000084
C	3.392559	-1.239434	0.233481
C	3.392549	1.239452	-0.233392
H	-4.582253	1.086886	0.883497
H	-2.908437	-1.378951	-1.652220
H	-4.582282	-1.086870	-0.883426
H	1.051036	2.128377	-0.458966
H	-1.413949	2.017058	-0.424310
H	-1.413953	-2.017054	0.424319
H	1.051032	-2.128385	0.458940
H	3.126470	-1.995809	-0.512324
H	4.459130	-1.037848	0.155716
H	3.183669	-1.636809	1.232634
H	3.183406	1.637183	-1.232345
H	3.126693	1.995581	0.512752
H	4.459133	1.037789	-0.156007
H	-2.908385	1.378958	1.652245

INT9

C	-2.692383	0.853485	0.310172
C	-1.580799	1.739830	0.275278
C	-1.564630	3.094365	0.357779
C	1.339452	-0.414476	1.061790
C	0.103321	0.169099	1.084056
N	-0.258265	1.114731	0.186640
C	0.602938	1.466807	-0.793855
C	1.850890	0.912115	-0.896688
C	2.277806	-0.062068	0.049950

N	3.495535	-0.621292	-0.010391
C	4.416686	-0.254972	-1.079404
C	3.893776	-1.618009	0.976667
H	-3.641163	1.266352	0.630322
H	-0.635671	3.641310	0.473829
H	-2.497187	3.647505	0.359039
H	1.570127	-1.152436	1.817812
H	-0.646635	-0.081561	1.824852
H	0.237095	2.204825	-1.497235
H	2.485598	1.229201	-1.713030
H	4.659759	0.812170	-1.038163
H	5.335871	-0.825191	-0.960647
H	3.987817	-0.484761	-2.060520
H	3.852255	-1.202665	1.988958
H	3.246155	-2.499994	0.927019
H	4.917524	-1.924673	0.771096
C	-2.678395	-0.480221	-0.157976
O	-1.740665	-1.131181	-0.642597
O	-3.913373	-1.080921	-0.015365
C	-3.999135	-2.420554	-0.475369
H	-3.319124	-3.076712	0.076136
H	-5.030769	-2.731136	-0.301643
H	-3.767394	-2.491902	-1.542274

INT3NH

C	-4.287400	1.947273	-1.382824
C	-3.995032	3.169861	-0.782462
C	-2.843927	3.304882	-0.008452
C	-1.985972	2.221593	0.158352
C	-2.268921	0.984471	-0.445186
C	-3.427290	0.862374	-1.214177
N	-0.791551	2.375894	0.918225
C	-1.871936	-1.528386	-0.629329
O	-1.495664	-2.137058	-1.614098
C	-1.271695	-0.151911	-0.299690
C	-0.031459	0.080792	-1.135725
C	0.108022	0.937815	-2.139928
C	2.749498	-1.469460	0.762455
C	1.672249	-0.700679	0.428182
N	1.084276	-0.781485	-0.796462
C	1.576504	-1.649277	-1.720097
C	2.655833	-2.443249	-1.458390
C	3.298266	-2.387970	-0.185098
N	4.353349	-3.151622	0.103492
C	4.891505	-4.068292	-0.898864
C	4.992280	-3.061321	1.413998
O	1.399471	2.654168	1.100570
C	2.728979	3.148447	0.732246
C	3.623036	2.520949	1.793625
C	2.772047	4.669253	0.823923
C	3.104721	2.636959	-0.654708
C	0.314916	2.987182	0.379850
O	0.295023	3.713563	-0.592797
C	-2.900496	-2.099701	0.292054
C	-3.496639	-3.317035	-0.062118
C	-4.460775	-3.890050	0.759829
C	-4.836288	-3.251526	1.943677
C	-4.246694	-2.039564	2.302383
C	-3.282726	-1.462264	1.479426
H	-5.182071	1.834390	-1.986759
H	-4.660749	4.017024	-0.912985
H	-2.595569	4.247725	0.468742
H	-3.661730	-0.081423	-1.700324
H	-0.957661	-0.209365	0.751420
H	1.048938	1.022349	-2.675197
H	-0.715765	1.573789	-2.444248
H	3.173700	-1.350713	1.750383
H	1.258219	0.031034	1.115765
H	1.048905	-1.674729	-2.665343
H	2.995593	-3.113135	-2.236125
H	5.229651	-3.520052	-1.784043
H	5.739765	-4.596288	-0.469468
H	4.136276	-4.801766	-1.197400
H	5.388241	-2.054834	1.583382
H	4.281670	-3.306961	2.208872
H	5.815328	-3.771659	1.452565
H	3.554805	1.428630	1.754688
H	4.662839	2.810670	1.619342
H	3.328956	2.857140	2.792349
H	2.165820	5.135425	0.046093
H	3.807953	5.002579	0.708193
H	2.414417	4.999359	1.804422
H	4.149505	2.892004	-0.857371
H	3.007106	1.545475	-0.697308
H	2.478501	3.083542	-1.428578
H	-3.196171	-3.801583	-0.985585
H	-4.921391	-4.832036	0.479354
H	-5.589884	-3.697994	2.585345
H	-4.539611	-1.540757	3.220698

H	-2.842377	-0.513905	1.772050
H	-0.620017	1.734181	1.683190

INT3CH

C	-4.583952	-1.981367	-1.295209
C	-3.917163	-3.183918	-1.054561
C	-2.535610	-3.215509	-0.843426
C	-1.853806	-2.009165	-0.867993
C	-2.511051	-0.802753	-1.113282
C	-3.881522	-0.772577	-1.327835
N	-0.441554	-1.797938	-0.712425
C	-1.540275	0.889198	0.342267
O	-0.840918	0.401725	1.212967
C	-1.488355	0.324709	-1.081002
C	-0.217227	-0.495752	-1.429945
C	-0.220245	-0.766355	-2.943554
C	2.400835	2.076023	-0.659434
C	1.191454	1.455864	-0.798345
N	1.081333	0.147118	-1.135762
C	2.218435	-0.552451	-1.409834
C	3.459192	-0.000377	-1.307690
C	3.609823	1.354679	-0.885672
N	4.809454	1.914062	-0.719658
C	6.023581	1.137754	-0.960520
C	4.918322	3.312339	-0.310918
O	1.276213	-1.703447	0.784304
C	1.945825	-1.971799	2.067431
C	3.246908	-1.190596	1.936297
C	2.232118	-3.462233	2.208011
C	1.110842	-1.421053	3.216289
C	0.066529	-2.191271	0.541280
O	-0.538971	-2.964122	1.251727
C	-2.497612	1.995373	0.644581
C	-2.622623	2.397767	1.982075
C	-3.492690	3.424958	2.326117
C	-4.245514	4.062061	1.336551
C	-4.126202	3.668149	0.004641
C	-3.255047	2.637630	-0.343646
H	-5.656290	-1.983519	-1.462301
H	-4.477425	-4.113471	-1.035989
H	-2.013286	-4.147122	-0.659704
H	-4.398263	0.164095	-1.514742
H	-0.043754	0.175347	-3.470575
H	0.567898	-1.474321	-3.205114
H	2.402956	3.121312	-0.382355
H	0.278829	2.018200	-0.660624
H	2.086987	-1.587250	-1.701884
H	4.313303	-0.623833	-1.535664
H	6.088693	0.830311	-2.009139
H	6.886621	1.755952	-0.722806
H	6.044446	0.248529	-0.322887
H	4.459285	3.971438	-1.054374
H	4.434473	3.470533	0.657905
H	5.971544	3.569205	-0.220761
H	3.041063	-0.131821	1.745358
H	3.815244	-1.274607	2.866774
H	3.856745	-1.585945	1.118358
H	1.319327	-4.034638	2.375041
H	2.902198	-3.612884	3.060068
H	2.733358	-3.838391	1.310195
H	1.683260	-1.523087	4.143491
H	0.894455	-0.362098	3.051509
H	0.169776	-1.961637	3.325756
H	-2.034206	1.891170	2.740291
H	-3.587961	3.729360	3.363620
H	-4.925872	4.864487	1.605098
H	-4.711398	4.161489	-0.764803
H	-3.182613	2.343391	-1.385309
H	-1.175158	-1.180522	-3.268319
H	-1.669263	1.088416	-1.839229

INT4CH

C	-2.409413	-3.863422	-1.769930
C	-3.577520	-3.103221	-1.770931
C	-3.539216	-1.737751	-1.506450
C	-2.319724	-1.106376	-1.230689
C	-1.127818	-1.863432	-1.248946
C	-1.196145	-3.237442	-1.508199
N	-2.250047	0.266912	-0.940712
C	0.998733	-1.937231	0.161394
O	2.075589	-2.446126	-0.093891
C	0.209660	-1.276666	-0.958044
C	0.772494	-0.309415	-1.698946
C	0.226648	0.318108	-2.942014
C	3.324239	1.293238	0.451600
C	2.135039	0.837542	-0.036380
N	2.038833	0.238250	-1.254495
C	3.150750	0.107462	-2.026766
C	4.372843	0.542402	-1.605839
C	4.518440	1.147122	-0.319132

N	5.703140	1.553016	0.136470
C	6.899354	1.405995	-0.689914
C	5.818957	2.126832	1.475452
O	-2.728043	2.250873	-0.113030
C	-3.547536	3.297884	0.508361
C	-2.577204	4.467836	0.604205
C	-3.990297	2.853578	1.897656
C	-4.723268	3.649159	-0.395899
C	-3.239174	1.038628	-0.372650
O	-4.375094	0.675519	-0.147521
C	0.417417	-1.972915	1.532570
C	0.997166	-2.822400	2.483370
C	0.496833	-2.858010	3.780125
C	-0.577641	-2.039062	4.136495
C	-1.153357	-1.186214	3.194762
C	-0.660184	-1.155572	1.892445
H	-2.440848	-4.928501	-1.973609
H	-4.533890	-3.572181	-1.980827
H	-4.450867	-1.156125	-1.504884
H	-0.275739	-3.816289	-1.510137
H	-1.339199	0.706008	-0.955408
H	0.025048	1.383578	-2.779995
H	0.959198	0.246834	-3.753018
H	3.328713	1.763284	1.425658
H	1.208438	0.931166	0.520563
H	3.015655	-0.388184	-2.981071
H	5.220221	0.395738	-2.261549
H	6.786427	1.951642	-1.631531
H	7.749880	1.816536	-0.150172
H	7.093562	0.350648	-0.905972
H	5.248796	3.058097	1.549417
H	5.456328	1.420848	2.228693
H	6.866694	2.340835	1.674113
H	-2.227830	4.760809	-0.390364
H	-3.078980	5.323924	1.063276
H	-1.712039	4.201019	1.218837
H	-4.704729	2.030559	1.848264
H	-4.465710	3.698265	2.405381
H	-3.123129	2.543626	2.490196
H	-5.219962	4.539880	0.000696
H	-4.369291	3.877065	-1.406389
H	-5.450532	2.837640	-0.444803
H	1.832440	-3.451241	2.191222
H	0.940182	-3.523584	4.514001
H	-0.967873	-2.068641	5.149312
H	-1.988971	-0.550925	3.471093
H	-1.118130	-0.490550	1.164980
H	-0.687412	-0.181095	-3.265535
H2O			
O	0.000000	-0.000000	0.116929
H	0.000000	0.767276	-0.467716
H	-0.000000	-0.767276	-0.467716
OH-			
O	-0.000000	-0.000000	0.107232
H	0.000000	0.000000	-0.857855
9			
C	1.527385	1.451218	-0.000014
C	2.599453	0.554705	0.000020
C	2.349165	-0.816561	0.000048
C	1.037047	-1.288548	0.000003
C	-0.043015	-0.396876	-0.000041
C	0.218105	0.981423	-0.000039
C	-1.419011	-0.936272	-0.000047
C	-2.514983	-0.210538	0.000017
C	-3.601545	0.514762	0.000065
H	1.714269	2.521111	-0.000019
H	3.620268	0.924520	0.000038
H	3.175023	-1.521887	0.000098
H	-0.611687	1.683744	-0.000061
H	-1.518331	-2.021374	-0.000172
H	-4.069236	0.826080	0.931912
H	-4.069049	0.826156	-0.931883
H	0.843132	-2.358226	0.000016
15			
C	1.308006	-0.000009	0.000027
H	1.867131	-0.659861	0.658616
H	1.867317	0.659687	-0.658554
C	0.000000	0.000047	-0.000036
C	-1.308006	0.000057	-0.000063
H	-1.867236	0.659275	0.659071
H	-1.867217	-0.659668	-0.658703
16			
C	0.858560	0.992822	0.000020
C	1.856354	0.137677	-0.000233
C	2.854286	-0.698532	0.000065
H	1.037666	2.064244	0.000118
H	3.277721	-1.058424	0.934610
H	3.278125	-1.058662	-0.934204

C	-0.565191	0.582314	0.000033
O	-1.482511	1.377225	0.000008
O	-0.736575	-0.743505	0.000071
C	-2.097593	-1.192062	-0.000042
H	-2.615879	-0.835344	-0.892713
H	-2.047357	-2.279674	0.000043
H	-2.616083	-0.835212	0.892458

TS1

C	3.032331	4.445854	0.730506
C	3.930311	3.478358	1.188937
C	3.600222	2.134101	1.044170
C	2.401921	1.766965	0.441124
C	1.486593	2.721046	-0.051060
C	1.841637	4.074643	0.117625
N	2.071443	0.365855	0.358772
C	1.058578	-0.107248	1.218080
O	0.787662	0.504586	2.233743
C	0.252232	2.292302	-0.701113
C	-0.809525	3.091307	-0.938274
C	-1.303973	4.260282	-1.336491
C	-4.538478	1.096208	-1.069201
C	-3.495663	1.985792	-1.241662
N	-2.398049	1.976863	-0.482242
C	-2.297184	1.067474	0.490118
C	-3.278398	0.132927	0.753538
C	-4.453962	0.117713	-0.042838
N	-5.440388	-0.786097	0.164221
C	-5.297686	-1.787220	1.209433
C	-6.638502	-0.758232	-0.659427
O	2.847883	-1.713006	0.009740
C	3.468717	-2.812353	-0.740121
C	2.980305	-4.038173	0.020336
C	4.984223	-2.680237	-0.661655
C	2.962271	-2.839037	-2.177581
C	2.896774	-0.457499	-0.422564
O	3.581058	-0.029738	-1.325153
C	0.231682	-1.281125	0.793014
C	-0.051930	-1.541640	-0.551029
C	-0.929484	-2.568165	-0.890121
C	-1.512330	-3.348785	0.109880
C	-1.225013	-3.093354	1.451787
C	-0.365444	-2.051638	1.793640
H	3.269240	5.500578	0.838805
H	4.866223	3.765583	1.656993
H	4.265201	1.354918	1.408235
H	1.167679	4.839042	-0.257164
H	0.169429	1.243804	-0.968504
H	-2.246443	4.652492	-0.967716
H	-0.742626	4.850735	-2.055644
H	-5.394795	1.152201	-1.729100
H	-3.521927	2.739949	-2.027666
H	-1.378867	1.101083	1.075593
H	-3.128811	-0.573300	1.561028
H	-5.227786	-1.322187	2.199995
H	-6.169329	-2.439870	1.195354
H	-4.402328	-2.399552	1.048449
H	-7.149486	0.208323	-0.581136
H	-6.402239	-0.944329	-1.713787
H	-7.320437	-1.535124	-0.317148
H	1.886127	-4.087874	-0.001475
H	3.383262	-4.943801	-0.441573
H	3.309227	-4.000176	1.063097
H	5.334220	-1.802406	-1.208090
H	5.443886	-3.571777	-1.099395
H	5.304877	-2.605199	0.382085
H	3.344455	-3.742238	-2.662997
H	1.868751	-2.880409	-2.197216
H	3.302035	-1.971465	-2.745110
H	0.398489	-0.939580	-1.336329
H	-1.157469	-2.758245	-1.934556
H	-2.190950	-4.153707	-0.156969
H	-1.675647	-3.700107	2.231497
H	-0.149169	-1.830048	2.834240

TS2

C	1.817687	-3.080023	-1.645569
C	0.743540	-3.800972	-1.125967
C	-0.402972	-3.129477	-0.693240
C	-0.467054	-1.744143	-0.798583
C	0.590480	-0.989199	-1.361867
C	1.738027	-1.692526	-1.765668
N	-1.538218	-0.964779	-0.270192
C	-1.117809	0.225920	0.491673
O	-0.447820	0.055602	1.501515
C	0.385168	0.451991	-1.434796
C	1.352709	1.464074	-1.254957
C	1.258179	2.797589	-1.531895
C	4.967539	0.899140	-0.585852
C	3.792856	1.296979	-1.165256

N	2.591850	1.049533	-0.591315
C	2.536552	0.386279	0.589105
C	3.668911	-0.040032	1.228753
C	4.950731	0.199235	0.655504
N	6.078956	-0.215286	1.248273
C	6.016346	-0.941503	2.511947
C	7.371979	0.044254	0.625746
O	-3.489807	-0.733224	0.775481
C	-4.932635	-0.882893	0.954777
C	-5.257976	0.228720	1.944936
C	-5.243844	-2.250023	1.553341
C	-5.658796	-0.648382	-0.365573
C	-2.811611	-1.467762	-0.116822
O	-3.250559	-2.431354	-0.718704
C	-1.773139	1.525182	0.169737
C	-2.696233	1.678170	-0.875204
C	-3.270448	2.917963	-1.127734
C	-2.927479	4.026693	-0.345536
C	-1.998750	3.883995	0.681940
C	-1.421685	2.638457	0.938436
H	2.713280	-3.598581	-1.976201
H	0.796160	-4.881851	-1.038905
H	-1.231132	-3.678842	-0.260839
H	2.564760	-1.143235	-2.209918
H	-0.531359	0.782050	-1.908375
H	2.010250	3.498816	-1.188837
H	0.398290	3.176365	-2.073987
H	5.891947	1.120655	-1.101857
H	3.761999	1.814217	-2.116647
H	1.542341	0.220777	0.994586
H	3.554299	-0.558172	2.171136
H	7.028845	-1.186414	2.826104
H	5.547137	-0.330535	3.290033
H	5.449572	-1.871609	2.399279
H	7.427937	-0.417398	-0.365752
H	7.550488	1.120408	0.528456
H	8.154327	-0.381884	1.250731
H	-4.984975	1.203180	1.526844
H	-6.329474	0.227450	2.164531
H	-4.708041	0.082985	2.879559
H	-5.039169	-3.051348	0.841669
H	-6.301786	-2.286693	1.831830
H	-4.645668	-2.411335	2.455827
H	-6.737488	-0.645272	-0.180263

H	-5.381873	0.325502	-0.782414
H	-5.433213	-1.429801	-1.093267
H	-2.961980	0.826033	-1.494939
H	-3.989667	3.022507	-1.934971
H	-3.379744	4.993798	-0.544089
H	-1.718959	4.741038	1.287372
H	-0.701376	2.516495	1.741339

TS2p

C	-2.303145	-1.519183	3.178231
C	-1.491632	-2.586062	2.792184
C	-0.315251	-2.358232	2.080647
C	0.040360	-1.050115	1.744073
C	-0.742554	0.051753	2.153317
C	-1.918679	-0.215392	2.865737
N	1.188743	-0.729898	0.970929
C	1.867291	0.511949	1.348585
O	2.334716	0.590980	2.479391
C	-0.303709	1.406065	1.742477
C	-1.016337	2.174183	0.794055
C	-0.839218	3.472026	0.406524
C	-2.749132	-0.425424	-1.235493
C	-1.781813	0.309244	-0.605221
N	-2.066143	1.450452	0.065663
C	-3.348384	1.879387	0.129807
C	-4.372346	1.201207	-0.475335
C	-4.108506	-0.001744	-1.191794
N	-5.086214	-0.699683	-1.785823
C	-6.466914	-0.236787	-1.709561
C	-4.779254	-1.943742	-2.482886
O	3.031965	-1.257775	-0.161693
C	3.819246	-1.901282	-1.213417
C	5.088516	-1.058838	-1.233490
C	3.099771	-1.809154	-2.554993
C	4.127234	-3.341180	-0.819023
C	1.776245	-1.630213	0.103054
O	1.219311	-2.613383	-0.352278
C	2.213991	1.480871	0.267820
C	1.786858	1.357382	-1.059716
C	2.167246	2.294930	-2.016255
C	2.971404	3.379907	-1.660394
C	3.380680	3.522646	-0.335197
C	3.005614	2.579625	0.621364
H	-3.220737	-1.700561	3.730209
H	-1.770095	-3.604822	3.045502

H	0.306309	-3.189535	1.771538
H	-2.536200	0.623515	3.178096
H	0.350043	1.970172	2.397649
H	-1.383659	3.887205	-0.433613
H	-0.125391	4.099289	0.929201
H	-2.448125	-1.326188	-1.753411
H	-0.740716	0.012137	-0.610143
H	-3.511825	2.784743	0.702049
H	-5.374587	1.595499	-0.376256
H	-6.570643	0.756650	-2.158037
H	-7.099724	-0.932458	-2.256663
H	-6.809422	-0.195741	-0.670191
H	-4.082726	-1.766649	-3.308846
H	-4.340343	-2.676923	-1.798058
H	-5.701752	-2.353760	-2.889374
H	5.586119	-1.091839	-0.259712
H	5.776186	-1.442893	-1.992334
H	4.849106	-0.016596	-1.468976
H	2.182732	-2.400752	-2.562399
H	3.765127	-2.188283	-3.336964
H	2.862146	-0.766053	-2.787354
H	4.844451	-3.761960	-1.530770
H	4.575970	-3.371085	0.178881
H	3.225449	-3.955740	-0.823458
H	1.169861	0.516434	-1.362255
H	1.835635	2.175949	-3.043961
H	3.267380	4.109657	-2.407991
H	3.999732	4.366256	-0.043792
H	3.331561	2.676698	1.652075

TS3p

C	2.609300	0.123382	3.427091
C	2.429418	1.385278	2.862022
C	1.415559	1.634091	1.931271
C	0.565169	0.587558	1.536118
C	0.792831	-0.699151	2.072805
C	1.780240	-0.927130	3.018481
N	-0.517018	0.604107	0.658545
C	-1.474512	-0.982561	1.210139
O	-2.093501	-0.713475	2.259714
C	-0.095257	-1.729749	1.435646
C	0.559829	-2.340031	0.204781
C	0.224381	-3.495512	-0.360858
C	2.447563	0.000070	-1.980048
C	1.456293	-0.789544	-1.466272
N	1.661453	-1.594364	-0.395554
C	2.895095	-1.646922	0.170900
C	3.933495	-0.884026	-0.282520
C	3.739351	0.008903	-1.378169
N	4.721459	0.800410	-1.823383
C	6.023624	0.795869	-1.164120
C	4.489513	1.690636	-2.956389
O	-2.326026	1.528053	-0.238933
C	-3.318135	2.559997	-0.458311
C	-4.430333	1.804860	-1.181142
C	-2.768683	3.668264	-1.353859
C	-3.828842	3.100103	0.874943
C	-1.182746	1.771314	0.443243
O	-0.841375	2.903600	0.778864
C	-2.292585	-1.468548	0.019185
C	-2.117721	-1.097215	-1.315495
C	-2.873686	-1.688507	-2.326022
C	-3.822869	-2.665529	-2.018115
C	-4.017627	-3.033021	-0.687779
C	-3.259328	-2.434242	0.320111
H	3.383738	-0.043547	4.169565
H	3.076667	2.205721	3.161508
H	1.273276	2.627659	1.529001
H	1.912796	-1.926924	3.427327
H	-0.330178	-2.551663	2.119738
H	0.743054	-3.868356	-1.239038
H	-0.592681	-4.083969	0.046095
H	2.212763	0.617212	-2.836443
H	0.462249	-0.815087	-1.889952
H	3.005890	-2.335809	0.998814
H	4.889767	-0.977210	0.213894
H	6.500689	-0.186384	-1.246318
H	6.661712	1.534241	-1.645133
H	5.922436	1.057552	-0.105944
H	4.221463	1.119537	-3.851220
H	3.688750	2.403108	-2.733675
H	5.403512	2.244744	-3.159675
H	-4.783560	0.968714	-0.569061
H	-5.270907	2.475832	-1.382632
H	-4.065551	1.405347	-2.133014
H	-2.002183	4.249405	-0.840035
H	-3.586156	4.335900	-1.645986
H	-2.338761	3.236950	-2.264493
H	-4.686304	3.757189	0.696093

H	-4.154476	2.271971	1.512824
H	-3.054570	3.664976	1.396517
H	-1.423103	-0.301399	-1.553137
H	-2.732443	-1.374845	-3.357020
H	-4.412274	-3.124644	-2.806593
H	-4.761573	-3.782019	-0.431098
H	-3.414086	-2.712514	1.358854

TS4

C	-4.221439	-1.302884	-2.305301
C	-4.539992	0.050977	-2.212163
C	-3.649075	0.975742	-1.656419
C	-2.405173	0.529247	-1.193751
C	-2.070168	-0.852513	-1.302078
C	-2.975713	-1.751465	-1.846149
N	-1.384511	1.228353	-0.577268
C	-0.533593	-2.198853	0.248668
O	0.409741	-2.994287	0.246404
C	-0.692180	-1.155911	-0.777011
C	0.377950	-1.151622	-1.803482
C	0.260632	-1.190629	-3.132288
C	3.269958	0.241795	0.054885
C	2.025920	0.072997	-0.487060
N	1.724546	-1.000825	-1.260020
C	2.670899	-1.938021	-1.503072
C	3.938084	-1.834407	-0.998861
C	4.292098	-0.724455	-0.178338
N	5.516767	-0.597029	0.347965
C	6.532461	-1.612586	0.092915
C	5.835190	0.544573	1.199229
O	-0.219604	2.860744	0.340503
C	0.032827	4.208874	0.813085
C	1.436362	4.105119	1.402490
C	-0.967012	4.591565	1.901573
C	0.026632	5.202868	-0.346363
C	-1.398014	2.535284	-0.269404
O	-2.289943	3.353182	-0.484436
C	-1.542375	-2.280078	1.363553
C	-1.747828	-3.518900	1.980082
C	-2.659588	-3.644063	3.025609
C	-3.361136	-2.524443	3.475729
C	-3.147905	-1.282715	2.875966
C	-2.247890	-1.160253	1.818658
H	-4.931340	-2.005101	-2.731587
H	-5.504289	0.401373	-2.571191
H	-3.909509	2.023675	-1.572868
H	-2.711877	-2.805029	-1.914572
H	-0.651405	0.115047	-0.316165
H	1.124287	-1.070164	-3.778925
H	-0.713049	-1.328879	-3.588949
H	3.448032	1.124387	0.653977
H	1.236059	0.804274	-0.339680
H	2.354286	-2.781835	-2.103247
H	4.642076	-2.623862	-1.223933
H	6.742850	-1.693677	-0.978626
H	7.448722	-1.328087	0.606019
H	6.210275	-2.589277	0.468757
H	5.723913	1.484642	0.648826
H	5.184292	0.567127	2.079422
H	6.867665	0.456616	1.531344
H	2.153767	3.814105	0.628198
H	1.743306	5.070646	1.815027
H	1.460901	3.359071	2.203185
H	-1.974222	4.692038	1.494701
H	-0.669827	5.545639	2.349004
H	-0.974438	3.831143	2.689700
H	0.389988	6.173290	0.007592
H	0.695491	4.856638	-1.141568
H	-0.976082	5.328415	-0.756322
H	-1.187502	-4.379312	1.626690
H	-2.822372	-4.612066	3.490263
H	-4.070624	-2.618844	4.292652
H	-3.684434	-0.407293	3.229334
H	-2.083693	-0.186759	1.364211

TS5

C	2.722111	3.370153	-1.972232
C	3.836214	2.562730	-1.712847
C	3.673181	1.268869	-1.240960
C	2.388156	0.738289	-0.985259
C	1.251081	1.543178	-1.281247
C	1.453358	2.851089	-1.760905
N	2.156661	-0.545875	-0.514095
C	-1.110686	2.035618	-0.461200
O	-2.278105	2.107441	-0.835209
C	-0.138752	1.081273	-1.061185
C	-0.559930	-0.155052	-1.490078
C	0.233051	-1.112012	-2.203220
C	-3.294483	-1.125697	0.823475
C	-2.090847	-0.701577	0.334737

N	-1.837310	-0.645218	-0.996005
C	-2.790746	-1.039428	-1.875158
C	-4.019977	-1.470572	-1.463072
C	-4.331111	-1.521184	-0.071575
N	-5.527452	-1.925146	0.370685
C	-6.566025	-2.319447	-0.575590
C	-5.802417	-1.969707	1.803422
O	2.658769	-2.567274	0.220615
C	3.428392	-3.570901	0.929427
C	2.580363	-4.828872	0.765367
C	3.551366	-3.214266	2.409404
C	4.793128	-3.774192	0.274598
C	3.089017	-1.275254	0.138309
O	4.146599	-0.898709	0.637620
C	-0.650578	2.920173	0.664027
C	-1.320372	4.128217	0.885046
C	-0.952584	4.950415	1.946686
C	0.074671	4.558773	2.807598
C	0.734787	3.346659	2.601735
C	0.380716	2.532563	1.527576
H	2.845517	4.383570	-2.341483
H	4.838777	2.946716	-1.881103
H	4.538678	0.652056	-1.032726
H	0.582275	3.466265	-1.978672
H	1.226056	-1.140125	-1.305988
H	0.783353	-0.703650	-3.054198
H	-0.246743	-2.066943	-2.407653
H	-3.428032	-1.153763	1.896144
H	-1.276339	-0.397664	0.983141
H	-2.522116	-0.972594	-2.923028
H	-4.738549	-1.759441	-2.217902
H	-6.248496	-3.185871	-1.164976
H	-7.462827	-2.585992	-0.020164
H	-6.807513	-1.494212	-1.252935
H	-5.112988	-2.652530	2.310507
H	-5.711001	-0.973709	2.248663
H	-6.819108	-2.326821	1.953331
H	2.458855	-5.072145	-0.294762
H	3.062105	-5.674431	1.265164
H	1.588685	-4.681602	1.204565
H	4.183821	-2.337698	2.555410
H	3.987610	-4.060035	2.951048
H	2.560472	-3.013468	2.830758
H	5.280026	-4.649636	0.716841
H	4.670925	-3.956671	-0.798367
H	5.434999	-2.903924	0.415902
H	-2.124363	4.414483	0.213518
H	-1.465572	5.894284	2.105117
H	0.360577	5.197837	3.637903
H	1.530361	3.037546	3.272697
H	0.902651	1.593132	1.363675

TS6

C	-4.308858	2.351914	-0.635380
C	-3.615524	3.301971	0.113919
C	-2.252043	3.156292	0.384748
C	-1.549563	2.043649	-0.105510
C	-2.273911	1.053154	-0.848518
C	-3.628497	1.228748	-1.114658
N	-0.218583	1.742869	0.078677
C	-1.868635	-1.505373	-0.812673
O	-1.276219	-2.499891	-1.253871
C	-1.465005	-0.146206	-1.139960
C	-0.136572	0.184930	-1.403760
C	0.303621	1.160749	-2.456338
C	1.843733	-1.971545	0.824868
C	0.910343	-1.105279	0.336147
N	0.897384	-0.720296	-0.966999
C	1.862109	-1.177764	-1.805200
C	2.829422	-2.045986	-1.387998
C	2.857329	-2.492135	-0.032632
N	3.791785	-3.337616	0.412421
C	4.831568	-3.825696	-0.488154
C	3.773588	-3.786878	1.801454
O	1.944015	1.978972	0.390870
C	3.177590	2.681104	0.665241
C	4.223639	1.572661	0.577376
C	3.165374	3.277575	2.071404
C	3.449965	3.741238	-0.400262
C	0.734717	2.632352	0.372492
O	0.636018	3.842514	0.590990
C	-3.071919	-1.739157	0.065239
C	-3.932657	-2.797407	-0.241849
C	-5.020809	-3.082852	0.580793
C	-5.238482	-2.328700	1.734852
C	-4.367905	-1.287409	2.060462
C	-3.295150	-0.985995	1.223522
H	-5.365621	2.481974	-0.847657
H	-4.135831	4.180919	0.485985

H	-1.717256	3.905698	0.956223
H	-4.159304	0.473122	-1.688957
H	0.394098	0.641824	-3.419106
H	-0.457127	1.932345	-2.576334
H	1.804747	-2.222210	1.876117
H	0.148439	-0.650064	0.956891
H	1.812547	-0.841549	-2.832301
H	3.556542	-2.384134	-2.113555
H	5.403878	-2.992310	-0.907487
H	5.509967	-4.463977	0.073954
H	4.396818	-4.409285	-1.306139
H	3.916485	-2.944190	2.485947
H	2.825806	-4.281400	2.035643
H	4.582870	-4.498913	1.949075
H	4.206496	1.112196	-0.416376
H	5.223553	1.978998	0.757187
H	4.021144	0.796989	1.323386
H	2.448387	4.096177	2.146113
H	4.163495	3.655602	2.316517
H	2.902104	2.506376	2.803303
H	4.454562	4.153226	-0.257814
H	3.404059	3.291968	-1.398465
H	2.723131	4.552589	-0.342990
H	-3.741431	-3.389830	-1.131960
H	-5.694697	-3.895455	0.325886
H	-6.082641	-2.553309	2.380274
H	-4.528194	-0.704739	2.962651
H	-2.628038	-0.165213	1.473950
H	1.261587	1.621358	-2.200320

TS7

C	2.886413	-1.610623	2.915667
C	1.793976	-2.414428	3.242708
C	0.702206	-2.518535	2.373134
C	0.754261	-1.812814	1.177754
C	1.855836	-1.007246	0.811704
C	2.923267	-0.899924	1.714321
N	-0.222735	-1.699858	0.150155
C	2.295411	0.563399	-1.224220
O	1.791250	1.313236	-2.080534
C	1.545555	-0.388272	-0.466281
C	0.193661	-0.742580	-0.821654
C	-0.168241	-0.974717	-2.267813
C	-2.747710	2.260519	-0.699329
C	-1.986802	1.173844	-1.079202
N	-0.883046	0.789949	-0.425171
C	-0.497442	1.502112	0.640301
C	-1.192230	2.595800	1.110803
C	-2.370774	3.017141	0.440964
N	-3.089736	4.080167	0.863271
C	-2.666176	4.822074	2.041329
C	-4.283840	4.486330	0.138045
O	-2.346361	-1.802317	-0.597552
C	-3.665675	-2.423284	-0.789811
C	-4.312685	-1.519527	-1.831570
C	-4.454474	-2.383100	0.513499
C	-3.499313	-3.836051	-1.337090
C	-1.448368	-2.354867	0.213942
O	-1.647576	-3.298393	0.951034
C	3.780065	0.675318	-0.989784
C	4.598531	-0.458328	-0.992177
C	5.978112	-0.328882	-0.839467
C	6.546021	0.933921	-0.662418
C	5.732792	2.068595	-0.659949
C	4.356234	1.939644	-0.838421
H	3.721877	-1.528986	3.605169
H	1.780738	-2.964237	4.178599
H	-0.150450	-3.134361	2.622815
H	3.774646	-0.265838	1.493850
H	-1.233328	-1.111157	-2.435411
H	0.342832	-1.890468	-2.583137
H	0.204929	-0.140035	-2.859374
H	-3.621809	2.513030	-1.285857
H	-2.273069	0.587161	-1.945044
H	0.420648	1.177072	1.123581
H	-0.816731	3.117207	1.981561
H	-1.672552	5.261479	1.897035
H	-3.375852	5.626995	2.224718
H	-2.638677	4.175715	2.925868
H	-5.029633	3.683207	0.123776
H	-4.720158	5.352335	0.633167
H	-4.045202	4.762050	-0.895575
H	-3.711130	-1.489750	-2.745893
H	-5.304487	-1.905205	-2.082967
H	-4.424168	-0.502256	-1.444406
H	-4.039093	-3.063548	1.257509
H	-5.489414	-2.674472	0.309206
H	-4.458832	-1.366061	0.918986
H	-4.482837	-4.221536	-1.622285

H	-2.864848	-3.824935	-2.229620
H	-3.064463	-4.508388	-0.596301
H	4.151382	-1.442022	-1.113278
H	6.609256	-1.212662	-0.853312
H	7.619600	1.033938	-0.531739
H	6.172348	3.052678	-0.525522
H	3.716921	2.817947	-0.857383

TS8

C	-4.356208	0.470953	-1.847419
C	-4.477269	1.779485	-1.380770
C	-3.480423	2.316299	-0.571674
C	-2.358936	1.558733	-0.223970
C	-2.220240	0.234148	-0.689415
C	-3.235407	-0.282460	-1.506078
N	-1.353004	2.128322	0.591671
C	-1.130794	-2.048933	-0.469612
O	-0.371099	-2.747834	-1.135720
C	-0.977139	-0.566799	-0.375060
C	0.210273	-0.069210	-1.139955
C	0.248384	0.898834	-2.058534
C	3.131811	-1.307765	0.791398
C	1.929132	-0.736940	0.470628
N	1.482047	-0.701897	-0.810612
C	2.225874	-1.262657	-1.795976
C	3.436787	-1.846053	-1.547445
C	3.949473	-1.889910	-0.218408
N	5.130807	-2.455118	0.064587
C	5.927670	-3.059459	-0.997014
C	5.612057	-2.494996	1.441176
O	0.371124	3.436089	1.045260
C	1.390100	4.434348	0.758376
C	2.334144	4.307011	1.948848
C	0.782946	5.833929	0.714651
C	2.118576	4.077470	-0.534510
C	-0.639973	3.210994	0.179116
O	-0.873294	3.887049	-0.811267
C	-2.205035	-2.721058	0.348142
C	-2.476873	-4.069572	0.089335
C	-3.449207	-4.748327	0.818738
C	-4.156308	-4.084905	1.822903
C	-3.888712	-2.742080	2.089998
C	-2.921888	-2.060163	1.353450
H	-5.124000	0.040240	-2.483065
H	-5.343720	2.379401	-1.642456
H	-3.555793	3.332529	-0.197612
H	-3.140309	-1.293187	-1.896035
H	-0.741211	-0.359750	0.873742
H	1.189614	1.227380	-2.488629
H	-0.660497	1.393595	-2.381127
H	3.433050	-1.299669	1.830249
H	1.275274	-0.298760	1.225552
H	1.792973	-1.235203	-2.787950
H	3.971982	-2.284267	-2.378843
H	6.197727	-2.316216	-1.754400
H	6.841399	-3.460935	-0.563556
H	5.381178	-3.877246	-1.478646
H	5.713244	-1.483410	1.847191
H	4.929254	-3.067248	2.077990
H	6.588899	-2.974015	1.456900
H	2.739267	3.292226	2.009288
H	3.164427	5.011193	1.842564
H	1.805875	4.527319	2.881441
H	0.142134	5.964225	-0.157966
H	1.589068	6.573749	0.677101
H	0.194186	6.015895	1.619762
H	2.969154	4.753346	-0.669523
H	2.500082	3.051914	-0.477777
H	1.459287	4.165878	-1.399872
H	-1.915825	-4.574598	-0.690657
H	-3.655774	-5.792916	0.605789
H	-4.914686	-4.612208	2.394254
H	-4.435514	-2.221947	2.870607
H	-2.730295	-1.013241	1.566341
H	-0.939678	1.508702	1.329508
O	-0.441719	0.125565	2.121492
H	-0.956709	-0.264373	2.836679

TS9

C	-2.468587	-3.391135	-2.241505
C	-3.522473	-2.482211	-2.341441
C	-3.333477	-1.157516	-1.963211
C	-2.098133	-0.712082	-1.475070
C	-1.028871	-1.625546	-1.371379
C	-1.237114	-2.955954	-1.761889
N	-1.935003	0.638906	-1.084612
C	0.763123	-1.842265	0.453695
O	1.943515	-2.089111	0.688779
C	0.316070	-1.249232	-0.838003
C	1.175954	-0.562021	-1.644815

C	0.956702	-0.102802	-2.998753
C	3.512309	1.220593	0.609646
C	2.372665	0.763499	0.010950
N	2.411961	-0.072390	-1.055438
C	3.607206	-0.466098	-1.557691
C	4.788979	-0.059365	-1.006554
C	4.788969	0.811635	0.123617
N	5.924928	1.227120	0.694136
C	7.214776	0.801742	0.160528
C	5.881939	2.080840	1.877164
O	-2.538437	2.539394	-0.124559
C	-3.280192	3.385936	0.794322
C	-2.626673	4.750295	0.599944
C	-3.089140	2.911642	2.233062
C	-4.753418	3.449016	0.399879
C	-2.815632	1.218281	-0.232237
O	-3.707357	0.653048	0.391019
C	-0.263850	-2.200620	1.487979
C	-0.032362	-3.316170	2.300669
C	-0.940354	-3.654161	3.300431
C	-2.074693	-2.866063	3.507955
C	-2.299133	-1.742431	2.712237
C	-1.399935	-1.414247	1.699605
H	-2.604236	-4.427985	-2.533658
H	-4.490340	-2.803066	-2.715295
H	-4.148931	-0.444630	-2.033593
H	-0.410172	-3.657461	-1.676694
H	-1.287441	1.310144	-1.686562
H	0.287244	-0.746903	-3.571415
H	1.884189	0.107306	-3.534889
H	3.412243	1.897245	1.447275
H	1.382645	1.048616	0.350639
H	3.566506	-1.138758	-2.406727
H	5.708519	-0.424516	-1.443245
H	7.307695	1.079361	-0.893796
H	8.005494	1.298288	0.719179
H	7.341223	-0.281812	0.258599
H	5.410727	3.042349	1.648249
H	5.327807	1.594164	2.685894
H	6.900524	2.262075	2.213703
H	-2.722380	5.074905	-0.440662
H	-3.109216	5.491116	1.244072
H	-1.563098	4.705444	0.854533
H	-3.589497	1.958154	2.407631
H	-3.503182	3.658595	2.918096
H	-2.021906	2.800142	2.453699
H	-5.255684	4.213599	1.001431
H	-4.847833	3.727008	-0.655037
H	-5.249047	2.490888	0.560983
H	0.858873	-3.914272	2.135507
H	-0.765104	-4.529821	3.918197
H	-2.782535	-3.128825	4.288624
H	-3.177032	-1.123437	2.869162
H	-1.581060	-0.538972	1.084978
O	-0.465032	2.079621	-2.622156
H	0.003459	2.800535	-2.183112
H	0.348891	1.020111	-2.863830

TS10

C	3.848558	-3.200403	-1.742891
C	4.464243	-1.964346	-1.939050
C	3.916121	-0.783043	-1.431049
C	2.720558	-0.876807	-0.716394
C	2.100479	-2.110879	-0.512105
C	2.653818	-3.274993	-1.022550
N	1.963993	0.144599	-0.102967
C	-0.406431	-2.472327	-0.366617
O	-0.394390	-2.823752	-1.530820
C	0.862997	-1.955577	0.324204
C	0.848842	-0.418400	0.702357
C	1.074710	-0.246243	2.171566
C	-2.588782	1.161001	0.515864
C	-1.402937	0.654560	0.977926
N	-0.429720	0.226721	0.146538
C	-0.611338	0.336656	-1.191908
C	-1.765397	0.830683	-1.734183
C	-2.832807	1.245418	-0.884107
N	-3.997742	1.684862	-1.377428
C	-4.206085	1.750407	-2.820283
C	-5.063147	2.104769	-0.473565
O	1.386383	2.215176	0.497946
C	1.563187	3.655227	0.688980
C	0.303863	4.037551	1.456940
C	1.602393	4.363223	-0.660617
C	2.808024	3.921086	1.527281
C	2.316857	1.475689	-0.113084
O	3.322774	1.903940	-0.648630
C	-1.682816	-2.491238	0.416421
C	-1.711704	-2.598150	1.811581

C	-2.930079	-2.556223	2.488155
C	-4.119566	-2.391317	1.778691
C	-4.095441	-2.291105	0.385717
C	-2.882367	-2.349881	-0.293309
H	4.298119	-4.102827	-2.144734
H	5.395679	-1.909668	-2.494815
H	4.404888	0.168705	-1.580225
H	2.164465	-4.230479	-0.856743
H	0.982046	-2.501624	1.265645
H	1.062022	0.807849	2.462945
H	0.316270	-0.795105	2.740937
H	-3.323704	1.479355	1.243136
H	-1.194031	0.570184	2.036423
H	0.208798	0.005702	-1.819771
H	-1.841483	0.885457	-2.811915
H	-4.089174	0.761293	-3.274981
H	-5.217339	2.103411	-3.011980
H	-3.498656	2.443348	-3.287369
H	-5.356753	1.283388	0.188593
H	-4.746009	2.957854	0.135460
H	-5.927477	2.401230	-1.064299
H	0.250570	3.490442	2.403522
H	0.312797	5.109649	1.672666
H	-0.588502	3.806800	0.865795
H	2.511752	4.122648	-1.212719
H	1.566427	5.444671	-0.495955
H	0.731752	4.079213	-1.261438
H	2.831279	4.979646	1.803973
H	2.780160	3.325335	2.445342
H	3.719819	3.683611	0.977323
H	-0.794270	-2.733050	2.375267
H	-2.948297	-2.652971	3.569221
H	-5.065723	-2.348036	2.310004
H	-5.021319	-2.167671	-0.168339
H	-2.847720	-2.270328	-1.376018
O	3.355230	-1.486344	2.614142
H	3.832808	-1.554600	1.777309
H	2.260585	-0.840896	2.399800

TS11

C	2.314206	-1.685340	1.485058
C	3.144689	-2.569541	0.793820
C	3.770992	-2.131519	-0.376577
C	3.559948	-0.841027	-0.851030
C	2.717923	0.064490	-0.170957
C	2.107446	-0.389530	1.017759
C	2.501732	1.403952	-0.694983
C	1.565496	2.274209	-0.233398
C	1.309257	3.513363	0.177165
C	-1.579001	-0.285882	-1.133504
C	-0.419217	0.461254	-1.112470
N	-0.172272	1.395532	-0.192867
C	-1.074734	1.607971	0.768217
C	-2.266419	0.915405	0.846609
C	-2.561971	-0.073189	-0.130202
N	-3.714972	-0.779681	-0.101227
C	-4.672813	-0.566413	0.972515
C	-3.975169	-1.790591	-1.114531
H	1.828238	-2.004085	2.403642
H	3.306978	-3.577688	1.162645
H	4.426691	-2.802650	-0.925203
H	1.474897	0.289624	1.583519
H	3.080182	1.711347	-1.562944
H	0.317728	3.953170	0.135343
H	2.127800	4.124992	0.545468
H	-1.712180	-1.028508	-1.909506
H	0.367445	0.314755	-1.852064
H	-0.814513	2.362897	1.508645
H	-2.950721	1.135392	1.655894
H	-5.049811	0.462675	0.969099
H	-5.514811	-1.242259	0.831592
H	-4.223830	-0.772108	1.951271
H	-3.961890	-1.353265	-2.119034
H	-3.233160	-2.596934	-1.073571
H	-4.961423	-2.217703	-0.940130
H	4.048894	-0.516273	-1.766957

TS12

C	-3.719308	1.181085	0.513526
C	-3.339861	0.000002	0.000001
C	-3.719312	-1.181070	-0.513544
C	0.650273	1.194382	-0.182034
C	-0.728620	1.136302	-0.172367
N	-1.406259	-0.000016	0.000020
C	-0.728606	-1.136327	0.172394
C	0.650288	-1.194396	0.182034
C	1.397726	-0.000003	-0.000006
N	2.750569	0.000004	-0.000017
C	3.477860	-1.246976	0.178705
C	3.477842	1.246999	-0.178707

H	-4.623887	1.651729	0.142652
H	-3.164807	-1.679358	-1.302506
H	-4.623932	-1.651681	-0.142729
H	1.137130	2.149130	-0.333951
H	-1.338123	2.028703	-0.310961
H	-1.338097	-2.028735	0.310999
H	1.137156	-2.149139	0.333942
H	3.231553	-1.965592	-0.611501
H	4.546190	-1.041480	0.135306
H	3.252054	-1.703084	1.149570
H	3.252002	1.703145	-1.149546
H	3.231550	1.965581	0.611536
H	4.546175	1.041512	-0.135351
H	-3.164833	1.679356	1.302520

TS13

C	2.868475	0.687506	-0.660438
C	2.107433	1.773620	-0.384702
C	1.986570	3.070699	-0.184248
C	-1.383826	-0.583976	-0.917358
C	-0.152922	0.040210	-0.982230
N	0.142148	1.156176	-0.316526
C	-0.791452	1.680314	0.481960
C	-2.054774	1.139698	0.630111
C	-2.397930	-0.033177	-0.091484
N	-3.623437	-0.601785	0.009927
C	-4.618171	-0.031460	0.903995
C	-3.912884	-1.832898	-0.707230
H	3.380615	0.612712	-1.613722
H	1.043664	3.599251	-0.263860
H	2.879560	3.638611	0.063371
H	-1.548477	-1.487028	-1.491048
H	0.652973	-0.372557	-1.590057
H	-0.506735	2.571194	1.038675
H	-2.754707	1.616390	1.304350
H	-4.847610	1.004118	0.628836
H	-5.534429	-0.615553	0.830883
H	-4.277040	-0.049062	1.946267
H	-3.795946	-1.696422	-1.788190
H	-3.254238	-2.648391	-0.384434
H	-4.943519	-2.122427	-0.508319
C	2.879204	-0.449200	0.234025
O	2.306387	-0.533875	1.311047
O	3.617358	-1.475649	-0.262676
C	3.691409	-2.636291	0.562506
H	2.698333	-3.064731	0.720950
H	4.322455	-3.343936	0.024838
H	4.137370	-2.396990	1.531241

TS-1-3

C	3.100695	-2.472364	2.356752
C	1.984200	-3.260496	2.614951
C	0.794569	-3.075865	1.898049
C	0.766000	-2.090271	0.917298
C	1.894864	-1.297299	0.623448
C	3.061061	-1.487857	1.361734
N	-0.323345	-1.683860	0.107869
C	2.182461	0.907043	-0.758946
O	1.554573	1.915793	-1.096613
C	1.554432	-0.383634	-0.494264
C	0.038629	-0.550386	-0.769063
C	0.059015	-0.888530	-2.238954
C	-2.355453	2.362733	-0.761317
C	-1.614883	1.277098	-1.152530
N	-0.798511	0.625918	-0.305339
C	-0.701487	1.044269	0.976551
C	-1.404668	2.118719	1.448534
C	-2.273138	2.837965	0.576598
N	-2.974626	3.901611	0.997025
C	-2.872013	4.348526	2.381569
C	-3.835814	4.621355	0.066358
O	-2.408542	-1.609929	-0.678551
C	-3.775669	-2.084350	-0.893493
C	-4.318717	-1.081546	-1.904342
C	-4.565673	-2.012418	0.408500
C	-3.758111	-3.486977	-1.490960
C	-1.565726	-2.268321	0.127092
O	-1.851295	-3.239791	0.805140
C	3.684003	0.967737	-0.738335
C	4.464400	-0.091772	-1.213476
C	5.853931	0.016813	-1.234128
C	6.471768	1.176634	-0.764641
C	5.696464	2.236506	-0.290014
C	4.307007	2.137237	-0.290438
H	4.014027	-2.618076	2.925679
H	2.023592	-4.027492	3.382492
H	-0.078321	-3.679610	2.101263
H	3.940671	-0.882447	1.174882
H	1.531936	-1.035443	-1.631896
H	-0.836802	-1.377242	-2.634813

H	0.300196	0.009434	-2.819026
H	-2.994034	2.836119	-1.494679
H	-1.651147	0.885885	-2.162001
H	-0.032453	0.481272	1.618562
H	-1.274773	2.402397	2.484067
H	-1.845554	4.644297	2.622877
H	-3.523502	5.209082	2.520974
H	-3.186751	3.558394	3.071294
H	-3.258111	5.007464	-0.780026
H	-4.632321	3.972307	-0.313228
H	-4.290780	5.461304	0.587429
H	-3.716068	-1.093476	-2.818057
H	-5.349718	-1.339469	-2.162478
H	-4.306203	-0.069977	-1.486524
H	-4.209069	-2.745166	1.133658
H	-5.621093	-2.210916	0.196998
H	-4.486027	-1.009792	0.842192
H	-4.773587	-3.753825	-1.799684
H	-3.112920	-3.512876	-2.375192
H	-3.406104	-4.226425	-0.770479
H	3.983007	-0.998155	-1.571920
H	6.453747	-0.804174	-1.615423
H	7.554820	1.256859	-0.772925
H	6.175333	3.140570	0.074235
H	3.692617	2.961619	0.059869

TS-L

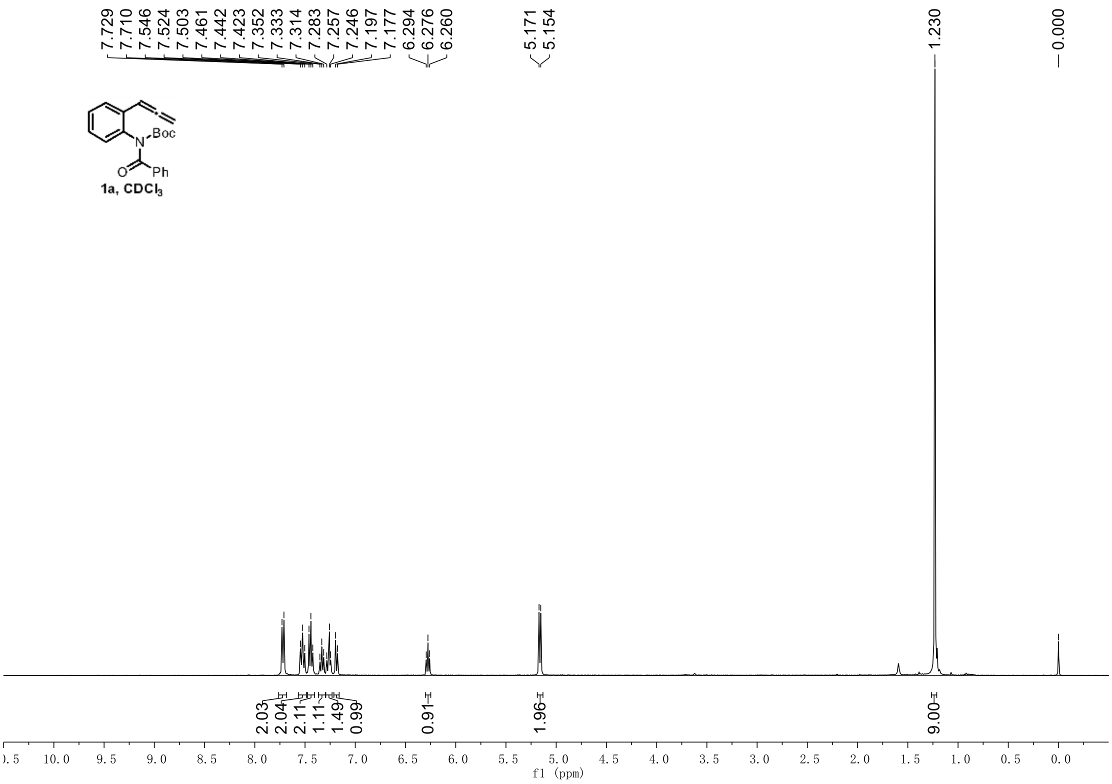
C	-4.275585	2.595997	-0.050725
C	-3.537477	3.463901	0.755782
C	-2.187819	3.214836	0.984316
C	-1.566600	2.110610	0.396930
C	-2.287069	1.242661	-0.446127
C	-3.650877	1.503547	-0.644551
N	-0.214051	1.825066	0.695270
C	-2.169545	-1.247775	-1.233357
O	-1.774683	-2.058120	-2.072467
C	-1.630863	0.112919	-1.163371
C	-0.500074	0.387054	-1.864202
C	0.175370	1.102899	-2.733635
C	1.673370	-2.368489	0.691591
C	0.794653	-1.488218	0.089833
N	1.052408	-0.834475	-1.043526
C	2.217118	-1.084212	-1.649996
C	3.173448	-1.945611	-1.145247
C	2.928783	-2.618274	0.080236
N	3.837552	-3.458592	0.629768
C	5.082018	-3.738264	-0.068845
C	3.512642	-4.178466	1.851152
O	1.977094	2.070443	0.723484
C	3.258917	2.709293	0.441428
C	4.263350	1.639503	0.851839
C	3.437917	3.962571	1.292605
C	3.366077	2.997825	-1.051658
C	0.815577	2.705223	0.486730
O	0.688198	3.871558	0.166619
C	-3.198978	-1.696404	-0.228639
C	-4.183049	-2.598932	-0.644340
C	-5.130853	-3.073632	0.259606
C	-5.085498	-2.668796	1.594515
C	-4.092117	-1.786183	2.020716
C	-3.158142	-1.293847	1.111139
H	-5.331274	2.776853	-0.228629
H	-4.012321	4.325094	1.215644
H	-1.603623	3.863931	1.628522
H	-4.219389	0.843505	-1.294973
H	0.061297	0.850349	0.678320
H	1.255553	1.190616	-2.735519
H	-0.388530	1.650150	-3.486238
H	1.380334	-2.858387	1.611173
H	-0.183459	-1.304070	0.539117
H	2.392693	-0.577360	-2.596810
H	4.090098	-2.094833	-1.701447
H	5.656867	-2.819590	-0.230058
H	5.683015	-4.414758	0.536807
H	4.898268	-4.211643	-1.041223
H	3.277535	-3.483715	2.664648
H	2.657378	-4.849845	1.705726
H	4.373855	-4.774362	2.149959
H	4.087856	0.716708	0.289273
H	5.280062	1.987773	0.648458
H	4.175875	1.419982	1.920365
H	2.779042	4.768044	0.966805
H	4.476005	4.300438	1.213271
H	3.231990	3.736228	2.343854
H	4.358116	3.404451	-1.271666
H	3.241691	2.070742	-1.621840
H	2.614091	3.721442	-1.373199
H	-4.197771	-2.919746	-1.681785
H	-5.901106	-3.762048	-0.075005

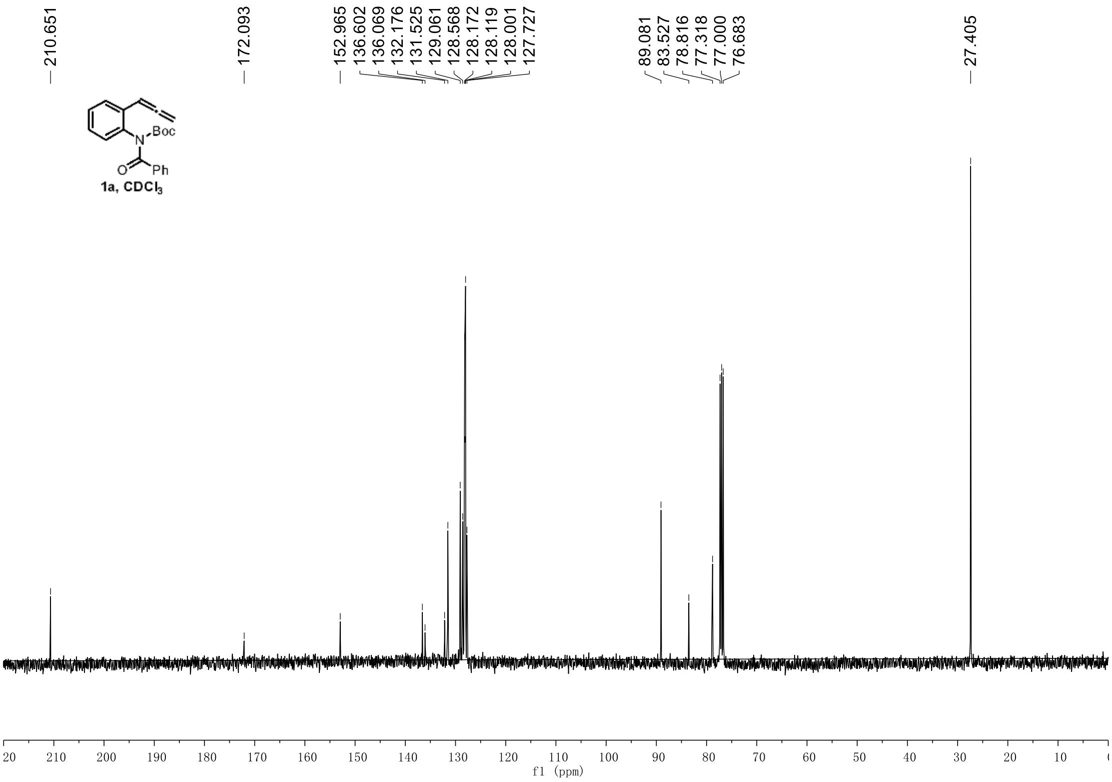
H	-5.820112	-3.042467	2.301715
H	-4.046606	-1.477353	3.060681
H	-2.391814	-0.601587	1.450032

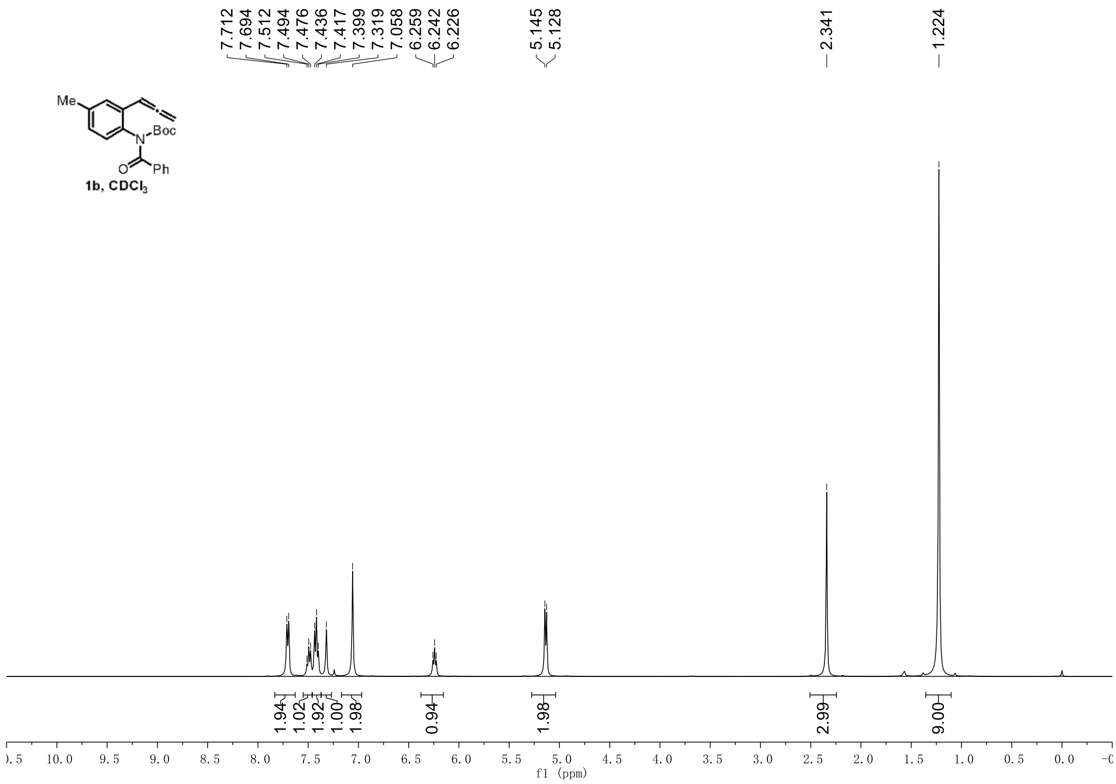
8. References

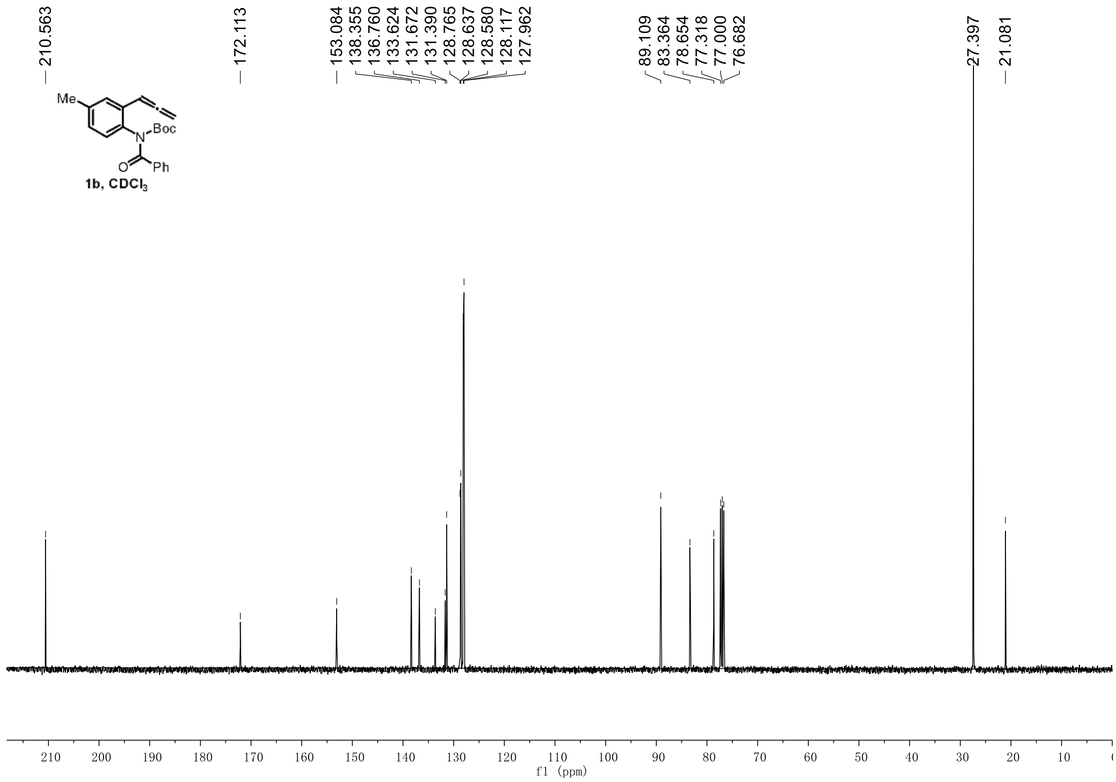
1. Nicolaou, K. C.; Roecker, A. J.; Hughes, R.; Summeren, R. v.; Pfefferkorna, J. A.; Winssinger, N. Novel Strategies for the Solid Phase Synthesis of Substituted Indolines and Indoles. *Bioorg. Med. Chem*. **2003**, *11*, 465–476.
2. Bhaskar, G.; Saikumar, C.; Perumal, P. T. Indium(III) Bromide-Catalyzed Hydroarylation of Alkynes with Indoles. *Tetrahedron Lett.* **2010**, *51*, 3141−3145.
3. Sharma, P.; Liu, R. S. [3 + 2]-Annulations of N-Hydroxy Allenylamines with Nitrosoarenes: One-Pot Synthesis of Substituted Indole Products. *Org. Lett.* **2016**, *18* , 412−415.
4. Mennie, K. M.; Banik, S. M.; Reichert, E. C.; Jacobsen, E. N. Catalytic Diastereo- and Enantioselective Fluoroamination of Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 4797−4802.
5. Jana, S.; Verma, A.; Kadu, R.; Kumar, S. Visible-Light-Induced Oxidant and Metal-Free Dehydrogenative Cascade Trifluoromethylation and Oxidation of 1,6-Enynes with Water. *Chem. Sci*. **2017**, *8*, 6633−6644.
6. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, Jr., J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador ,P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski J.; Fox, D. J. *Gaussian 09, Revision E.01*, Gaussian, Inc., Wallingford, CT, 2013.
7. Zhao, Y.; Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157−167.
8. Marenich,A. V.; Cramer,C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B*, **2009**, *113*, 6378−6396.
9. (a) Zhao, Y.; Truhlar, D. G. Computational Characterization and Modeling of Buckyball Tweezers: Density Functional Study of Concave–Convex $\pi\cdots\pi$ Interactions. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2813−2818; (b) Ribeiro, R. F.; Marenich, A. V.; Cramer,C. J.; Truhlar, D. G. Use of Solution-Phase Vibrational Frequencies in Continuum Models for the Free Energy of Solvation. *J. Phys. Chem. B*, **2011**, *115*, 14556−14562.

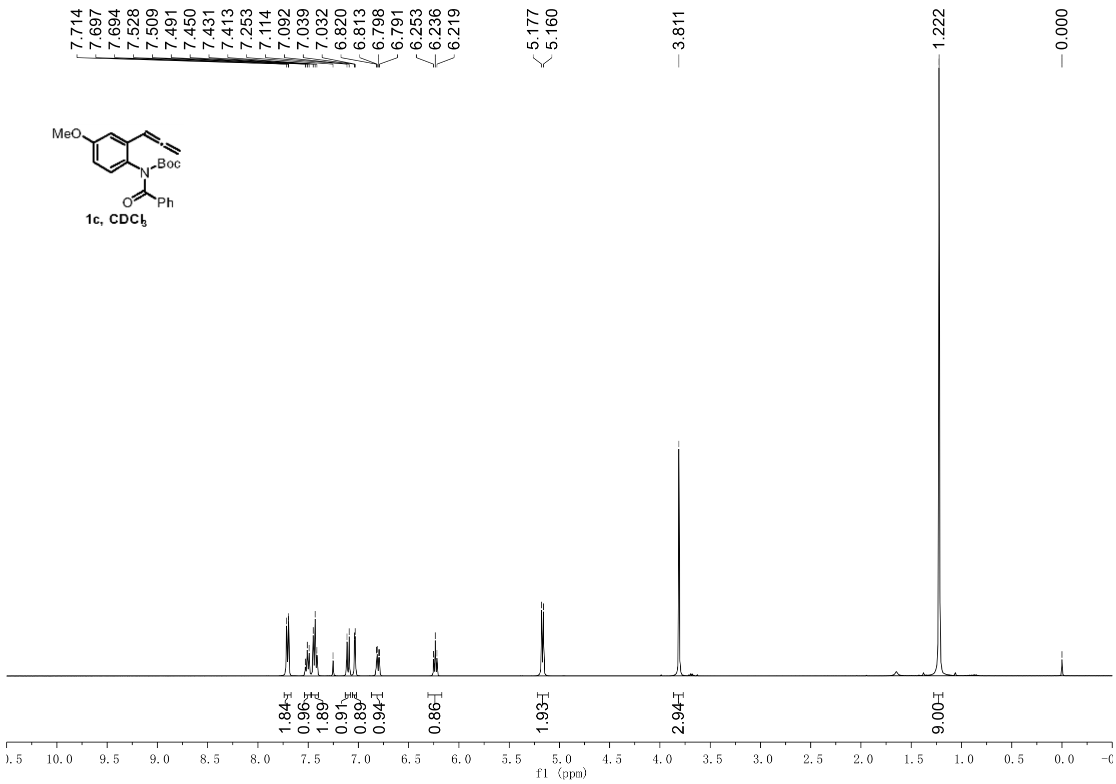
9. NMR Spectra

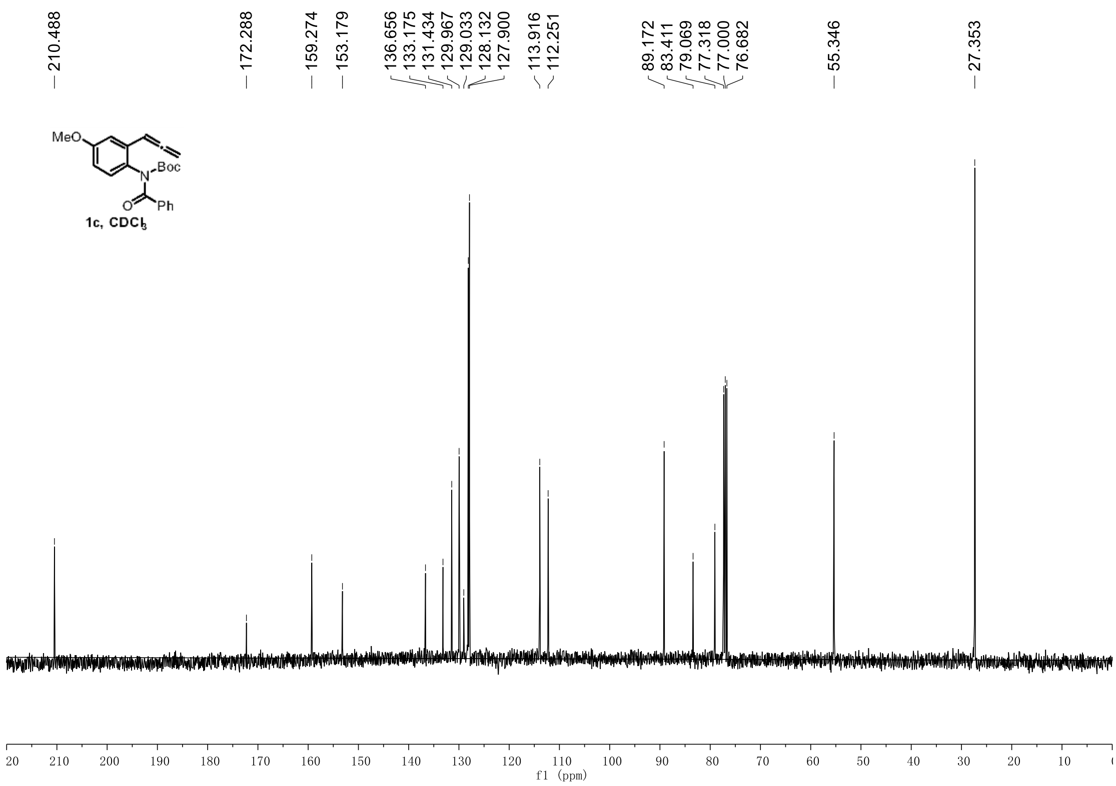


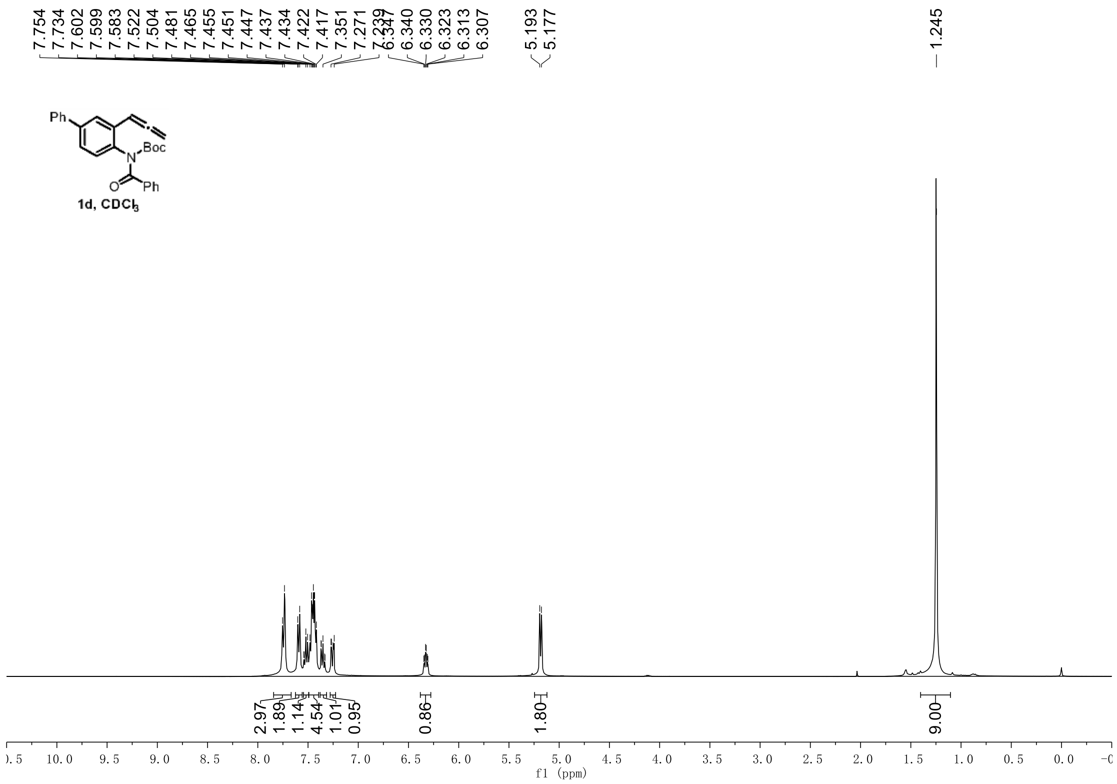


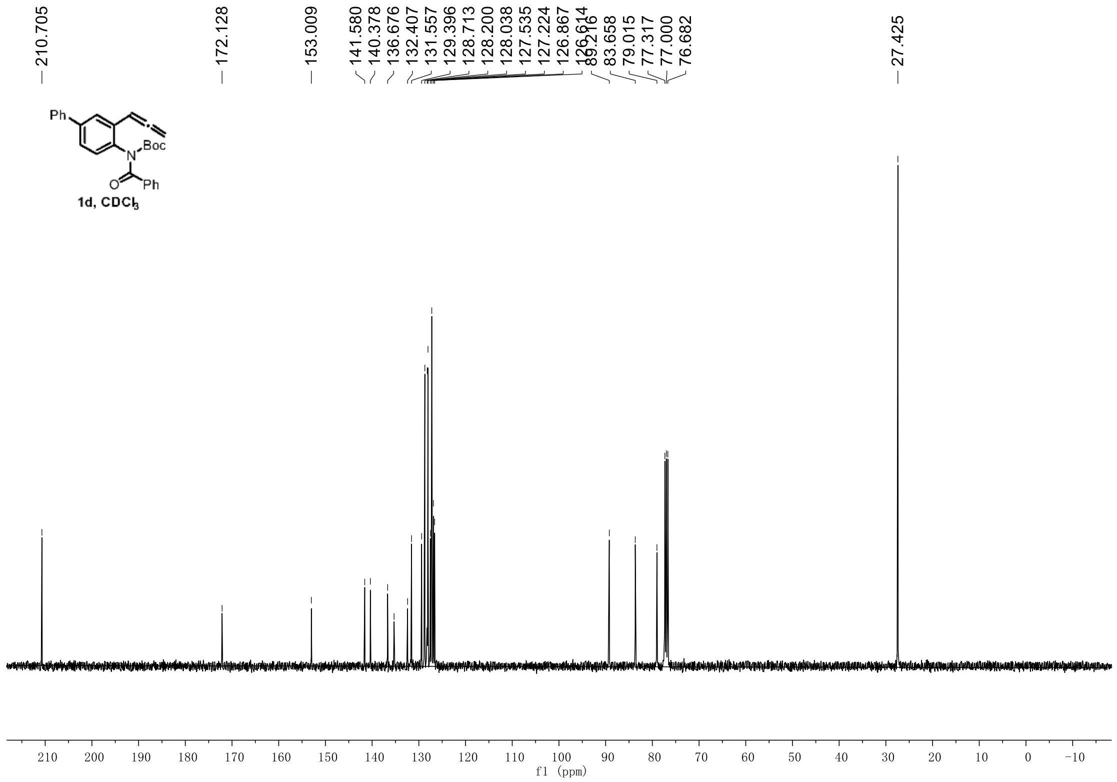

Me
Boc
N
O
Ph
1b, CDCl3
7.712
7.694
7.512
7.494
7.476
7.436
7.417
7.399
7.319
7.058
6.259
6.242
6.226
5.145
5.128
2.341
1.224
1.94
1.02
1.92
1.00
1.98
0.94
1.98
2.99
9.00
f1 (ppm)

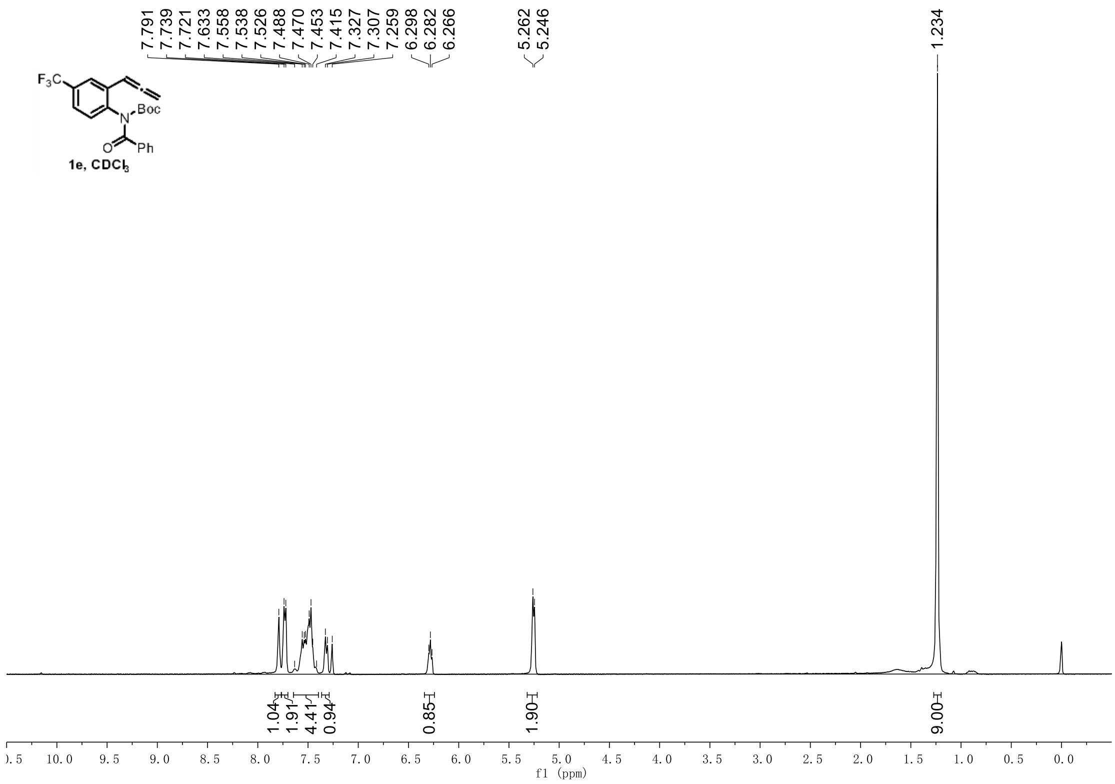

Me
Boc
N
O
Ph
1b, CDCl3
210.563
172.113
153.084
138.355
136.760
133.624
131.672
131.390
128.765
128.637
128.580
128.117
127.962
89.109
83.364
78.654
77.318
77.000
76.682
27.397
21.081
f1 (ppm)

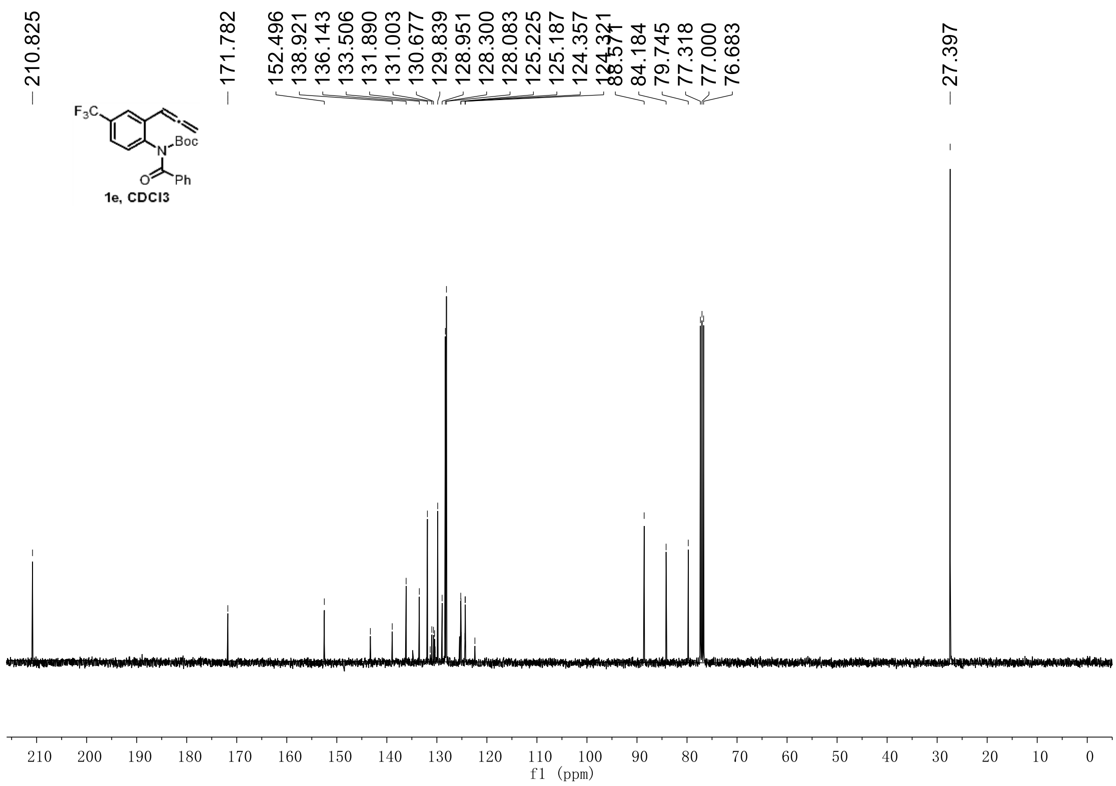

7.714
7.697
7.694
7.528
7.509
7.491
7.450
7.431
7.413
7.253
7.114
7.092
7.039
7.032
6.820
6.813
6.798
6.791
6.253
6.236
6.219
5.177
5.160
3.811
1.222
0.000
MeO
Boc
N
O
Ph
1c, CDCl3
1.84
0.96
1.89
0.91
0.89
0.94
0.86
1.93
2.94
9.00
f1 (ppm)

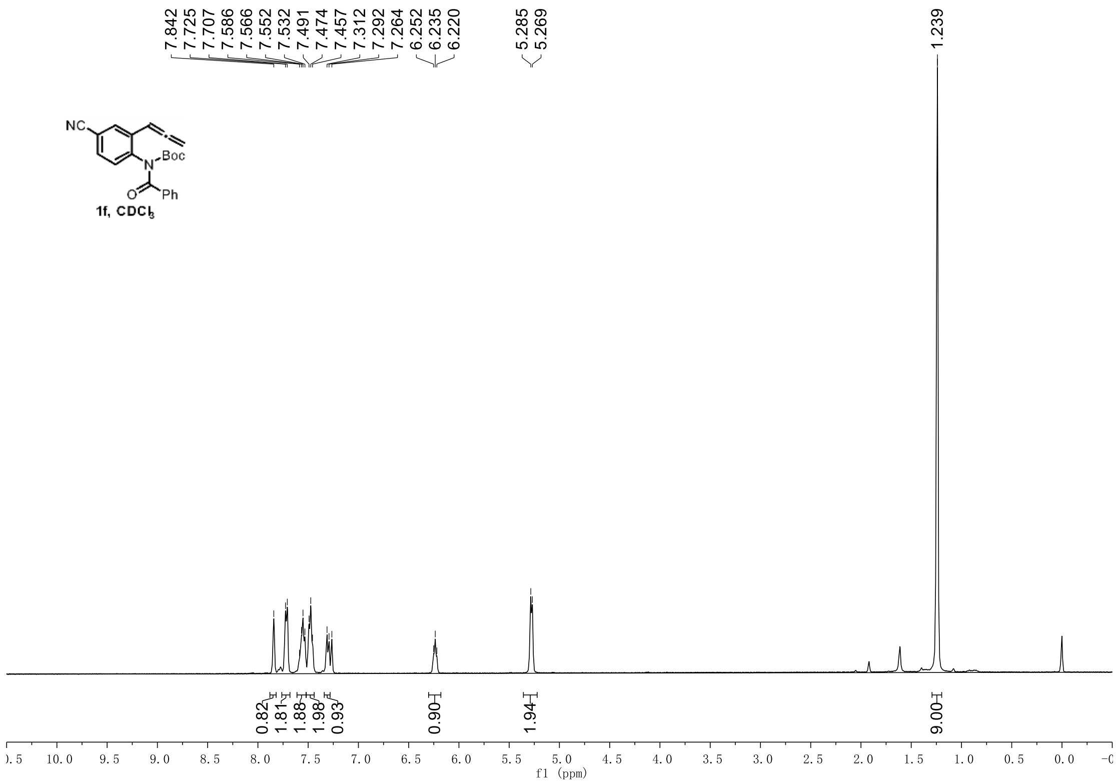

210.488
172.288
159.274
153.179
136.656
133.175
131.434
129.967
129.033
128.132
127.900
113.916
112.251
89.172
83.411
79.069
77.318
77.000
76.682
55.346
27.353
MeO
Boc
N
O
Ph
1c, CDCl3
f1 (ppm)

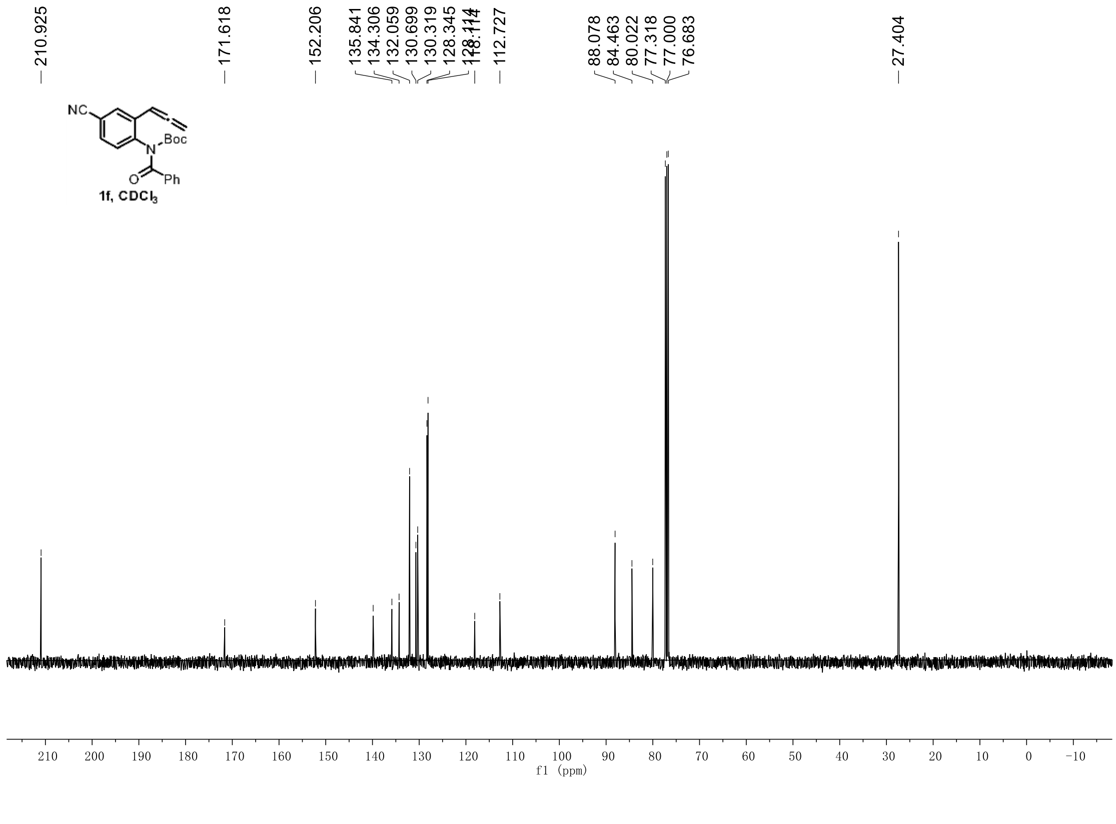

7.754
7.734
7.602
7.599
7.583
7.522
7.504
7.481
7.465
7.455
7.451
7.447
7.437
7.434
7.422
7.417
7.351
7.271
7.239
6.347
6.340
6.330
6.323
6.313
6.307
5.193
5.177
1.245
Ph
Boc
N
O
Ph
1d, CDCl3
2.97
1.89
1.14
4.54
1.01
0.95
0.86
1.80
9.00
f1 (ppm)

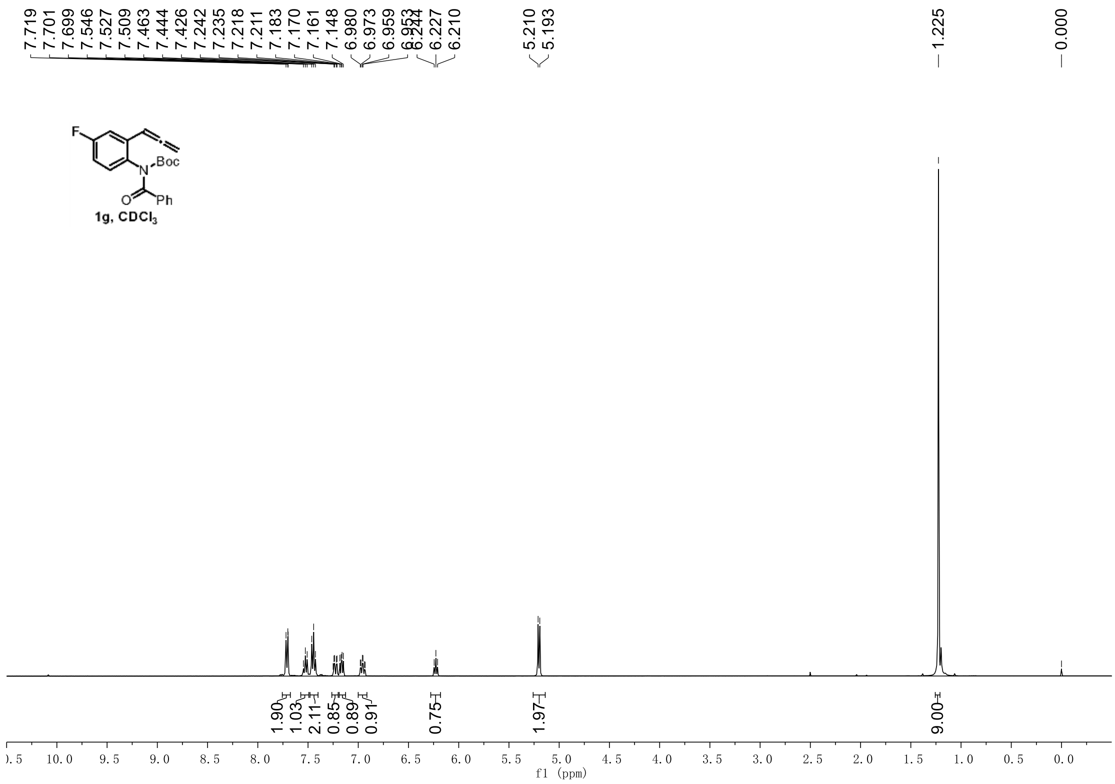

210.705
172.128
153.009
141.580
140.378
136.676
132.407
131.557
129.396
128.713
128.200
128.038
127.535
127.224
126.867
126.614
89.216
83.658
79.015
77.317
77.000
76.682
27.425
Ph
Boc
N
O
Ph
1d, CDCl3
f1 (ppm)

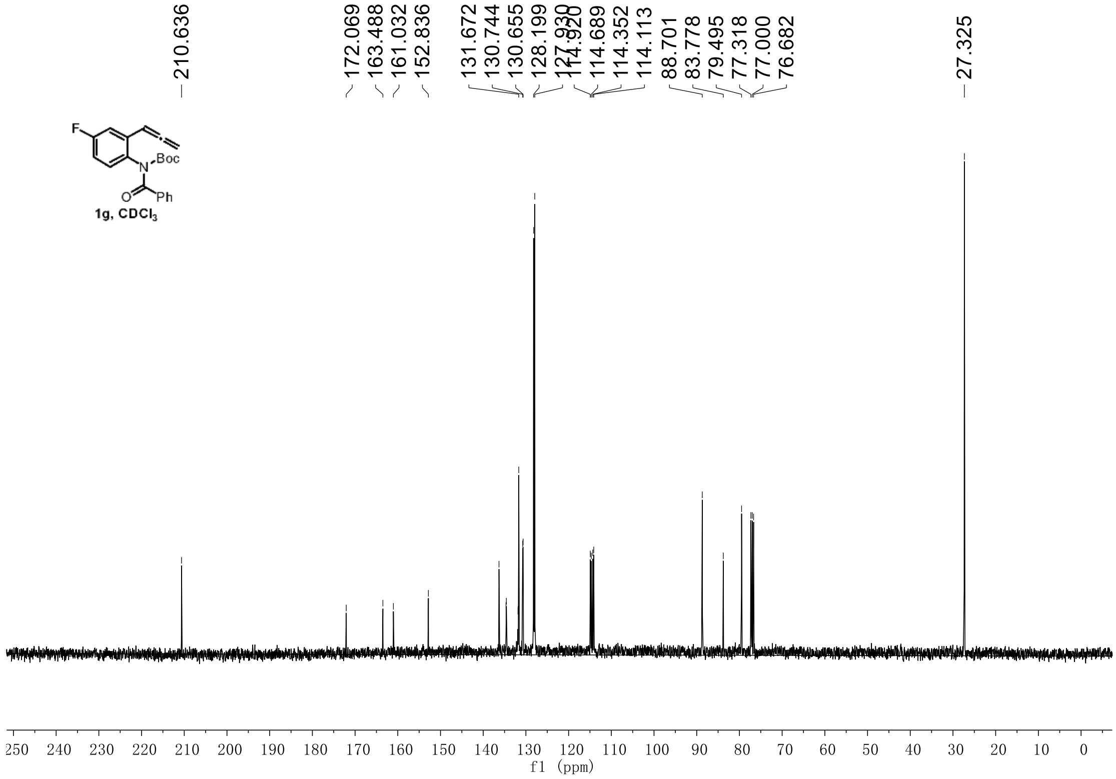

7.791
7.739
7.721
7.633
7.558
7.538
7.526
7.488
7.470
7.453
7.415
7.327
7.307
7.259
6.298
6.282
6.266
5.262
5.246
1.234
F_3C
N
Boc
O
Ph
1e, $CDCl_3$
1.04
1.91
4.41
0.94
0.85
1.90
9.00
f1 (ppm)

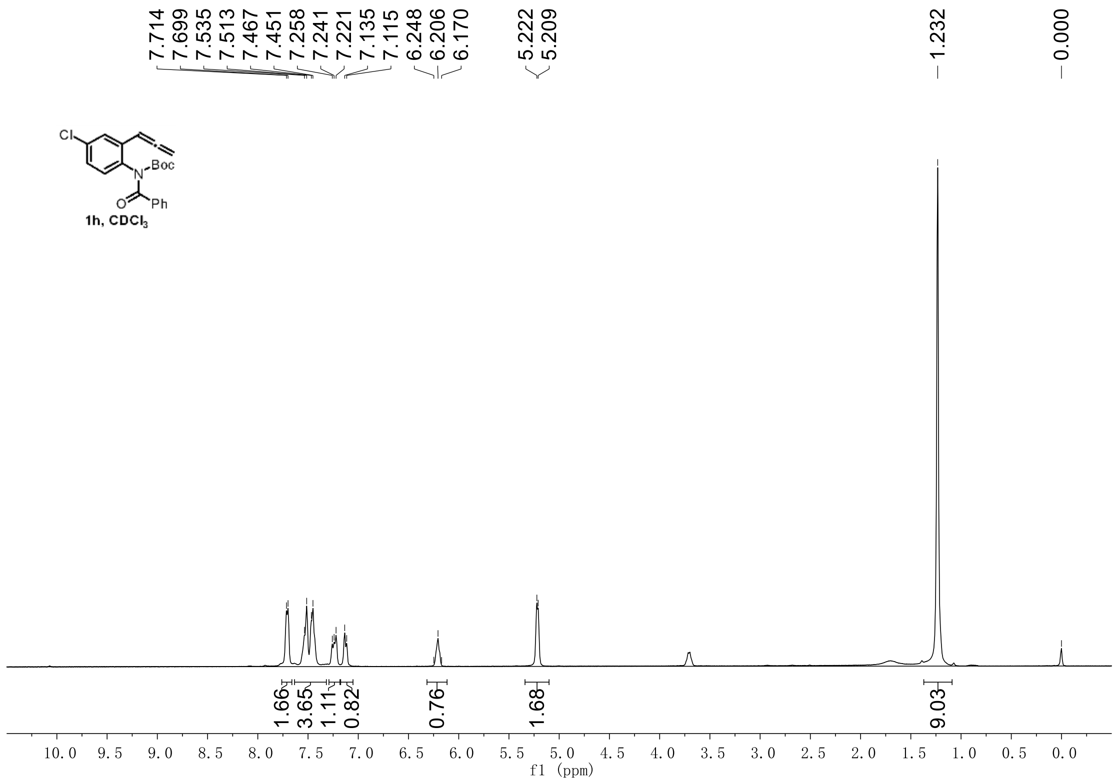

210.825
171.782
152.496
138.921
136.143
133.506
131.890
131.003
130.677
129.839
128.951
128.300
128.083
125.225
125.187
124.357
124.321
88.571
84.184
79.745
77.318
77.000
76.683
27.397
F_3C
N
Boc
O
Ph
1e, CDCl3
f1 (ppm)

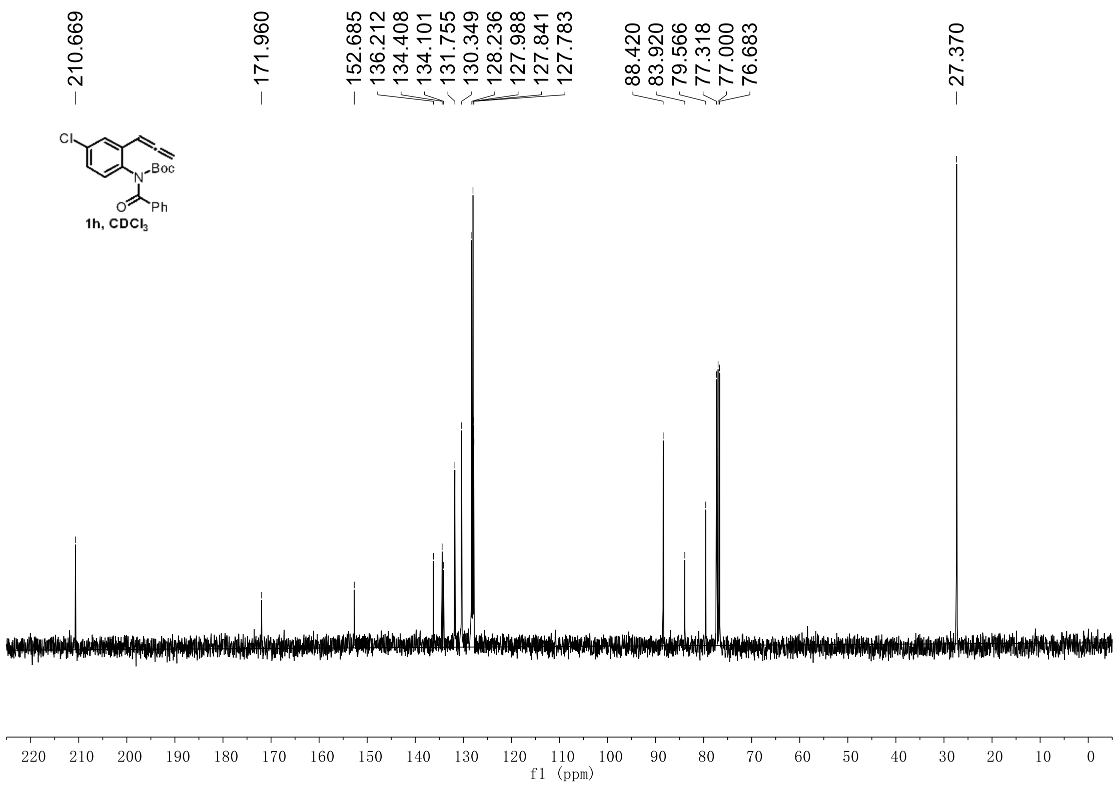

7.842
7.725
7.707
7.586
7.566
7.552
7.532
7.491
7.474
7.457
7.312
7.292
7.264
6.252
6.235
6.220
5.285
5.269
1.239
NC
N
Boc
O
Ph
1f, CDCl3
0.82
1.81
1.88
1.98
0.93
0.90
1.94
9.00
f1 (ppm)

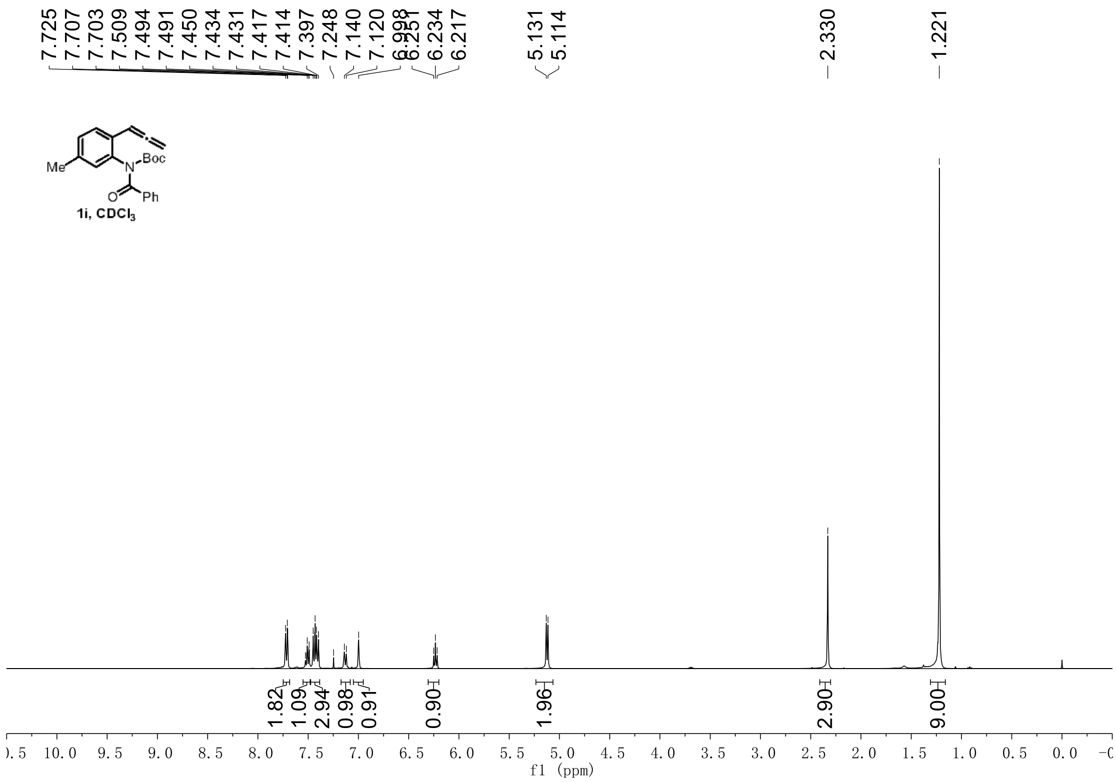

210.925
171.618
152.206
135.841
134.306
132.059
130.699
130.319
128.345
128.114
112.727
88.078
84.463
80.022
77.318
77.000
76.683
27.404
NC
N
Boc
O
Ph
1f, CDCl3
f1 (ppm)

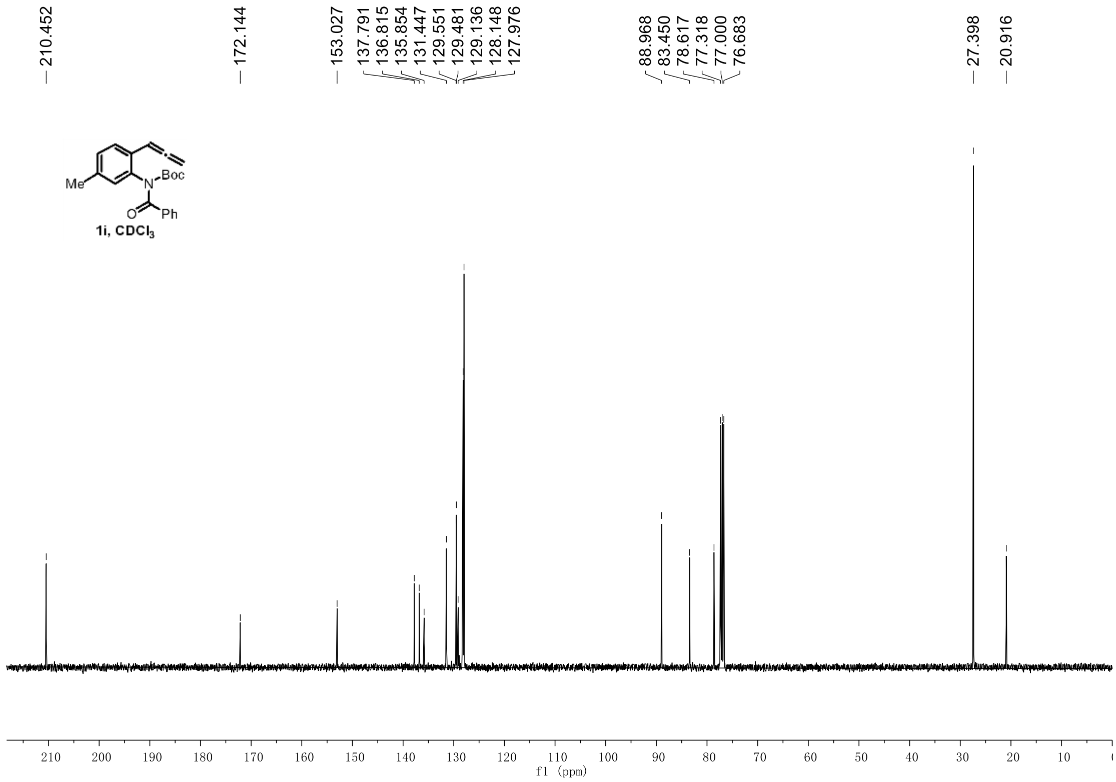

7.719 7.701 7.699 7.546 7.527 7.509 7.463 7.444 7.426 7.242 7.235 7.218 7.211 7.183 7.170 7.161 7.148 6.980 6.973 6.959 6.953 6.244 6.227 6.210
5.210 5.193
1.225
0.000
F
N
Boc
O
Ph
1g, CDCl3
1.90 1.03 2.11 0.85 0.89 0.91
0.75
1.97
9.00
f1 (ppm)

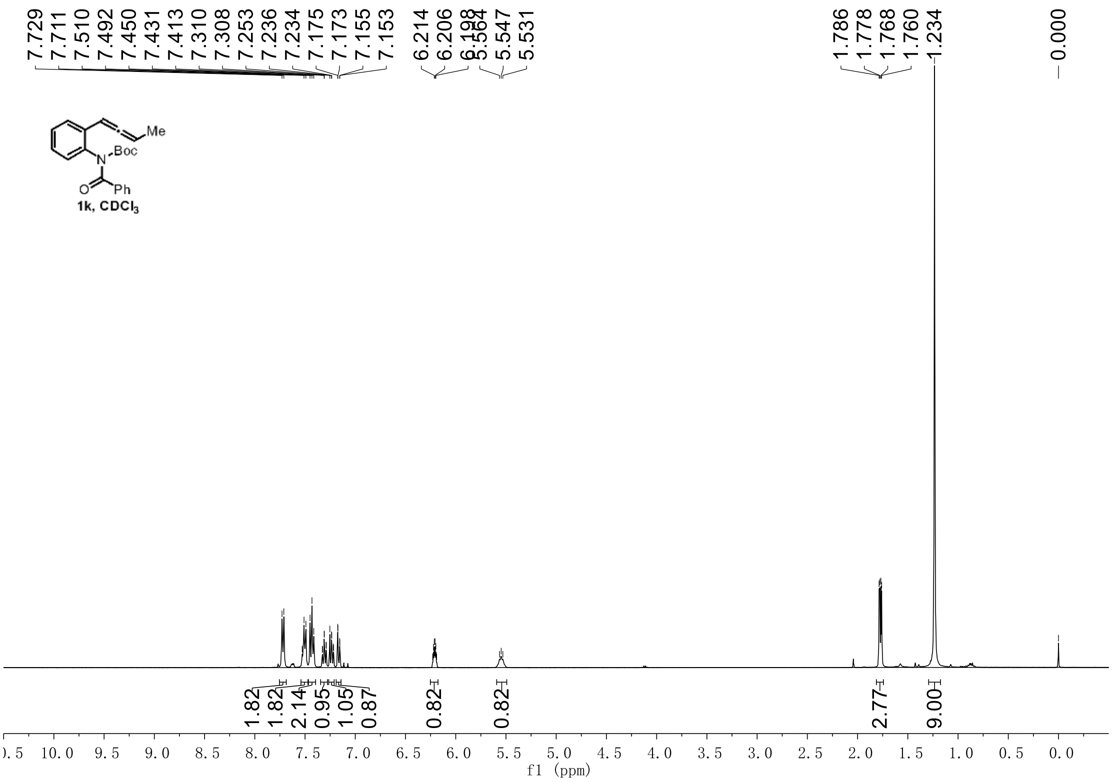

210.636
172.069 163.488 161.032 152.836
131.672 130.744 130.655 128.199 127.930 114.920 114.689 114.352 114.113
88.701 83.778 79.495 77.318 77.000 76.682
27.325
F
N
Boc
O
Ph
1g, CDCl3
f1 (ppm)

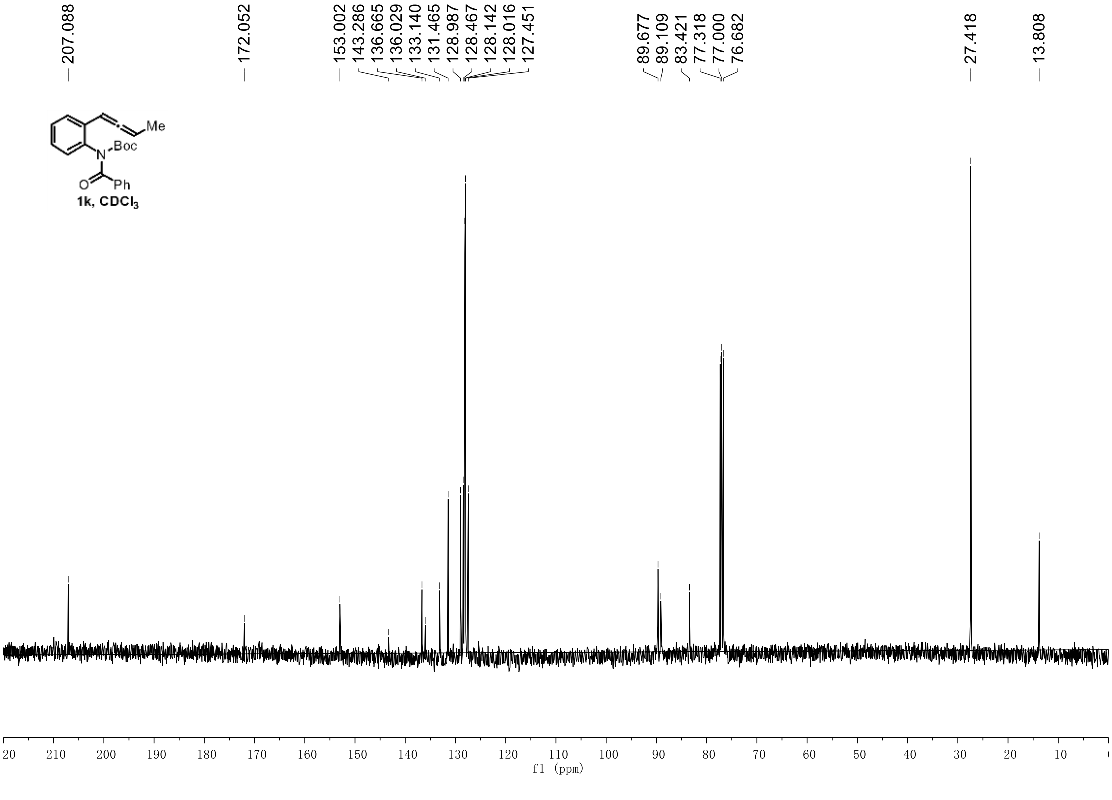

7.714
7.699
7.535
7.513
7.467
7.451
7.258
7.241
7.221
7.135
7.115
6.248
6.206
6.170
5.222
5.209
1.232
0.000
Cl
N
Boc
O
Ph
1h, CDCl3
1.66
3.65
1.11
0.82
0.76
1.68
9.03
f1 (ppm)

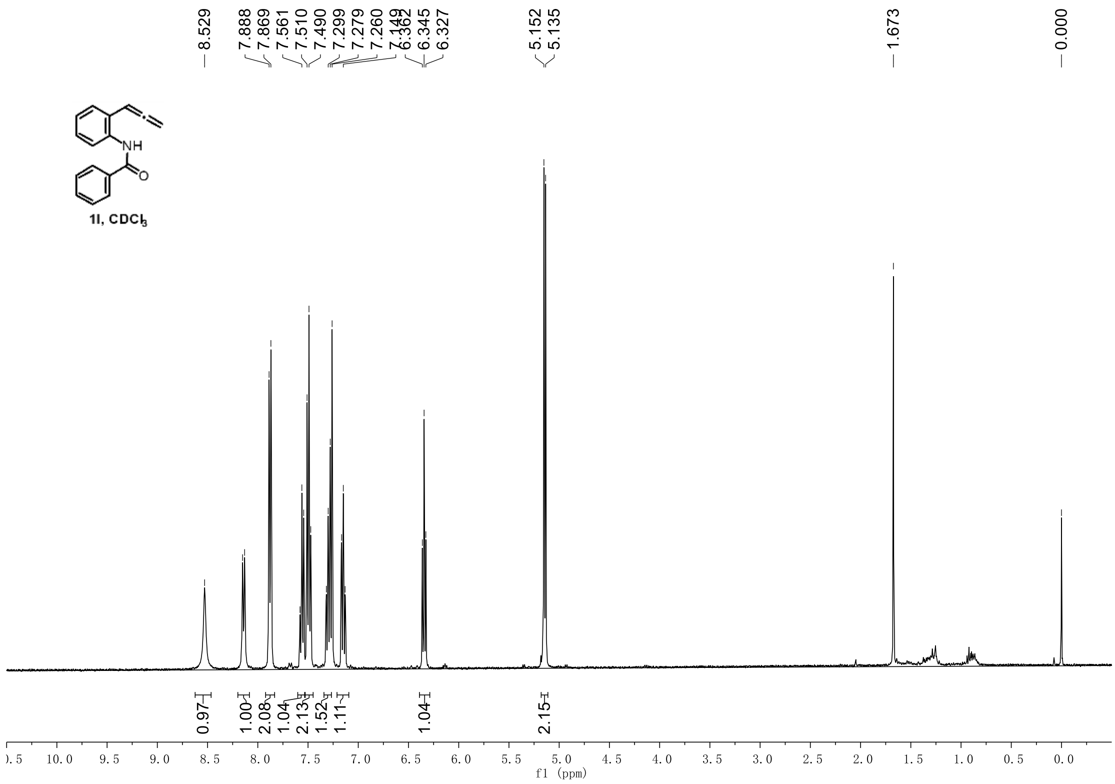

210.669
171.960
152.685
136.212
134.408
134.101
131.755
130.349
128.236
127.988
127.841
127.783
88.420
83.920
79.566
77.318
77.000
76.683
27.370
Cl
N
Boc
O
Ph
1h, CDCl3
f1 (ppm)

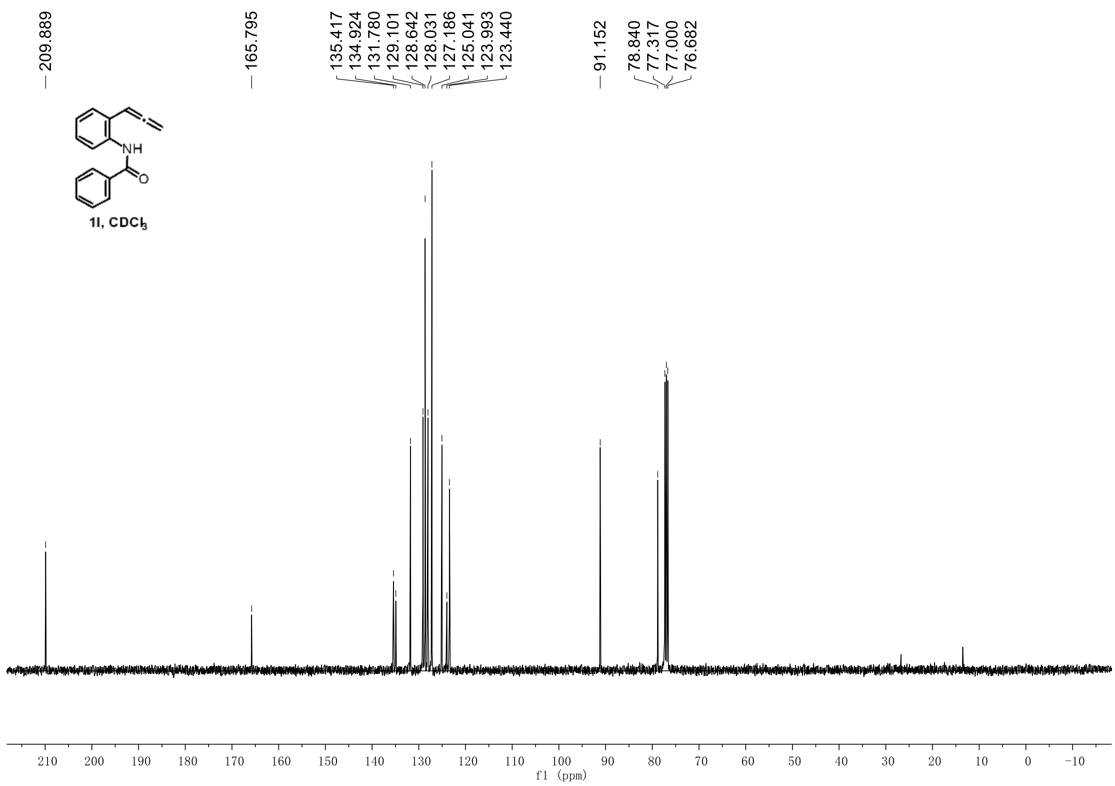

7.725
7.707
7.703
7.509
7.494
7.491
7.450
7.434
7.431
7.417
7.414
7.397
7.248
7.140
7.120
6.998
6.251
6.234
6.217
5.131
5.114
2.330
1.221
Me
N
Boc
O
Ph
1i, CDCl3
1.82
1.09
2.94
0.98
0.91
0.90
1.96
2.90
9.00
f1 (ppm)

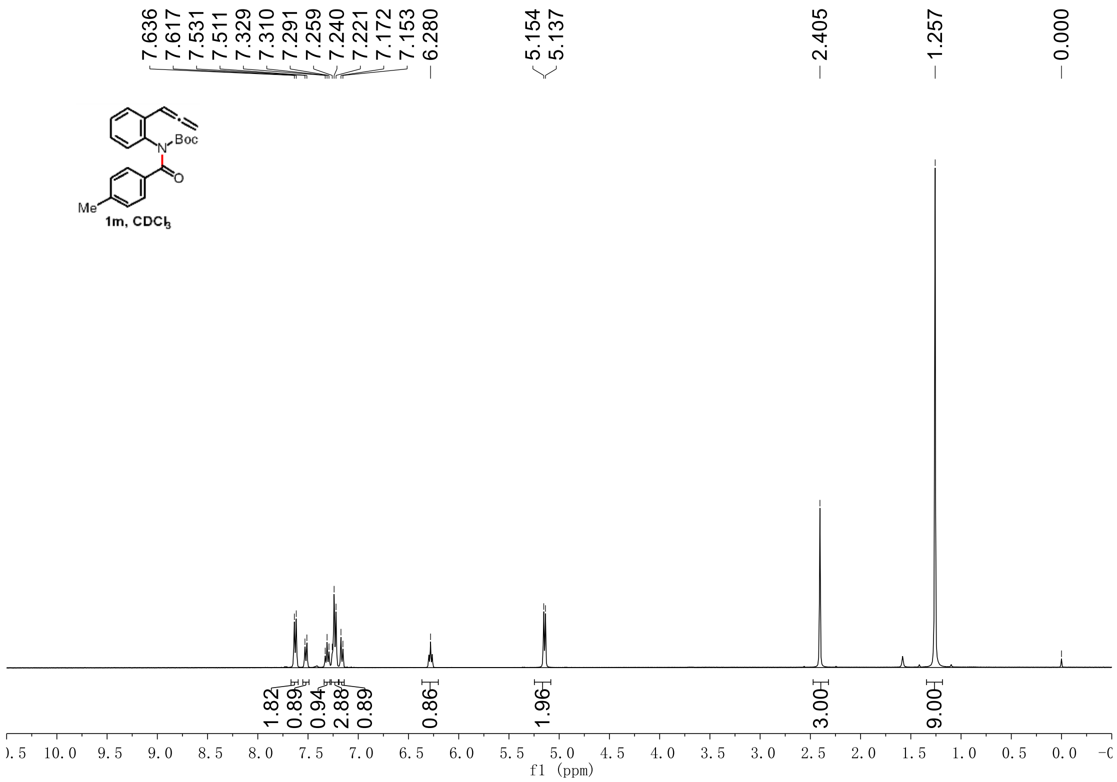

210.452
172.144
153.027
137.791
136.815
135.854
131.447
129.551
129.481
129.136
128.148
127.976
88.968
83.450
78.617
77.318
77.000
76.683
27.398
20.916
Me
N
Boc
O
Ph
1i, CDCl3
f1 (ppm)

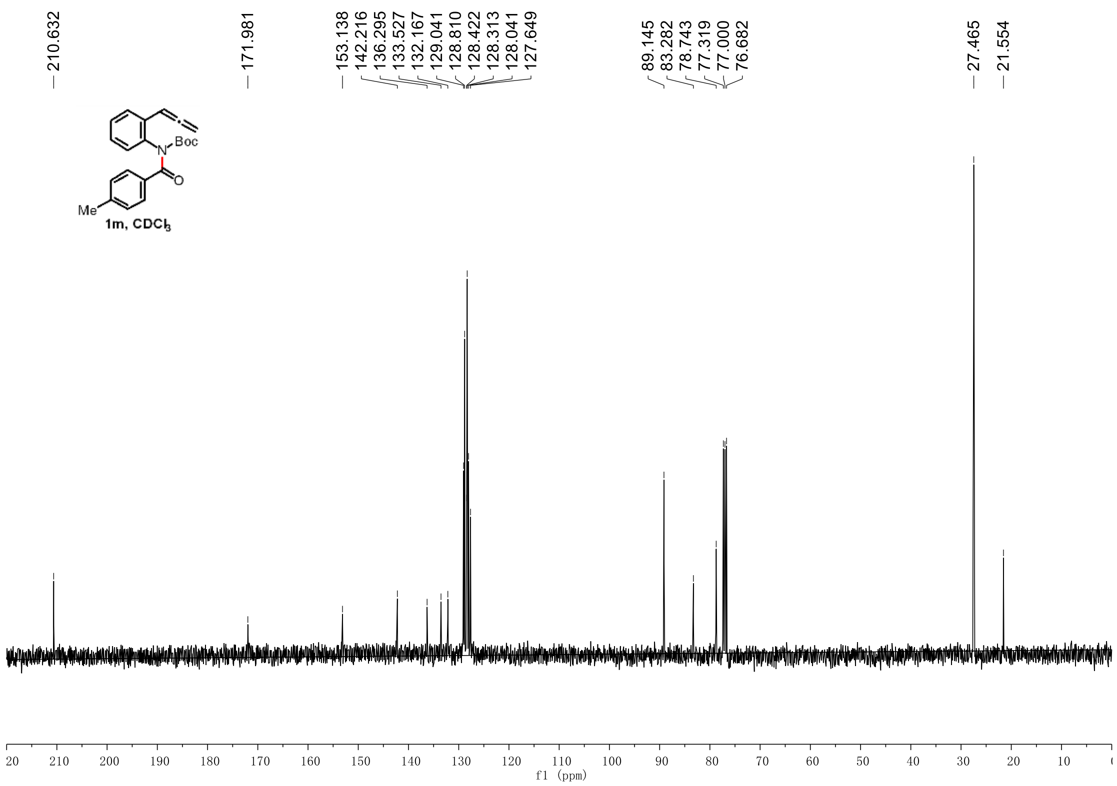

7.729
7.711
7.510
7.492
7.450
7.431
7.413
7.310
7.308
7.253
7.236
7.234
7.175
7.173
7.155
7.153
6.214
6.206
6.198
5.564
5.547
5.531
1.786
1.778
1.768
1.760
1.234
0.000
Me
N
Boc
O
Ph
1k, CDCl3
1.82
1.82
2.14
0.95
1.05
0.87
0.82
0.82
2.77
9.00
f1 (ppm)

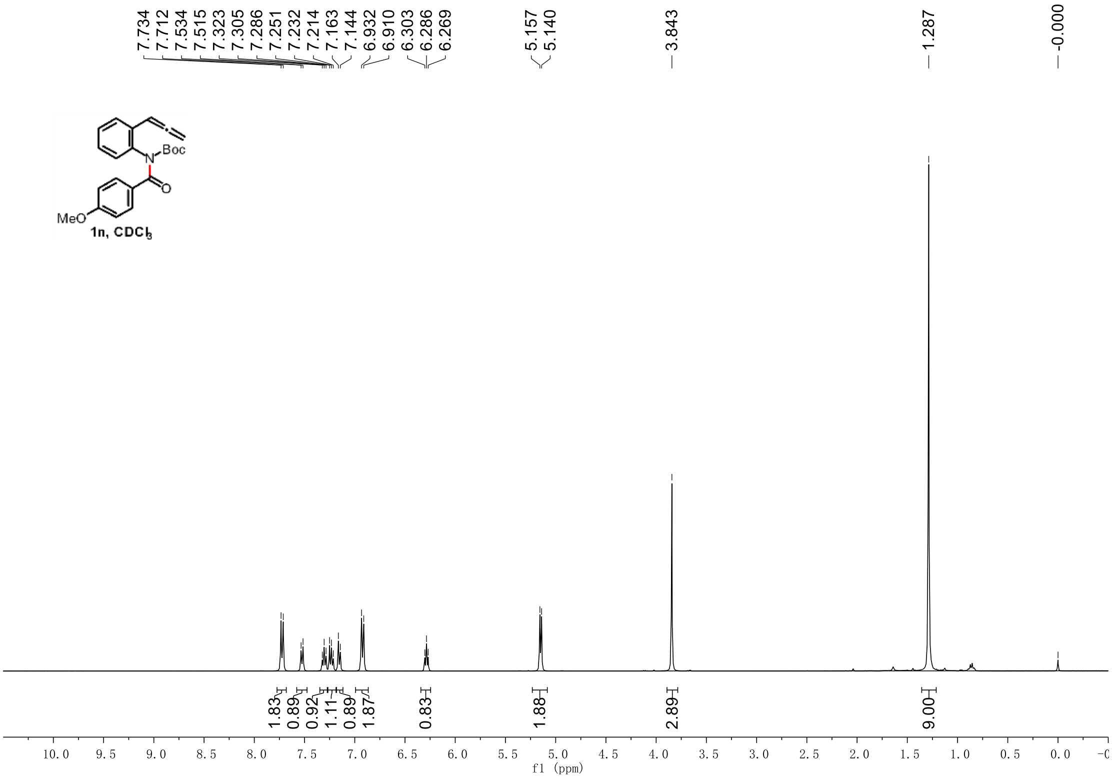

207.088
172.052
153.002
143.286
136.665
136.029
133.140
131.465
128.987
128.467
128.142
128.016
127.451
89.677
89.109
83.421
77.318
77.000
76.682
27.418
13.808
Me
N
Boc
O
Ph
1k, CDCl3
f1 (ppm)

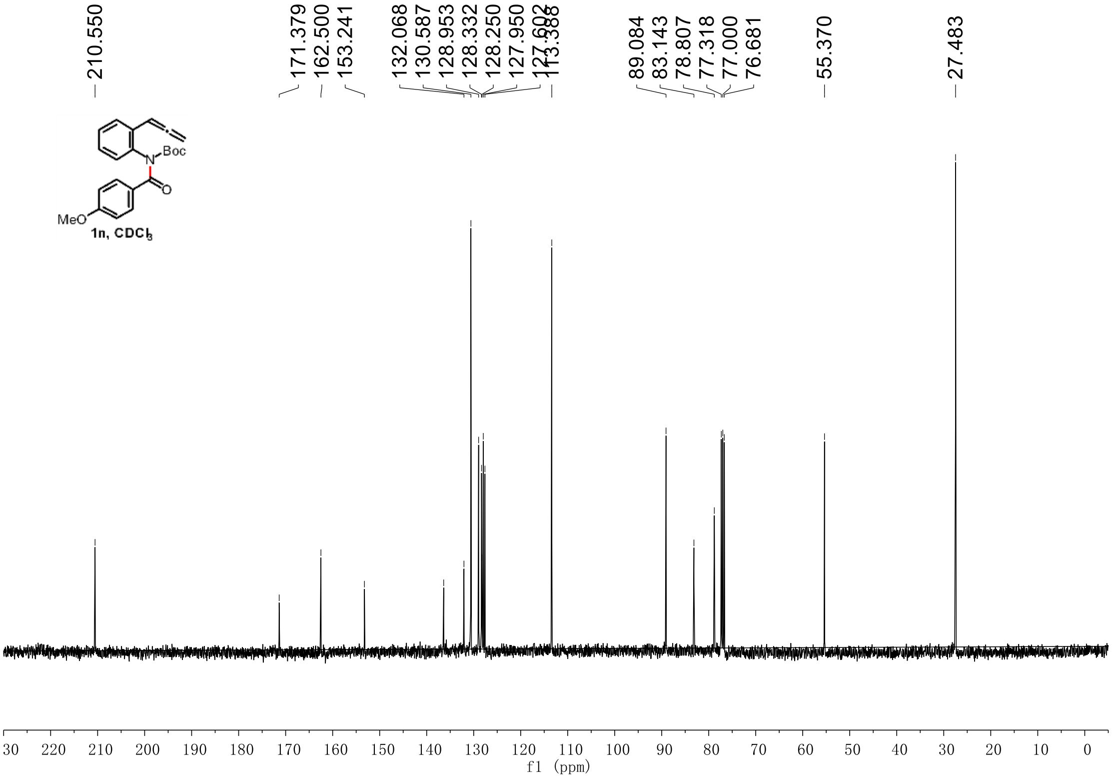

8.529
7.888
7.869
7.561
7.510
7.490
7.299
7.279
7.260
7.149
6.362
6.345
6.327
5.152
5.135
1.673
0.000
NH
O
1l, CDCl3
0.97
1.00
2.08
1.04
2.13
1.52
1.11
1.04
2.15
f1 (ppm)

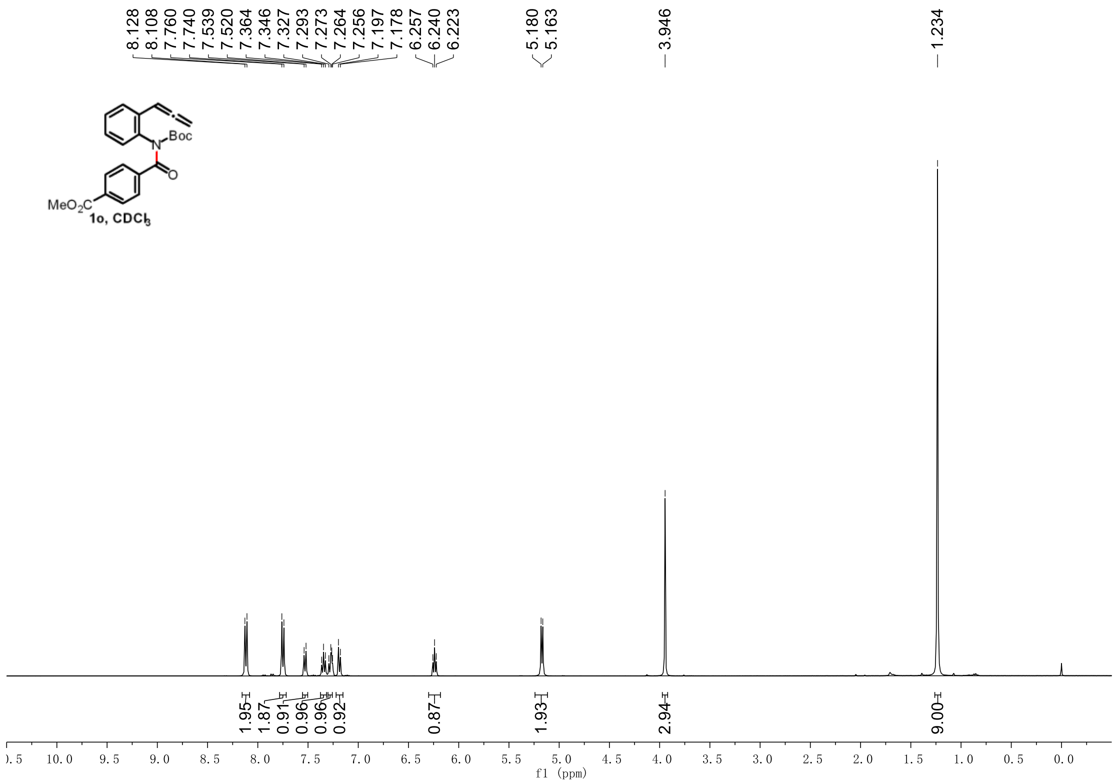

209.889
165.795
135.417
134.924
131.780
129.101
128.642
128.031
127.186
125.041
123.993
123.440
91.152
78.840
77.317
77.000
76.682
NH
O
1l, CDCl3
f1 (ppm)

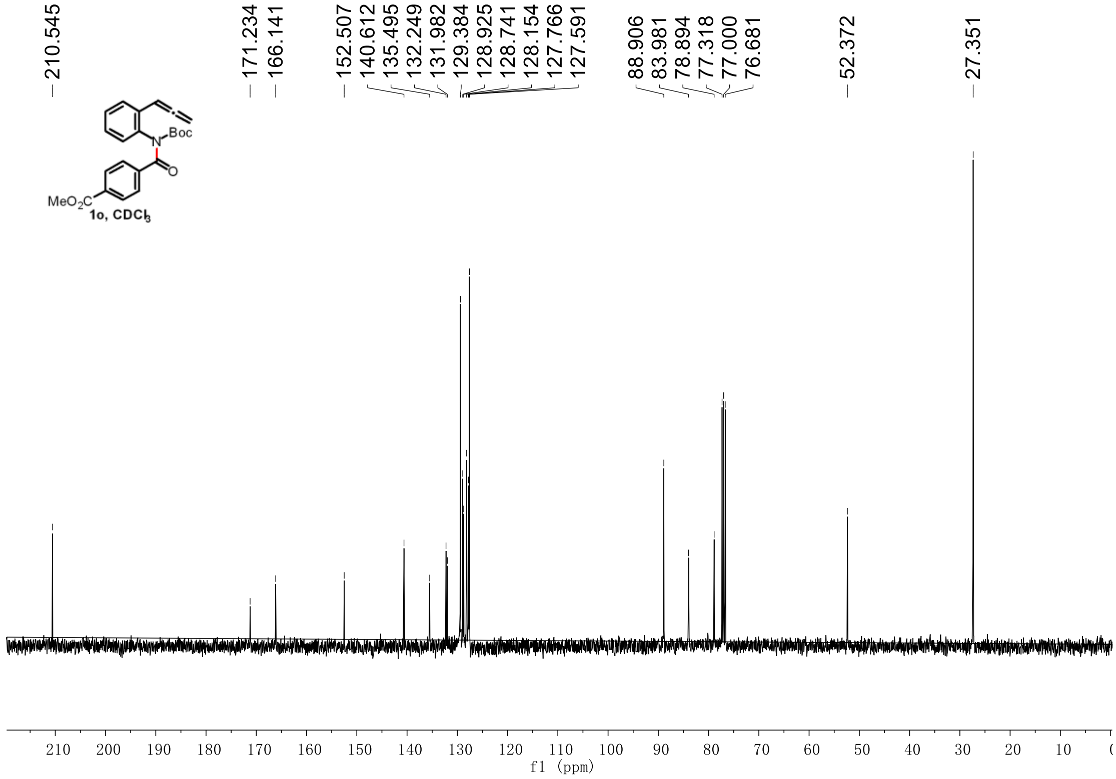

1m, CDCl3
f1 (ppm)

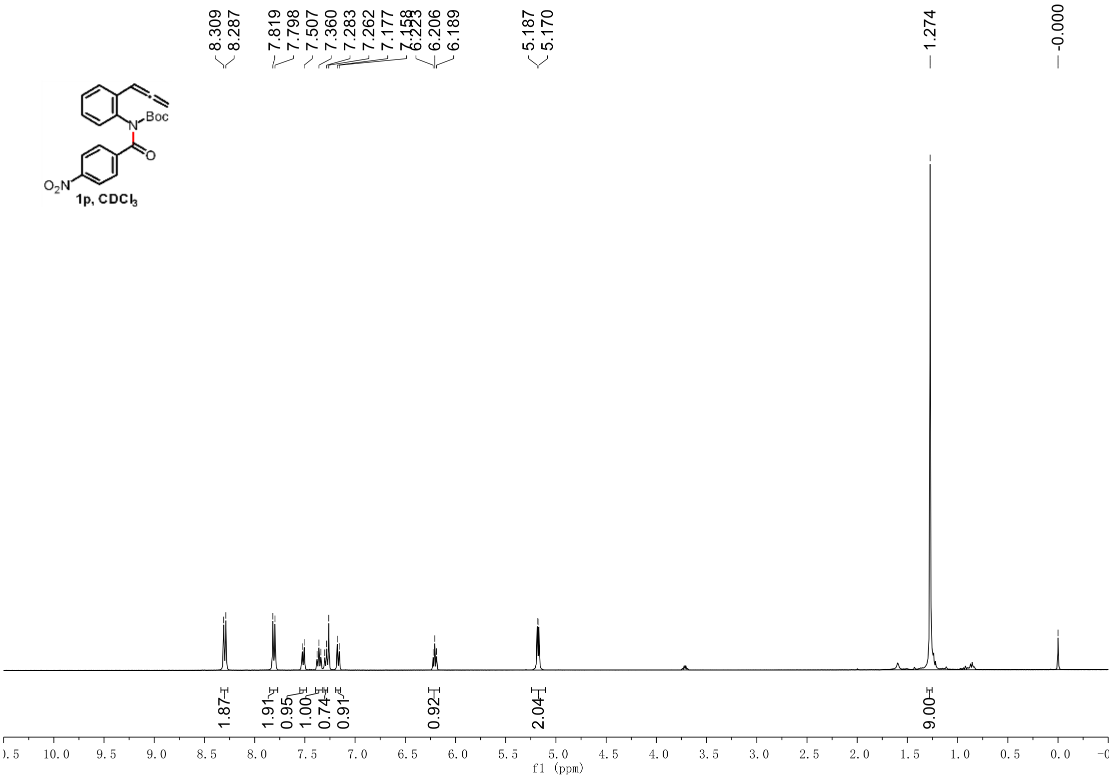

1m, CDCl3
f1 (ppm)

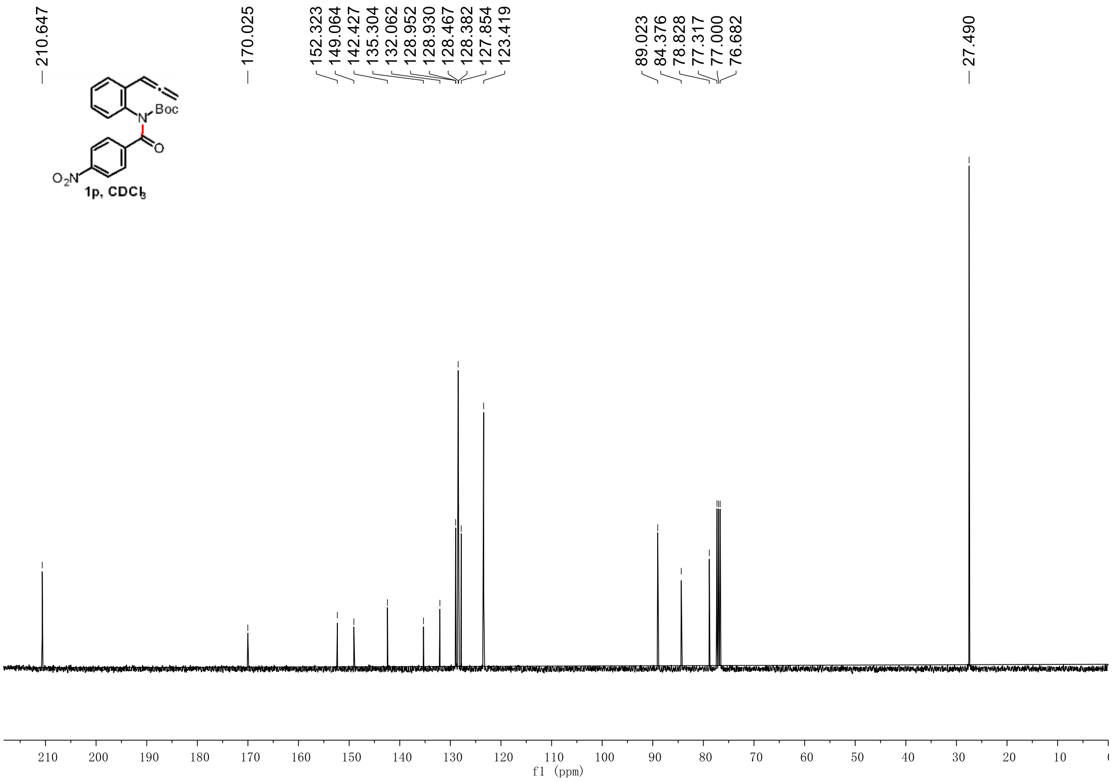

7.734
7.712
7.534
7.515
7.323
7.305
7.286
7.251
7.232
7.214
7.163
7.144
6.932
6.910
6.303
6.286
6.269
5.157
5.140
3.843
1.287
-0.000
Boc
N
O
MeO
1n, CDCl3
1.83
0.89
0.92
1.11
0.89
1.87
0.83
1.88
2.89
9.00
f1 (ppm)

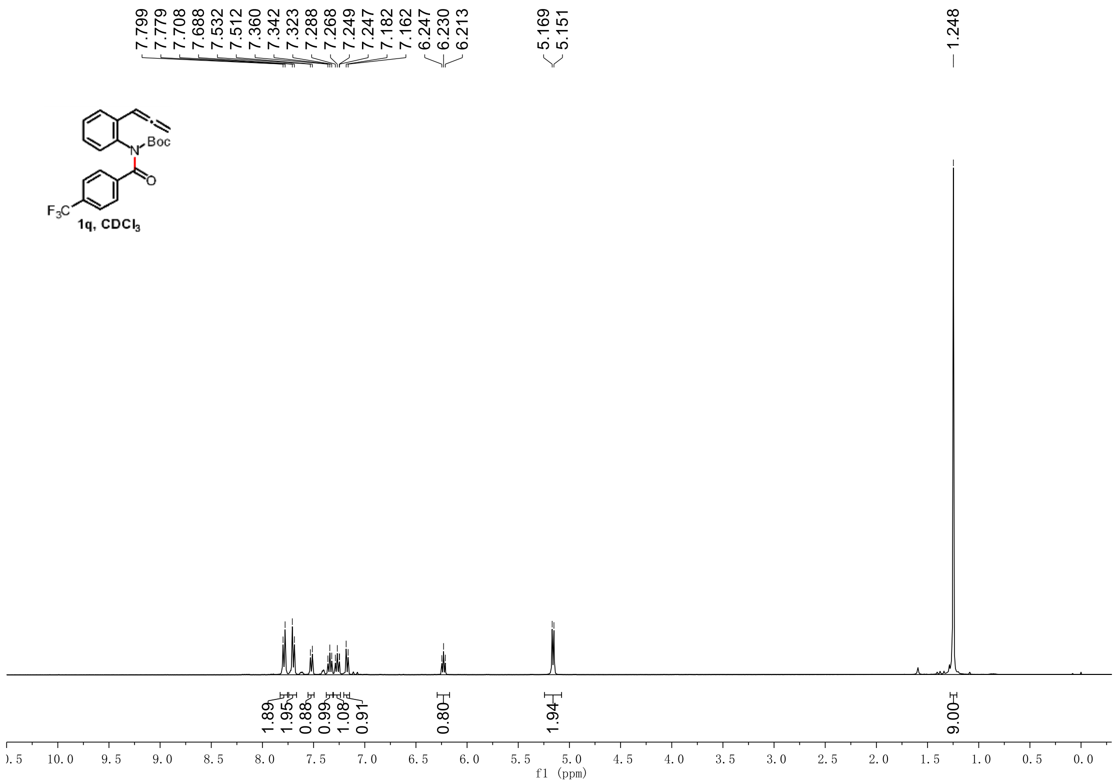

210.550
171.379
162.500
153.241
132.068
130.587
128.953
128.332
128.250
127.950
127.602
113.388
89.084
83.143
78.807
77.318
77.000
76.681
55.370
27.483
Boc
N
O
MeO
1n, CDCl3
f1 (ppm)

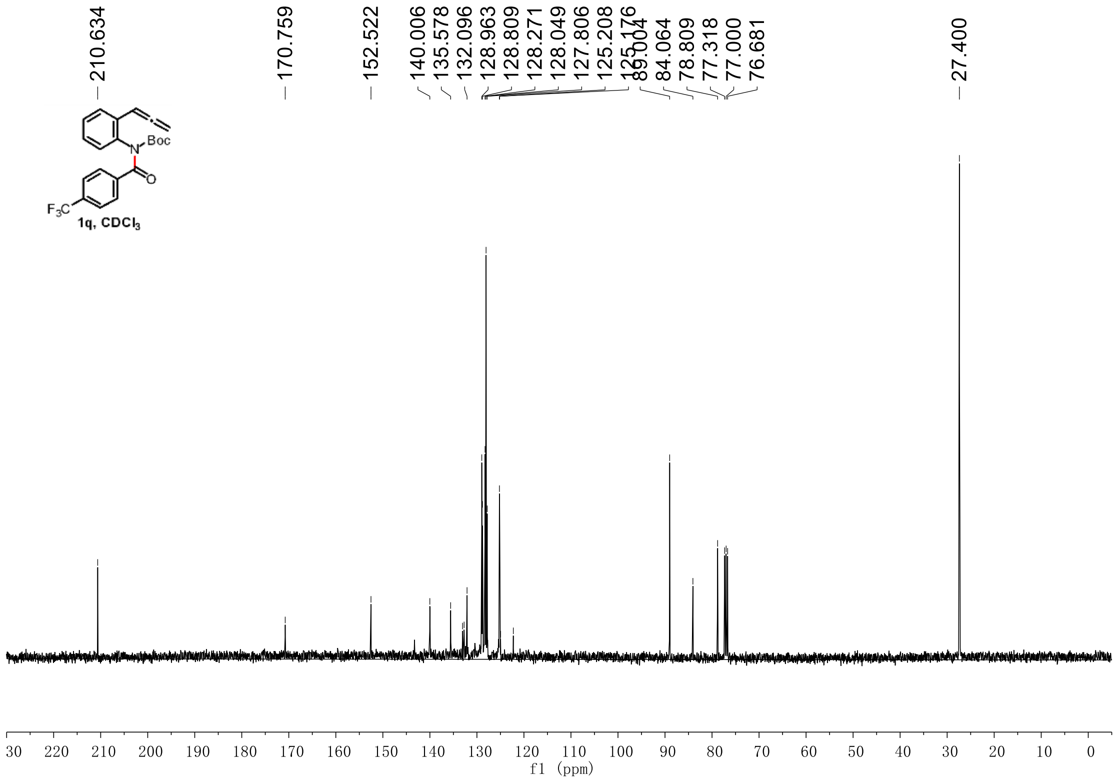

8.128
8.108
7.760
7.740
7.539
7.520
7.364
7.346
7.327
7.293
7.273
7.264
7.256
7.197
7.178
6.257
6.240
6.223
5.180
5.163
3.946
1.234
Boc
N
O
MeO2C
1o, CDCl3
1.95
1.87
0.91
0.96
0.96
0.92
0.87
1.93
2.94
9.00
f1 (ppm)

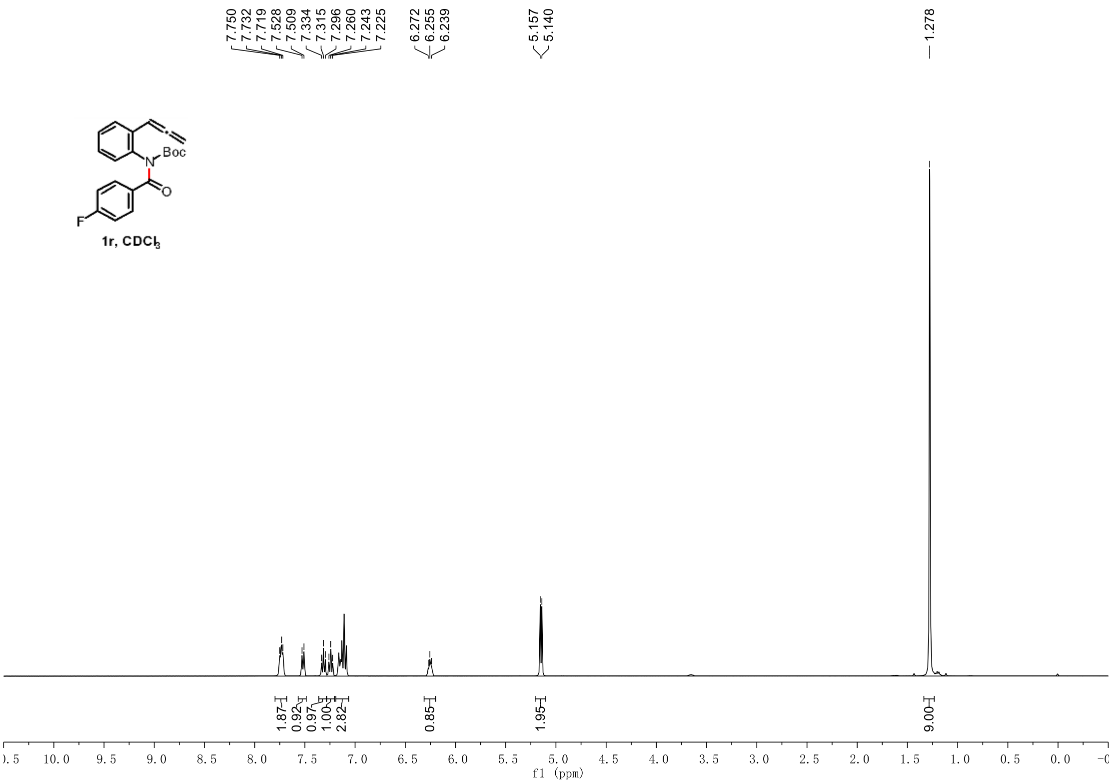

210.545
171.234
166.141
152.507
140.612
135.495
132.249
131.982
129.384
128.925
128.741
128.154
127.766
127.591
88.906
83.981
78.894
77.318
77.000
76.681
52.372
27.351
Boc
N
O
MeO2C
1o, CDCl3
f1 (ppm)

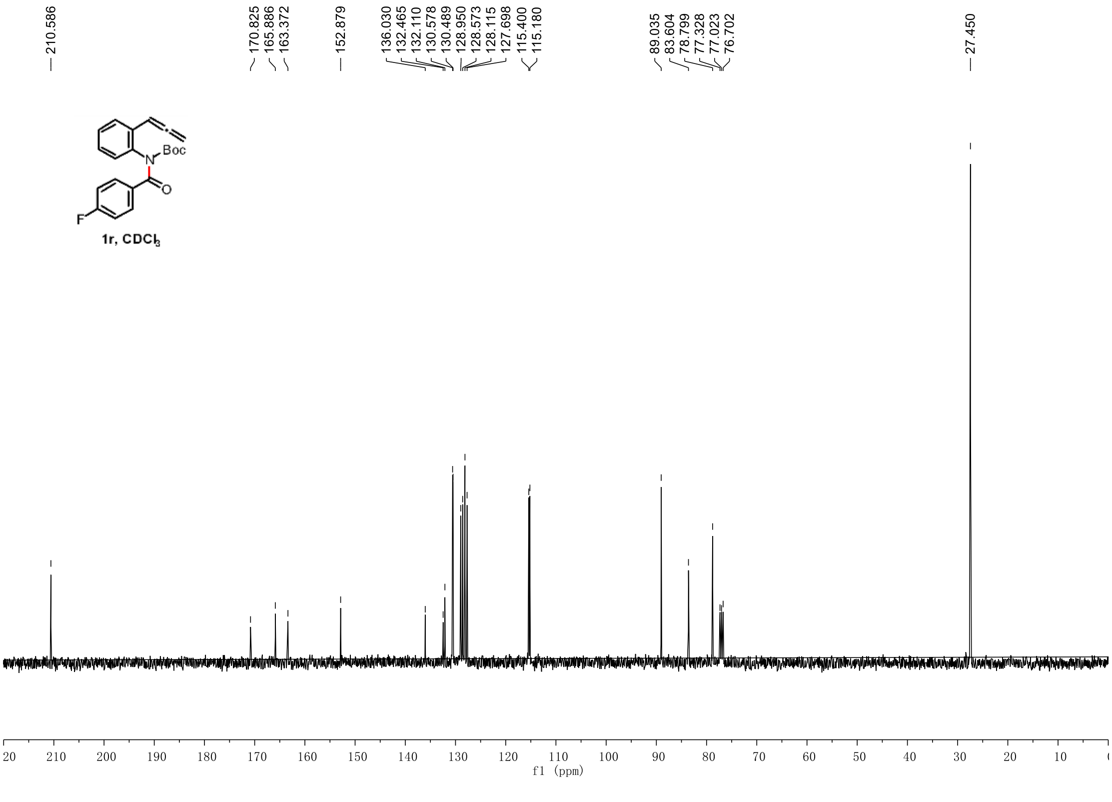


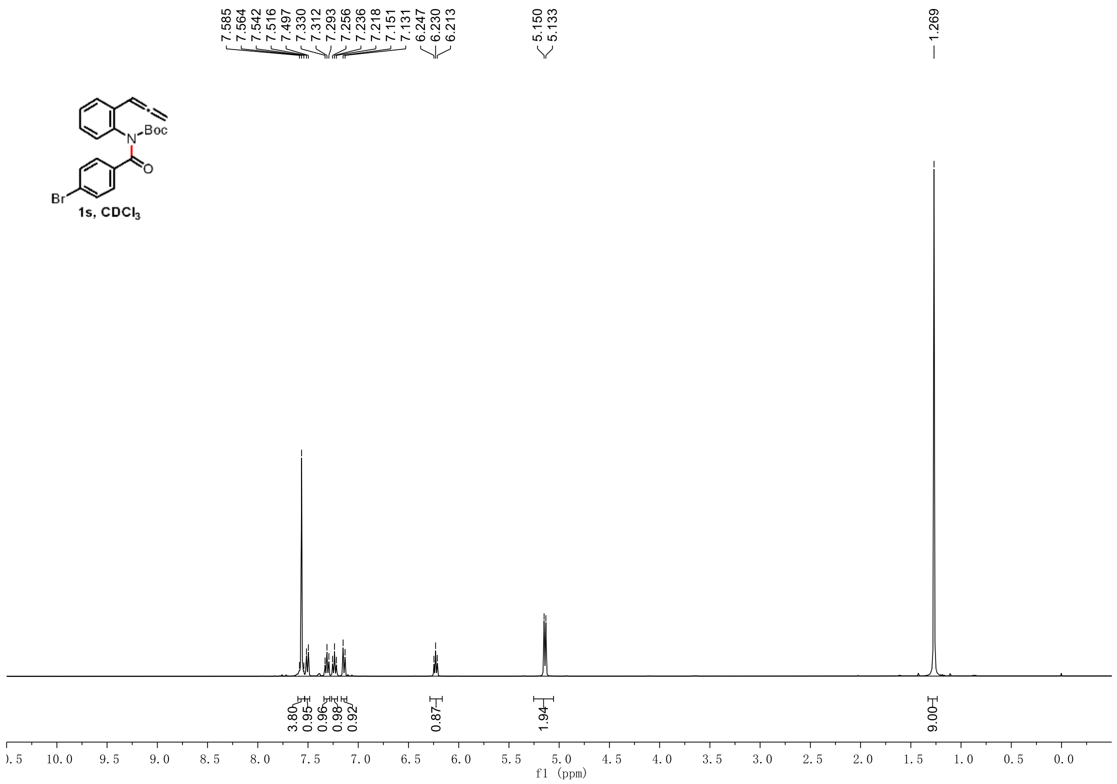


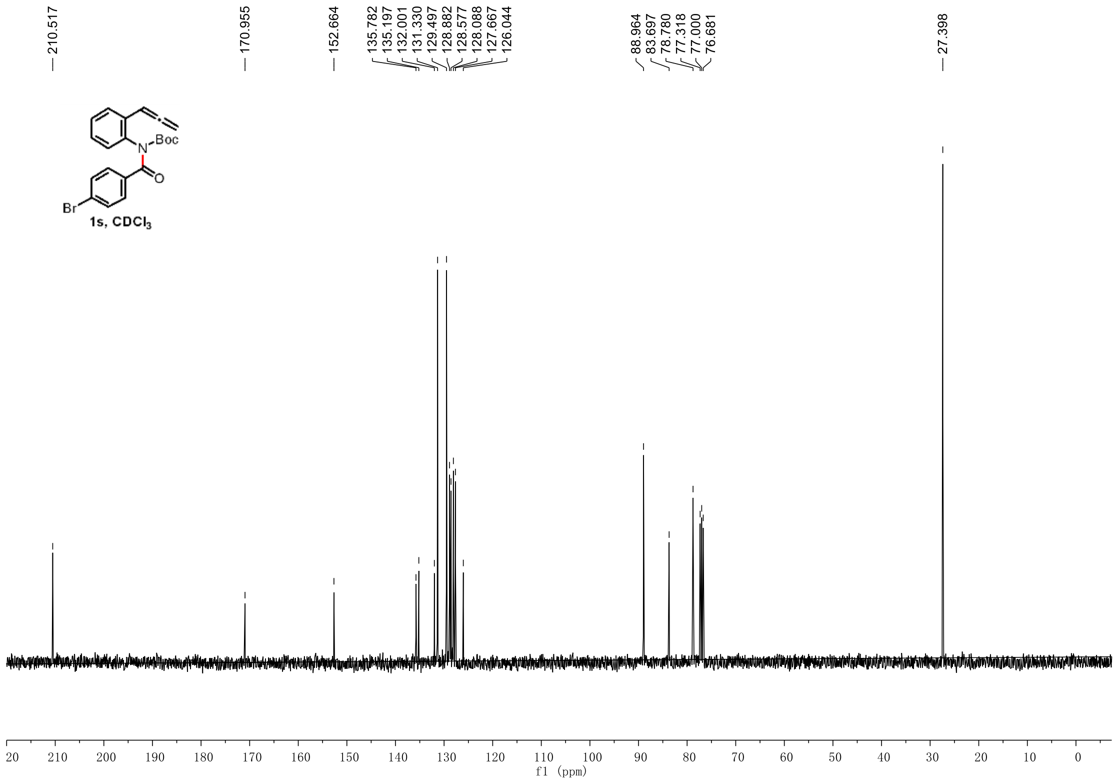

7.799
7.779
7.708
7.688
7.532
7.512
7.360
7.342
7.323
7.288
7.268
7.249
7.247
7.182
7.162
6.247
6.230
6.213
5.169
5.151
1.248
Boc
O
F_3C
1q, $CDCl_3$
1.89
1.95
0.88
0.99
1.08
0.91
0.80
1.94
9.00
f1 (ppm)

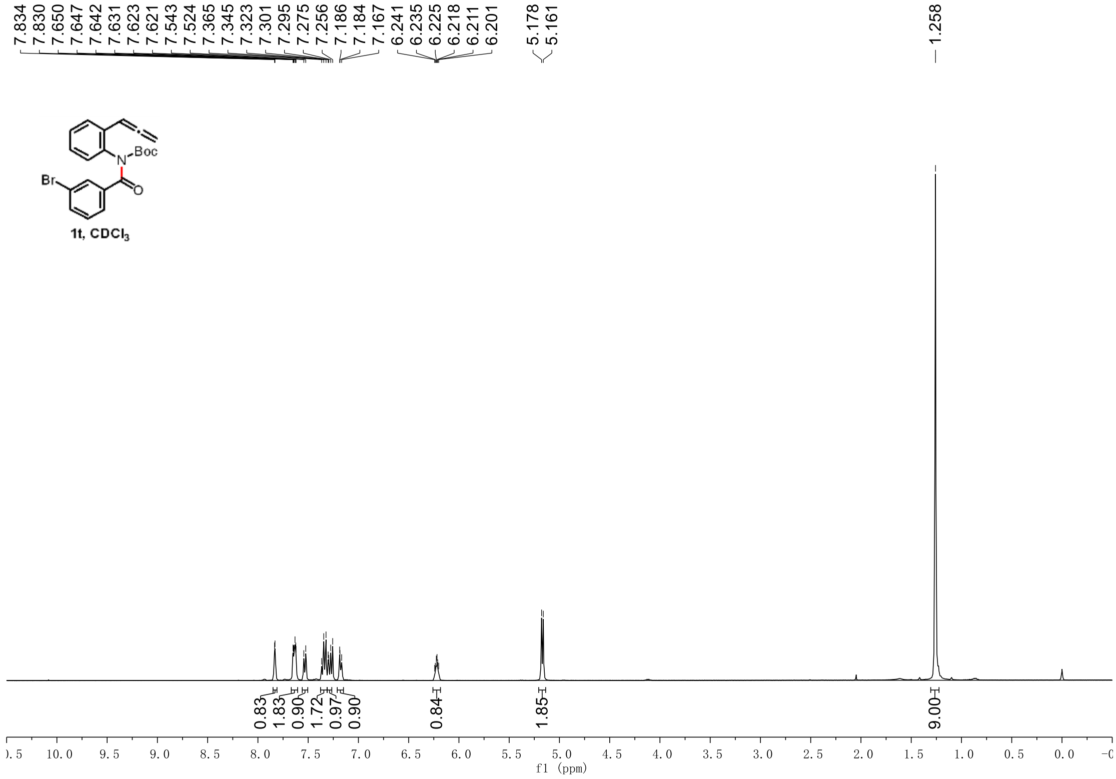

210.634
170.759
152.522
140.006
135.578
132.096
128.963
128.809
128.271
128.049
127.806
125.208
125.176
89.004
84.064
78.809
77.318
77.000
76.681
27.400
Boc
O
F_3C
1q, $CDCl_3$
f1 (ppm)

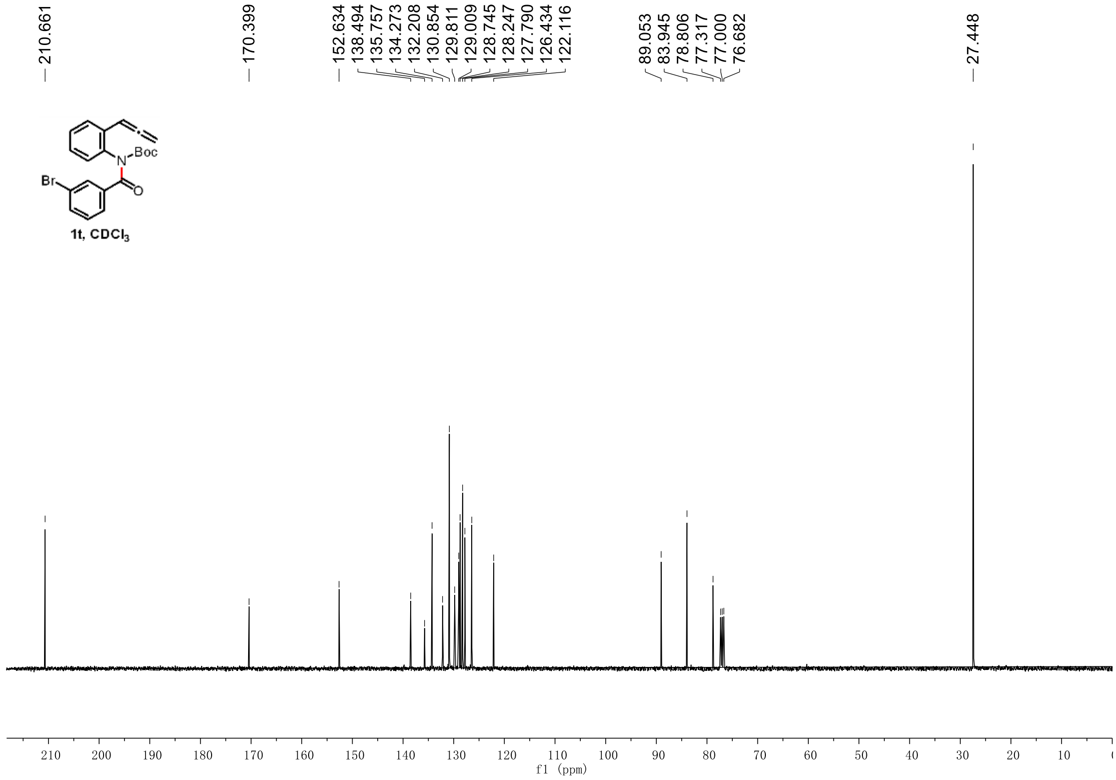

7.750
7.732
7.719
7.528
7.509
7.334
7.315
7.296
7.260
7.243
7.225
6.272
6.255
6.239
5.157
5.140
1.278
Boc
N
O
F
1r, CDCl3
1.87
0.92
0.97
1.00
2.82
0.85
1.95
9.00
f1 (ppm)

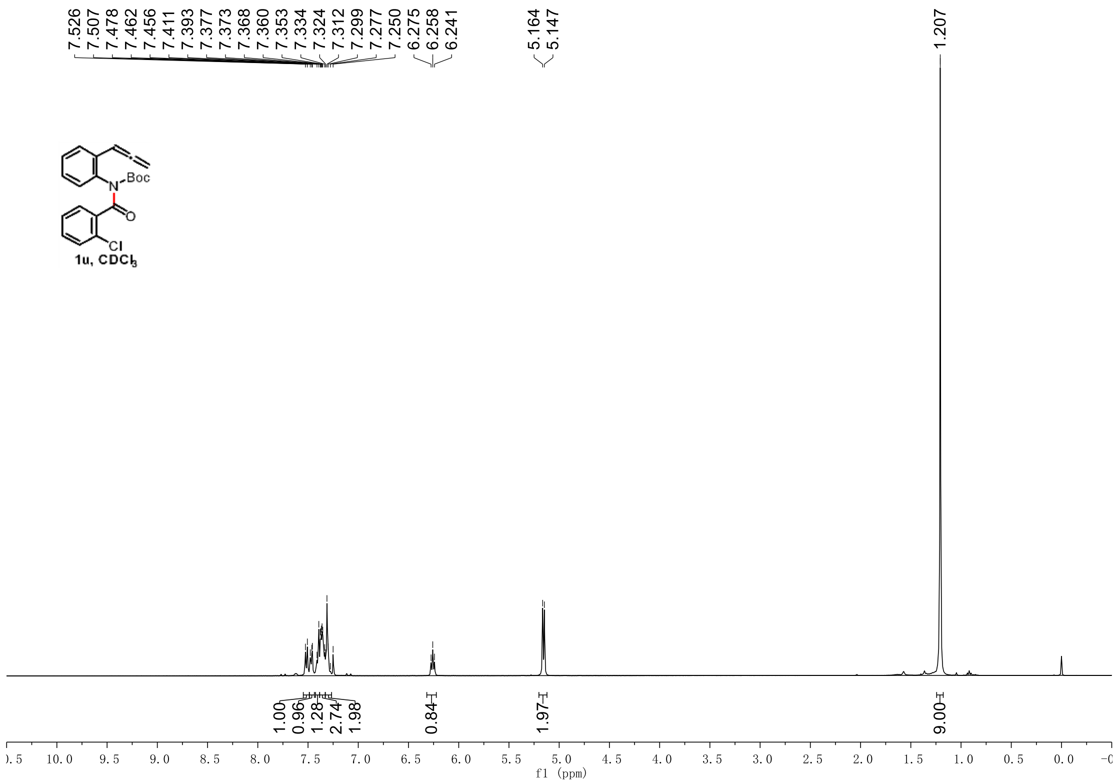

210.586
170.825
165.886
163.372
152.879
136.030
132.465
132.110
130.578
130.489
128.950
128.573
128.115
127.698
115.400
115.180
89.035
83.604
78.799
77.328
77.023
76.702
27.450
Boc
N
O
F
1r, CDCl3
f1 (ppm)

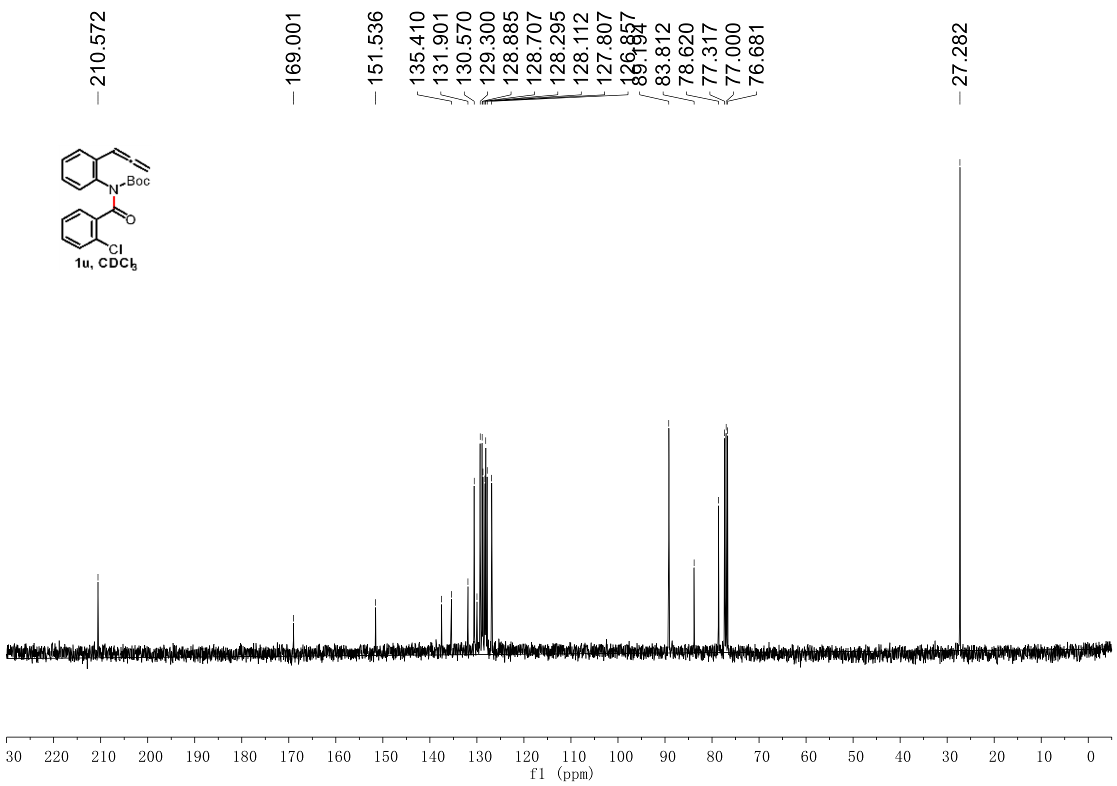

7.585
7.564
7.542
7.516
7.497
7.330
7.312
7.293
7.256
7.236
7.218
7.151
7.131
6.247
6.230
6.213
5.150
5.133
1.269
Boc
N
O
Br
1s, CDCl3
3.80
0.95
0.96
0.98
0.92
0.87
1.94
9.00
f1 (ppm)

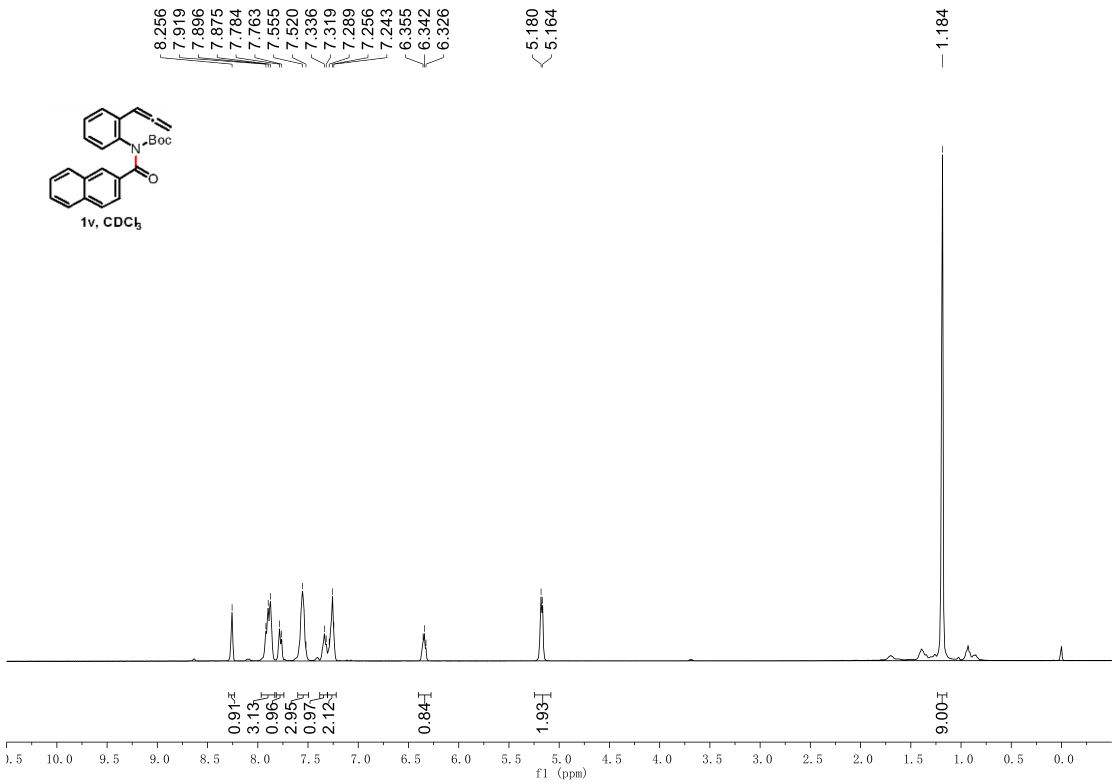

210.517
170.955
152.664
135.782
135.197
132.001
131.330
129.497
128.882
128.577
128.088
127.667
126.044
88.964
83.697
78.780
77.318
77.000
76.681
27.398
Boc
N
O
Br
1s, CDCl3
f1 (ppm)

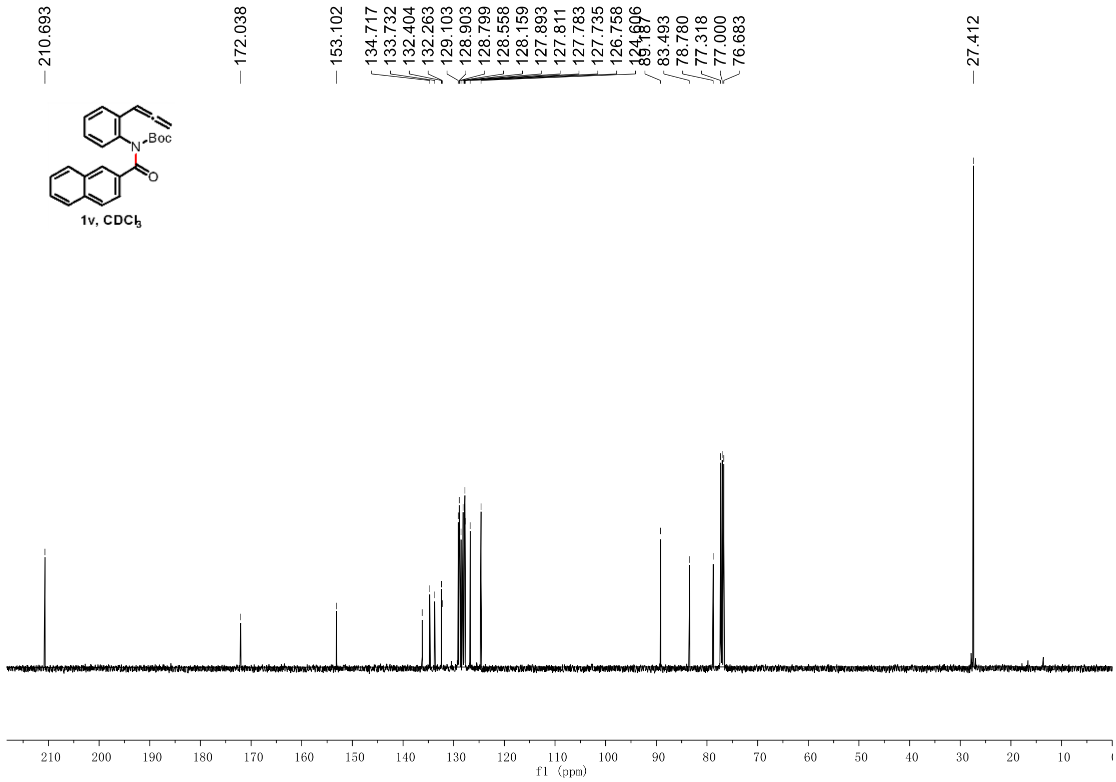

7.834 7.830 7.650 7.647 7.642 7.631 7.623 7.621 7.543 7.524 7.365 7.345 7.323 7.301 7.295 7.275 7.256 7.186 7.184 7.167 6.241 6.235 6.225 6.218 6.211 6.201
5.178 5.161
1.258
N
Boc
Br
O
1t, CDCl3
0.83 1.83 0.90 1.72 0.97 0.90
0.84
1.85
9.00
f1 (ppm)

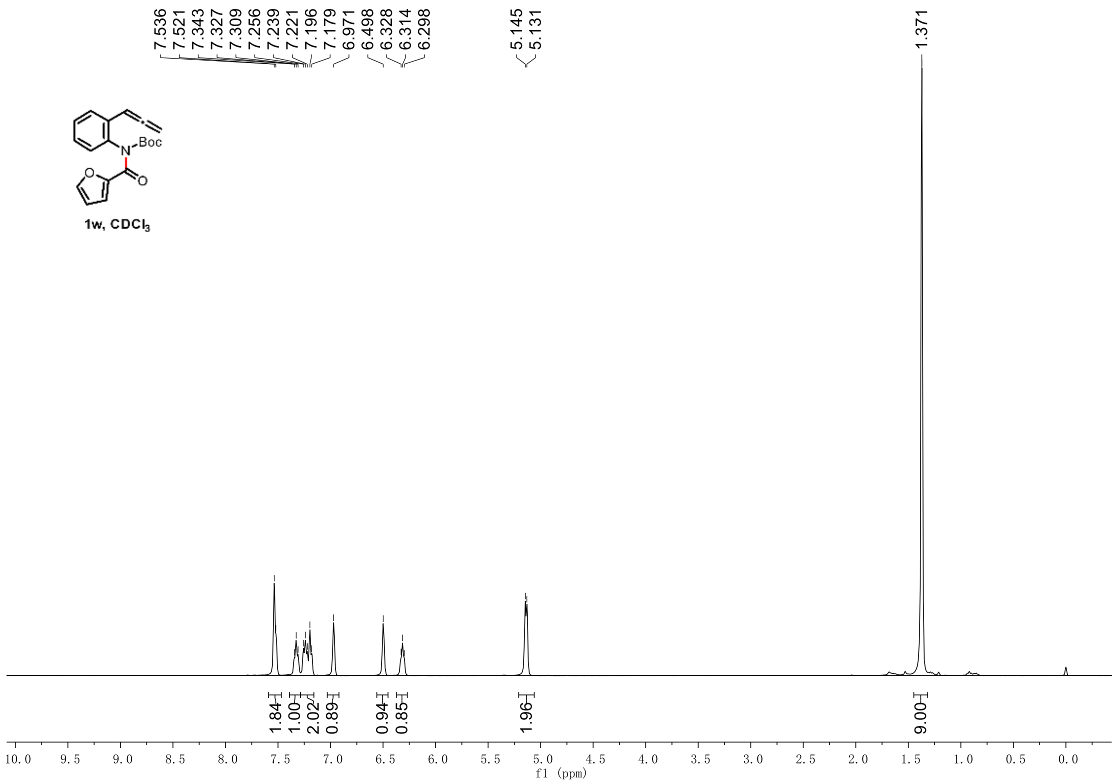

210.661
170.399
152.634 138.494 135.757 134.273 132.208 130.854 129.811 129.009 128.745 128.247 127.790 126.434 122.116
89.053 83.945 78.806 77.317 77.000 76.682
27.448
N
Boc
Br
O
1t, CDCl3
f1 (ppm)

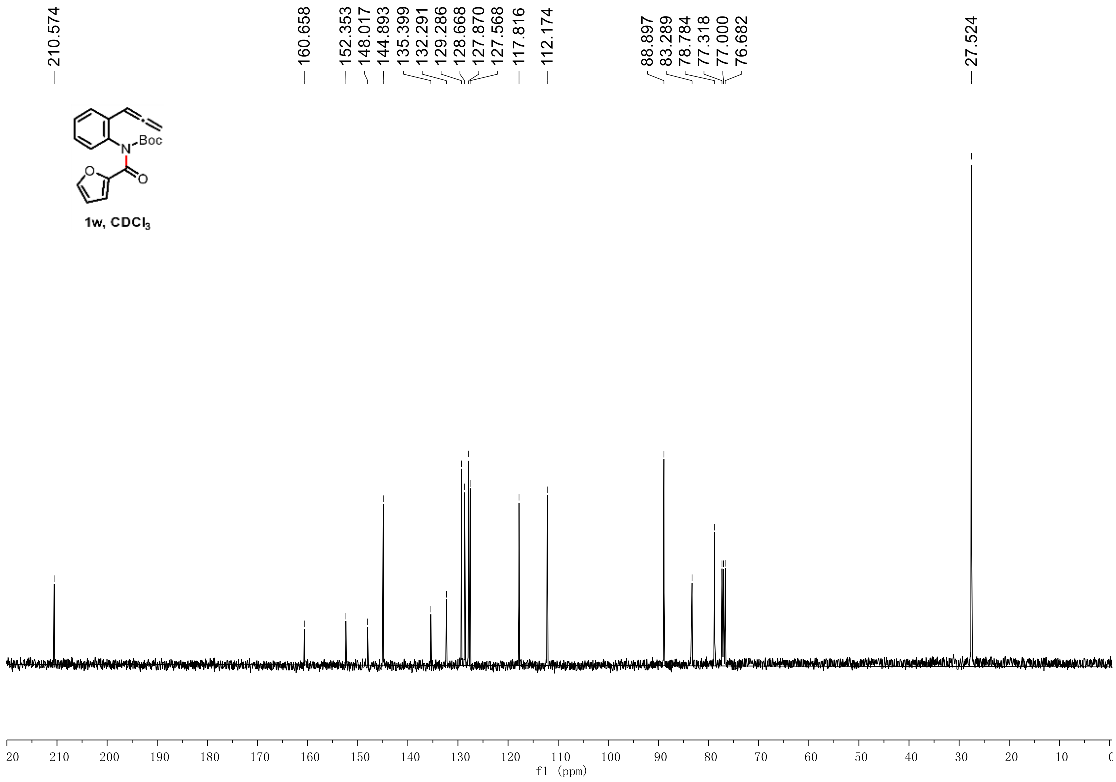

7.526
7.507
7.478
7.462
7.456
7.411
7.393
7.377
7.373
7.368
7.360
7.353
7.334
7.324
7.312
7.299
7.277
7.250
6.275
6.258
6.241
5.164
5.147
1.207
Boc
N
O
Cl
1u, CDCl3
1.00
0.96
1.28
2.74
1.98
0.84
1.97
9.00
f1 (ppm)

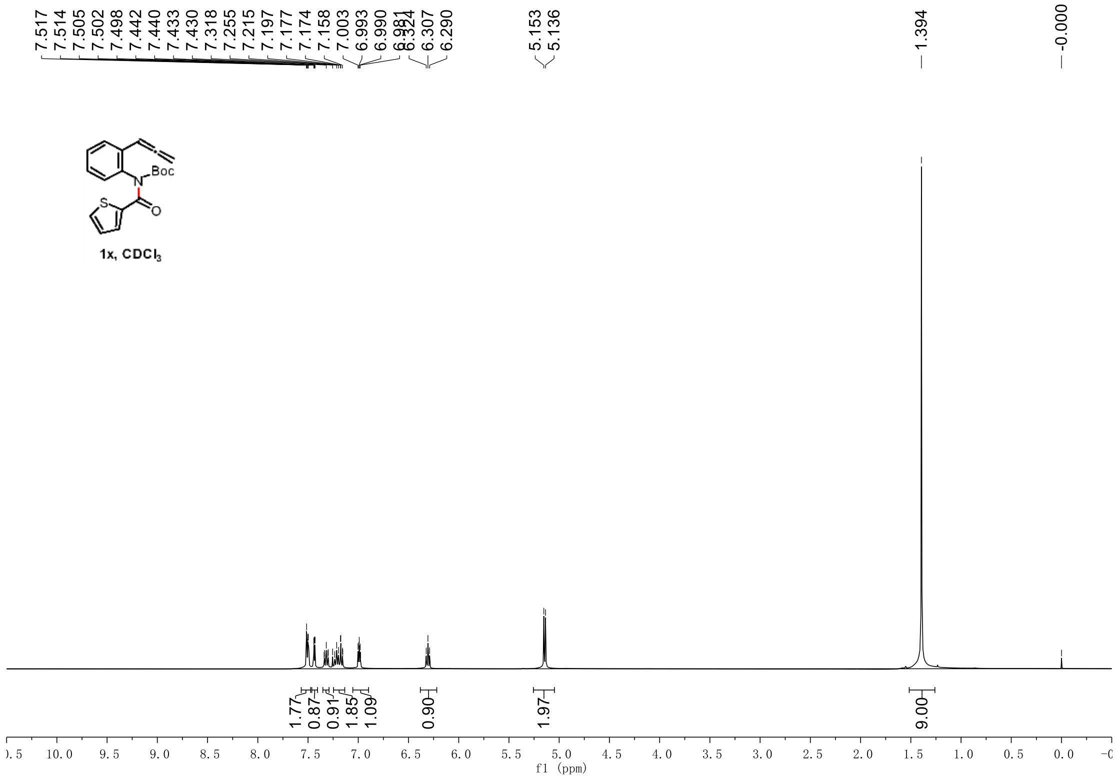

210.572
169.001
151.536
135.410
131.901
130.570
129.300
128.885
128.707
128.295
128.112
127.807
126.857
89.194
83.812
78.620
77.317
77.000
76.681
27.282
Boc
N
O
Cl
1u, CDCl3
f1 (ppm)

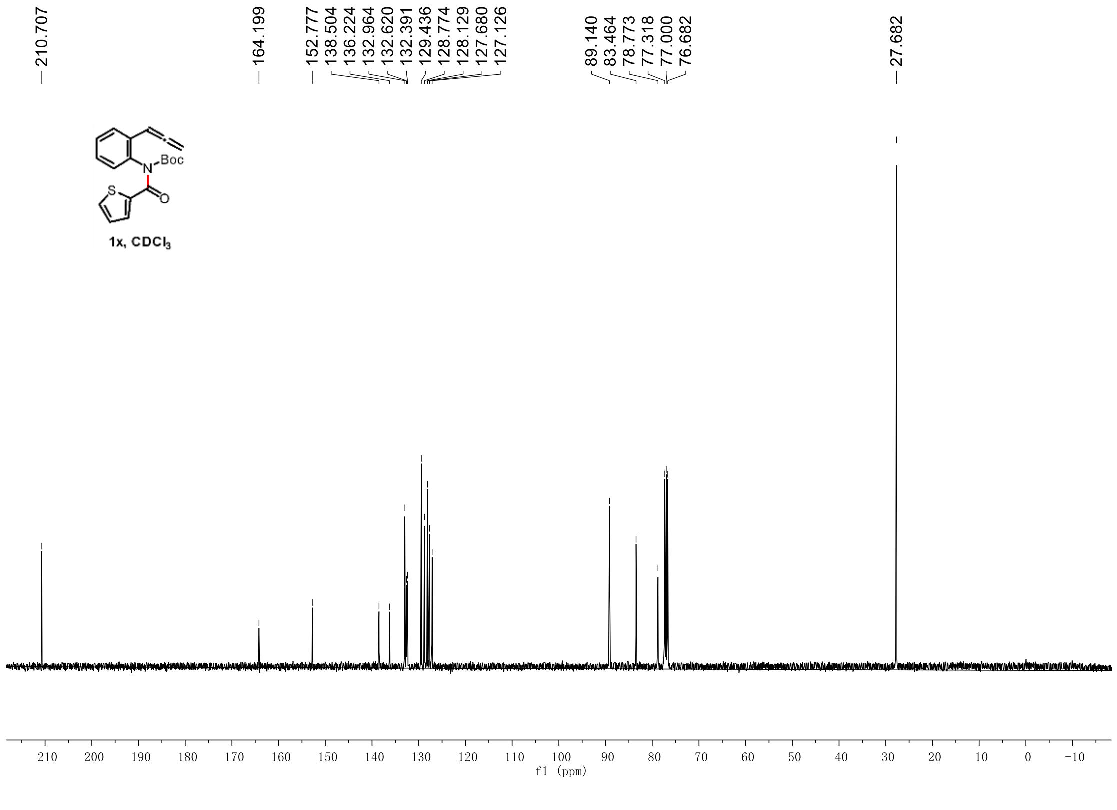

8.256
7.919
7.896
7.875
7.784
7.763
7.555
7.520
7.336
7.319
7.289
7.256
7.243
6.355
6.342
6.326
5.180
5.164
1.184
Boc
N
O
1v, CDCl3
0.91
3.13
0.96
2.95
0.97
2.12
0.84
1.93
9.00
f1 (ppm)

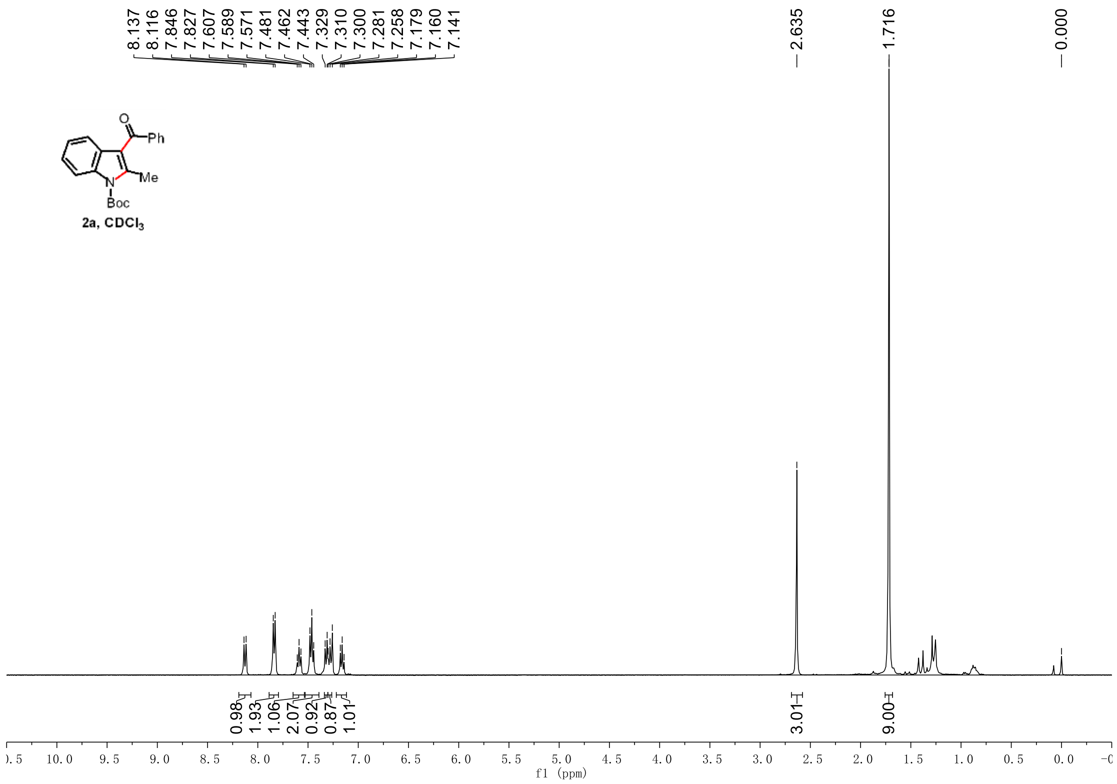

210.693
172.038
153.102
134.717
133.732
132.404
132.263
129.103
128.903
128.799
128.558
128.159
127.893
127.811
127.783
127.735
126.758
124.606
89.187
83.493
78.780
77.318
77.000
76.683
27.412
Boc
N
O
1v, CDCl3
f1 (ppm)

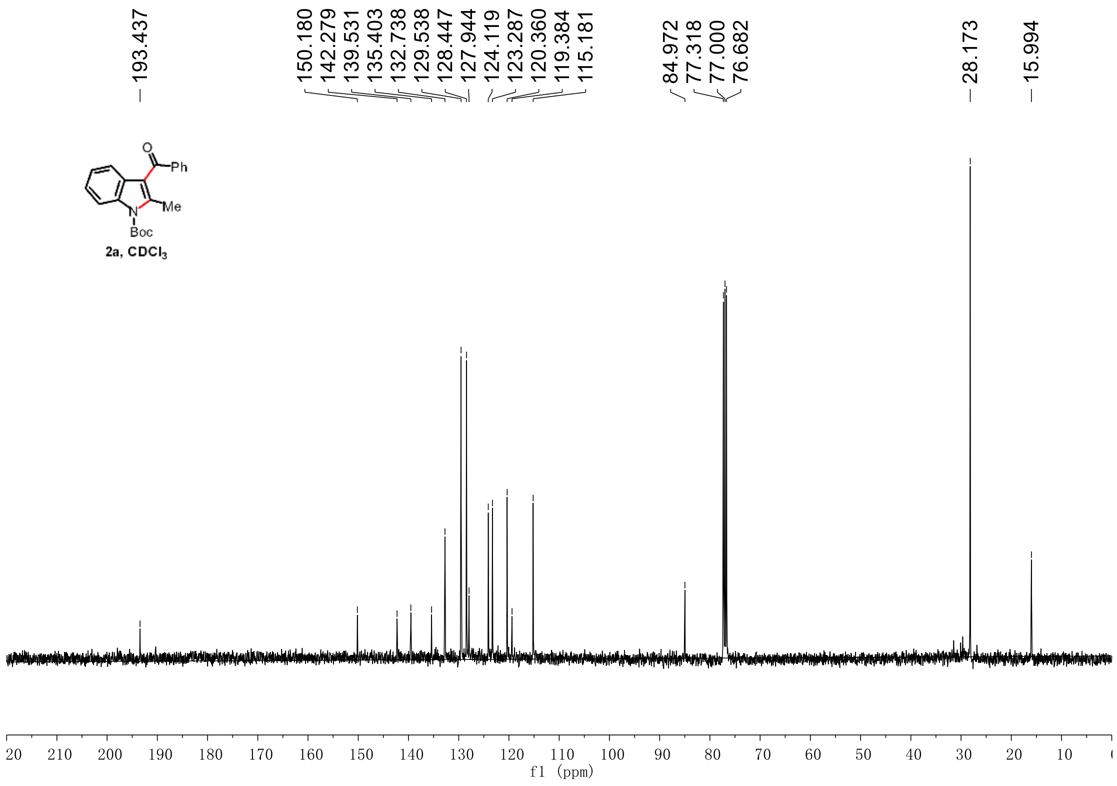

7.536
7.521
7.343
7.327
7.309
7.256
7.239
7.221
7.196
7.179
6.971
6.498
6.328
6.314
6.298
5.145
5.131
1.371
Boc
1w, CDCl3
1.84
1.00
2.02
0.89
0.94
0.85
1.96
9.00
f1 (ppm)

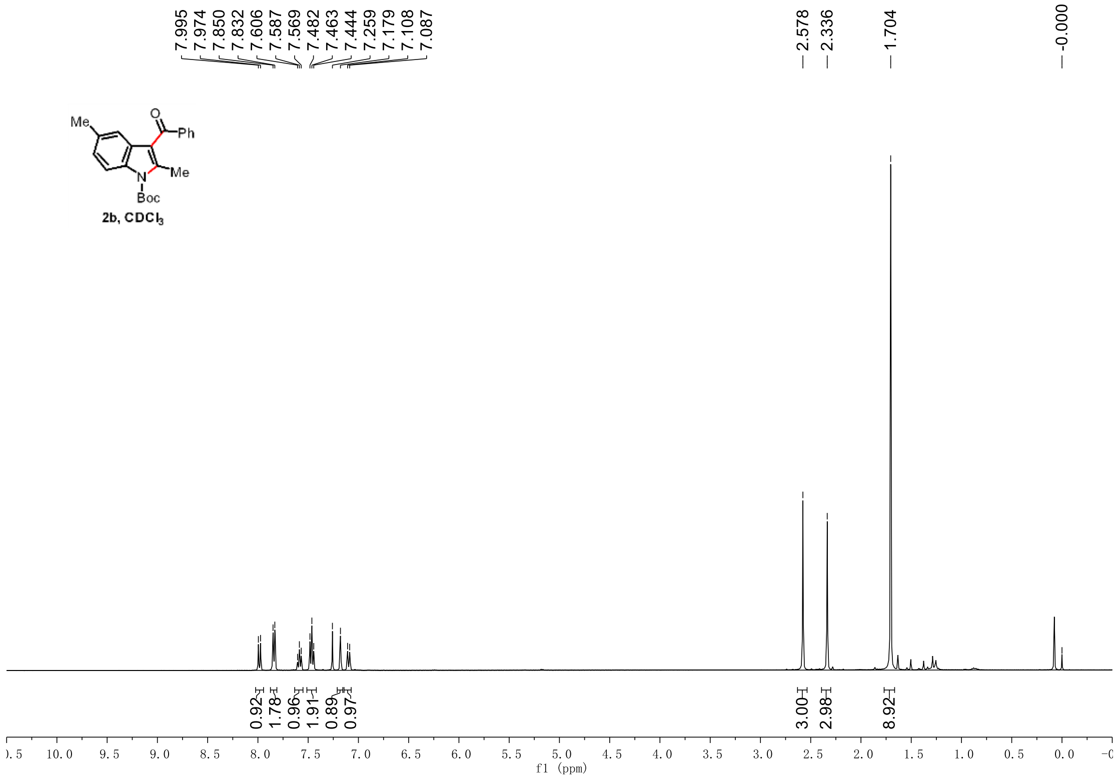

210.574
160.658
152.353
148.017
144.893
135.399
132.291
129.286
128.668
127.870
127.568
117.816
112.174
88.897
83.289
78.784
77.318
77.000
76.682
27.524
Boc
1w, CDCl3
f1 (ppm)

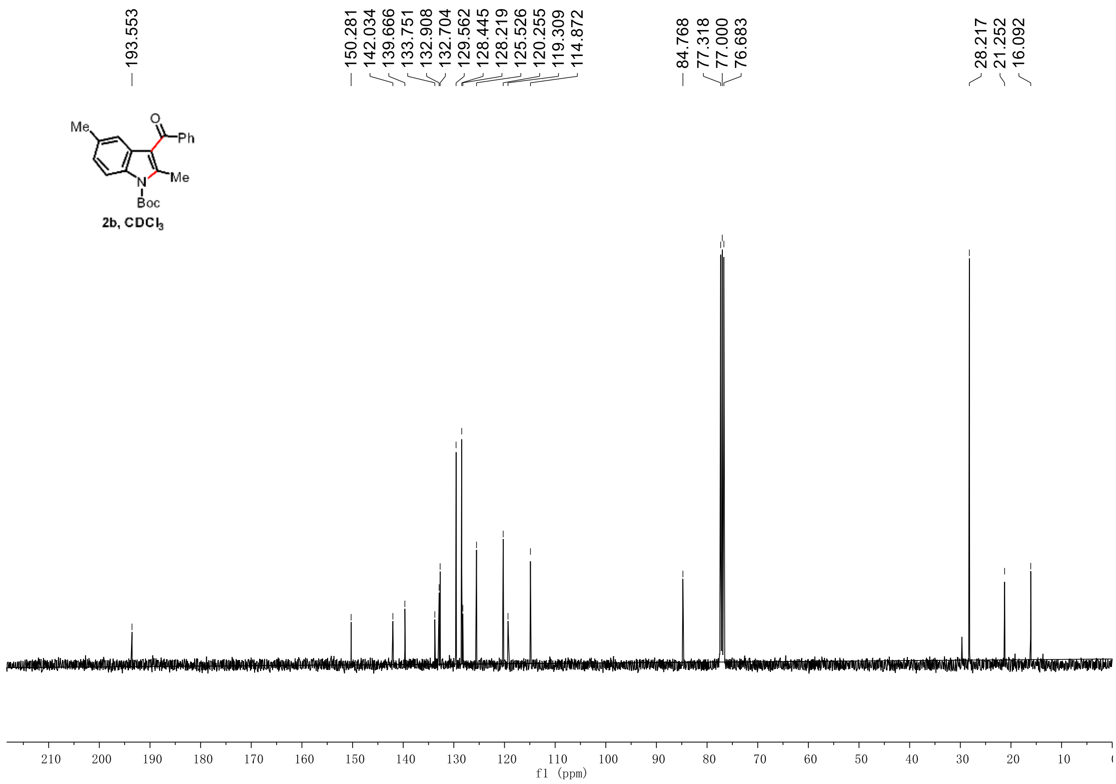

7.517
7.514
7.505
7.502
7.498
7.442
7.440
7.433
7.430
7.318
7.255
7.215
7.197
7.177
7.174
7.158
7.003
6.993
6.990
6.981
6.324
6.307
6.290
5.153
5.136
1.394
-0.000
Boc
N
S
O
1x, CDCl3
1.77
0.87
0.91
1.85
1.09
0.90
1.97
9.00
f1 (ppm)

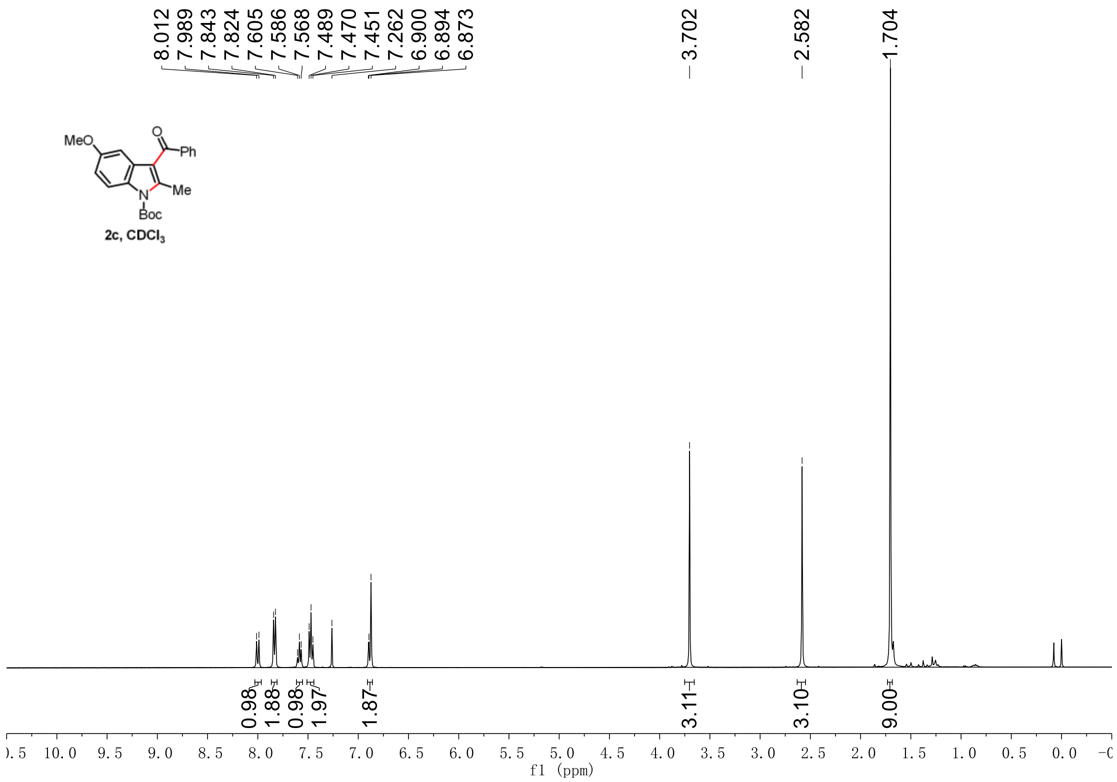

210.707
164.199
152.777
138.504
136.224
132.964
132.620
132.391
129.436
128.774
128.129
127.680
127.126
89.140
83.464
78.773
77.318
77.000
76.682
27.682
Boc
N
S
O
1x, CDCl3
f1 (ppm)

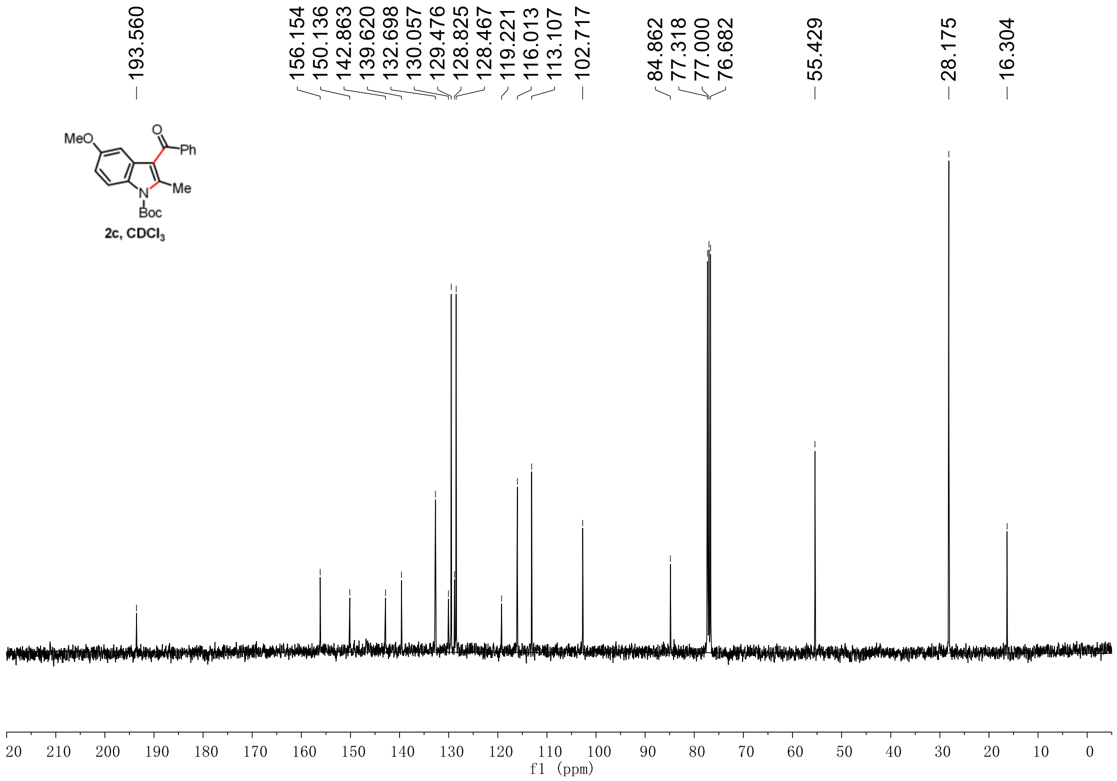

8.137
8.116
7.846
7.827
7.607
7.589
7.571
7.481
7.462
7.443
7.329
7.310
7.300
7.281
7.258
7.179
7.160
7.141
2.635
1.716
0.000
Ph
Me
N
Boc
2a, CDCl3
0.98
1.93
1.06
2.07
0.92
0.87
1.01
3.01
9.00
f1 (ppm)

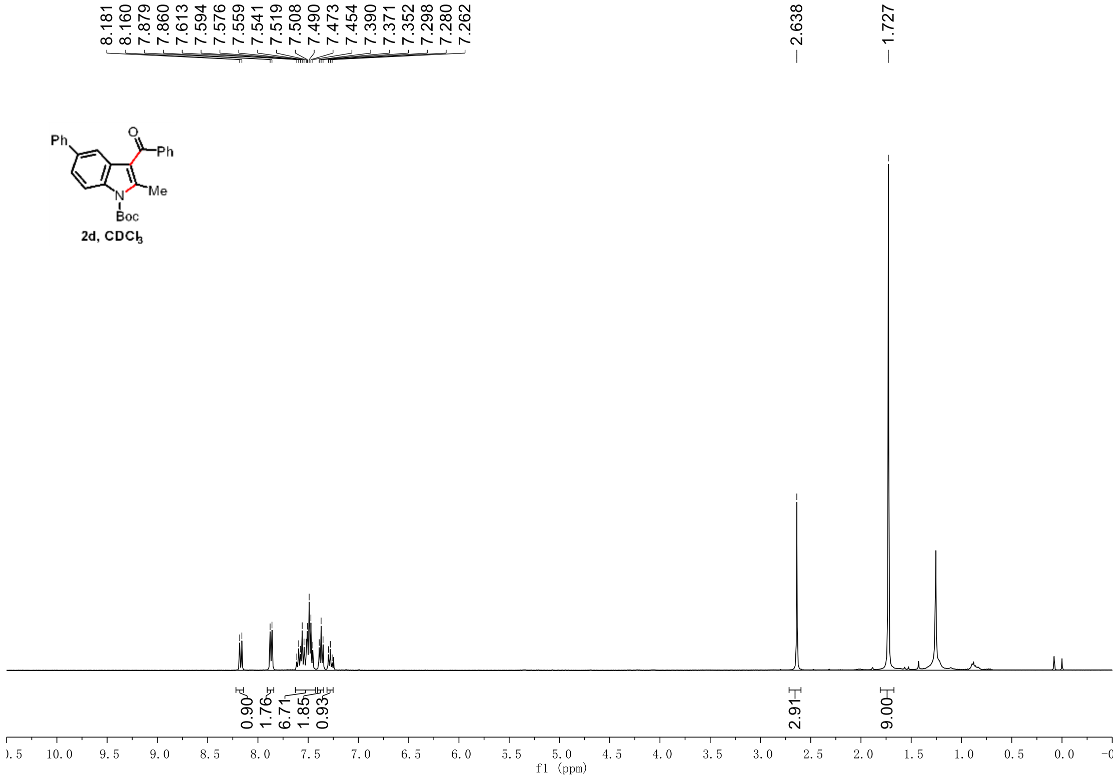

193.437
150.180
142.279
139.531
135.403
132.738
129.538
128.447
127.944
124.119
123.287
120.360
119.384
115.181
84.972
77.318
77.000
76.682
28.173
15.994
Ph
Me
N
Boc
2a, CDCl3
f1 (ppm)

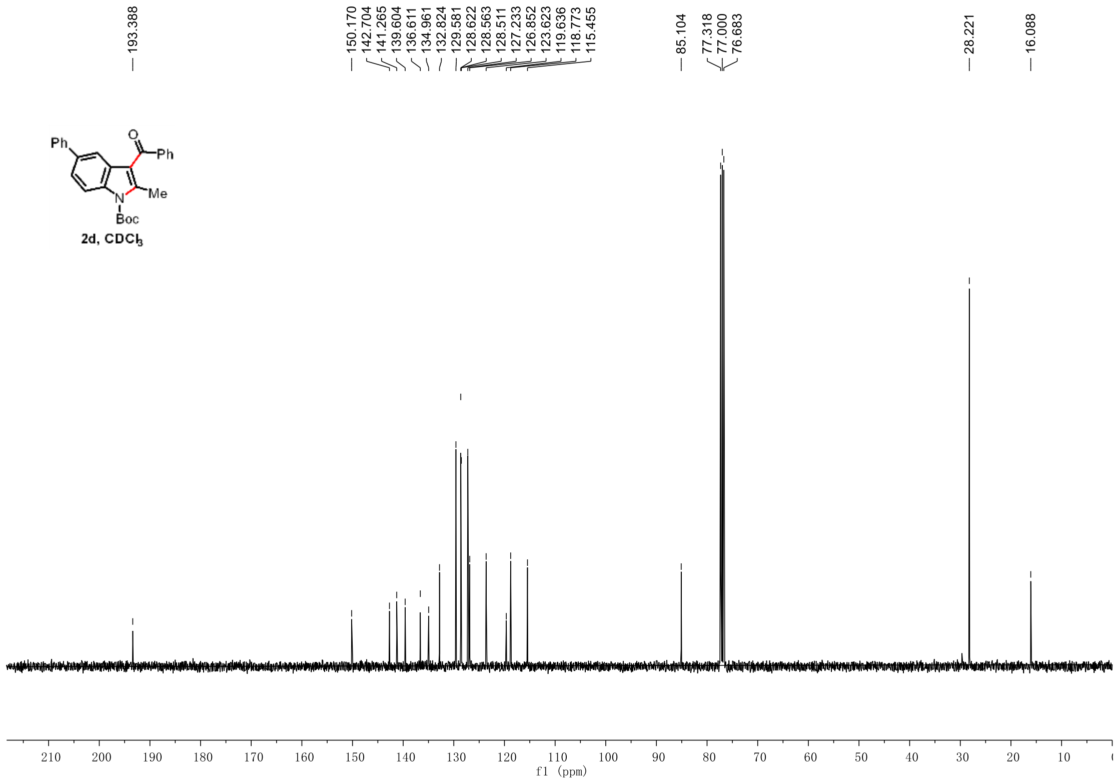

7.995
7.974
7.850
7.832
7.606
7.587
7.569
7.482
7.463
7.444
7.259
7.179
7.108
7.087
2.578
2.336
1.704
-0.000
Me
O
Ph
N
Me
Boc
2b, CDCl3
0.92
1.78
0.96
1.91
0.89
0.97
3.00
2.98
8.92
f1 (ppm)

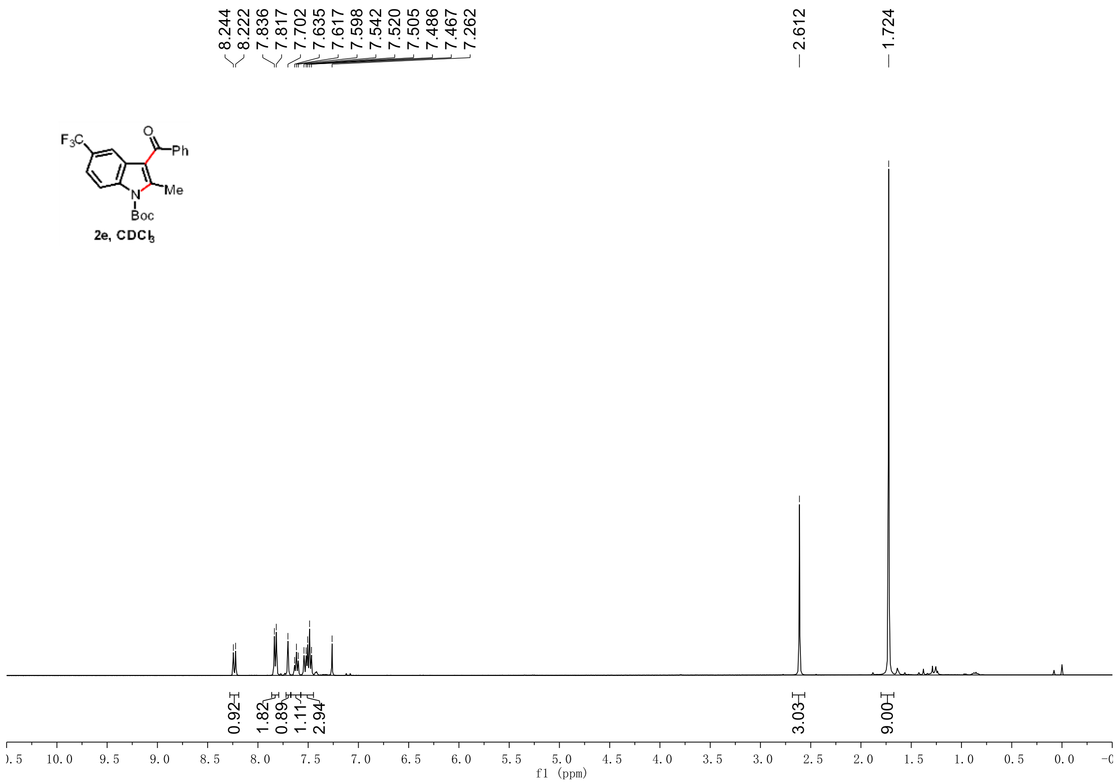

193.553
150.281
142.034
139.666
133.751
132.908
132.704
129.562
128.445
128.219
125.526
120.255
119.309
114.872
84.768
77.318
77.000
76.683
28.217
21.252
16.092
Me
O
Ph
N
Me
Boc
2b, CDCl3
f1 (ppm)

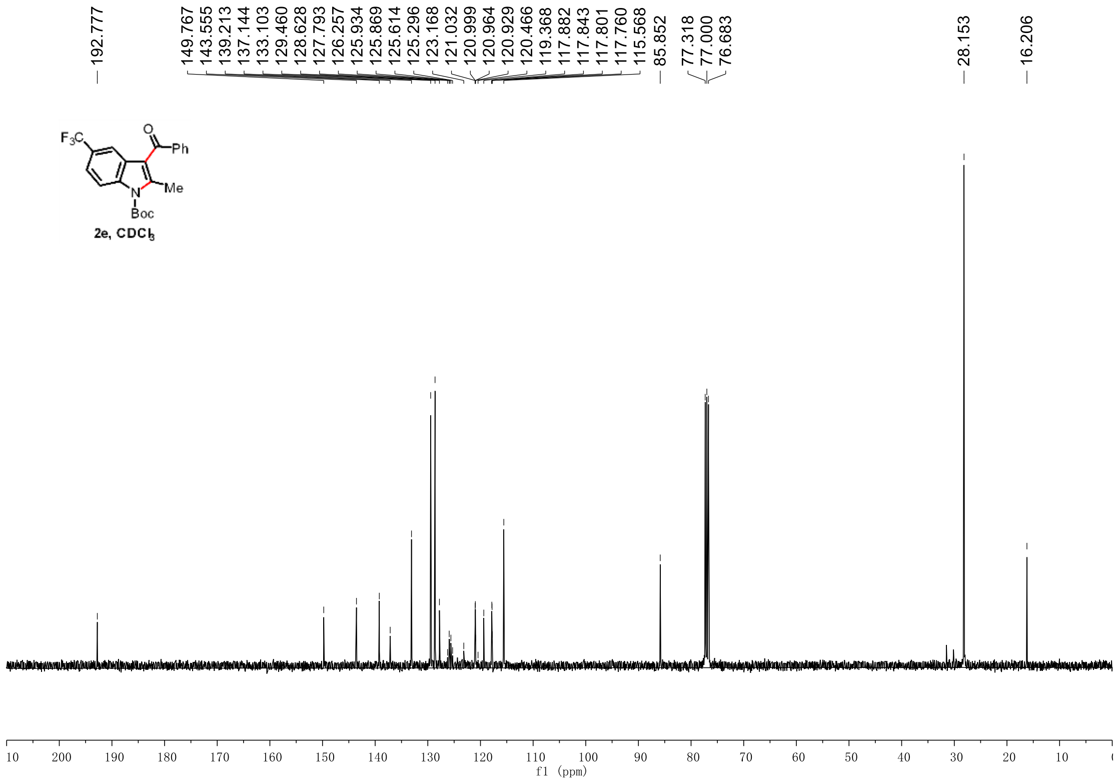

8.012
7.989
7.843
7.824
7.605
7.586
7.568
7.489
7.470
7.451
7.262
6.900
6.894
6.873
3.702
2.582
1.704
MeO
O
Ph
N
Me
Boc
2c, CDCl$_3$
0.98
1.88
0.98
1.97
1.87
3.11
3.10
9.00
f1 (ppm)

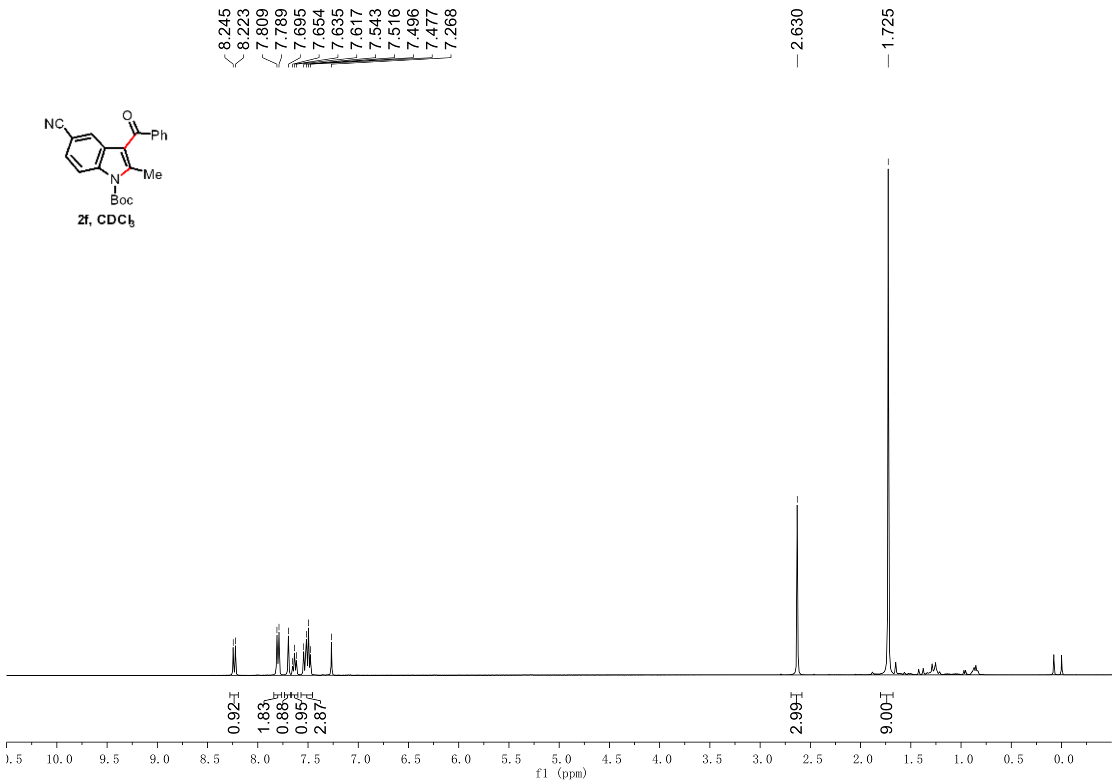

193.560
156.154
150.136
142.863
139.620
132.698
130.057
129.476
128.825
128.467
119.221
116.013
113.107
102.717
84.862
77.318
77.000
76.682
55.429
28.175
16.304
MeO
O
Ph
N
Me
Boc
2c, CDCl$_3$
f1 (ppm)

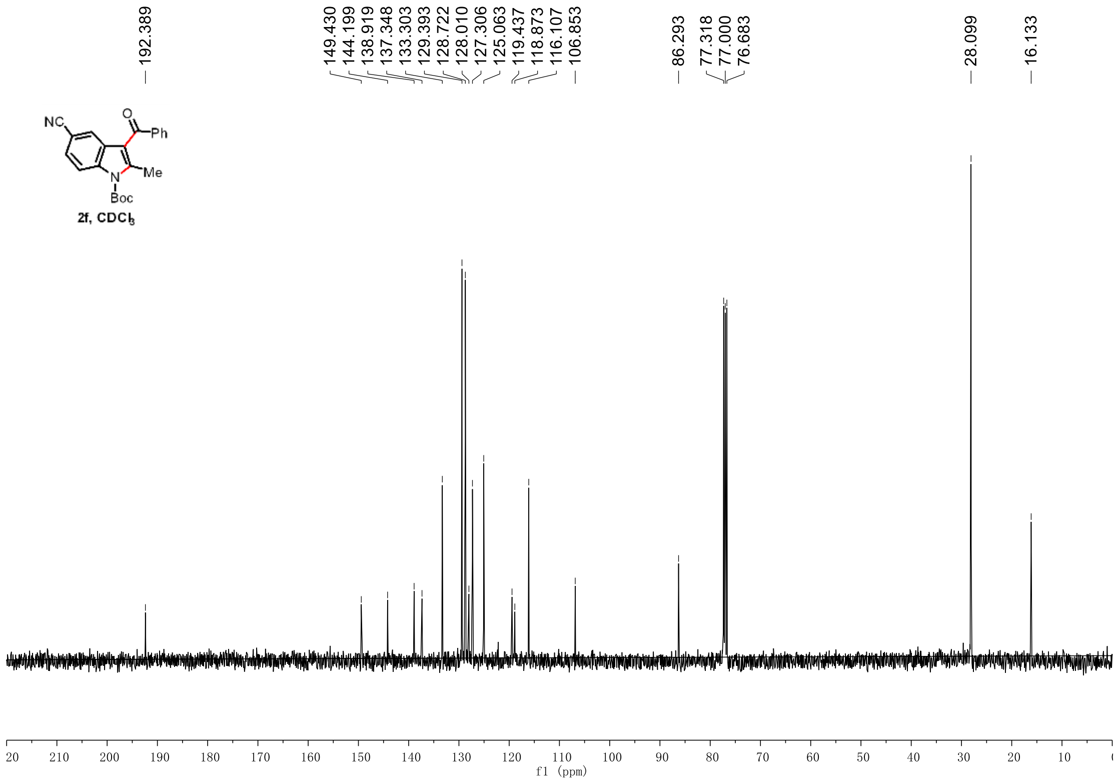

8.181
8.160
7.879
7.860
7.613
7.594
7.576
7.559
7.541
7.519
7.508
7.490
7.473
7.454
7.390
7.371
7.352
7.298
7.280
7.262
2.638
1.727
Ph
O
Ph
Me
N
Boc
2d, CDCl3
0.90
1.76
6.71
1.85
0.93
2.91
9.00
f1 (ppm)

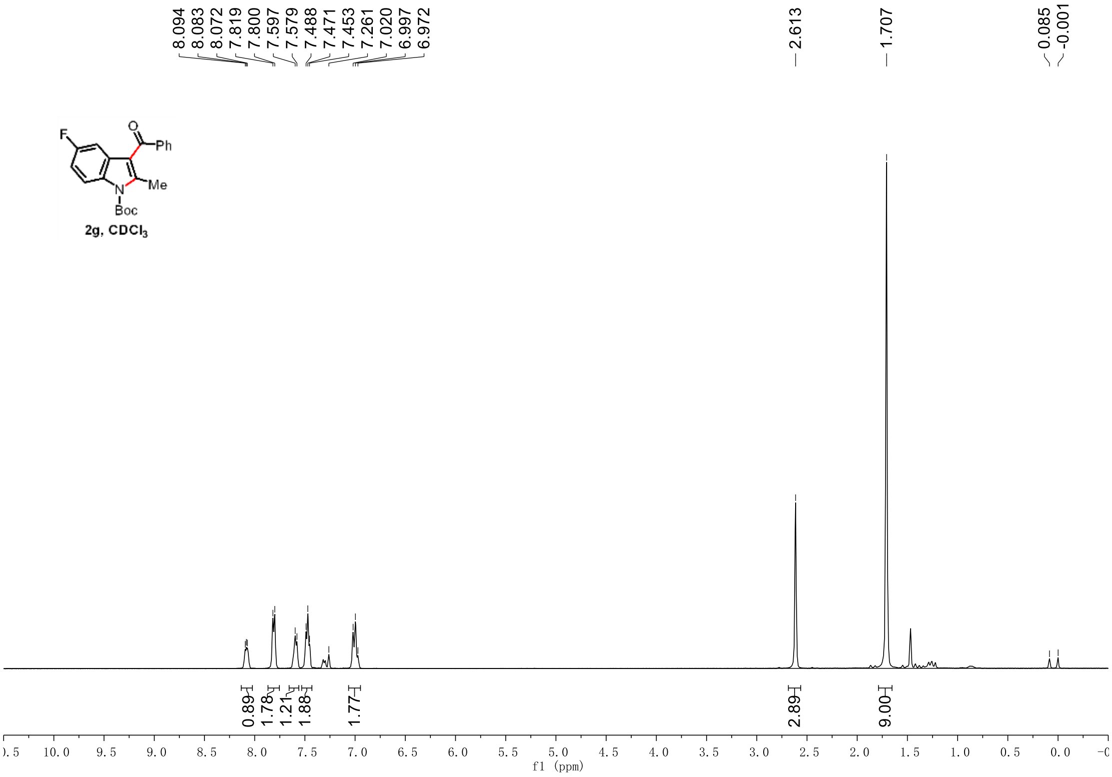

193.388
150.170
142.704
141.265
139.604
136.611
134.961
132.824
129.581
128.622
128.563
128.511
127.233
126.852
123.623
119.636
118.773
115.455
85.104
77.318
77.000
76.683
28.221
16.088
Ph
O
Ph
Me
N
Boc
2d, CDCl3
f1 (ppm)

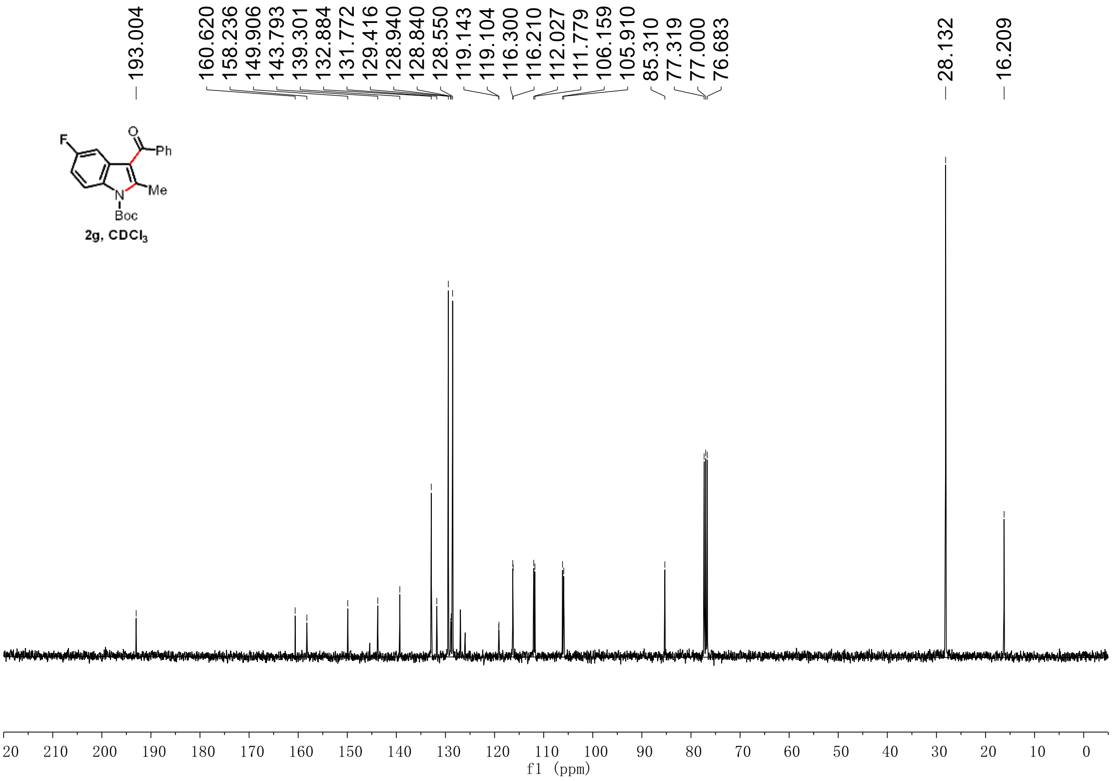

8.244
8.222
7.836
7.817
7.702
7.635
7.617
7.598
7.542
7.520
7.505
7.486
7.467
7.262
2.612
1.724
2e, CDCl3
0.92
1.82
0.89
1.11
2.94
3.03
9.00
f1 (ppm)

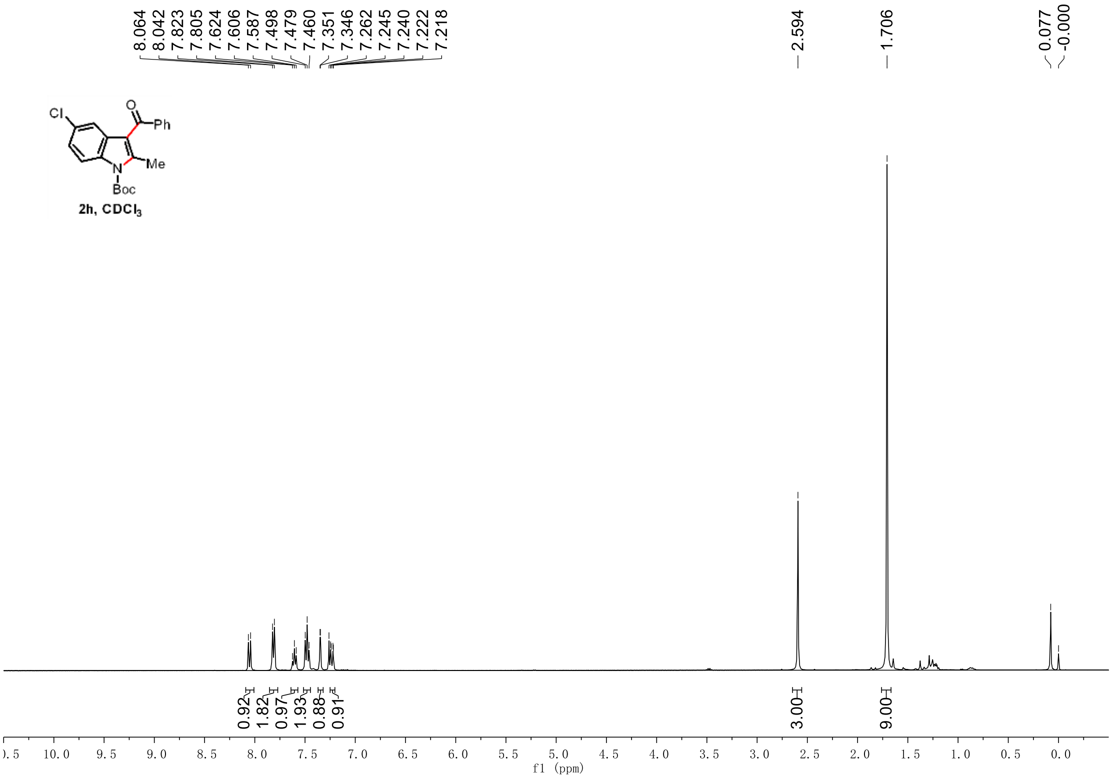

192.777
149.767
143.555
139.213
137.144
133.103
129.460
128.628
127.793
126.257
125.934
125.869
125.614
125.296
123.168
121.032
120.999
120.964
120.929
120.466
119.368
117.882
117.843
117.801
117.760
115.568
85.852
77.318
77.000
76.683
28.153
16.206
2e, CDCl3
f1 (ppm)

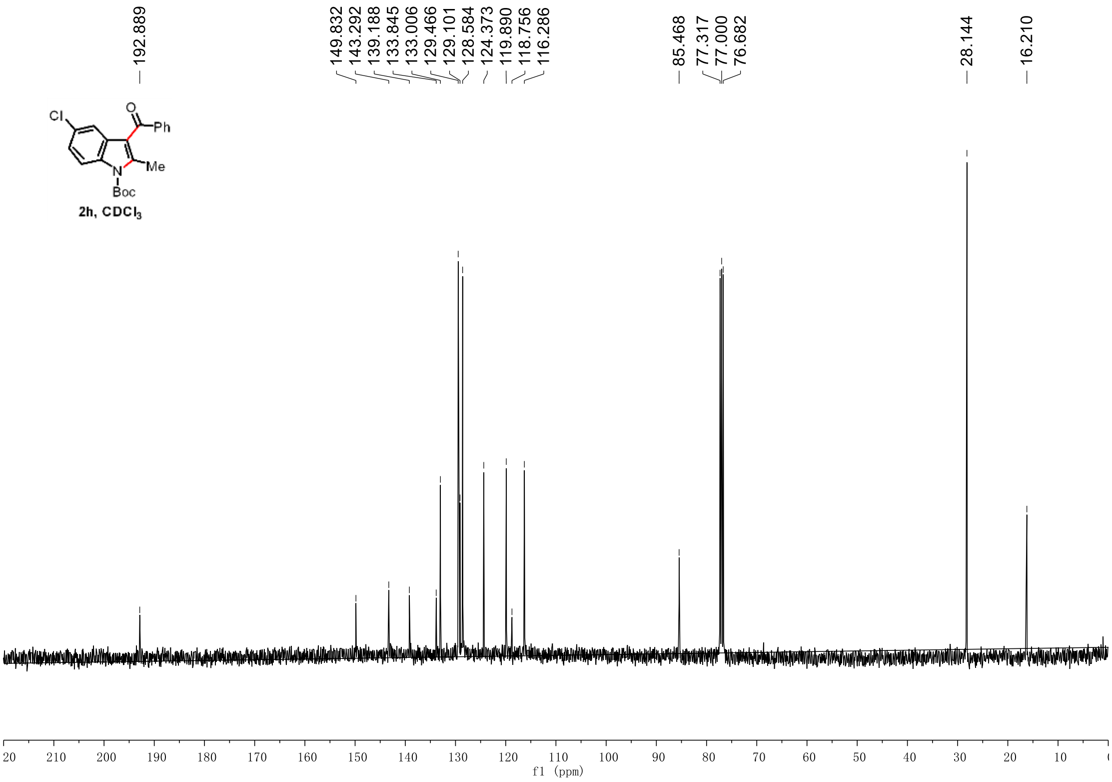

8.245
8.223
7.809
7.789
7.695
7.654
7.635
7.617
7.543
7.516
7.496
7.477
7.268
2.630
1.725
NC
O
Ph
Me
N
Boc
2f, CDCl3
0.92
1.83
0.88
0.95
2.87
2.99
9.00
f1 (ppm)

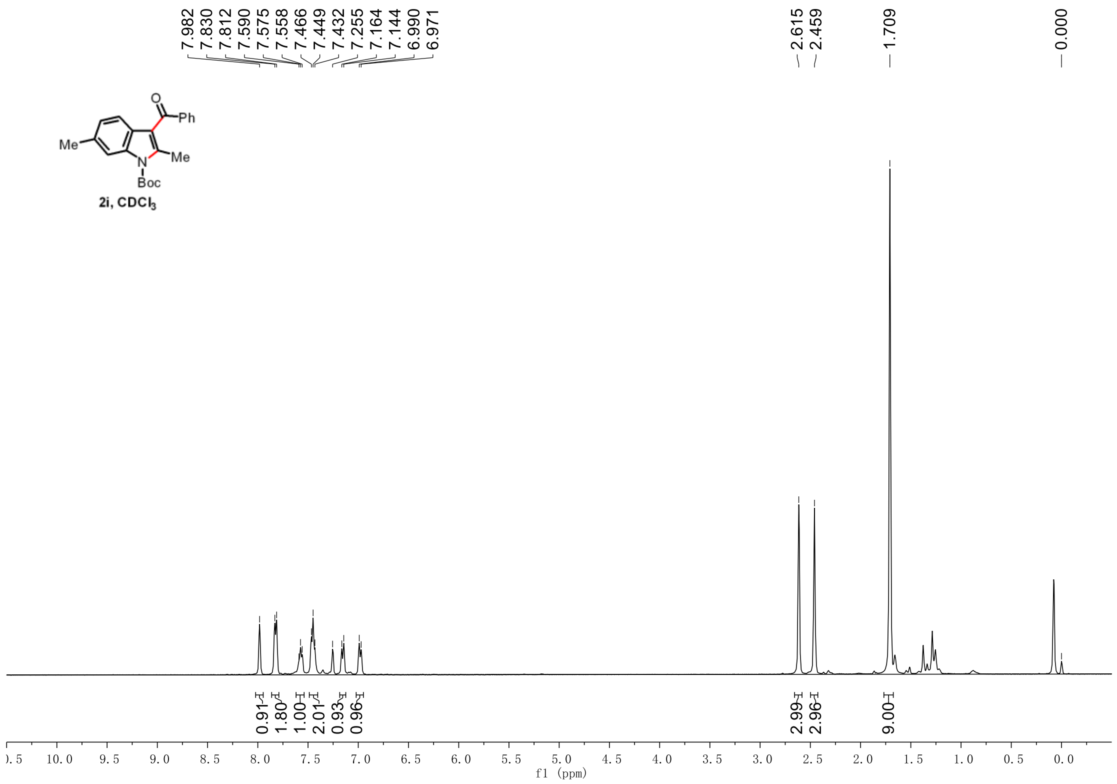

192.389
149.430
144.199
138.919
137.348
133.303
129.393
128.722
128.010
127.306
125.063
119.437
118.873
116.107
106.853
86.293
77.318
77.000
76.683
28.099
16.133
NC
O
Ph
Me
N
Boc
2f, CDCl3
f1 (ppm)

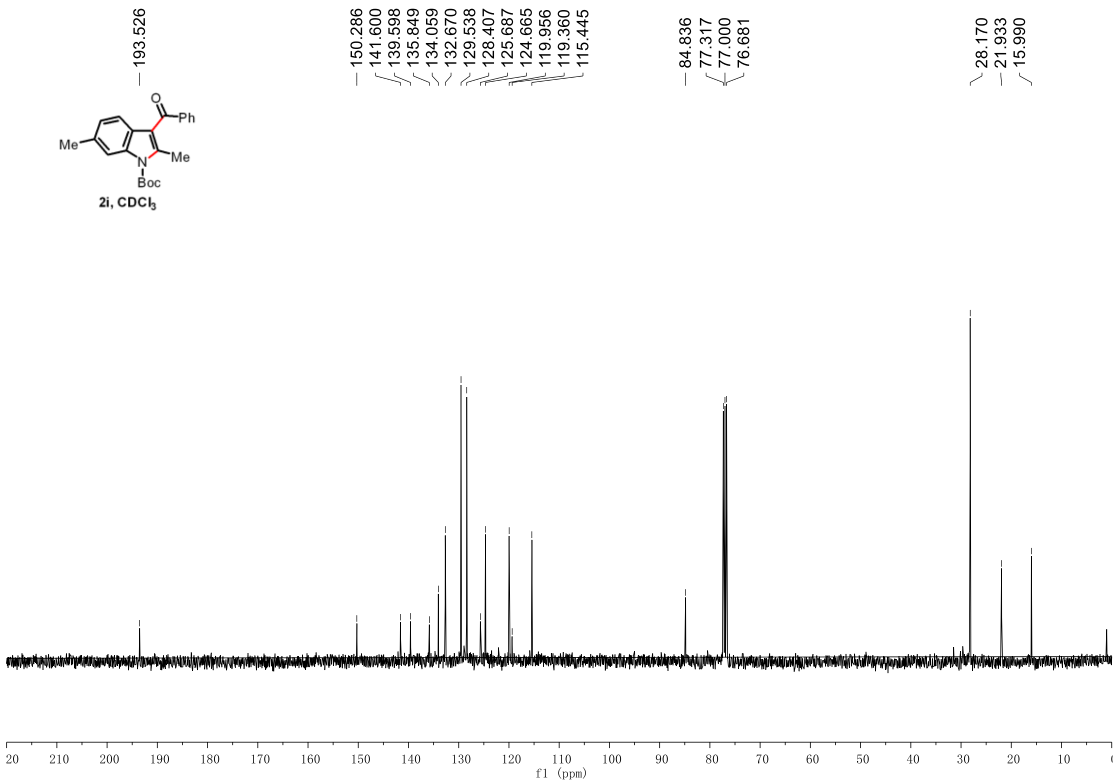

8.094
8.083
8.072
7.819
7.800
7.597
7.579
7.488
7.471
7.453
7.261
7.020
6.997
6.972
2.613
1.707
0.085
-0.001
F
O
Ph
Me
N
Boc
2g, CDCl3
0.89
1.78
1.21
1.88
1.77
2.89
9.00
f1 (ppm)

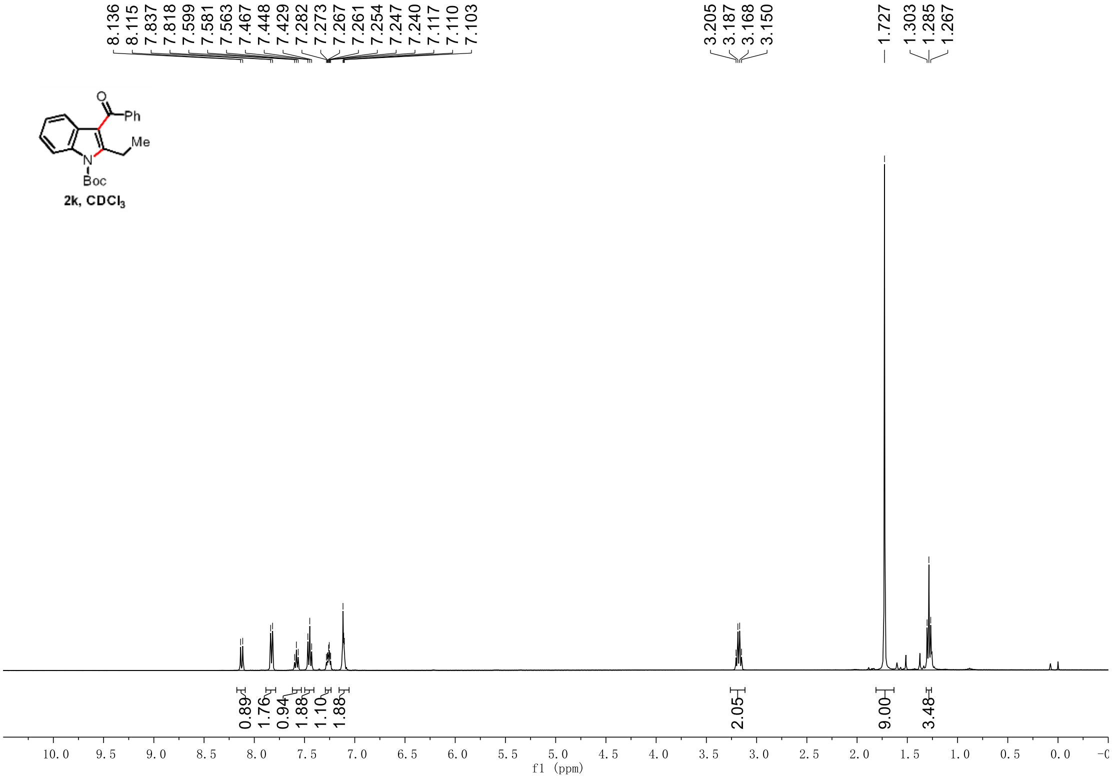

193.004
160.620
158.236
149.906
143.793
139.301
132.884
131.772
129.416
128.940
128.840
128.550
119.143
119.104
116.300
116.210
112.027
111.779
106.159
105.910
85.310
77.319
77.000
76.683
28.132
16.209
F
O
Ph
Me
N
Boc
2g, CDCl3
f1 (ppm)

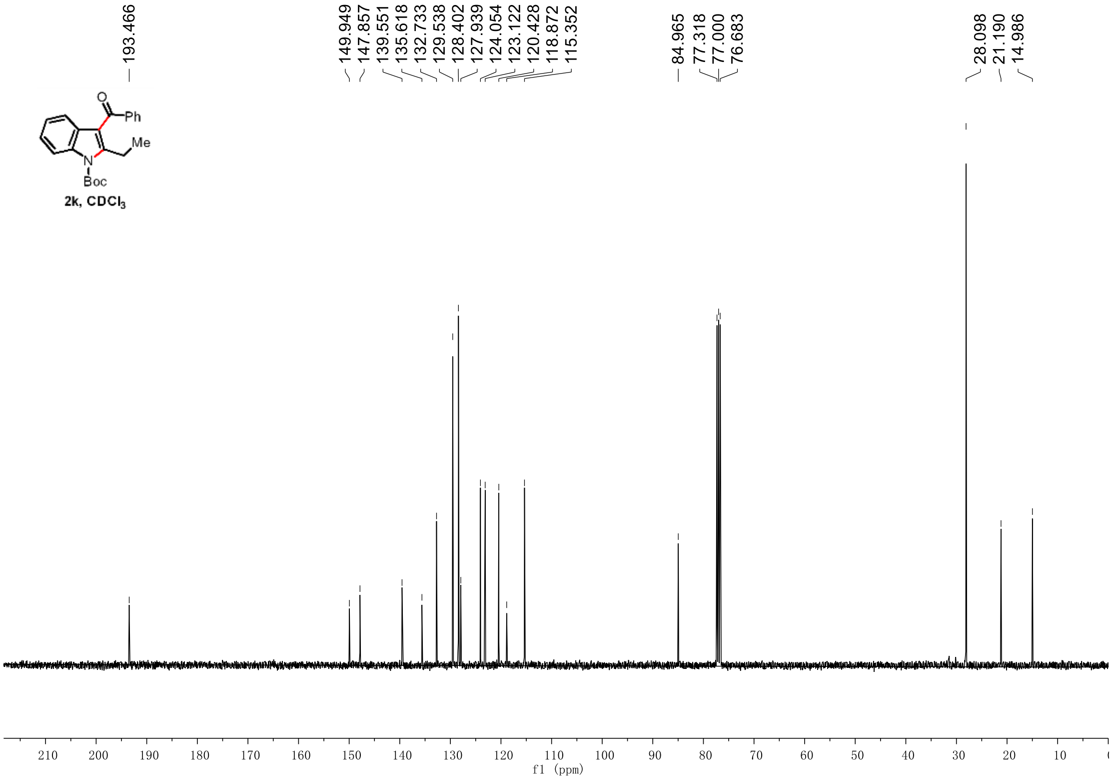

8.064
8.042
7.823
7.805
7.624
7.606
7.587
7.498
7.479
7.460
7.351
7.346
7.262
7.245
7.240
7.222
7.218
2.594
1.706
0.077
-0.000
Cl
O
Ph
N
Me
Boc
2h, CDCl3
0.92
1.82
0.97
1.93
0.88
0.91
3.00
9.00
f1 (ppm)

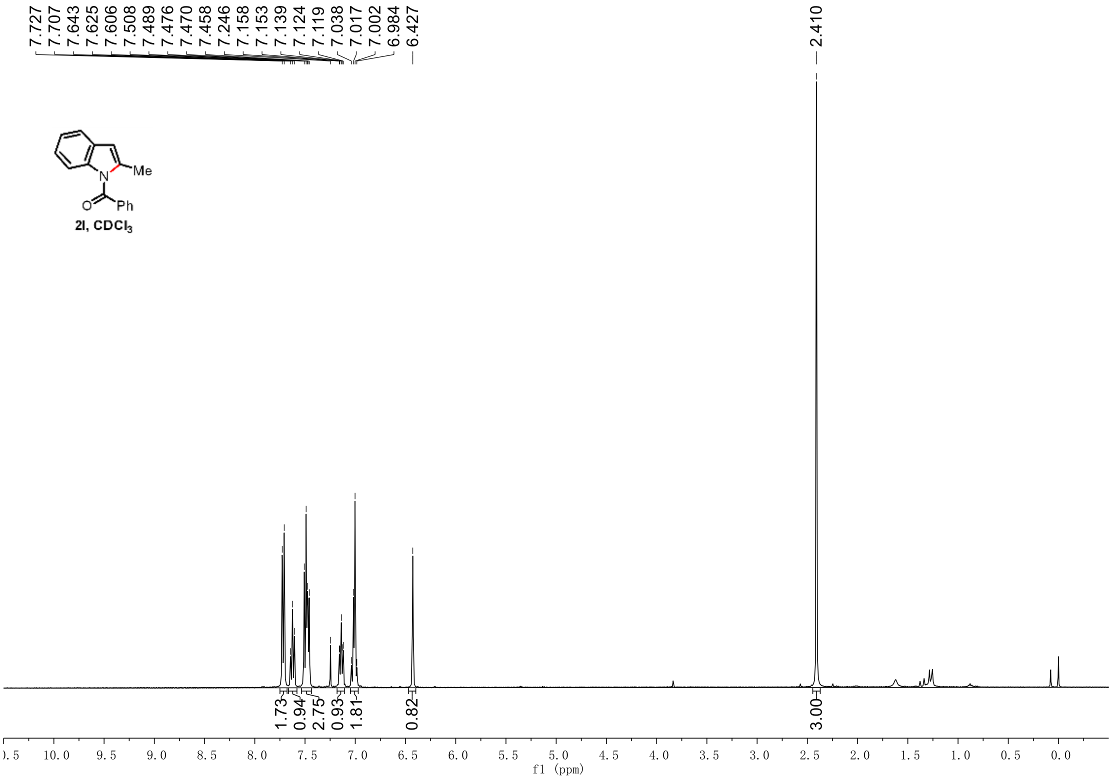

192.889
149.832
143.292
139.188
133.845
133.006
129.466
129.101
128.584
124.373
119.890
118.756
116.286
85.468
77.317
77.000
76.682
28.144
16.210
Cl
O
Ph
N
Me
Boc
2h, CDCl3
f1 (ppm)

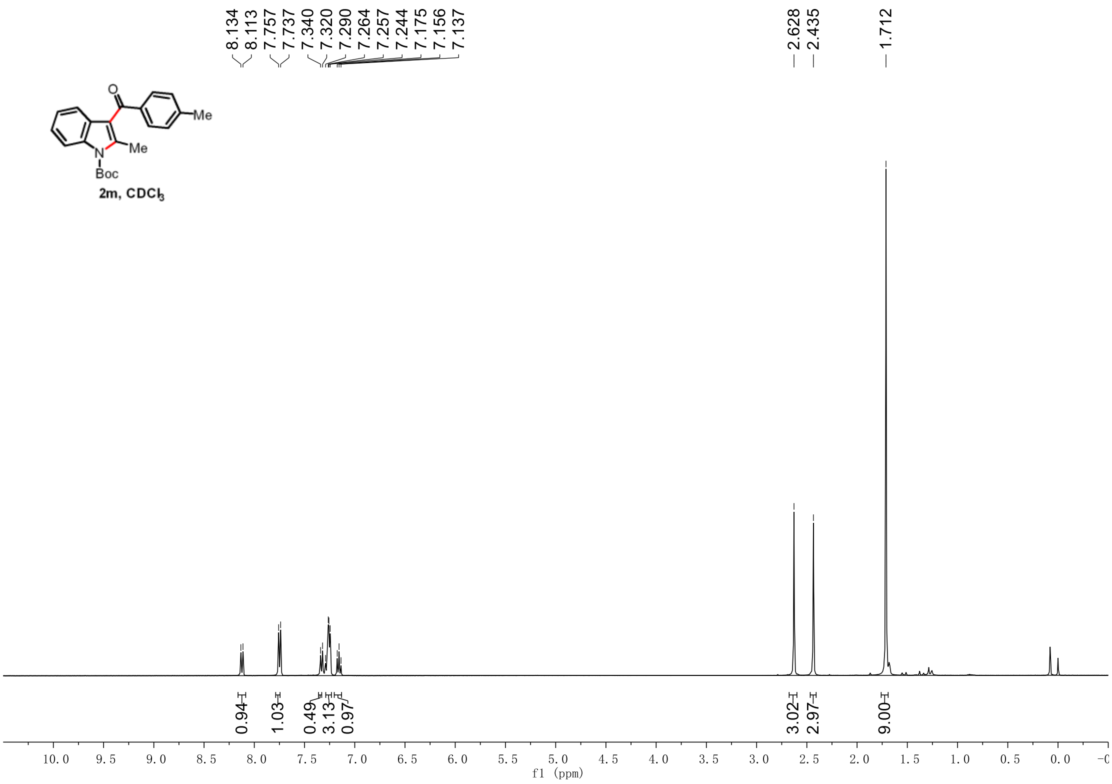

2i, CDCl3
7.982
7.830
7.812
7.590
7.575
7.558
7.466
7.449
7.432
7.255
7.164
7.144
6.990
6.971
2.615
2.459
1.709
0.000
0.91
1.80
1.00
2.01
0.93
0.96
2.99
2.96
9.00
f1 (ppm)

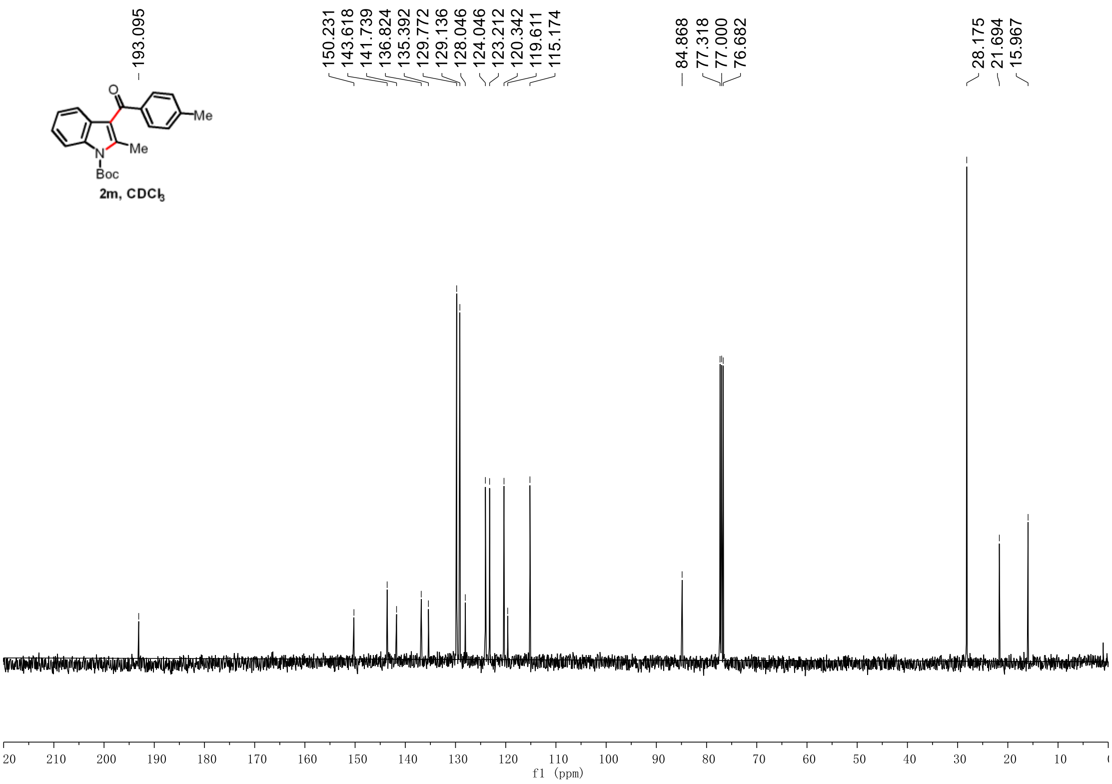

2i, CDCl3
193.526
150.286
141.600
139.598
135.849
134.059
132.670
129.538
128.407
125.687
124.665
119.956
119.360
115.445
84.836
77.317
77.000
76.681
28.170
21.933
15.990
f1 (ppm)

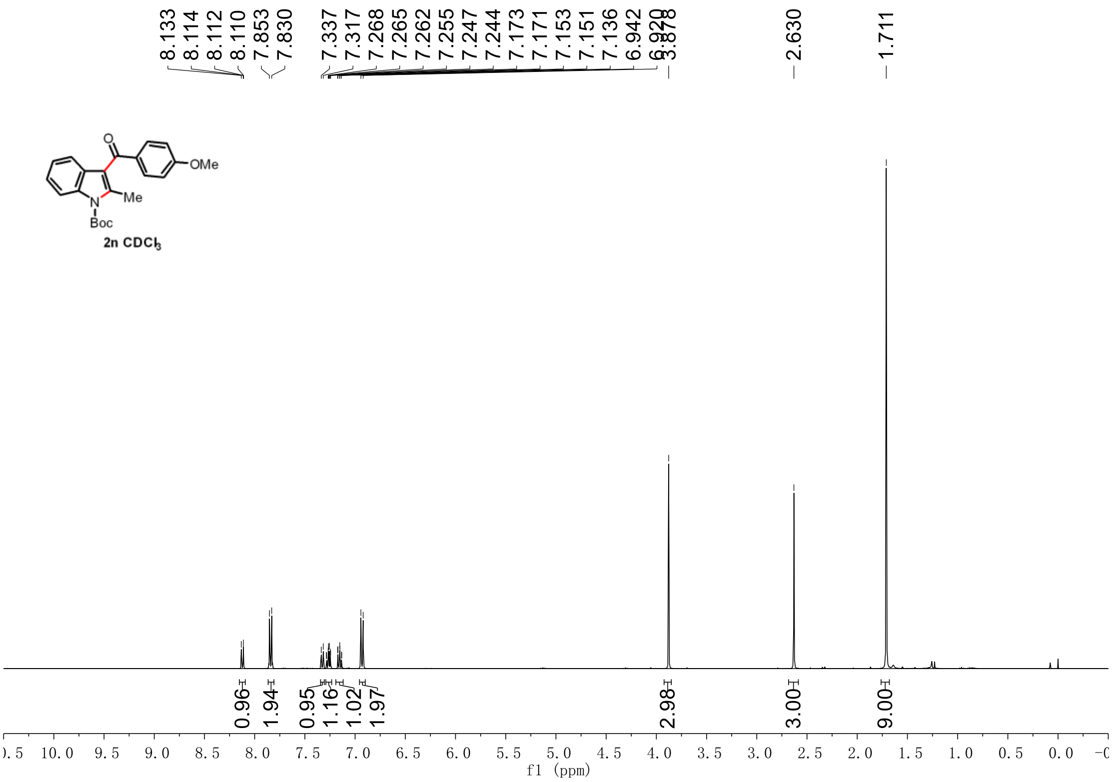

Ph
Me
N
Boc
2k, CDCl3
8.136
8.115
7.837
7.818
7.599
7.581
7.563
7.467
7.448
7.429
7.282
7.273
7.267
7.261
7.254
7.247
7.240
7.117
7.110
7.103
3.205
3.187
3.168
3.150
1.727
1.303
1.285
1.267
0.89
1.76
0.94
1.88
1.10
1.88
2.05
9.00
3.48
f1 (ppm)


Ph
Me
N
Boc
2k, CDCl3
193.466
149.949
147.857
139.551
135.618
132.733
129.538
128.402
127.939
124.054
123.122
120.428
118.872
115.352
84.965
77.318
77.000
76.683
28.098
21.190
14.986
f1 (ppm)

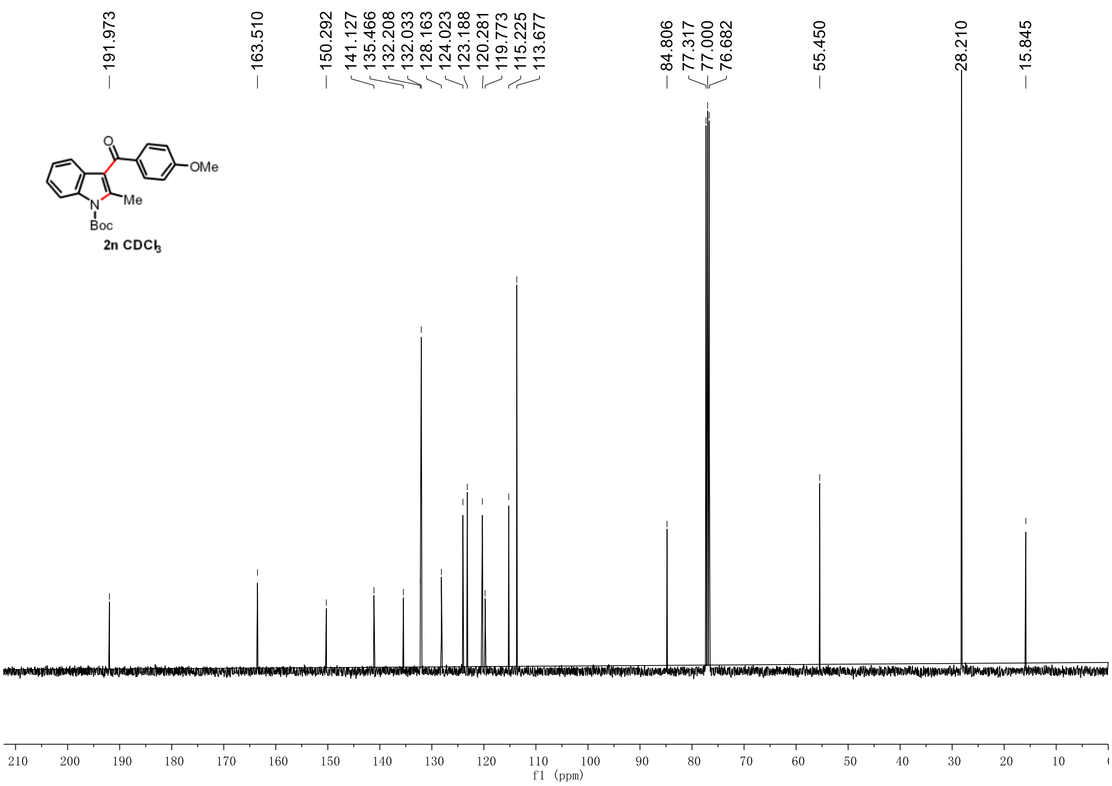

7.727
7.707
7.643
7.625
7.606
7.508
7.489
7.476
7.470
7.458
7.246
7.158
7.153
7.139
7.124
7.119
7.038
7.017
7.002
6.984
6.427
2.410
Me
N
O
Ph
2l, CDCl3
1.73
0.94
2.75
0.93
1.81
0.82
3.00
f1 (ppm)


8.134
8.113
7.757
7.737
7.340
7.320
7.290
7.264
7.257
7.244
7.175
7.156
7.137
2.628
2.435
1.712
O
Me
N
Me
Boc
2m, CDCl3
0.94
1.03
0.49
3.13
0.97
3.02
2.97
9.00
f1 (ppm)

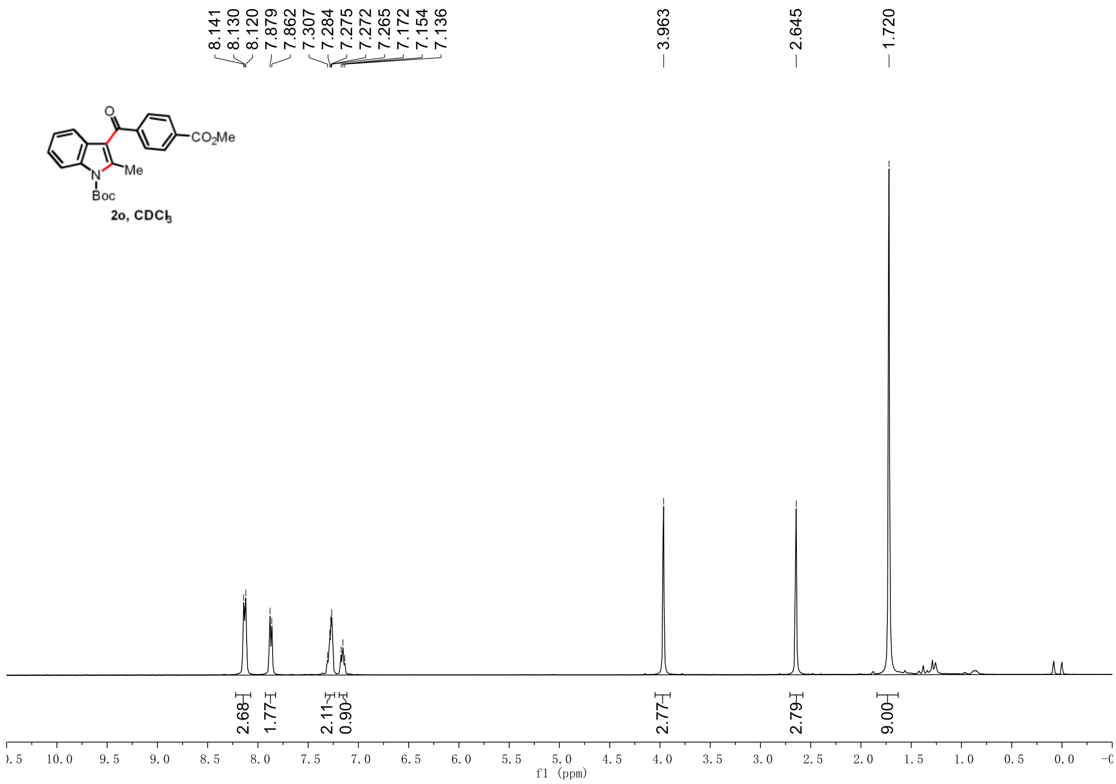

193.095
150.231
143.618
141.739
136.824
135.392
129.772
129.136
128.046
124.046
123.212
120.342
119.611
115.174
84.868
77.318
77.000
76.682
28.175
21.694
15.967
O
Me
N
Me
Boc
2m, CDCl3
f1 (ppm)

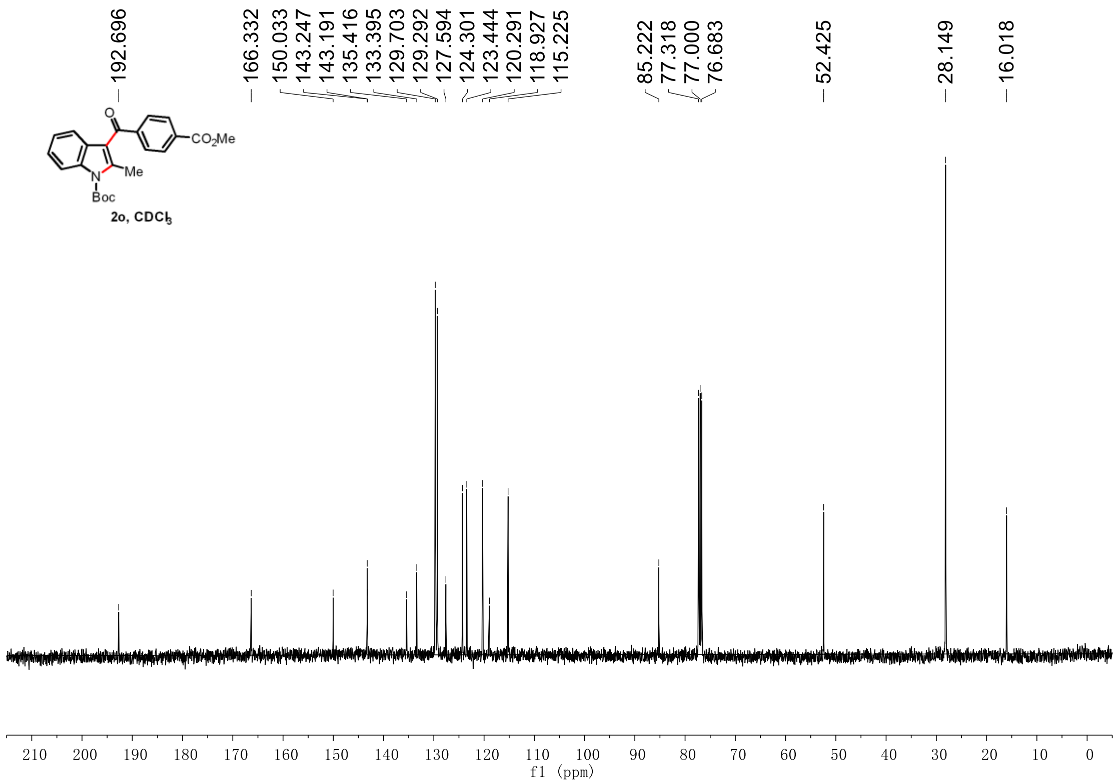


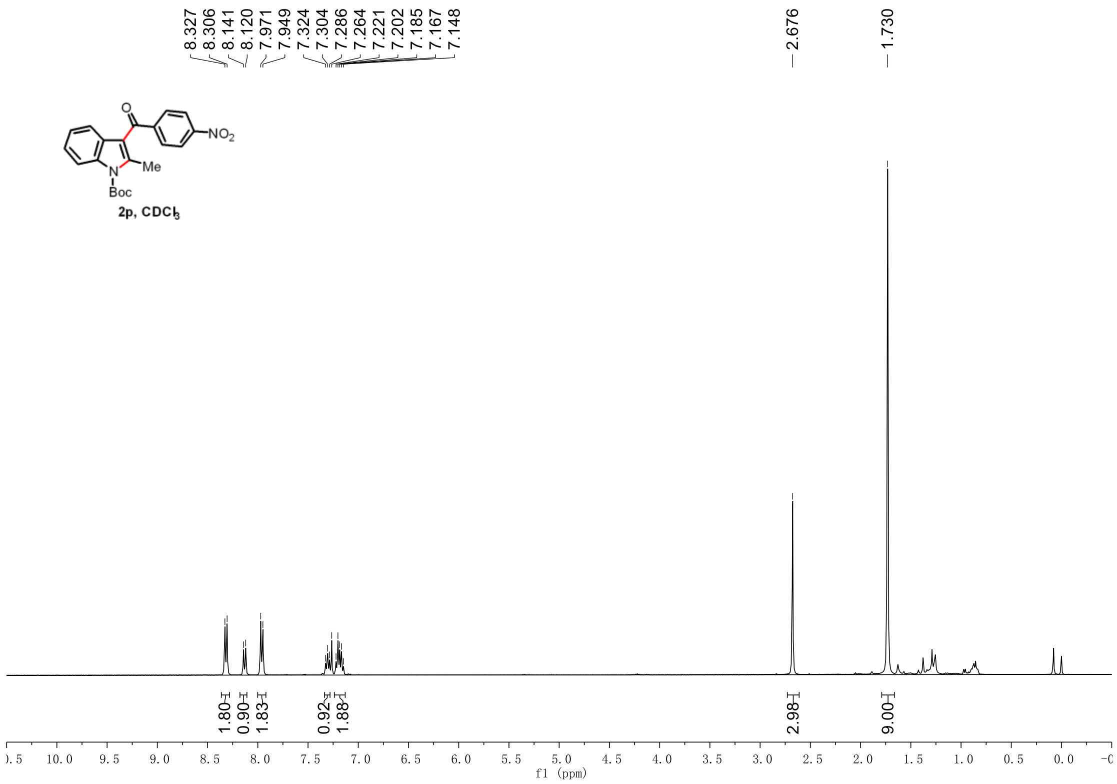
8.133
8.114
8.112
8.110
7.853
7.830
7.337
7.317
7.268
7.265
7.262
7.255
7.247
7.244
7.173
7.171
7.153
7.151
7.136
6.942
6.920
3.878
2.630
1.711
OMe
Me
Boc
2n CDCl3
0.96
1.94
0.95
1.16
1.02
1.97
2.98
3.00
9.00
f1 (ppm)

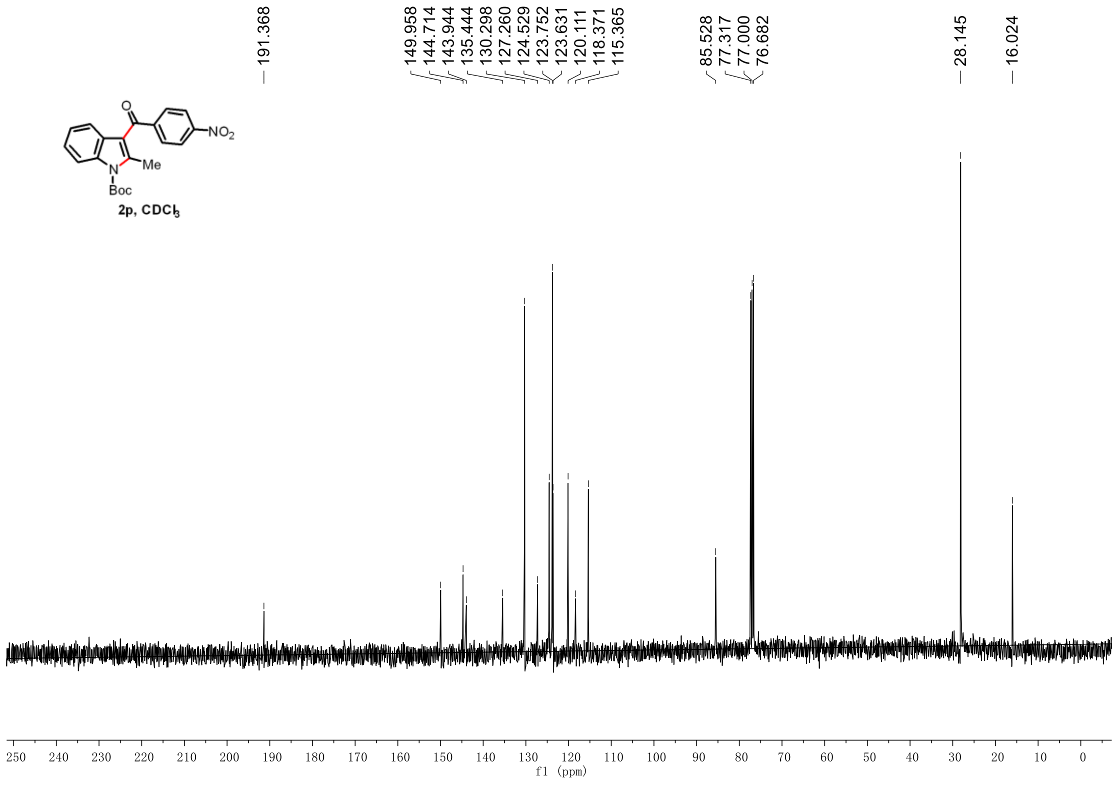


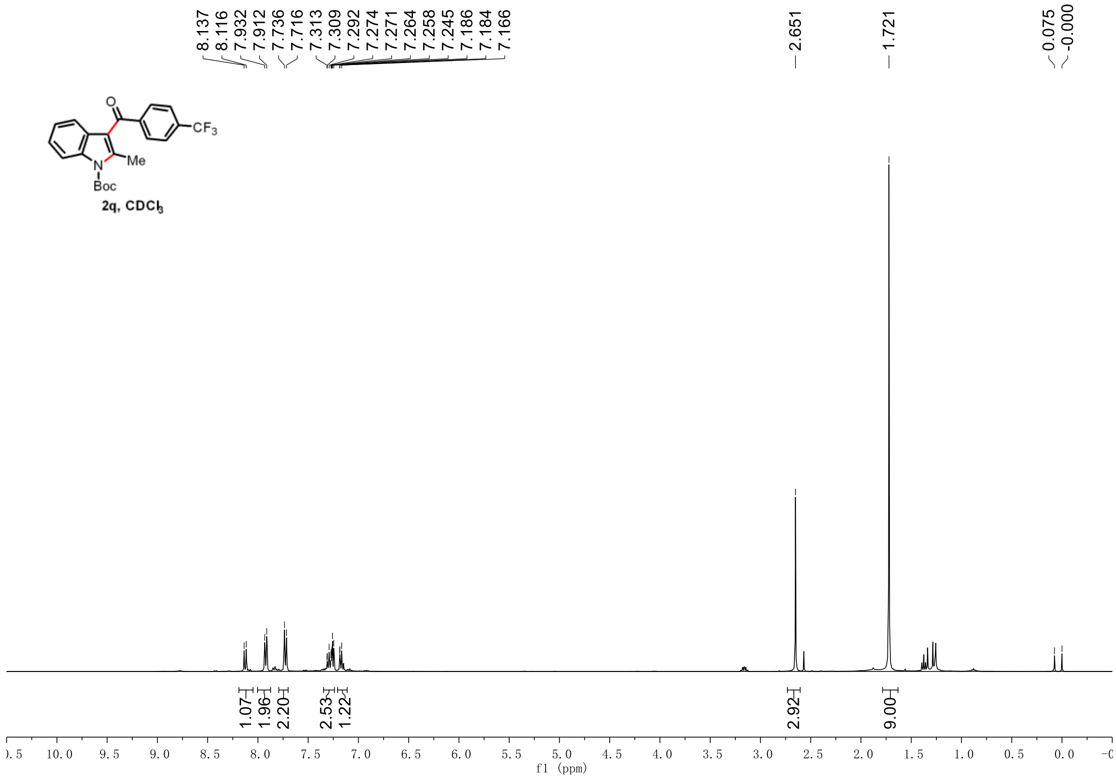
191.973
163.510
150.292
141.127
135.466
132.208
132.033
128.163
124.023
123.188
120.281
119.773
115.225
113.677
84.806
77.317
77.000
76.682
55.450
28.210
15.845
OMe
Me
Boc
2n CDCl3
f1 (ppm)

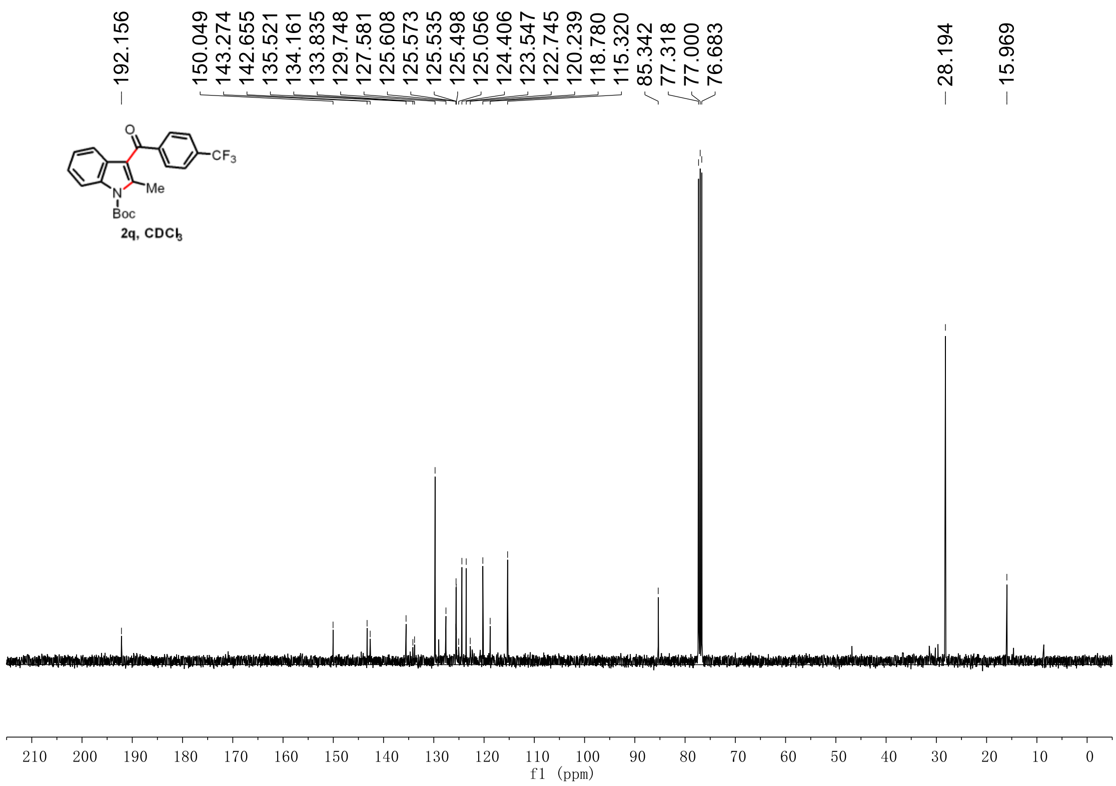

8.141
8.130
8.120
7.879
7.862
7.307
7.284
7.275
7.272
7.265
7.172
7.154
7.136
3.963
2.645
1.720
CO2Me
Me
N
Boc
O
2o, CDCl3
2.68
1.77
2.11
0.90
2.77
2.79
9.00
f1 (ppm)

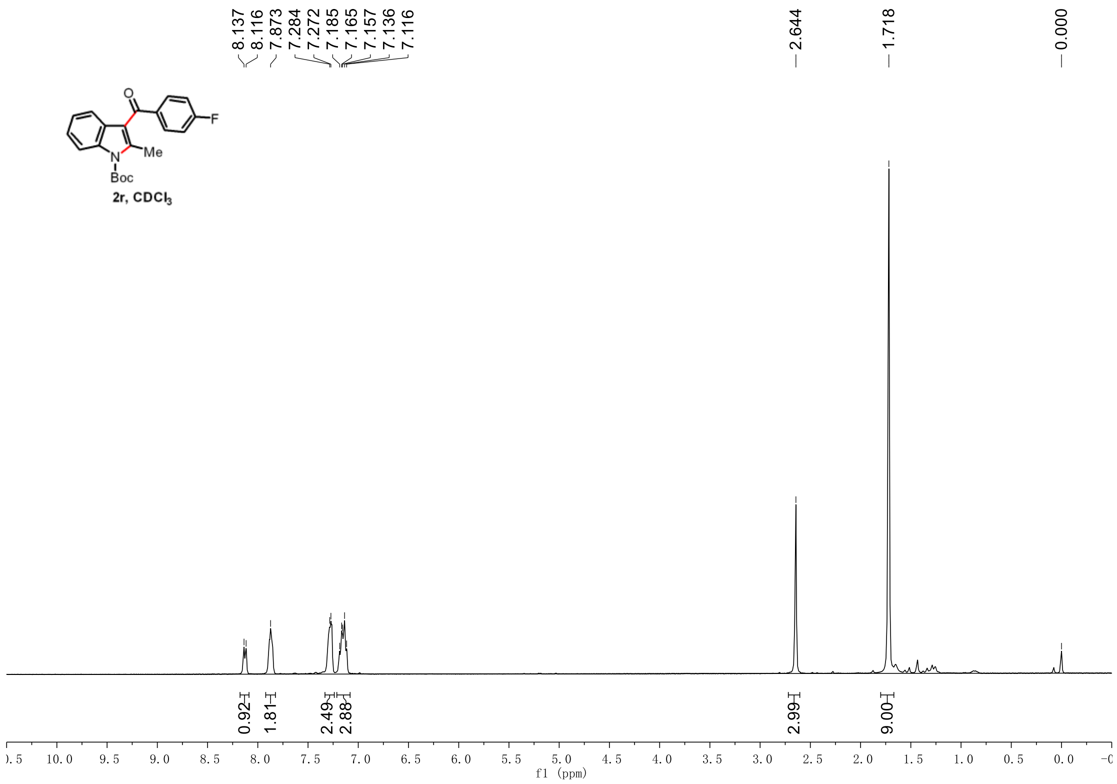

192.696
166.332
150.033
143.247
143.191
135.416
133.395
129.703
129.292
127.594
124.301
123.444
120.291
118.927
115.225
85.222
77.318
77.000
76.683
52.425
28.149
16.018
CO2Me
Me
N
Boc
O
2o, CDCl3
f1 (ppm)

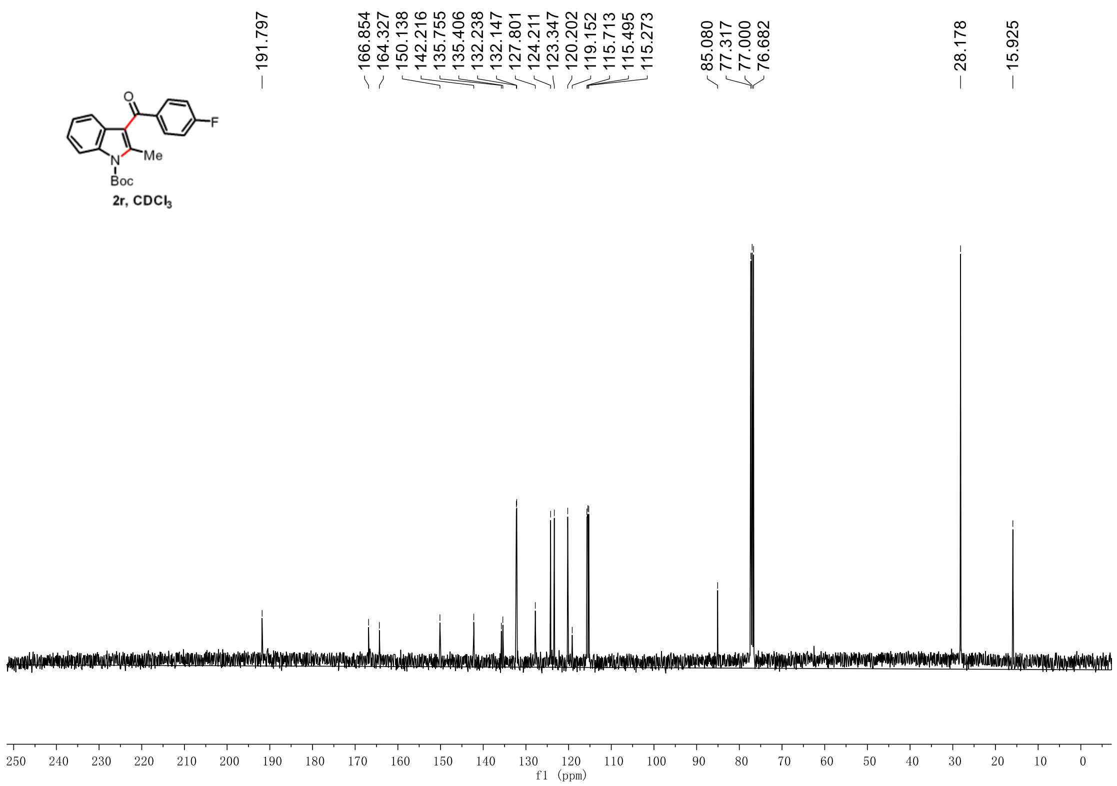

8.327
8.306
8.141
8.120
7.971
7.949
7.324
7.304
7.286
7.264
7.221
7.202
7.185
7.167
7.148
2.676
1.730
O
NO2
Me
N
Boc
2p, CDCl3
1.80
0.90
1.83
0.92
1.88
2.98
9.00
f1 (ppm)

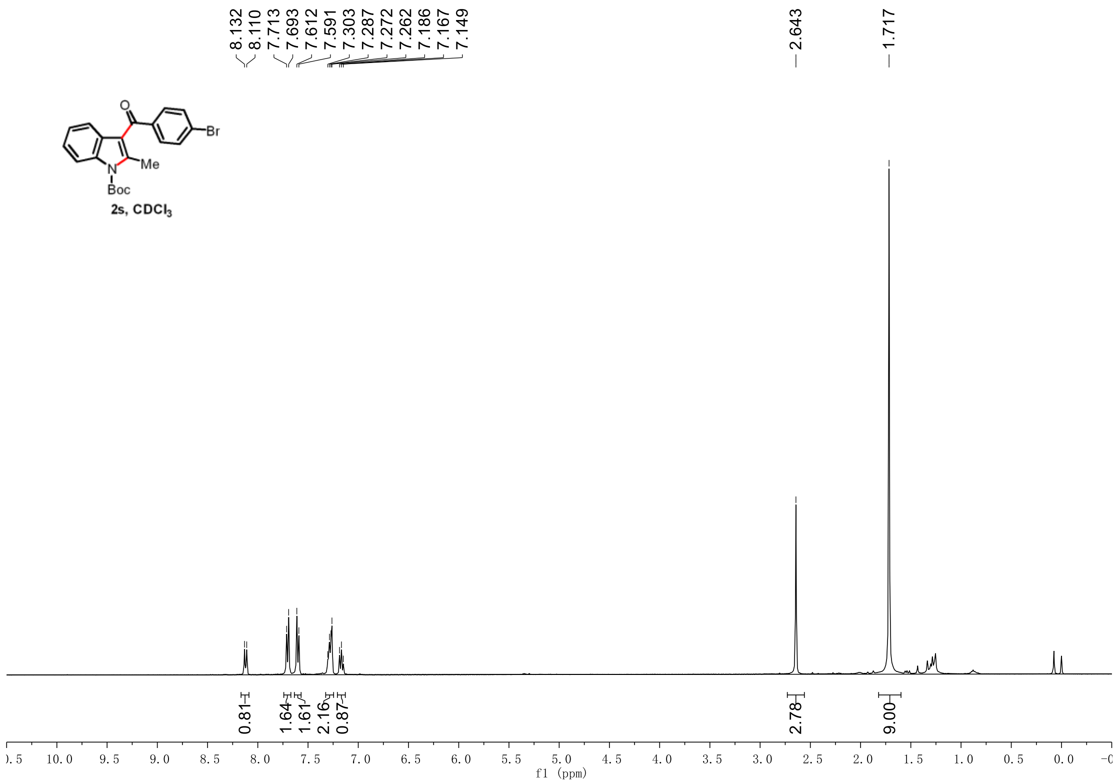

191.368
149.958
144.714
143.944
135.444
130.298
127.260
124.529
123.752
123.631
120.111
118.371
115.365
85.528
77.317
77.000
76.682
28.145
16.024
O
NO2
Me
N
Boc
2p, CDCl3
f1 (ppm)

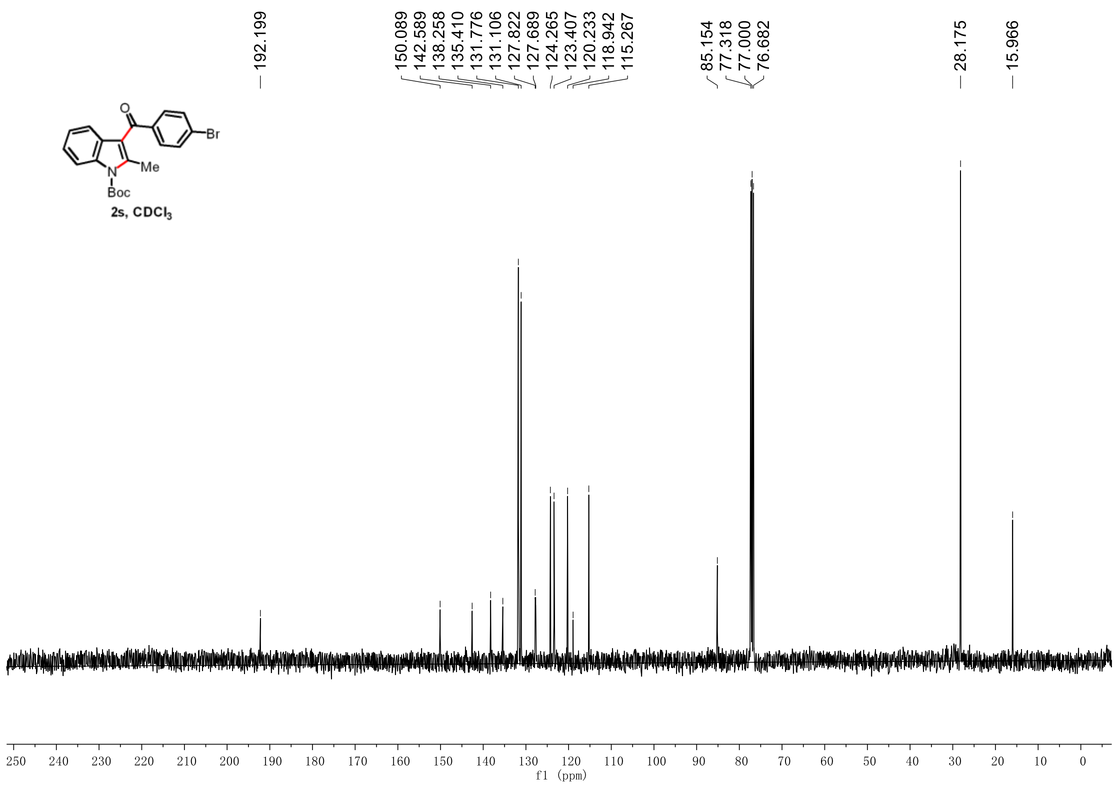

8.137
8.116
7.932
7.912
7.736
7.716
7.313
7.309
7.292
7.274
7.271
7.264
7.258
7.245
7.186
7.184
7.166
2.651
1.721
0.075
-0.000
CF3
Me
N
Boc
O
2q, CDCl3
1.07
1.96
2.20
2.53
1.22
2.92
9.00
f1 (ppm)

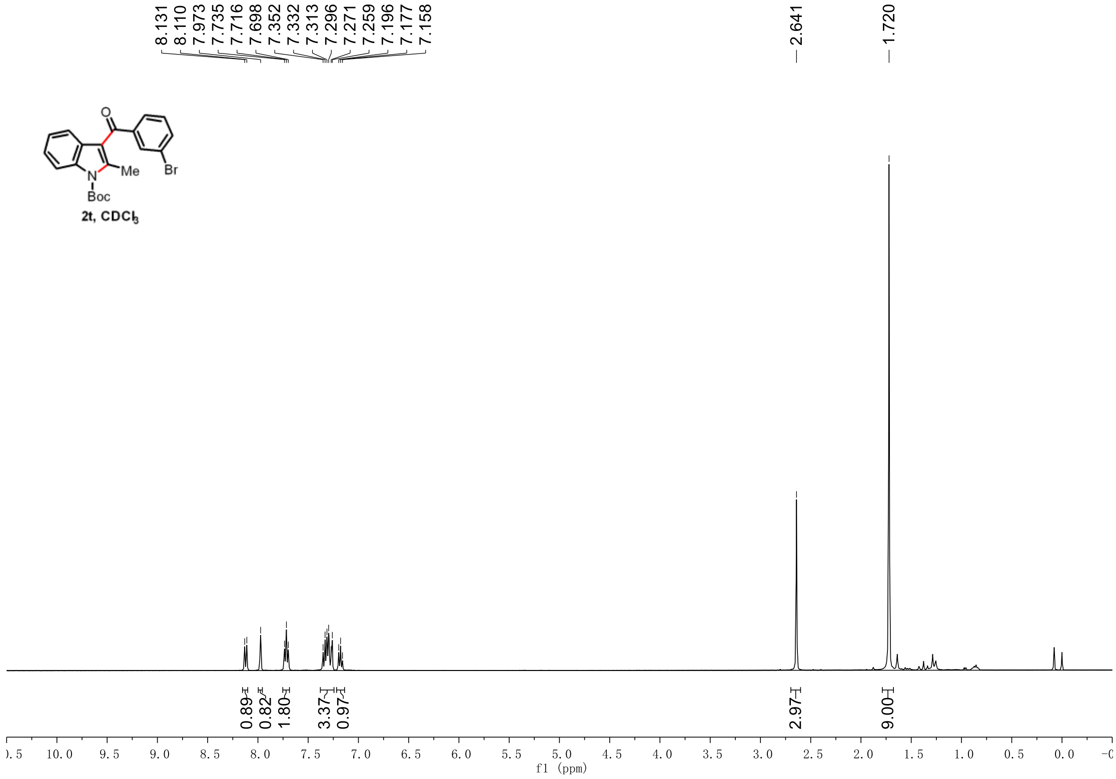

192.156
150.049
143.274
142.655
135.521
134.161
133.835
129.748
127.581
125.608
125.573
125.535
125.498
125.056
124.406
123.547
122.745
120.239
118.780
115.320
85.342
77.318
77.000
76.683
28.194
15.969
CF3
Me
N
Boc
O
2q, CDCl3
f1 (ppm)

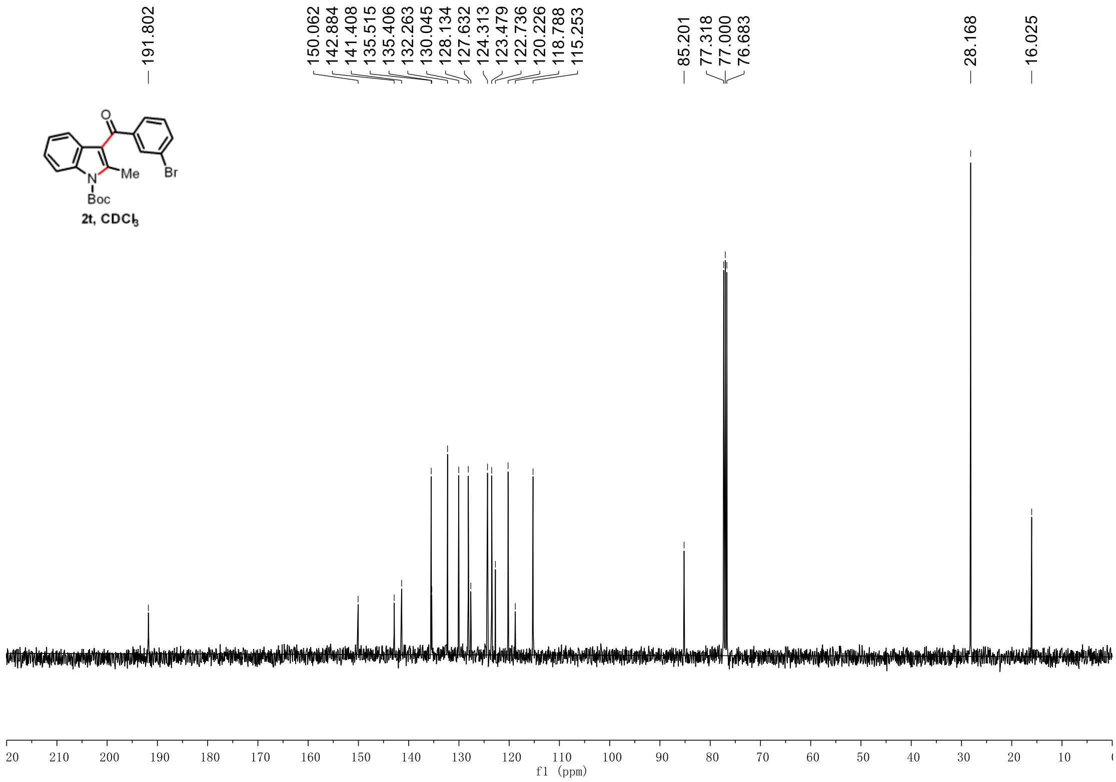

8.137
8.116
7.873
7.284
7.272
7.185
7.165
7.157
7.136
7.116
2.644
1.718
0.000
O
F
Me
N
Boc
2r, CDCl3
0.92
1.81
2.49
2.88
2.99
9.00
f1 (ppm)

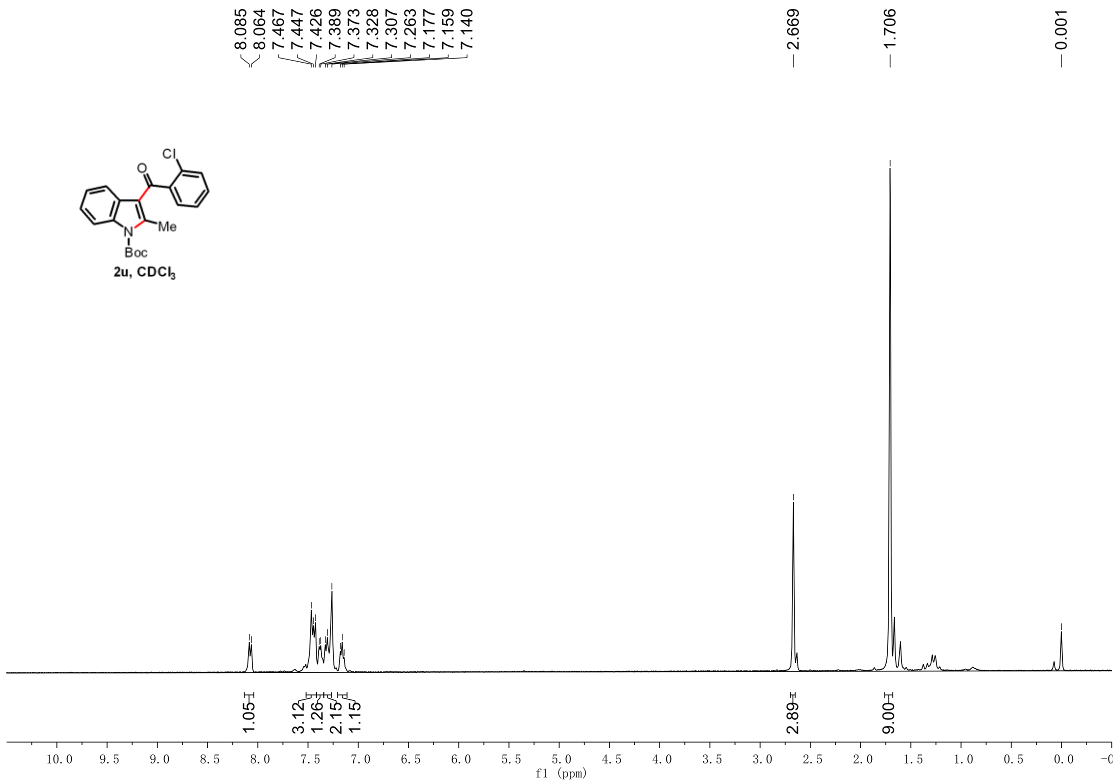

191.797
166.854
164.327
150.138
142.216
135.755
135.406
132.238
132.147
127.801
124.211
123.347
120.202
119.152
115.713
115.495
115.273
85.080
77.317
77.000
76.682
28.178
15.925
O
F
Me
N
Boc
2r, CDCl3
f1 (ppm)

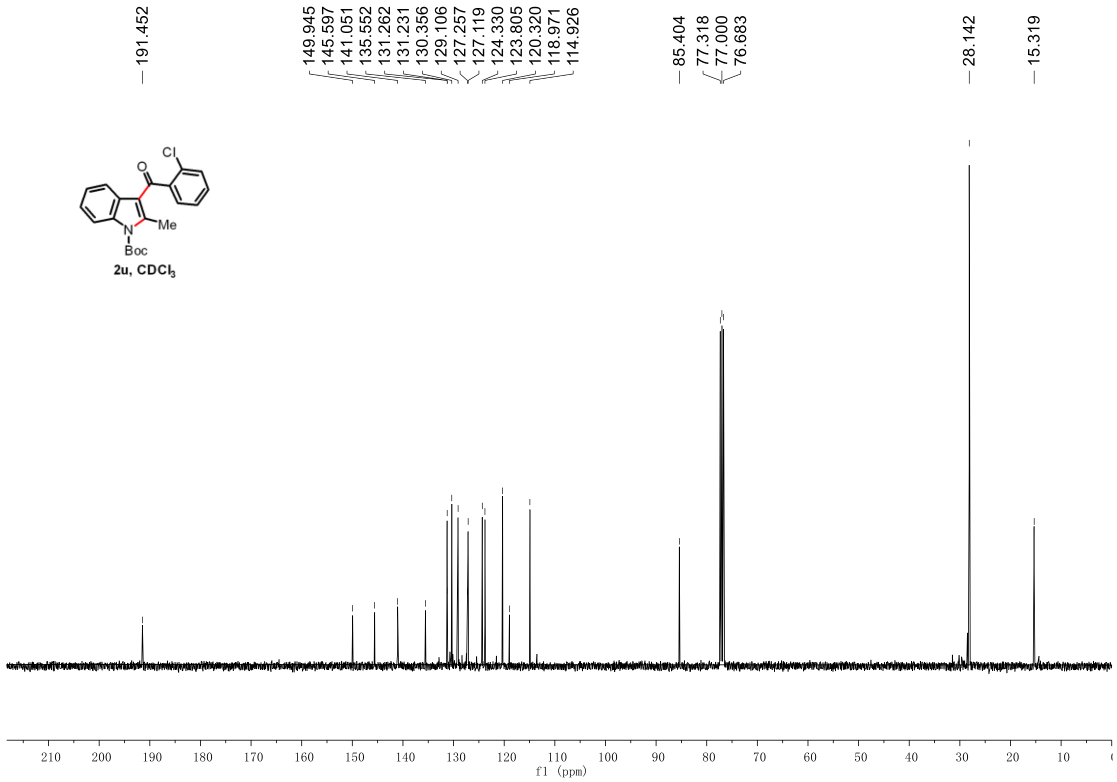

8.132
8.110
7.713
7.693
7.612
7.591
7.303
7.287
7.272
7.262
7.186
7.167
7.149
2.643
1.717
O
Br
Me
N
Boc
2s, CDCl3
0.81
1.64
1.61
2.16
0.87
2.78
9.00
f1 (ppm)

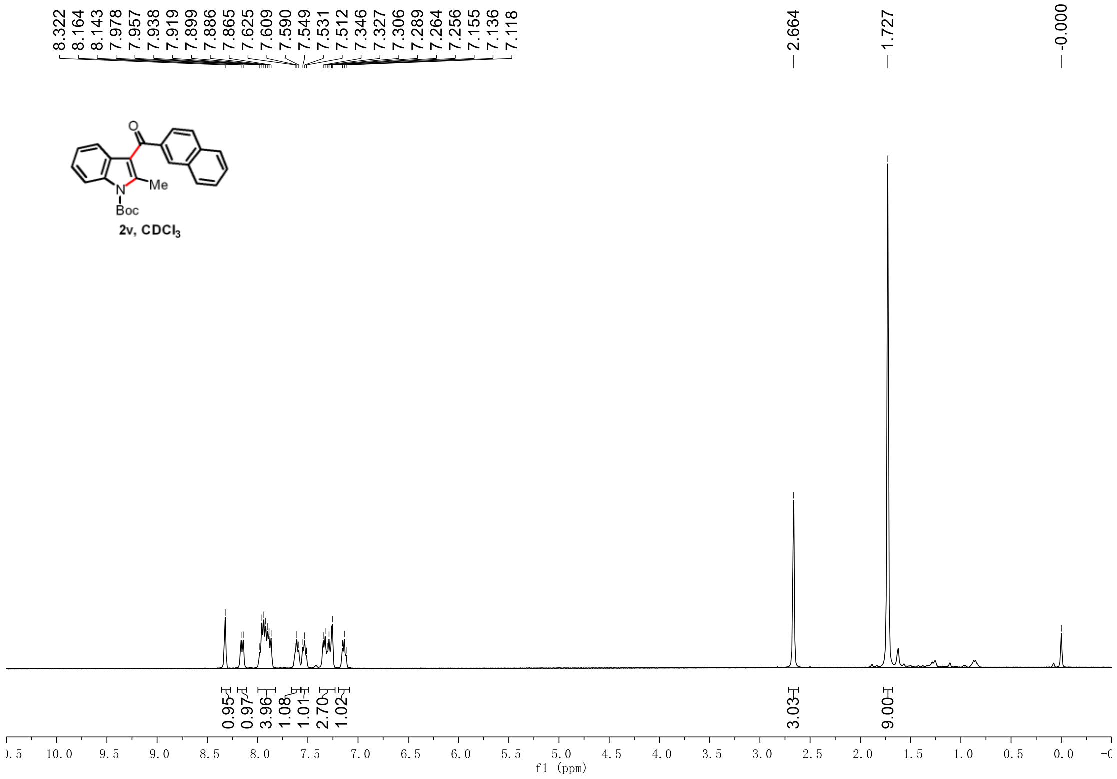

192.199
150.089
142.589
138.258
135.410
131.776
131.106
127.822
127.689
124.265
123.407
120.233
118.942
115.267
85.154
77.318
77.000
76.682
28.175
15.966
O
Br
Me
N
Boc
2s, CDCl3
f1 (ppm)

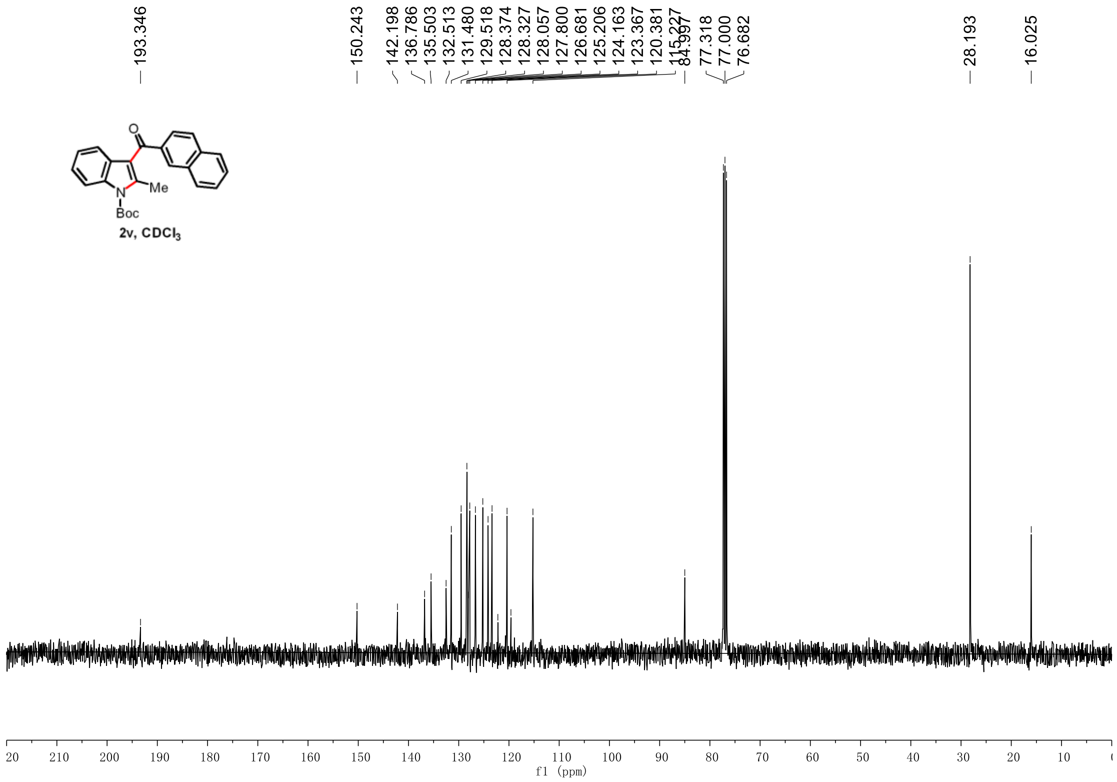

8.131
8.110
7.973
7.735
7.716
7.698
7.352
7.332
7.313
7.296
7.271
7.259
7.196
7.177
7.158
2.641
1.720
Me
Br
Boc
2t, CDCl3
0.89
0.82
1.80
3.37
0.97
2.97
9.00
f1 (ppm)

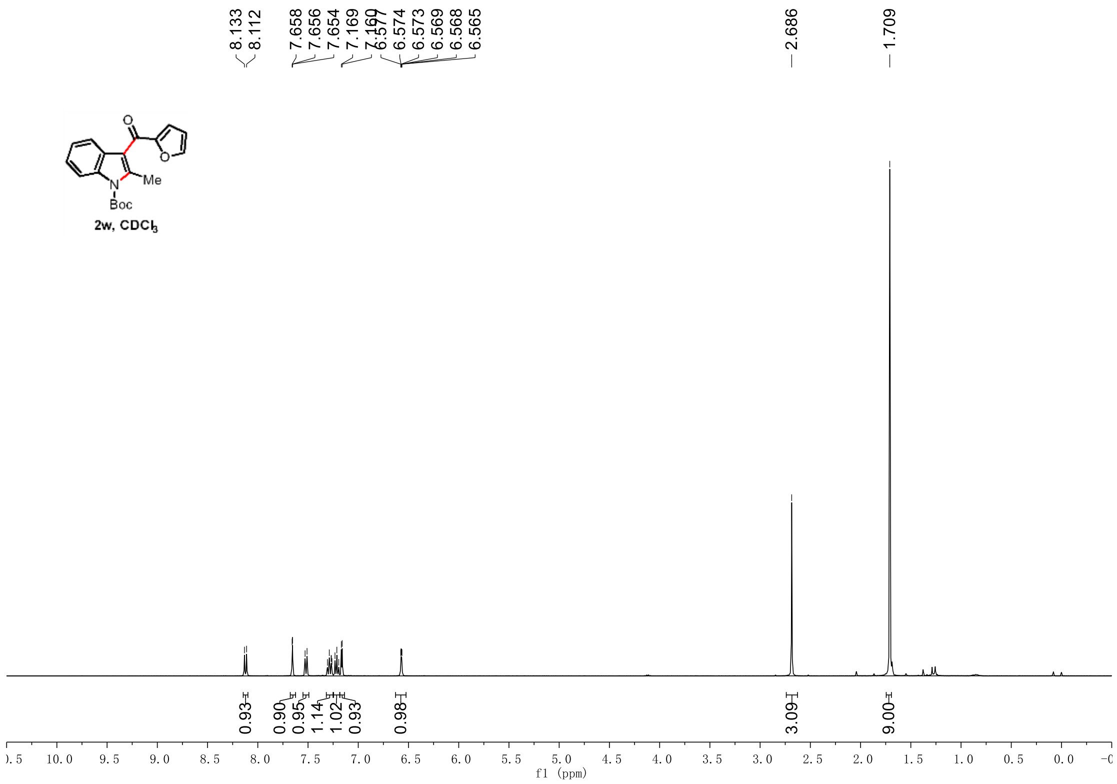

191.802
150.062
142.884
141.408
135.515
135.406
132.263
130.045
128.134
127.632
124.313
123.479
122.736
120.226
118.788
115.253
85.201
77.318
77.000
76.683
28.168
16.025
Me
Br
Boc
2t, CDCl3
f1 (ppm)

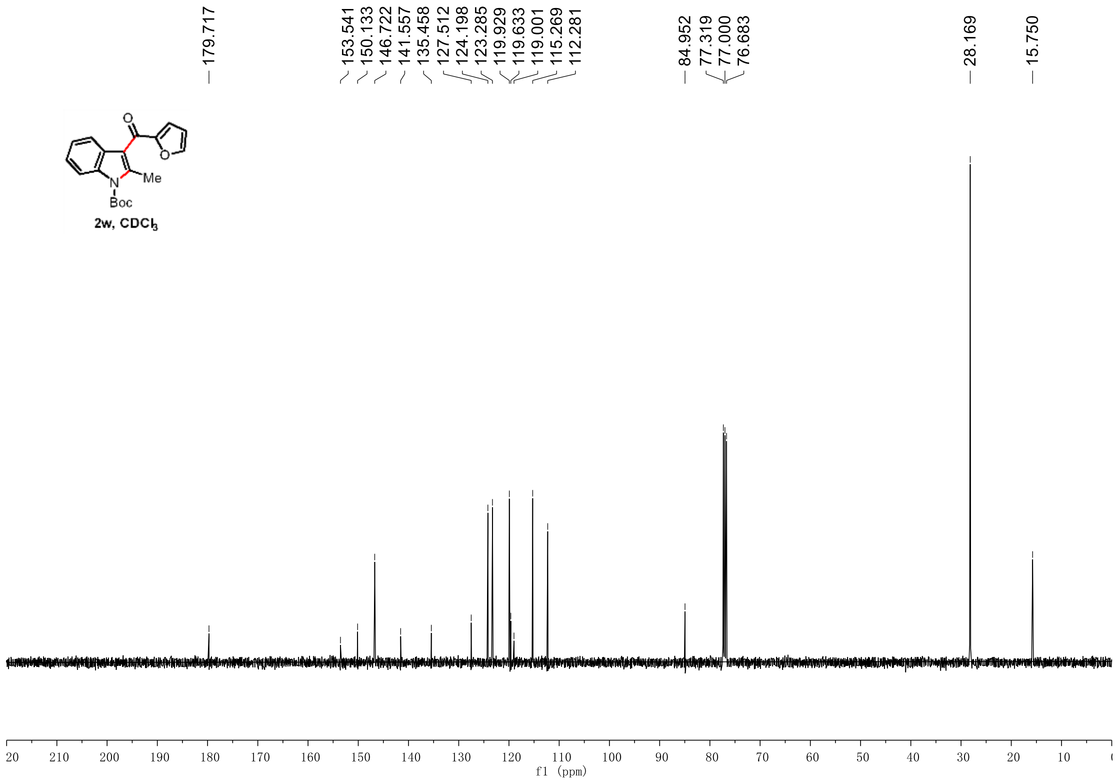

8.085
8.064
7.467
7.447
7.426
7.389
7.373
7.328
7.307
7.263
7.177
7.159
7.140
2.669
1.706
0.001
Cl
O
N
Me
Boc
2u, CDCl3
1.05
3.12
1.26
2.15
1.15
2.89
9.00
f1 (ppm)

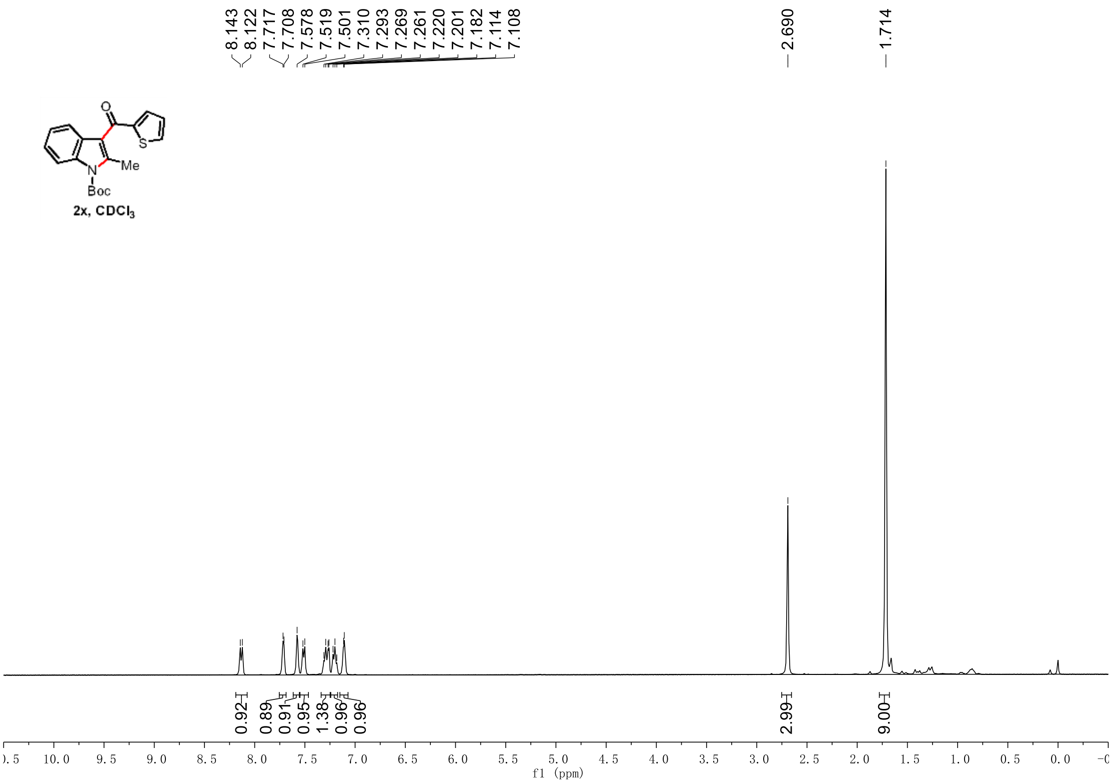

191.452
149.945
145.597
141.051
135.552
131.262
131.231
130.356
129.106
127.257
127.119
124.330
123.805
120.320
118.971
114.926
85.404
77.318
77.000
76.683
28.142
15.319
Cl
O
N
Me
Boc
2u, CDCl3
f1 (ppm)


8.322
8.164
8.143
7.978
7.957
7.938
7.919
7.899
7.886
7.865
7.625
7.609
7.590
7.549
7.531
7.512
7.346
7.327
7.306
7.289
7.264
7.256
7.155
7.136
7.118
2.664
1.727
-0.000
O
Me
N
Boc
2v, CDCl3
0.95
0.97
3.96
1.08
1.01
2.70
1.02
3.03
9.00
f1 (ppm)

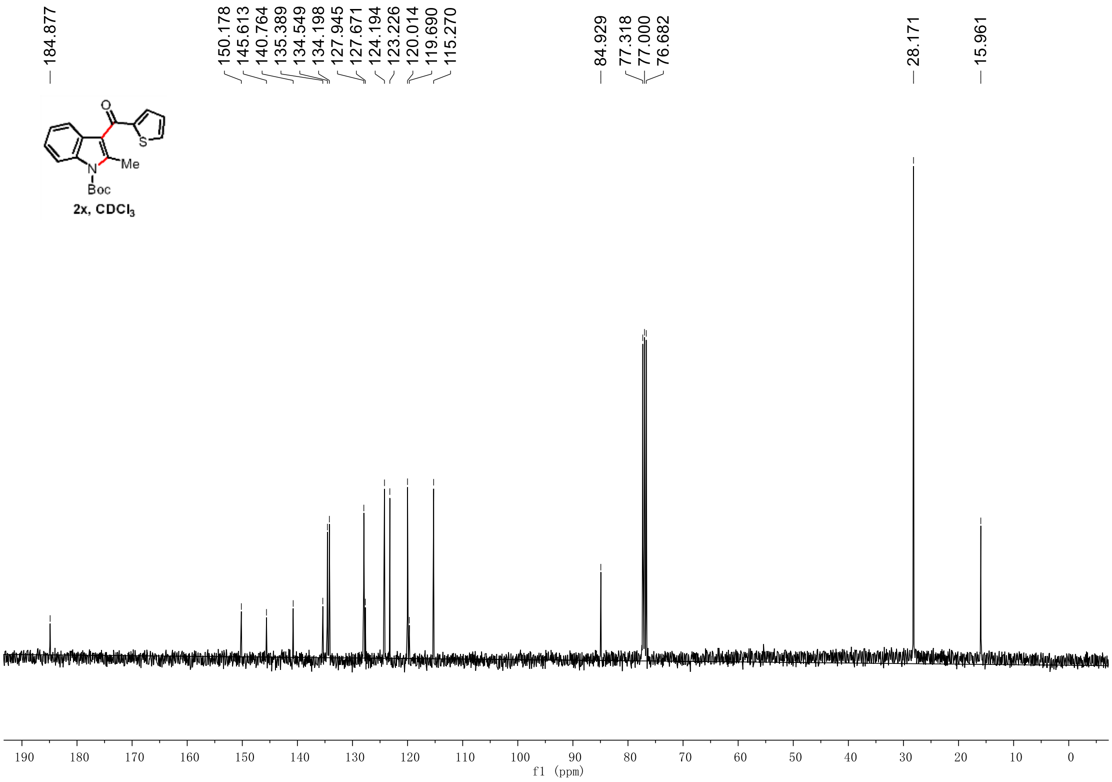

193.346
150.243
142.198
136.786
135.503
132.513
131.480
129.518
128.374
128.327
128.057
127.800
126.681
125.206
124.163
123.367
120.381
115.227
84.997
77.318
77.000
76.682
28.193
16.025
O
Me
N
Boc
2v, CDCl3
f1 (ppm)



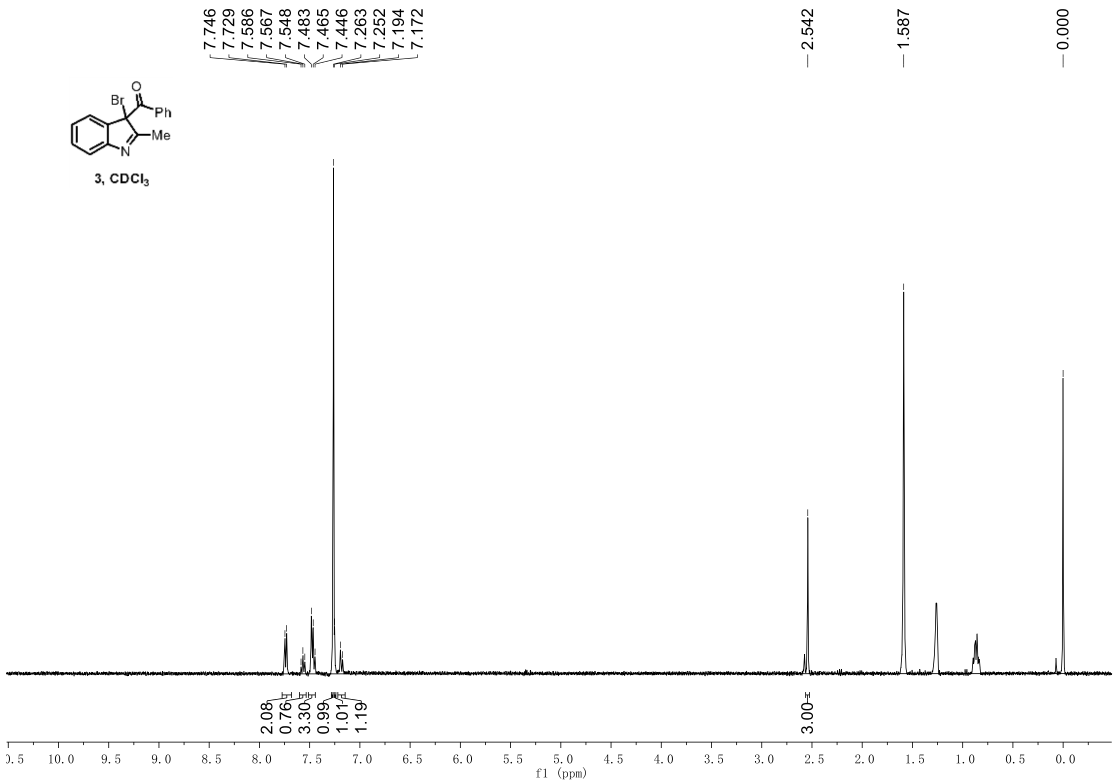


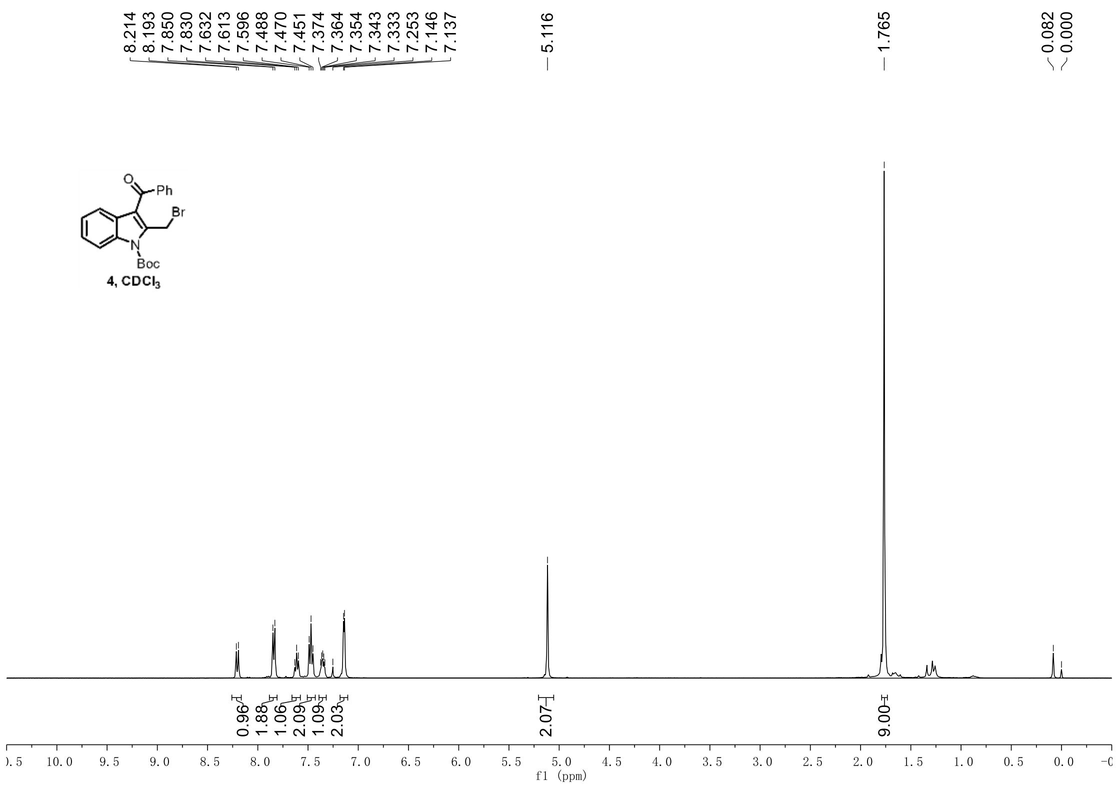


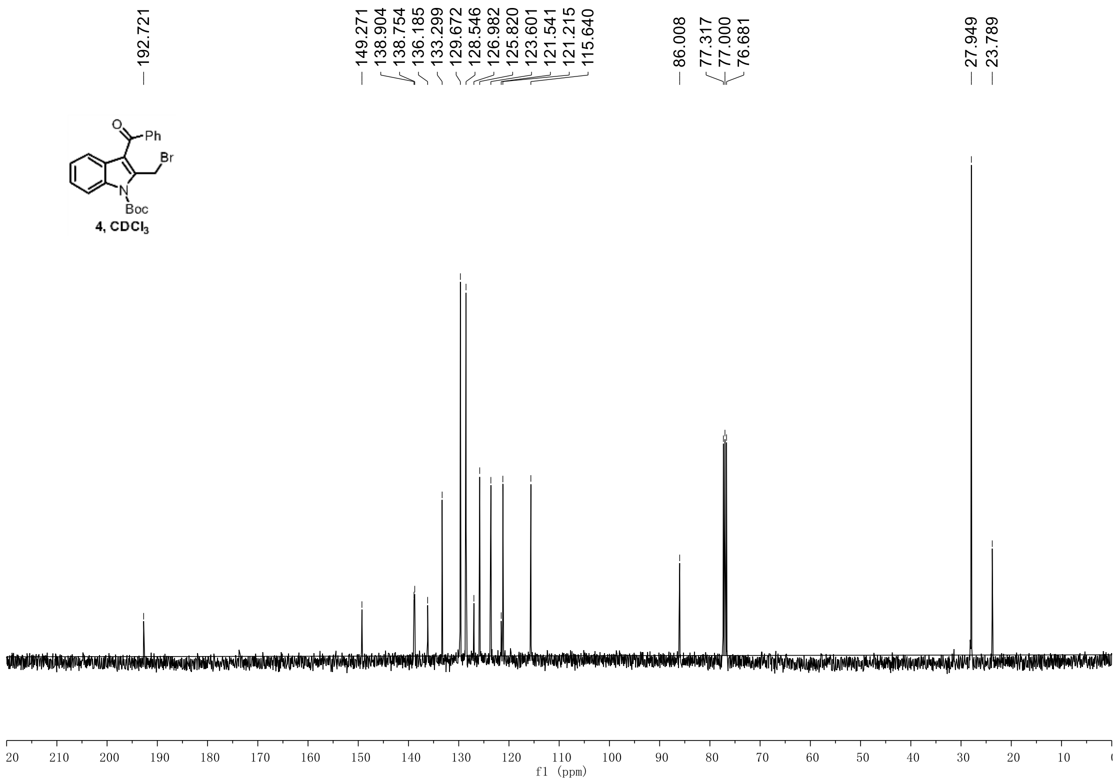
8.143
8.122
7.717
7.708
7.578
7.519
7.501
7.310
7.293
7.269
7.261
7.220
7.201
7.182
7.114
7.108
2.690
1.714
Me
Boc
2x, CDCl3
0.92
0.89
0.91
0.95
1.38
0.96
0.96
2.99
9.00
f1 (ppm)

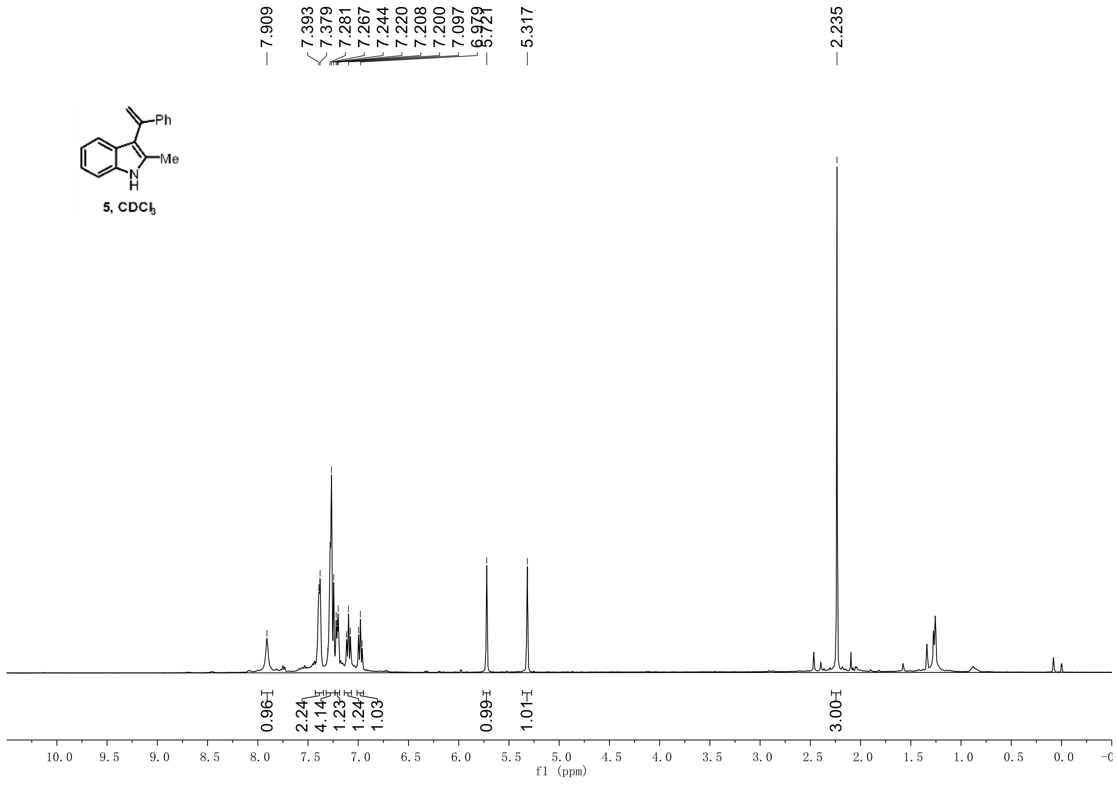


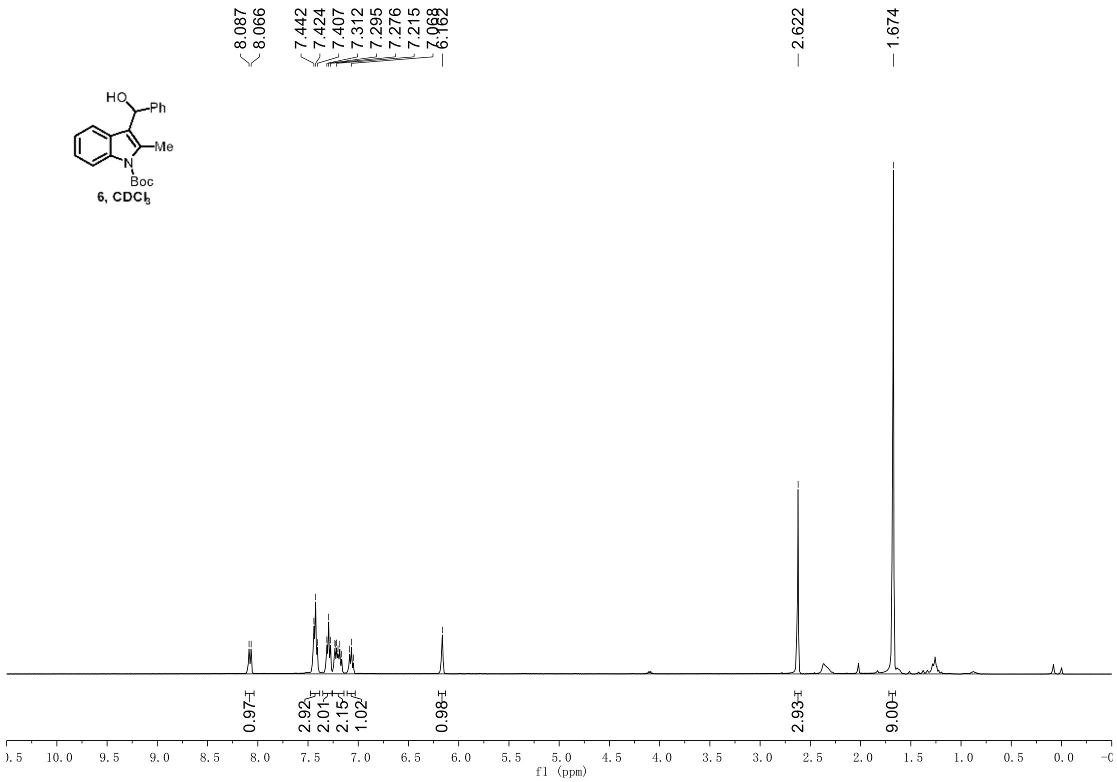
184.877
150.178
145.613
140.764
135.389
134.549
134.198
127.945
127.671
124.194
123.226
120.014
119.690
115.270
84.929
77.318
77.000
76.682
28.171
15.961
Me
Boc
2x, CDCl3
f1 (ppm)

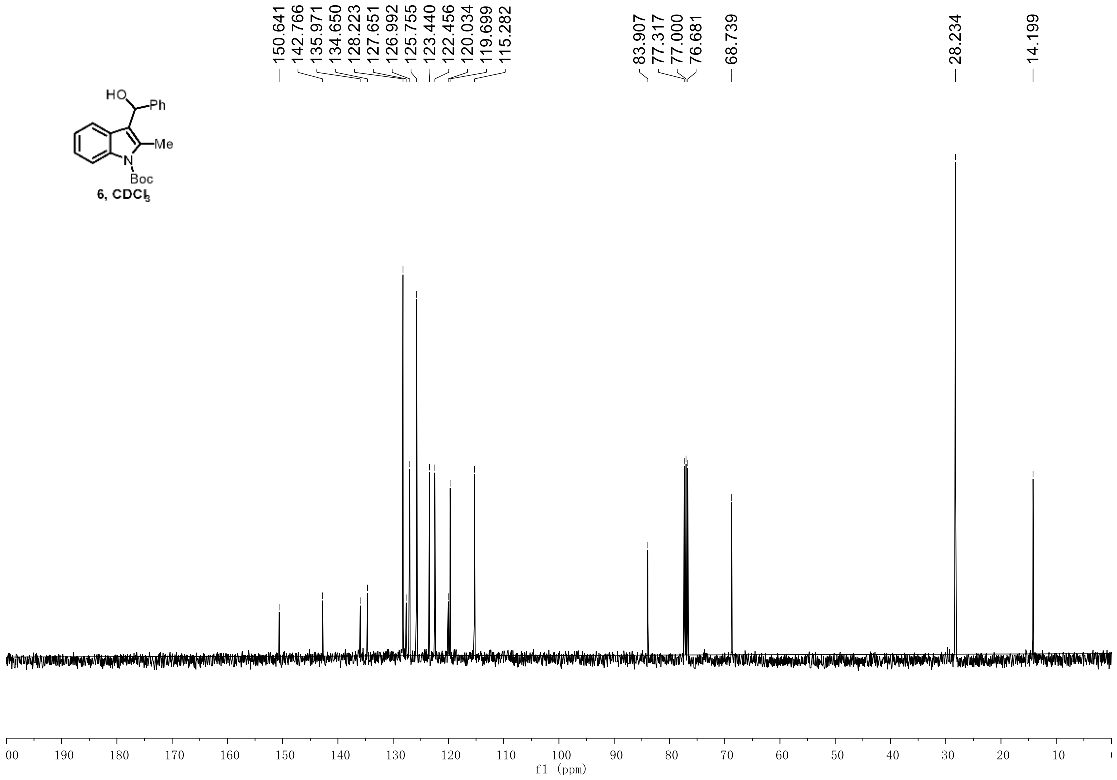

7.746
7.729
7.586
7.567
7.548
7.483
7.465
7.446
7.263
7.252
7.194
7.172
2.542
1.587
0.000
Br
O
Ph
Me
N
3, CDCl3
2.08
0.76
3.30
0.99
1.01
1.19
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

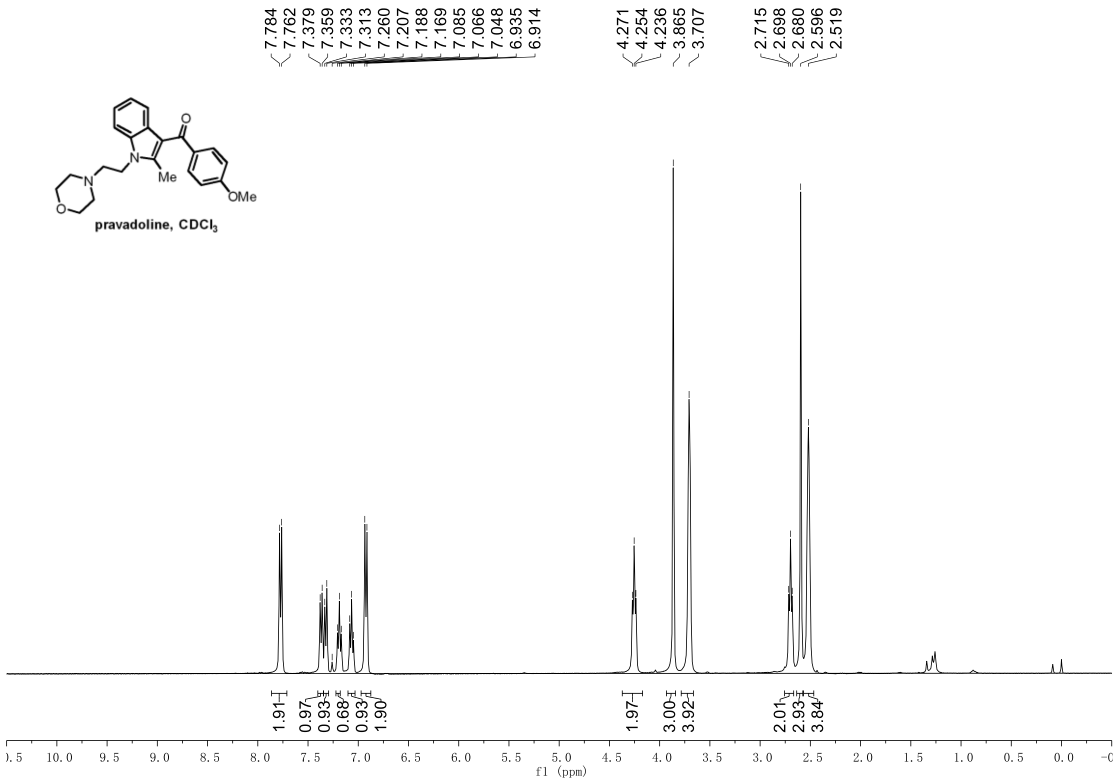

8.214
8.193
7.850
7.830
7.632
7.613
7.596
7.488
7.470
7.451
7.374
7.364
7.354
7.343
7.333
7.253
7.146
7.137
5.116
1.765
0.082
0.000
O
Ph
Br
N
Boc
4, CDCl3
0.96
1.88
1.06
2.09
1.09
2.03
2.07
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

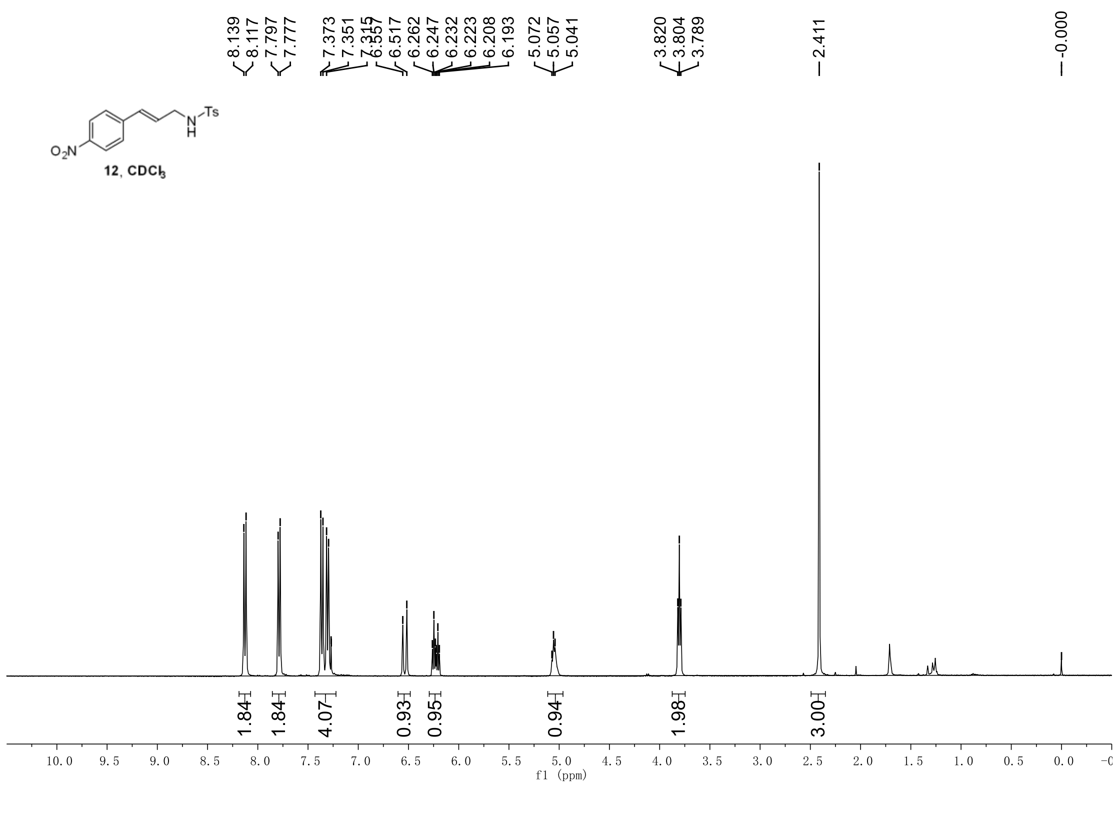


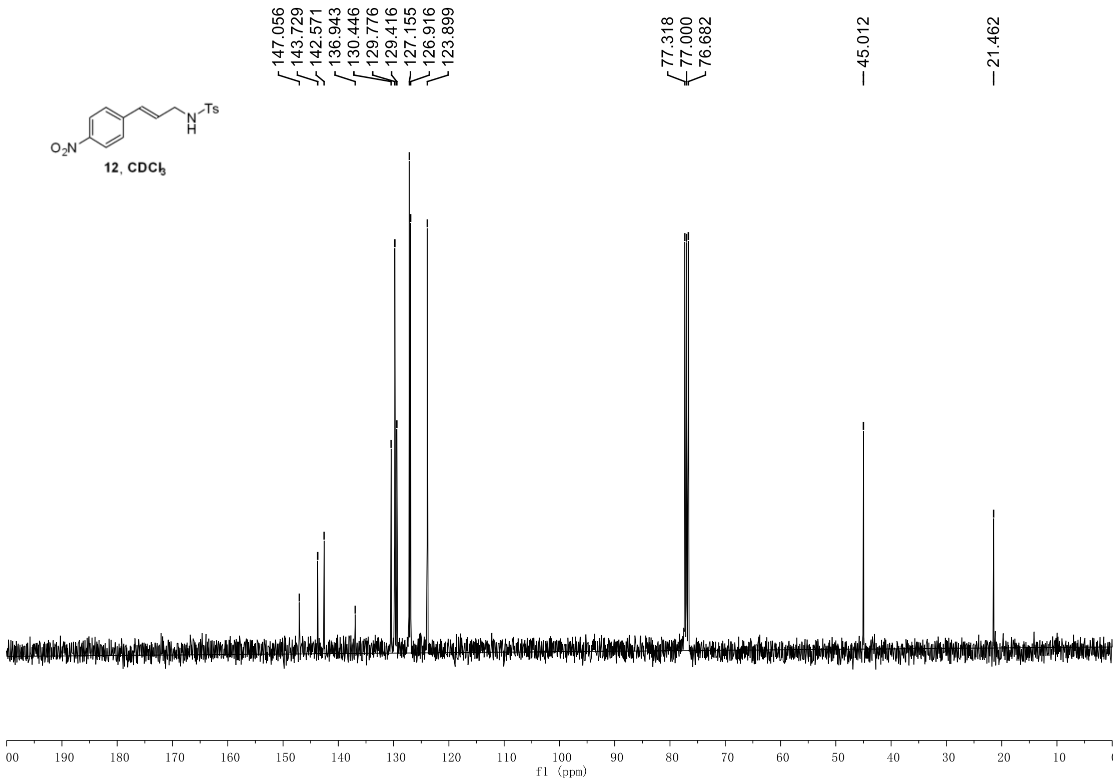




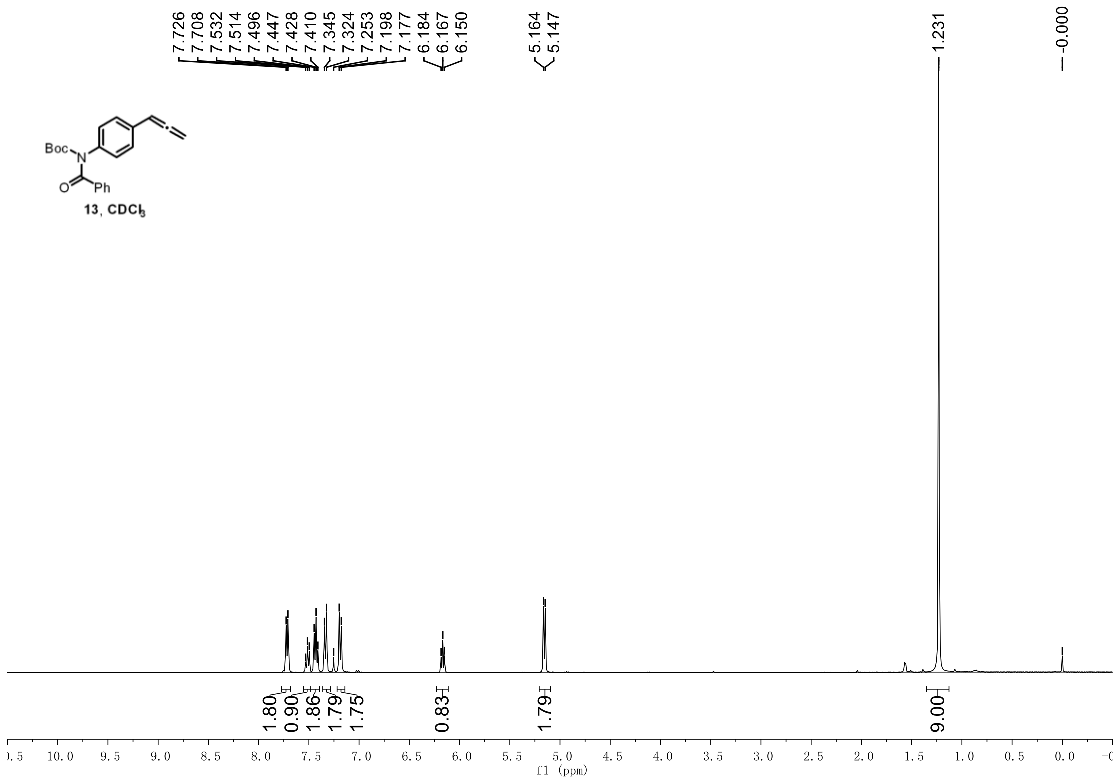



7.784
7.762
7.379
7.359
7.333
7.313
7.260
7.207
7.188
7.169
7.085
7.066
7.048
6.935
6.914
4.271
4.254
4.236
3.865
3.707
2.715
2.698
2.680
2.596
2.519
O
N
Me
N
O
OMe
pravadoline, CDCl3
1.91
0.97
0.93
0.68
0.93
1.90
1.97
3.00
3.92
2.01
2.93
3.84
f1 (ppm)

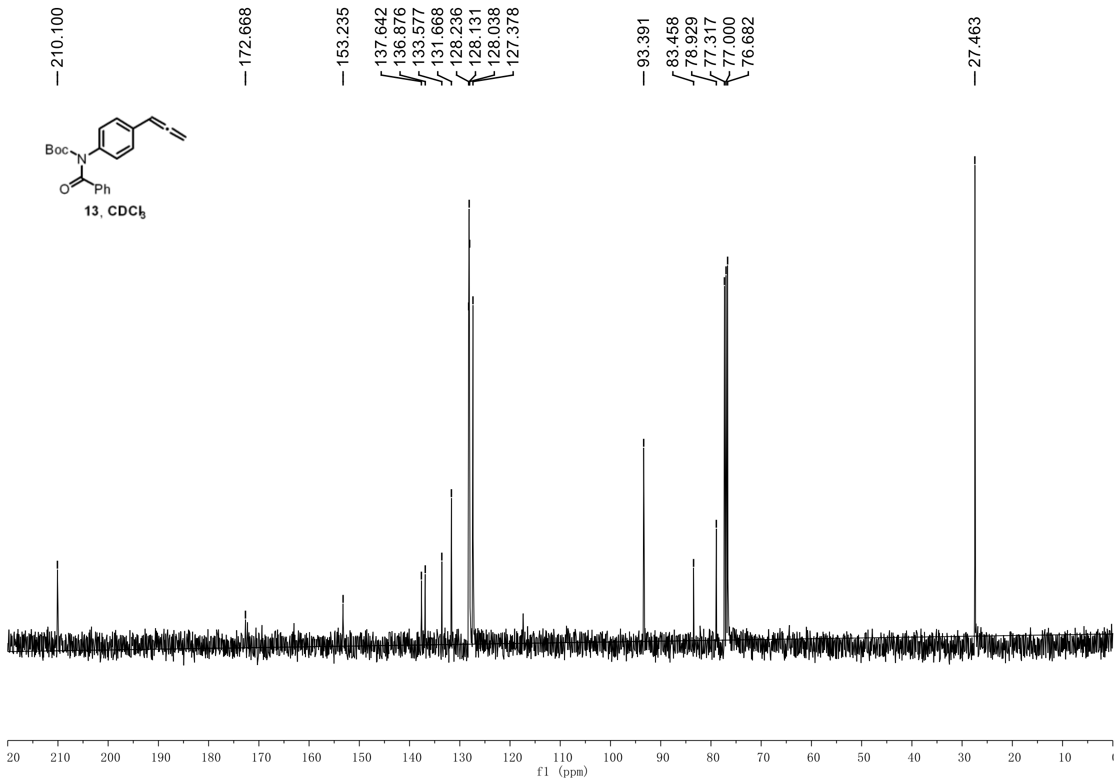

8.139
8.117
7.797
7.777
7.373
7.351
7.315
6.557
6.517
6.262
6.247
6.232
6.223
6.208
6.193
5.072
5.057
5.041
3.820
3.804
3.789
2.411
-0.000
O2N
N
H
Ts
12, CDCl3
1.84
1.84
4.07
0.93
0.95
0.94
1.98
3.00
f1 (ppm)



12, $CDCl_3$



13, $CDCl_3$


210.100
172.668
153.235
137.642
136.876
133.577
131.668
128.236
128.131
128.038
127.378
93.391
83.458
78.929
77.317
77.000
76.682
27.463
Boc
N
O
Ph
13, CDCl3
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)