

Supporting Information

C3-Arylation of Indoles with Aryl Ketones

via C-C/C-H Activations

Zi-Qiong Guo, Hui Xu, Xing Wang, Zhen-Yu Wang, Han-Yuan Li, Biao Ma, Hui-Xiong Dai*

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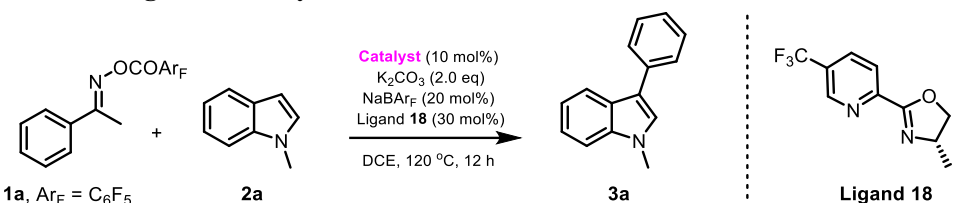
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1. General information

Unless otherwise noted, all reactions were carried out under an N₂ atmosphere in sealed tube with magnetic stirring. All reagents were purchased from commercial suppliers with the highest purity grade, and used directly without further purification. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker 400 and 500 MHz spectrometer in CDCl₃. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublets, td = triple doublet, dt = double triplet, tt = triple of triplets and br = broad. HRMS were recorded at the Center for Mass Spectrometry, Shanghai Institute of Material Medica. Solvents were purified prior to use according to conventional procedures. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Column chromatography was performed on silica gel (200–300 mesh) using a mixture of petroleum ether-ethyl acetate as the eluent. The aryl ketones were commercially available or readily prepared according to the known method.¹

2. Optimization of the Reaction Conditions

Table S1. Screening of the catalysts^a



Entry	Catalysts	Yield (%)
1	/	nd
2	Pd(MeCN) ₂ Cl ₂	65
3	Pd(dppf)Cl ₂	trace
4	PdCl ₂	74
5	Pd(cod)Cl ₂	14
6	Pd(OAc) ₂	48
7	Pd(TFA) ₂	49
8	Pd(acac) ₂	trace
9	Pd(MeCN) ₄ (BF ₄) ₂	30
10	Pd ₂ dba ₃	26
11	Pd(PPh ₃) ₄	nd

^aReaction conditions: **1a** (0.11 mmol), **2a** (0.1 mmol), Catalyst (10 mol%), ligand **18** (30 mol%), NaBARF (20 mol%), K₂CO₃ (0.2 mmol), DCE (2.0 mL), N₂, 120 °C, 12 h. Yields were determined by ¹H NMR spectroscopy using CH₂Br₂ as internal standard. NaBARF = Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate.

Table S2. Screening of the bases^a

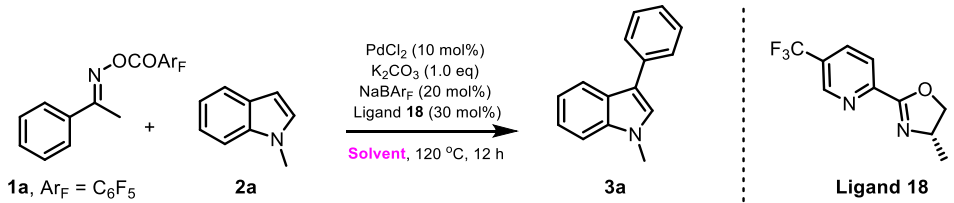
Entry	Bases	Yield (%)
1	/	nd
2	Na ₂ CO ₃	64
3	NaHCO ₃	24
4	K ₂ CO ₃	74
5	KHCO ₃	72
6	Cs ₂ CO ₃	nd
7	Na ₃ PO ₄	60
8	K ₃ PO ₄	29
9	NaOAc	13
10	KOAc	13
11	CF ₃ COONa	nd
12	CF ₃ COOK	nd

^aReaction conditions: **1a** (0.11mmol), **2a** (0.1 mmol), PdCl₂ (10 mol%), ligand **18** (30 mol%), NaBAR_F (20 mol%), Base (0.2 mmol), DCE (2.0 mL), N₂, 120 °C, 12 h. Yields were determined by ¹H NMR spectroscopy using CH₂Br₂ as internal standard.

Table S3. Screening of the base loading^a

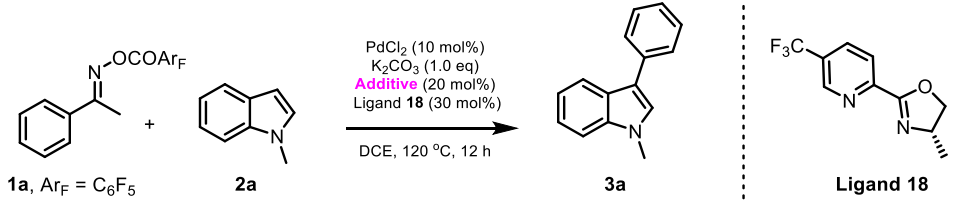
Entry	K ₂ CO ₃ (n equiv.)	Yield (%)
1	1.0	77
2	1.5	74
3	2.0	74
4	2.5	65
5	3.0	47

^aReaction conditions: **1a** (0.11mmol), **2a** (0.1 mmol), PdCl₂ (10 mol%), ligand **18** (30 mol%), NaBAR_F (20 mol%), K₂CO₃ (n eq), DCE (2.0 mL), N₂, 120 °C, 12 h. Yields were determined by ¹H NMR spectroscopy using CH₂Br₂ as internal standard.

Table S4. Screening of the solvents^a


Entry	Solvents	Yield (%)
1	DCE	77
2	DCM	35
3	Toluene	43
4	PhCF ₃	42
5	CH ₃ CN	nd
6	1, 4-dioxane	nd
7	THF	nd
8	MeOH	nd
9	DMF	nd
10	DMSO	nd

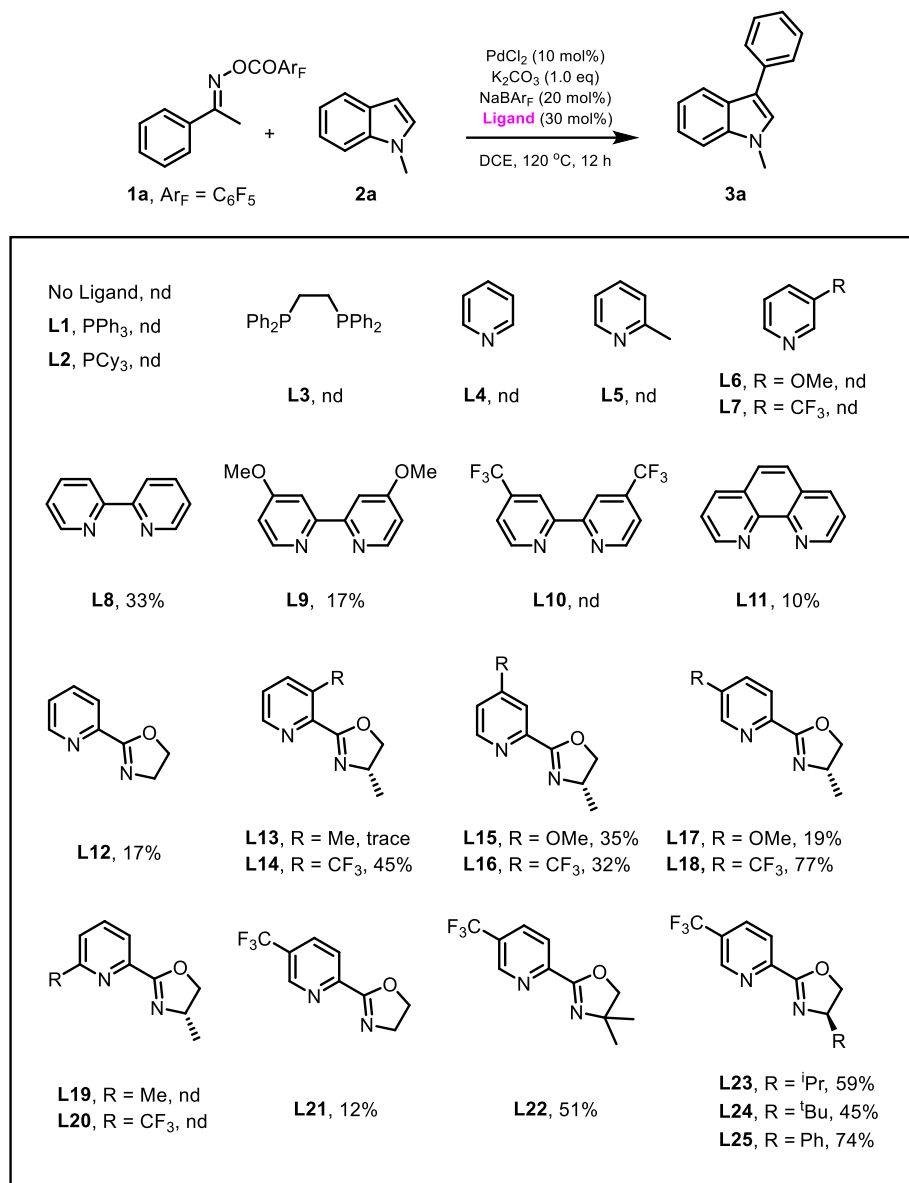
^aReaction conditions: **1a** (0.11mmol), **2a** (0.1 mmol), PdCl₂ (10 mol%), ligand **18** (30 mol%), NaBAr_F (20 mol%), K₂CO₃ (0.1 mmol), Solvent (2.0 mL), N₂, 120 °C, 12 h. Yields were determined by ¹H NMR spectroscopy using CH₂Br₂ as internal standard.

Table S5. Screening of the additives^a


Entry	Additives	Yield (%)
1	/	nd
2	NaBAr _F	77
3	AgNTf ₂	20
4	AgOTf	nd
5	AgOAc	nd
6	AgOTs	nd
7	AgSbF ₆	nd
8	Ag ₂ SO ₄	nd
9	AgNO ₃	nd
10	AgBF ₄	nd

^aReaction conditions: **1a** (0.11mmol), **2a** (0.1 mmol), PdCl₂ (10 mol%), ligand **18** (30 mol%), Additive (20 mol%), K₂CO₃ (0.1 mmol), DCE (2.0 mL), N₂, 120 °C, 12 h. Yields were determined by ¹H NMR spectroscopy using CH₂Br₂ as internal standard.

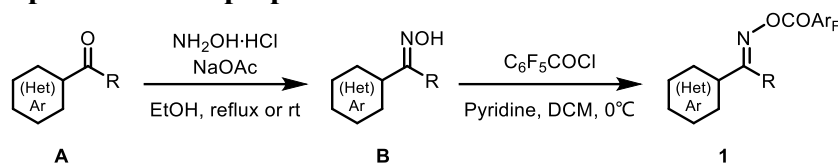
Table S6. Screening of the ligands^a



^aReaction conditions: **1a** (0.11mmol), **2a** (0.1 mmol), PdCl₂ (10 mol%), ligand (30 mol%), NaBArF (20 mol%), K₂CO₃ (0.1 mmol), DCE (2.0 mL), N₂, 120 °C, 12 h. Yields were determined by ¹H NMR spectroscopy using CH₂Br₂ as internal standard.

3. Experimental Procedures

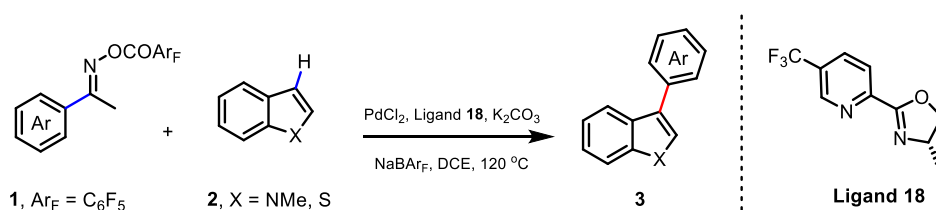
3.1 Typical procedure for preparation of ketoxime esters²



To a mixture of hydroxylamine hydrochloride (278 mg, 4 mmol), NaOAc (640 mg, 8 mmol), EtOH (10 mL) was added aryl ketone **A** (2 mmol), and the mixture was stirred at 90 °C for 2 h or at room temperature for overnight. The reaction mixture was cooled down to room temperature, and then EtOH was removed under reduced pressure. The resulting mixture was extracted with EtOAc. The organic layer was then washed with brine and dried over Na₂SO₄. The solvent was removed under vacuum to give oxime **B** (> 99% yield), not further purified.

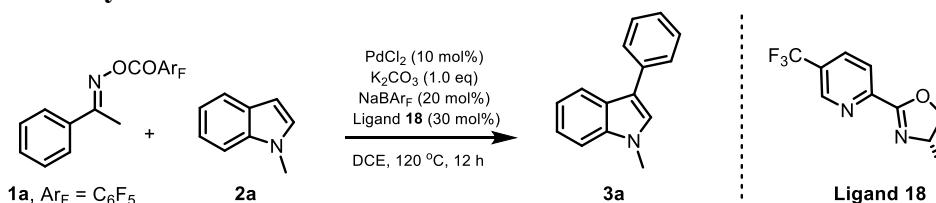
To a mixture of oxime **B** (2 mmol) and CH₂Cl₂ (10 mL) was slowly added pentafluorobenzoyl chloride (552 mg, 2.4 mmol), pyridine (221.2 mg, 2.8 mmol) at 0 °C. After a special time, aq. HCl (1.0 M) was added to the above solution, and the aqueous phase was discarded. The organic portion was washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was isolated by column chromatography (petroleum ether/ethyl acetate 20:1-5:1) or recrystallization to give starting material **1**.

3.2 Typical procedure for preparation of **3**



Under N₂ atmosphere, a mixture consisting of **1** (36.2 mg, 0.11 mmol), **2** (12.5 μl, 0.1 mmol), PdCl₂ (1.8 mg, 10 mol%), ligand **18** (6.9 mg, 30 mol%), NaBAR_F (17.7 mg, 20 mol%), and K₂CO₃ (13.8 mg, 0.1 mmol) in DCE (2.0 mL) was stirred at 120 °C for 12 h. After cooling to room temperature, solvent and other volatile components were removed on a rotary evaporator under reduced pressure, and the residue was subjected to column chromatography for isolation (gradient eluent: petroleum ether/ethyl acetate 100:1-1- 50:1) to give product **3**.

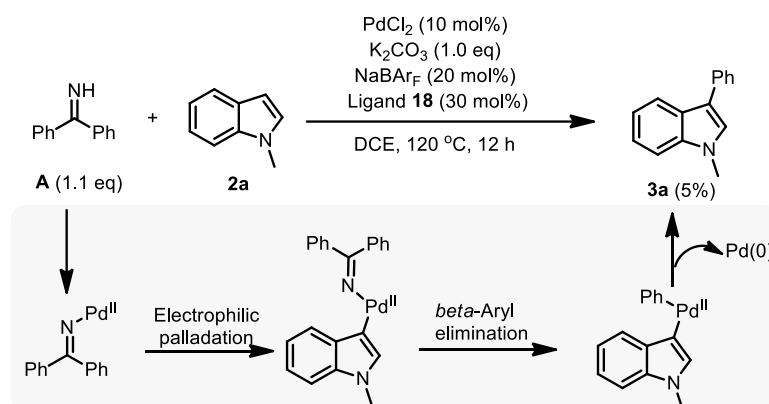
3.3 Scalable synthesis



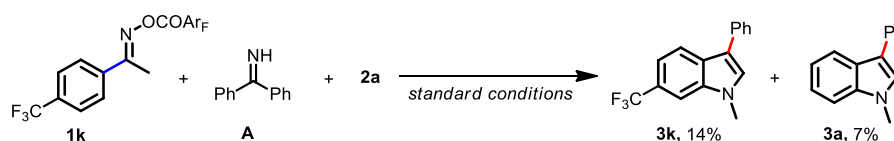
Under N₂ atmosphere, a mixture consisting of **1a** (2.17 g, 6.6 mmol), **2a** (750 μl, 6.0 mmol), PdCl₂ (106 mg, 10 mol%), ligand **18** (414 mg, 30 mol%), NaBAR_F (1.06 g, 20 mol%), and K₂CO₃ (828 mg, 6.0 mmol) in DCE (100 mL) was stirred at 120 °C for 12 h. After cooling to room temperature, solvent and other volatile components were removed on a rotary evaporator under reduced pressure, and the residue was subjected to column chromatography for isolation (gradient

eluent: petroleum ether/ethyl acetate 100:1:1- 50:1) to give product **3a** 0.81 g (65%).

4. Mechanism Experiments



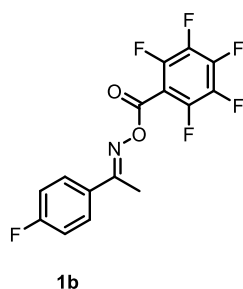
Under N₂ atmosphere, a mixture consisting of benzophenone imine **A** (18.4 μ l, 0.11 mmol), **2a** (12.5 μ l, 0.1 mmol), PdCl₂ (1.8 mg, 10 mol%), ligand **18** (6.9 mg, 30 mol%), NaBAR_F (17.7 mg, 20 mol%), and K₂CO₃ (13.8 mg, 0.1 mmol) in DCE (2.0 mL) was stirred at 120 °C for 12 h. Yields of products **3a** (5%) were determined by GC-MS using n-hexadecane as internal standard.



Under N₂ atmosphere, a mixture consisting of **1k** (45.4 mg, 0.11 mmol), benzophenone imine **A** (1.7 μ l, 0.01 mmol), **2a** (12.5 μ l, 0.1 mmol), PdCl₂ (1.8 mg, 10 mol%), ligand **18** (6.9 mg, 30 mol%), NaBAR_F (17.7 mg, 20 mol%), and K₂CO₃ (13.8 mg, 0.1 mmol) in DCE (2.0 mL) was stirred at 120 °C for 12 h. Yields of products **3k** (14%) and **3a** (7%) were determined by GC-MS using n-hexadecane as internal standard.

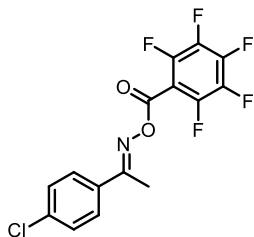
5. Analytical Data

Substrates **1a**, **1f**, **1u-1v**, **1ai** and **1am** were known products and synthesized according to the literatures^{1d,3}. Substrates **2a**, **2m**, and **2o** were commercially available. Substrates **2b-2l** and **2n** were known products and synthesized according to the literatures^{4,5}.



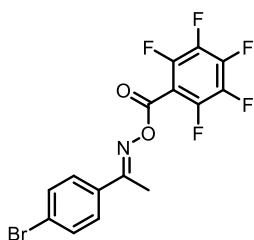
(*E*)-1-(4-fluorophenyl)ethan-1-one *O*-perfluorobenzoyl oxime (**1b**) as a white solid (0.489 g, 70% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ

7.84 – 7.78 (m, 2H), 7.16 – 7.10 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.67 (d, $J = 252$ Hz), 164.05, 156.44, 146.70 (m), 144.66 (m), 142.62 (m), 138.92 (m), 136.90 (m), 130.18 (d, $J = 3.5$ Hz), 129.41 (d, $J = 8.6$ Hz), 115.91 (d, $J = 21.9$ Hz), 107.03, 14.88; ^{19}F NMR (470 MHz, CDCl_3) δ -108.62 – -108.68 (m), -136.99 – -137.08 (m), -147.46 (tt, $J = 20.9, 5.5$ Hz), -159.70 – -159.89 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_7\text{F}_6\text{NO}_2$: 347.0375, found: 347.0380.



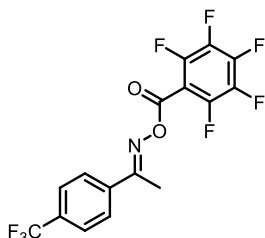
1c

(E)-1-(4-chlorophenyl)ethan-1-one O-perfluorobenzoyl oxime (1c) as a white solid (0.620 g, 85% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, $J = 8.7$ Hz, 2H), 7.42 (d, $J = 8.6$ Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.00, 156.34, 146.70 (m), 144.67 (m), 142.61 (m), 138.91 (m), 137.47, 136.87 (m), 132.47, 129.04, 128.56, 106.94 (m), 14.74; ^{19}F NMR (470 MHz, CDCl_3) δ -136.91 – -137.01 (m), -147.32 (tt, $J = 20.8, 5.2$ Hz), -157.96 – -161.65 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_7\text{F}_5\text{ClNO}_2$: 363.0080, found: 363.0061.



1d

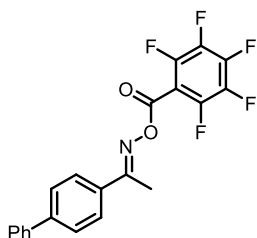
(E)-1-(4-bromophenyl)ethan-1-one O-perfluorobenzoyl oxime (1d) as a white solid (0.593 g, 73% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.67 (d, $J = 8.6$ Hz, 2H), 7.58 (d, $J = 8.7$ Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.08, 156.31, 146.69 (m), 144.64 (m), 142.61 (m), 138.90 (m), 136.87 (m), 132.92, 132.01, 128.74, 125.87, 106.91 (m), 14.70; ^{19}F NMR (470 MHz, CDCl_3) δ -136.95 (d, $J = 21.2$ Hz), -147.29 (t, $J = 22.0$ Hz), -159.67 – -160.08 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_7\text{F}_5\text{BrNO}_2$: 406.9575, found: 406.9584.



1e

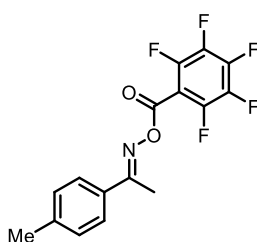
(E)-1-(4-(trifluoromethyl)phenyl)ethan-1-one O-perfluorobenzoyl oxime (1e) as a white solid (0.548 g, 69% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, $J = 8.1$ Hz, 2H), 7.70 (d, $J = 7.5$ Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.13, 156.58,

146.88 (m), 144.90 (m), 142.82 (m), 139.00 (m), 137.54, 136.98 (m), 132.97 (q, $J = 32.7$ Hz), 127.74, 125.78 (q, $J = 5.0$ Hz), 123.82 (q, $J = 272.3$ Hz), 106.66 (m), 15.03; ^{19}F NMR (470 MHz, CDCl_3) δ -63.09, -136.90 – -136.99 (m), -147.17 (tt, $J = 21.0, 5.3$ Hz), -159.66 – -159.84 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{16}\text{H}_7\text{F}_8\text{NO}_2$: 397.0344, found: 397.0377.



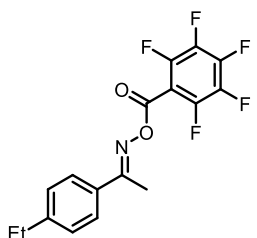
1g

(E)-1-([1,1'-biphenyl]-4-yl)ethan-1-one O-perfluorobenzoyl oxime (1g) as a white solid (0.605 g, 75% yield). Purification condition (crystallization from DCM/PE). ^1H NMR (500 MHz, CDCl_3) δ 7.87 (d, $J = 8.4$ Hz, 2H), 7.67 (d, $J = 8.4$ Hz, 2H), 7.65 – 7.59 (m, 2H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.42 – 7.36 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.77, 156.62, 146.74 (m), 144.68 (m), 144.11, 142.62 (m), 140.11, 138.99 (m), 136.95 (m), 132.87, 129.07, 128.16, 127.81, 127.50, 127.28, 107.28 (m), 14.96; ^{19}F NMR (470 MHz, CDCl_3) δ -134.02 – -144.07 (m), -147.60 (tt, $J = 20.6, 5.1$ Hz), -156.94 – -162.62 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{21}\text{H}_{12}\text{F}_5\text{NO}_2$: 405.0783, found: 405.0784.



1h

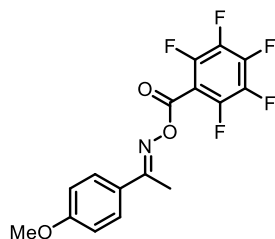
(E)-1-(p-tolyl)ethan-1-one O-perfluorobenzoyl oxime (1h) as a white solid (0.617 g, 90% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.68 (d, $J = 8.3$ Hz, 2H), 7.24 (d, $J = 7.8$ Hz, 2H), 2.44 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.01, 156.61, 146.63 (m), 144.58 (m), 142.51 (m), 141.71, 138.91 (m), 136.88 (m), 131.15, 129.52, 127.21, 107.28 (m), 21.49, 14.86; ^{19}F NMR (470 MHz, CDCl_3) δ -137.07 – -137.16 (m), -147.80 (tt, $J = 21.2, 5.3$ Hz), -159.82 – -160.00 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{16}\text{H}_{10}\text{F}_5\text{NO}_2$: 343.0626, found: 343.0632.



1i

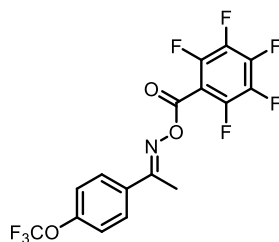
(E)-1-(4-ethylphenyl)ethan-1-one O-perfluorobenzoyl oxime (1i) as a white solid (0.604 g, 85% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.71

(d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 8.2$ Hz, 2H), 2.69 (q, $J = 7.6$ Hz, 2H), 2.44 (s, 3H), 1.25 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.03, 156.60, 147.94, 146.60 (m), 144.55 (m), 142.47 (m), 138.87 (m), 136.84 (m), 131.33, 128.30, 127.27, 107.26 (m), 28.82, 15.35, 14.83; ^{19}F NMR (470 MHz, CDCl_3) δ -132.67 – -142.83 (m), -144.96 – -150.66 (m), -155.94 – -163.43 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{12}\text{F}_5\text{NO}_2$: 357.0783, found: 357.0787.



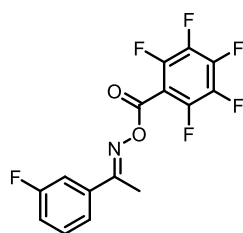
1j

(*E*)-1-(4-ethylphenyl)ethan-1-one *O*-perfluorobenzoyl oxime (1j) as a white solid (0.617 g, 86% yield). Purification condition (hexane: ethyl acetate = 10: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, $J = 8.9$ Hz, 2H), 6.94 (d, $J = 8.9$ Hz, 2H), 3.86 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.51, 162.14, 156.67, 146.63 (m), 144.57 (m), 142.50 (m), 138.92 (m), 136.88 (m), 128.92, 126.23, 114.18, 107.35 (m), 55.51, 14.76; ^{19}F NMR (470 MHz, CDCl_3) δ -137.14 – -137.23 (m), -147.90 (tt, $J = 20.8, 5.2$ Hz), -159.86 – -160.05 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{16}\text{H}_{10}\text{F}_5\text{NO}_3$: 359.0575, found: 359.0569.



1k

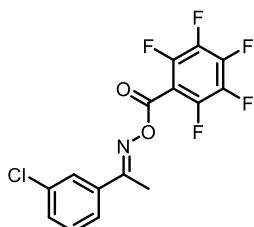
(*E*)-1-(4-(trifluoromethoxy)phenyl)ethan-1-one *O*-perfluorobenzoyl oxime (1k) as a white solid (0.735 g, 89% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, $J = 8.9$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.84, 156.36, 151.36, 146.75 (m), 144.70 (m), 142.67 (m), 138.95 (m), 136.93 (m), 132.63, 129.01, 120.92, 120.45 (q, $J = 258.2$ Hz), 106.94 (m), 14.78; ^{19}F NMR (470 MHz, CDCl_3) δ -57.78, -136.87 – -137.04 (m), -147.25 (t, $J = 20.7$ Hz), -159.62 – -159.85 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{16}\text{H}_7\text{F}_8\text{NO}_3$: 413.0293, found: 413.0305.



1l

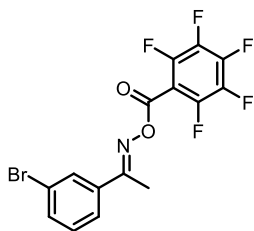
(*E*)-1-(3-fluorophenyl)ethan-1-one *O*-perfluorobenzoyl oxime (1l) as a white solid (0.628 g,

91% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.57 (dt, $J = 7.9, 1.1$ Hz, 1H), 7.53 – 7.50 (m, 1H), 7.42 (td, $J = 8.0, 5.7$ Hz, 1H), 7.22 – 7.17 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.04 (d, $J = 2.6$ Hz), 162.91 (d, $J = 247.2$ Hz), 156.42, 146.61 (m), 144.73 (m), 142.88 (m), 138.79 (m), 137.13 (m), 136.24 (d, $J = 7.7$ Hz), 130.51 (d, $J = 8.1$ Hz), 123.09 (d, $J = 3.1$ Hz), 118.29 (d, $J = 21.1$ Hz), 114.40 (d, $J = 23.4$ Hz), 106.99 (m), 15.04; ^{19}F NMR (470 MHz, CDCl_3) δ -111.88 (q, $J = 8.3$ Hz), -136.90 – -136.99 (m), -147.30 (tt, $J = 20.8, 5.4$ Hz), -159.65 – -159.84 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_7\text{F}_6\text{NO}_2$: 347.0375, found: 347.0389.



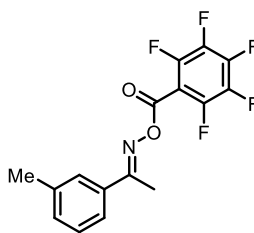
1m

(*E*)-1-(3-chlorophenyl)ethan-1-one *O*-perfluorobenzoyl oxime (1m) as a white solid (0.590 g, 81% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.79 (t, $J = 1.9$ Hz, 1H), 7.67 (dt, $J = 7.8, 1.3$ Hz, 1H), 7.48 – 7.46 (m, 1H), 7.39 (t, $J = 7.9$ Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.96, 156.30, 146.73 (m), 144.72 (m), 142.65 (m), 138.92 (m), 136.88 (m), 135.80, 134.91, 131.21, 130.09, 127.31, 125.42, 106.87 (m), 14.90; ^{19}F NMR (470 MHz, CDCl_3) δ -136.86 – -136.95 (m), -145.90 – -148.62 (m), -158.22 – -161.86 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_7\text{ClF}_5\text{NO}_2$: 363.0080, found: 363.0072.



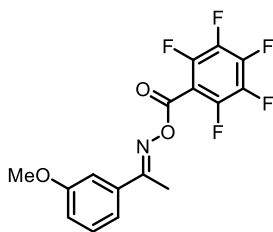
1n

(*E*)-1-(3-bromophenyl)ethan-1-one *O*-perfluorobenzoyl oxime (1n) as a white solid (0.585 g, 72% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.94 (t, $J = 1.8$ Hz, 1H), 7.72 (dt, $J = 7.8, 1.4$ Hz, 1H), 7.62 – 7.60 (m, 1H), 7.32 (t, $J = 7.9$ Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.91, 156.34, 146.59 (m), 144.70 (m), 142.86 (m), 138.78 (m), 137.09 (m), 136.07, 134.19, 130.35, 130.24, 125.90, 122.99, 106.92 (m), 14.97; ^{19}F NMR (470 MHz, CDCl_3) δ -136.86 – -136.95 (m), -147.27 (tt, $J = 20.9, 5.2$ Hz), -159.64 – -159.82 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_7\text{BrF}_5\text{NO}_2$: 406.9575, found: 406.9582.



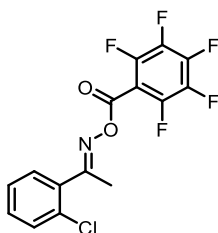
1o

(E)-1-(*m*-tolyl)ethan-1-one *O*-perfluorobenzoyl oxime (1o) as a white solid (0.638 g, 93% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.62 (s, 1H), 7.55 (dt, *J* = 7.5, 1.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.30 (dt, *J* = 6.4, 1.4 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.45, 156.63, 146.52 (m), 144.57 (m), 142.75 (m), 138.78 (m), 138.67, 137.09 (m), 134.04, 132.07, 128.74, 127.84, 124.51, 107.24 (m), 21.50, 15.16; ¹⁹F NMR (470 MHz, CDCl₃) δ -137.02 – -137.10 (m), -147.70 (t, *J* = 21.3 Hz), -159.82 – -159.96 (m); HRMS (EI) *m/z*: [M]⁺ calcd for C₁₆H₁₀F₅NO₂: 343.0626, found: 343.0626.



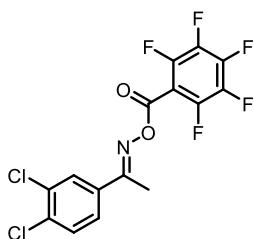
1p

(E)-1-(3-methoxyphenyl)ethan-1-one *O*-perfluorobenzoyl oxime (1p) as a white solid (0.538 g, 75% yield). Purification condition (hexane: ethyl acetate = 10: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.30 (m, 3H), 7.03 (dt, *J* = 7.2, 2.4 Hz, 1H), 3.86 (s, 3H), 2.45 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.14, 159.88, 156.59, 146.52 (m), 144.62 (m), 142.77 (m), 138.79 (m), 137.10 (m), 135.46, 129.89, 119.85, 117.23, 112.44, 107.24 (m), 55.57, 15.21; ¹⁹F NMR (470 MHz, CDCl₃) δ -137.00 – -137.10 (m), -147.58 – -147.69 (m), -159.80 – -159.92 (m); HRMS (EI) *m/z*: [M]⁺ calcd for C₁₆H₁₀F₅NO₃: 359.0575, found: 359.0584.



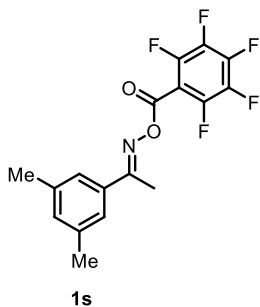
1q

(E)-1-(2-chlorophenyl) ethan-1-one *O*-perfluorobenzoyl oxime (1q) as a white solid (0.568 g, 78% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.46 – 7.43 (m, 2H), 7.40 (td, *J* = 7.7, 1.8 Hz, 1H), 7.33 (td, *J* = 7.5, 1.3 Hz, 1H), 2.46 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.89, 156.46, 146.58 (m), 144.67 (m), 142.85 (m), 138.78 (m), 137.10 (m), 134.51, 132.59, 131.32, 130.38, 130.29, 127.18, 106.99 (m), 18.51; ¹⁹F NMR (470 MHz, CDCl₃) δ -136.75 – -136.84 (m), -147.38 (t, *J* = 20.9 Hz), -159.77 – -159.88 (m); HRMS (EI) *m/z*: [M]⁺ calcd for C₁₅H₇ClF₅NO₂: 363.0080, found: 363.0130.

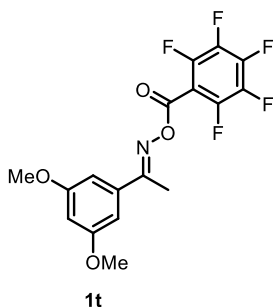


1r

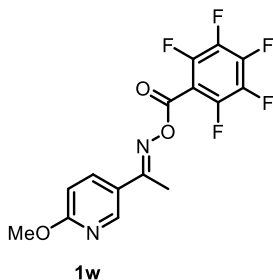
(E)-1-(3,4-dichlorophenyl)ethan-1-one O-perfluorobenzoyl oxime (1r) as a white solid (0.659 g, 83% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 2.1$ Hz, 1H), 7.65 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.00, 156.16, 146.77 (m), 144.79 (m), 142.72 (m), 138.94 (m), 136.90 (m), 135.59, 133.93, 133.26, 130.79, 129.07, 126.39, 106.73 (m), 14.67; ^{19}F NMR (470 MHz, CDCl_3) δ -136.79 – -136.88 (m), -147.02 (tt, $J = 20.7, 5.2$ Hz), -159.54 – -159.73 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_6\text{Cl}_2\text{F}_5\text{NO}_2$: 396.9690, found: 396.9700.



(E)-1-(3,5-dimethylphenyl)ethan-1-one O-perfluorobenzoyl oxime (1s) as a white solid (0.558 g, 78% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.39 (s, 2H), 7.12 (s, 1H), 2.44 (s, 3H), 2.36 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.52, 156.49, 146.63 (m), 144.55 (m), 142.48 (m), 138.87 (m), 138.42, 136.84 (m), 133.90, 132.85, 124.98, 107.20 (m), 21.25, 15.04; ^{19}F NMR (470 MHz, CDCl_3) δ -136.98 – -137.16 (m), -147.77 (t, $J = 20.9$ Hz), -159.86 – -159.98 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{12}\text{F}_5\text{NO}_2$: 357.0783, found: 357.0790.

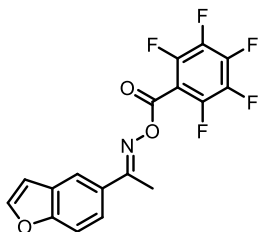


(E)-1-(3,5-dimethoxyphenyl)ethan-1-one O-perfluorobenzoyl oxime (1t) as a white solid (0.663 g, 85% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 6.90 (d, $J = 2.2$ Hz, 2H), 6.57 (t, $J = 2.3$ Hz, 1H), 3.84 (s, 6H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.05, 160.91, 156.39, 146.64 (m), 144.58 (m), 142.50 (m), 138.86 (m), 136.83 (m), 135.92, 107.06 (m), 105.29, 103.08, 55.50, 15.02; ^{19}F NMR (470 MHz, CDCl_3) δ -136.99 – -137.08 (m), -147.61 (tt, $J = 20.9, 5.2$ Hz), -159.76 – -159.95 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{12}\text{F}_5\text{NO}_4$: 389.0681, found: 389.0678.



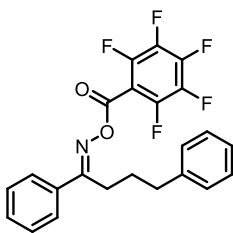
(E)-1-(6-methoxypyridin-3-yl)ethan-1-one O-perfluorobenzoyl oxime (1w) as a white solid

(0.469 mg, 65% yield). Purification condition (crystallization from DCM/PE). ^1H NMR (500 MHz, CDCl_3) δ 8.52 (d, $J = 2.5$ Hz, 1H), 8.11 (dd, $J = 8.8, 2.5$ Hz, 1H), 6.80 (d, $J = 8.8$ Hz, 1H), 3.99 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.91, 162.55, 156.25, 146.62 (m), 146.45, 144.56 (m), 142.49 (m), 138.82, 136.92, 136.81 (m), 123.15, 111.12, 106.91, 53.75, 14.12; ^{19}F NMR (470 MHz, CDCl_3) δ -136.99 – -137.08 (m), -147.43 (tt, $J = 22.0, 5.8$ Hz), -159.69 – -159.82 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_9\text{F}_5\text{N}_2\text{O}_3$: 360.0528, found: 360.0527.



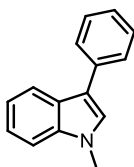
1x

(E)-1-(benzofuran-5-yl)ethan-1-one O-perfluorobenzoyl oxime (1x) as a white solid (0.458 g, 62% yield). Purification condition (crystallization from DCM/PE). ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 2.0$ Hz, 1H), 7.78 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.68 (d, $J = 2.2$ Hz, 1H), 7.55 (d, $J = 8.7$ Hz, 1H), 6.85 – 6.80 (m, 1H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.36, 156.65, 156.60, 146.68 (m), 146.33, 144.66 (m), 142.59 (m), 138.98 (m), 136.95 (m), 129.08, 127.95, 123.72, 120.92, 111.89, 107.34 (m), 107.09, 15.43; ^{19}F NMR (470 MHz, CDCl_3) δ -136.97 – -137.15 (m), -147.68 (t, $J = 21.1$ Hz), -159.78 – -159.91 (m); HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_8\text{F}_5\text{NO}_3$: 369.0419, found: 369.0424.



1a-1

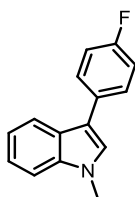
(E)-1,4-diphenylbutan-1-one O-perfluorobenzoyl oxime (1a-1) as a white solid (0.607 g, 70% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.69 (d, $J = 7.7$ Hz, 2H), 7.48 (t, $J = 7.2$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 2H), 7.23 (t, $J = 7.4$ Hz, 2H), 7.16 (d, $J = 7.4$ Hz, 1H), 7.12 (d, $J = 7.6$ Hz, 2H), 2.94 – 2.86 (m, 2H), 2.69 (t, $J = 7.4$ Hz, 2H), 1.95 – 1.89 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.76, 156.64, 146.65 (m), 144.61 (m), 142.59 (m), 140.98, 138.95 (m), 136.92 (m), 133.17, 131.24, 128.96, 128.50, 128.48, 127.55, 126.23, 107.17 (m), 35.71, 28.34, 28.30; ^{19}F NMR (470 MHz, Chloroform-d) δ -137.04 – -137.13 (m), -147.59 – -147.74 (m), -159.63 – -159.82 (m).



3a

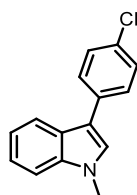
1-methyl-3-phenyl-1H-indole (3a)⁵ as a yellow oil (14.5 mg, 70% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.94 (dt, $J = 8.2, 1.0$ Hz, 1H), 7.67 – 7.63 (m, 2H), 7.45 – 7.40 (m, 2H), 7.37 – 7.33 (m, 1H), 7.29 – 7.24 (m, 2H), 7.22 (s, 1H), 7.20 – 7.17 (m, 1H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 137.55, 135.75, 128.82, 127.40, 126.62,

126.23, 125.77, 122.04, 120.01, 119.96, 116.79, 109.61, 32.94.



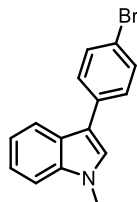
3b

3-(4-fluorophenyl)-1-methyl-1H-indole (3b)⁶ as a yellow solid (14.6 mg, 65% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.21 – 7.16 (m, 2H), 7.15 – 7.08 (m, 2H), 3.82 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 161.40 (d, *J* = 244.3 Hz), 137.45, 131.73 (d, *J* = 3.2 Hz), 128.79 (d, *J* = 7.8 Hz), 126.43, 126.17, 122.14, 120.03, 119.70, 115.87, 115.64 (d, *J* = 21.3 Hz), 109.65, 32.95; ¹⁹F NMR (470 MHz, CDCl₃) δ -117.33 – 117.39 (m).



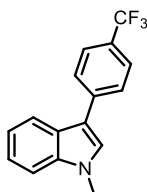
3c

3-(4-chlorophenyl)-1-methyl-1H-indole (3c)⁷ as a yellow solid (17.4 mg, 72% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.88 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.41 – 7.34 (m, 3H), 7.30 – 7.27 (m, 1H), 7.22 – 7.17 (m, 2H), 3.82 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.55, 134.24, 131.34, 128.94, 128.47, 126.71, 126.00, 122.23, 120.19, 119.74, 115.61, 109.72, 32.99.



3d

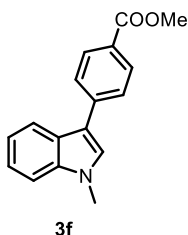
3-(4-bromophenyl)-1-methyl-1H-indole (3d)⁵ as a yellow solid (14 mg, 49% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.88 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.56 – 7.49 (m, 4H), 7.36 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.22 (s, 1H), 7.21 – 7.18 (m, 1H), 3.83 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.56, 134.70, 131.88, 128.83, 126.71, 125.95, 122.25, 120.22, 119.74, 119.34, 115.61, 109.74, 33.02.



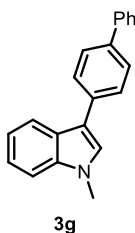
3e

1-methyl-3-(4-(trifluoromethyl)phenyl)-1H-indole (3e)⁵ as a yellow solid (15.5 mg, 56% yield). **L22** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H),

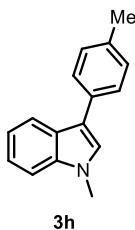
7.36 (d, $J = 8.3$ Hz, 1H), 7.31 – 7.27 (m, 1H), 7.24 (s, 1H), 7.23 – 7.19 (m, 1H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.55, 137.70, 127.48 (q, $J = 32.4$ Hz), 127.46, 127.12, 125.94, 125.81 (q, $J = 3.8$ Hz), 124.68 (q, $J = 271.7$ Hz), 122.47, 120.56, 119.77, 115.39, 109.94, 33.07; ^{19}F NMR (470 MHz, CDCl_3) δ -62.14.



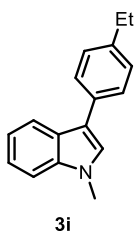
methyl 4-(1-methyl-1H-indol-3-yl) benzoate (3f) as a yellow solid (20.0 mg, 75% yield). **L23** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, $J = 8.0$ Hz, 2H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.73 (d, $J = 8.5$ Hz, 2H), 7.38 (d, $J = 8.2$ Hz, 1H), 7.33 (s, 1H), 7.32 – 7.27 (m, 1H), 7.23 (t, $J = 7.4$ Hz, 1H), 3.93 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.29, 140.67, 137.70, 130.25, 127.63, 127.00, 126.63, 125.91, 122.39, 120.52, 119.95, 115.70, 109.85, 52.07, 33.11; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{NO}_2$: 266.1176, found: 266.1174.



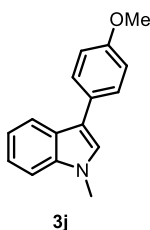
3-([1,1'-biphenyl]-4-yl)-1-methyl-1H-indole (3g)⁸ as a yellow solid (16.1 mg, 57% yield). **L23** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.99 (d, $J = 8.0$ Hz, 1H), 7.76 – 7.72 (m, 2H), 7.69 – 7.64 (m, 4H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.37 (d, $J = 8.2$ Hz, 1H), 7.36 – 7.32 (m, 1H), 7.32 – 7.26 (m, 2H), 7.23 – 7.20 (m, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.12, 138.49, 137.60, 134.84, 128.85, 127.62, 127.53, 127.11, 127.00, 126.72, 126.21, 122.11, 120.06, 116.29, 109.67, 33.01.



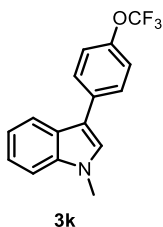
1-methyl-3-(p-tolyl)-1H-indole (3h)⁶ as a yellow solid (14.6 mg, 66% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.92 (dt, $J = 8.0, 1.0$ Hz, 1H), 7.57 – 7.52 (m, 2H), 7.35 (dt, $J = 8.2, 1.0$ Hz, 1H), 7.29 – 7.23 (m, 3H), 7.20 – 7.15 (m, 2H), 3.81 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 137.50, 135.38, 132.77, 129.53, 127.33, 126.34, 126.30, 121.96, 120.04, 119.82, 116.74, 109.55, 32.91, 21.23.



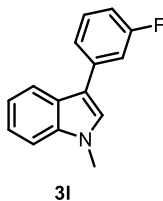
3-(4-ethylphenyl)-1-methyl-1H-indole (3i) as a yellow oil (14.1 mg, 60% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.93 (dt, $J = 8.1, 1.0$ Hz, 1H), 7.59 – 7.55 (m, 2H), 7.35 (dt, $J = 8.3, 0.9$ Hz, 1H), 7.29 – 7.24 (m, 3H), 7.20 – 7.15 (m, 2H), 3.82 (s, 3H), 2.69 (q, $J = 7.6$ Hz, 2H), 1.29 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.79, 137.50, 133.04, 128.32, 127.39, 126.37, 126.31, 121.94, 120.07, 119.80, 116.78, 109.53, 32.92, 28.66, 15.74; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{18}\text{N}$: 236.1434, found: 236.1435.



3-(4-methoxyphenyl)-1-methyl-1H-indole (3j)⁵ as a yellow solid (10.0 mg, 42% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.89 (dt, $J = 8.0, 1.0$ Hz, 1H), 7.59 – 7.54 (m, 2H), 7.35 (dt, $J = 8.2, 0.9$ Hz, 1H), 7.30 – 7.25 (m, 1H), 7.20 – 7.14 (m, 2H), 7.01 – 6.96 (m, 2H), 3.85 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.00, 137.43, 128.54, 128.31, 126.35, 126.02, 121.94, 119.92, 119.75, 116.49, 114.32, 109.52, 55.44, 32.90.

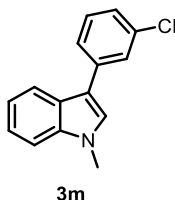


1-methyl-3-(4-(trifluoromethoxy)phenyl)-1H-indole (3k) as a yellow oil (13.1 mg, 45% yield). **L22** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.89 (dt, $J = 7.9, 1.0$ Hz, 1H), 7.66 – 7.61 (m, 2H), 7.36 (dt, $J = 8.3, 0.9$ Hz, 1H), 7.32 – 7.25 (m, 3H), 7.22 – 7.18 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 147.25, 137.50, 134.62, 128.37, 126.81, 125.99, 122.25, 121.49, 120.68 (q, $J = 255.0$ Hz), 120.22, 119.66, 115.42, 109.75, 32.98; ^{19}F NMR (470 MHz, CDCl_3) δ -57.81; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NO}$: 292.0944, found: 292.0930.

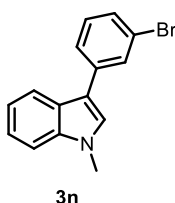


3-(3-fluorophenyl)-1-methyl-1H-indole (3l) as a yellow oil (11.0 mg, 49% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, $J = 8.1$ Hz, 1H), 7.43 (dt, $J = 7.7, 1.3$ Hz, 1H), 7.40 – 7.32 (m, 3H), 7.31 – 7.27 (m, 1H), 7.24 (d, $J = 0.7$ Hz,

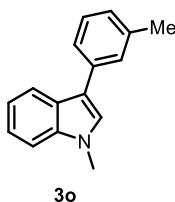
1H), 7.22 – 7.19 (m, 1H), 6.96 – 6.92 (m, 1H), 3.83 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 163.37 (d, *J* = 245.0 Hz), 138.02 (d, *J* = 8.2 Hz), 137.58, 130.20 (d, *J* = 9.0 Hz), 127.01, 125.97, 122.84, 122.28, 120.29, 119.81, 115.69, 113.87 (d, *J* = 21.8 Hz), 112.41 (d, *J* = 21.1 Hz), 109.75, 33.01; ¹⁹F NMR (470 MHz, CDCl₃) δ -113.41 (q, *J* = 8.6 Hz); HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₅H₁₃FN: 226.1027, found:226.1021.



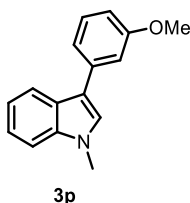
3-(3-chlorophenyl)-1-methyl-1H-indole (3m)⁹ as a yellow oil (14.5 mg, 60% yield). **L23** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.91 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.63 (t, *J* = 1.9 Hz, 1H), 7.53 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 7.23 – 7.18 (m, 3H), 3.82 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.63, 137.56, 134.60, 130.02, 127.13, 127.01, 125.93, 125.66, 125.32, 122.29, 120.30, 119.75, 115.44, 109.75, 33.01.



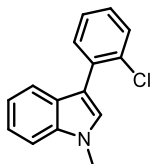
3-(3-bromophenyl)-1-methyl-1H-indole (3n) as a yellow oil (10.8 mg, 38% yield). **L23** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.79 (t, *J* = 1.9 Hz, 1H), 7.58 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 (s, 1H), 7.23 – 7.19 (m, 1H), 3.84 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.92, 137.53, 130.31, 130.04, 128.56, 127.02, 125.90, 125.77, 122.92, 122.30, 120.31, 119.72, 115.31, 109.76, 33.05; HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₅H₁₃BrN: 286.0226, found: 286.0025.



1-methyl-3-(m-tolyl)-1H-indole (3o)⁹ as a yellow oil (15.0 mg, 68% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.29 – 7.25 (m, 1H), 7.21 (s, 1H), 7.20 – 7.17 (m, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 2.42 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 138.35, 137.54, 135.65, 128.73, 128.16, 126.60, 126.28, 124.52, 121.99, 120.08, 119.88, 116.85, 109.57, 32.92, 21.68.

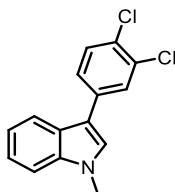


3-(3-methoxyphenyl)-1-methyl-1H-indole (3p)¹⁰ as a yellow oil (17.1 mg, 72% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.24 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.22 (s, 1H), 7.21 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.20 – 7.16 (m, 1H), 6.83 – 6.81 (m, 1H), 3.86 (s, 3H), 3.81 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.03, 137.54, 137.13, 129.78, 126.76, 126.19, 122.07, 120.03, 120.00, 119.96, 116.64, 112.98, 111.24, 109.62, 55.32, 32.94.



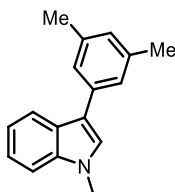
3q

3-(2-chlorophenyl)-1-methyl-1H-indole (3q)⁹ as a yellow oil (16.4 mg, 68% yield). **L24** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.65 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.51 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.37 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.29 – 7.26 (m, 1H), 7.24 – 7.20 (m, 1H), 7.18 – 7.14 (m, 1H), 3.85 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 136.74, 133.96, 133.12, 131.89, 130.22, 128.92, 127.39, 127.09, 126.72, 121.99, 120.25, 119.87, 113.19, 109.56, 33.06.



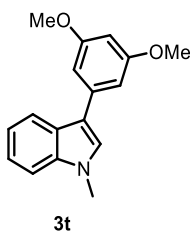
3r

3-(3,4-dichlorophenyl)-1-methyl-1H-indole (3r) as a yellow solid (11.6 mg, 42% yield). **L23** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.87 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.72 (t, *J* = 1.2 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.24 – 7.19 (m, 2H), 3.84 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.52, 135.91, 132.68, 130.66, 129.19, 128.67, 127.08, 126.38, 125.71, 122.42, 120.46, 119.54, 114.41, 109.86, 33.09; HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₅H₁₂Cl₂N: 276.0341, found: 276.0340.

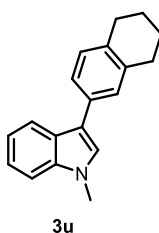


3s

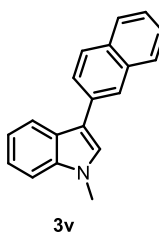
3-(3,5-dimethylphenyl)-1-methyl-1H-indole (3s) as a yellow solid (15.0 mg, 64% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.95 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.21 (s, 1H), 7.20 – 7.17 (m, 1H), 6.92 (s, 1H), 3.82 (s, 3H), 2.38 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 138.28, 137.47, 135.54, 127.54, 126.60, 126.26, 125.26, 121.92, 120.13, 119.78, 116.84, 109.53, 32.94, 21.57; HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₇H₁₈N: 236.1434, found: 236.1435.



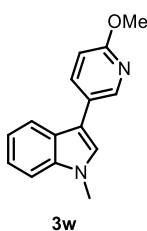
3-(3,5-dimethoxyphenyl)-1-methyl-1H-indole (3t) as a yellow oil (15.5 mg, 58% yield). **L23** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.95 (dt, $J = 8.1, 1.0$ Hz, 1H), 7.36 (dt, $J = 8.1, 0.9$ Hz, 1H), 7.31 – 7.26 (m, 1H), 7.25 (s, 1H), 7.21 – 7.17 (m, 1H), 6.82 (d, $J = 2.3$ Hz, 2H), 6.41 (t, $J = 2.3$ Hz, 1H), 3.86 (s, 6H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 161.11, 137.62, 137.49, 126.84, 126.12, 122.09, 120.04, 120.02, 116.70, 109.65, 105.47, 98.01, 55.45, 32.98; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_2$: 268.1332, found: 268.1325.



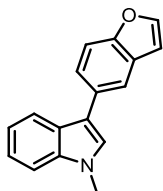
1-methyl-3-(5,6,7,8-tetrahydronaphthalen-2-yl)-1H-indole (3u) as a yellow oil (17.0 mg, 65% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, $J = 8.0$ Hz, 1H), 7.39 (dd, $J = 7.8, 1.9$ Hz, 1H), 7.37 – 7.32 (m, 2H), 7.29 – 7.24 (m, 1H), 7.20 – 7.15 (m, 2H), 7.13 (d, $J = 7.8$ Hz, 1H), 3.81 (s, 3H), 2.86 – 2.79 (m, 4H), 1.86 – 1.82 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 137.48, 134.81, 132.83, 129.58, 128.02, 126.33, 124.78, 121.89, 120.11, 119.73, 116.87, 109.50, 32.90, 29.68, 29.24, 23.45, 23.41; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{20}\text{N}$: 262.1590, found: 262.1564.



1-methyl-3-(naphthalen-2-yl)-1H-indole (3v)⁵ as a yellow solid (20.0 mg, 78% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 8.11 (s, 1H), 8.06 (d, $J = 7.9$ Hz, 1H), 7.90 – 7.82 (m, 3H), 7.79 (dd, $J = 8.5, 1.8$ Hz, 1H), 7.49 – 7.46 (m, 1H), 7.45 – 7.41 (m, 1H), 7.38 (dt, $J = 8.1, 0.9$ Hz, 1H), 7.34 (s, 1H), 7.32 – 7.29 (m, 1H), 7.25 – 7.23 (m, 1H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 137.66, 134.11, 133.24, 131.98, 128.30, 127.80, 127.76, 127.08, 126.51, 126.33, 126.18, 125.18, 124.97, 122.18, 120.13, 120.10, 116.67, 109.70, 32.99.

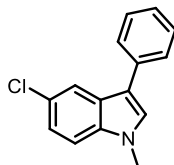


3-(6-methoxypyridin-3-yl)-1-methyl-1H-indole (3w) as a yellow oil (5.7 mg, 27% yield). **L24** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 10: 1). ^1H NMR (500 MHz, CDCl_3) δ 8.44 (dd, $J = 2.5, 0.8$ Hz, 1H), 7.86 – 7.82 (m, 2H), 7.38 (dt, $J = 8.2, 0.9$ Hz, 1H), 7.31 – 7.28 (m, 1H), 7.21 – 7.18 (m, 1H), 7.18 (s, 1H), 6.84 (dd, $J = 8.5, 0.8$ Hz, 1H), 3.99 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.57, 144.88, 138.01, 137.39, 126.17, 124.81, 122.21, 120.06, 119.54, 113.09, 110.87, 109.68, 53.53, 33.00; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}$: 239.1179, found: 239.1177.



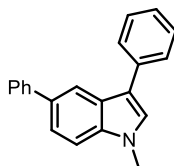
3x

3-(benzofuran-5-yl)-1-methyl-1H-indole (3x) as a yellow solid (9.5 mg, 36% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, $J = 8.0$ Hz, 1H), 7.84 (t, $J = 1.2$ Hz, 1H), 7.64 (d, $J = 2.2$ Hz, 1H), 7.58 – 7.55 (m, 2H), 7.37 (d, $J = 8.2$ Hz, 1H), 7.30 – 7.27 (m, 1H), 7.22 – 7.17 (m, 2H), 6.80 (d, $J = 2.1$ Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.75, 145.32, 137.41, 130.48, 128.00, 126.44, 126.42, 124.48, 122.00, 119.87, 119.84, 119.68, 117.03, 111.58, 109.57, 106.76, 32.92; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{14}\text{NO}$: 248.1070, found: 248.1063.



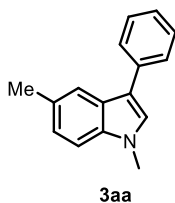
3y

5-chloro-1-methyl-3-phenyl-1H-indole (3y)⁸ as a yellow oil (13.0 mg, 54% yield). Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, $J = 2.0$ Hz, 1H), 7.62 – 7.57 (m, 2H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.30 – 7.25 (m, 2H), 7.24 – 7.19 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.94, 135.03, 129.00, 127.83, 127.39, 127.19, 126.17, 125.94, 122.37, 119.47, 116.55, 110.71, 33.23.

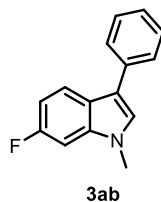


3z

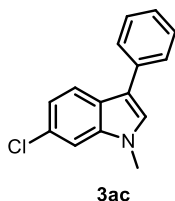
1-methyl-3,5-diphenyl-1H-indole (3z) as a yellow solid (17.8 mg, 63% yield). **L23** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ^1H NMR (500 MHz, CDCl_3) δ 8.13 (d, $J = 1.7$ Hz, 1H), 7.67 (td, $J = 8.4, 1.3$ Hz, 4H), 7.52 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.47 – 7.39 (m, 5H), 7.33 – 7.26 (m, 2H), 7.24 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.75, 137.10, 135.64, 133.69, 128.95, 128.78, 127.63, 127.56, 127.32, 126.73, 126.51, 125.95, 122.01, 118.64, 117.27, 109.93, 33.13; HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{18}\text{N}$: 284.1434, found: 284.1426.



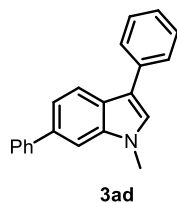
1,5-dimethyl-3-phenyl-1H-indole (3aa)⁵ as a yellow solid (12.2 mg, 55% yield). **L22** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (s, 1H), 7.65 – 7.63 (m, 2H), 7.44 – 7.41 (m, 2H), 7.27 – 7.23 (m, 2H), 7.18 (s, 1H), 7.10 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.80 (s, 3H), 2.48 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 135.97, 135.91, 129.24, 128.78, 127.38, 126.71, 126.40, 125.64, 123.63, 119.59, 116.20, 109.29, 32.98, 21.67.



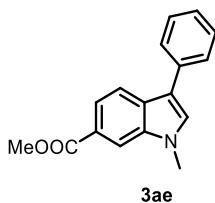
6-fluoro-1-methyl-3-phenyl-1H-indole (3ab)⁷ as a yellow solid (11.3 mg, 50% yield). **L22** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.83 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.61 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.18 (s, 1H), 7.01 (dd, *J* = 9.7, 2.3 Hz, 1H), 6.97 – 6.91 (m, 1H), 3.76 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.99 (d, *J* = 238.3 Hz), 137.56 (d, *J* = 11.8 Hz), 135.25, 128.88, 127.32, 126.75, 126.01, 122.72, 120.85 (d, *J* = 10.1 Hz), 116.97, 108.59 (d, *J* = 24.3 Hz), 95.95 (d, *J* = 26.0 Hz), 33.07; ¹⁹F NMR (470 MHz, CDCl₃) δ -120.51 – 120.57 (m).



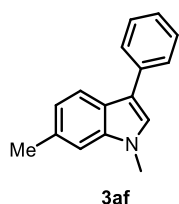
6-chloro-1-methyl-3-phenyl-1H-indole (3ac)⁷ as a yellow solid (7.7 mg, 32% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 6.9 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 1.9 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.19 (s, 1H), 7.14 (dd, *J* = 8.5, 1.9 Hz, 1H), 3.77 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.88, 135.07, 128.90, 128.01, 127.32, 127.13, 126.08, 124.72, 120.90, 120.55, 116.96, 109.63, 33.04.



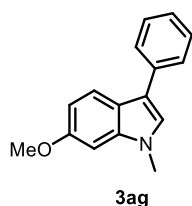
1-methyl-3,6-diphenyl-1H-indole (3ad) as a yellow solid (20.1 mg, 71% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.70 – 7.66 (m, 4H), 7.54 (d, *J* = 1.5 Hz, 1H), 7.45 (td, *J* = 8.4, 7.9, 6.8 Hz, 5H), 7.36 – 7.31 (m, 1H), 7.29 – 7.26 (m, 1H), 7.23 (d, *J* = 10.5 Hz, 1H), 3.84 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 142.35, 138.06, 135.63, 135.61, 128.86, 128.81, 127.53, 127.33, 127.26, 126.79, 125.84, 125.50, 120.25, 119.88, 116.69, 108.15, 33.00; HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₂₁H₁₈N: 284.1434, found: 284.1429.



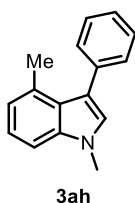
methyl 1-methyl-3-phenyl-1H-indole-6-carboxylate (3ae)⁵ as a yellow solid (9.6 mg, 36% yield). **L24** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 10: 1). ¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, *J* = 1.5 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.63 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.37 (s, 1H), 7.32 – 7.27 (m, 1H), 3.96 (s, 3H), 3.89 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.16, 136.88, 134.93, 129.78, 129.57, 128.93, 127.40, 126.18, 123.57, 120.92, 119.53, 117.17, 112.12, 52.11, 33.19.



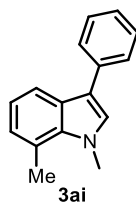
1,6-dimethyl-3-phenyl-1H-indole (3af)⁵ as a yellow oil (15.2 mg, 69% yield). **L22** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 10: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.65 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.16 (s, 1H), 7.15 (s, 1H), 7.02 (dd, *J* = 8.1, 1.5 Hz, 1H), 3.79 (s, 3H), 2.52 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 138.03, 135.97, 131.96, 128.84, 127.31, 126.09, 125.70, 124.12, 121.79, 119.75, 116.63, 109.64, 32.93, 21.97.



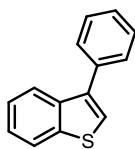
6-methoxy-1-methyl-3-phenyl-1H-indole (3ag)⁷ as a yellow solid (14.2 mg, 60% yield). **L23** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 10: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8.7 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.12 (s, 1H), 6.86 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.80 (d, *J* = 2.2 Hz, 1H), 3.90 (s, 3H), 3.77 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 156.50, 138.25, 135.74, 128.80, 127.19, 125.70, 125.41, 120.72, 120.50, 116.68, 109.77, 92.96, 55.77, 32.98.



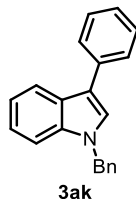
1,4-dimethyl-3-phenyl-1H-indole (3ah)⁵ as a yellow oil (12.6 mg, 57% yield). **L22** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.46 – 7.41 (m, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.17 (dd, *J* = 8.3, 6.9 Hz, 1H), 6.97 (s, 1H), 6.88 (d, *J* = 6.9 Hz, 1H), 3.80 (s, 3H), 2.29 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.03, 131.43, 130.74, 127.75, 127.61, 126.27, 125.62, 121.93, 121.22, 118.18, 107.22, 32.93, 20.89.



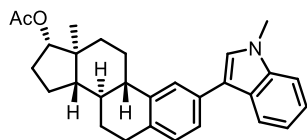
1,7-dimethyl-3-phenyl-1H-indole (3ai)⁵ as a white solid (8.4 mg, 38% yield). **L22** was used instead of **L18**. Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.09 (s, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 4.10 (s, 3H), 2.80 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 136.11, 135.66, 128.76, 128.41, 127.64, 127.28, 125.77, 124.68, 121.60, 120.16, 118.00, 116.52, 37.03, 19.94.



3-phenylbenzo[b]thiophene (3aj)⁵ as a yellow oil (9.2 mg, 44% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 7.95 – 7.88 (m, 2H), 7.61 – 7.56 (m, 2H), 7.51 – 7.45 (m, 2H), 7.42 – 7.35 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 140.75, 138.16, 137.95, 136.07, 128.81, 128.79, 127.63, 124.49, 124.41, 123.49, 123.00.

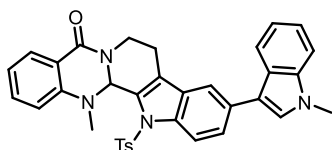


1-benzyl-3-phenyl-1H-indole (3ak)⁵ as a white solid (15.0 mg, 53% yield). Purification condition (hexane: ethyl acetate = 20: 1). ¹H NMR (500 MHz, CDCl₃) δ 8.00 – 7.95 (m, 1H), 7.70 – 7.64 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.23 (m, 7H), 7.21 – 7.15 (m, 3H), 5.35 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 137.24, 137.11, 135.56, 128.89, 128.83, 127.78, 127.41, 126.94, 126.43, 126.01, 125.89, 122.21, 120.18, 120.10, 117.36, 110.09, 50.17.



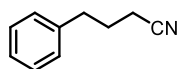
(8*R*,9*S*,13*S*,14*S*,17*S*)-13-methyl-2-(1-methyl-1*H*-indol-3-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl acetate (3al) as a white solid (27.0 mg, 63% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.61 (s, 1H), 7.43 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.29 (dd, *J* = 8.2, 6.9 Hz, 1H), 7.21 (s, 1H), 7.21 – 7.16 (m, 2H), 4.73 (t, *J* = 8.4 Hz, 1H), 3.84 (s, 3H), 2.97 – 2.90 (m, 2H), 2.43 (dt, *J* = 12.8, 3.6 Hz, 1H), 2.36 (td, *J* = 10.8, 3.9 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.08 (s, 3H), 1.97 – 1.92 (m, 2H), 1.82 – 1.76 (m, 1H), 1.61 – 1.31 (m, 7H), 0.88 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.38, 140.59, 137.52, 134.32, 133.04, 129.56, 126.38, 124.96, 124.59, 121.97, 120.09, 119.85, 117.16, 109.59, 82.88, 50.08, 44.55,

43.02, 38.53, 37.08, 32.97, 29.41, 27.72, 27.42, 26.20, 23.43, 21.35, 12.21; HRMS (EI) m/z: [M]⁺ calcd for C₂₉H₃₃NO₂: 427.2506, found: 427.2511.



3am

14-methyl-10-(1-methyl-1*H*-indol-3-yl)-13-tosyl-8,13,13b,14-tetrahydroindolo[2',3':3,4]pyrido[2,1-*b*]quinazolin-5(7*H*)-one (3am) as a white solid (35.7 mg, 61% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.35 (d, *J* = 8.6 Hz, 1H), 8.12 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 1.6 Hz, 1H), 7.74 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.49 (td, *J* = 7.6, 1.6 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.25 (m, 4H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.35 (s, 1H), 4.88 (dd, *J* = 12.7, 4.3 Hz, 1H), 3.84 (s, 3H), 3.12 (td, *J* = 12.2, 3.6 Hz, 1H), 3.00 – 2.94 (m, 1H), 2.83 – 2.76 (m, 1H), 2.39 (s, 3H), 2.20 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 164.57, 150.80, 145.13, 137.54, 135.91, 135.83, 133.21, 131.89, 129.60, 129.25, 129.09, 128.75, 127.16, 126.75, 126.19, 126.02, 124.06, 123.12, 122.99, 122.21, 120.58, 120.11, 119.68, 117.38, 116.25, 115.59, 109.77, 67.90, 38.42, 35.41, 33.01, 21.74, 20.98; HRMS (EI) m/z: [M]⁺ calcd for C₃₅H₃₀N₄O₃S: 586.2033, found: 586.2029.



4

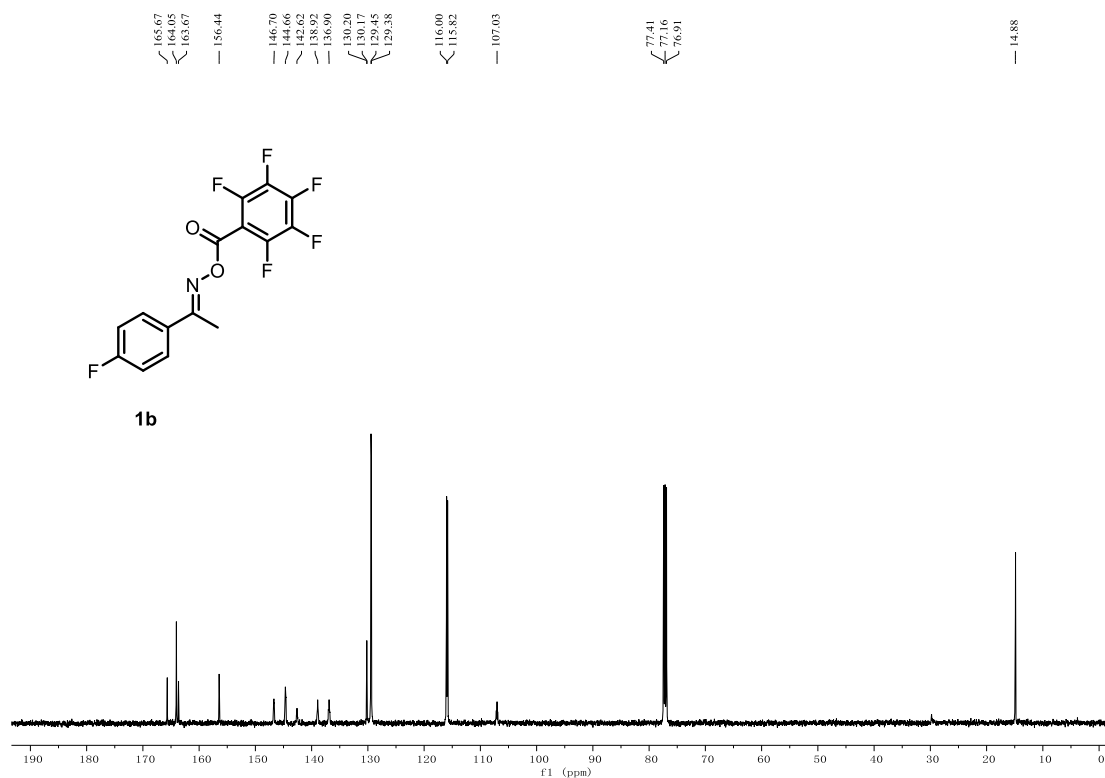
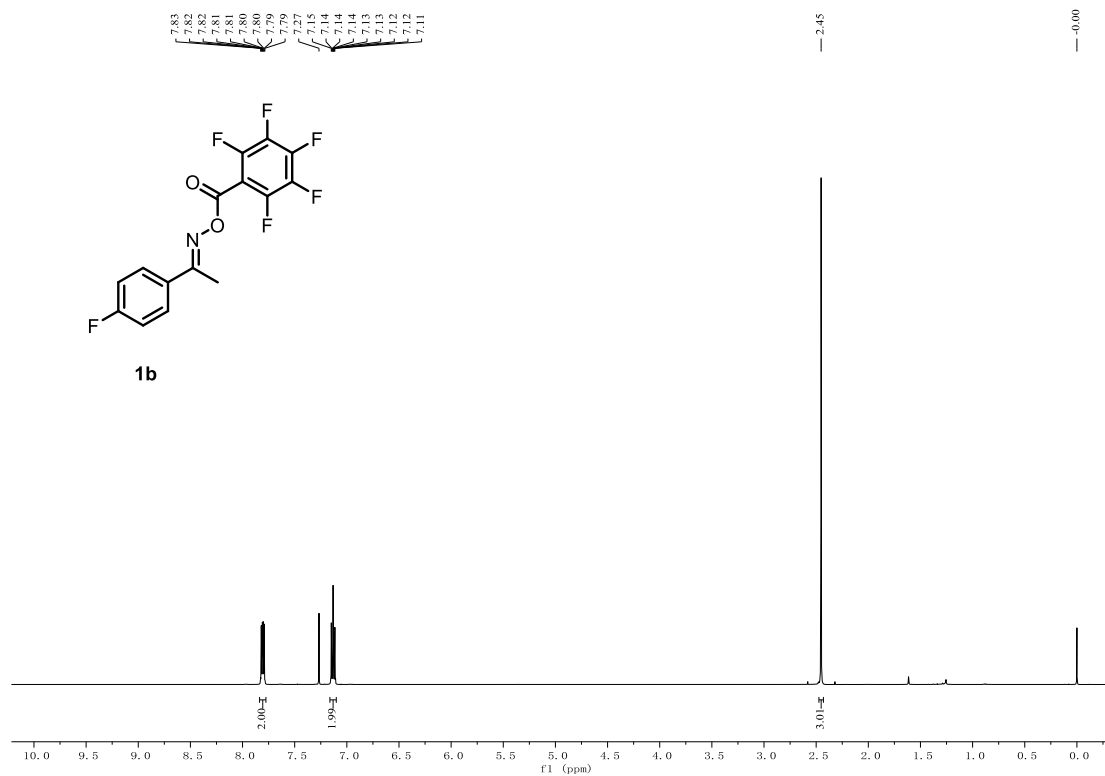
4-phenylbutanenitrile (4) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.32 (t, *J* = 7.1 Hz, 2H), 2.02 – 1.96 (m, 2H).

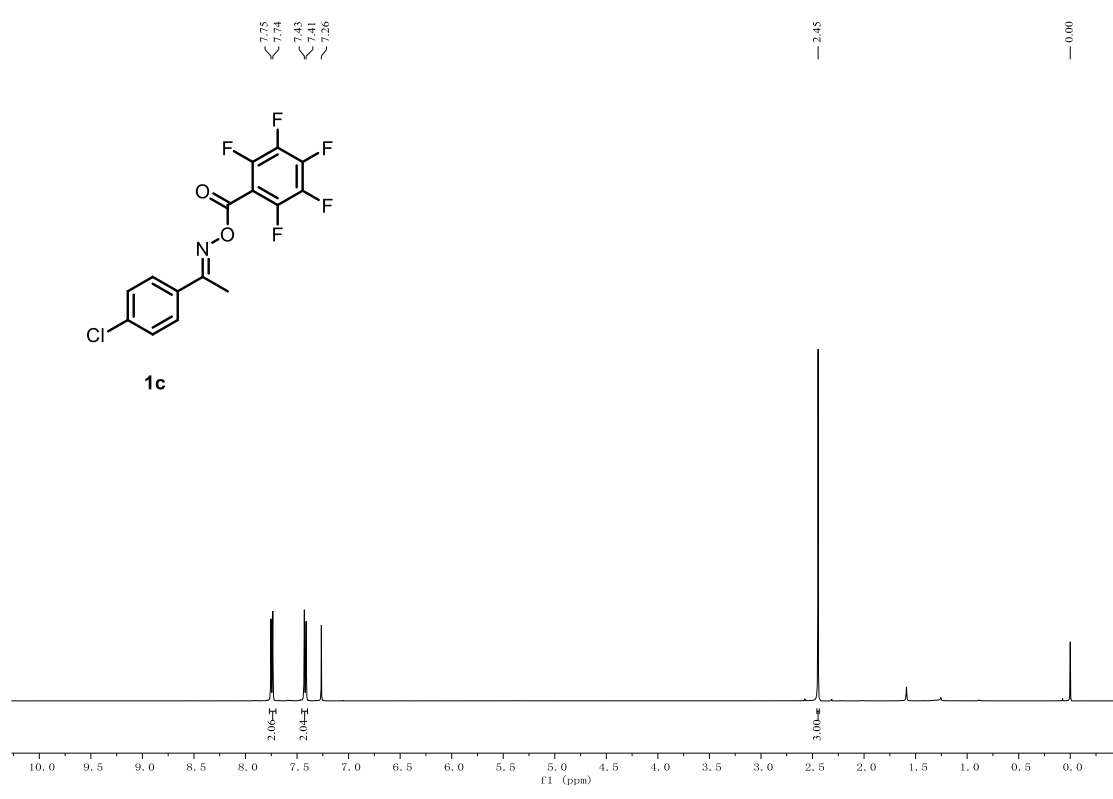
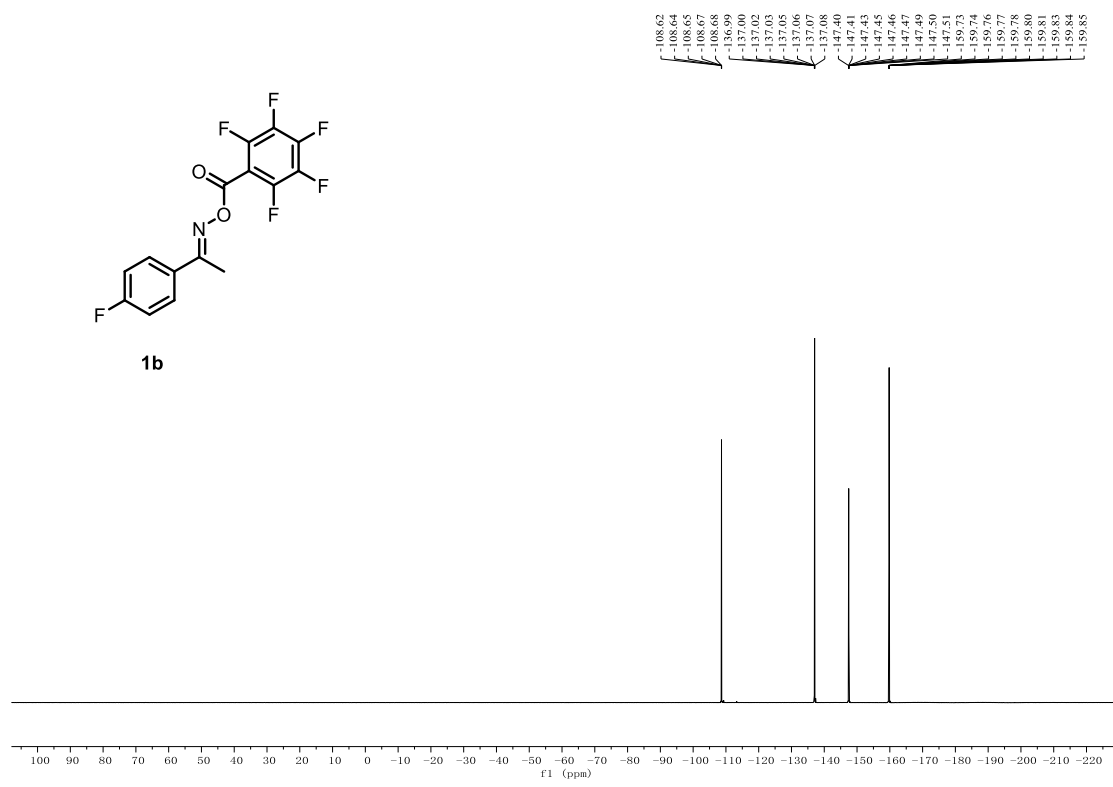
6. References

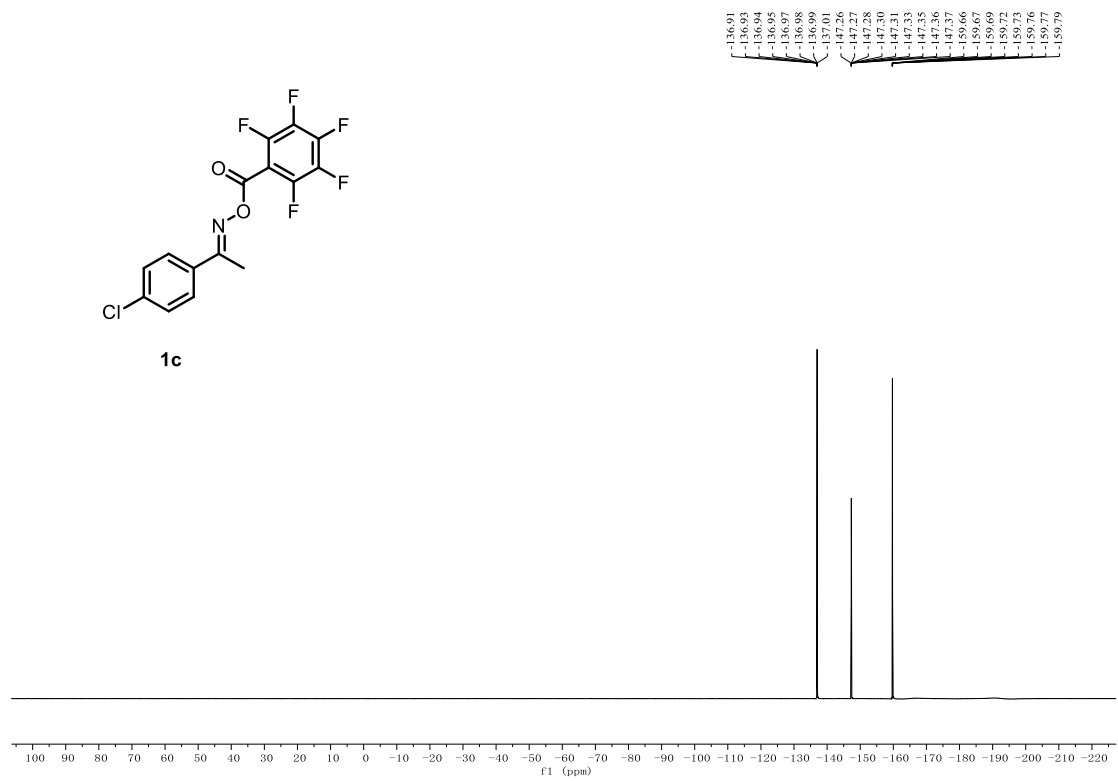
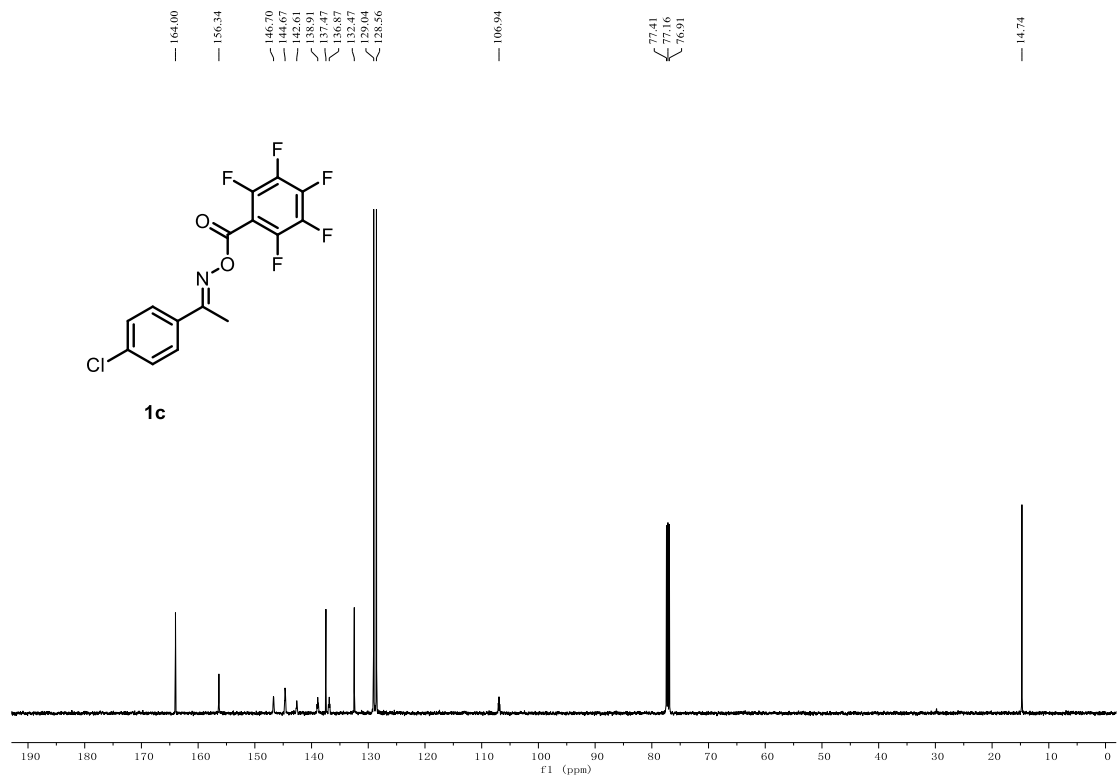
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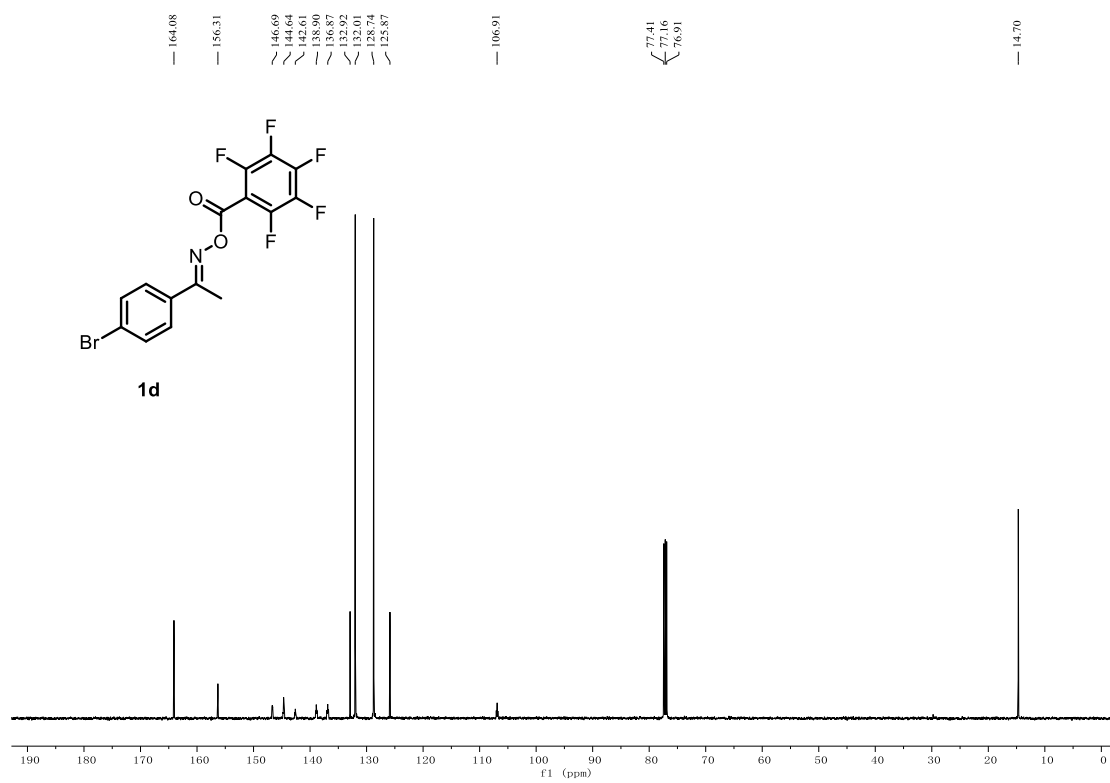
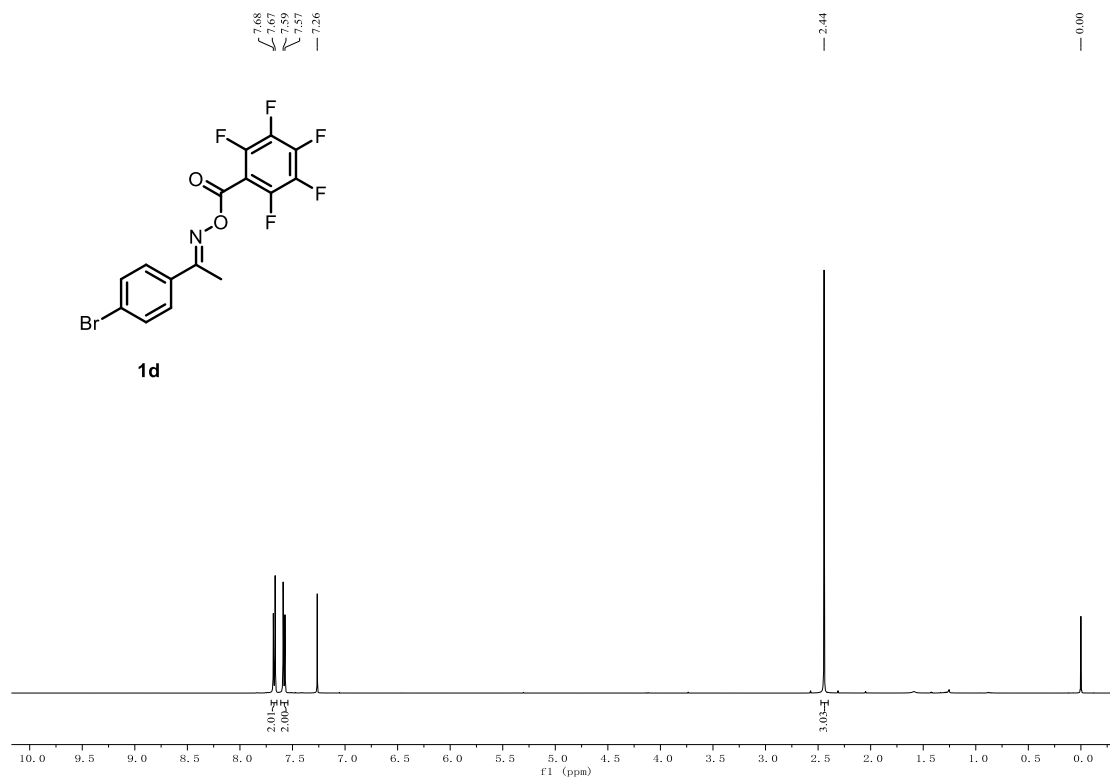
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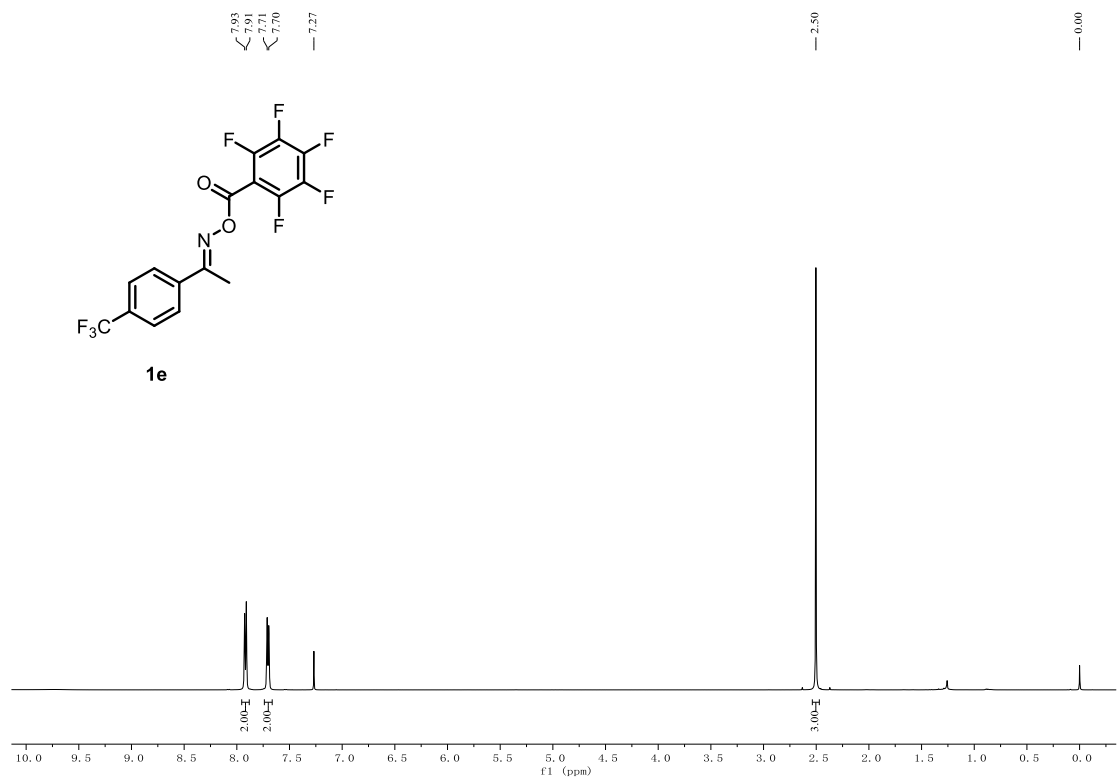
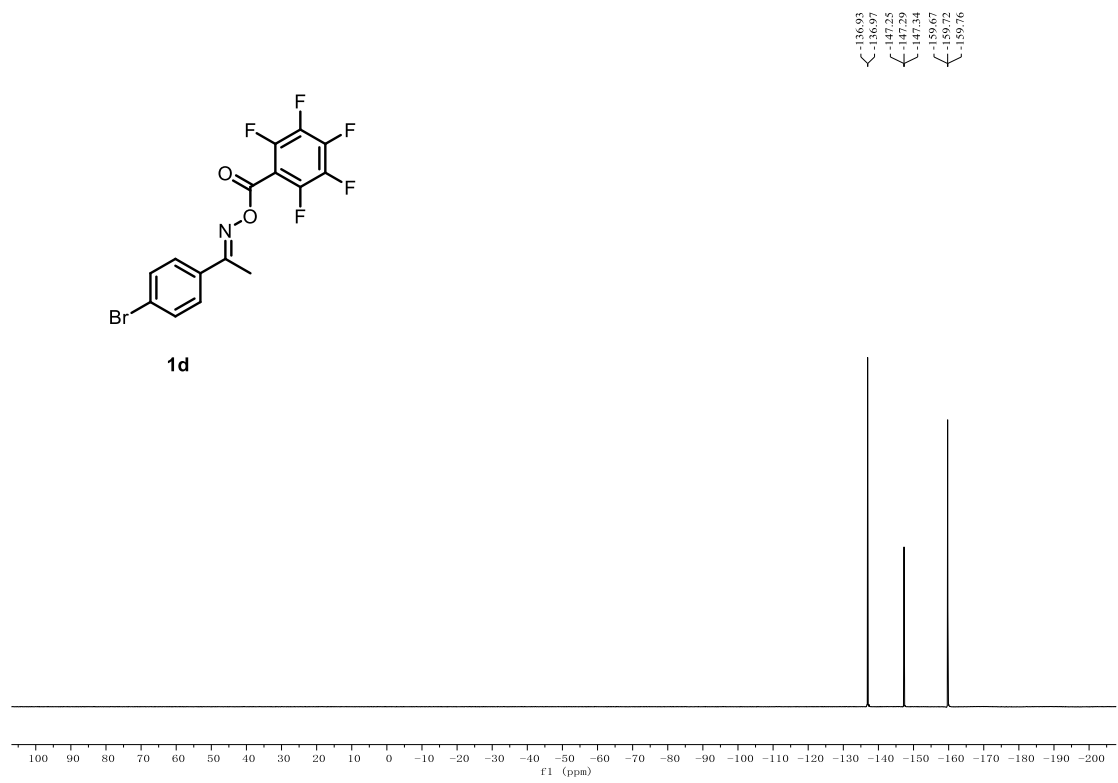
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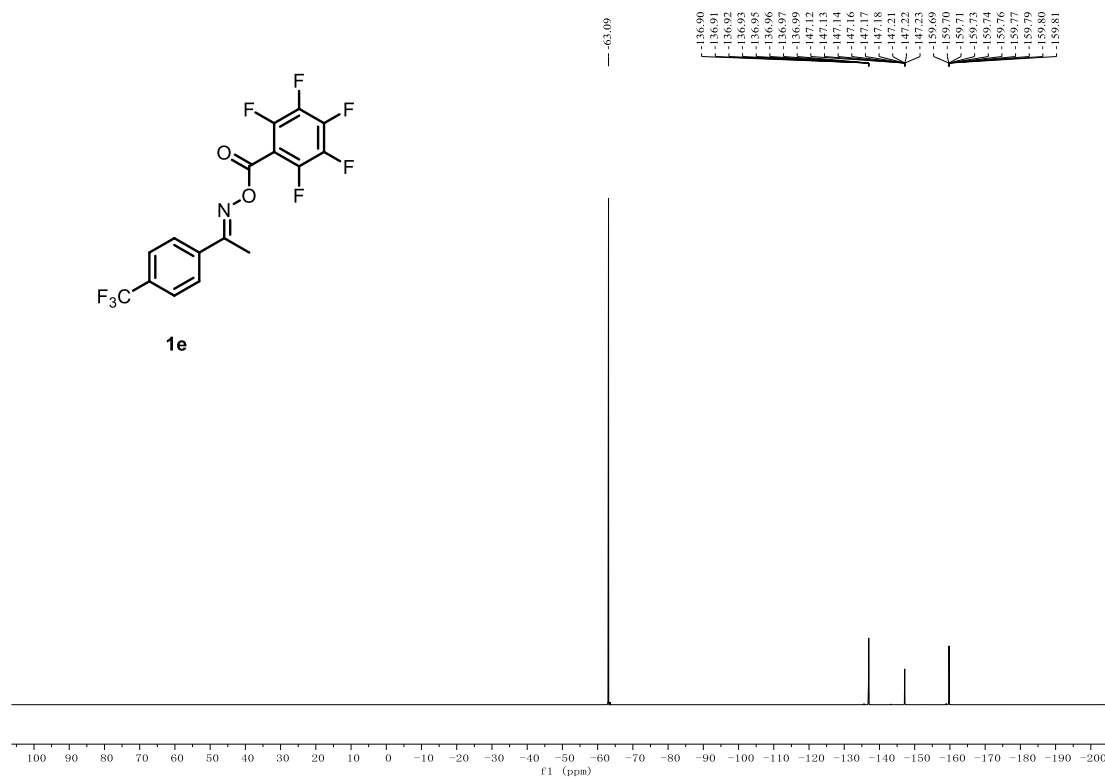
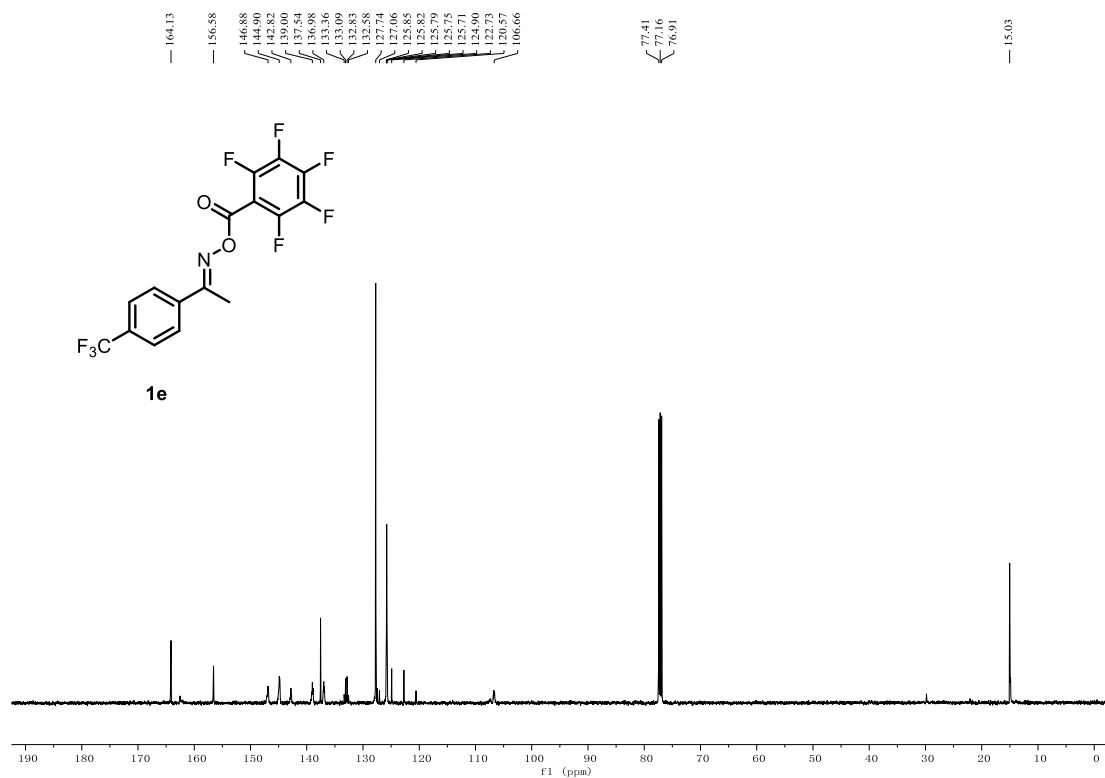


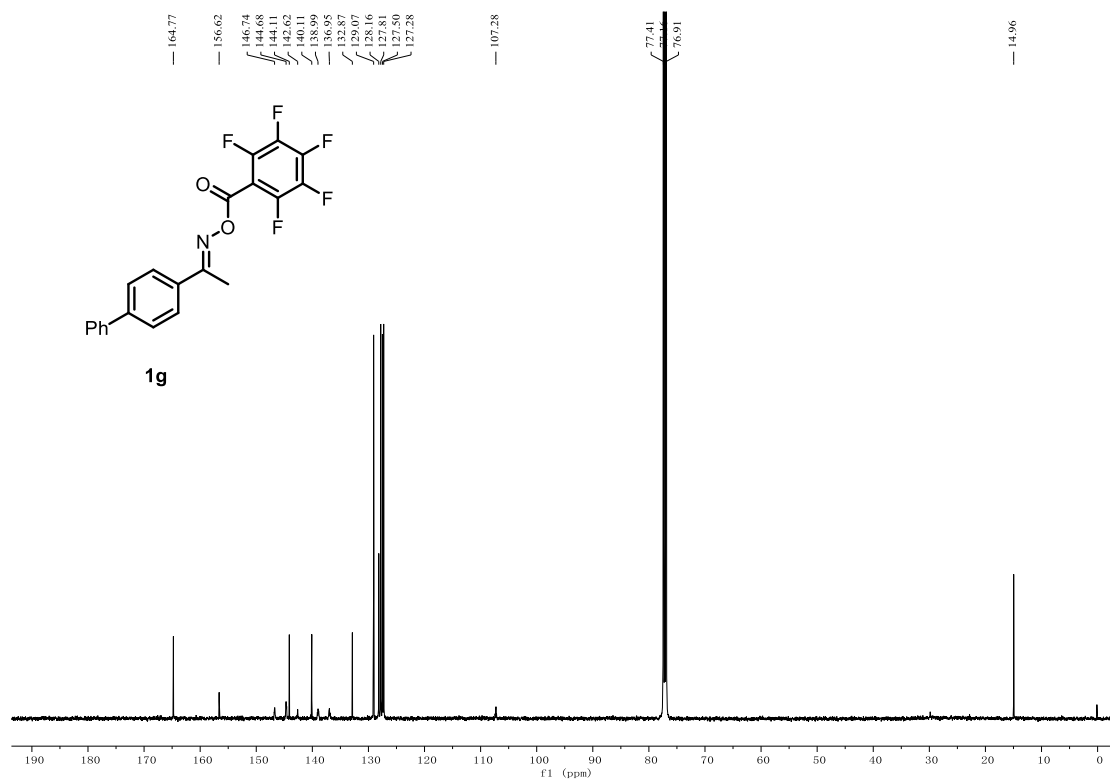
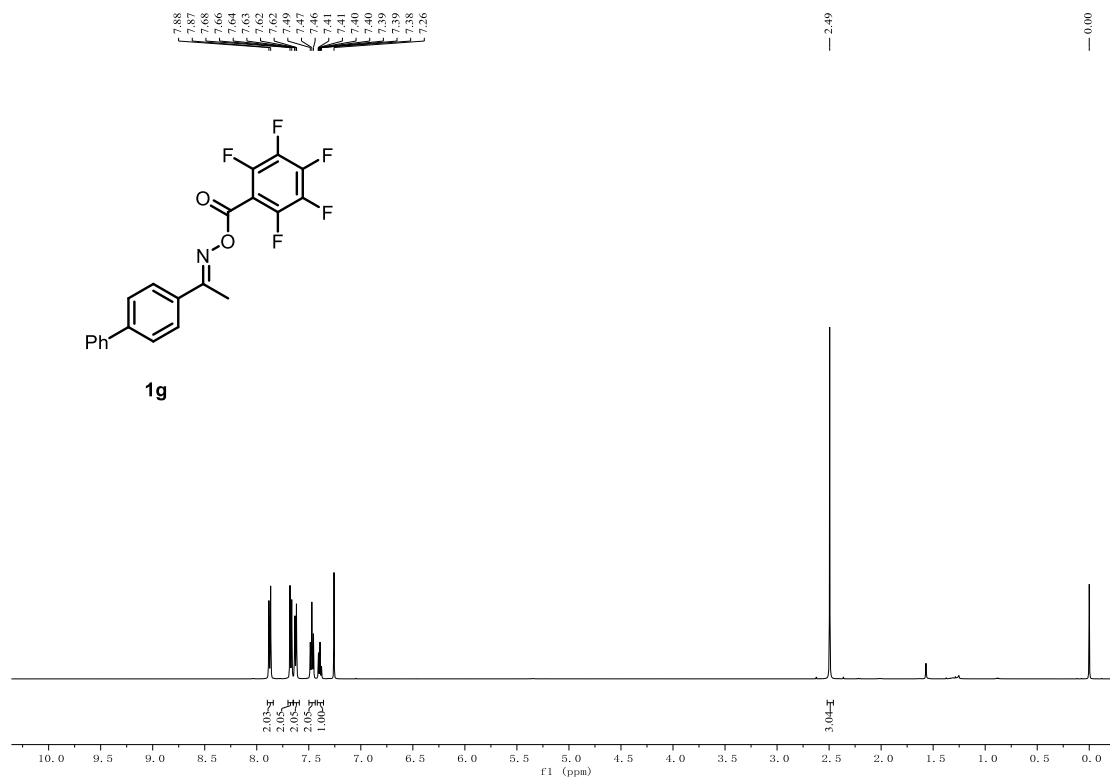


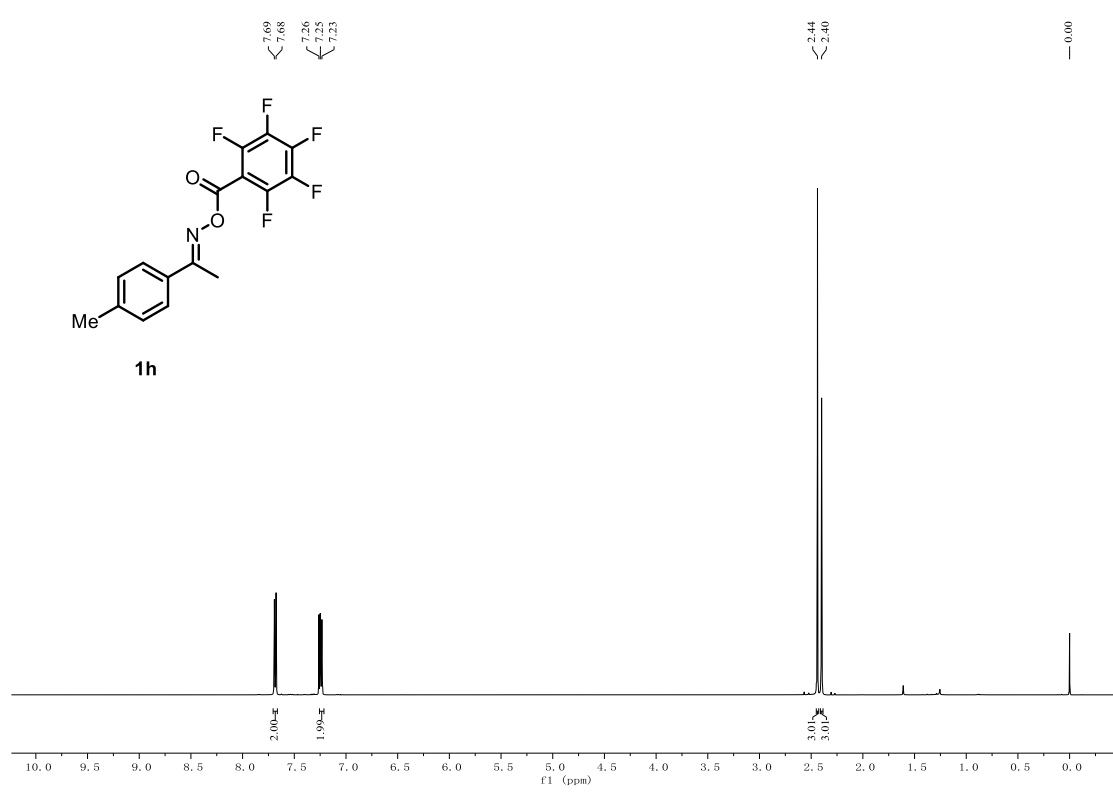
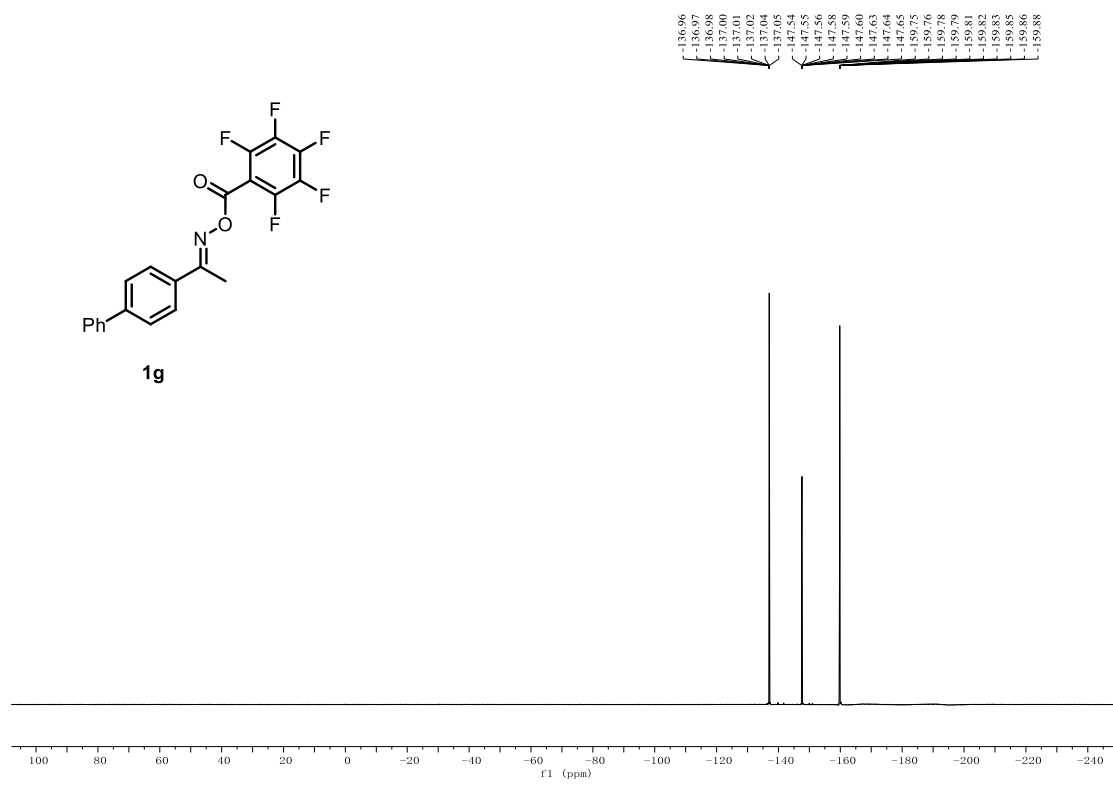


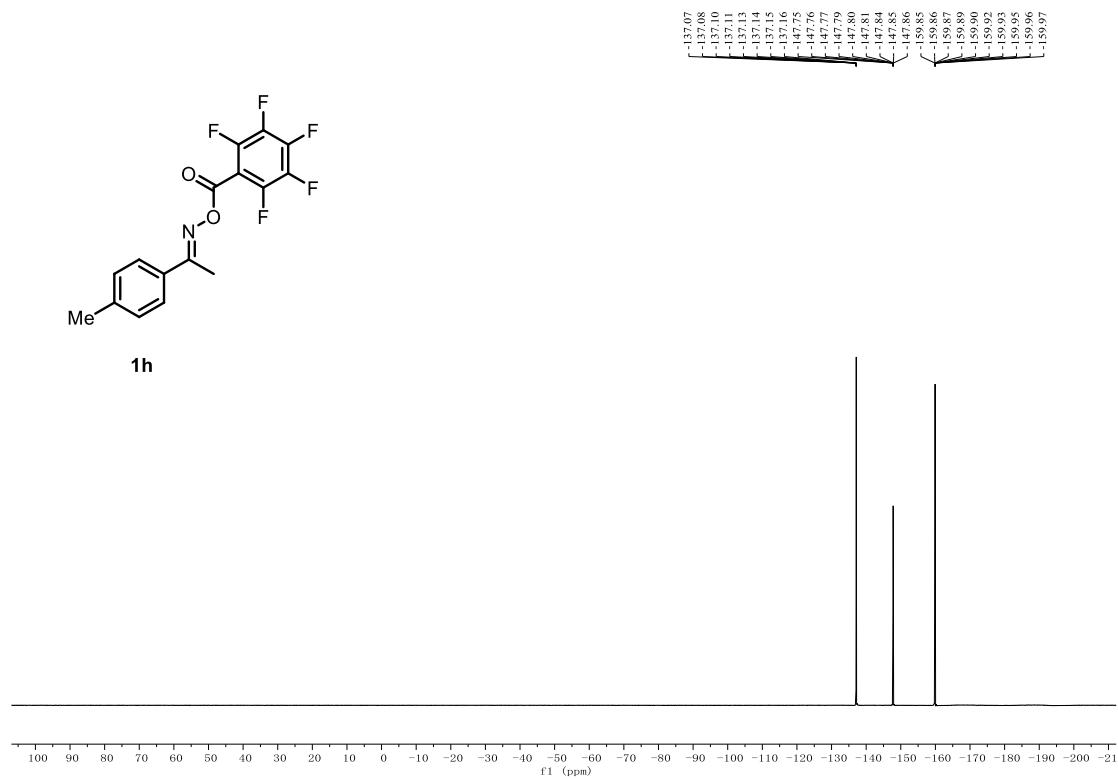
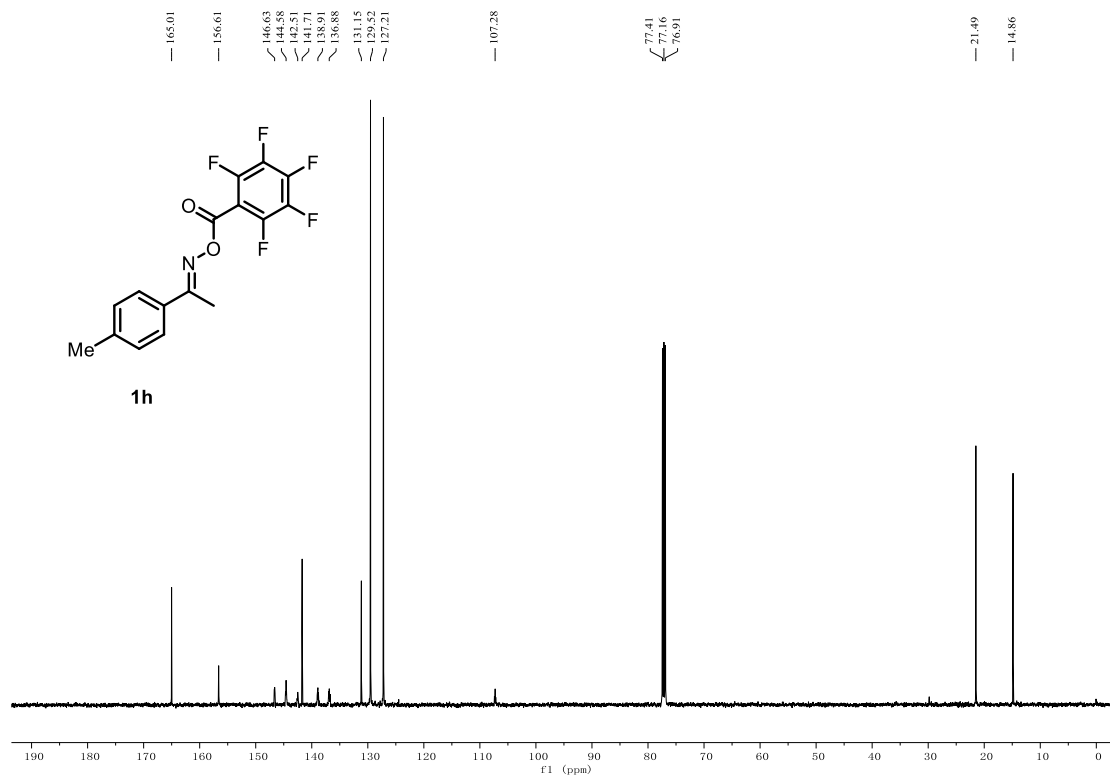


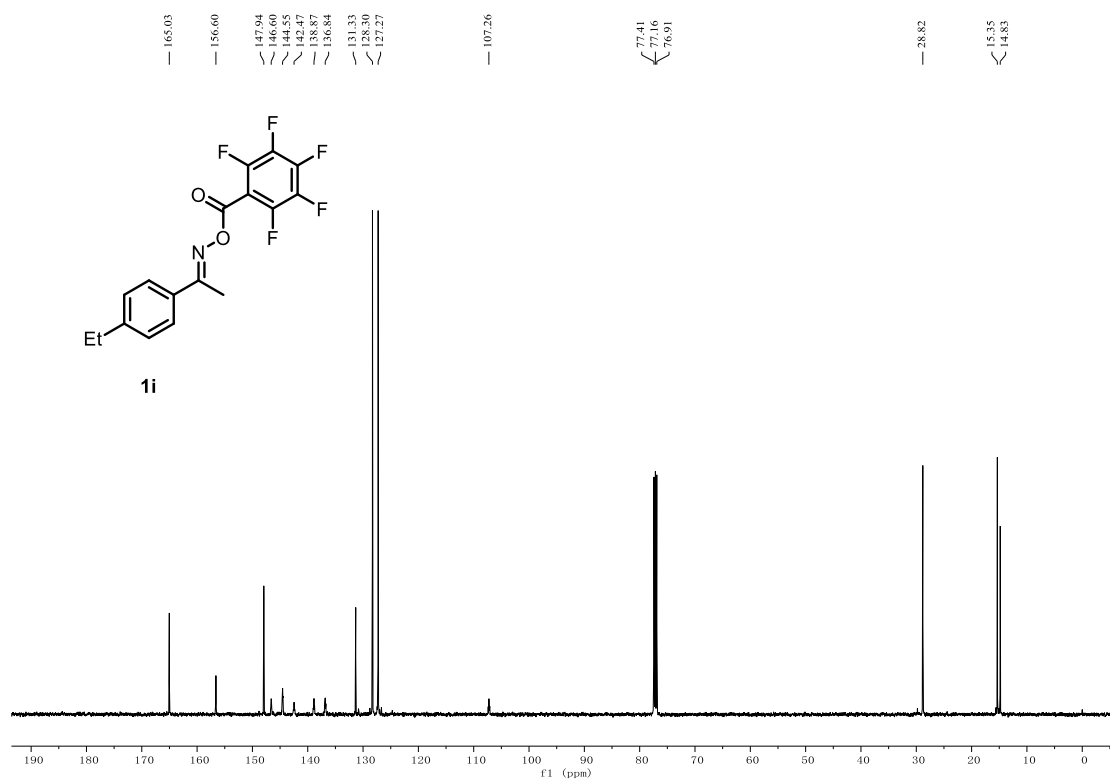
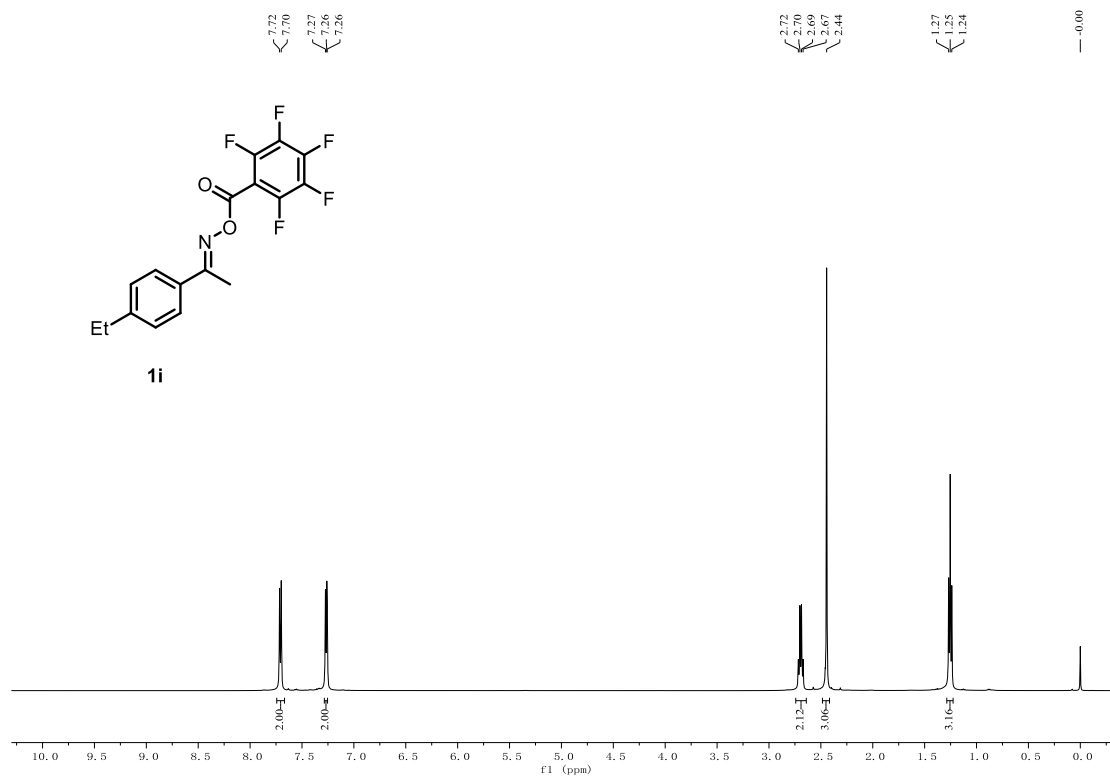


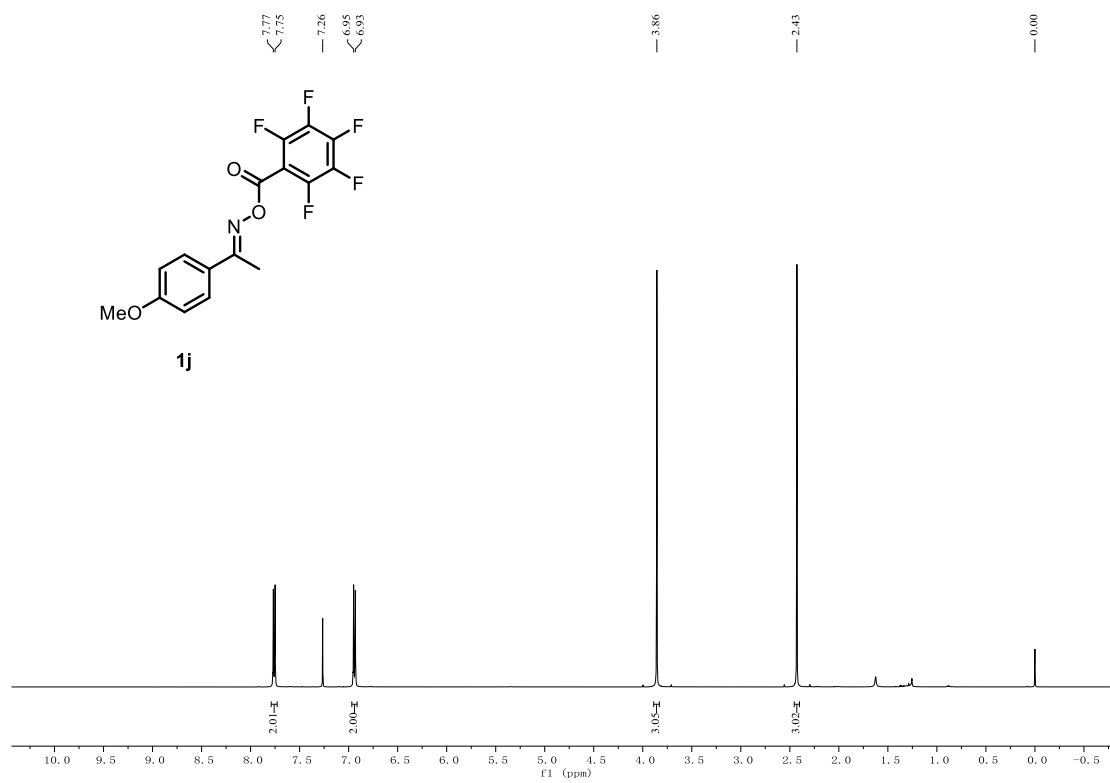
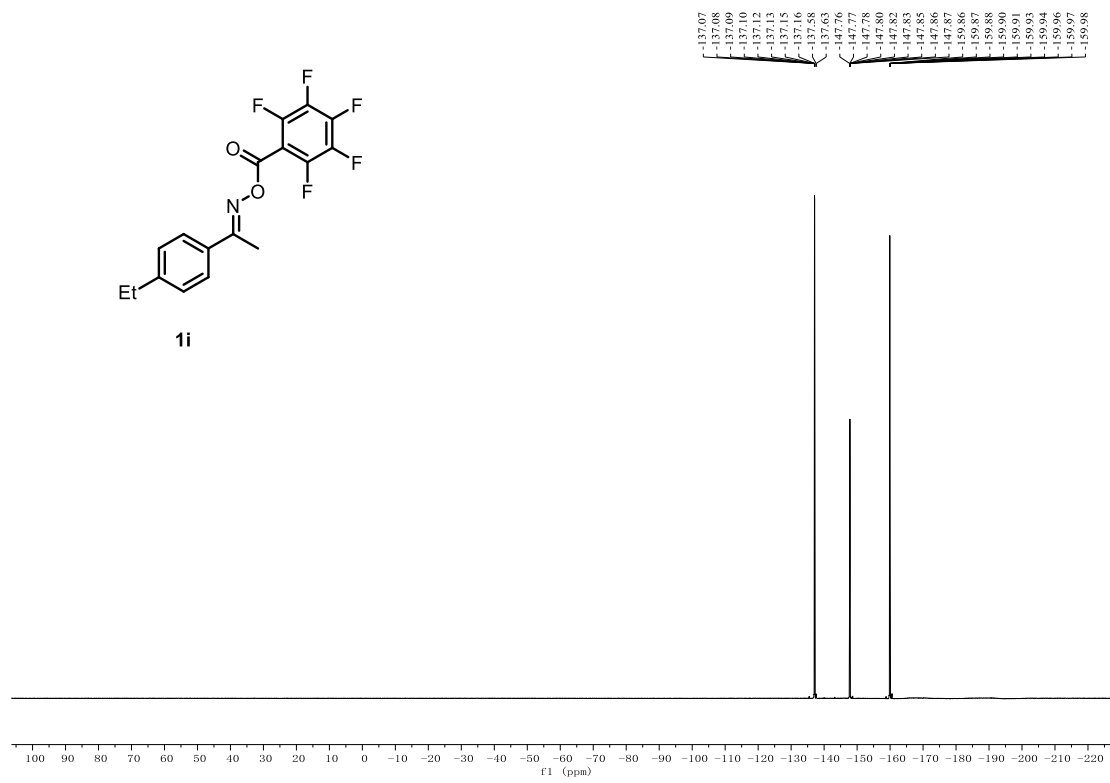


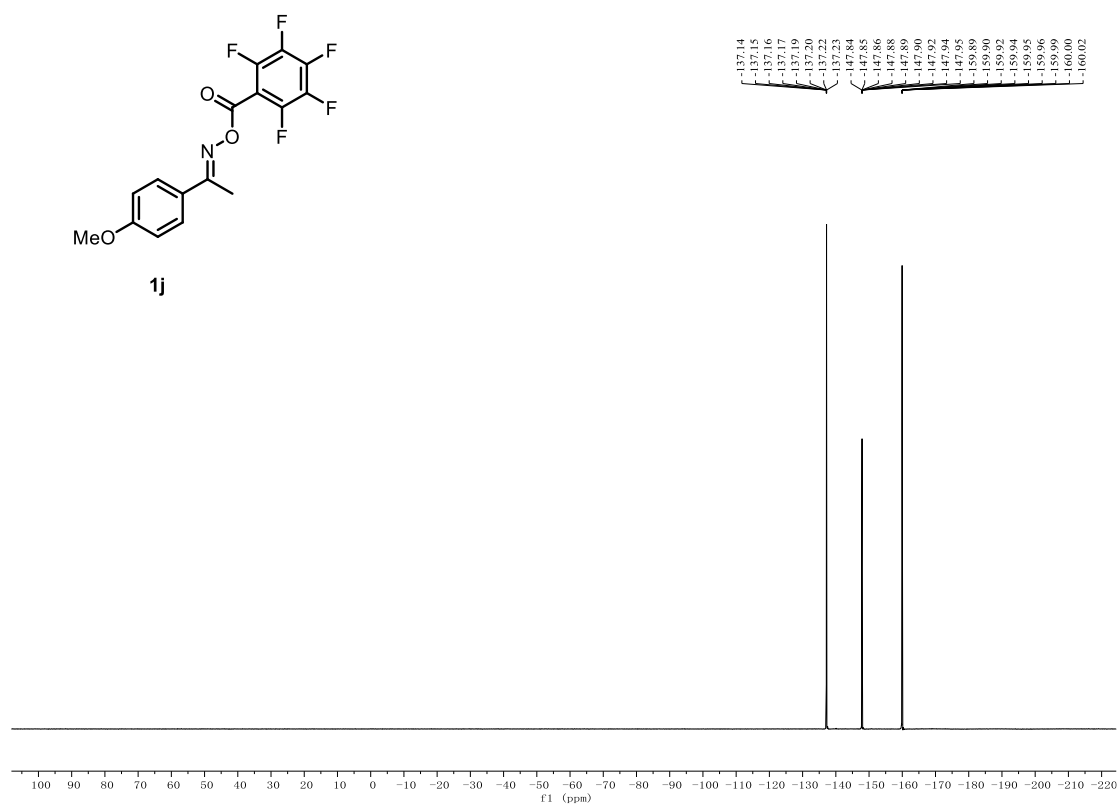
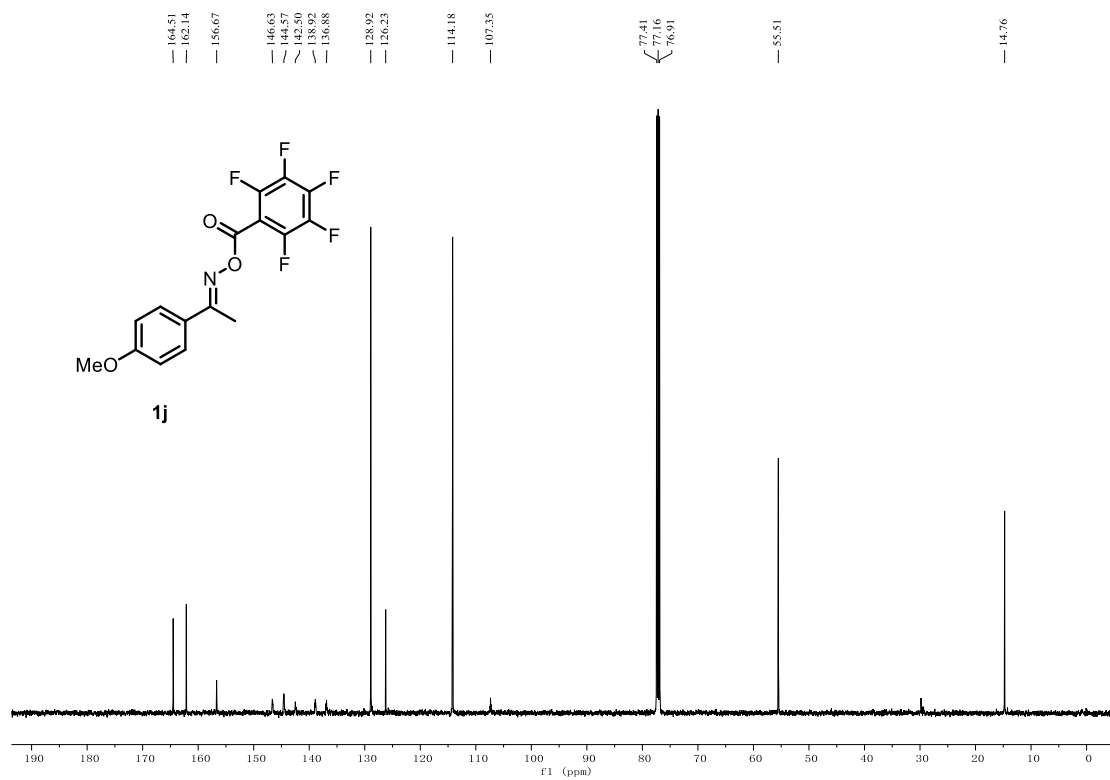


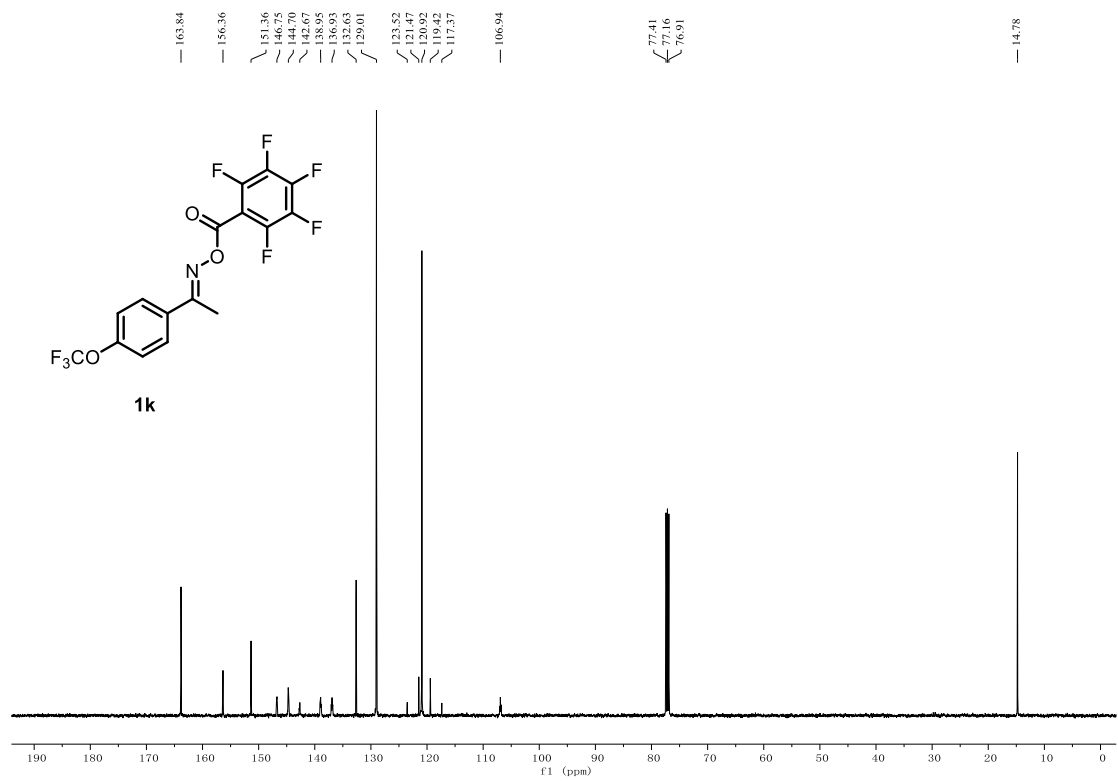
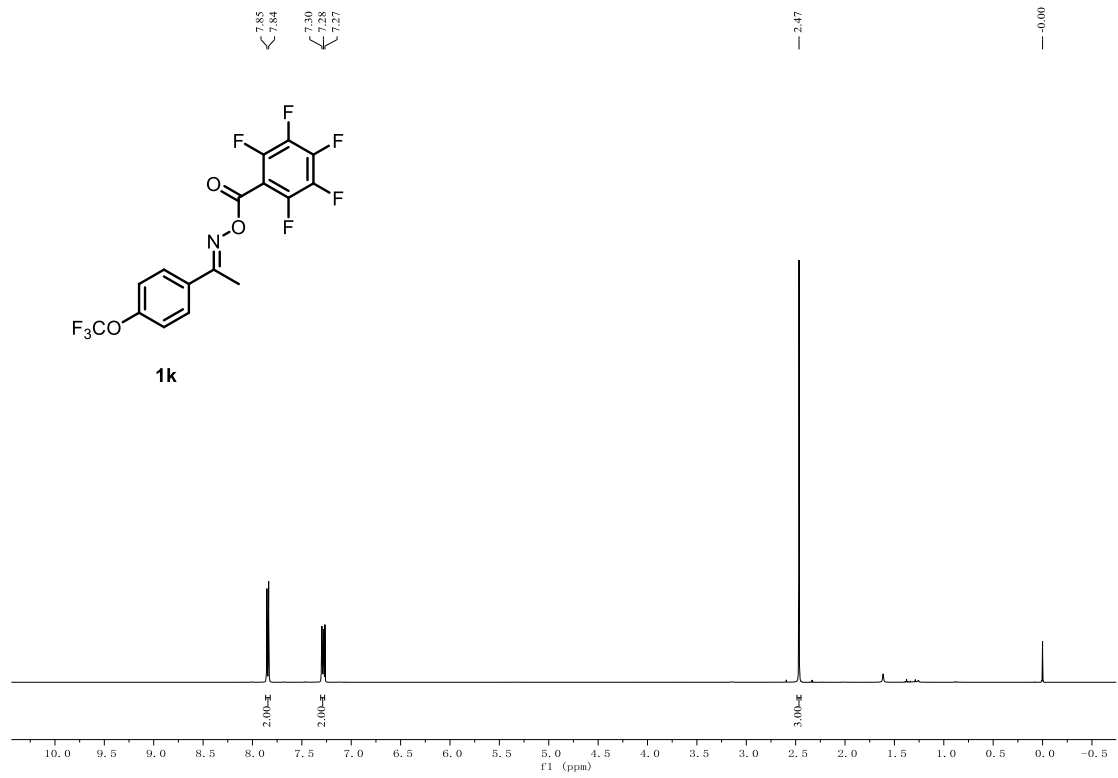


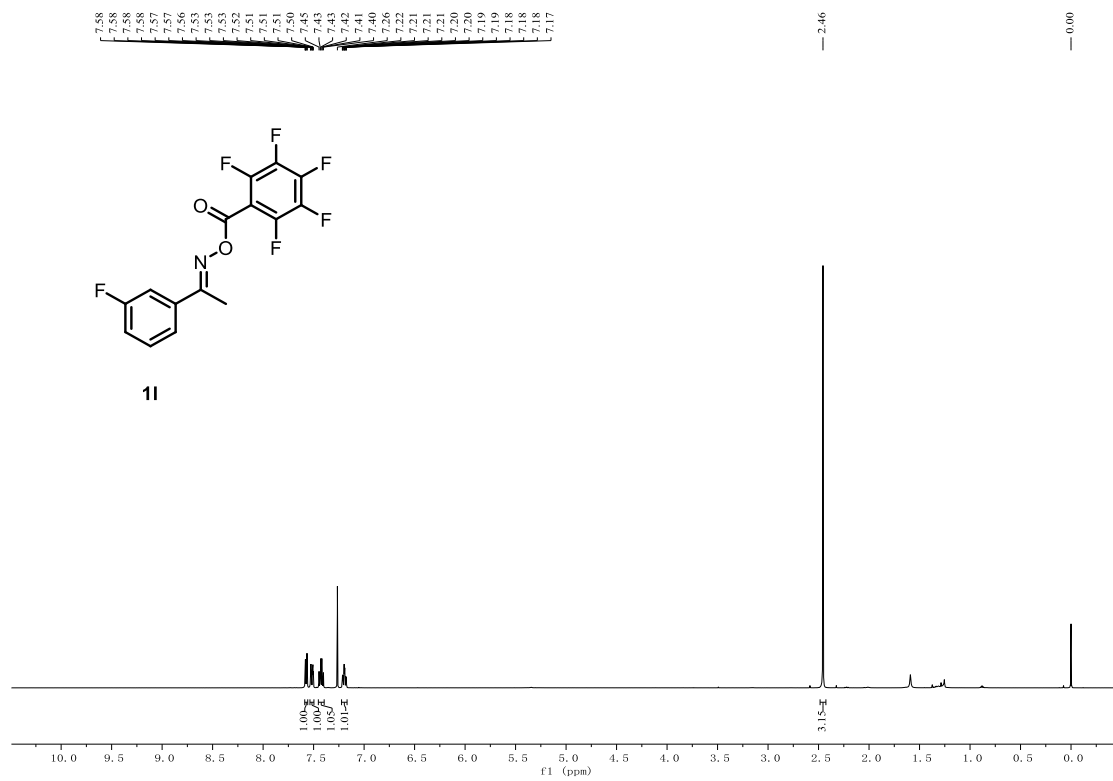
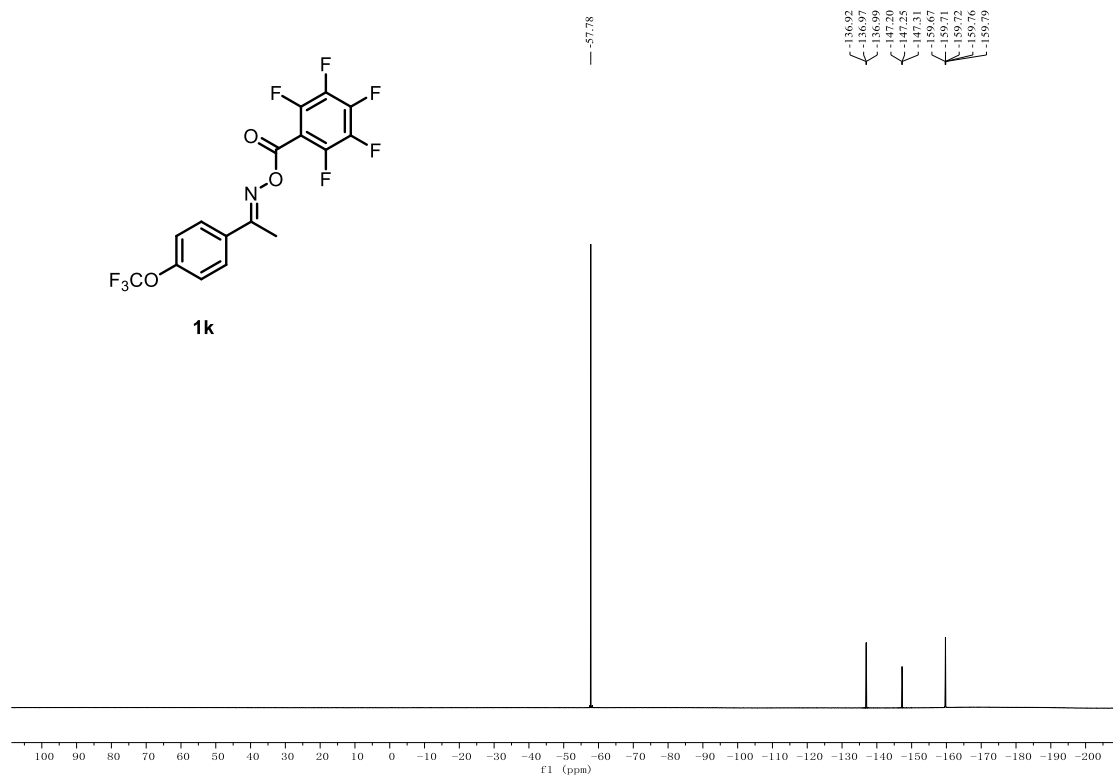


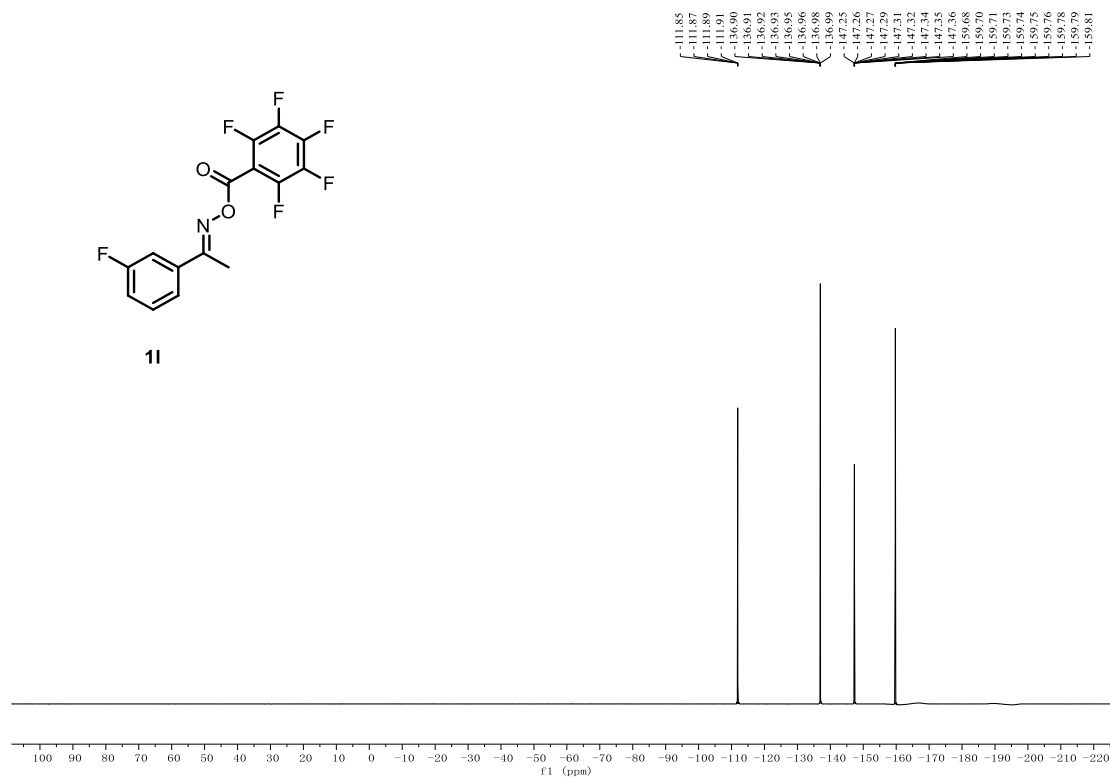
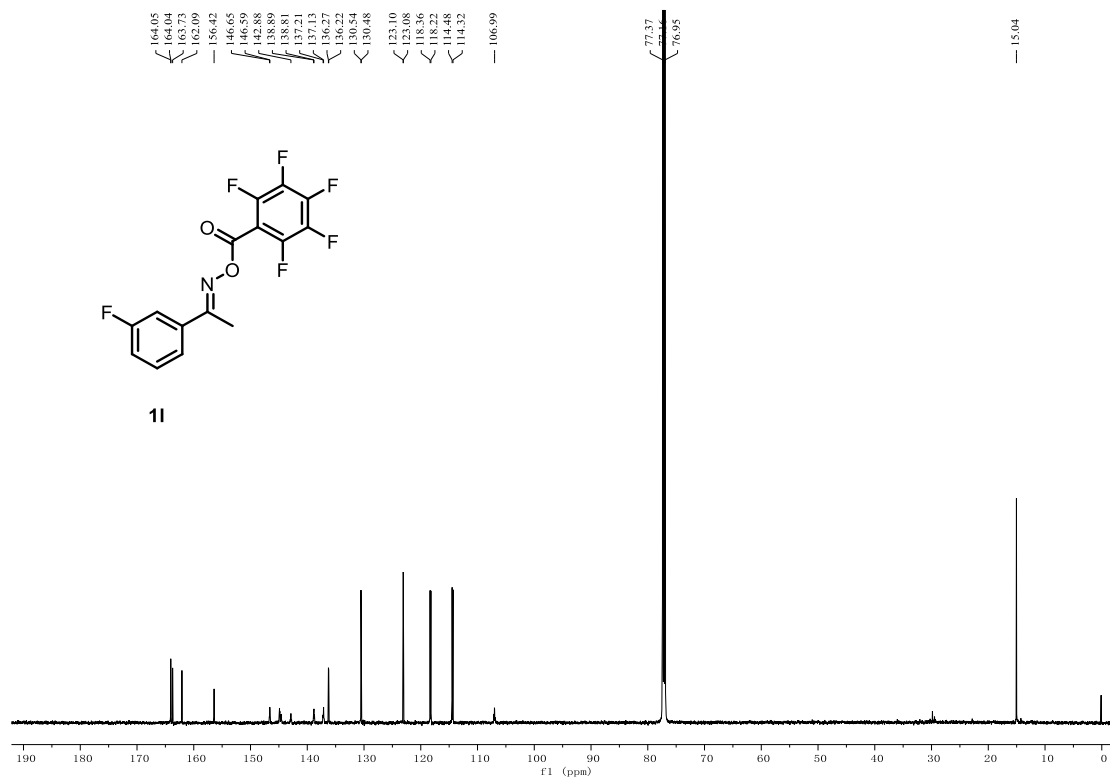


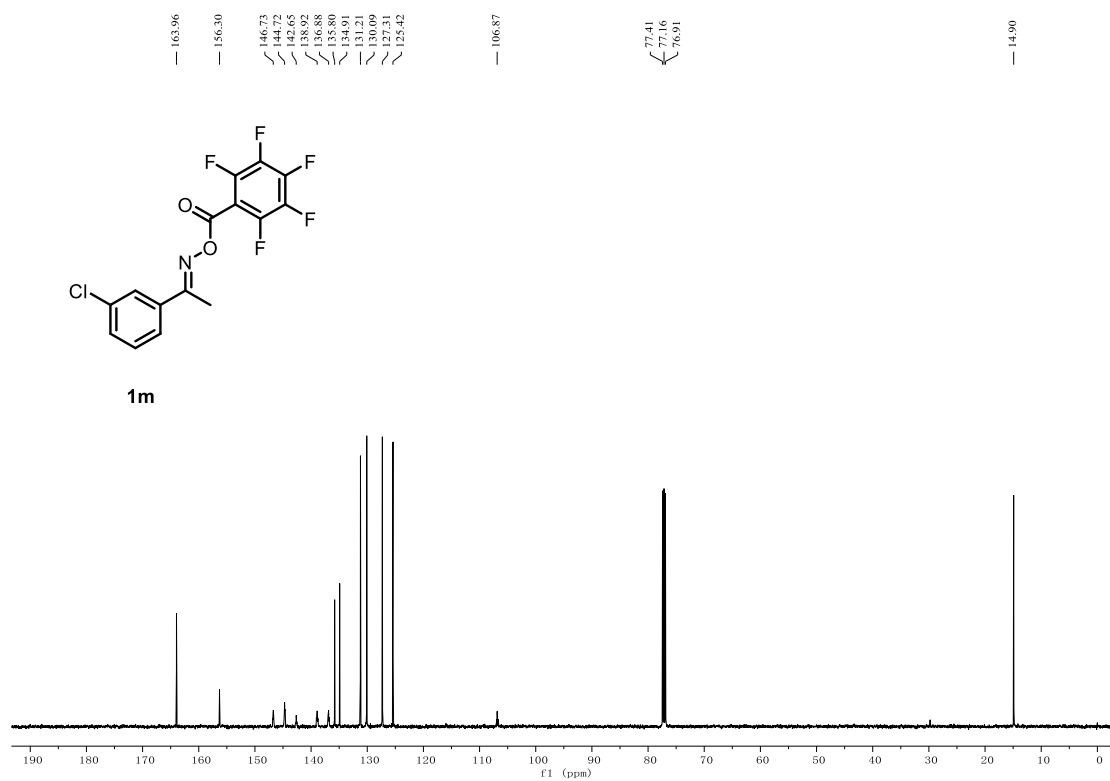
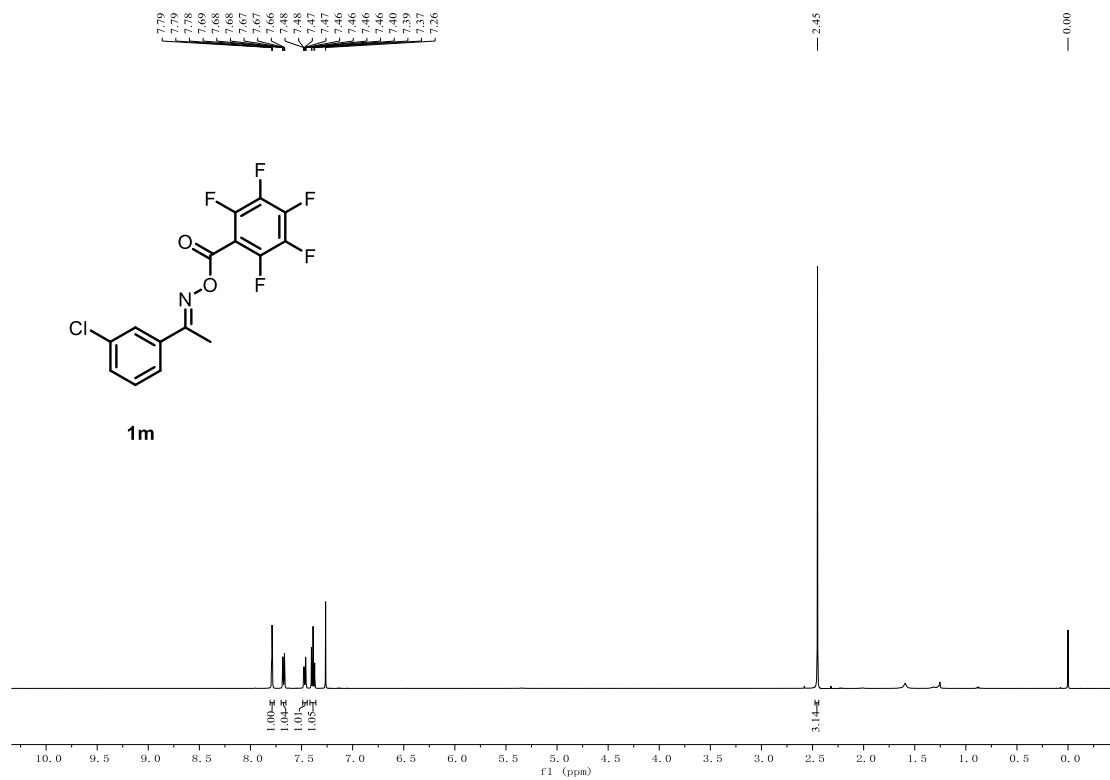


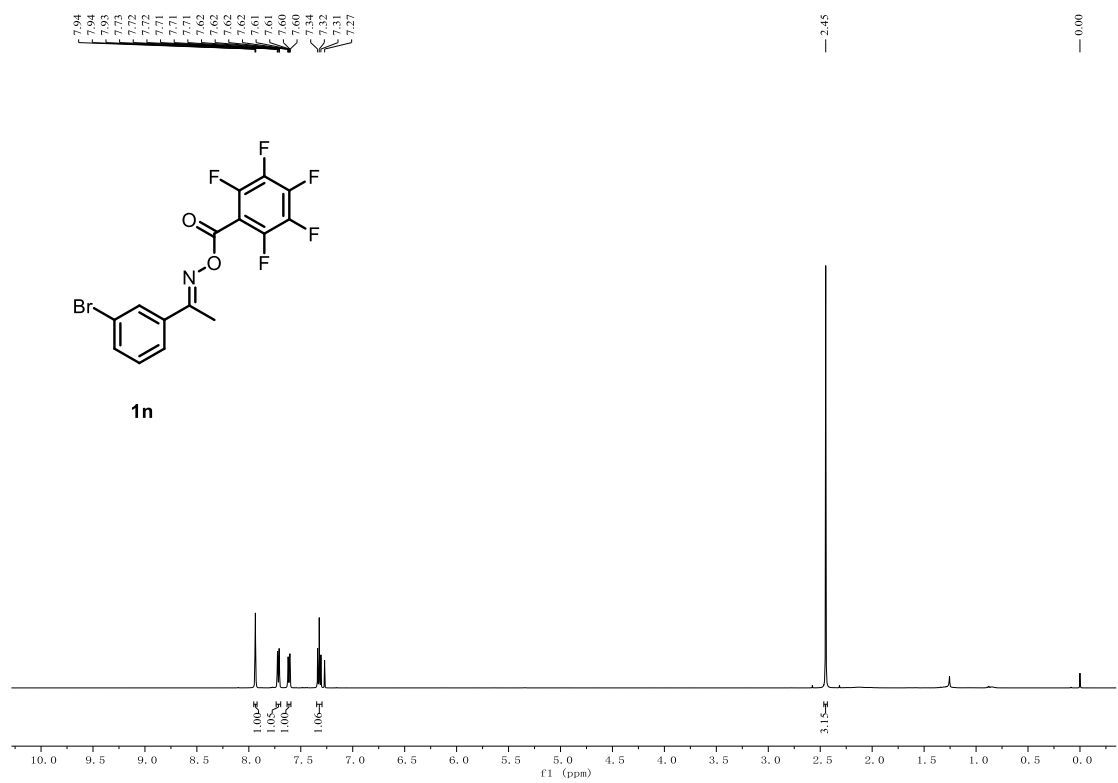
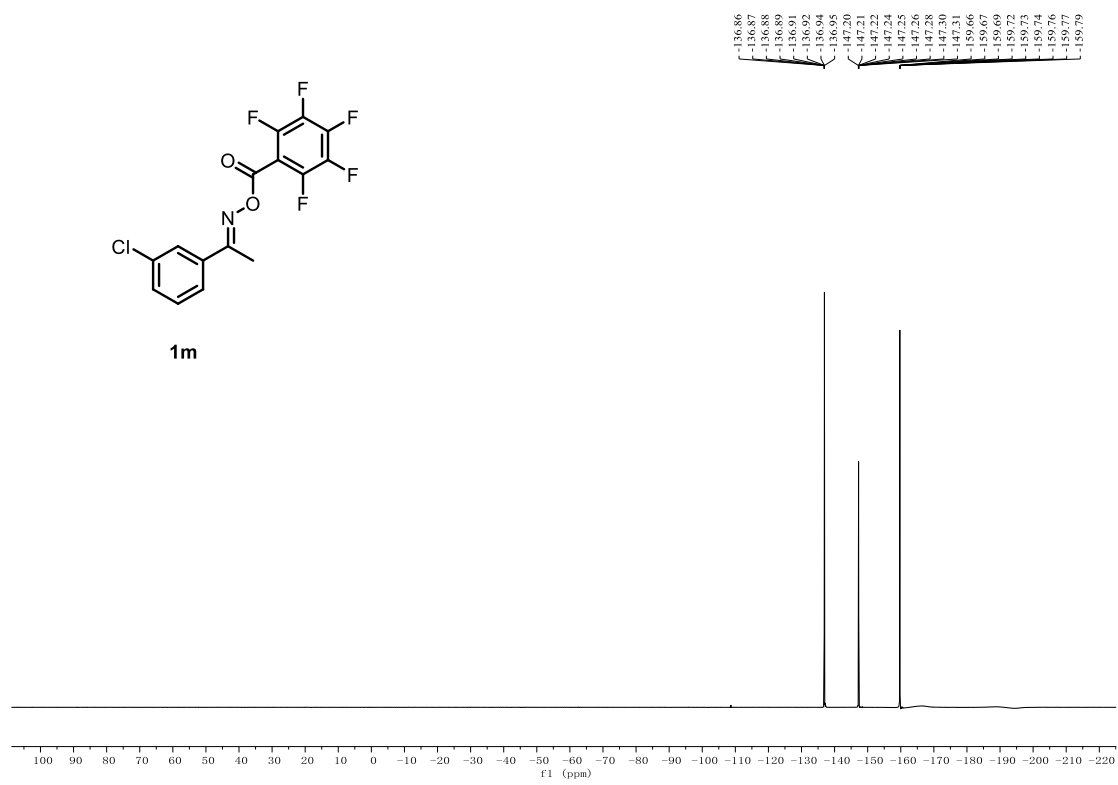


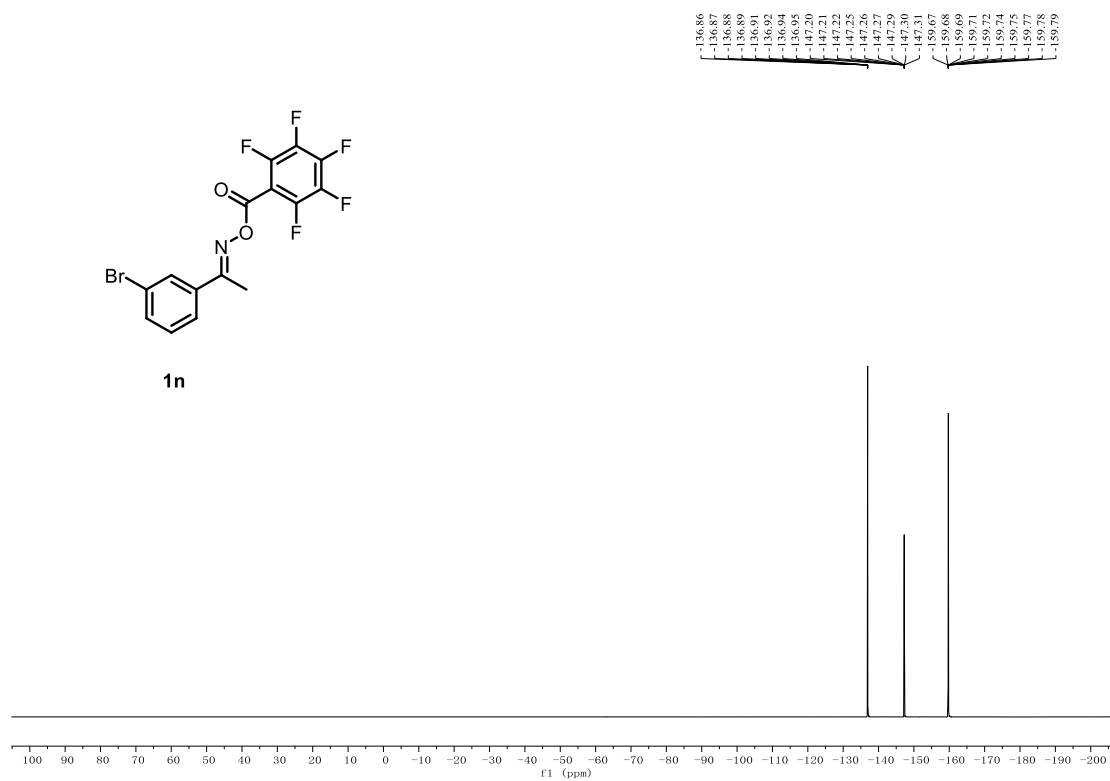
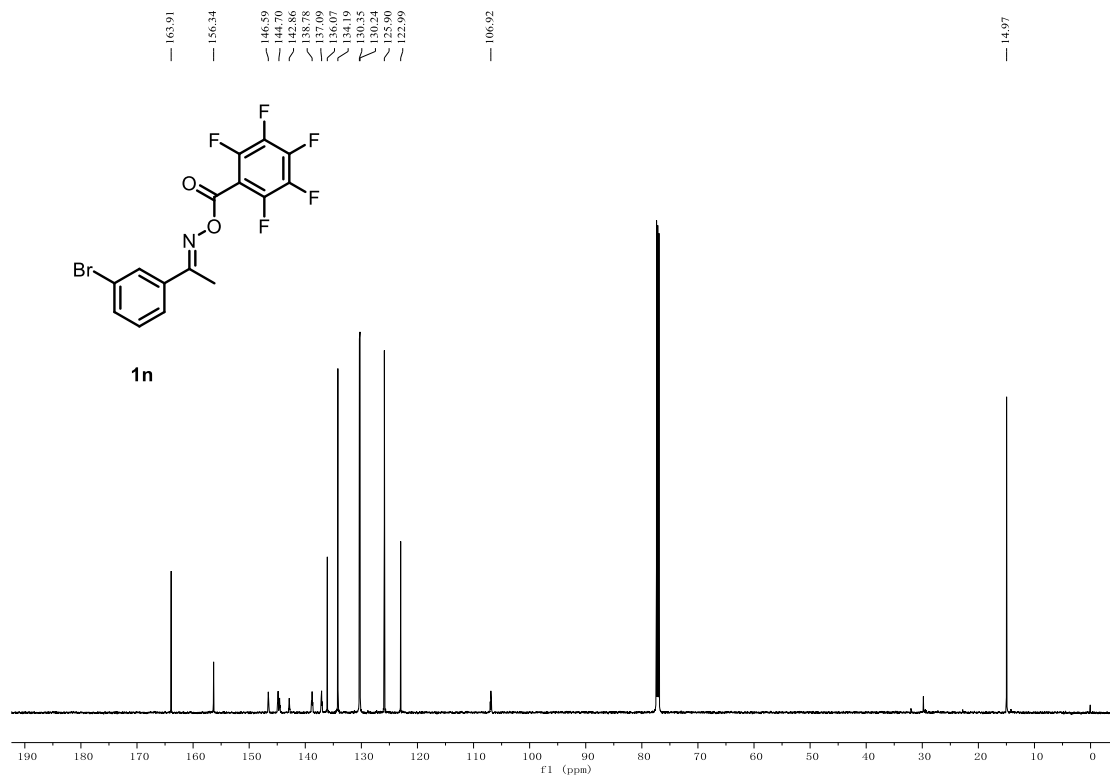


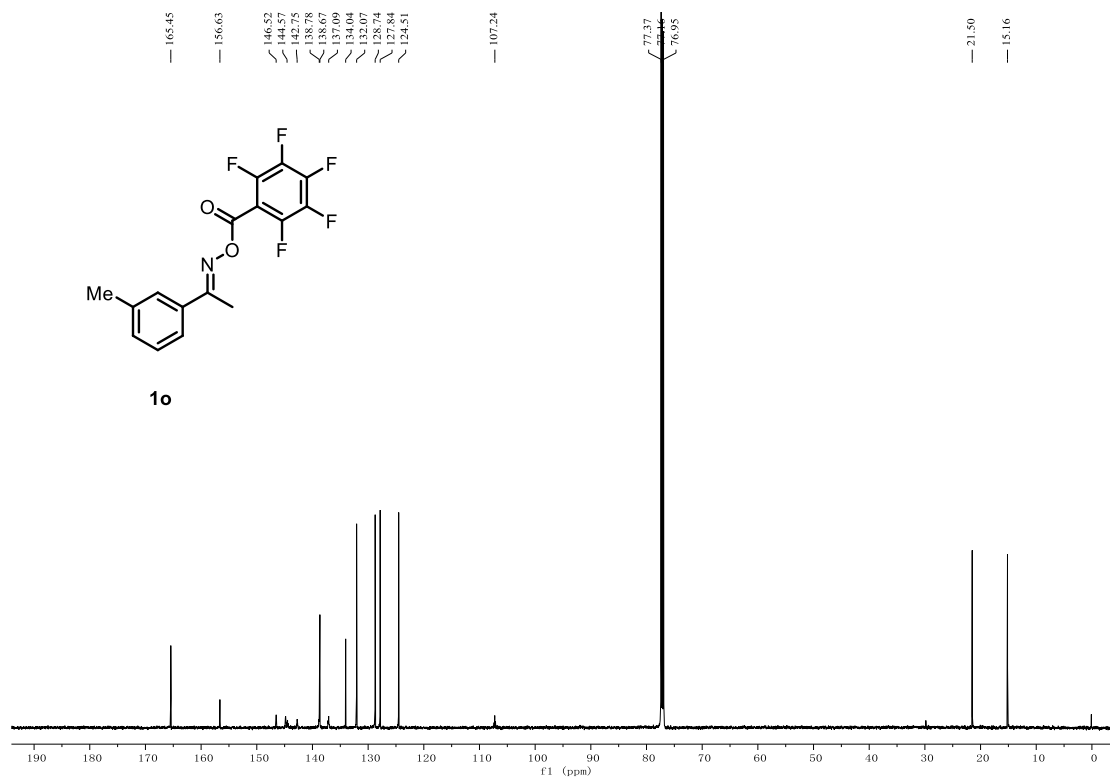
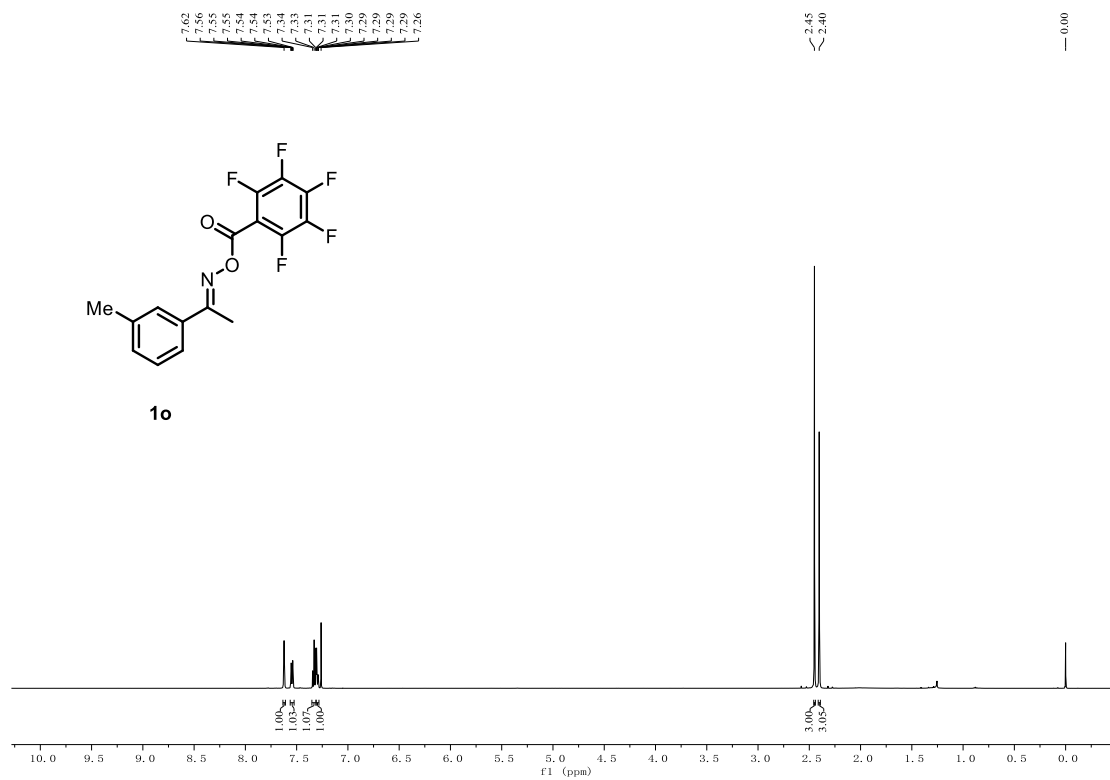


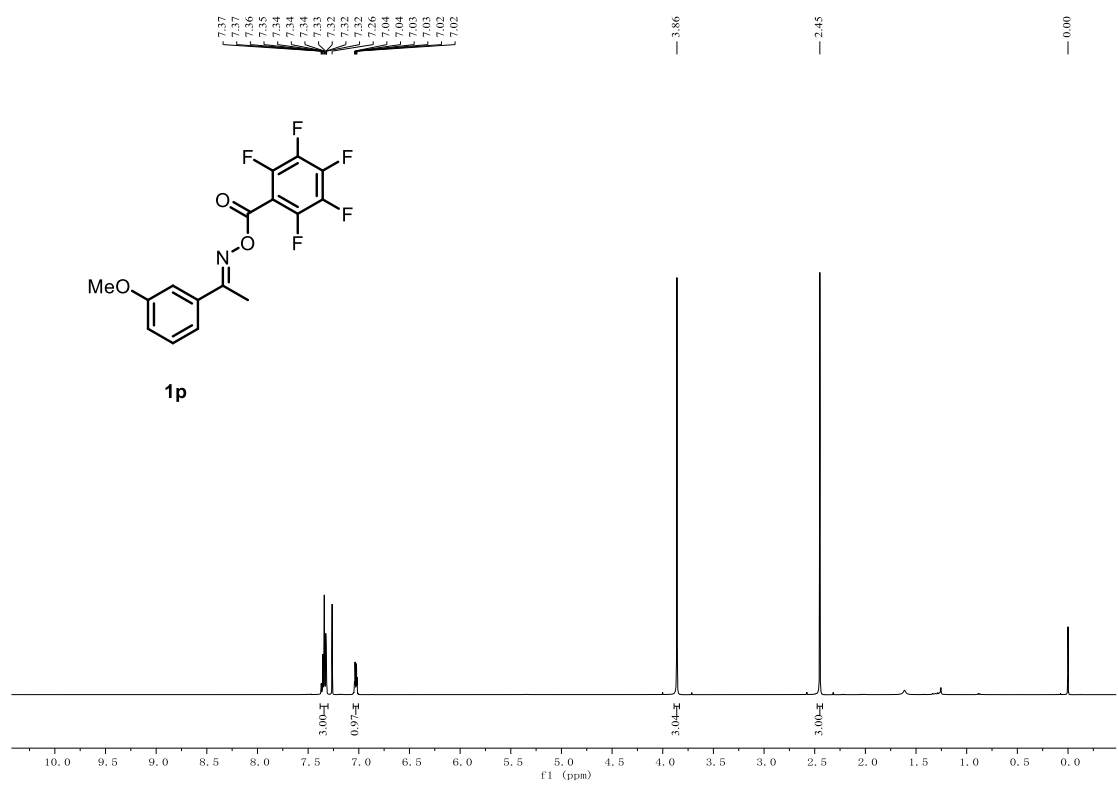
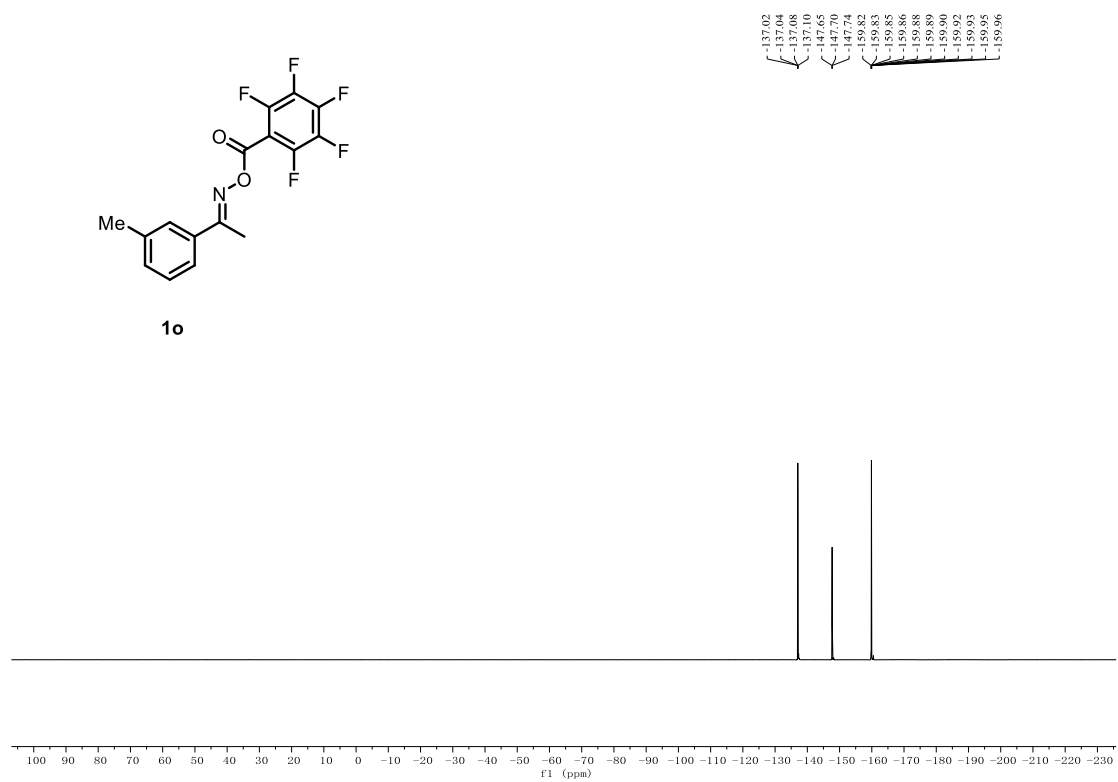


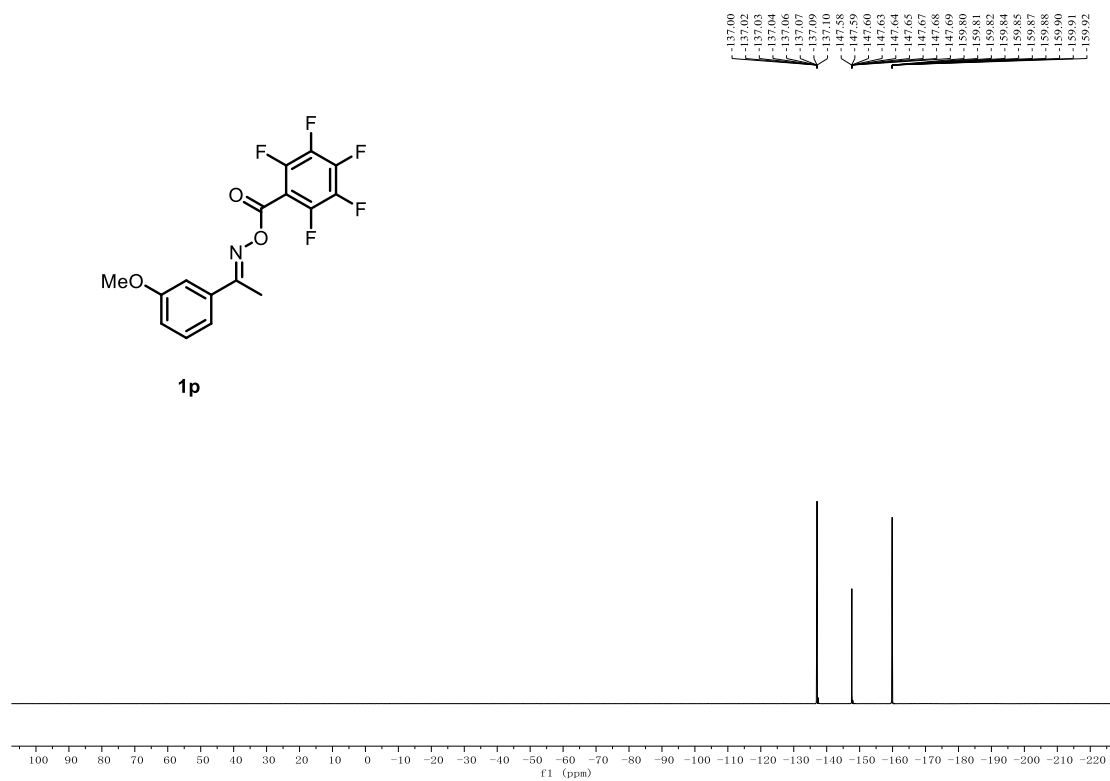
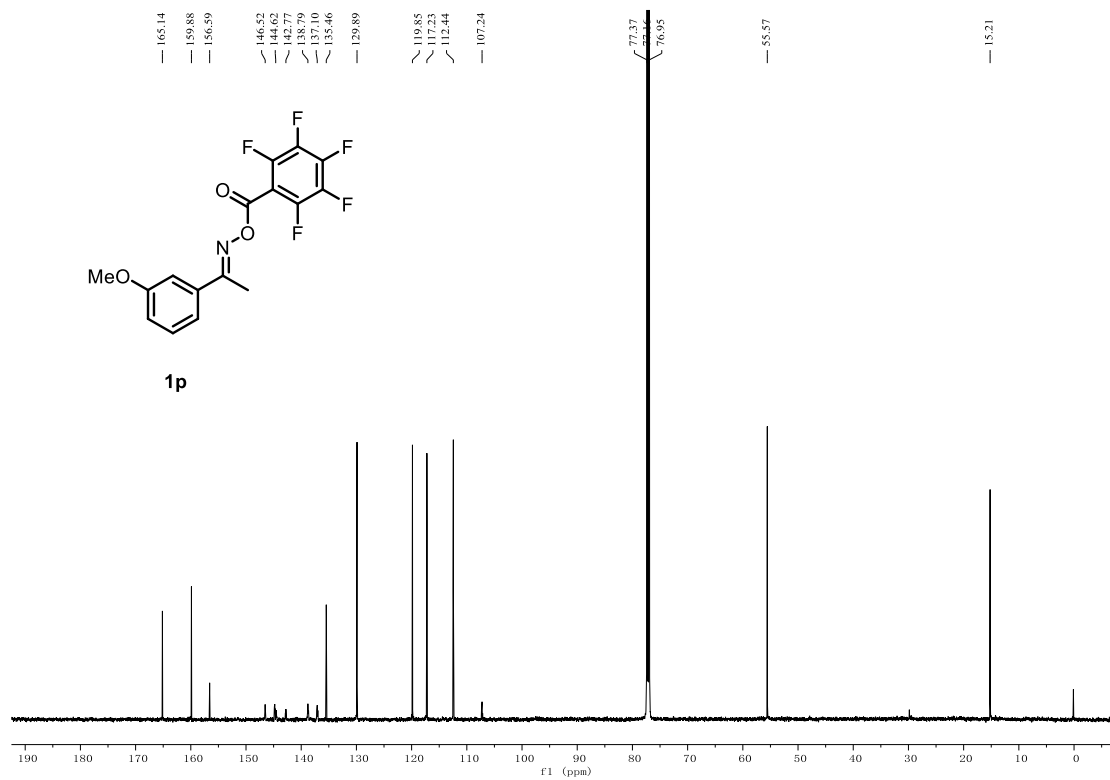


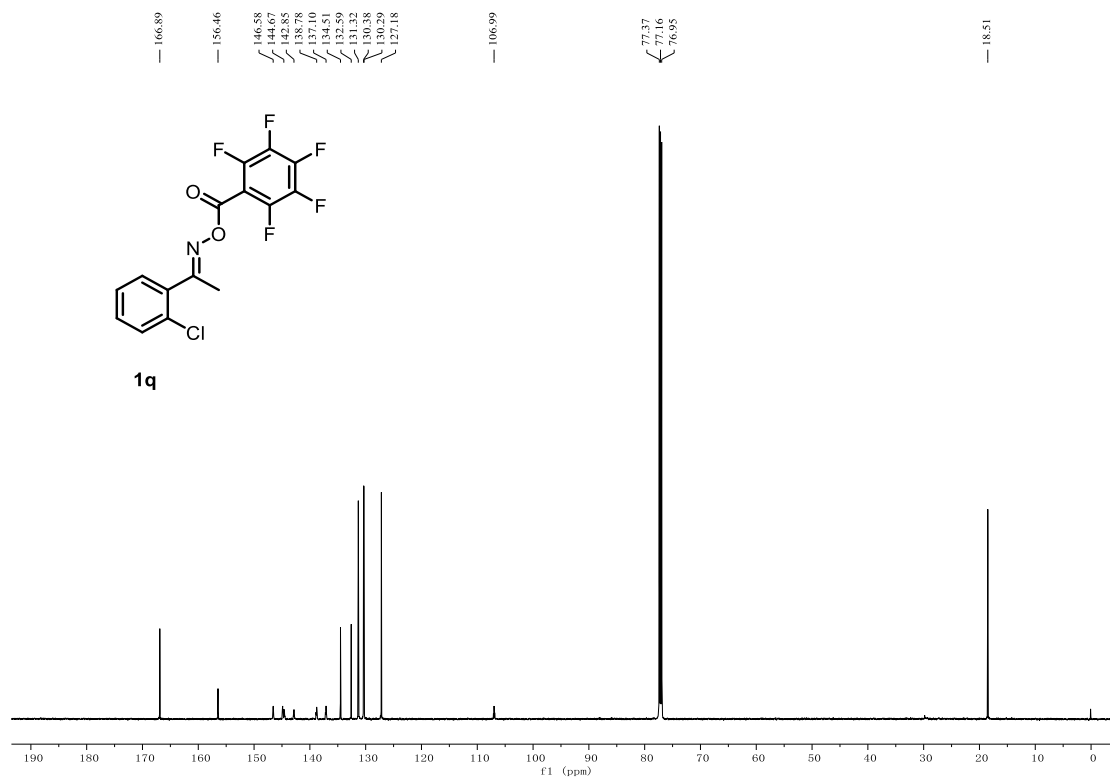
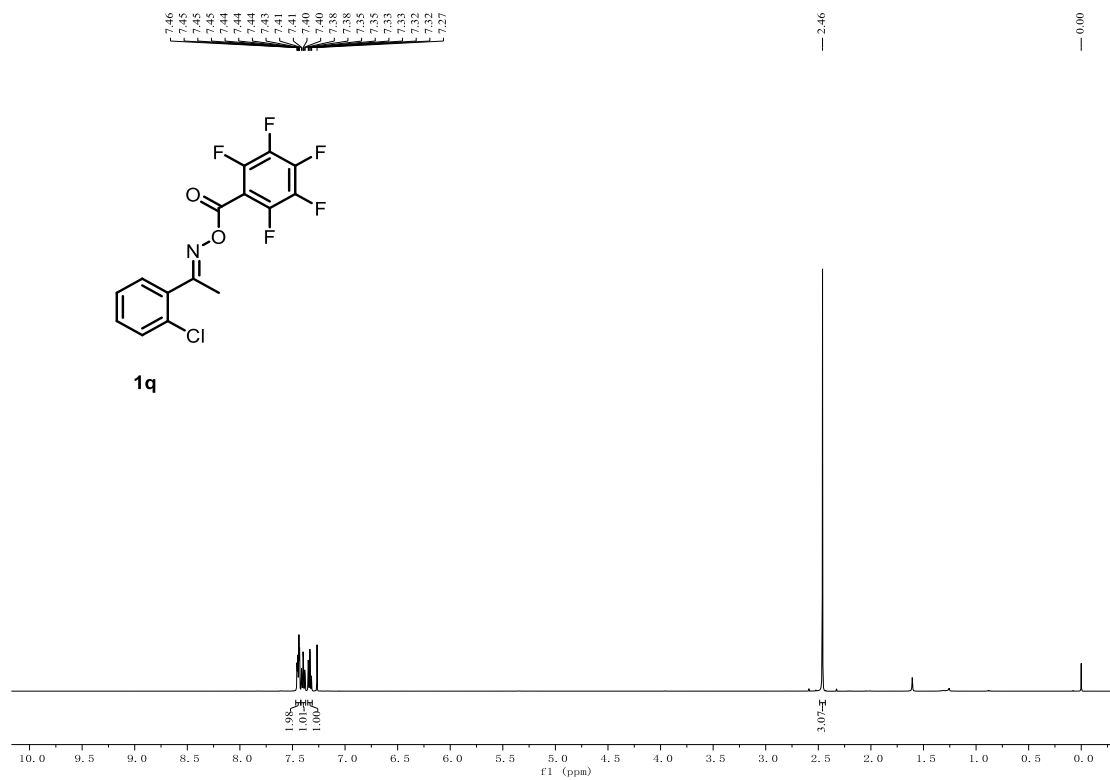


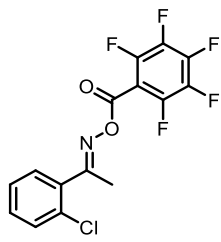




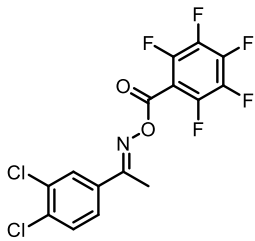
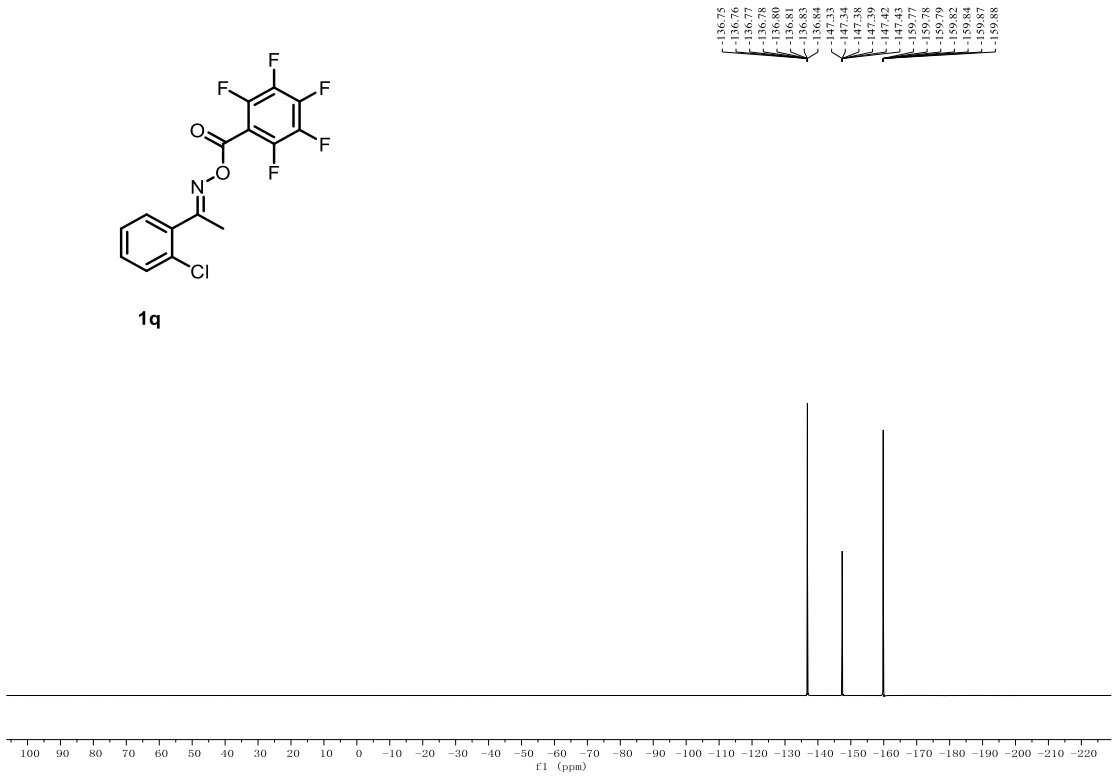




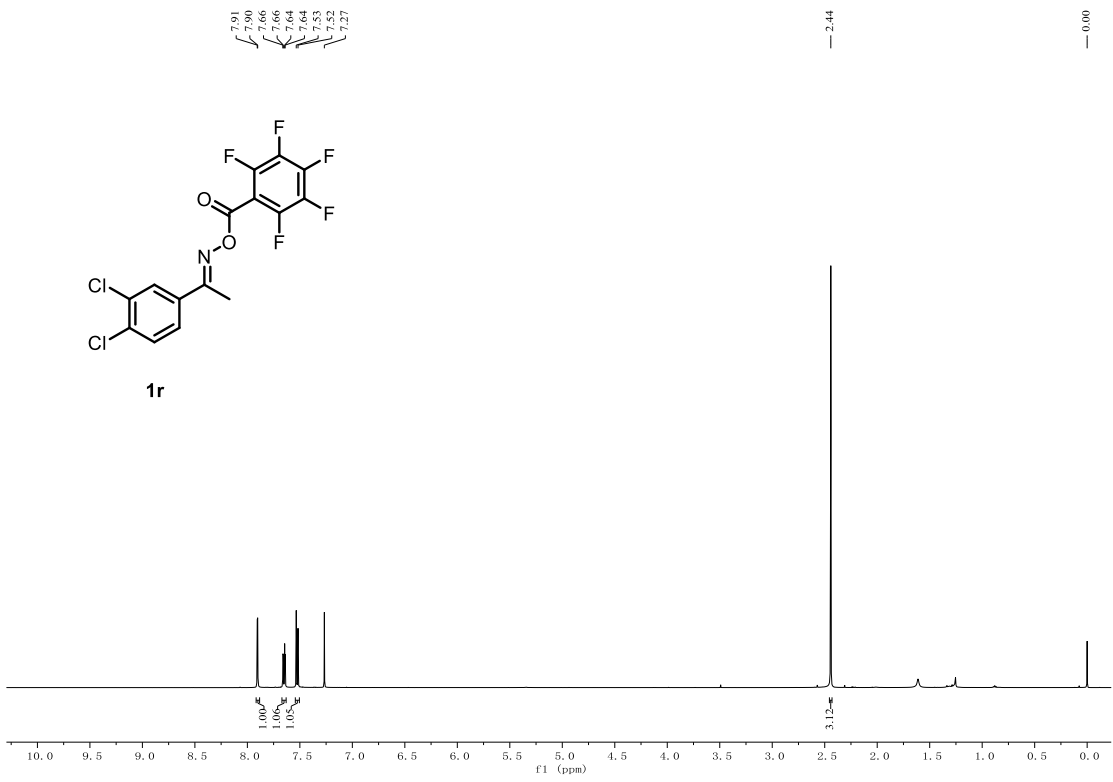


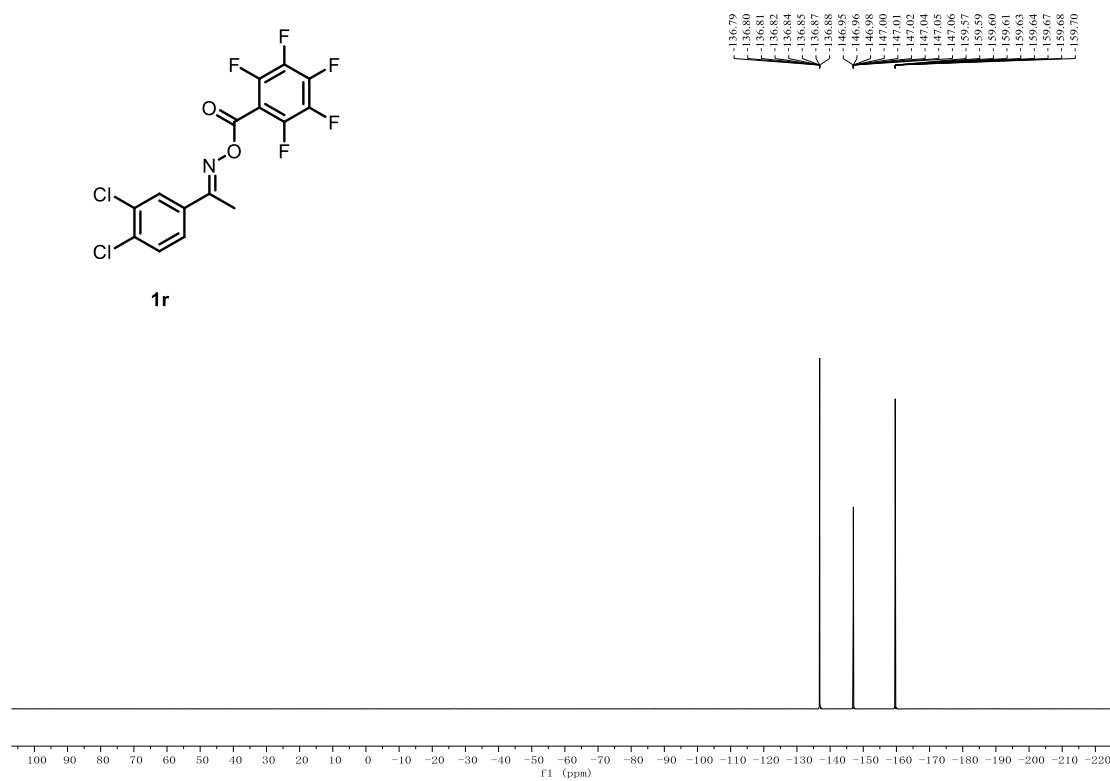
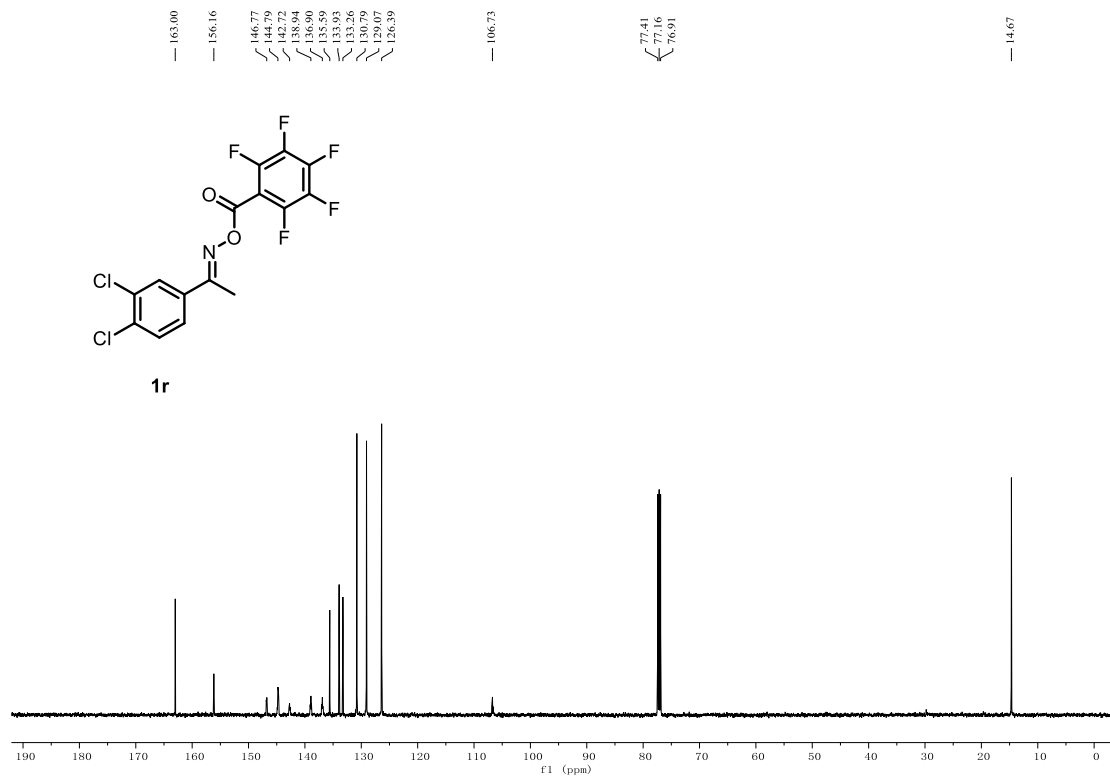


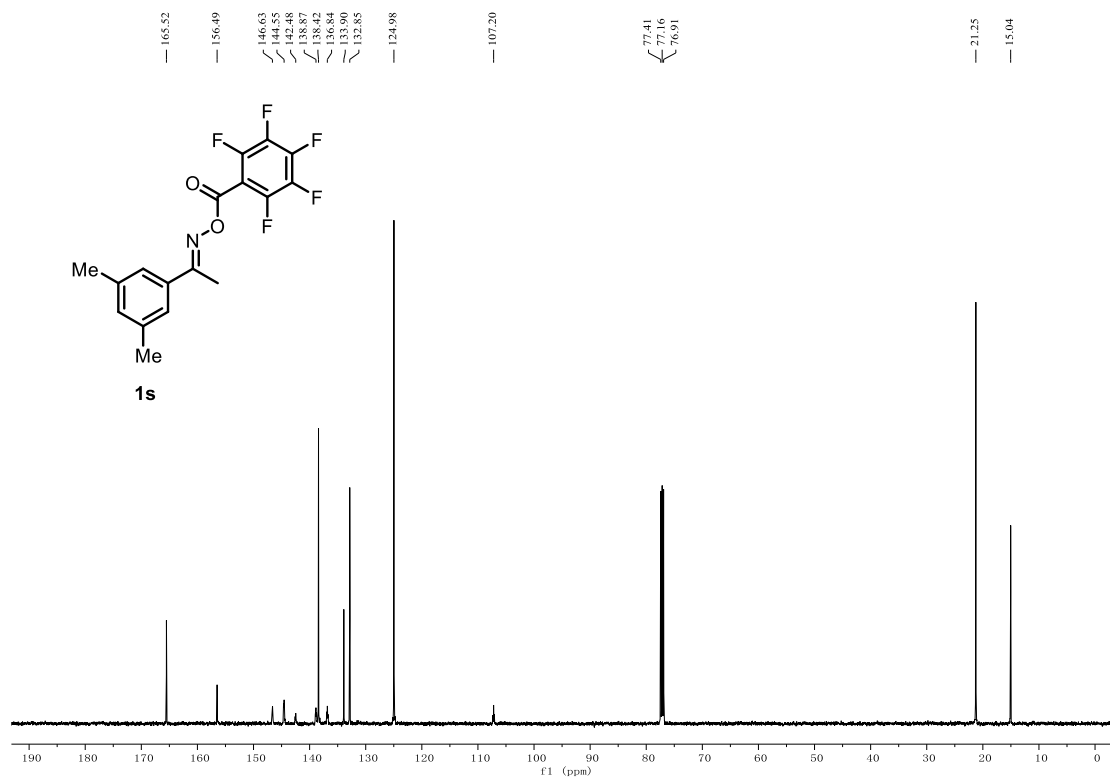
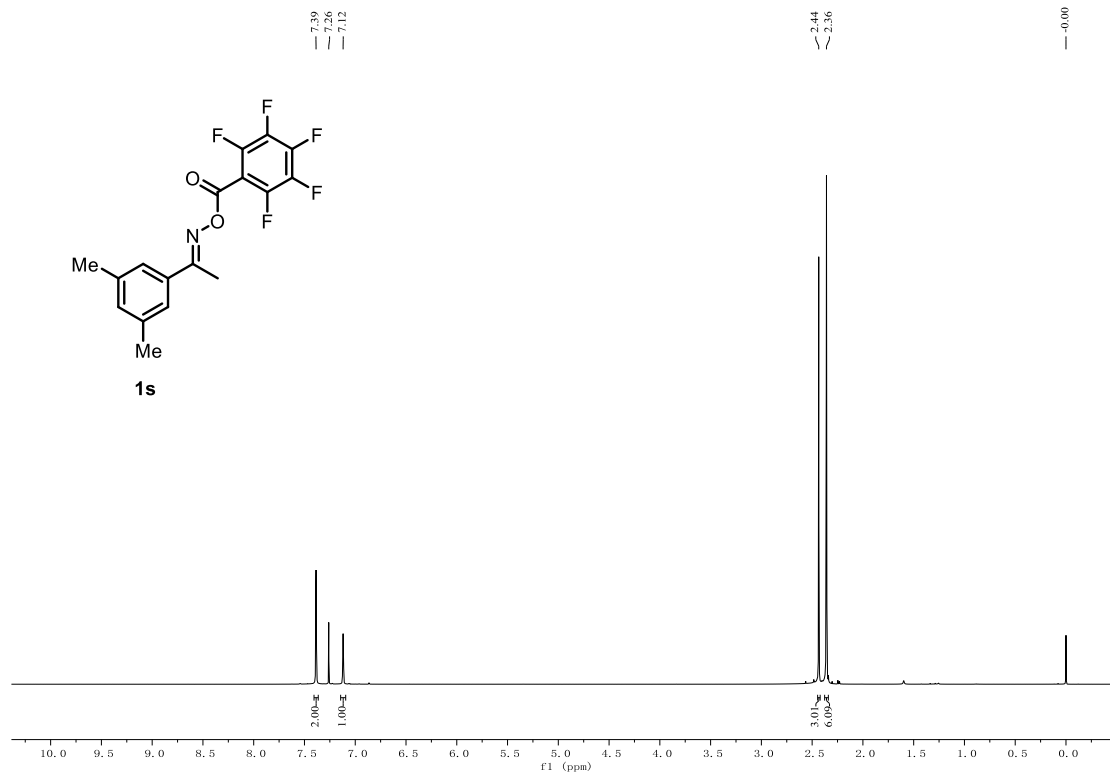
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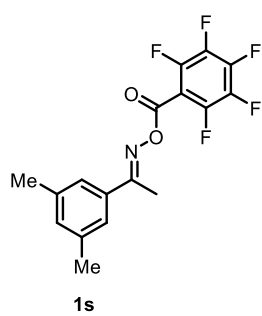


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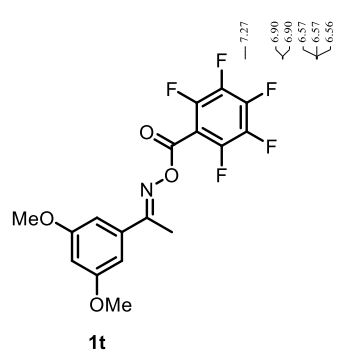
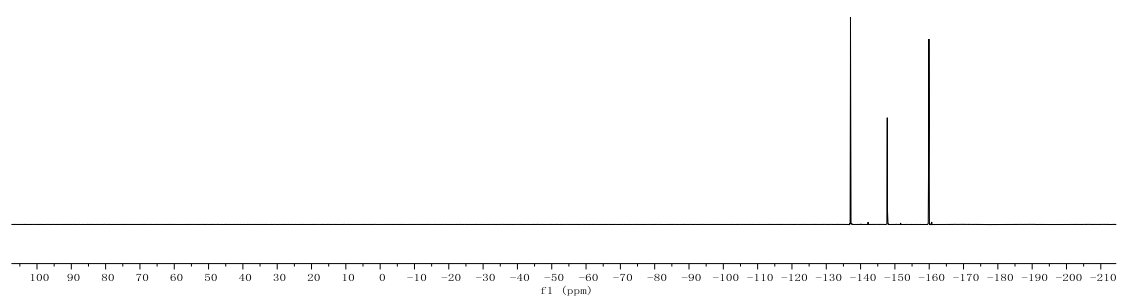




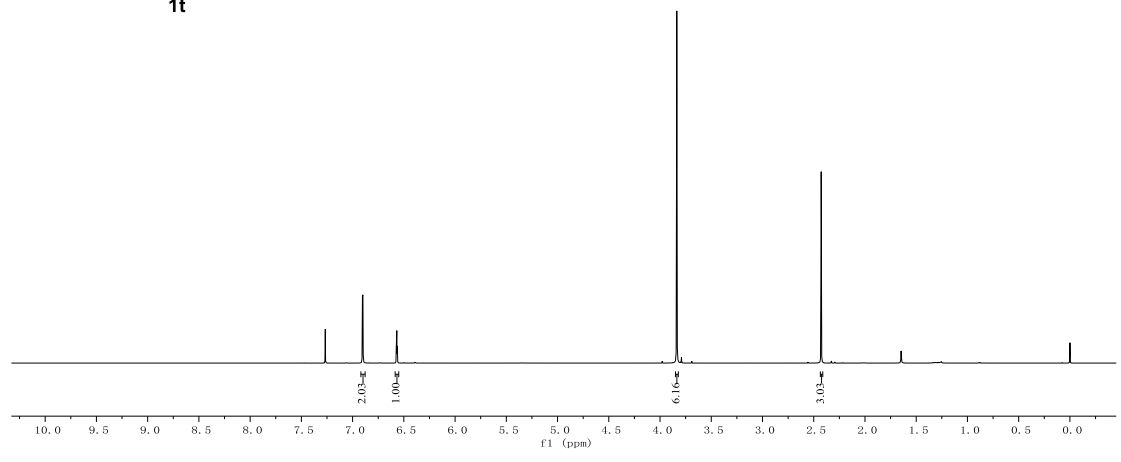


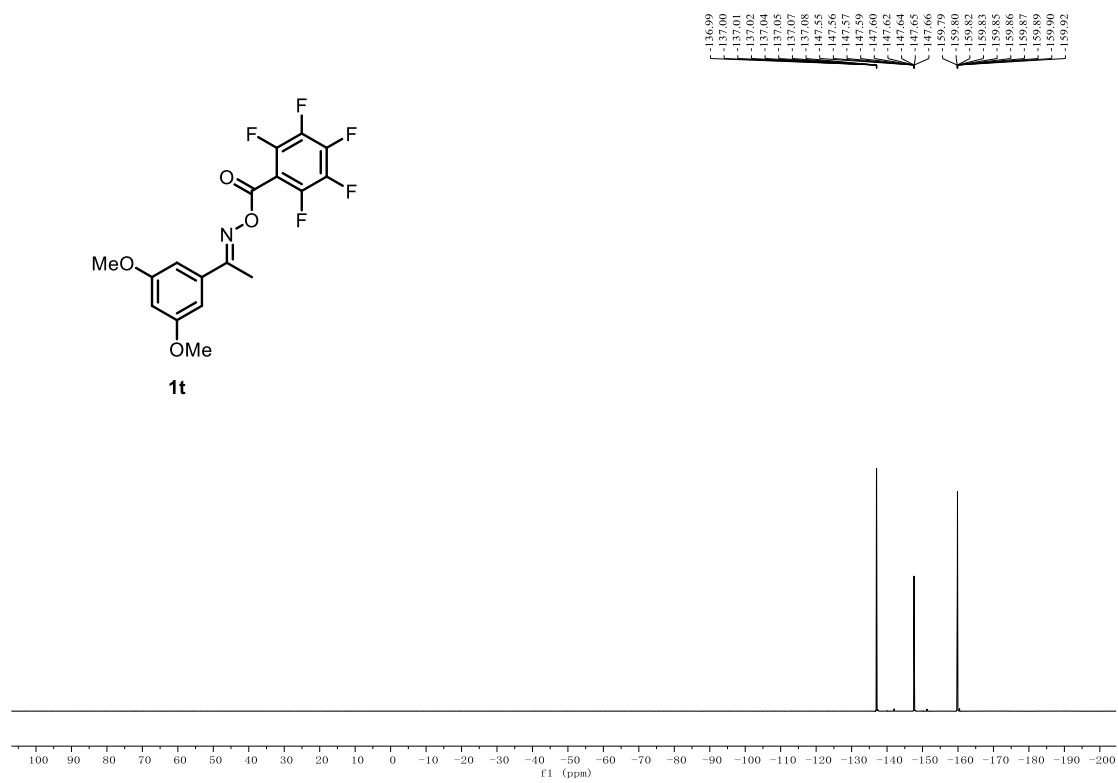
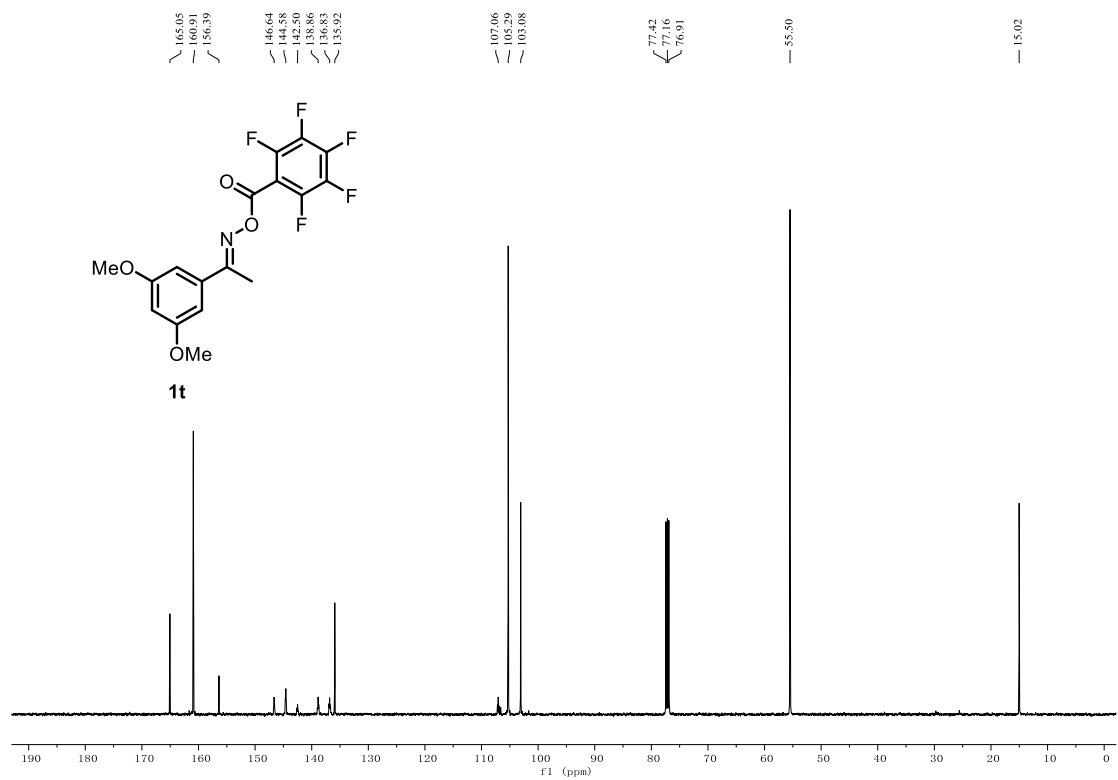


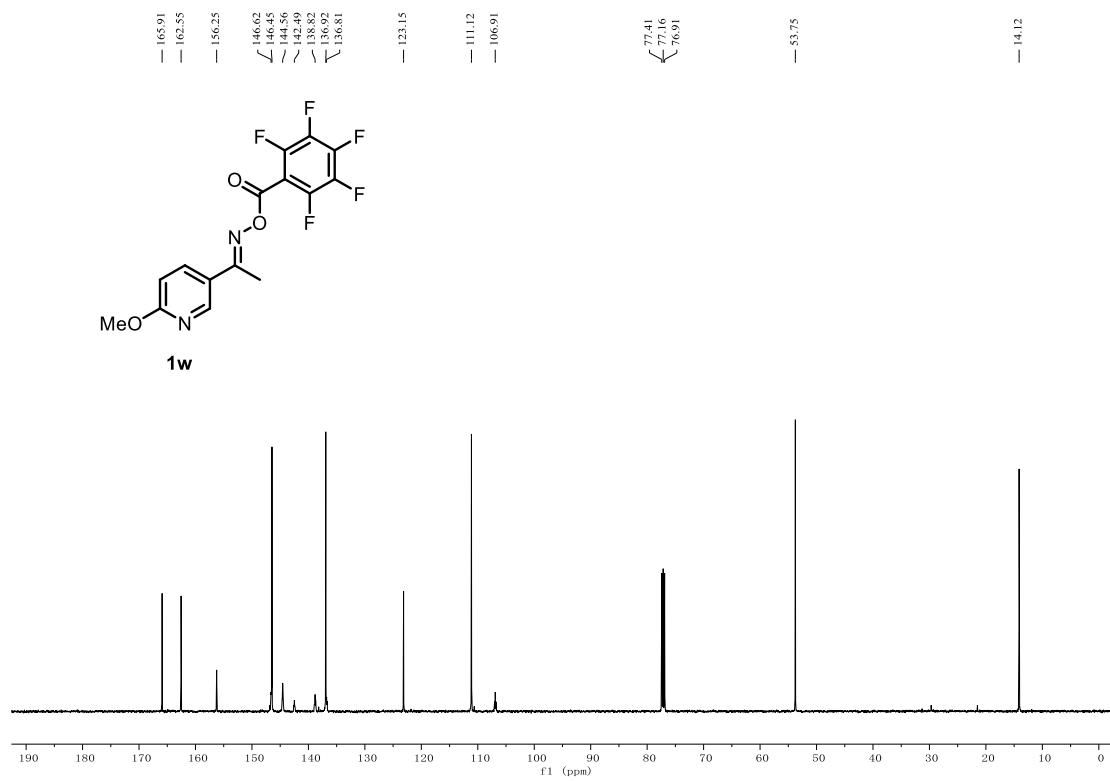
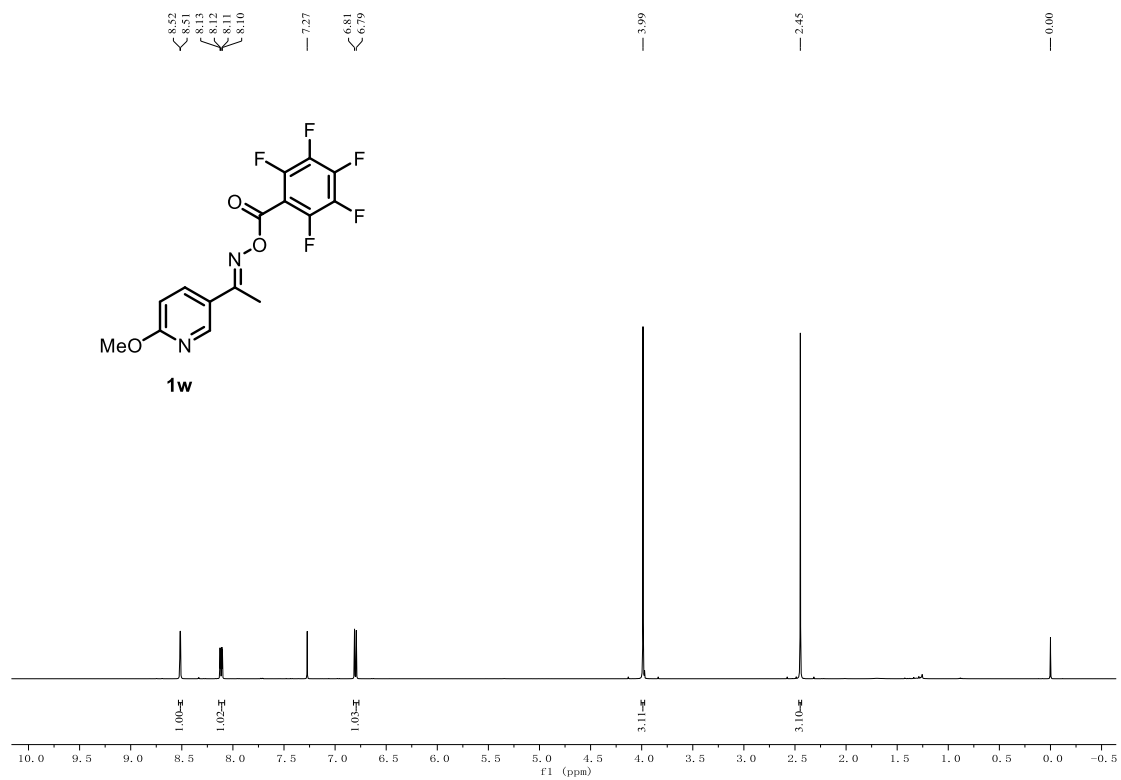
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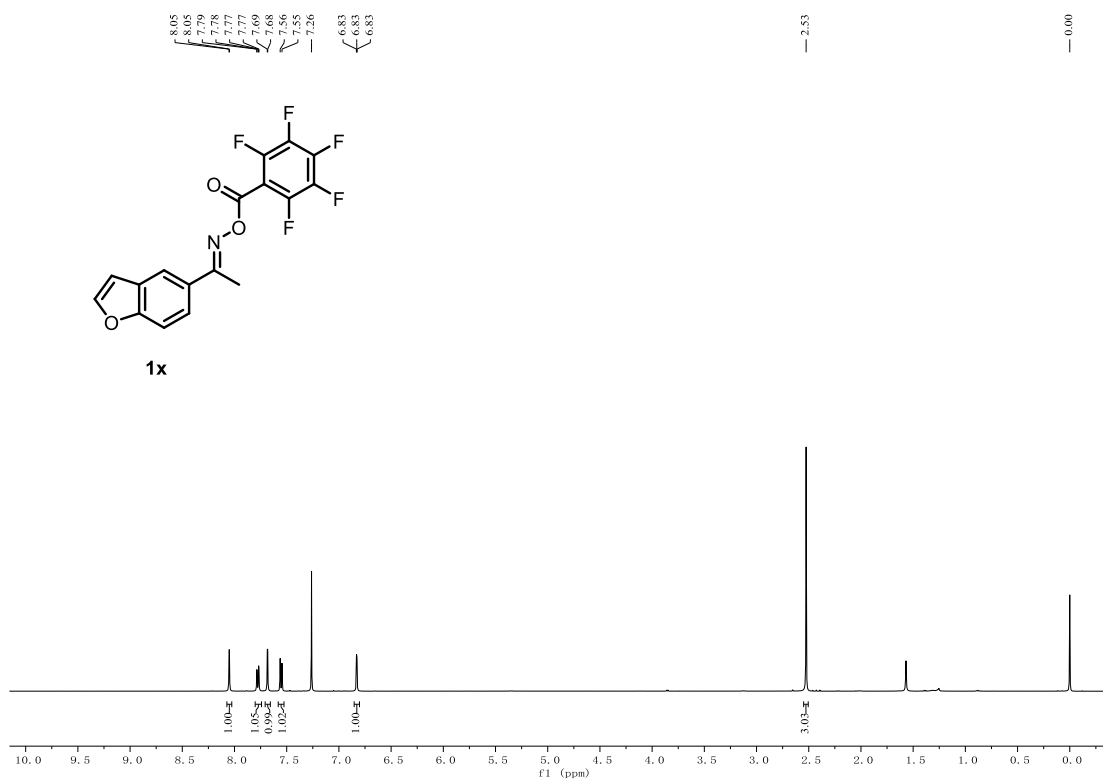
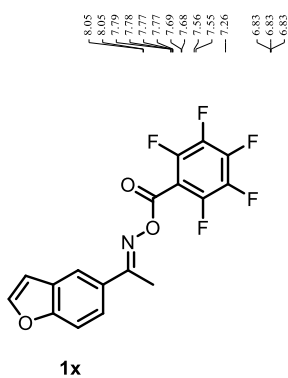
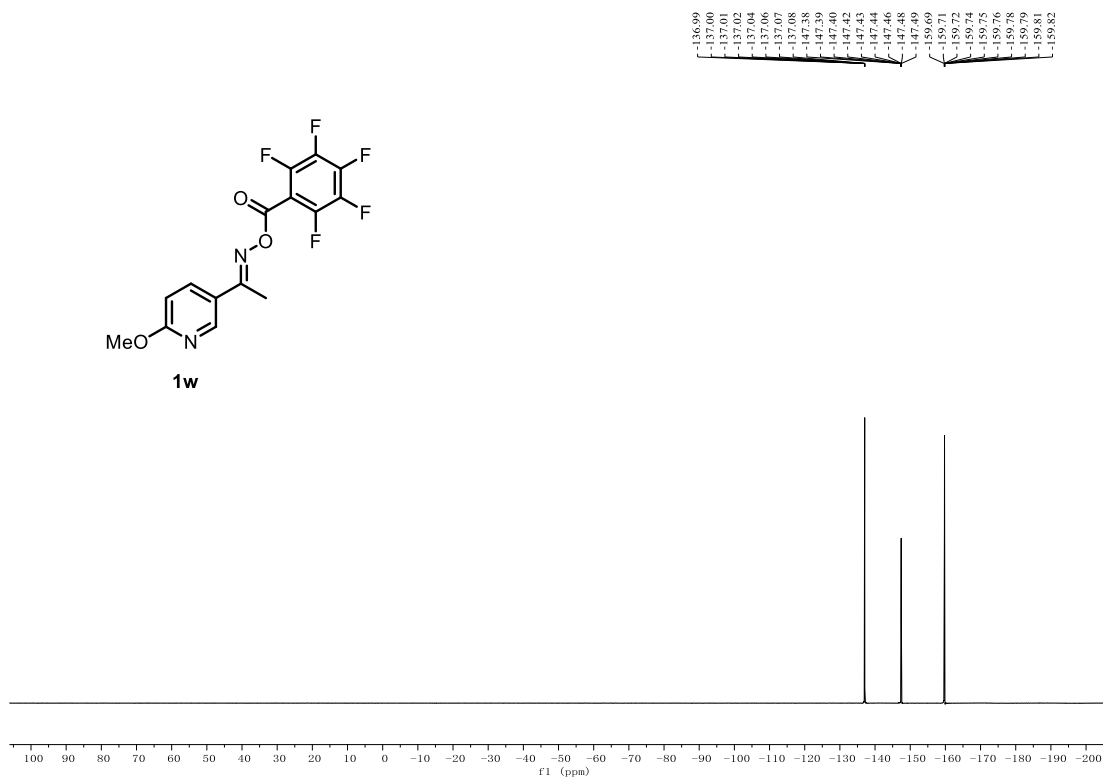
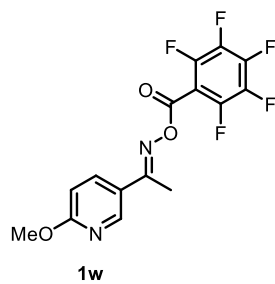


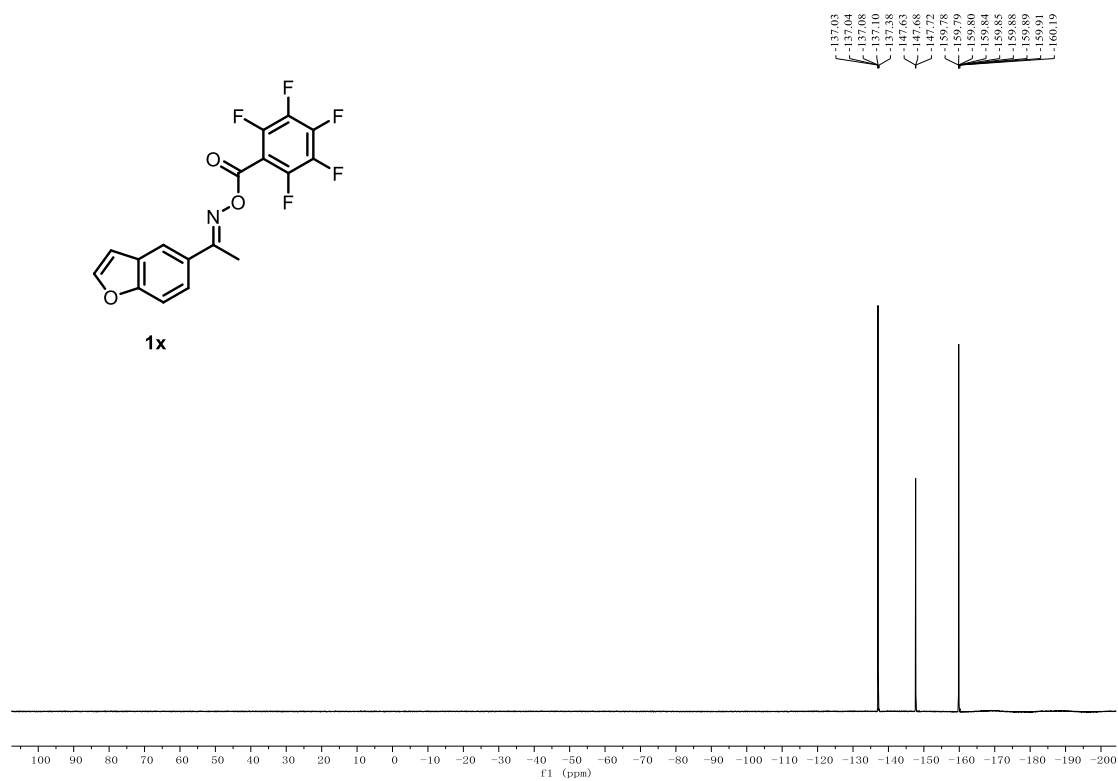
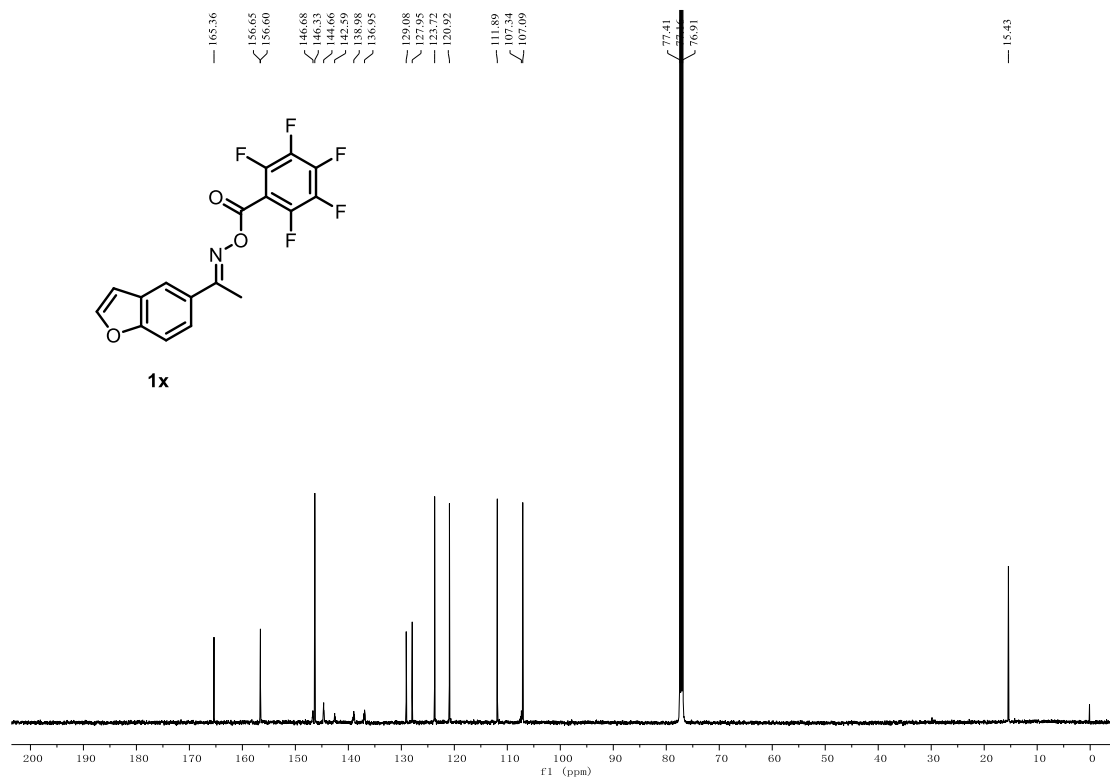
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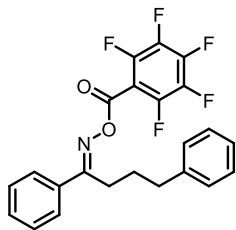




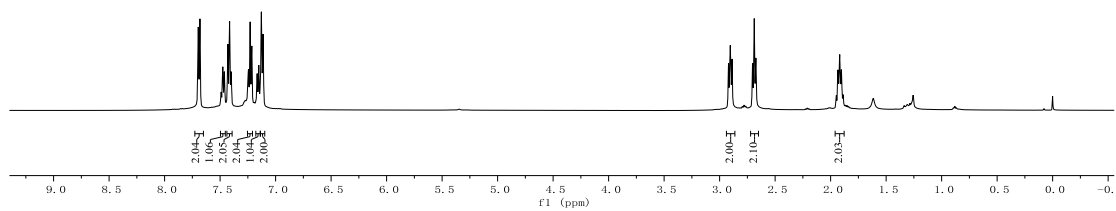
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7.15
7.13
7.11

2.92
2.90
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1.89

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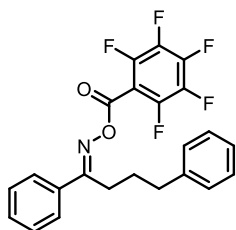


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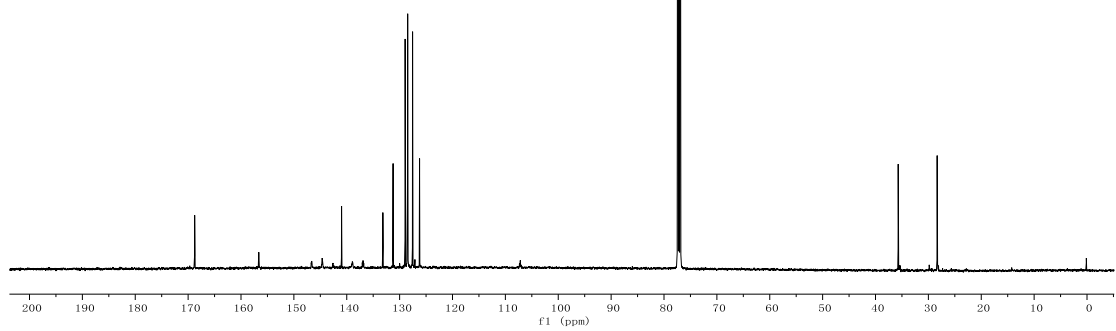


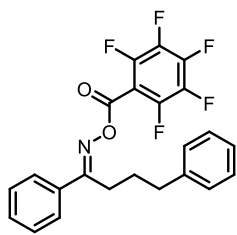
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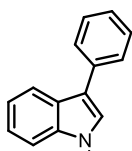
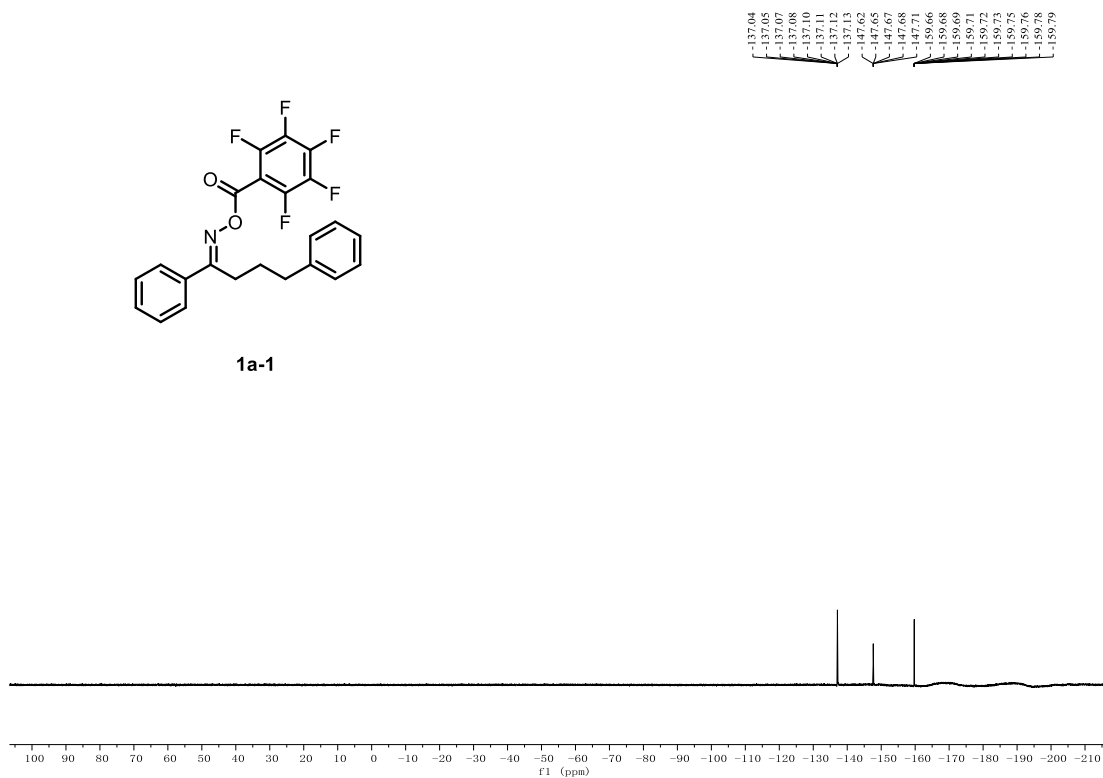


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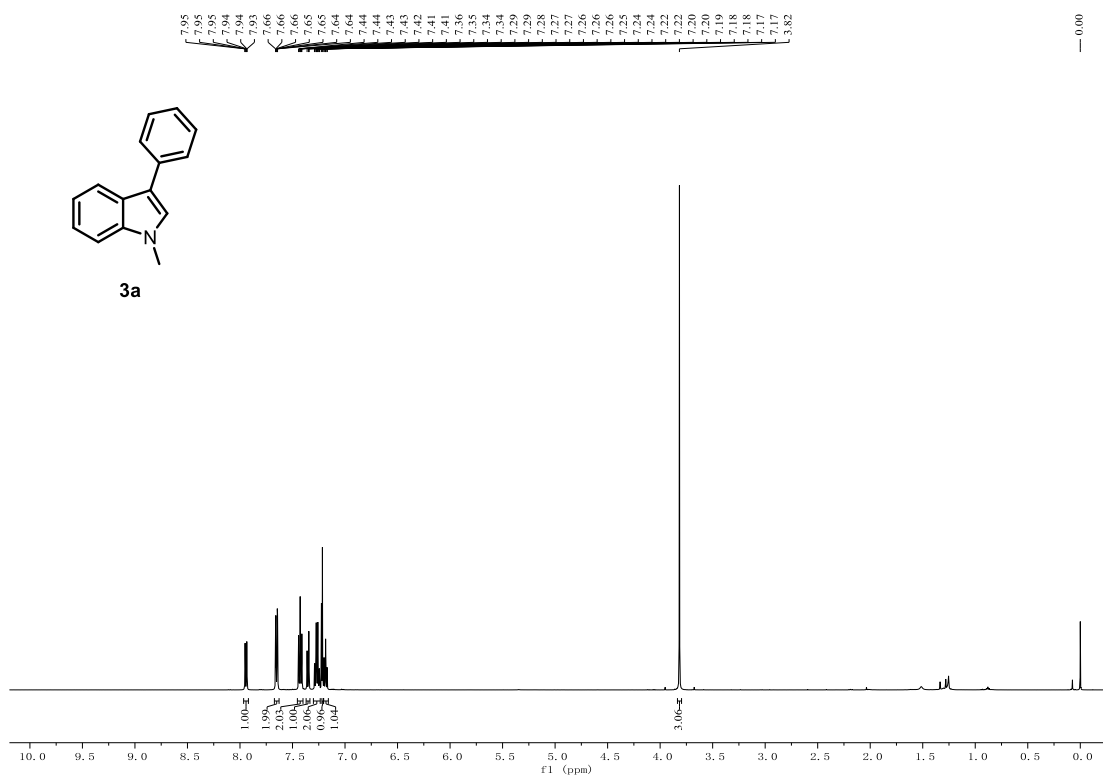


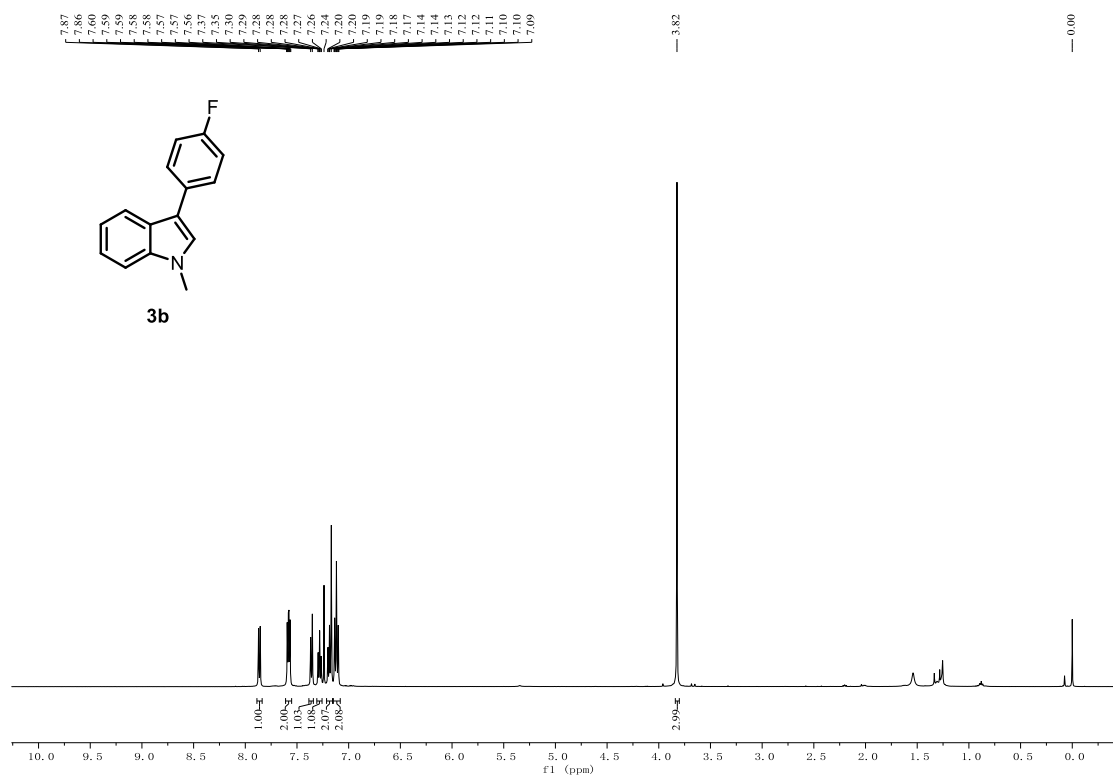
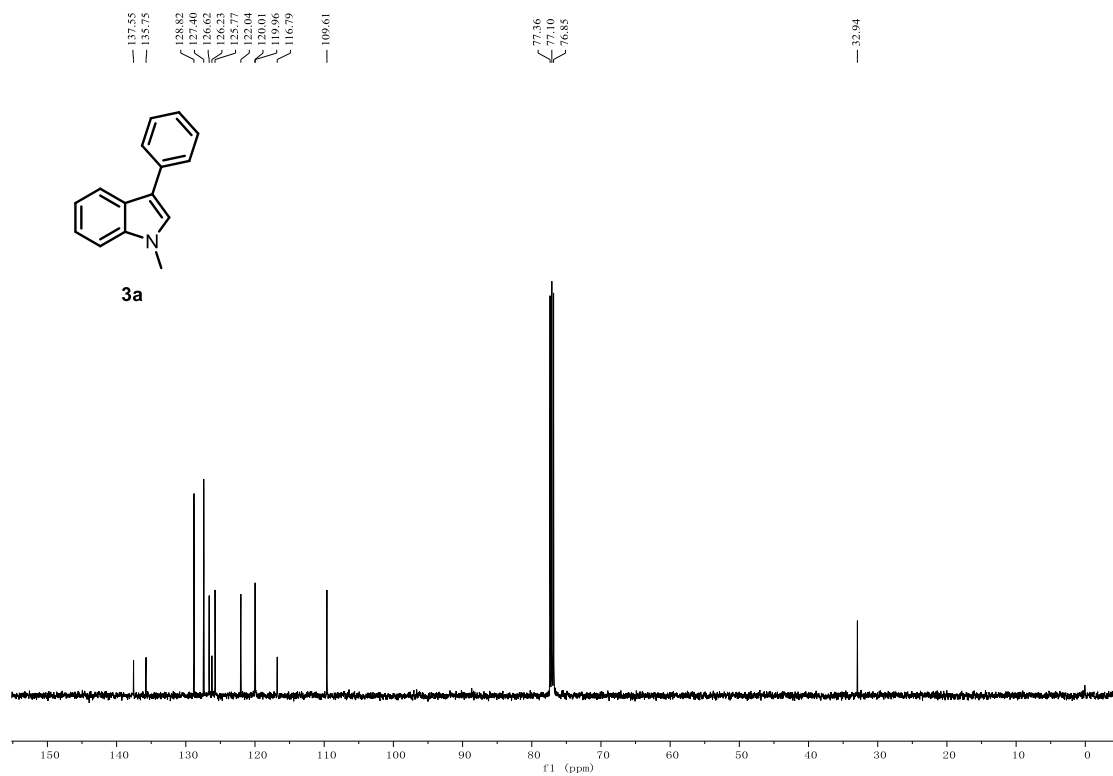


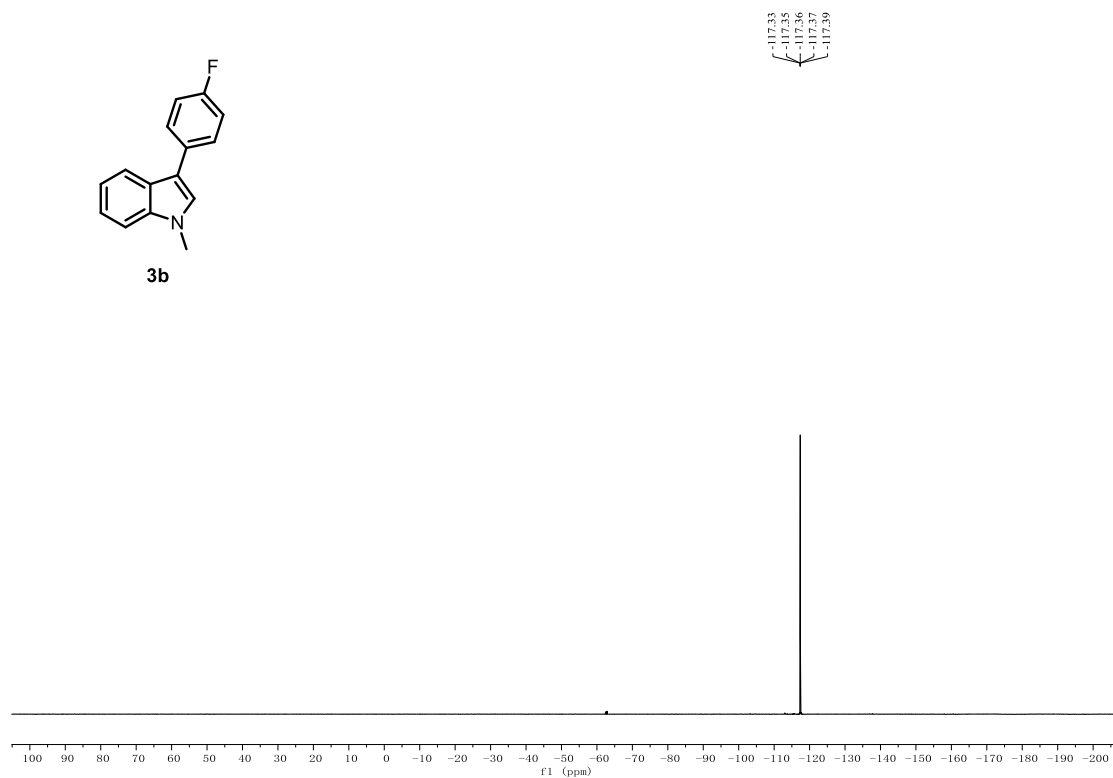
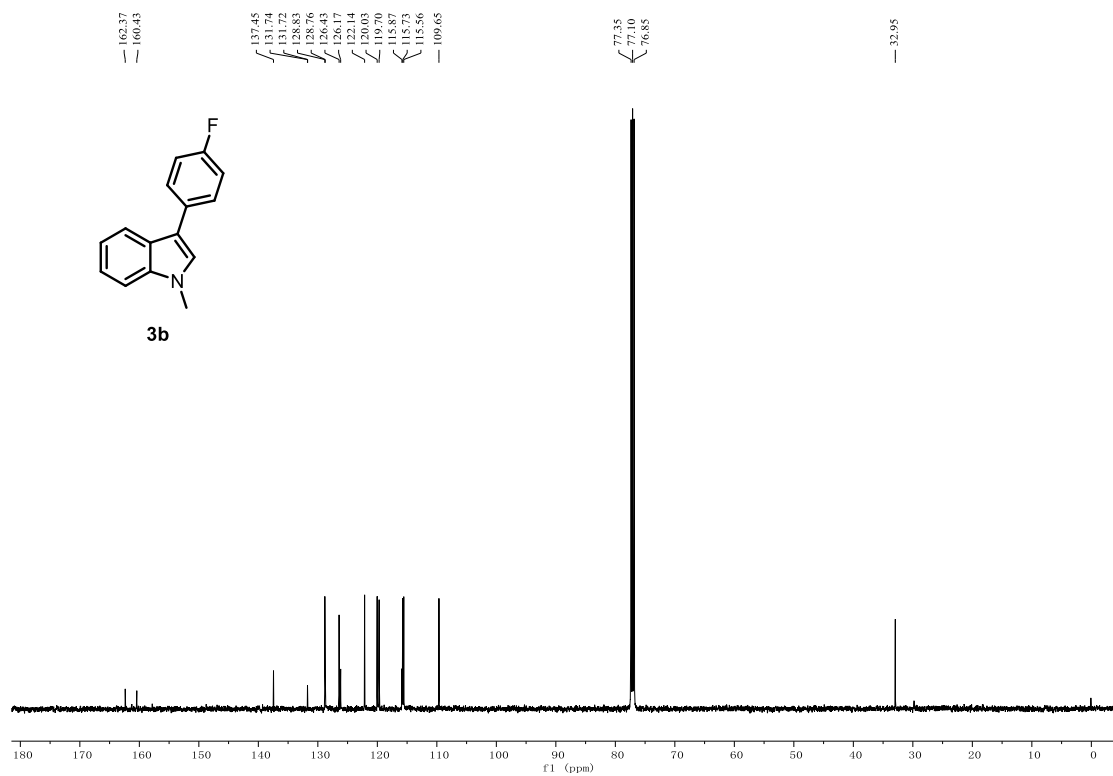
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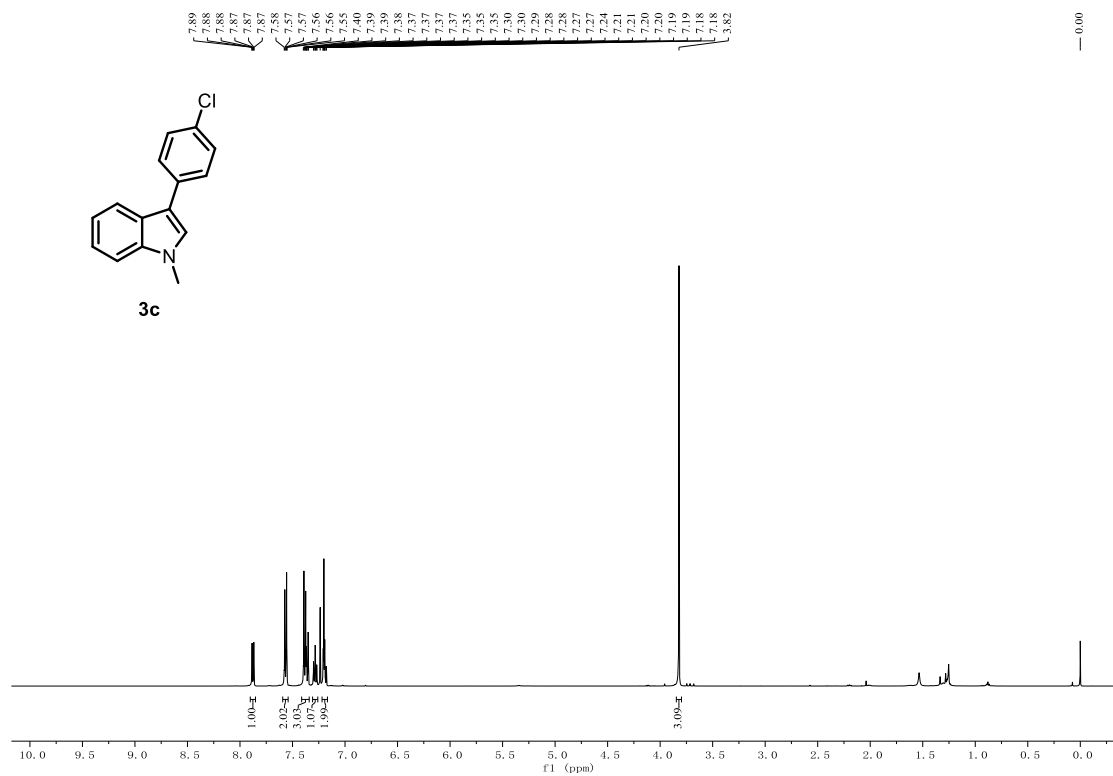


3a

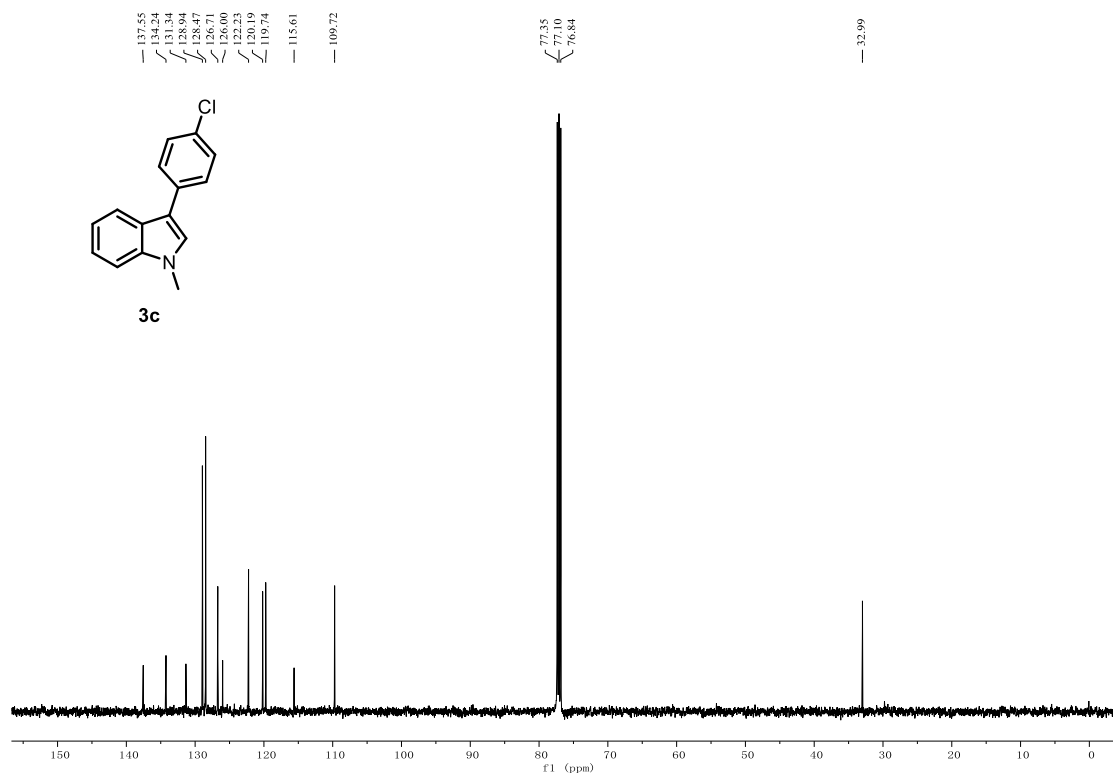


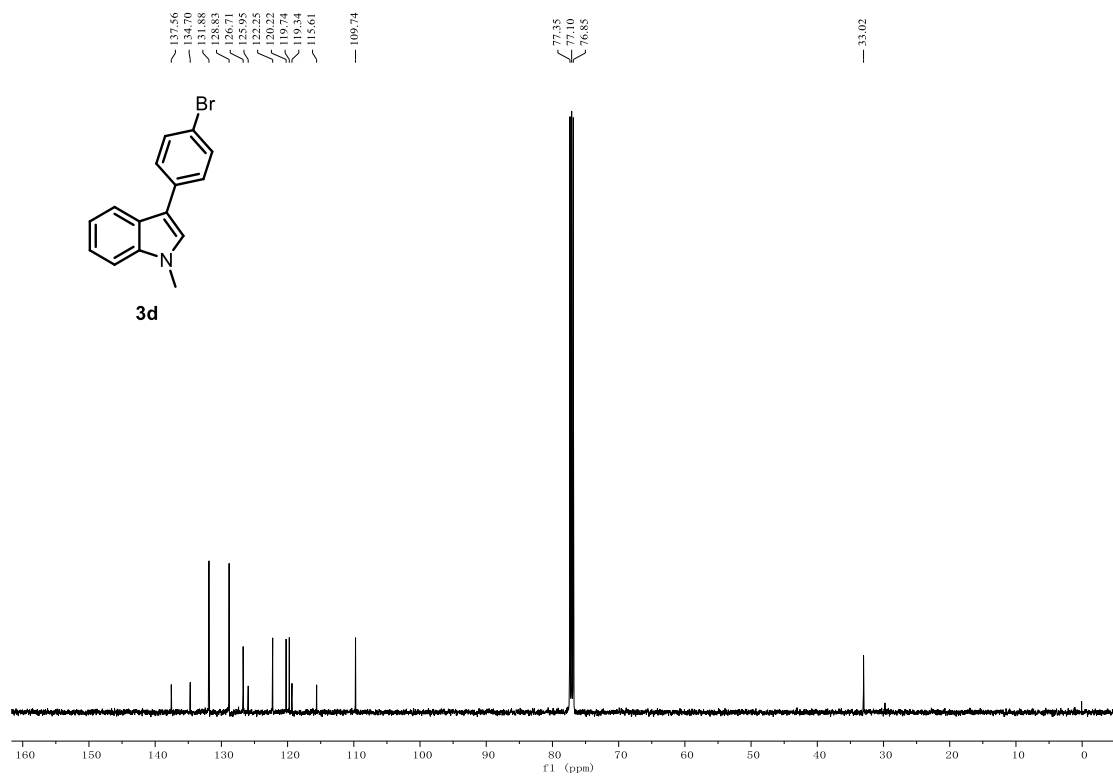
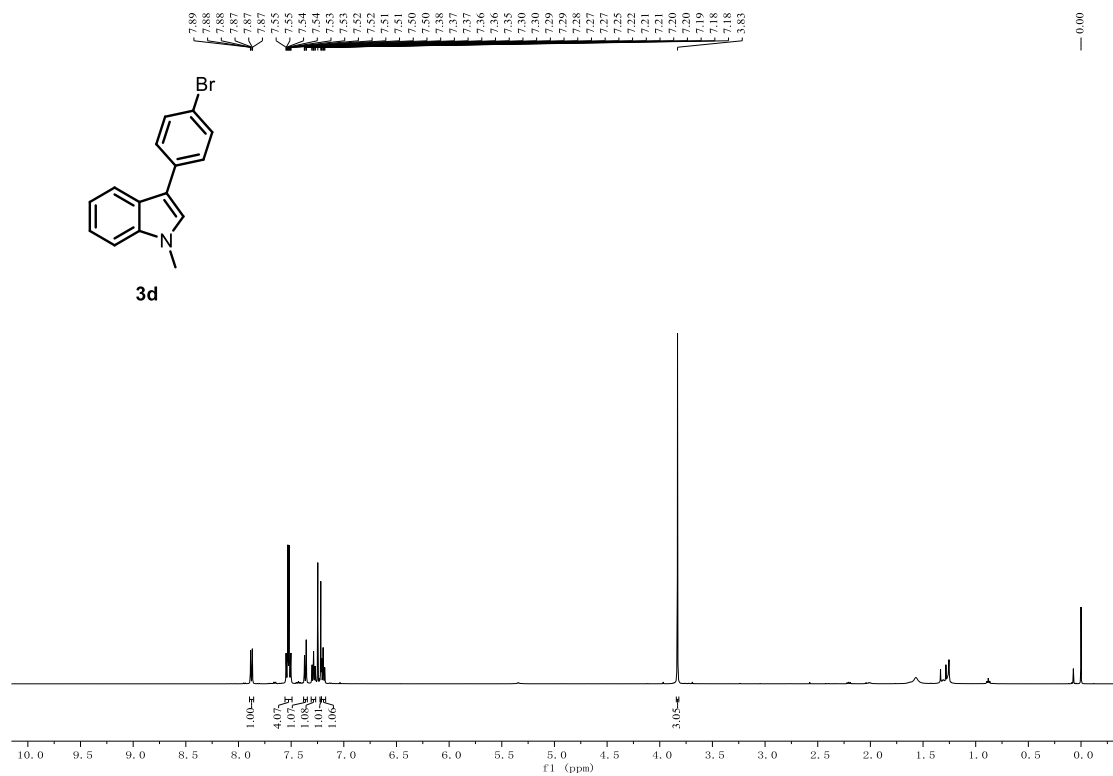


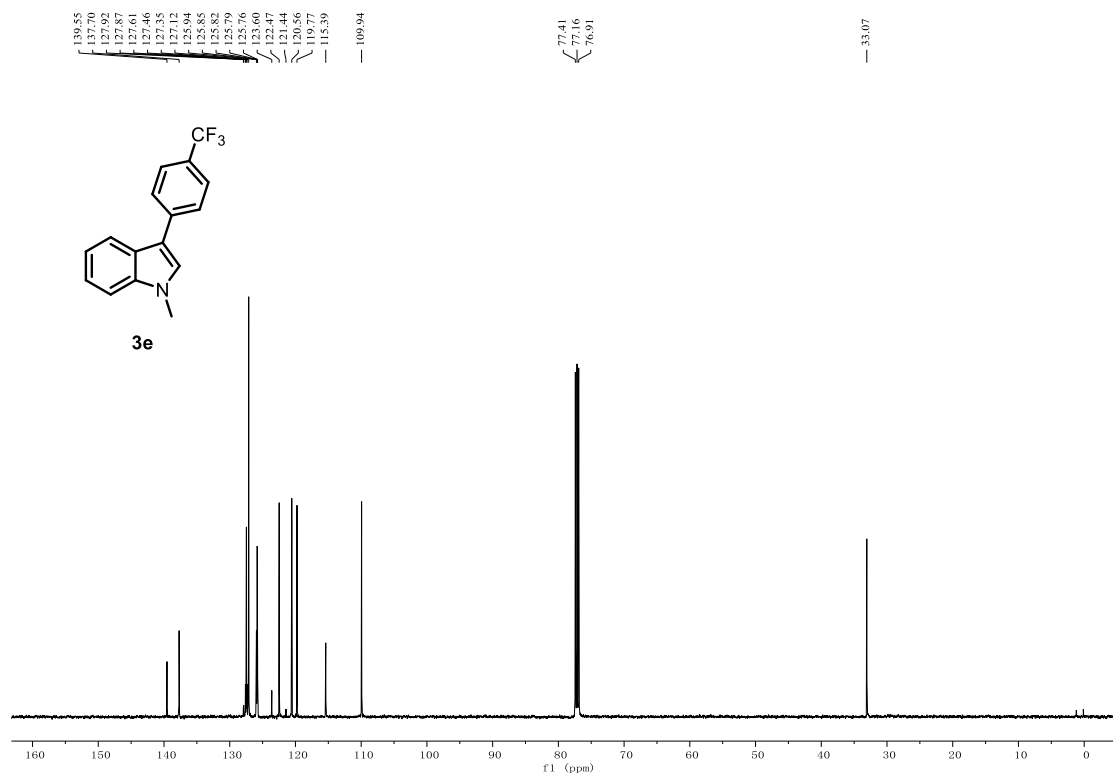
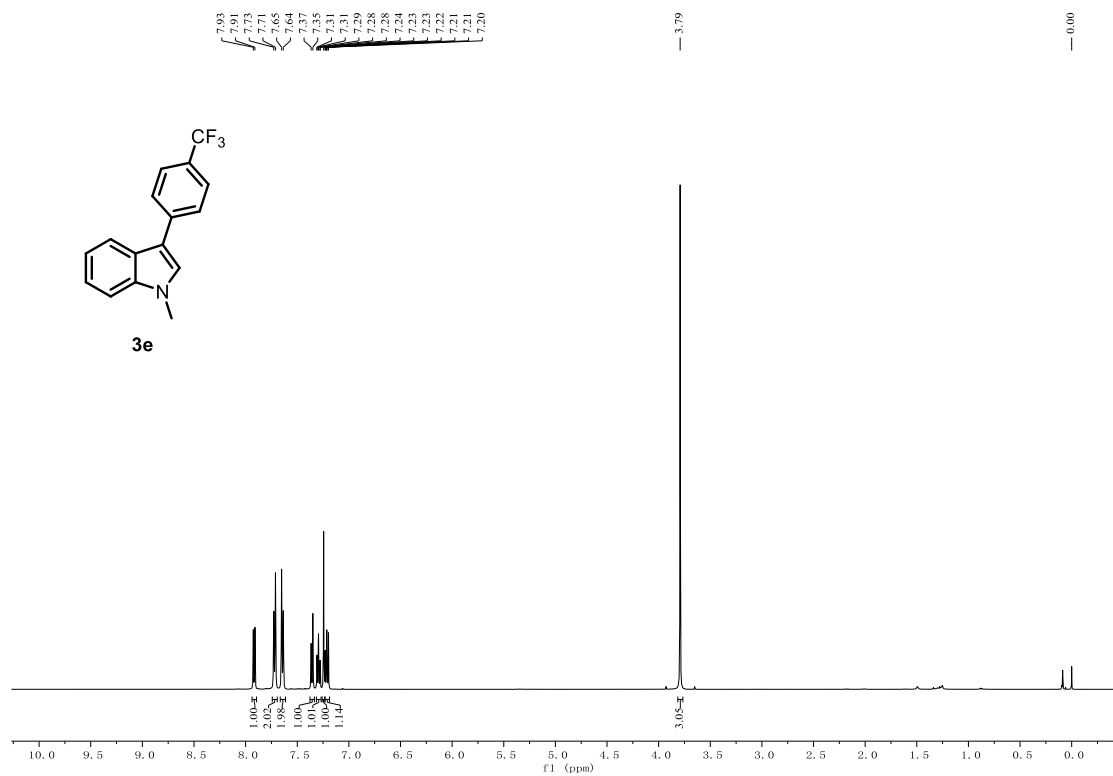


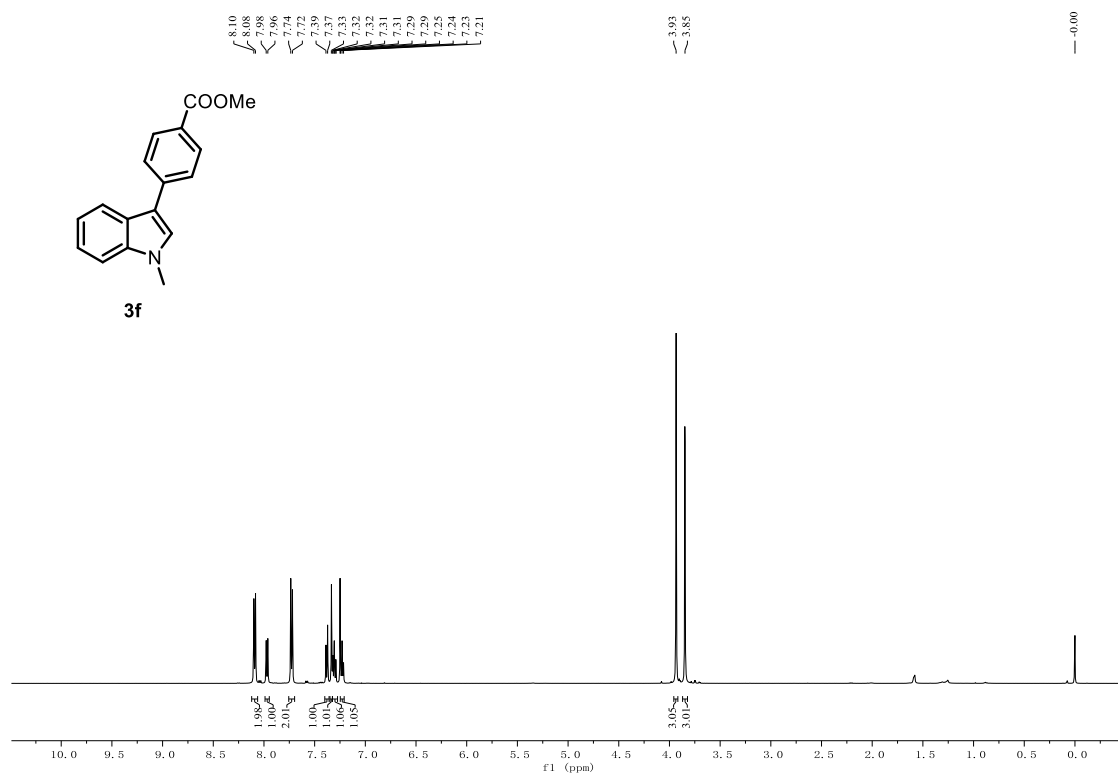
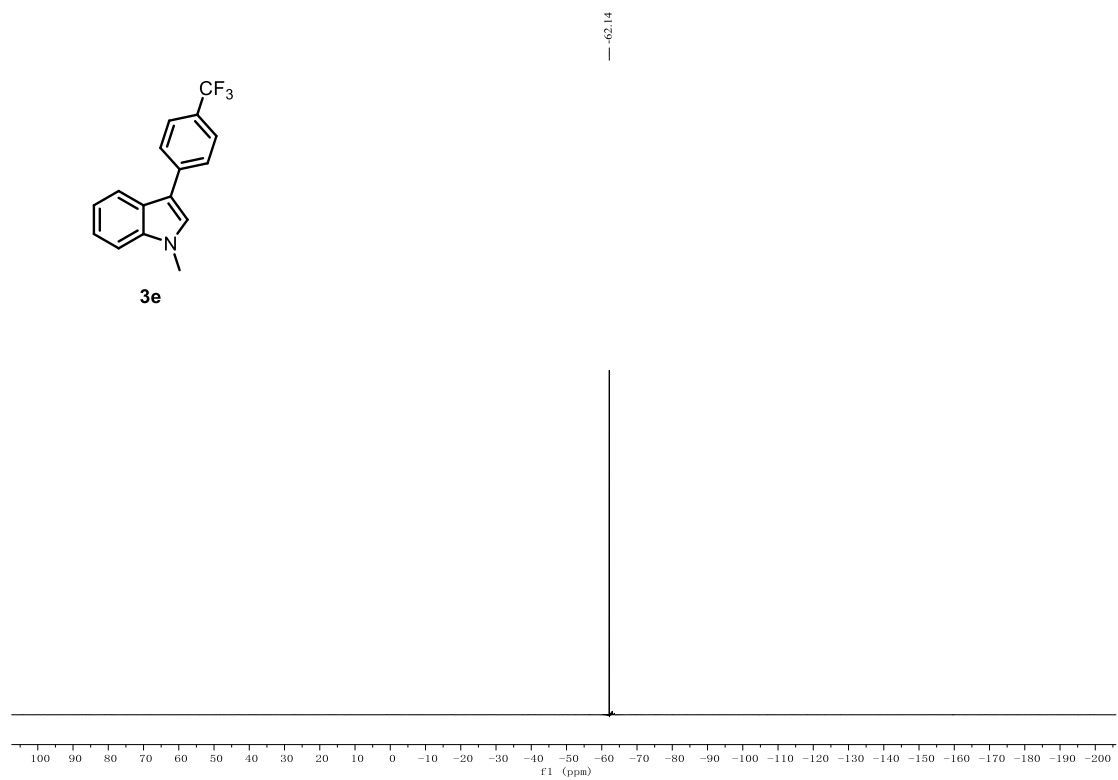


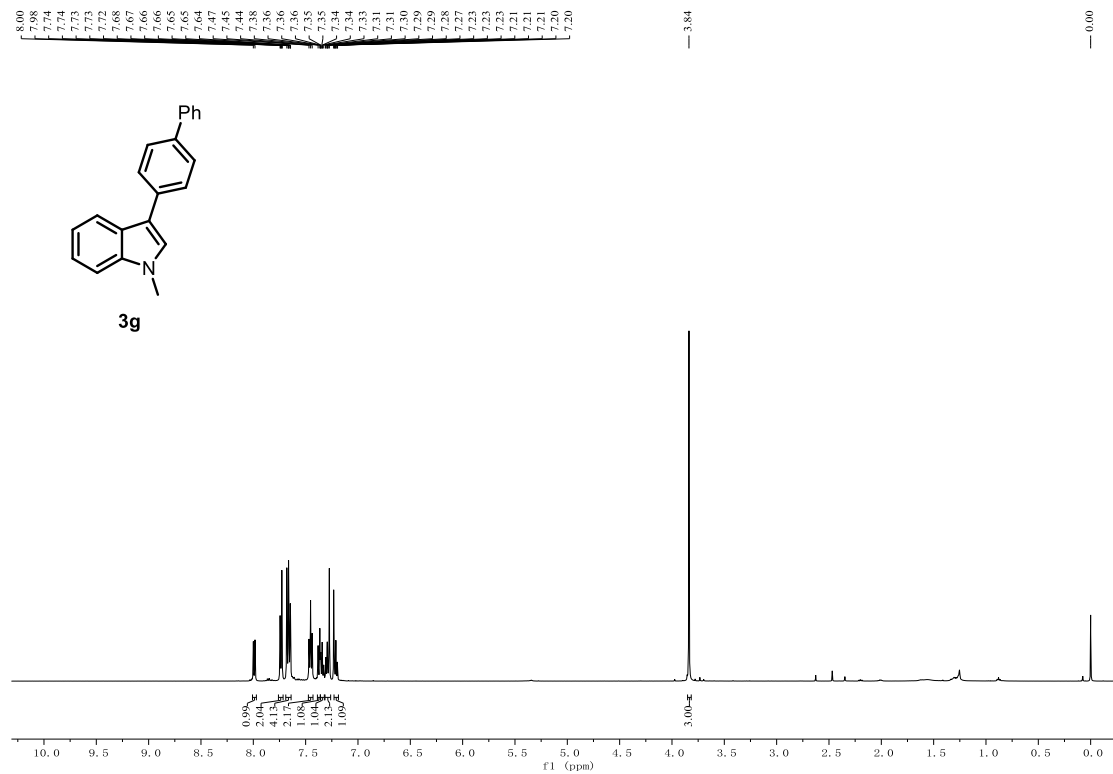
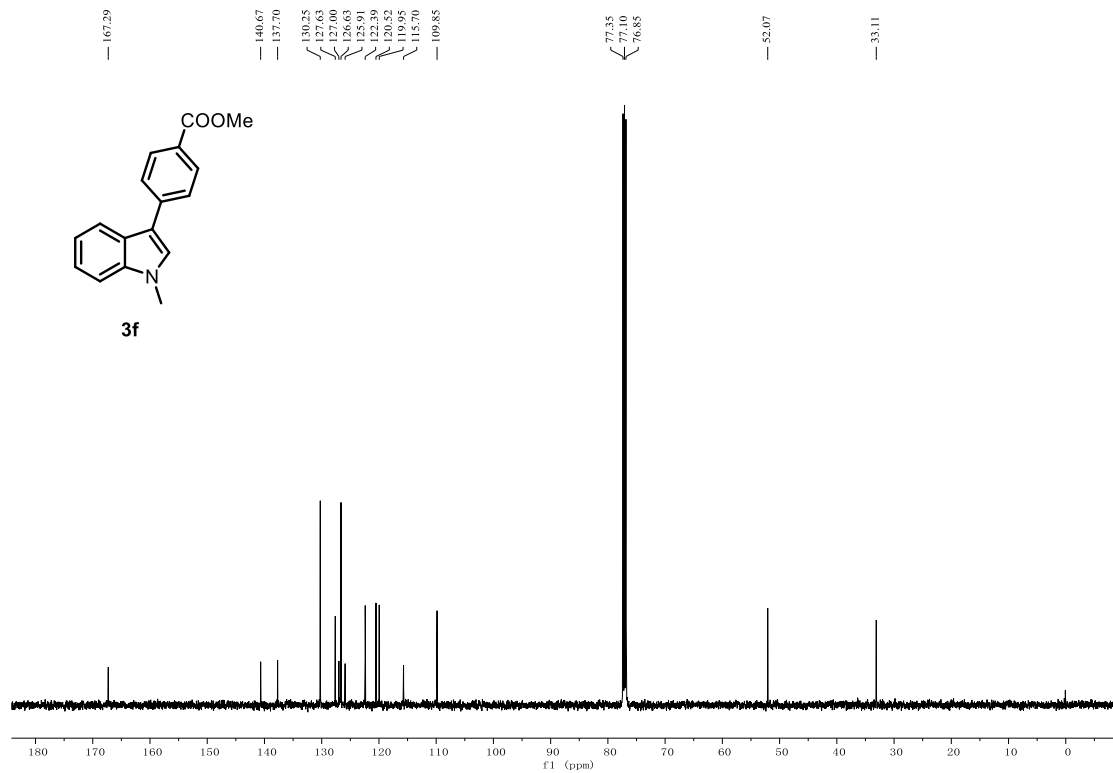
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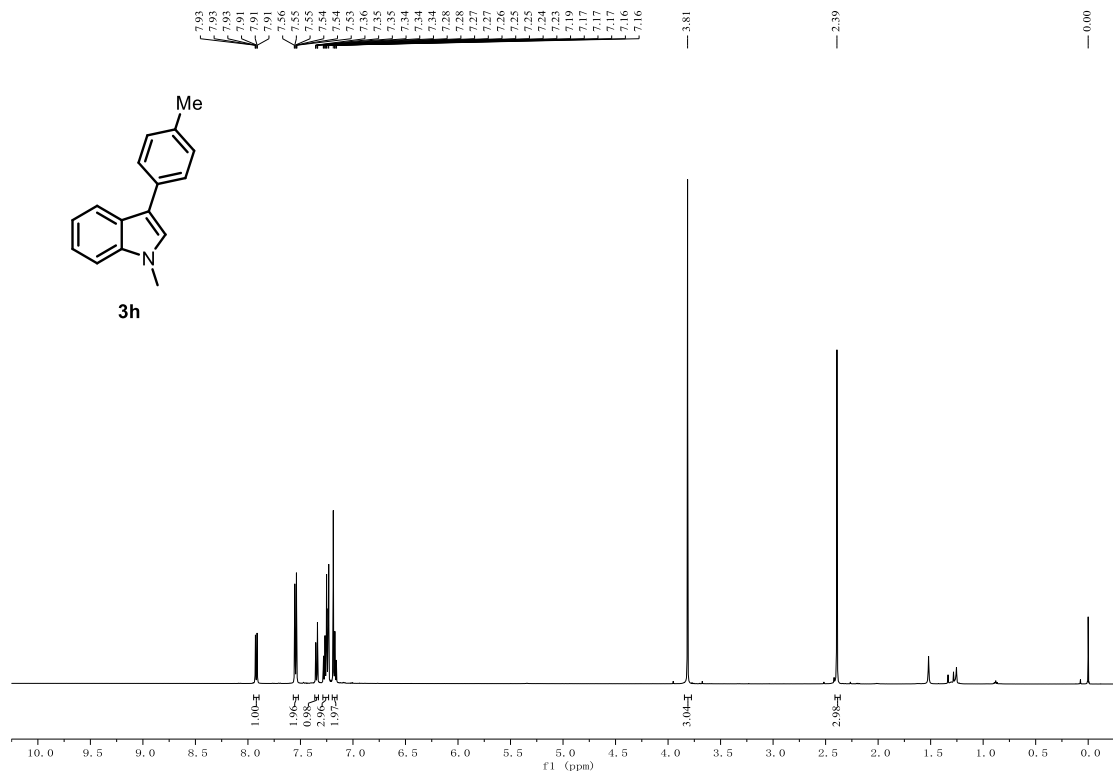
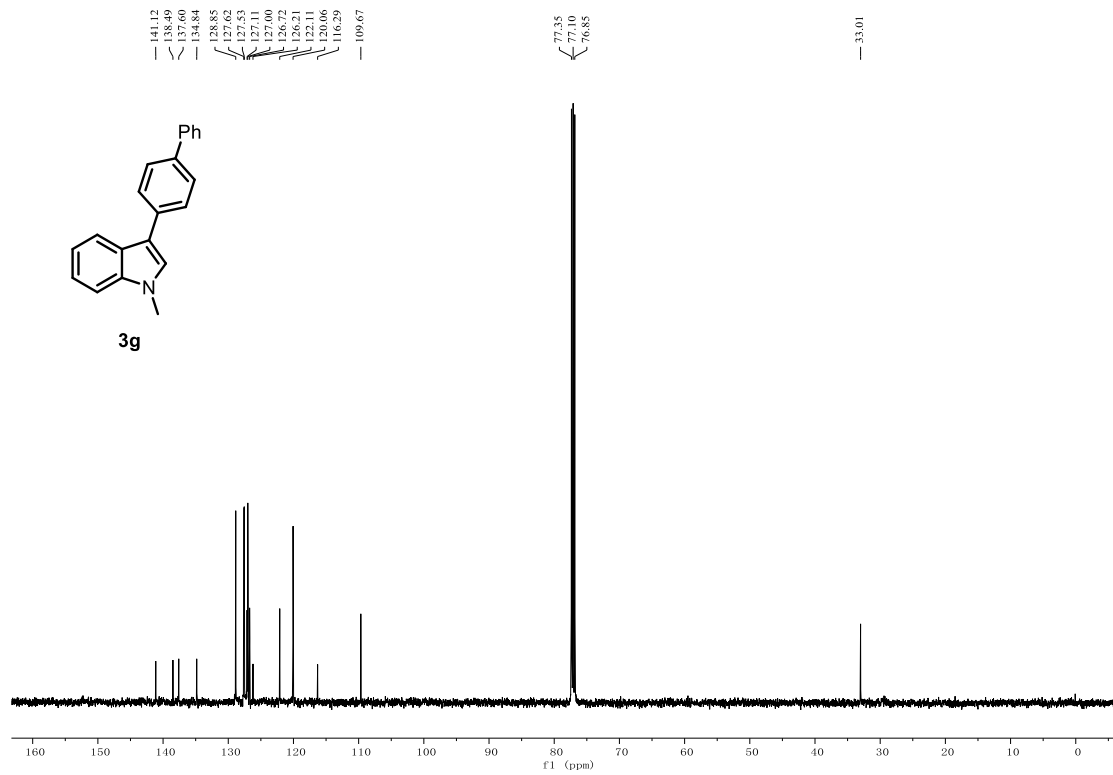


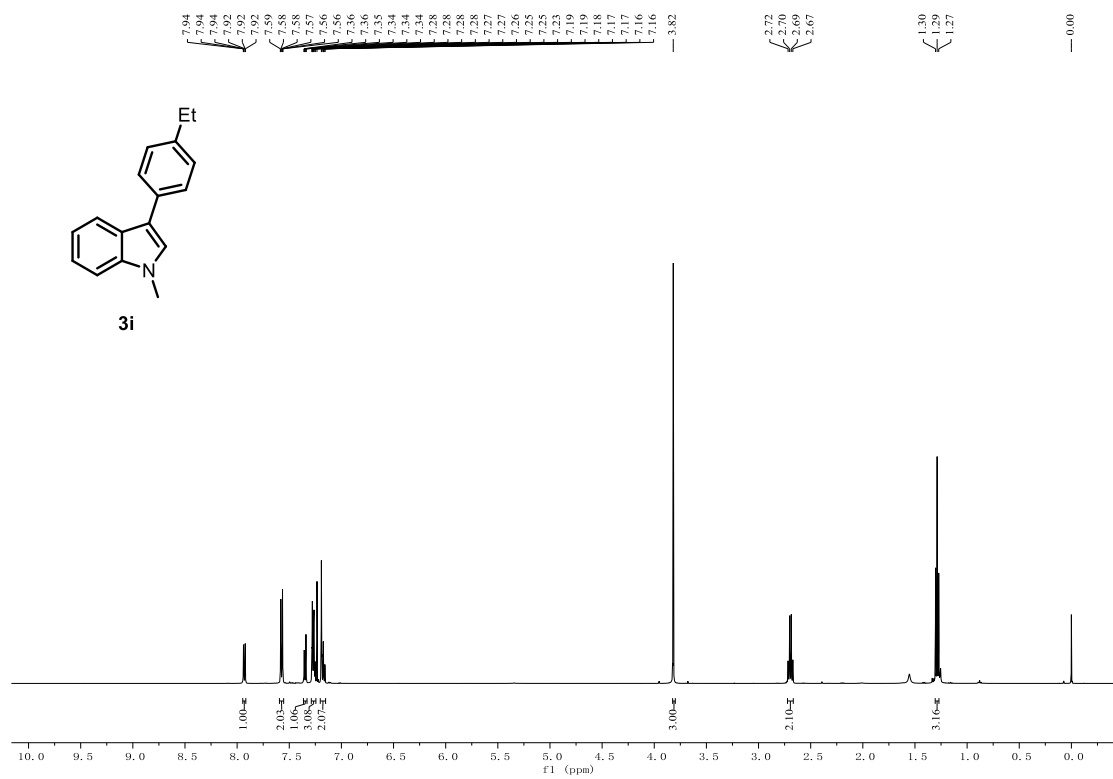
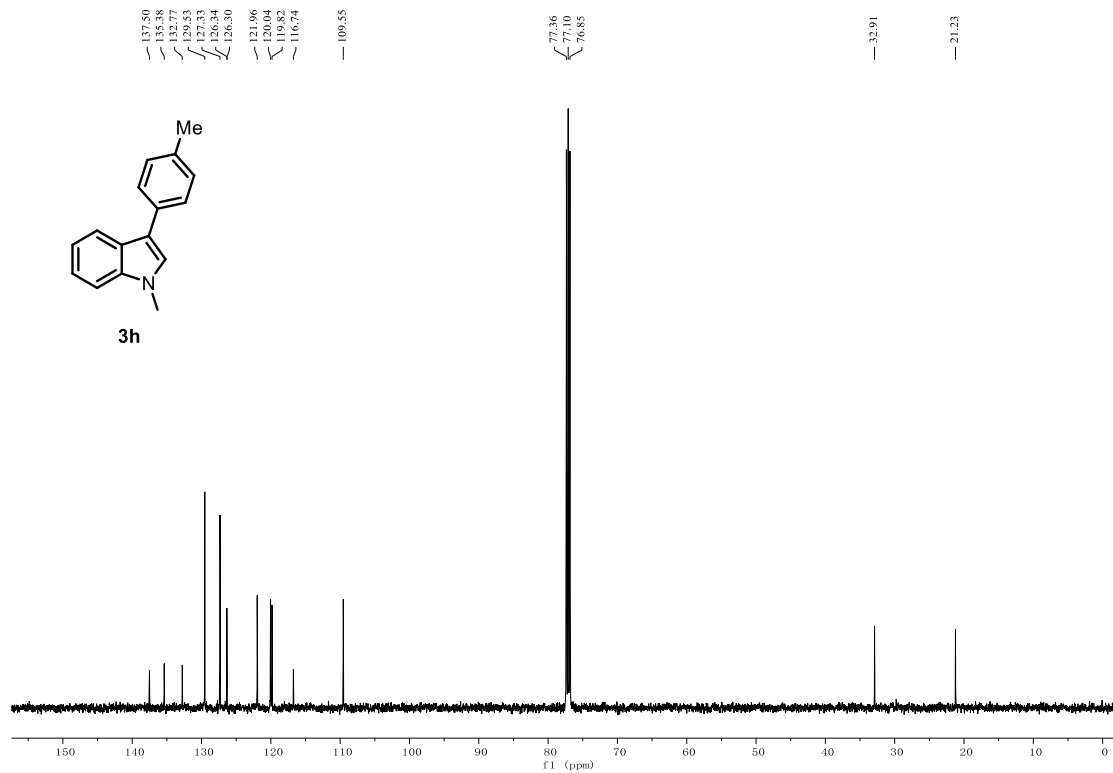


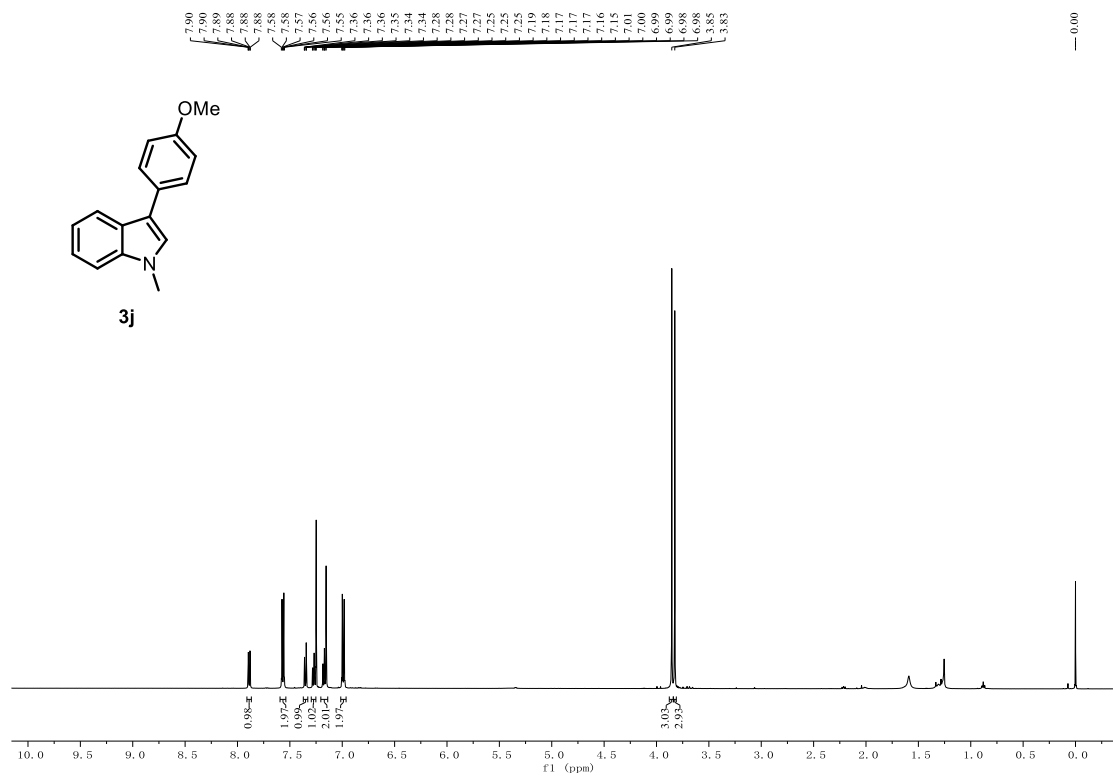
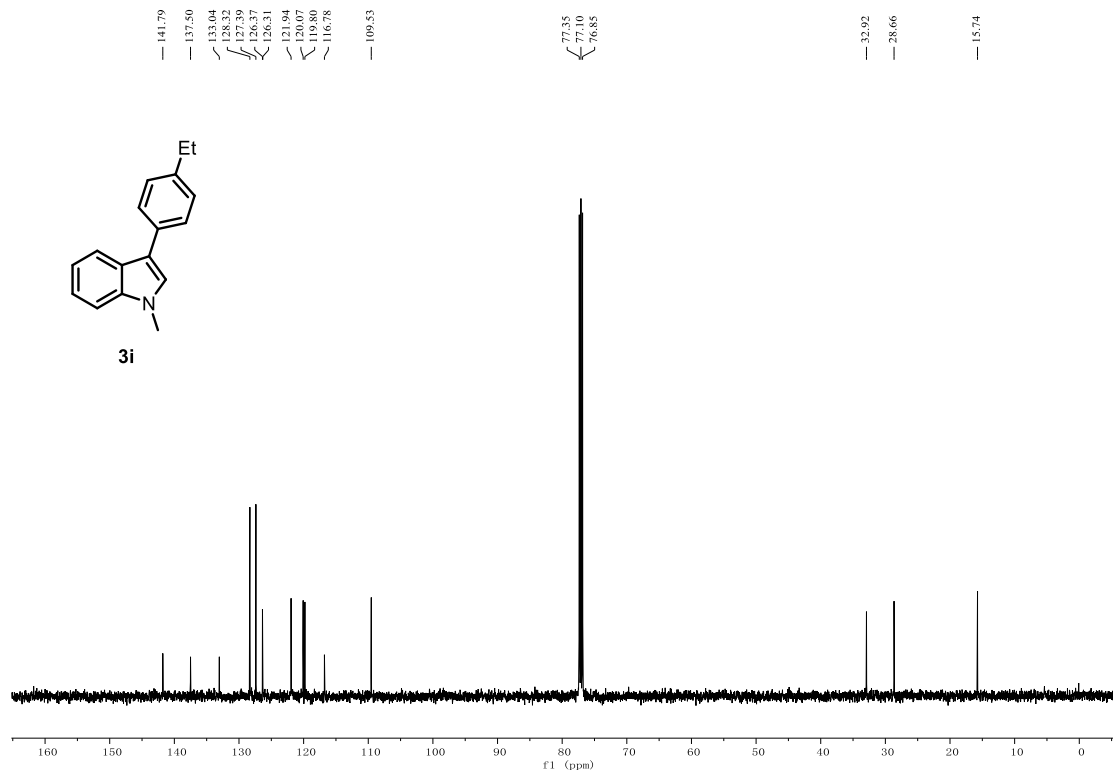


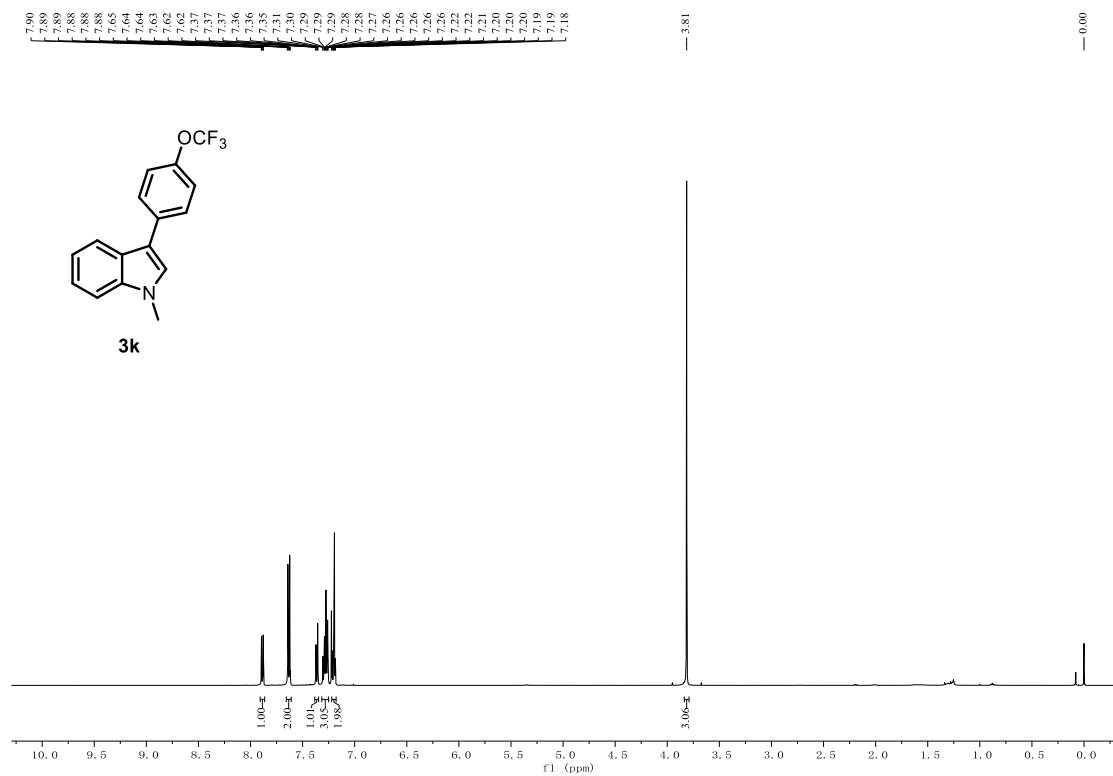
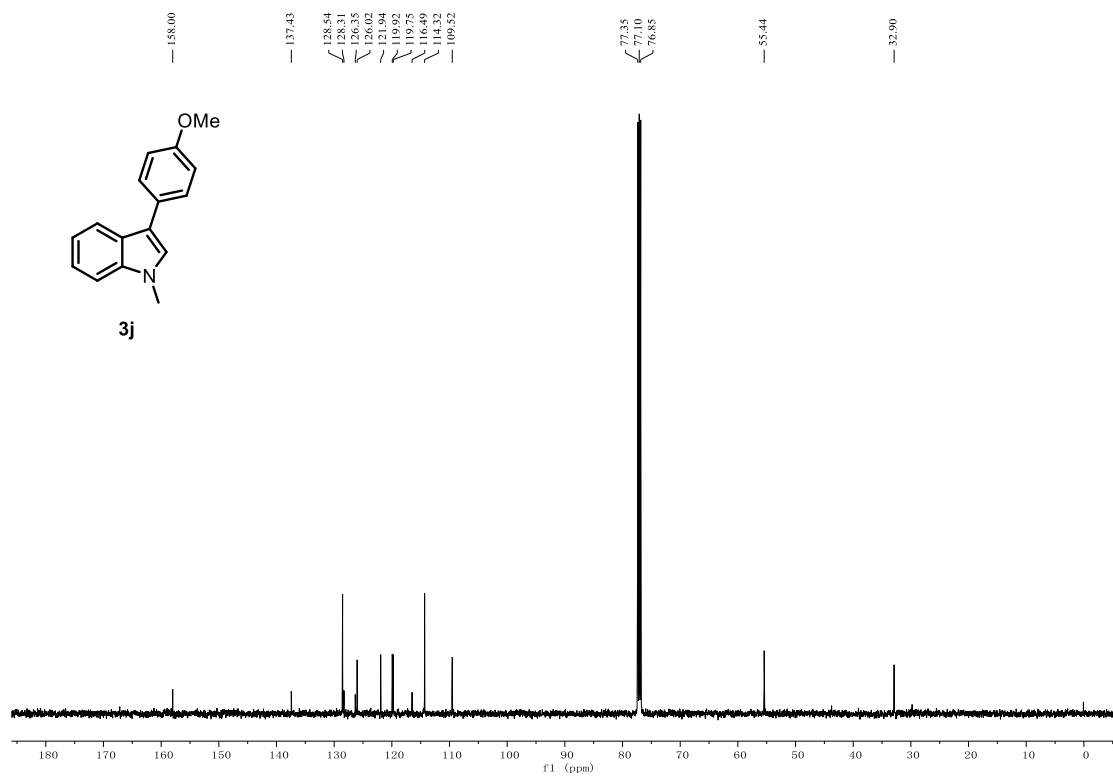


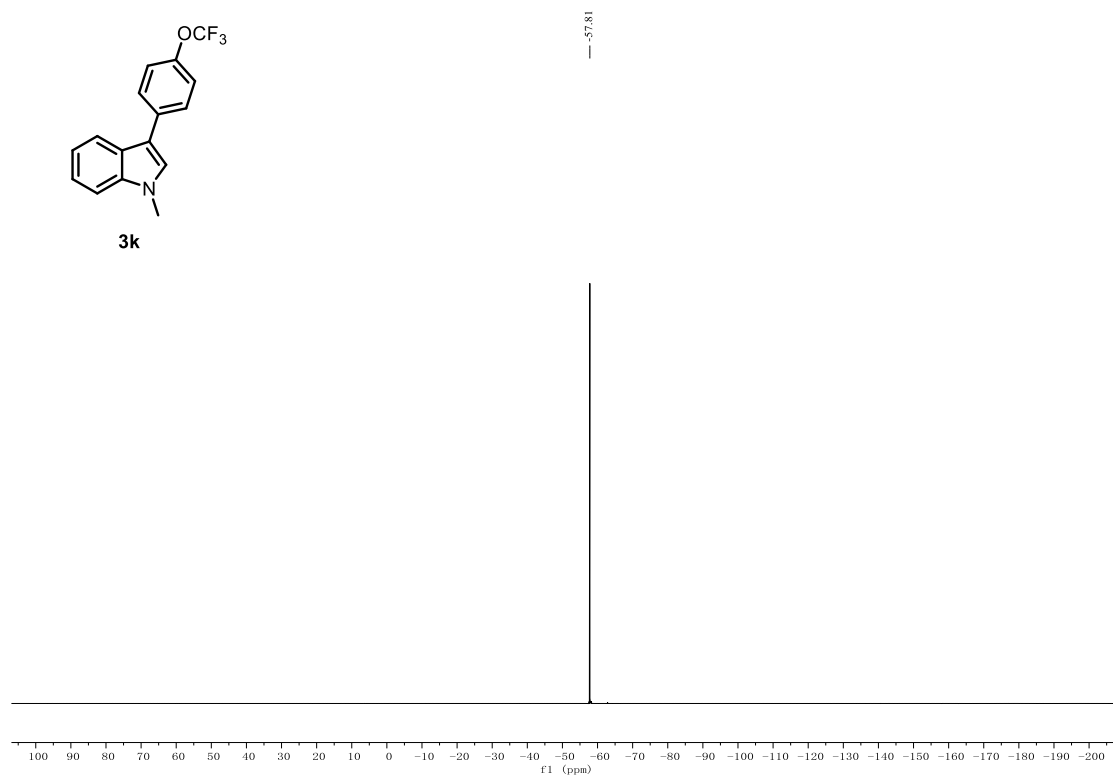
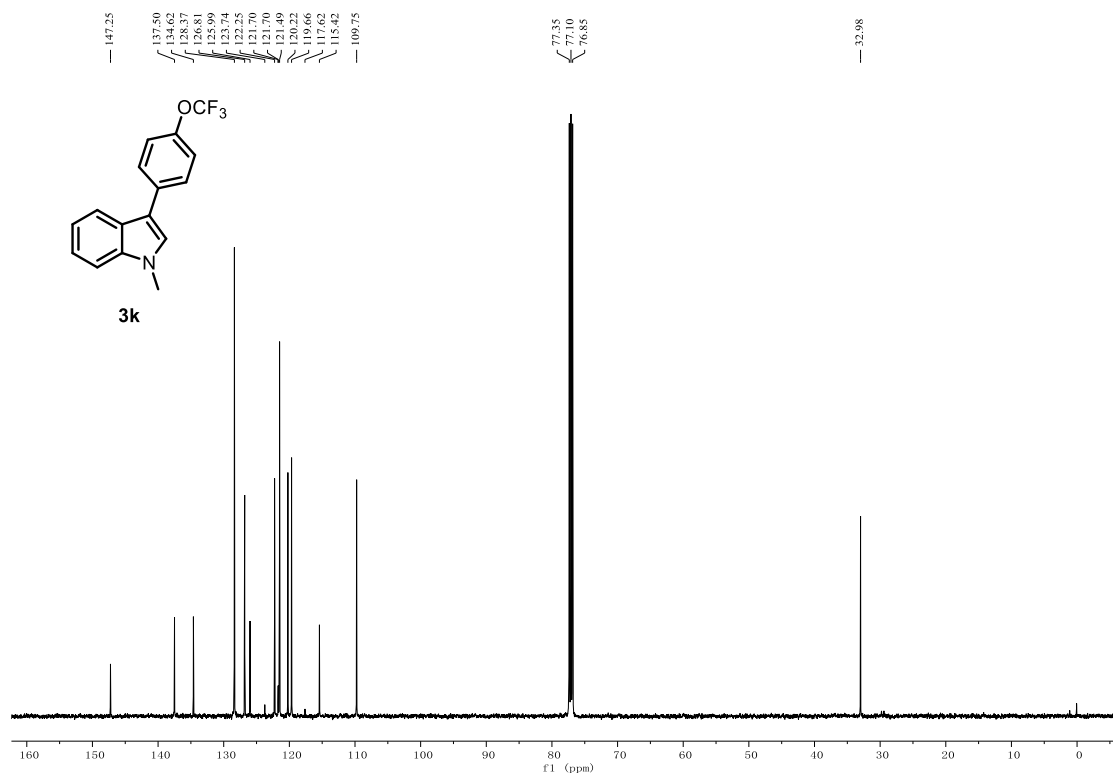


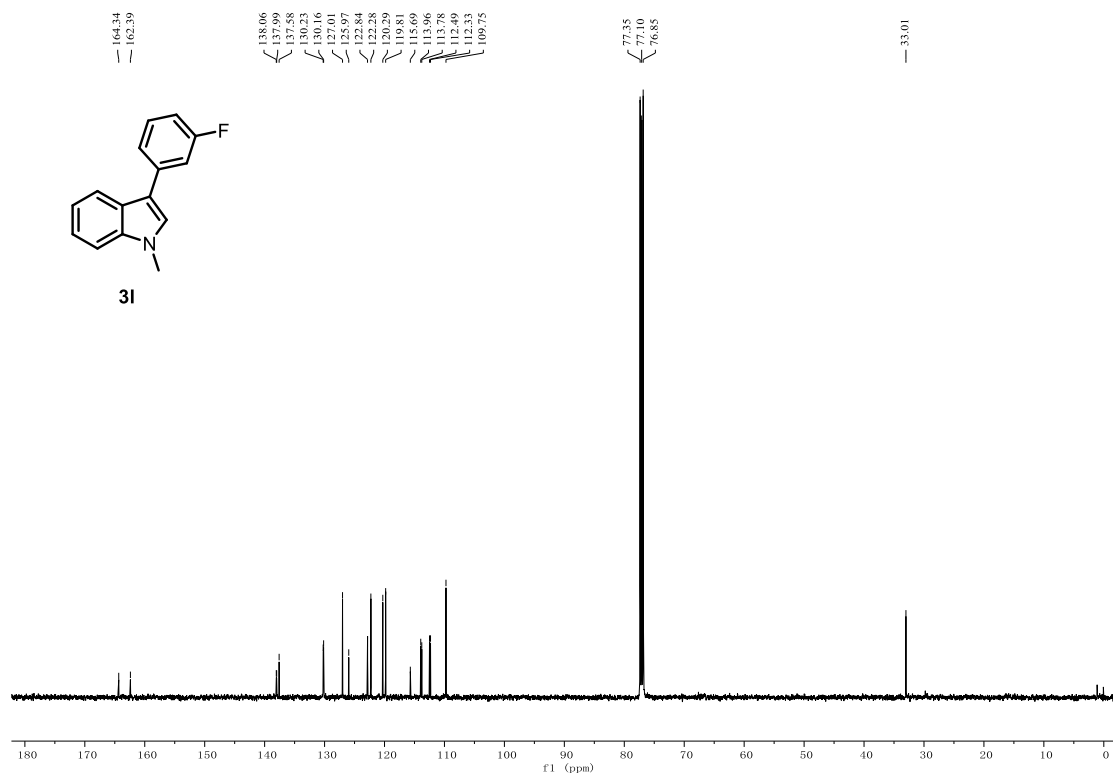
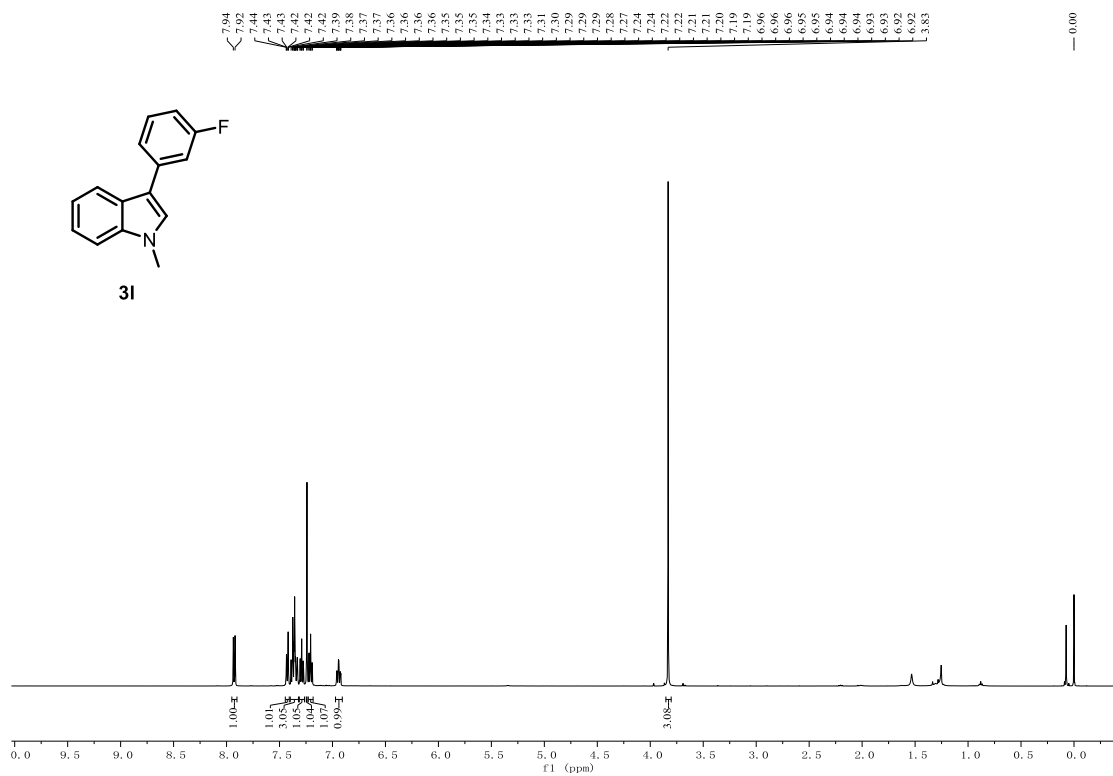


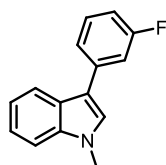




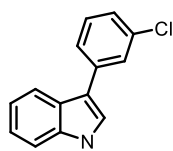
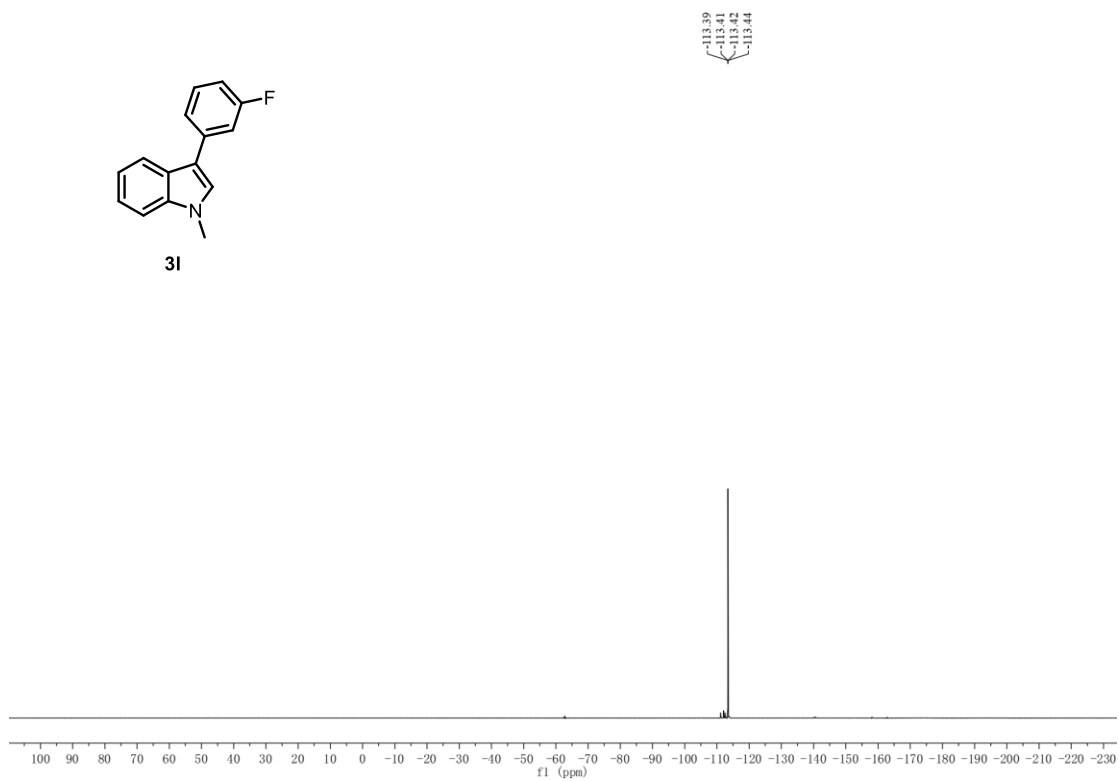




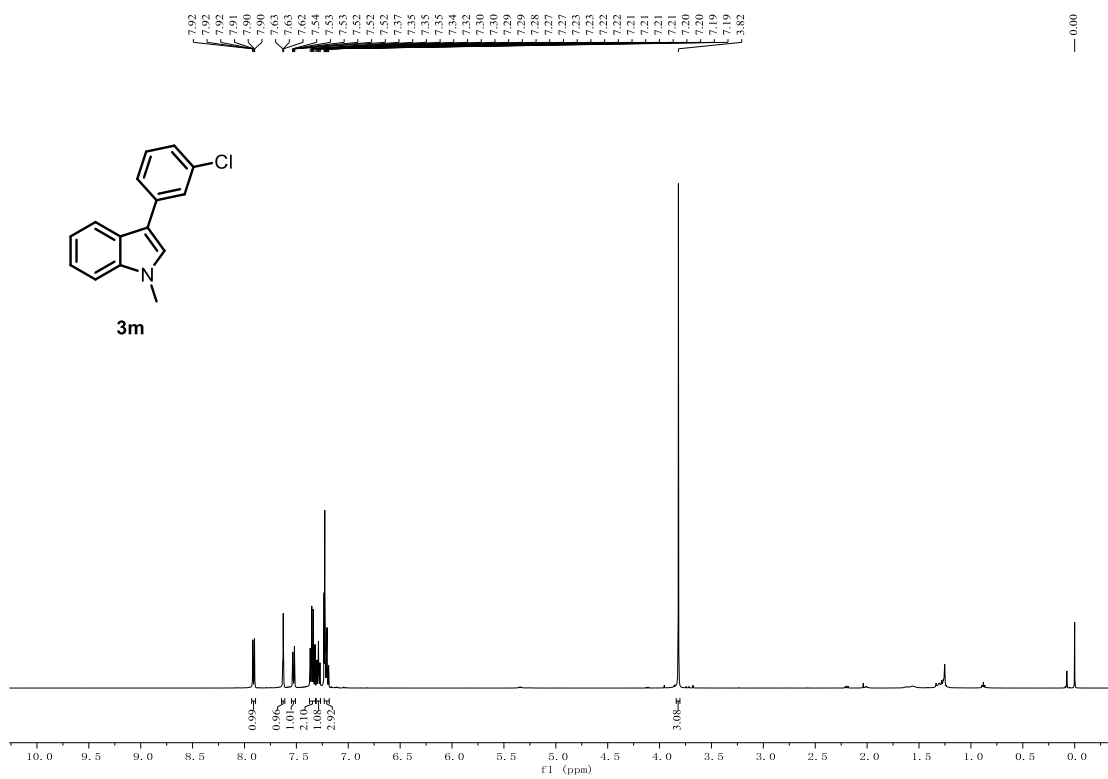


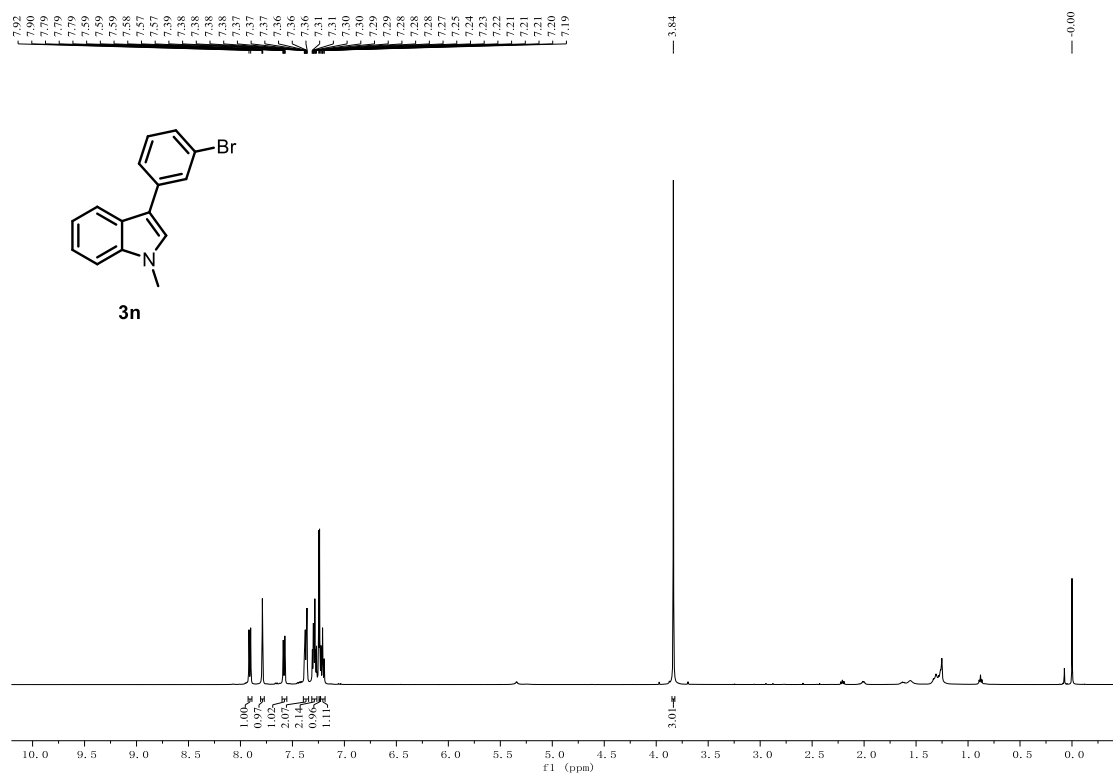
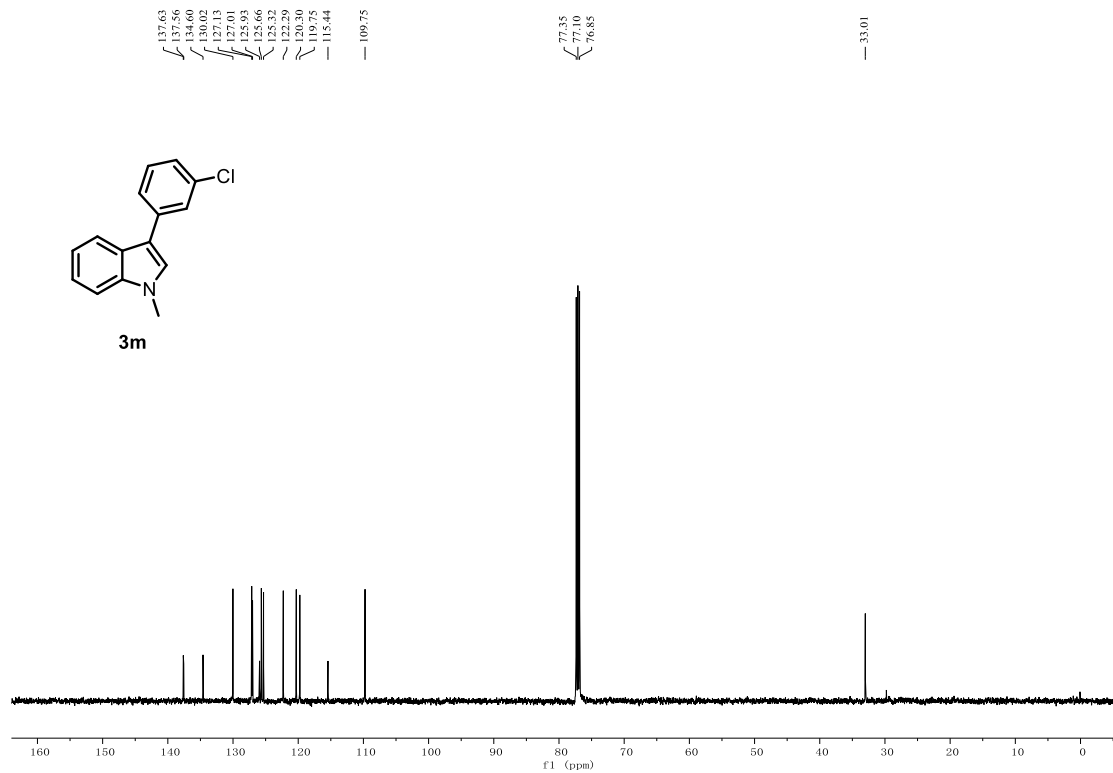


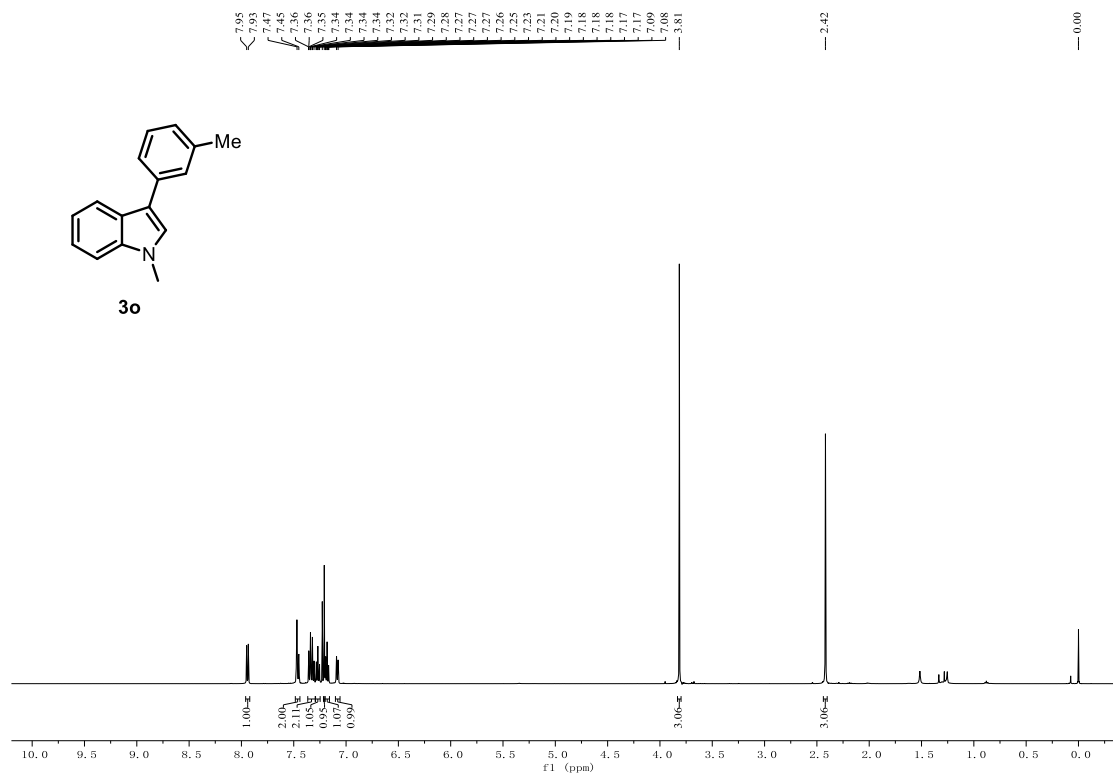
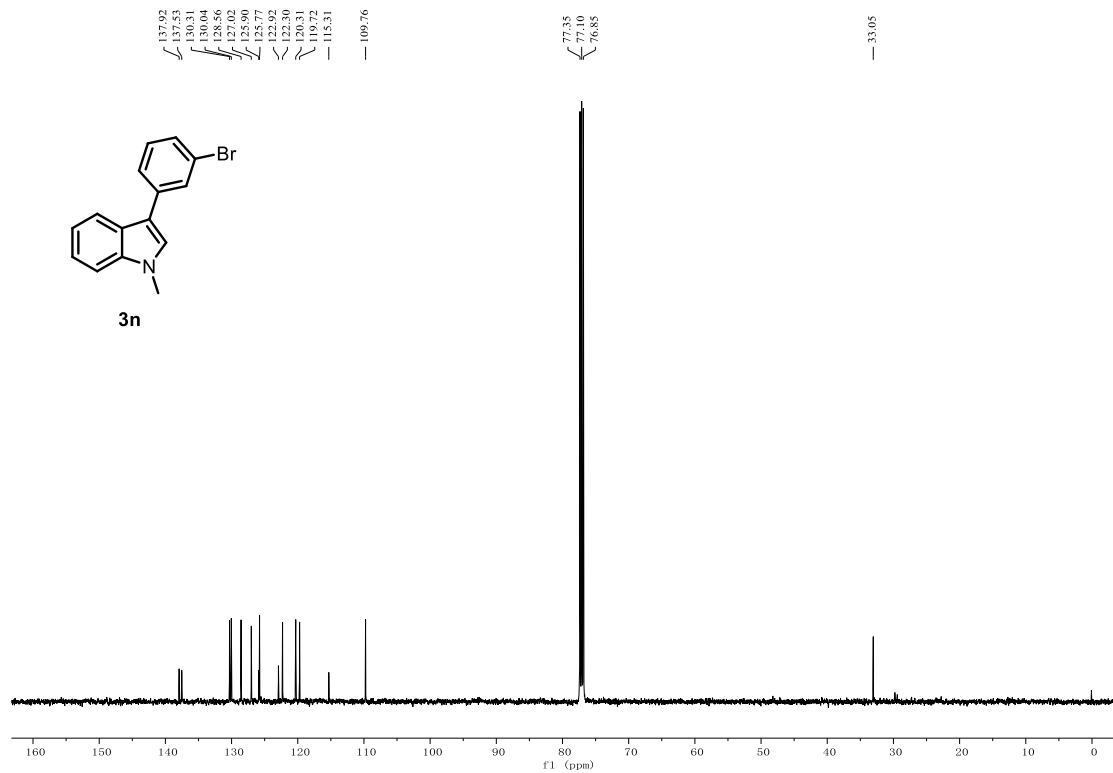
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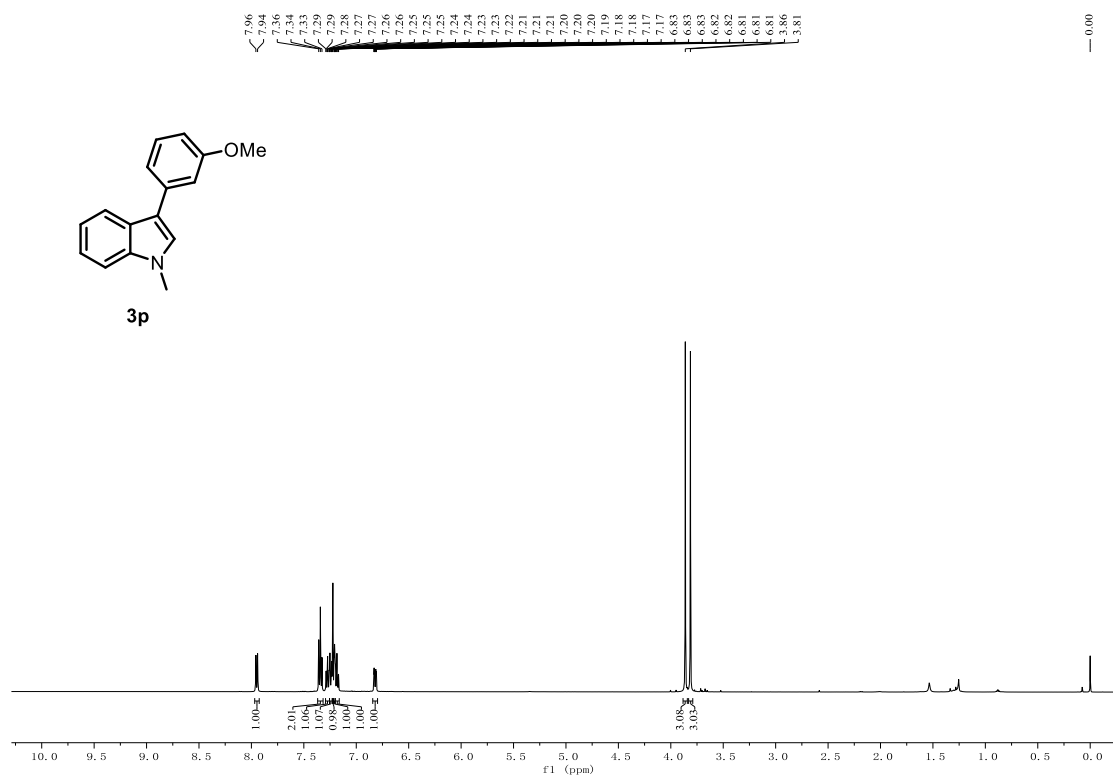
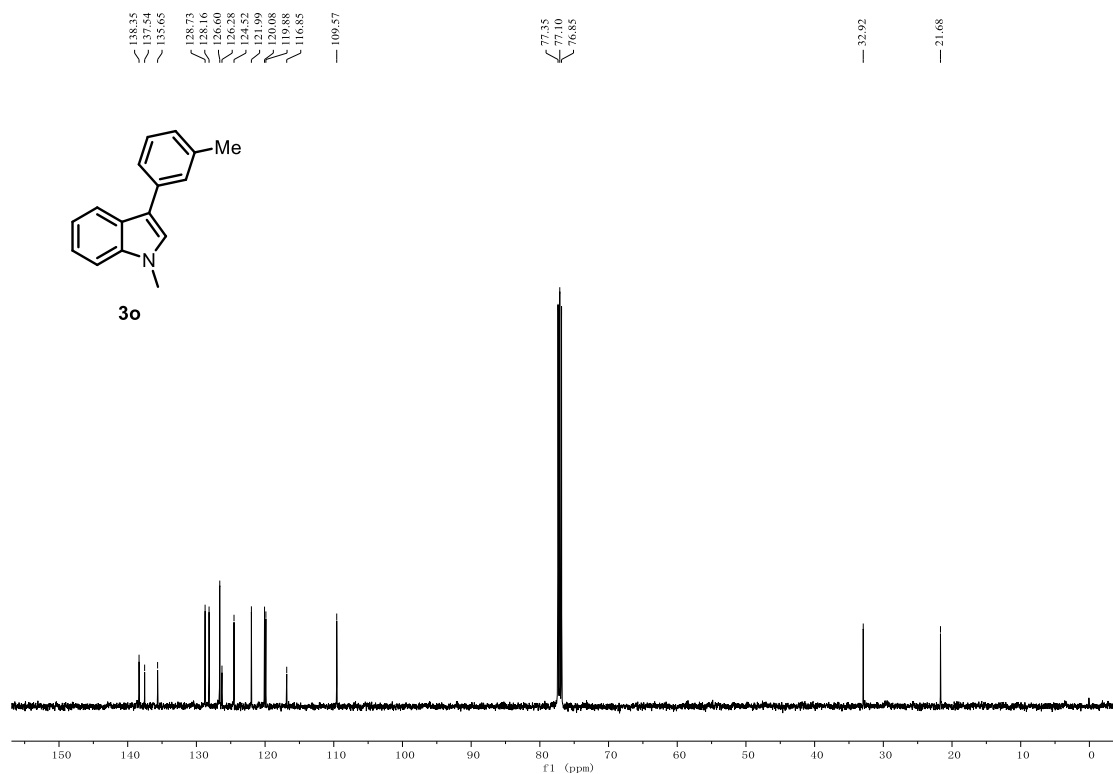


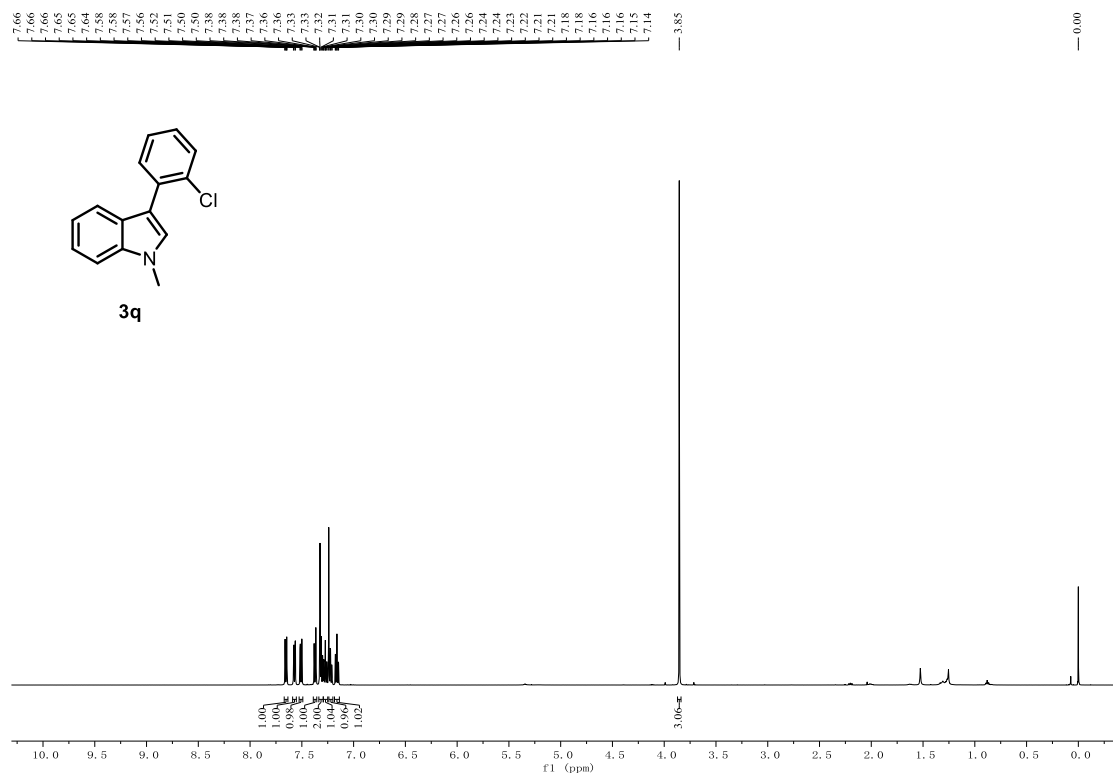
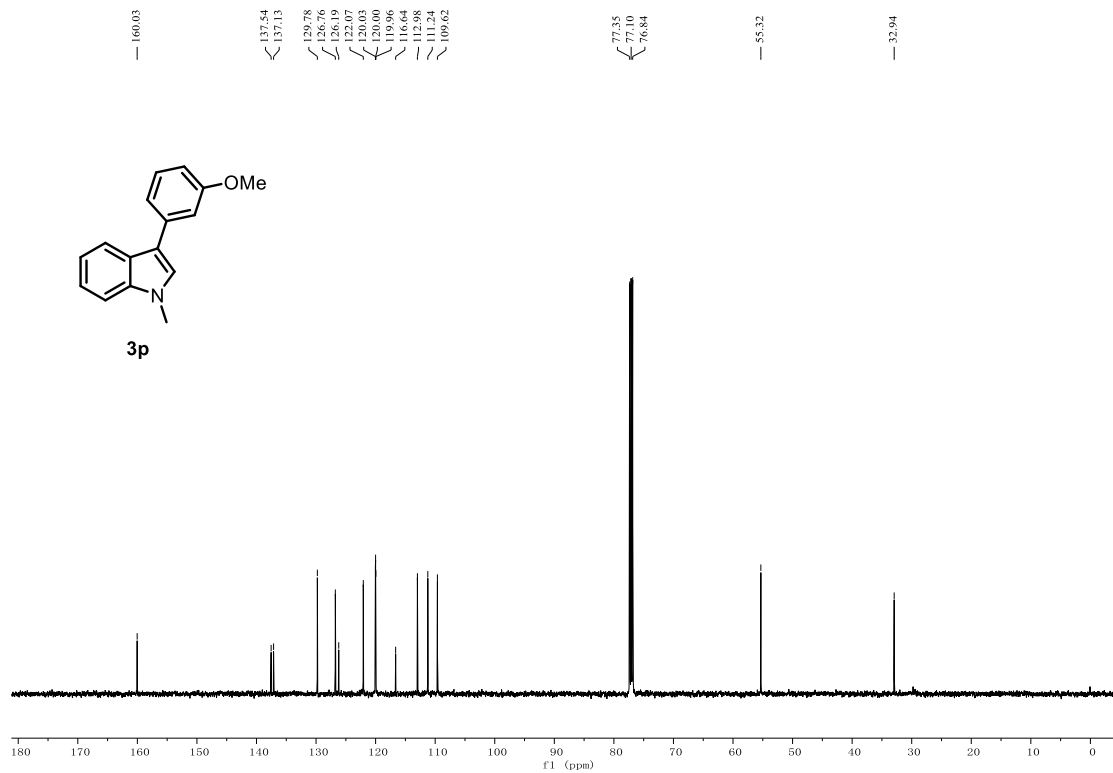
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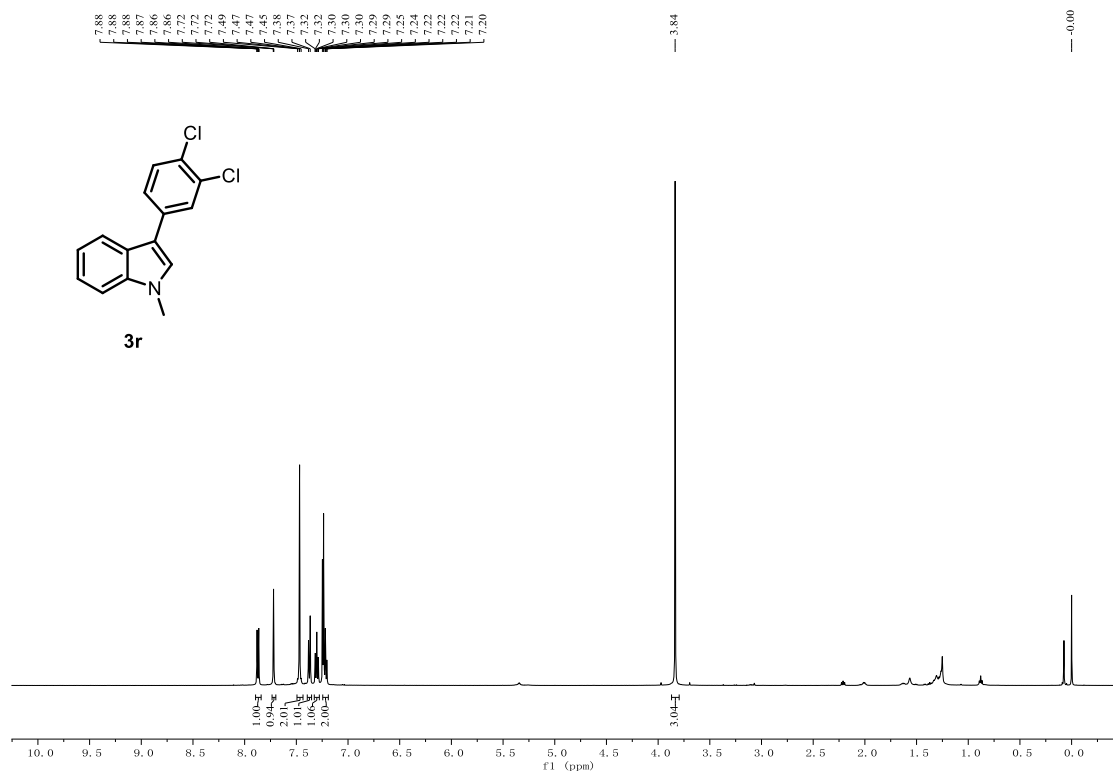
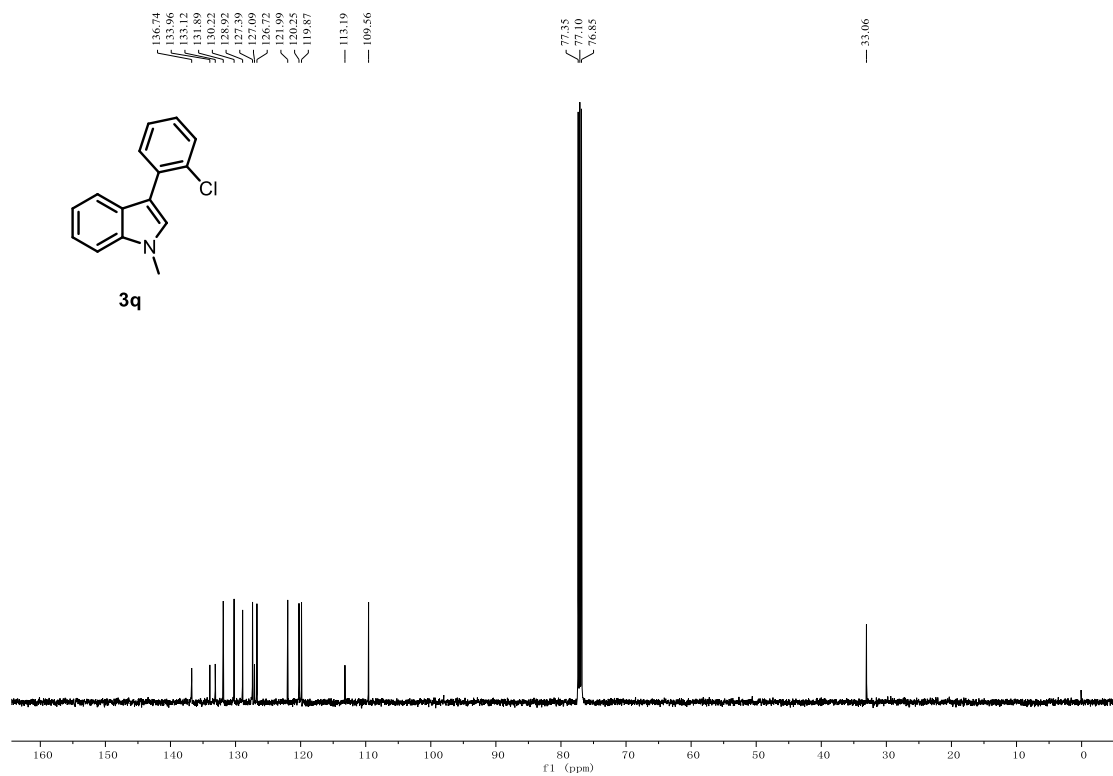


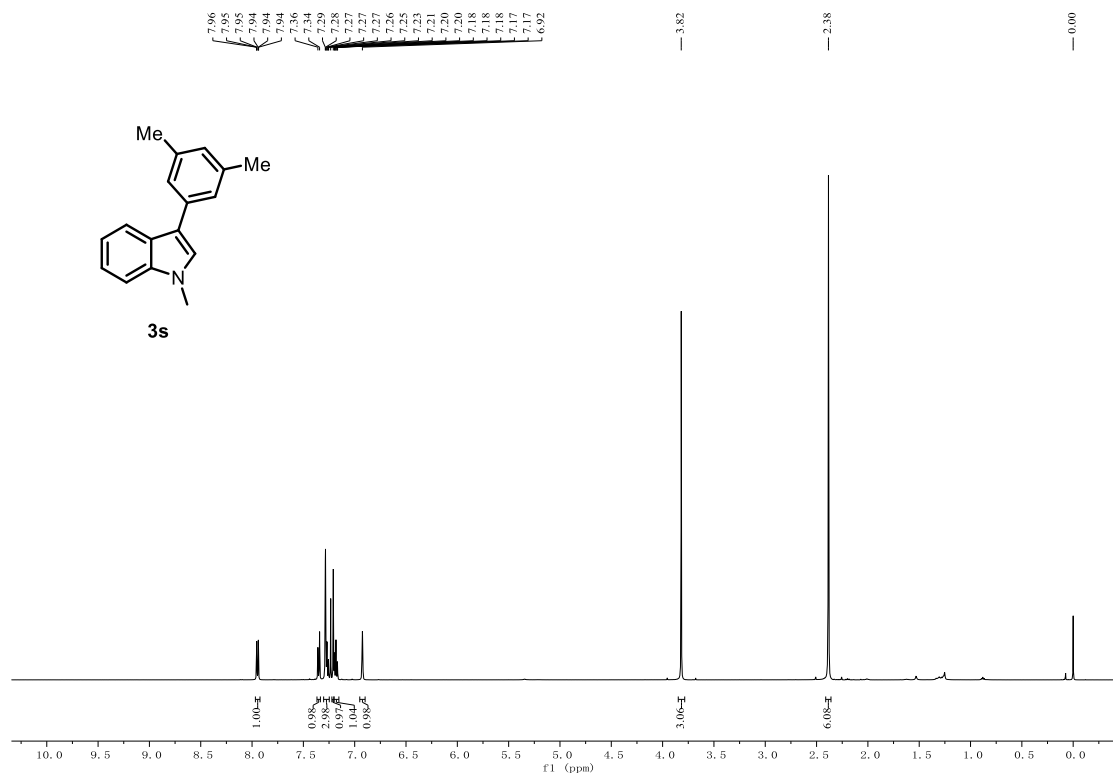
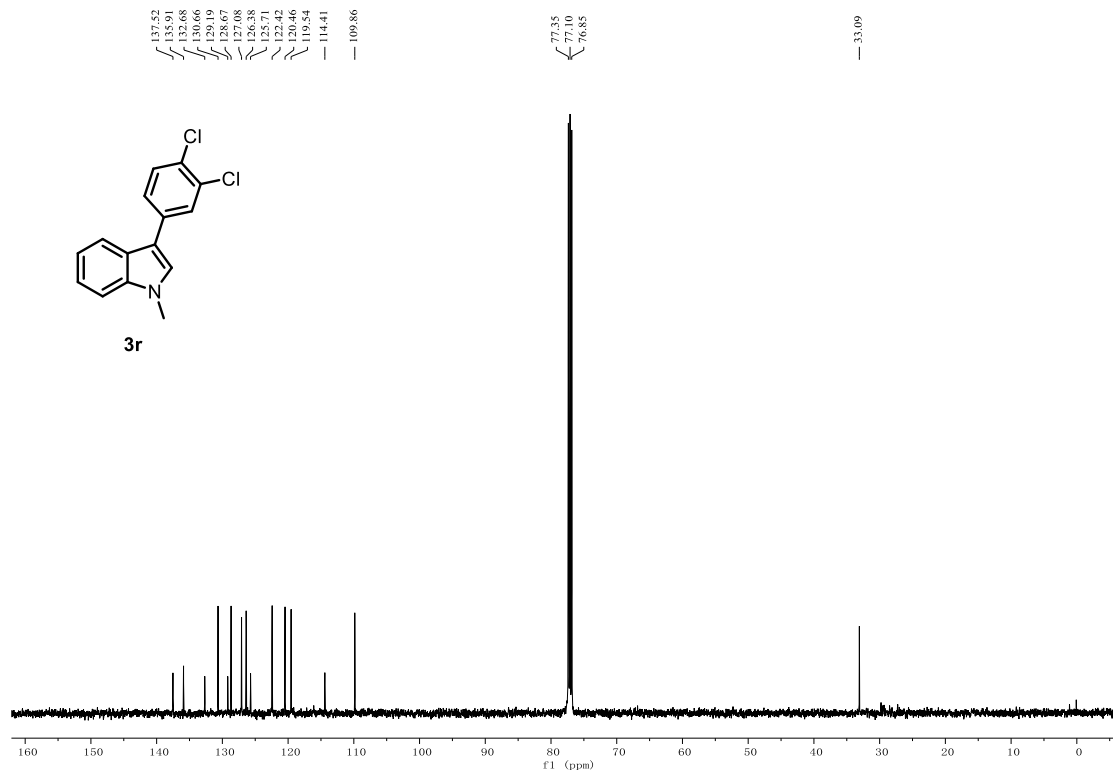


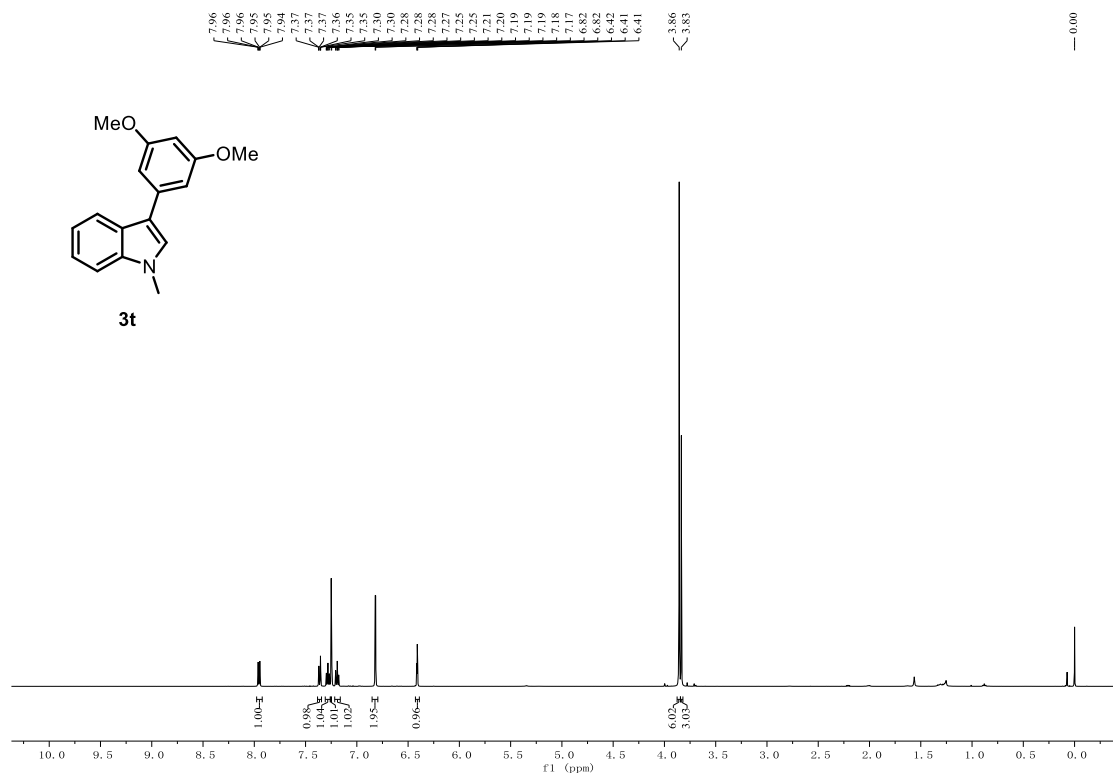
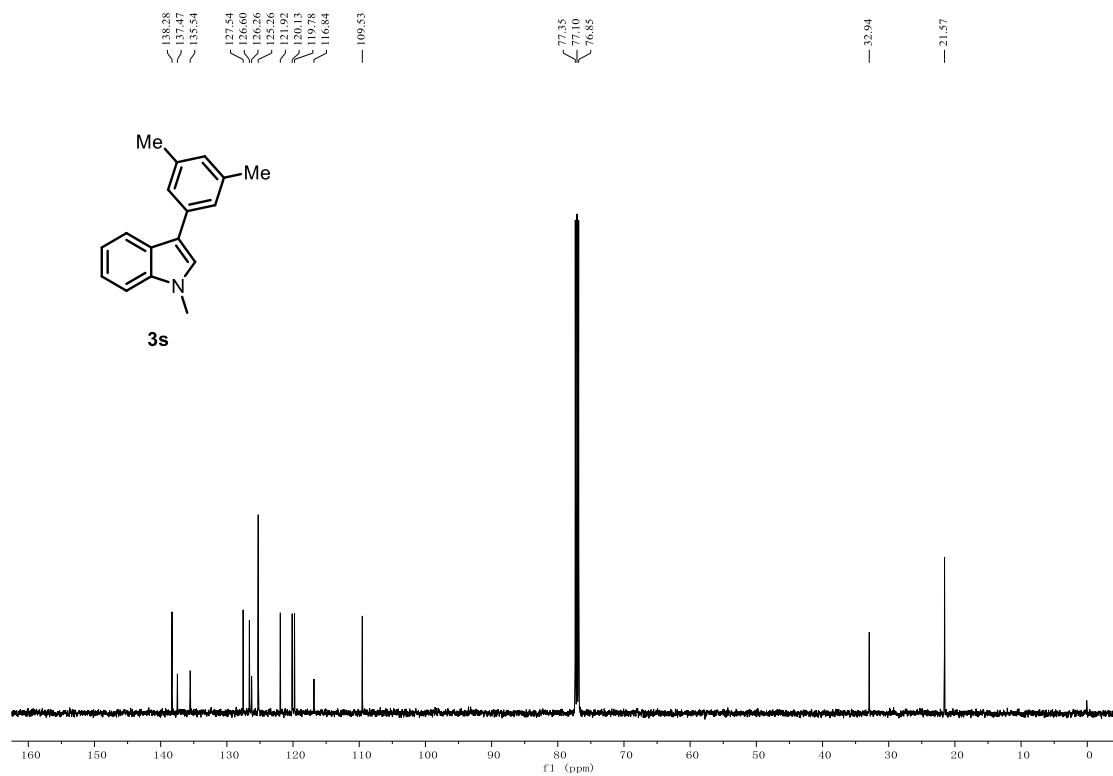


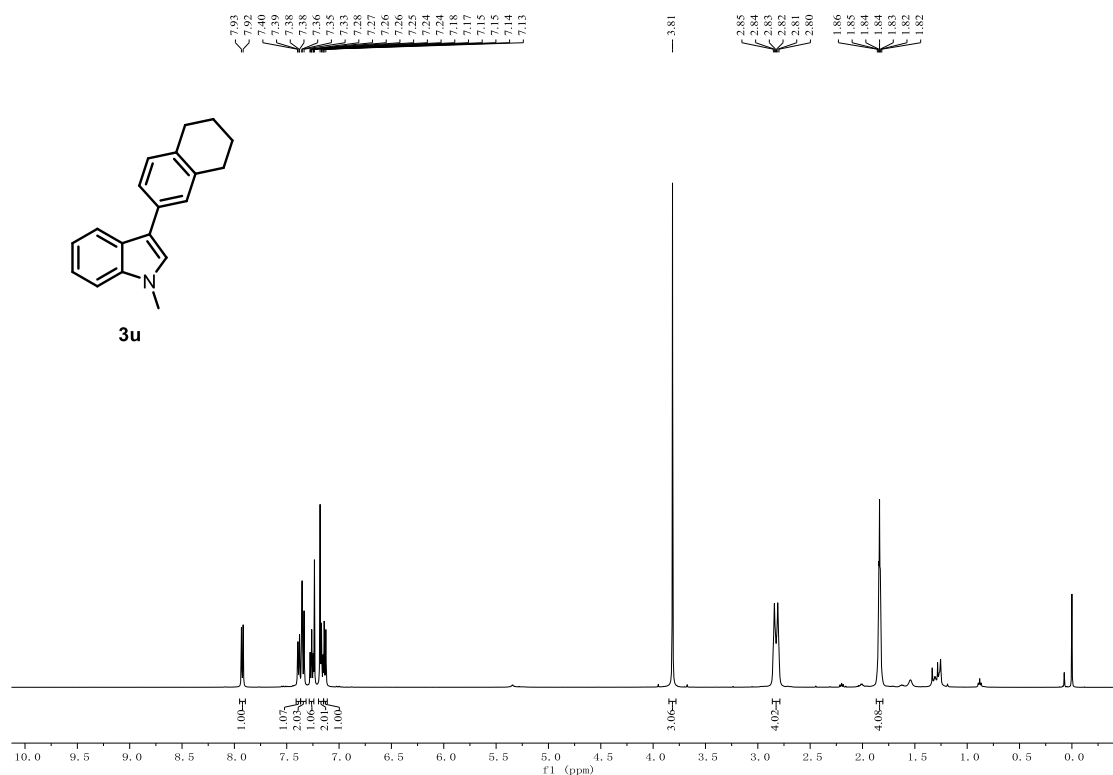
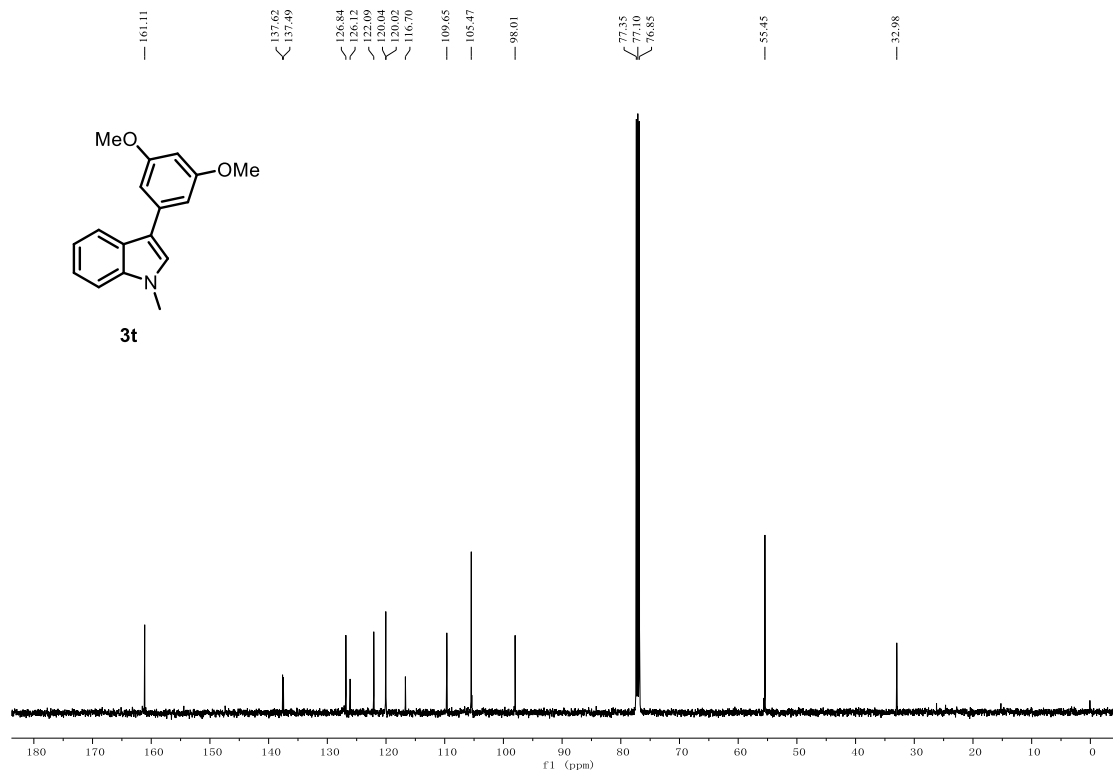


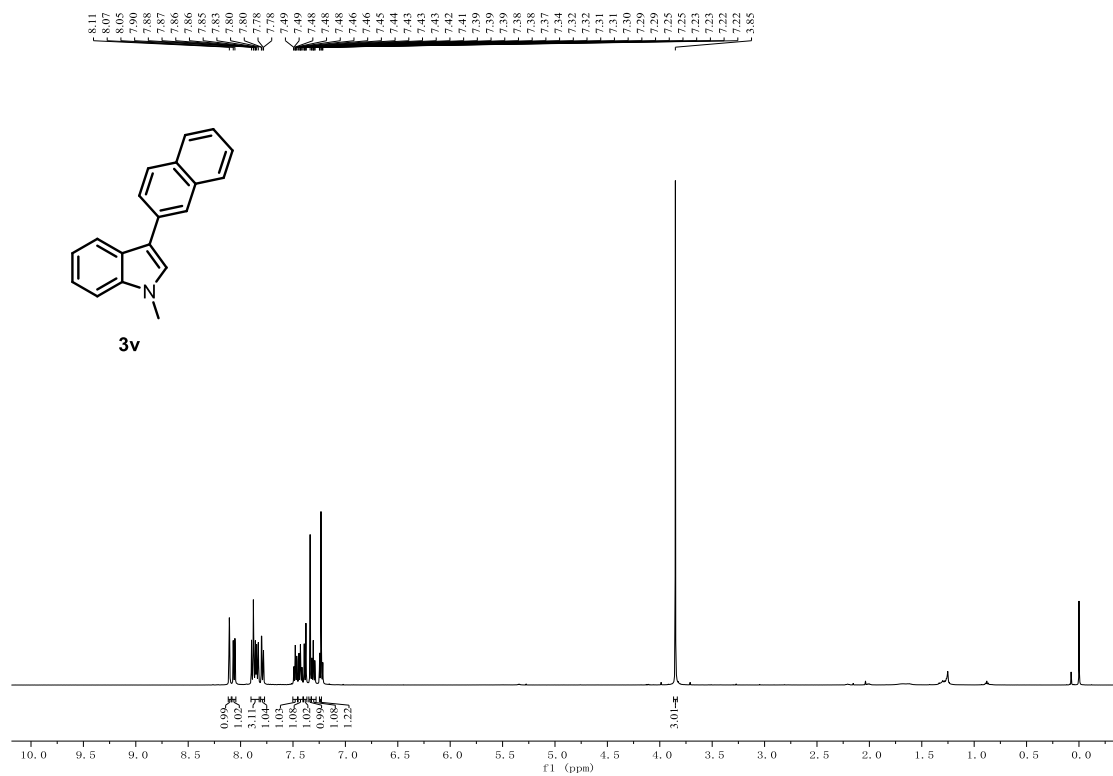
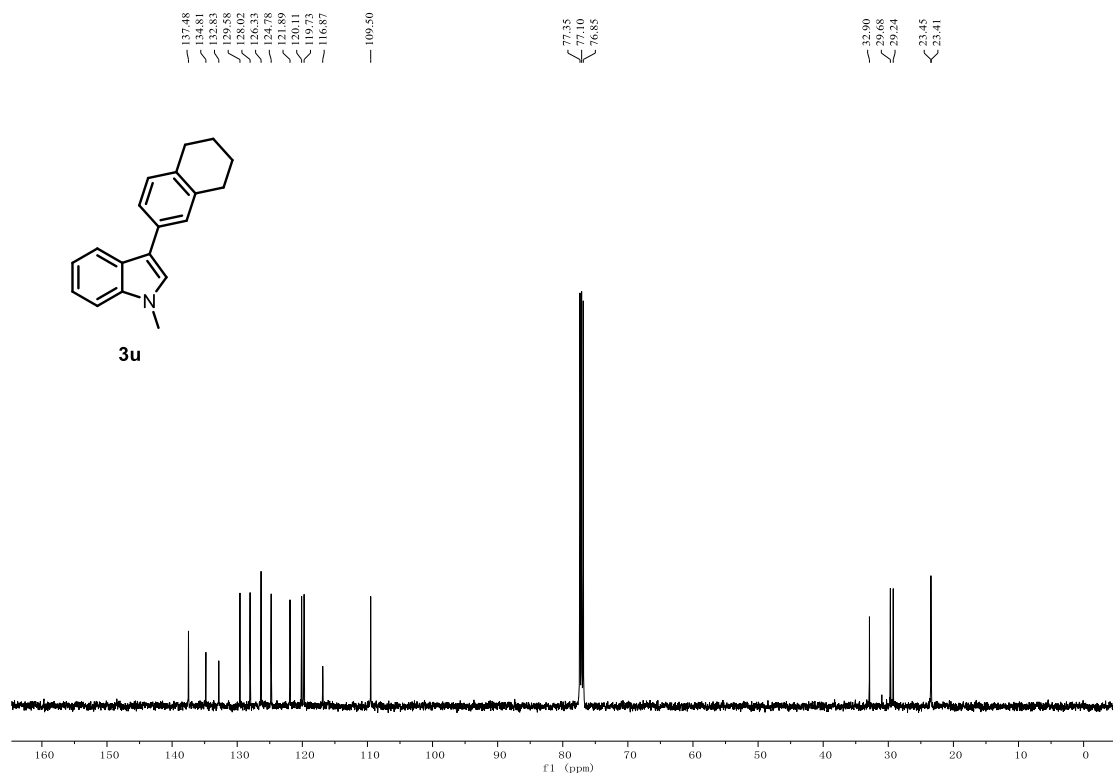


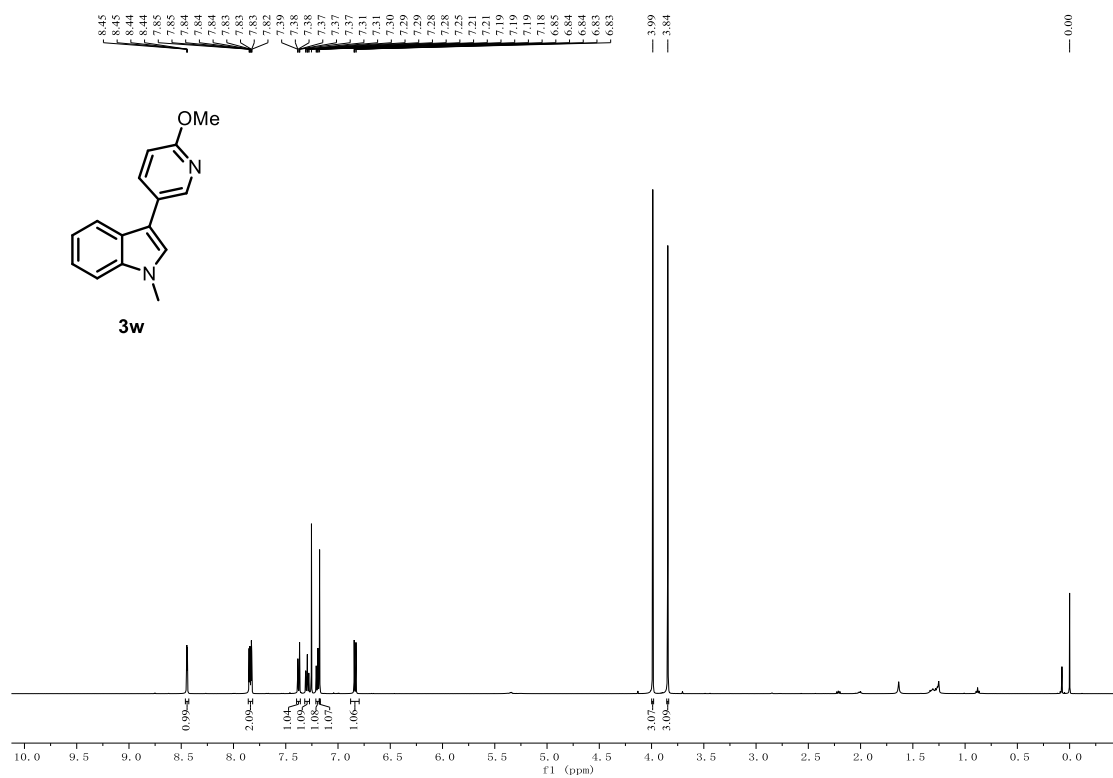
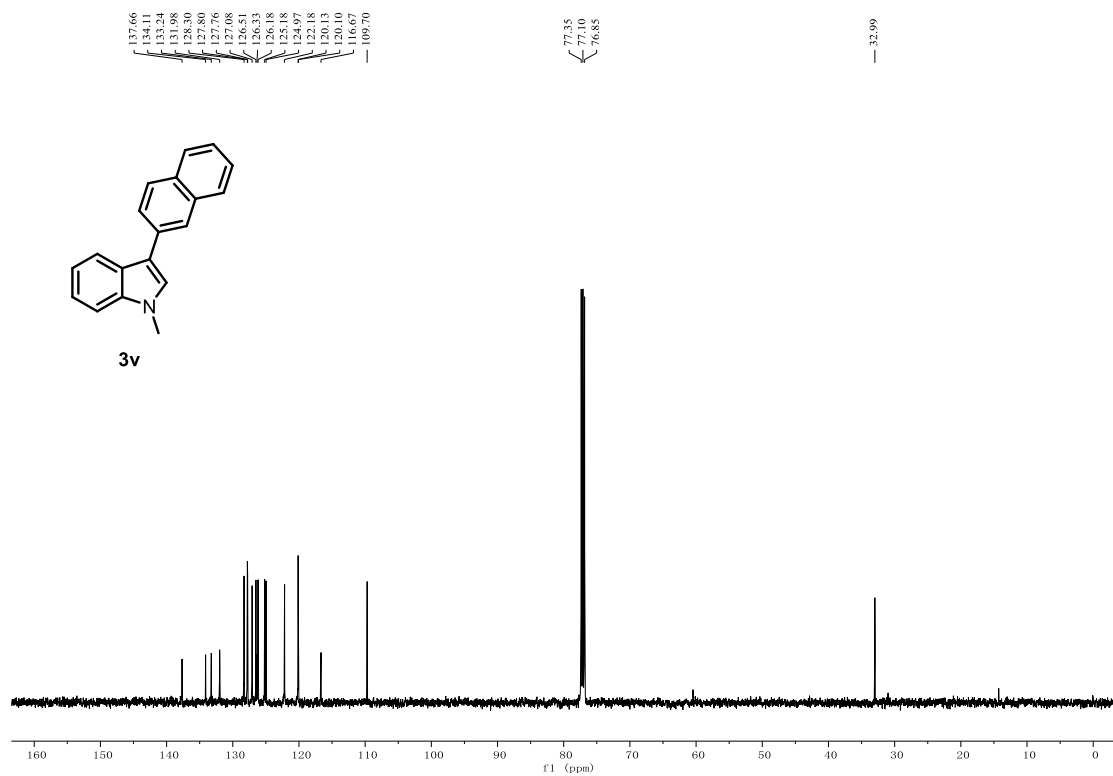


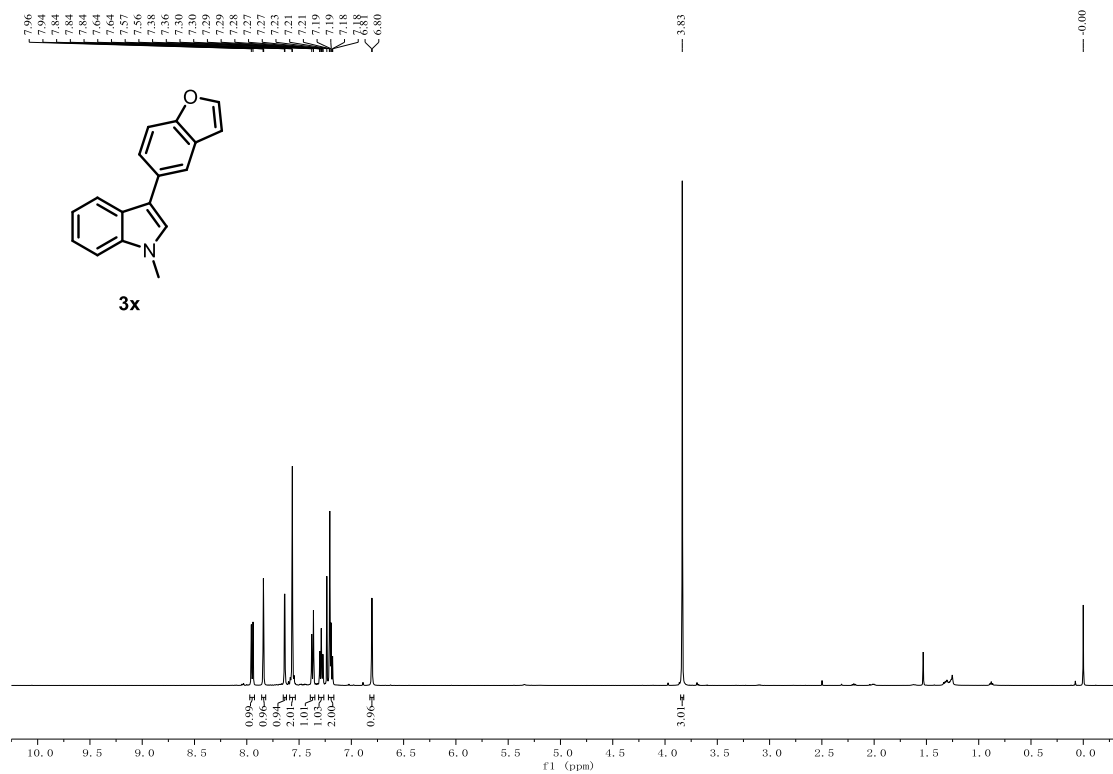
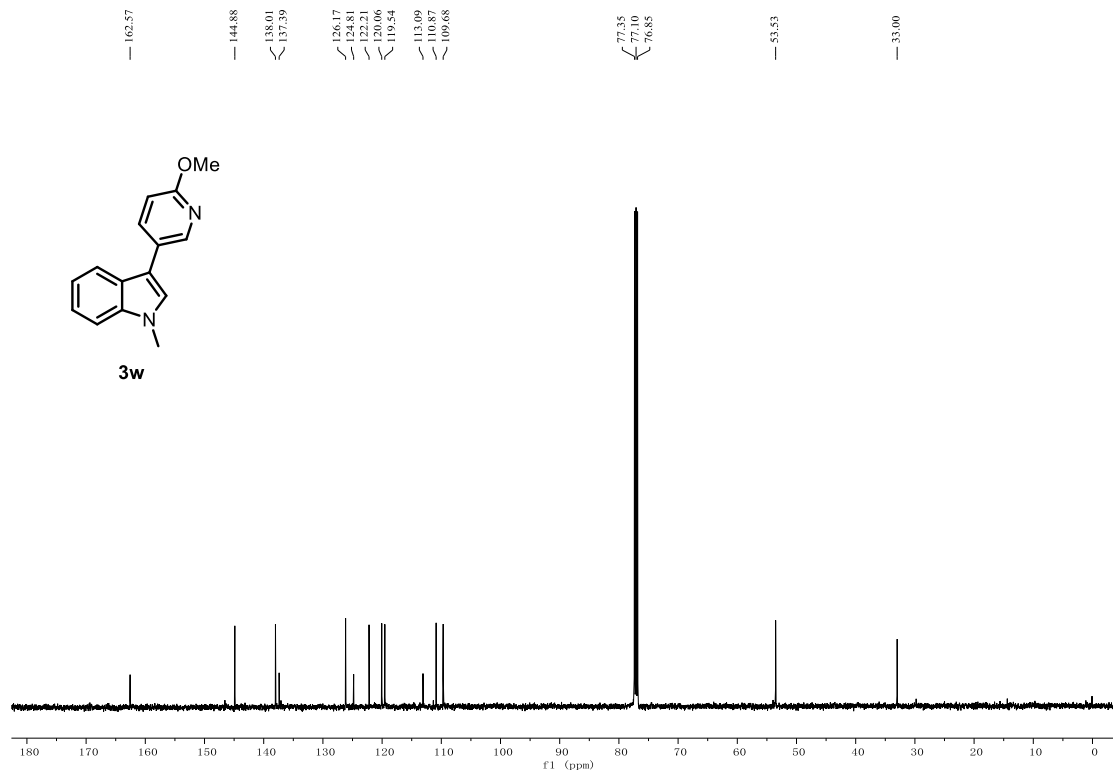


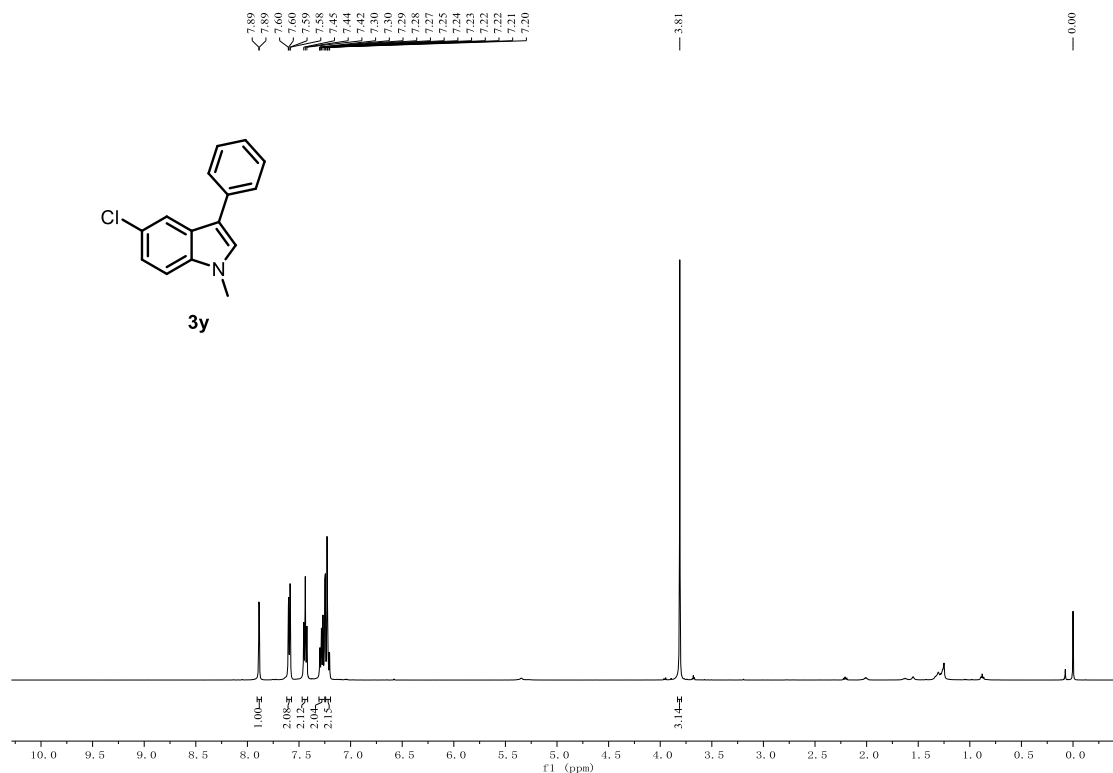
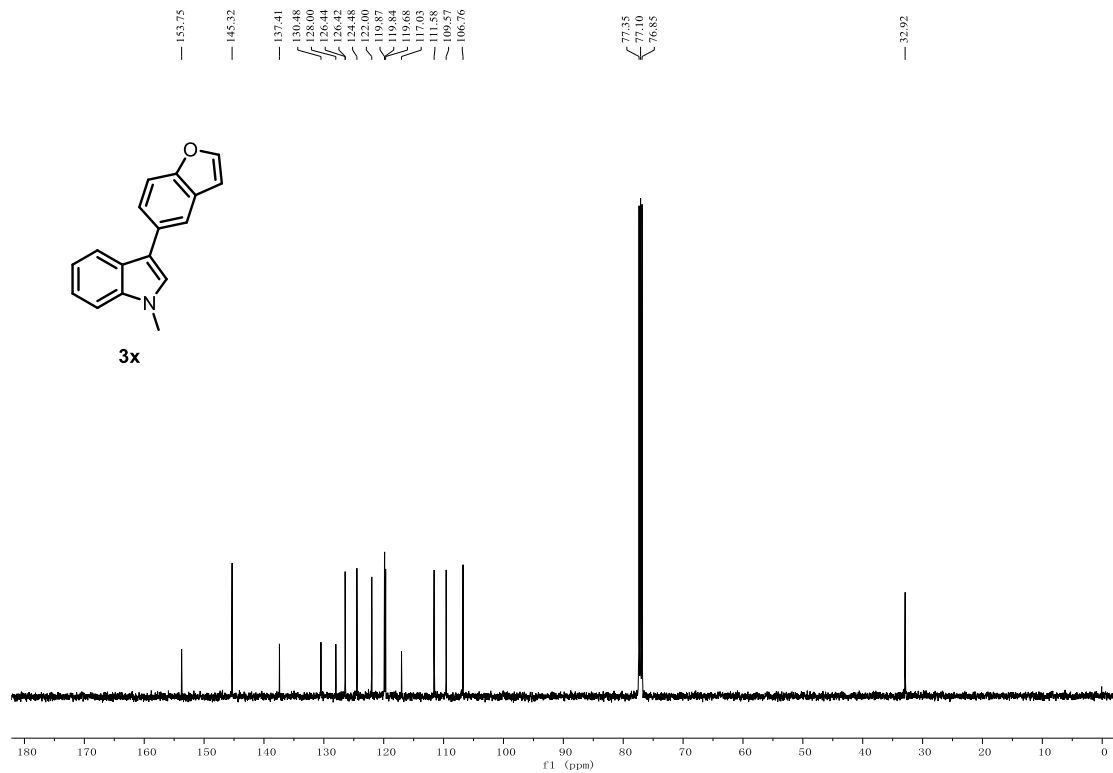


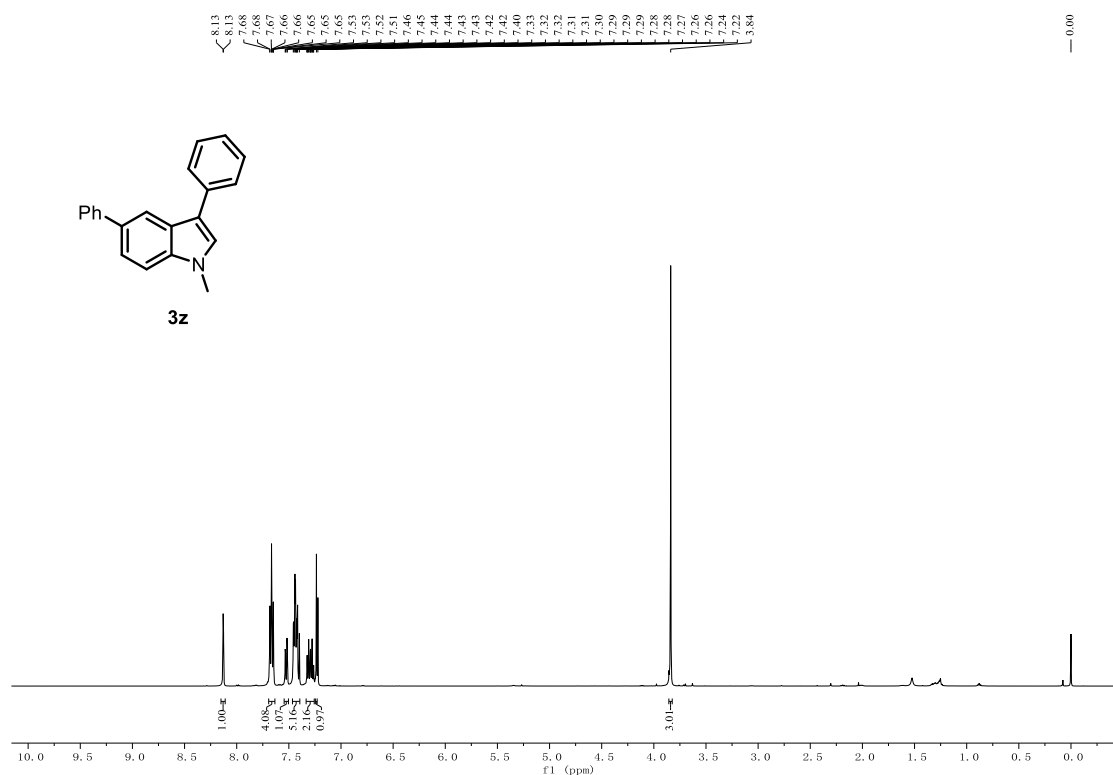
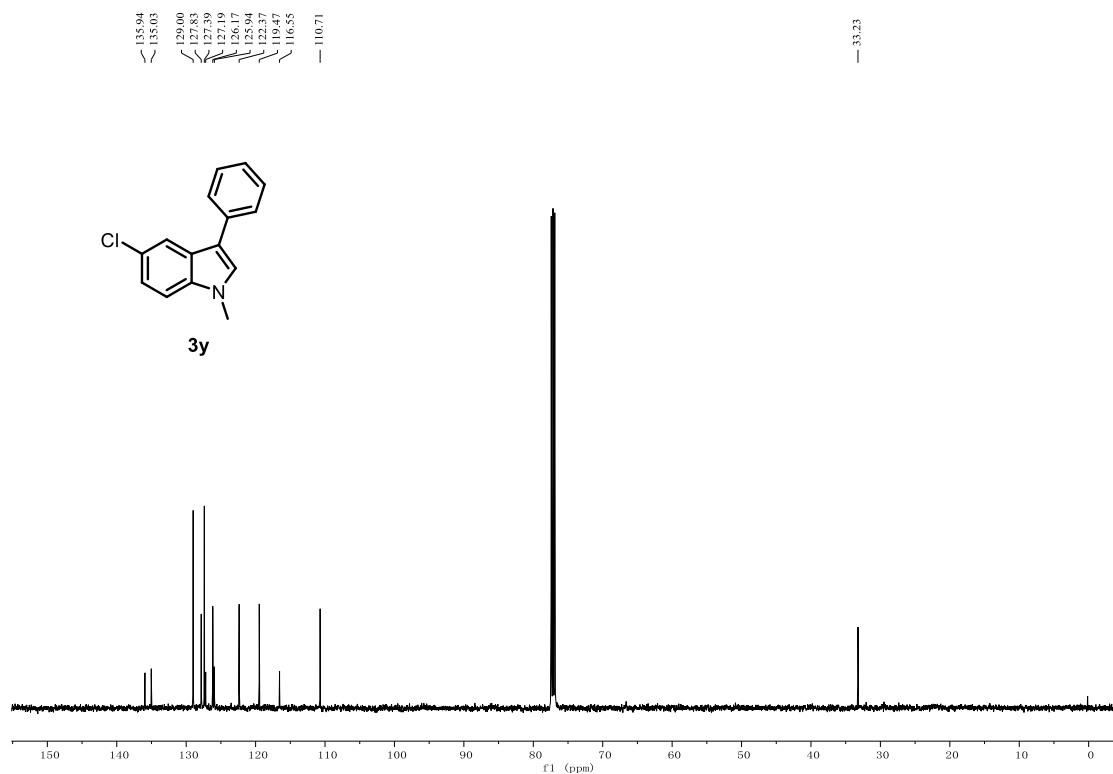


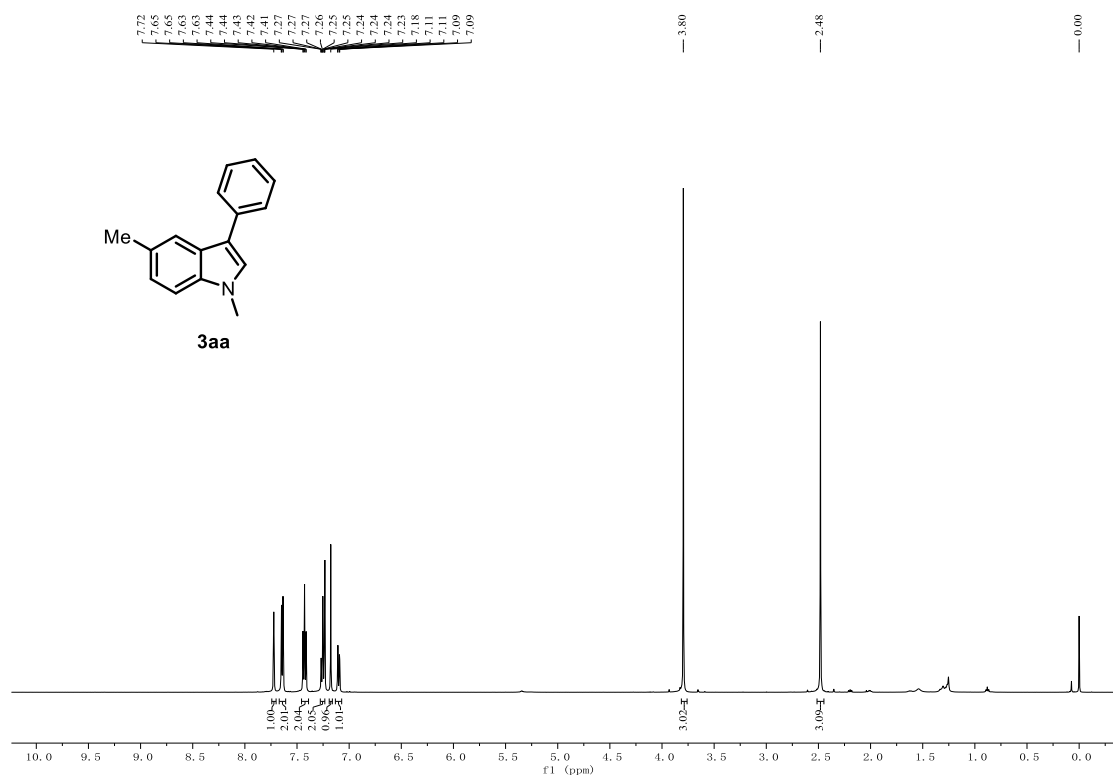
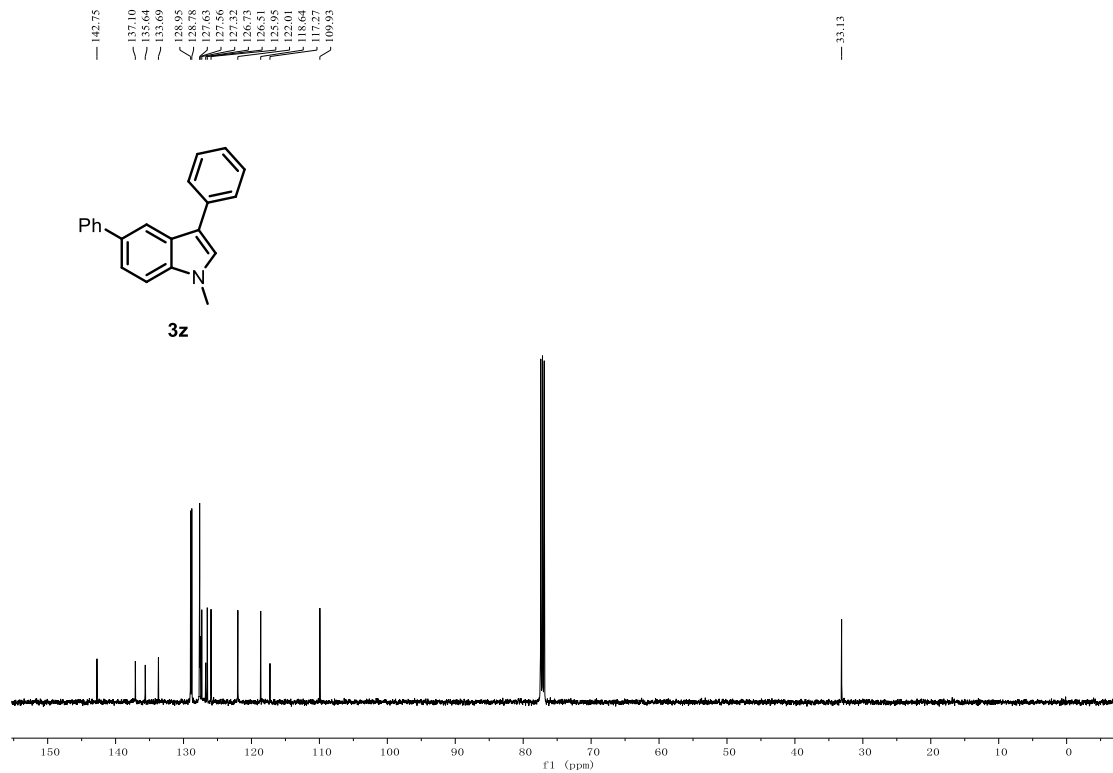


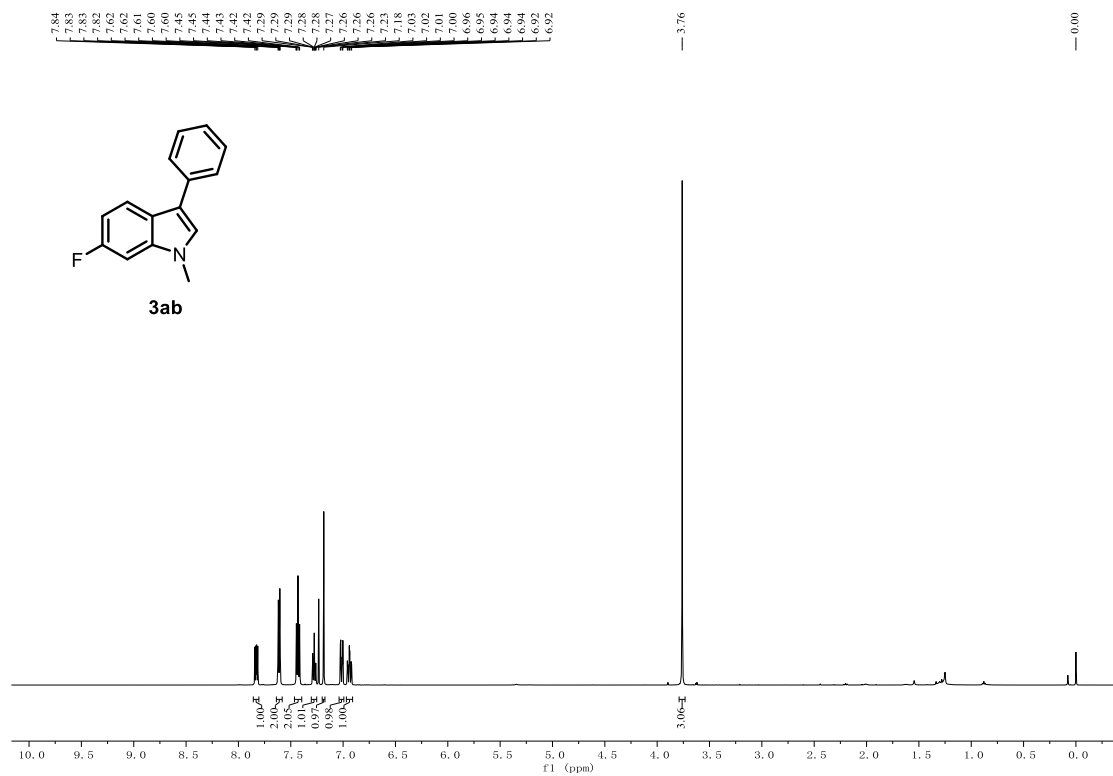
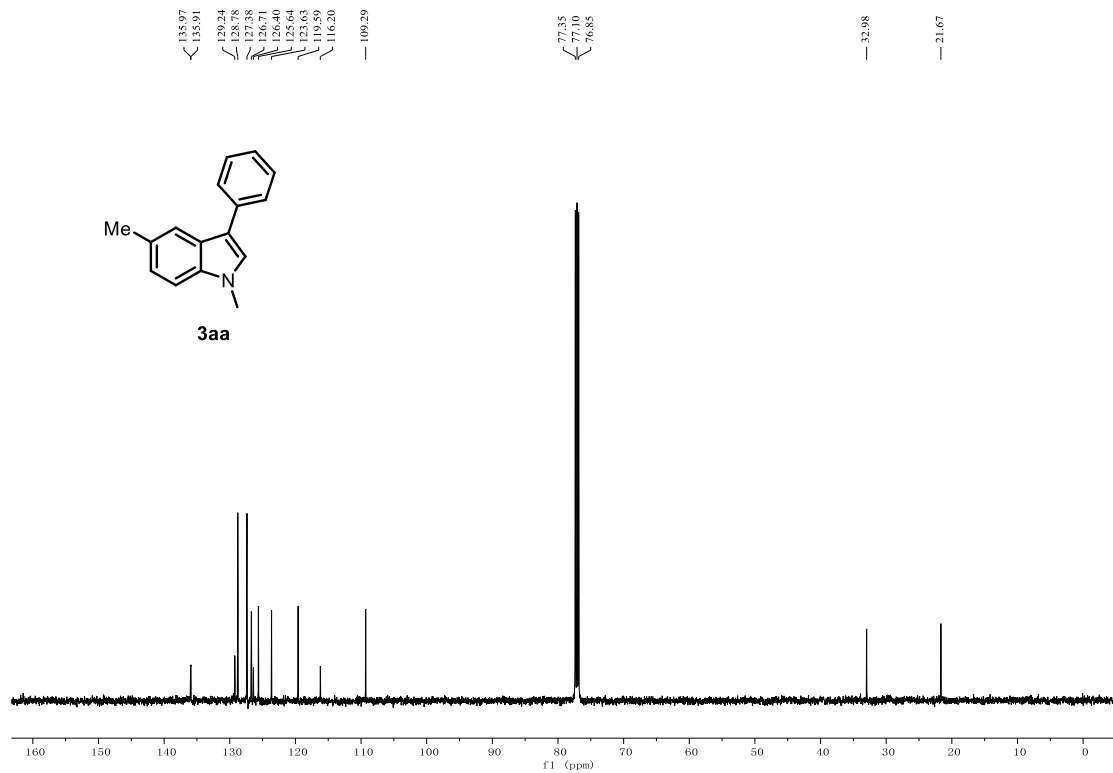


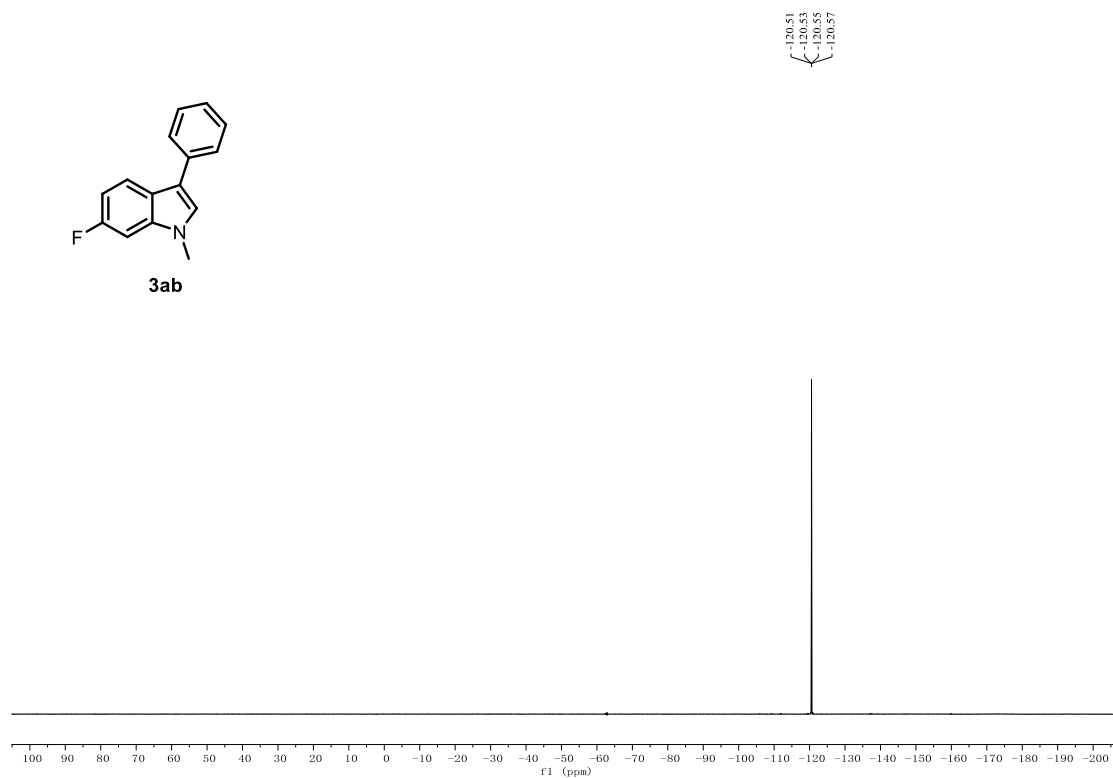
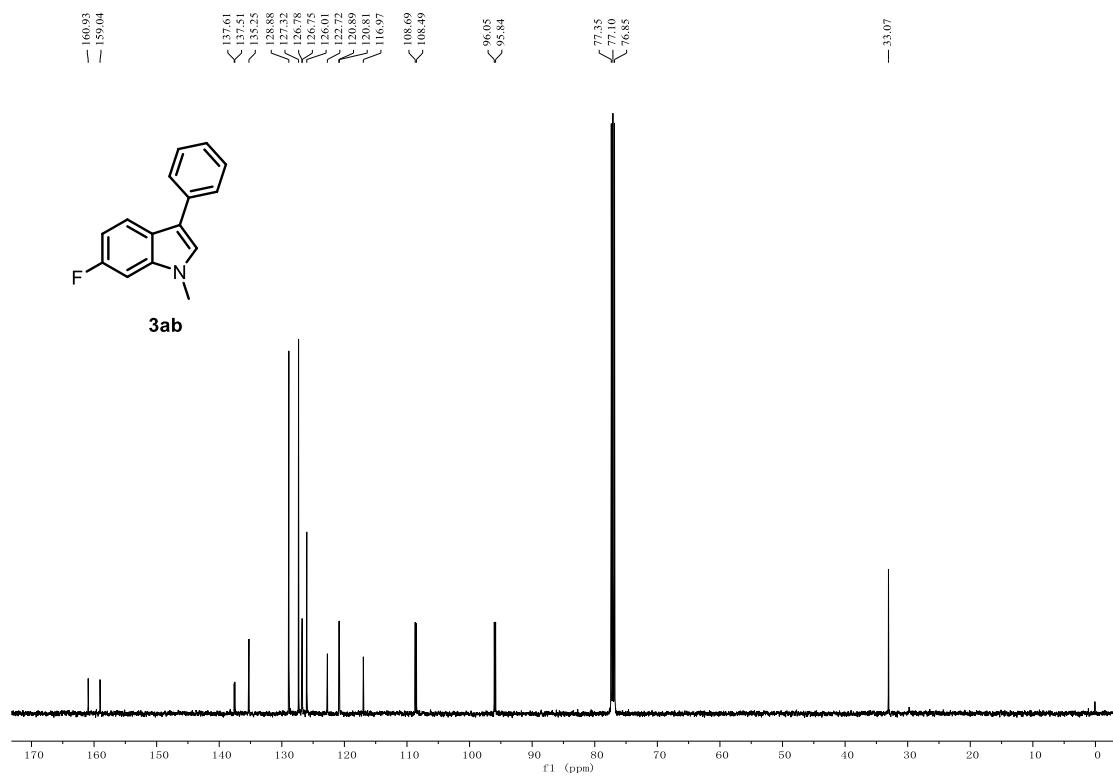


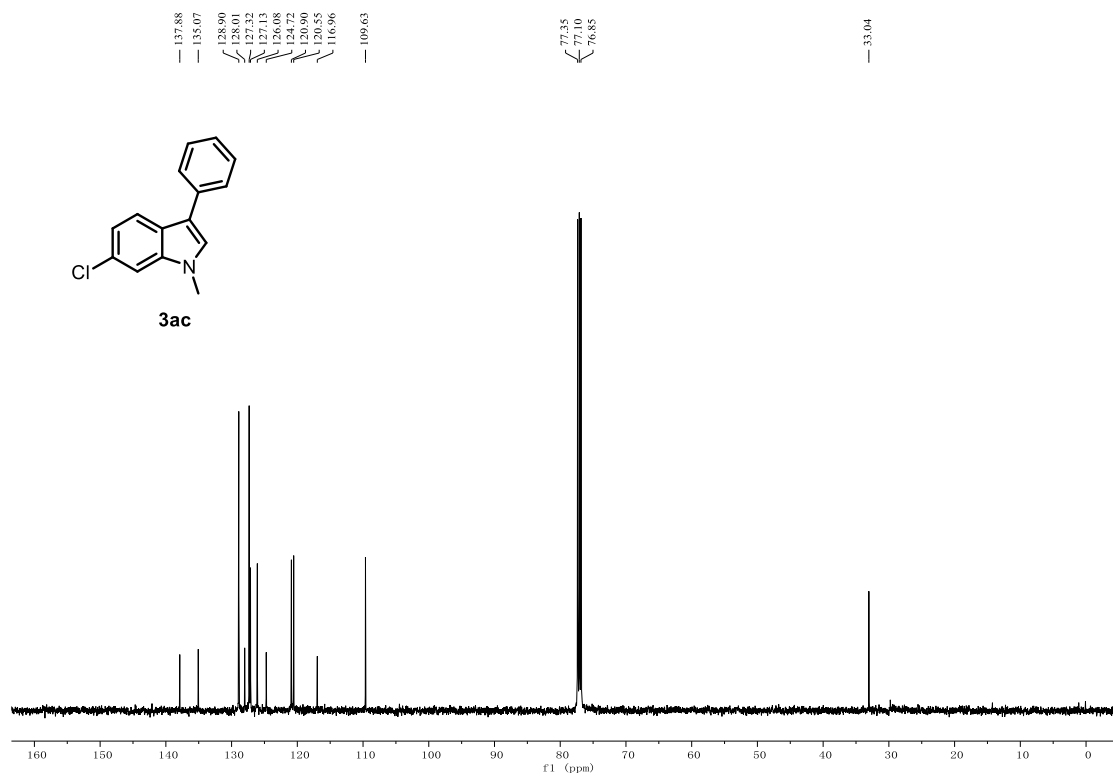
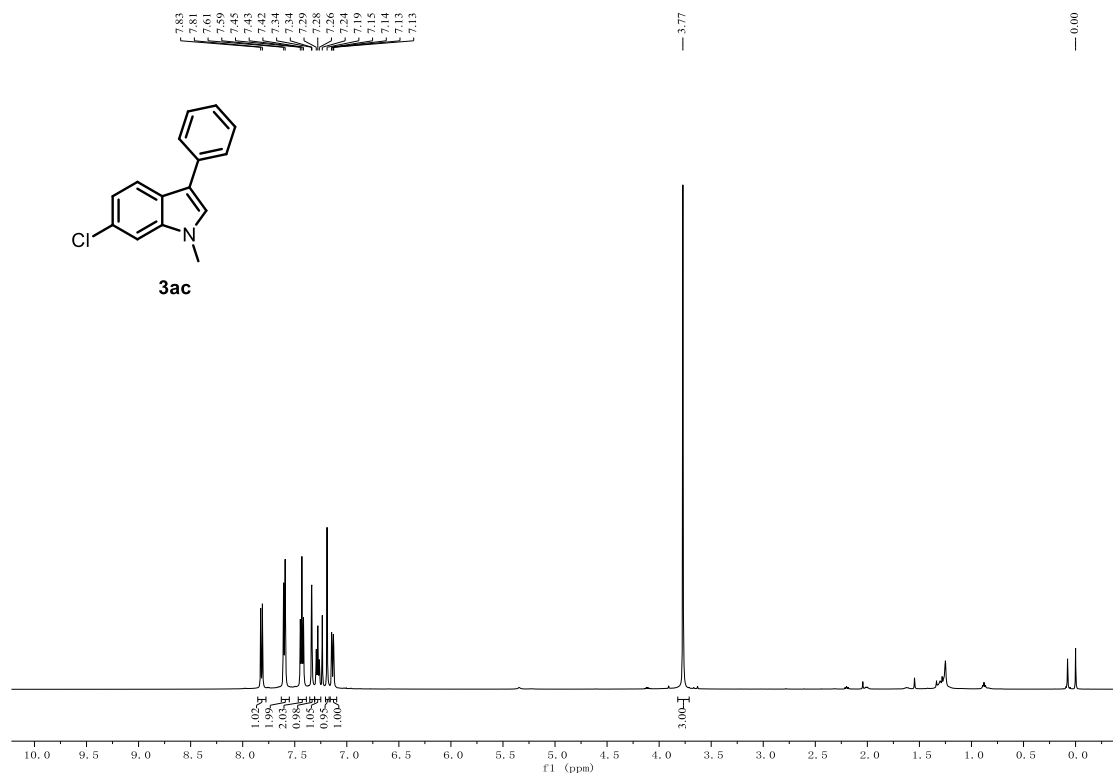


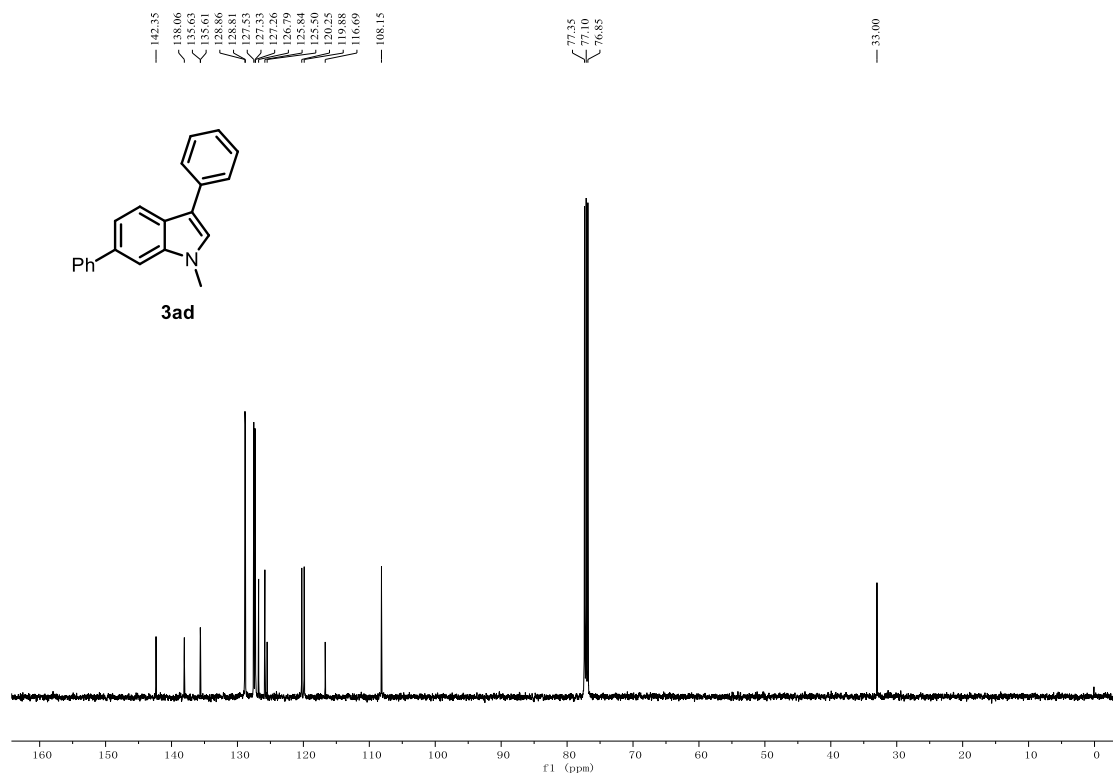
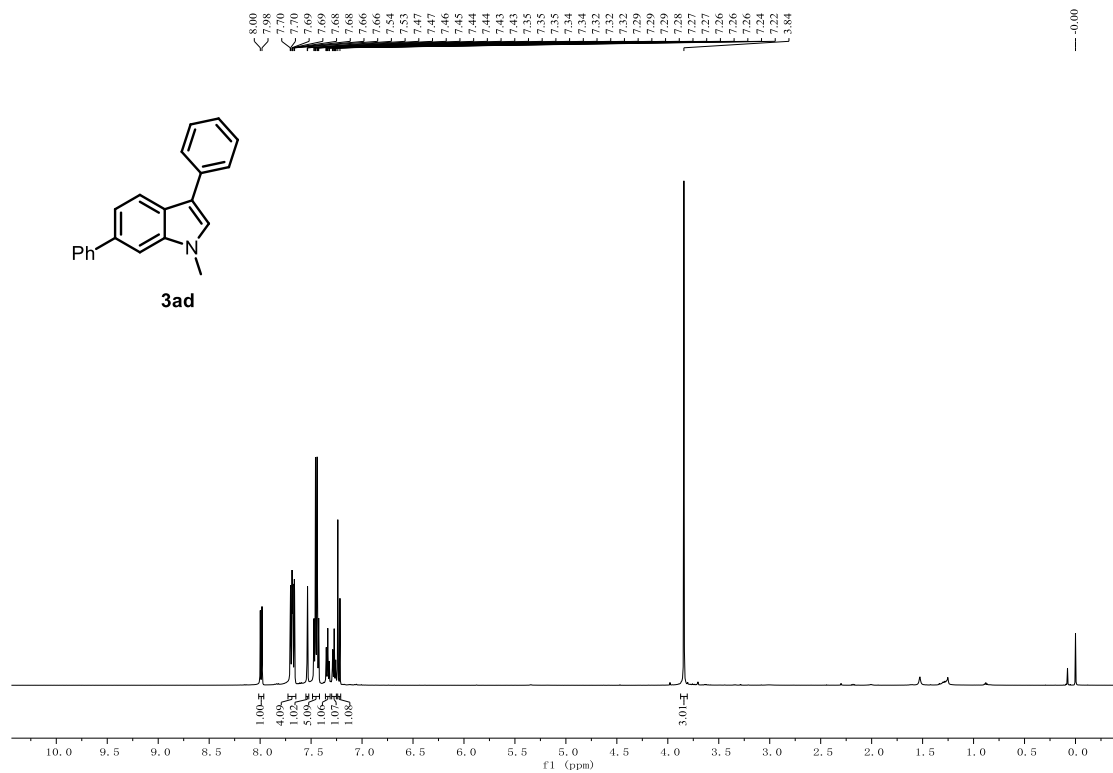


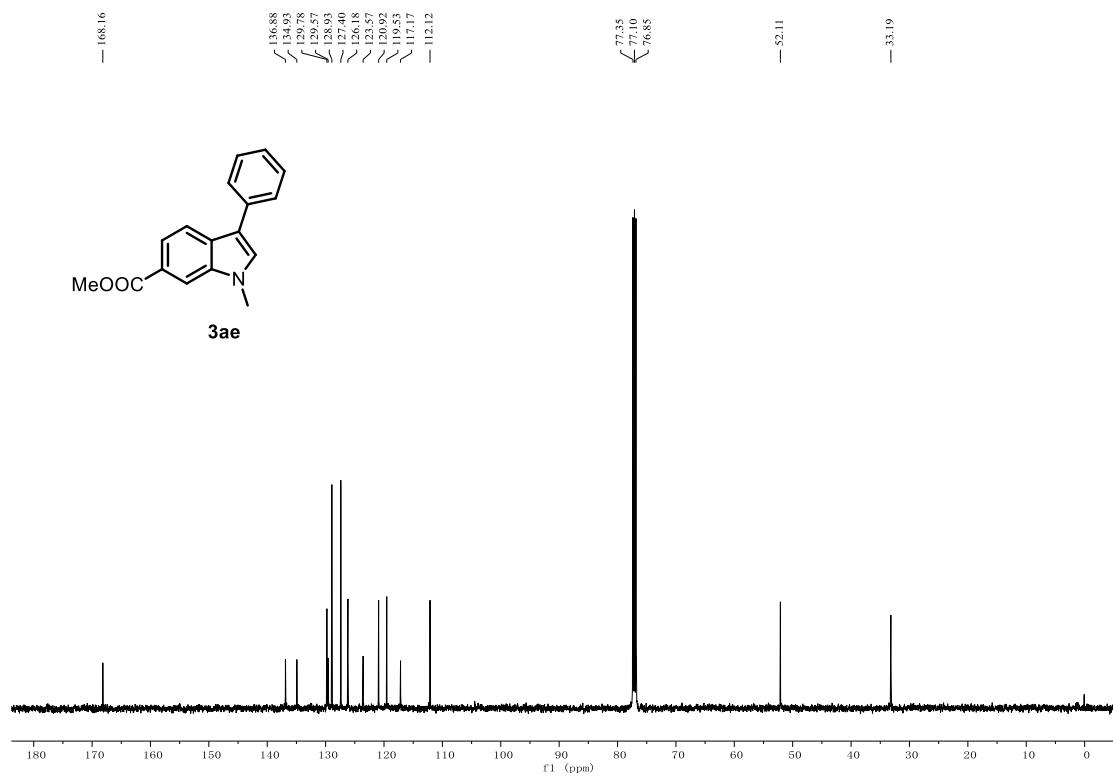
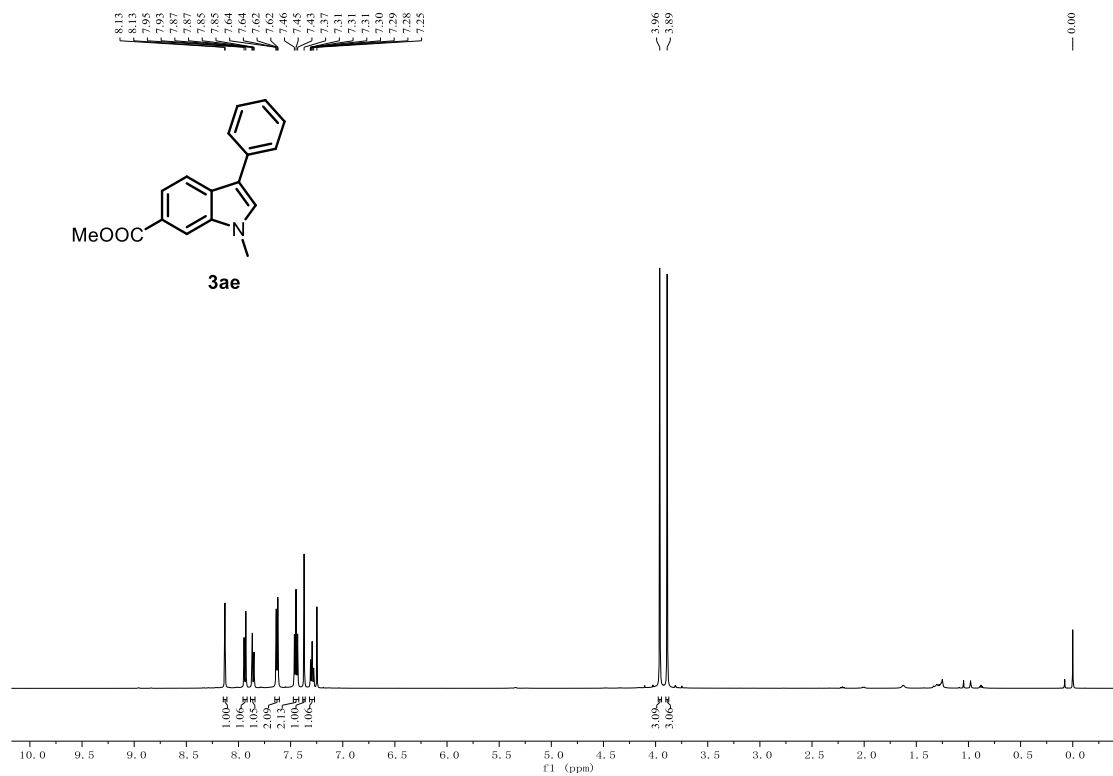


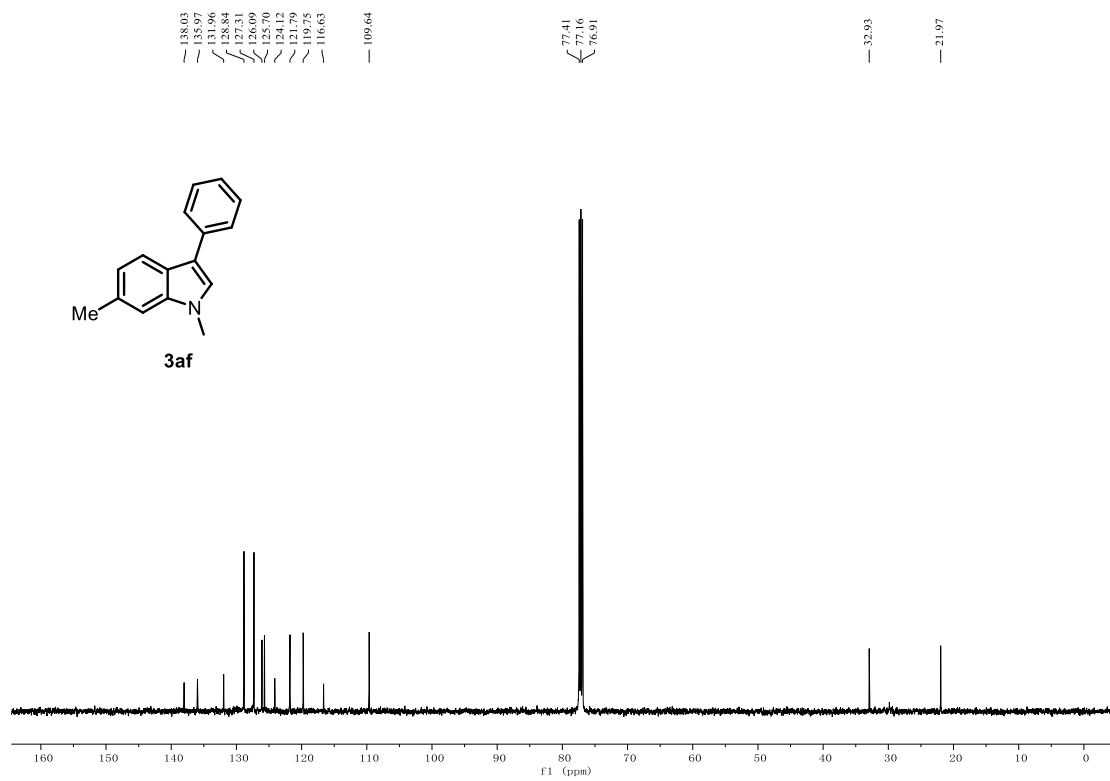
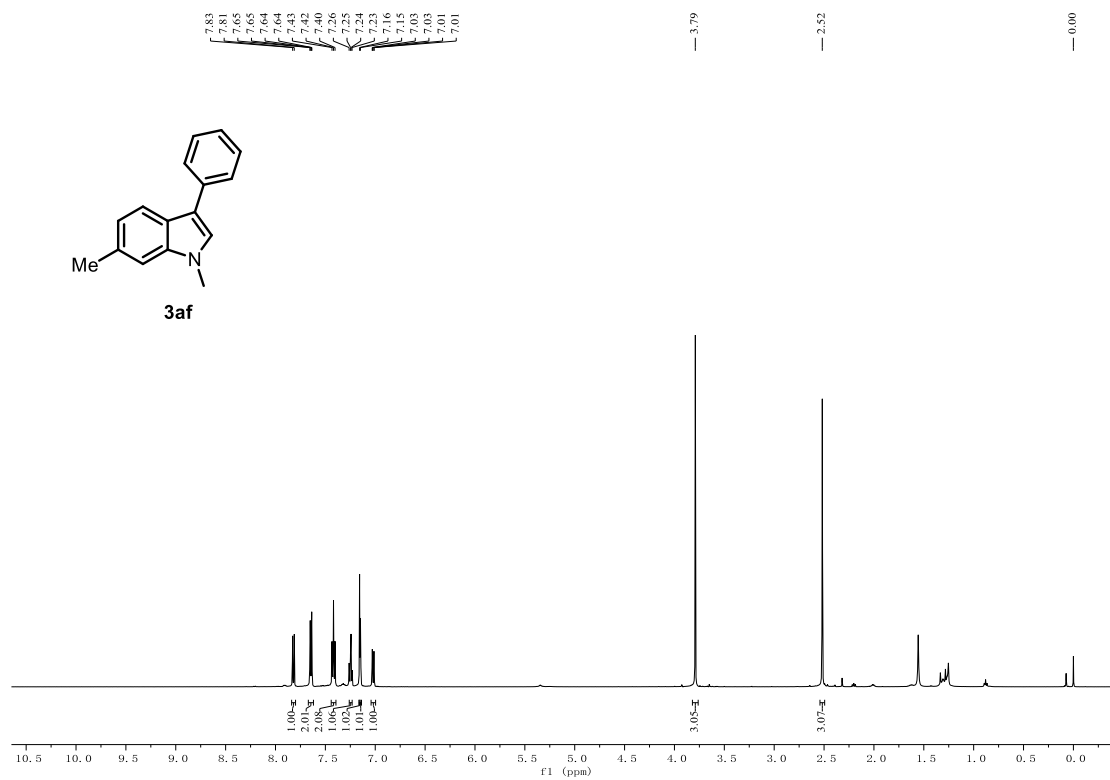


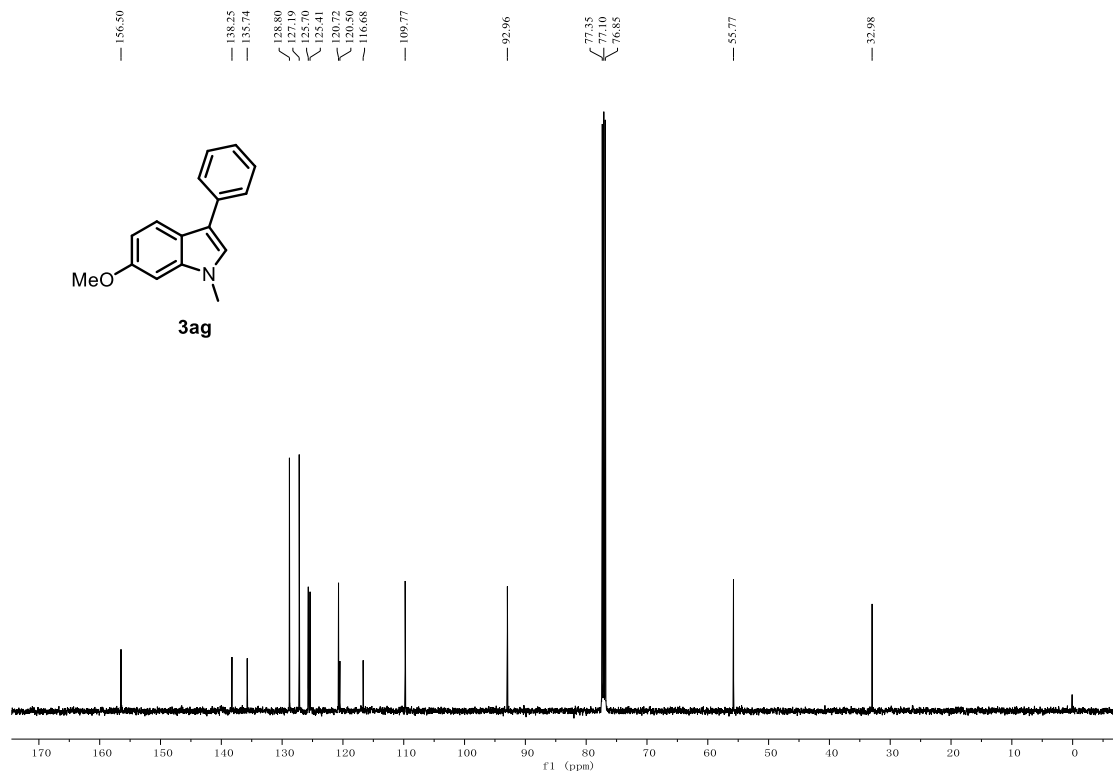
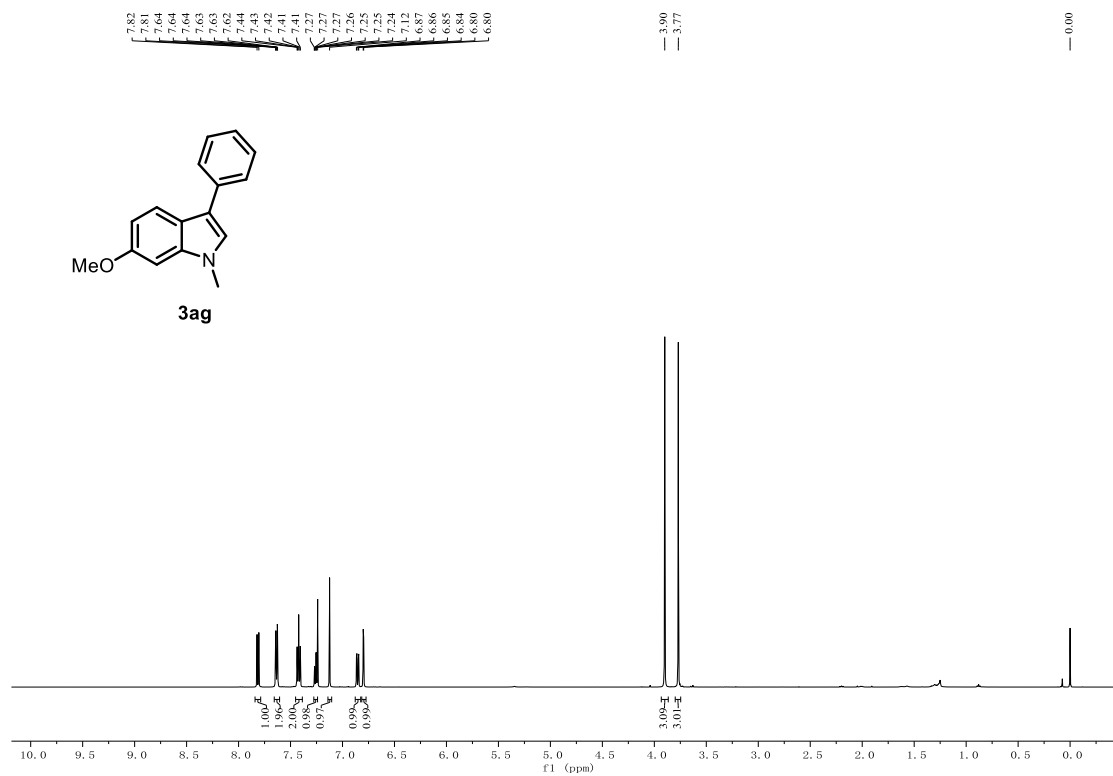


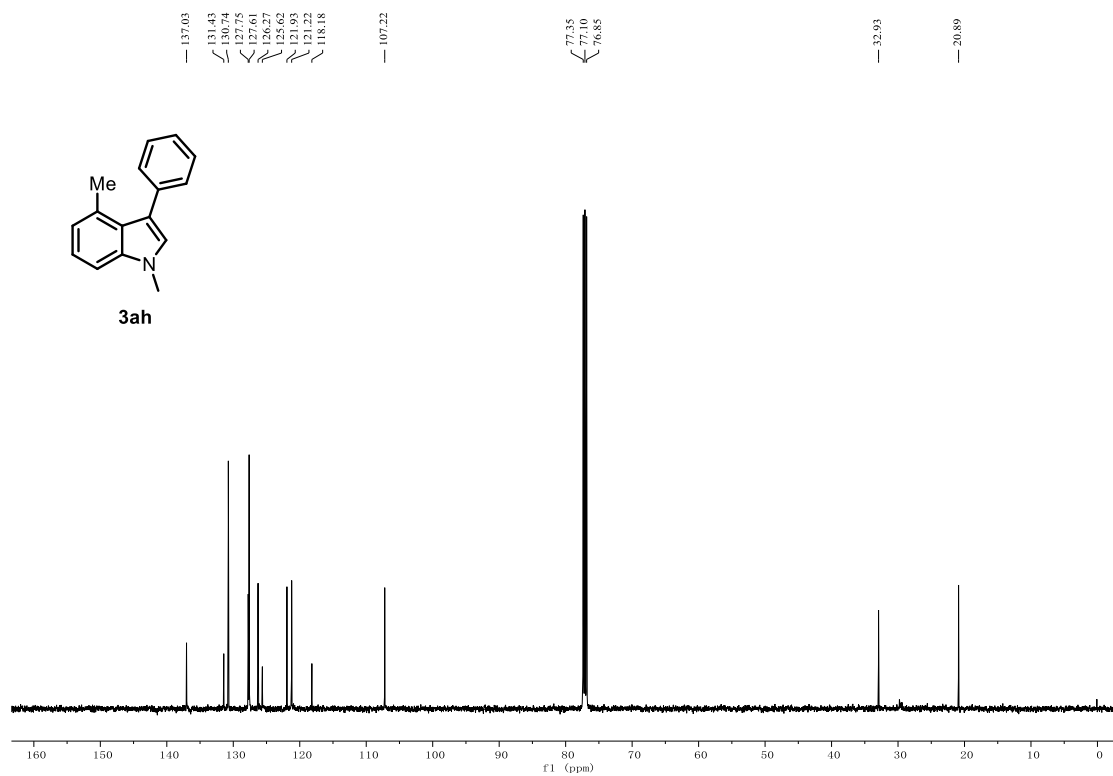
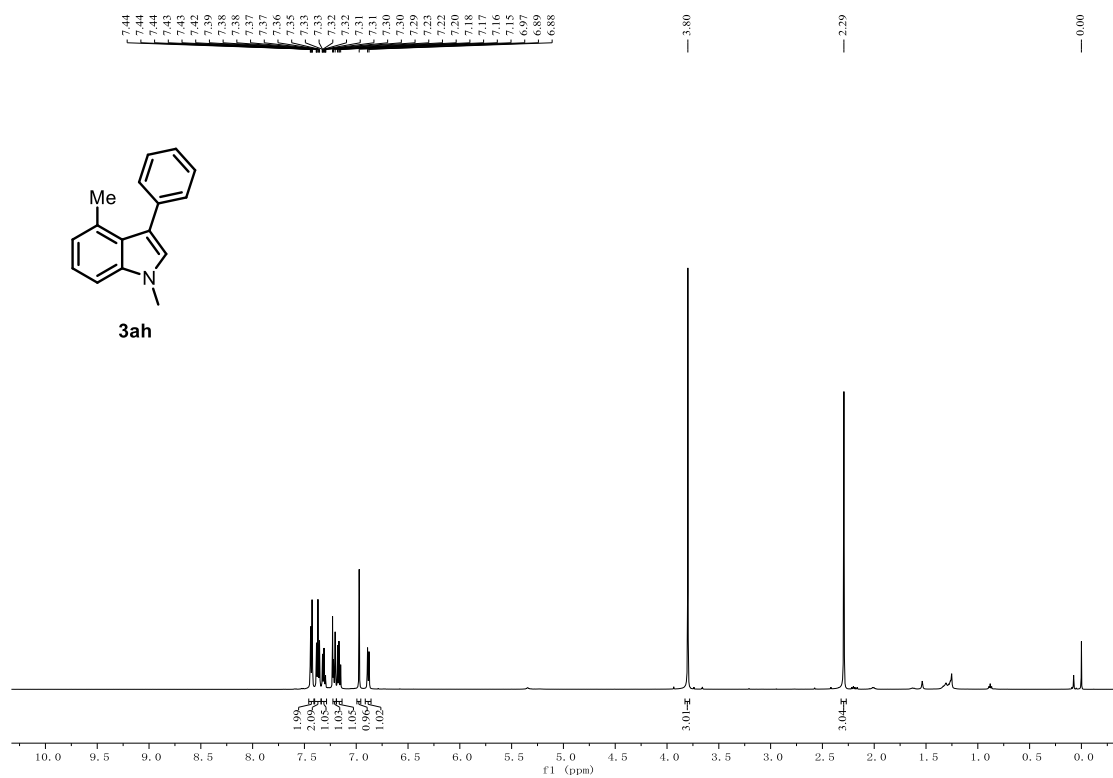


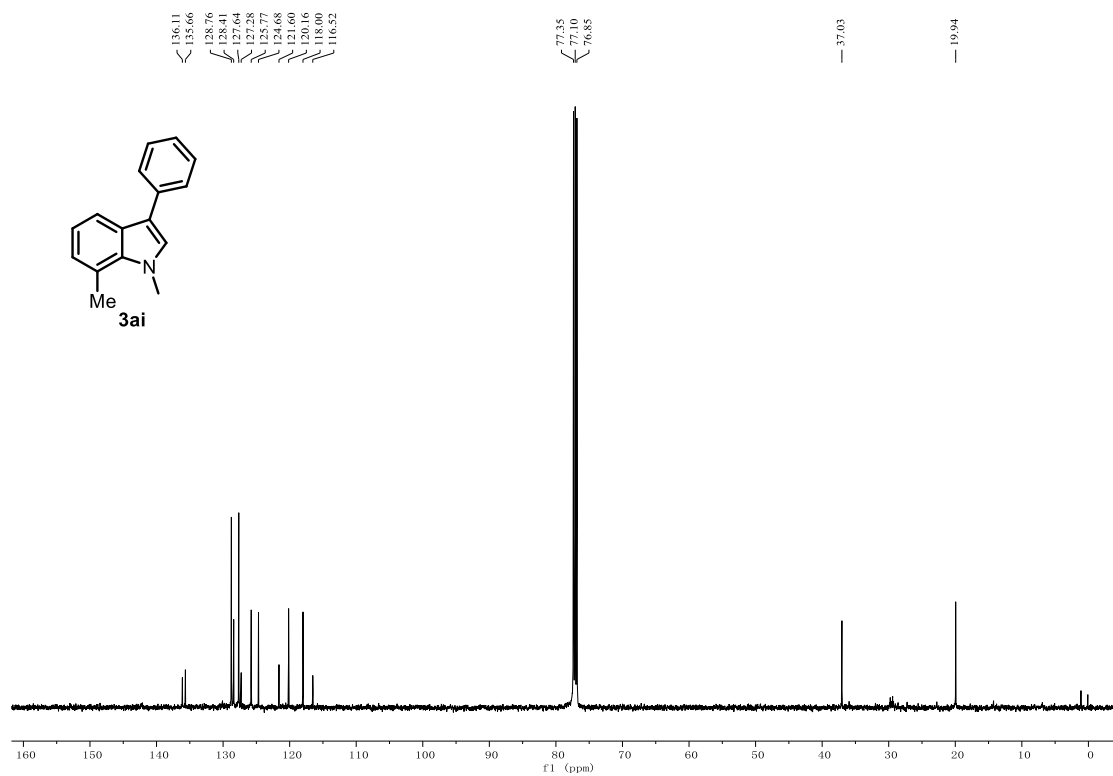
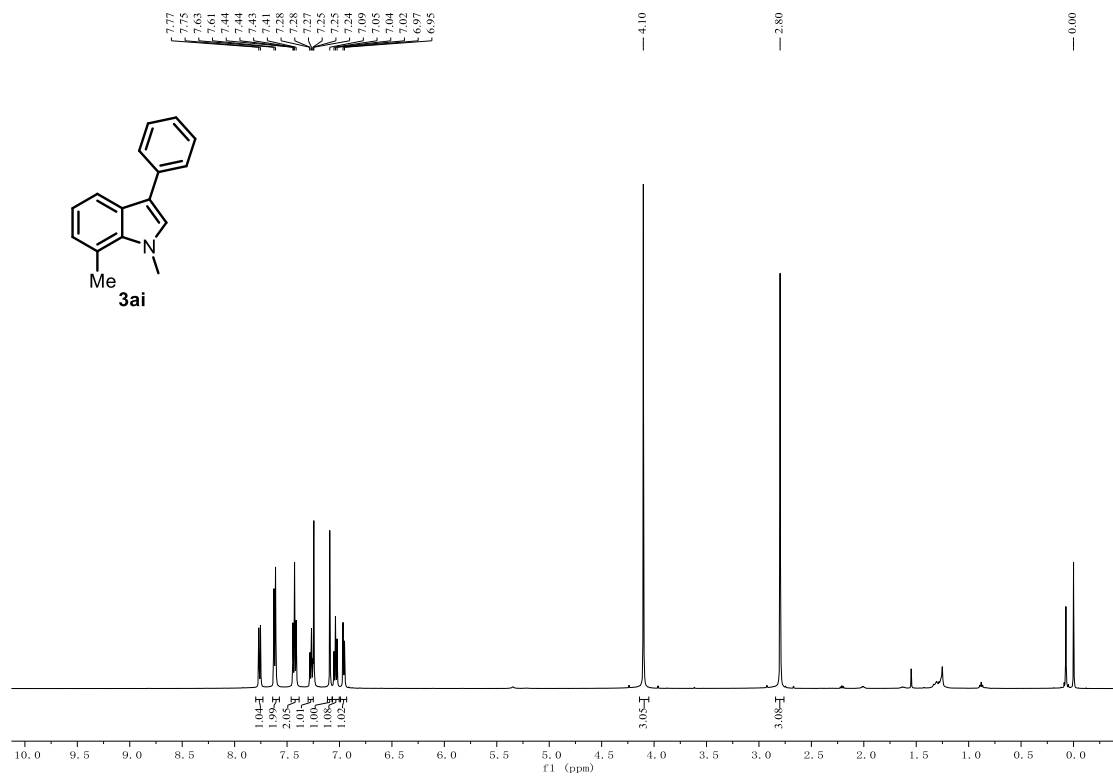


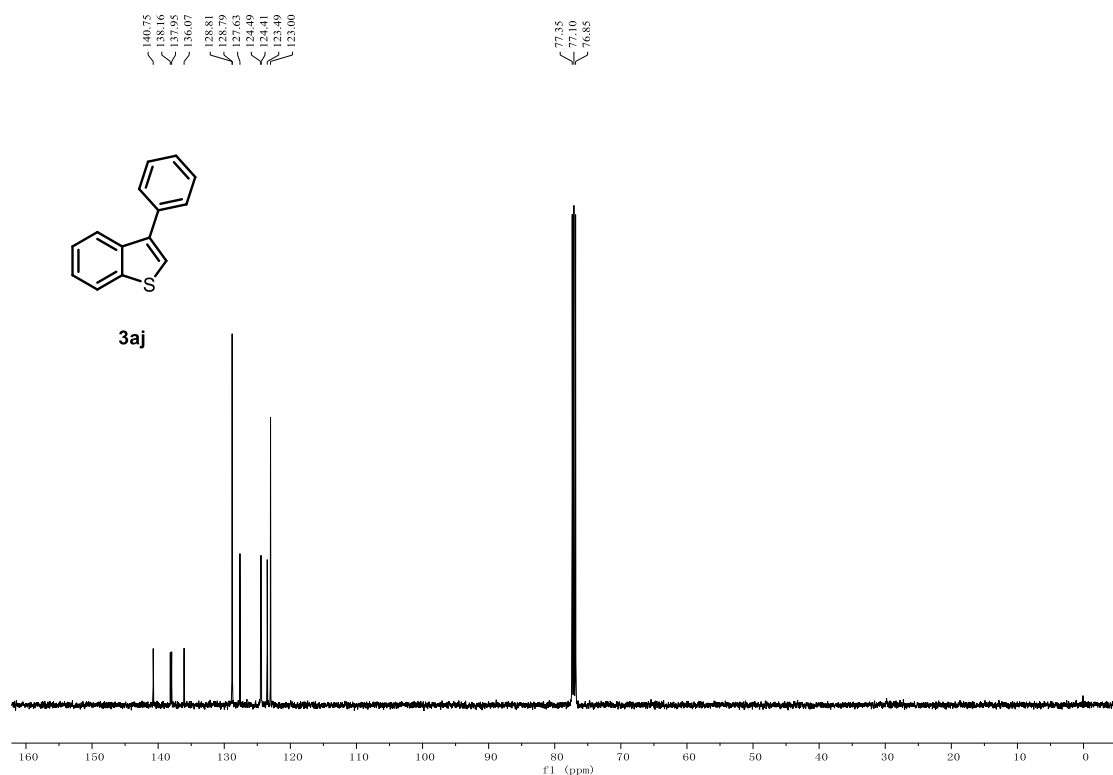
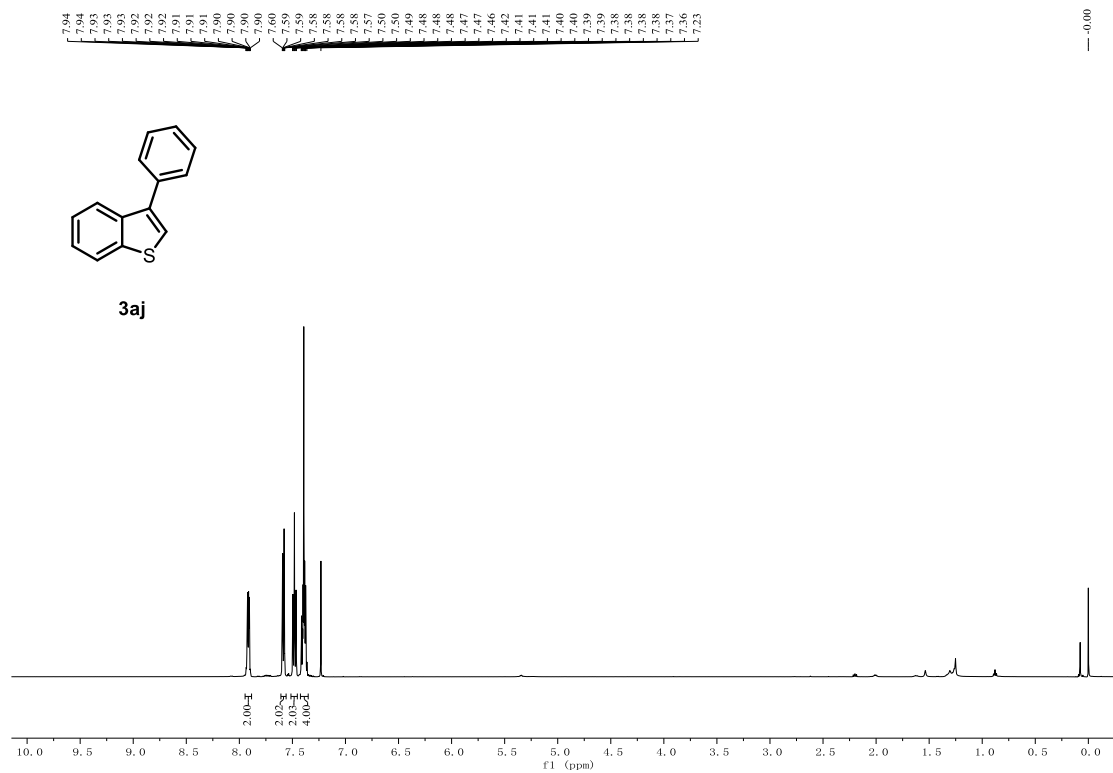


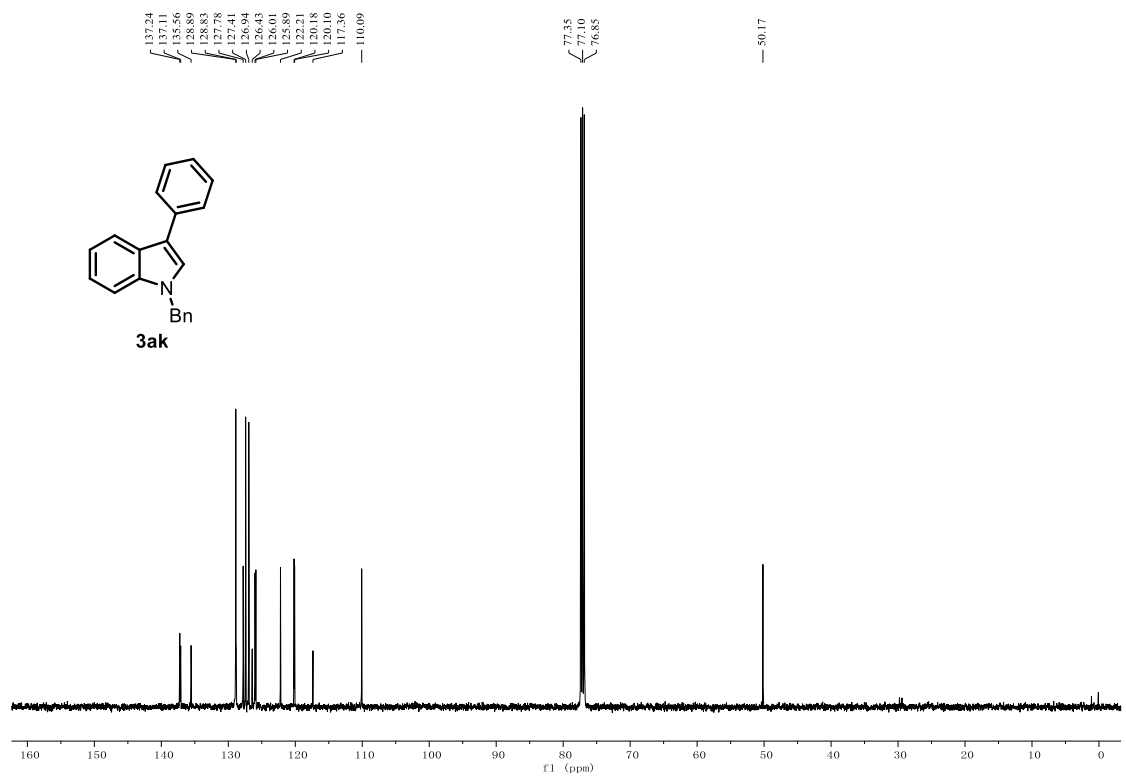
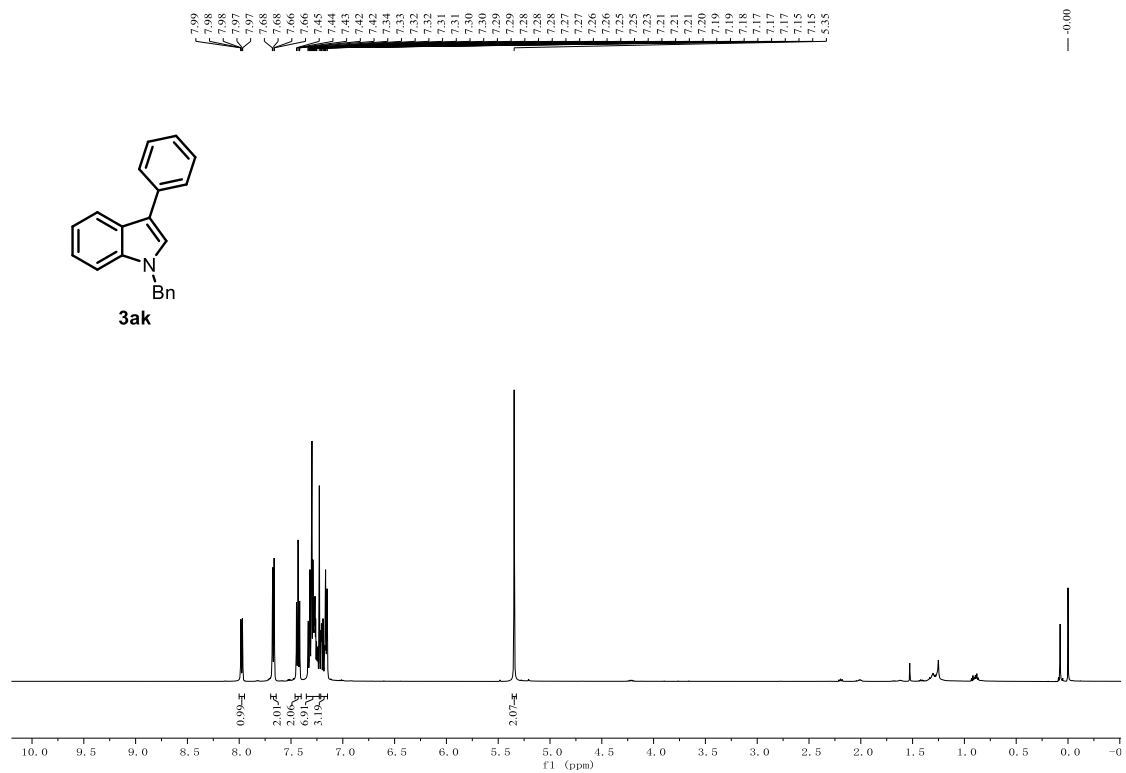


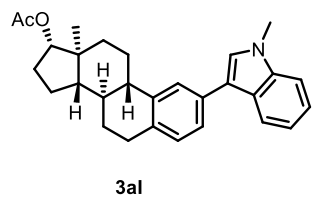
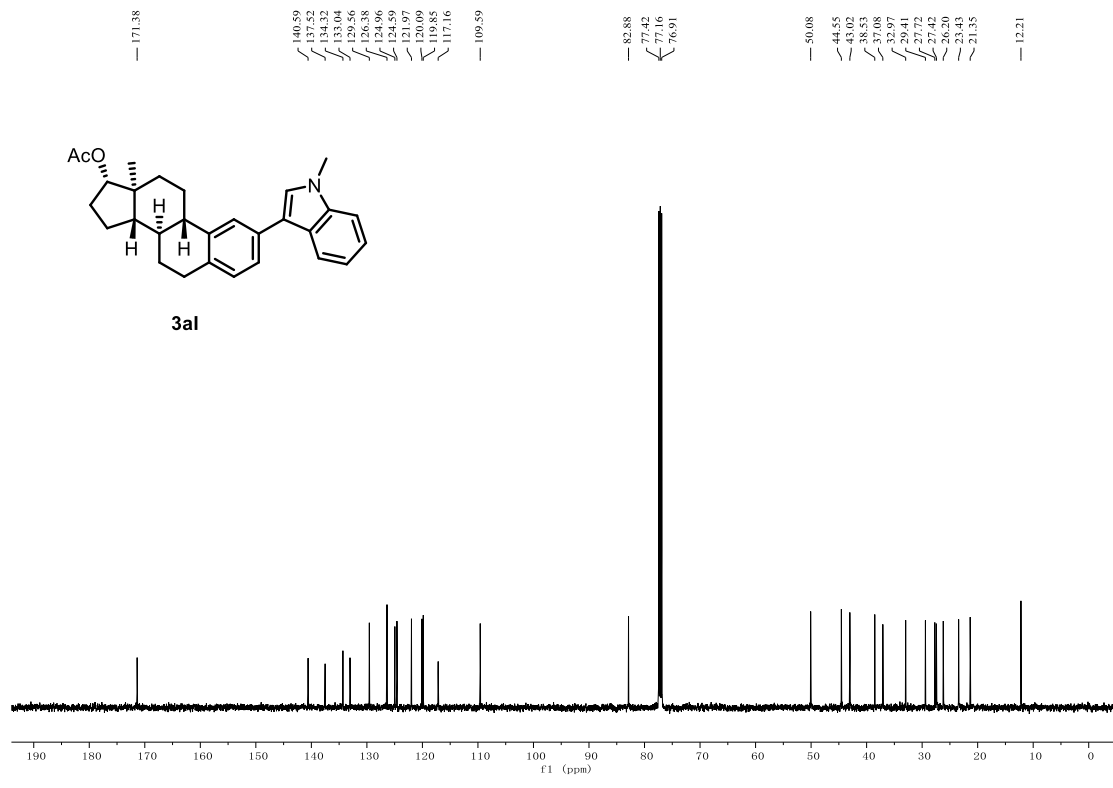
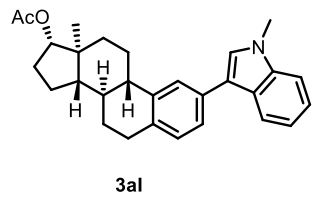
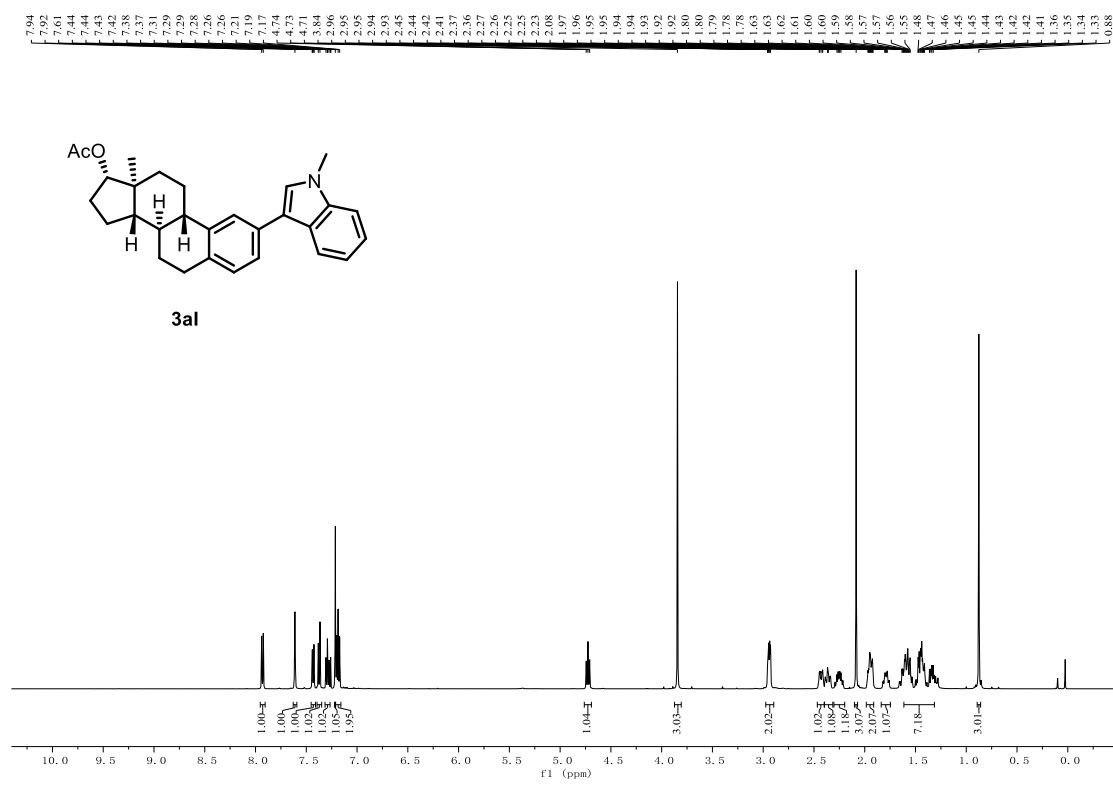


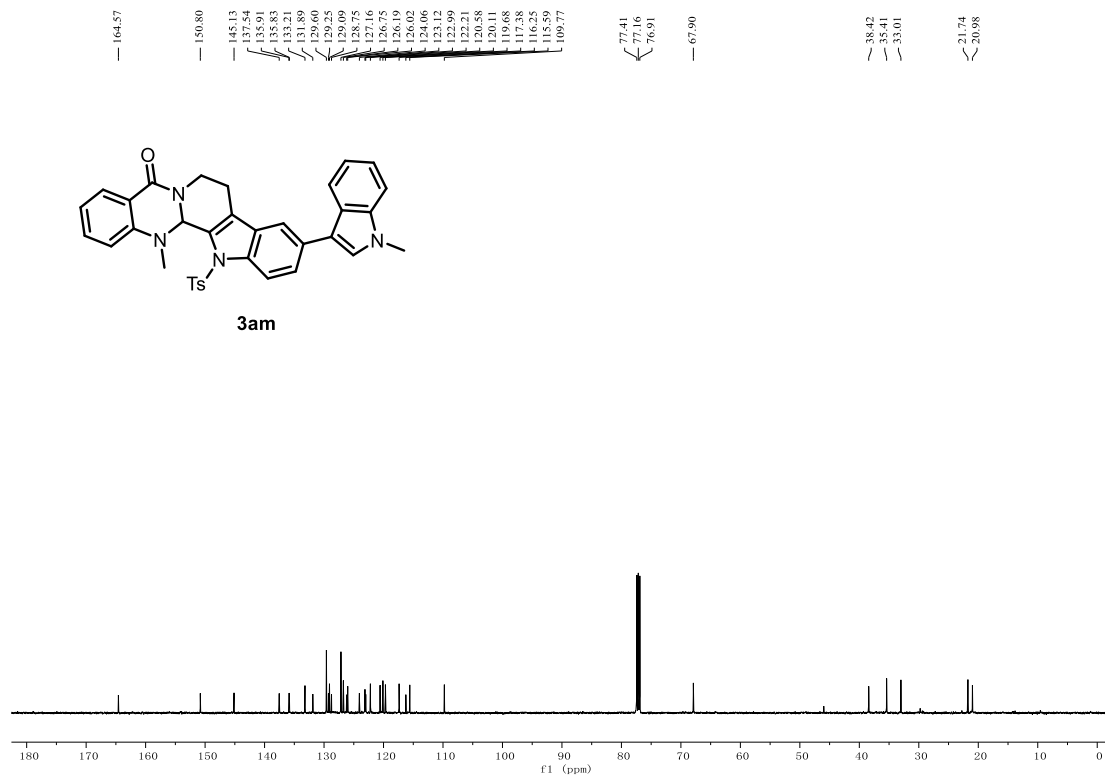
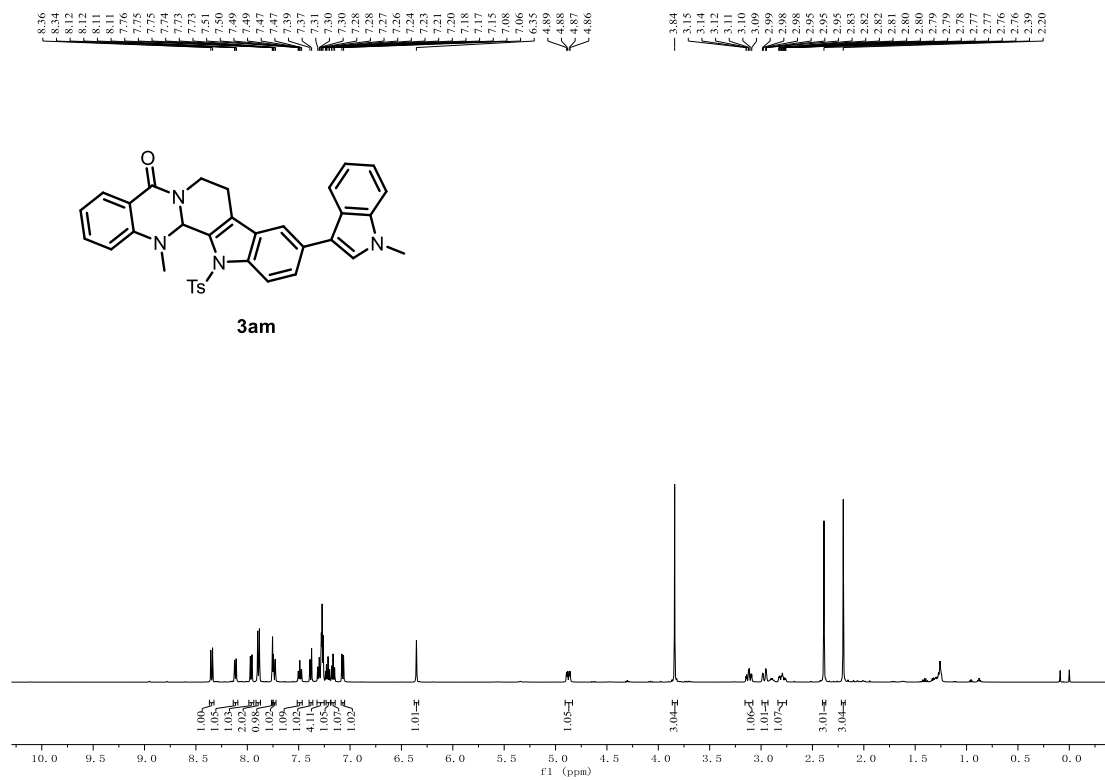








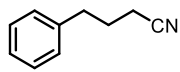




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