
Supporting Information

Rapid construction of cyclopenta[*b*]naphthalene frameworks from propargylic alcohol tethered methylenecyclopropanes

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Content

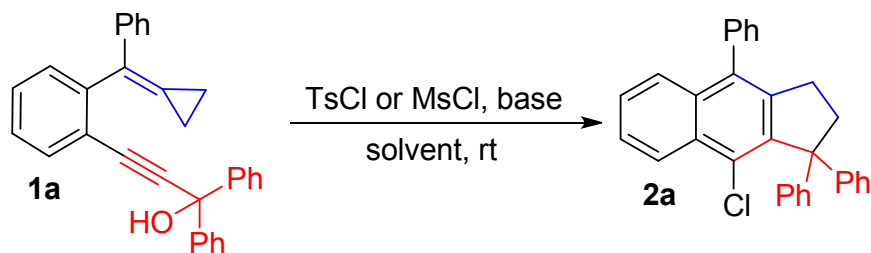
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1. General remarks

^1H NMR spectra were recorded on Varian Mercury-400 and Bruker-400 spectrometer for solution in CDCl_3 with tetramethylsilane (TMS) as an internal standard; coupling constants J are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-400 and Bruker-400 spectrophotometers with complete proton decoupling spectrophotometers (CDCl_3 ; 77.0 ppm). The reference of ^{19}F NMR (376 MHz) spectra is trichlorofluoromethane (δ ppm 0). Mass and HRMS spectra were recorded by DART or EI method. Organic solvents used were dried by standard methods when necessary. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1} . Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

2. Optimization of reaction conditions

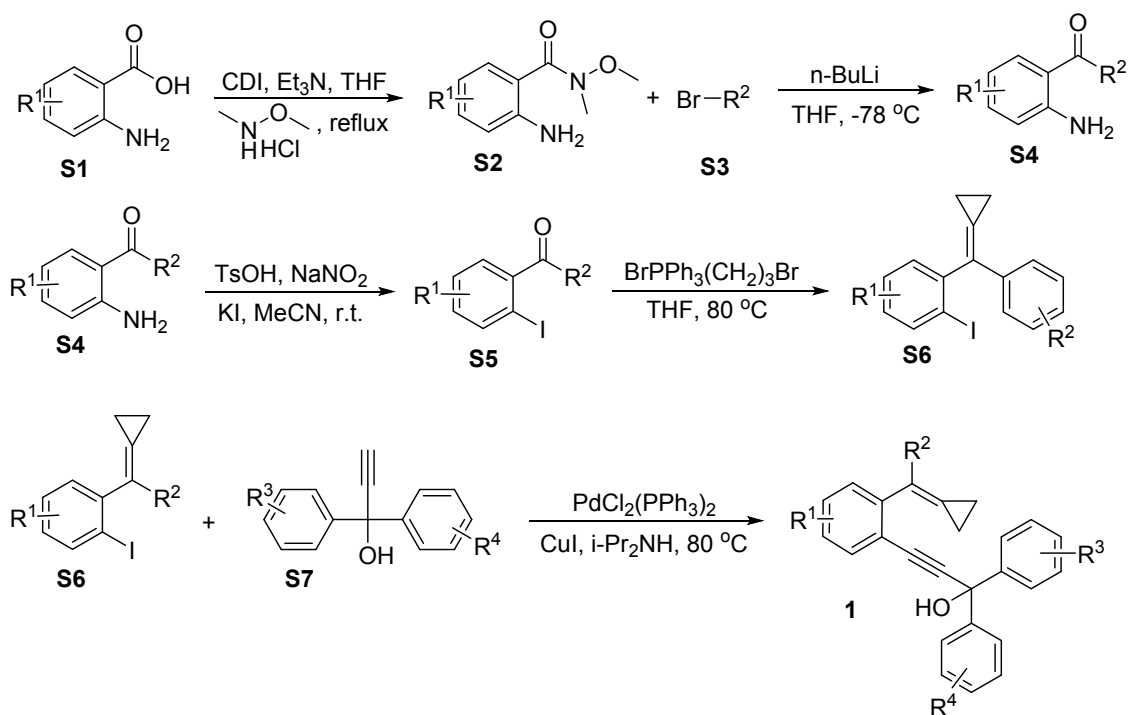
Table S1. Screening of reaction conditions



Entry	Reaction conditions ^a	Yield of 2a [%] ^b
1	TsCl (1.5 equiv), pyridine (1.6 equiv), DCM	NR
2	TsCl (1.5 equiv), Et ₃ N (1.6 equiv), DCM	NR
3	MsCl (1.5 equiv), Et ₃ N (1.6 equiv), DCM	79
4	MsCl (1.5 equiv), pyridine (1.6 equiv), DCM	NR
5	MsCl (1.5 equiv), K ₂ CO ₃ (1.6 equiv), DCM	NR
6	MsCl (1.5 equiv), <i>i</i> -Pr ₂ NH (1.6 equiv), DCM	Trace
7	MsCl (1.5 equiv), Et ₃ N (1.6 equiv), DMSO	Trace
8	MsCl (1.5 equiv), Et ₃ N (1.6 equiv), MeCN	84
9	MsCl (1.5 equiv), Et ₃ N (1.6 equiv), THF	45
10	MsCl (1.5 equiv), Et ₃ N (1.6 equiv), Et ₂ O	Trace
11	MsCl (1.5 equiv), Et ₃ N (1.6 equiv), Dioxane	Trace
12	MsCl (1.5 equiv), Et ₃ N (1.6 equiv), DMF	Trace
13	MsCl (1.5 equiv), Et ₃ N (1.6 equiv), PhMe	34
14	MsCl (2.0 equiv), Et ₃ N (2.1 equiv), MeCN	86
15	MsCl (2.5 equiv), Et ₃ N (2.6 equiv), MeCN	90
16	MsCl (3.0 equiv), Et ₃ N (3.1 equiv), MeCN	85
17	MsCl (2.5 equiv), Et ₃ N (2.6 equiv), MeCN	81 ^c

^a Reaction conditions: **1a** (0.20 mmol, 1.0 equiv), MsCl or TsCl, base, solvent, rt, for 8 h. ^b ¹H NMR yield using 1,3,5-trimethoxybenzene as an internal standard. ^c Isolated yield.

3. Preparation of reactants

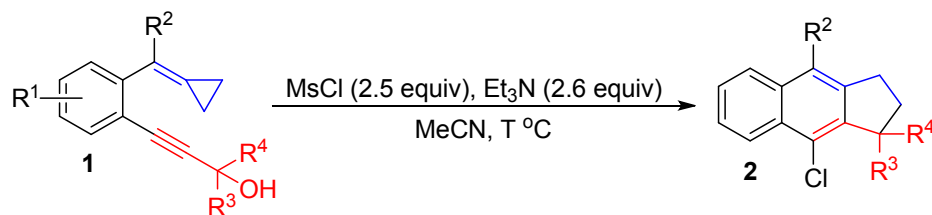


Propargylic alcohol-tethered methylenecyclopropanes were prepared according to the previous literature.¹

1) Q. Li, L. Yu, Y. Wei and M. Shi, *J. Org. Chem.*, 2019, **84**, 9282–9296.

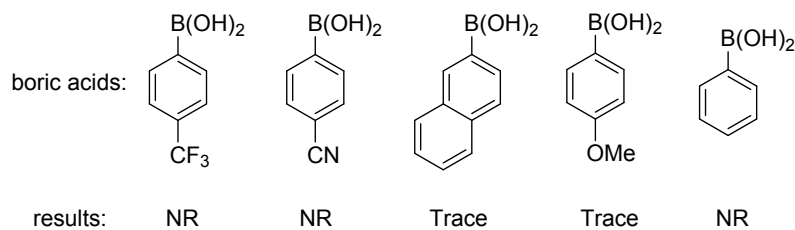
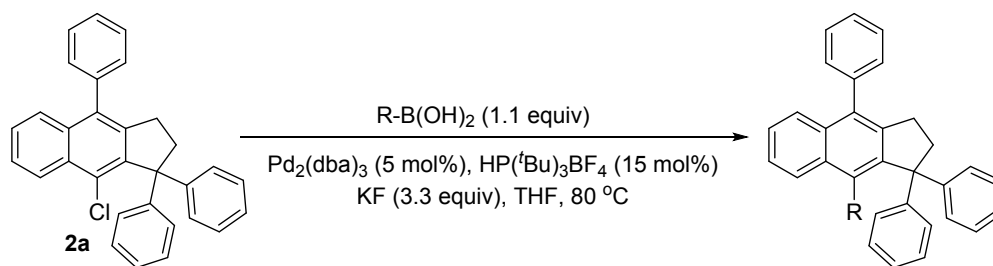
4. General procedures of cyclization reactions

General procedure for the preparation of compounds **2**:



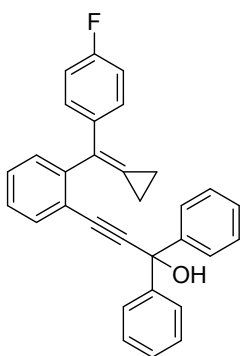
To a stirred solution of **1** (1.0 equiv) and Et₃N (2.6 equiv) in dry MeCN (2 mL) was added MsCl (2.5 equiv), and the resulting mixture was stirred at T °C for 8 h. After washing by water and removing the solvent under reduced pressure, the residue was purified by a column chromatography on silica gel with petroleum to afford the corresponding products **2**.

5. Unsuccessful coupling experiments

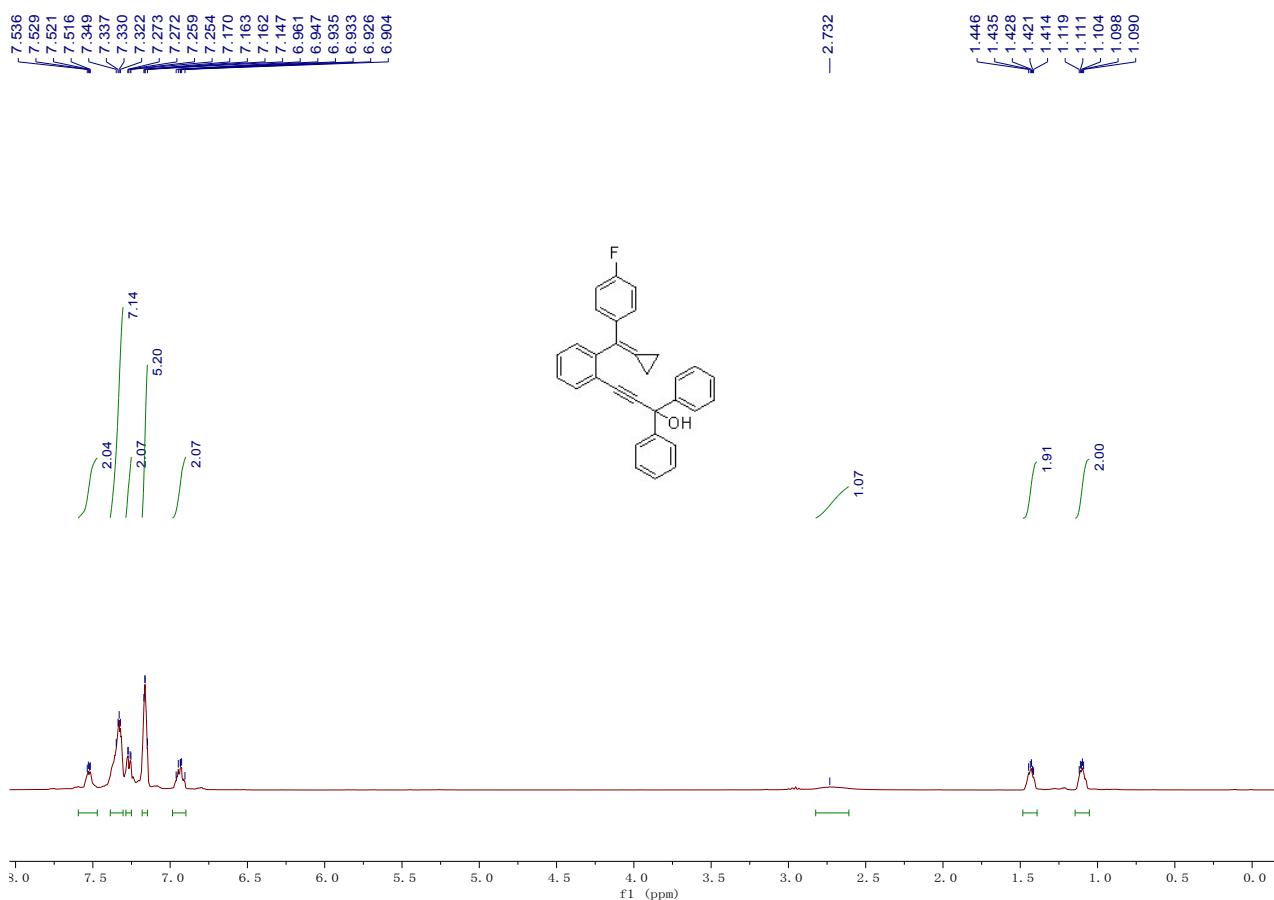


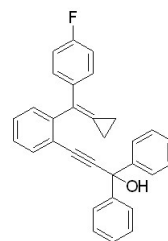
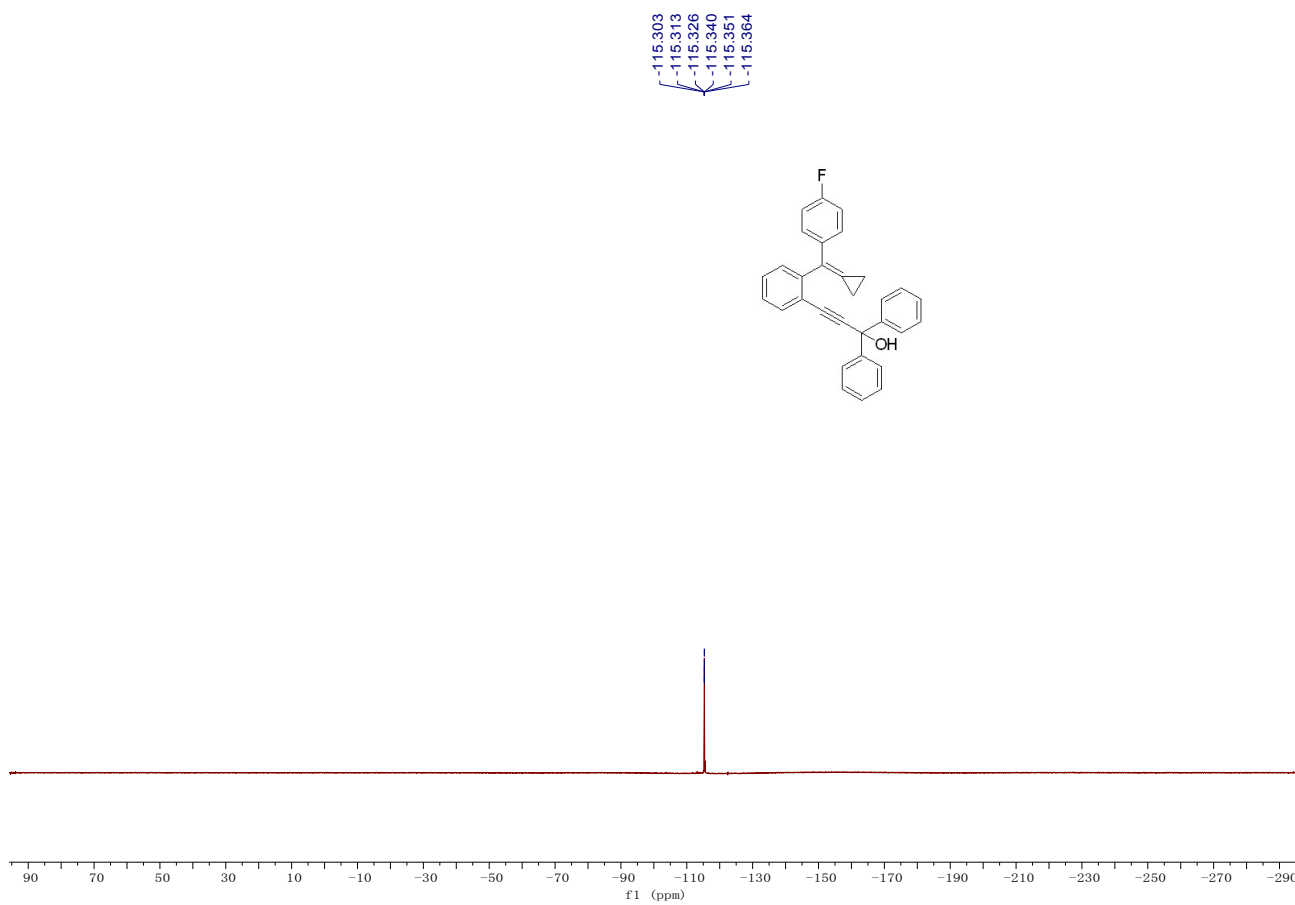
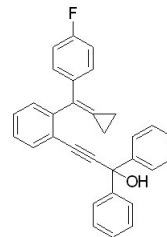
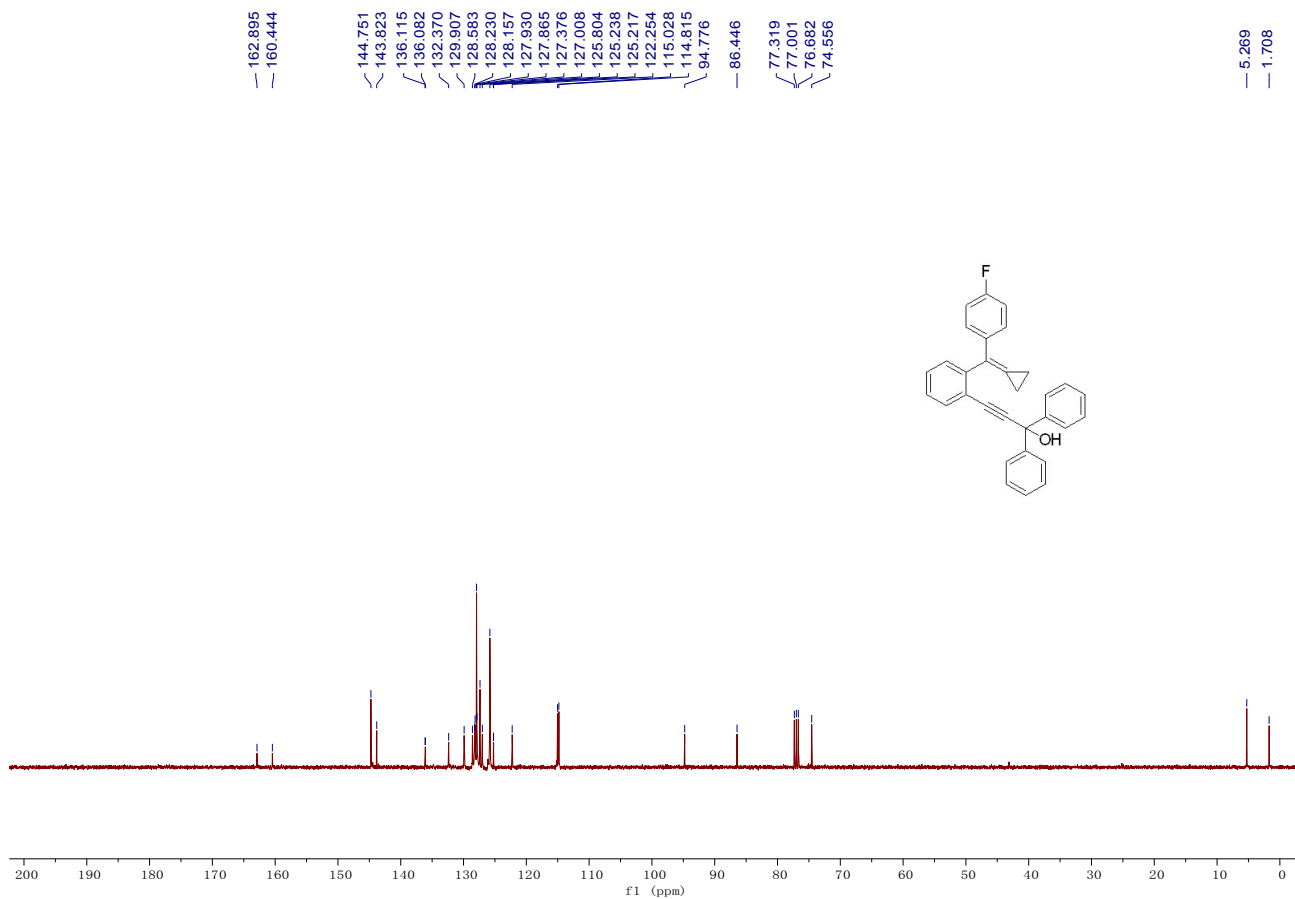
To a degassed solution of **2a** (1.0 equiv), KF (3.3 equiv) and boric acids (1.1 equiv) in dry THF (2 mL) was added $\text{Pd}_2(\text{dba})_3$ (5 mol%) and $\text{HP}(\text{tBu})_3\text{BF}_4$ (15 mol%), and the resulting mixture was stirred at $80\text{ }^\circ\text{C}$ for 8 h. After removing the solvent under reduced pressure, the crude ^1H NMR spectrum was determined.

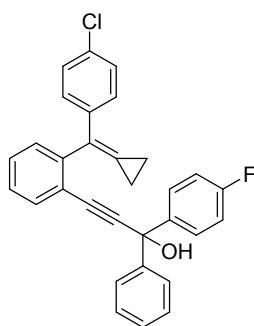
6. Characterization and spectra charts



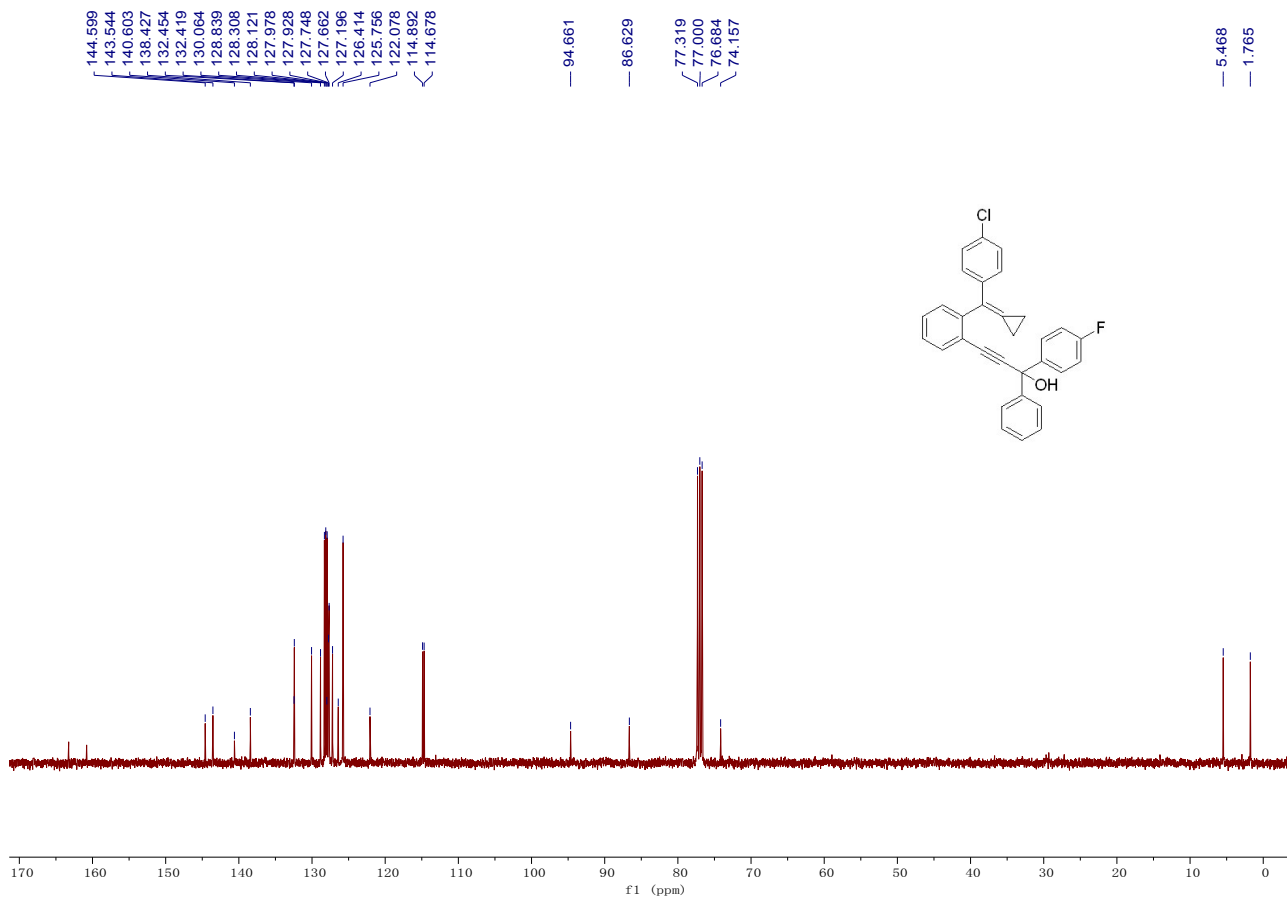
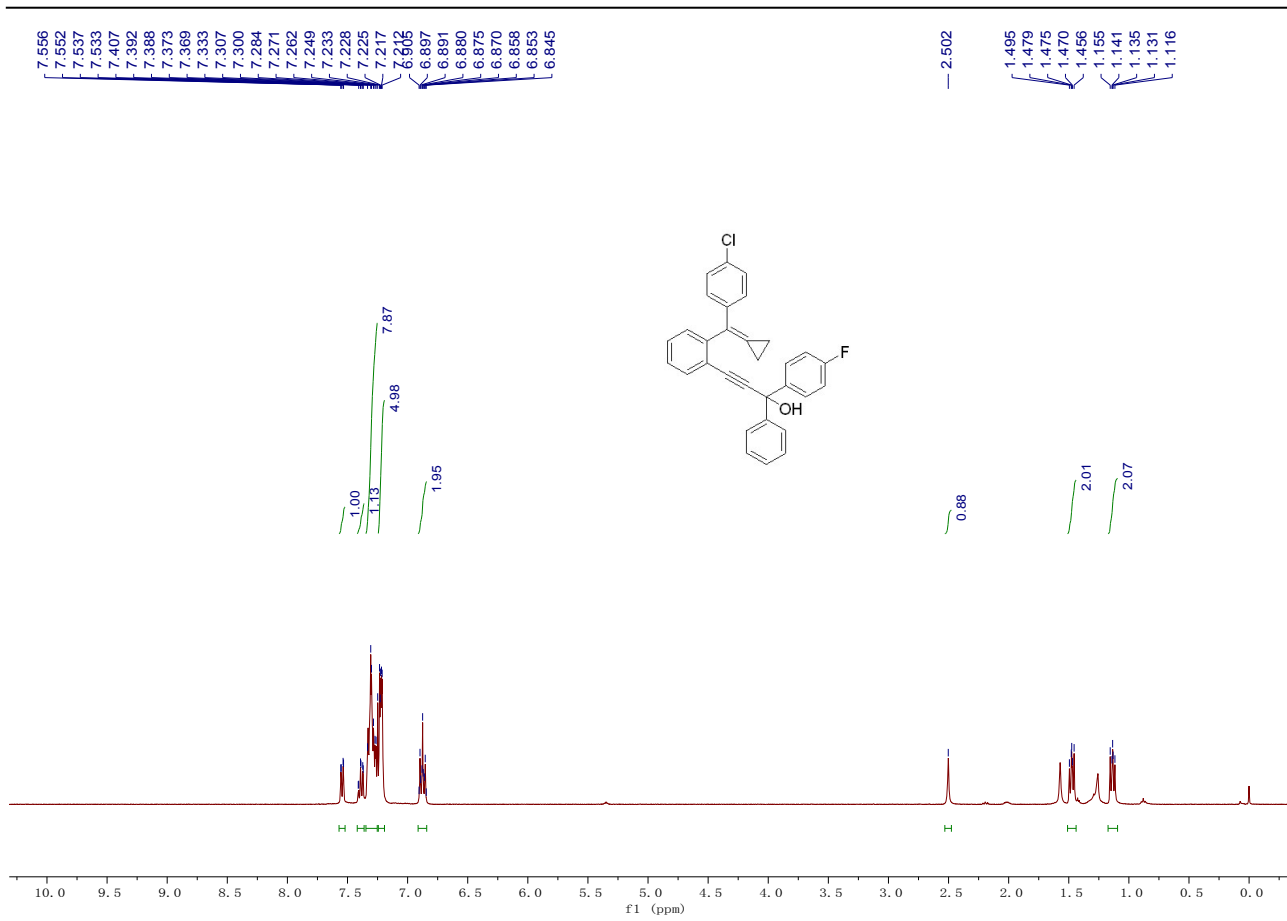
Compound 1f: Yield: 1.3 g, 80%; A white solid; Mp: 89 - 91 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.47 (m, 2H), 7.39 – 7.30 (m, 7H), 7.29 – 7.25 (m, 2H), 7.18 – 7.15 (m, 5H), 6.98 – 6.90 (m, 2H), 2.73 (s, 1H), 1.48 – 1.39 (m, 2H), 1.15 – 1.05 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.7 (d, $J = 246.3$ Hz), 144.8, 143.8, 136.1, 136.1, 132.4, 129.9, 128.6, 128.2 (d, $J = 7.4$ Hz), 127.9, 127.4, 127.0, 125.8, 125.2 (d, $J = 2.1$ Hz), 122.3, 114.9 (d, $J = 21.3$ Hz), 94.8, 86.4, 74.6, 5.3, 1.7; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.25 – -115.42 (m); IR (neat): ν 2925, 2857, 1501, 1089, 834, 757 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{31}\text{H}_{23}\text{FO}$ $[\text{M}]^+$: 430.1727, Found: 430.1737.

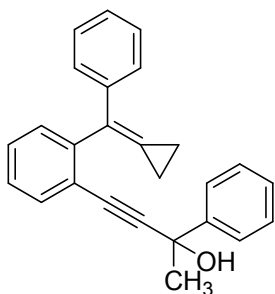
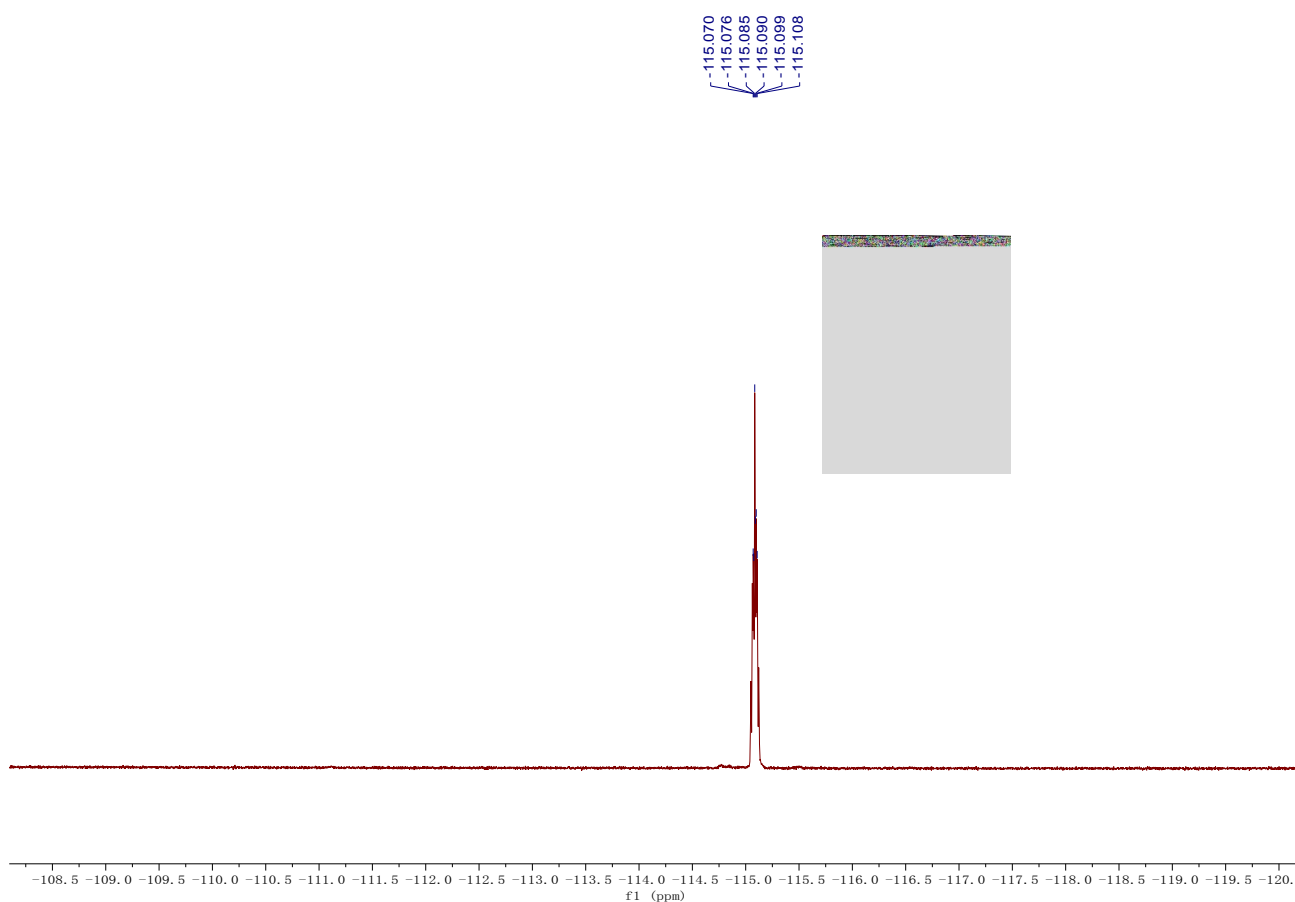




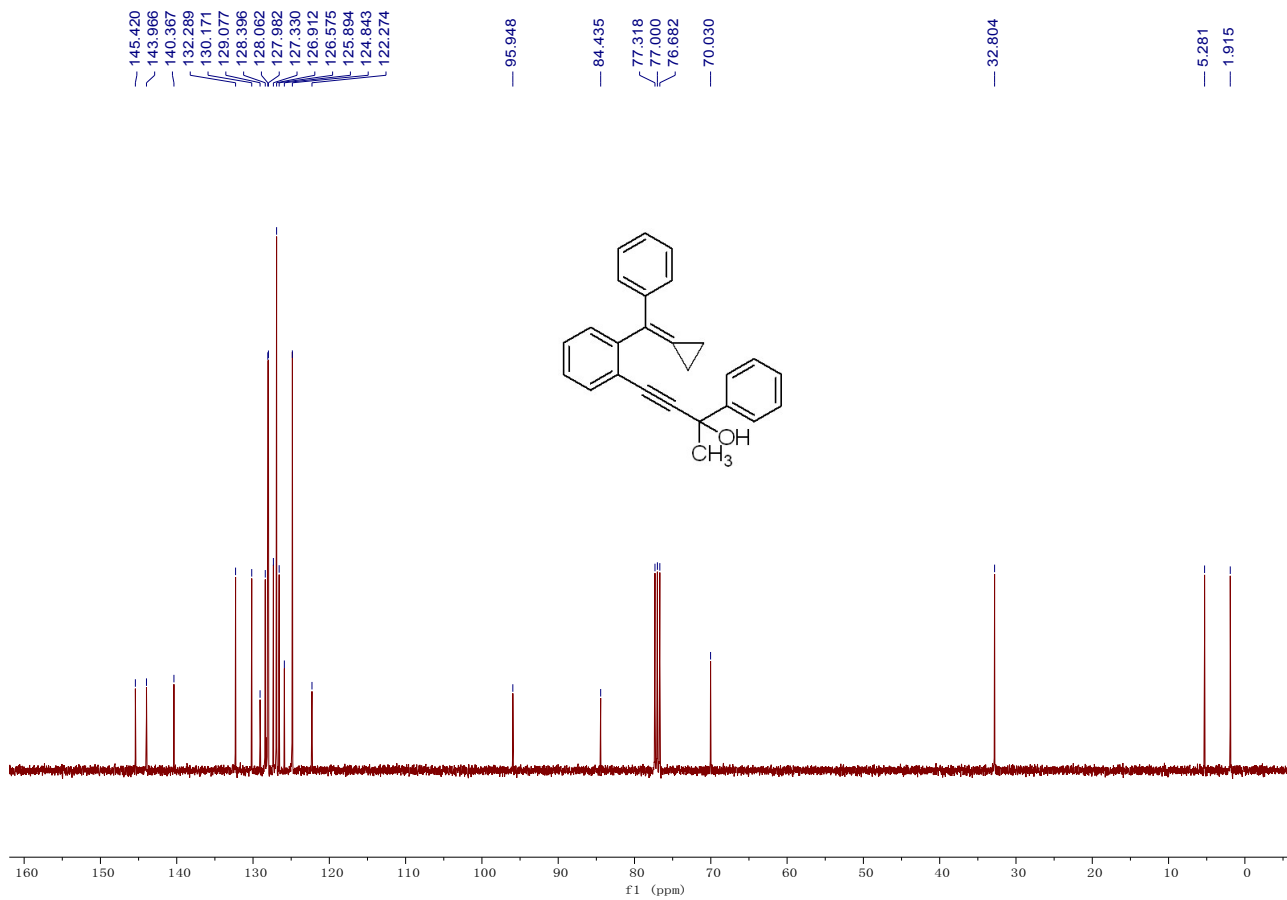
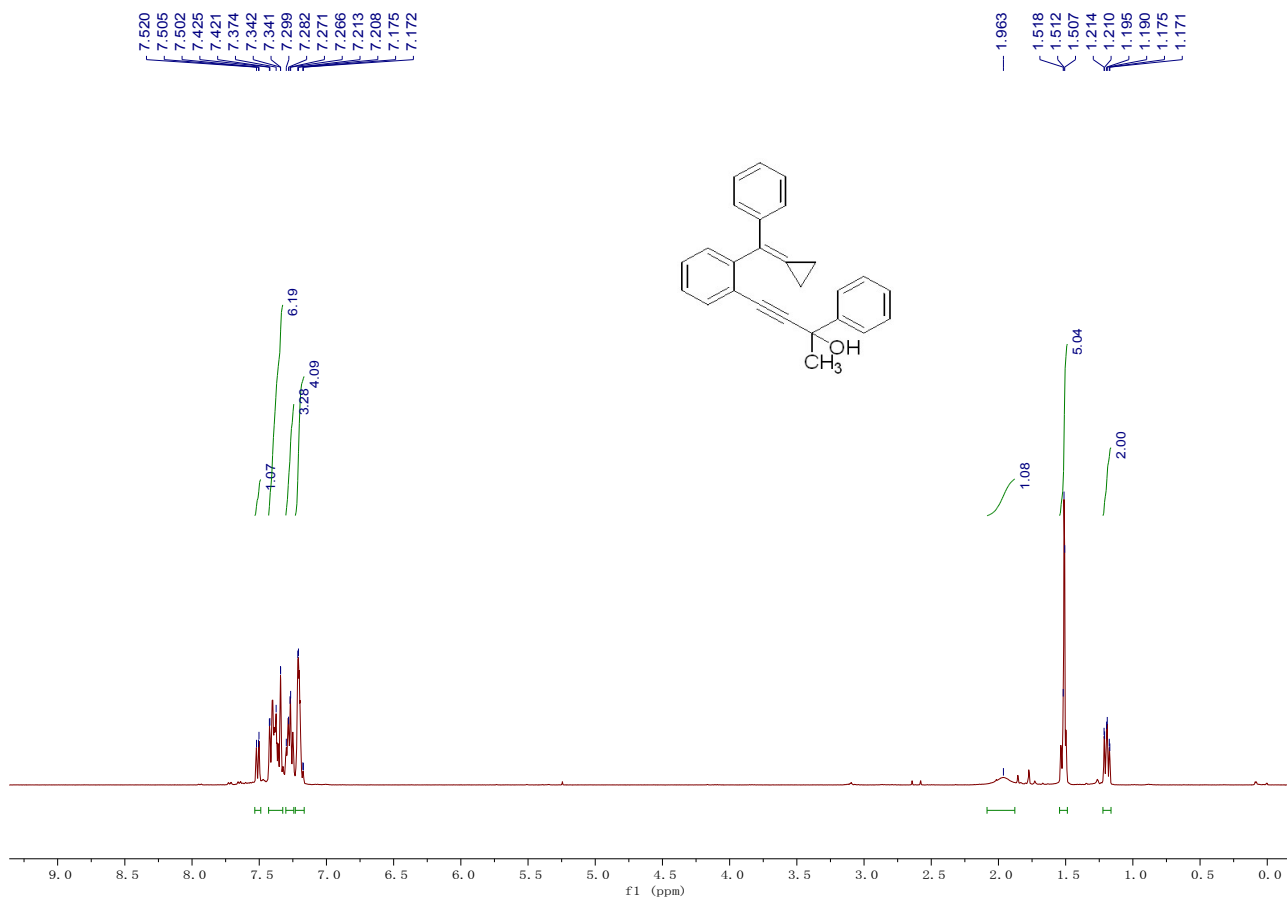


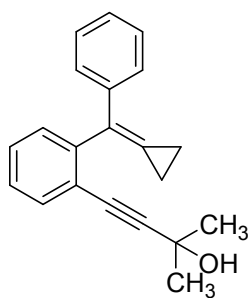
Compound 1k: Yield: 1.9 g, 85%; A white solid; Mp: 98 - 100 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.41 – 7.36 (m, 1H), 7.35 – 7.25 (m, 8H), 7.24 – 7.19 (m, 5H), 6.91 – 6.84 (m, 2H), 2.50 (s, 1H), 1.51 – 1.44 (m, 2H), 1.17 – 1.09 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.0 (d, $J = 246.6$ Hz), 144.6, 143.5, 140.6, 138.4, 132.5, 132.4, 130.1, 128.8, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 127.2, 126.4, 125.8, 122.1, 114.8 (d, $J = 21.5$ Hz), 94.7, 86.6, 74.2, 5.5, 1.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.05 – -115.13 (m); IR (neat): ν 2927, 1599, 1505, 1484, 1218, 1153, 754 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{31}\text{H}_{22}\text{ClFO}$ $[\text{M}]^+$: 464.1338, Found: 464.1339.



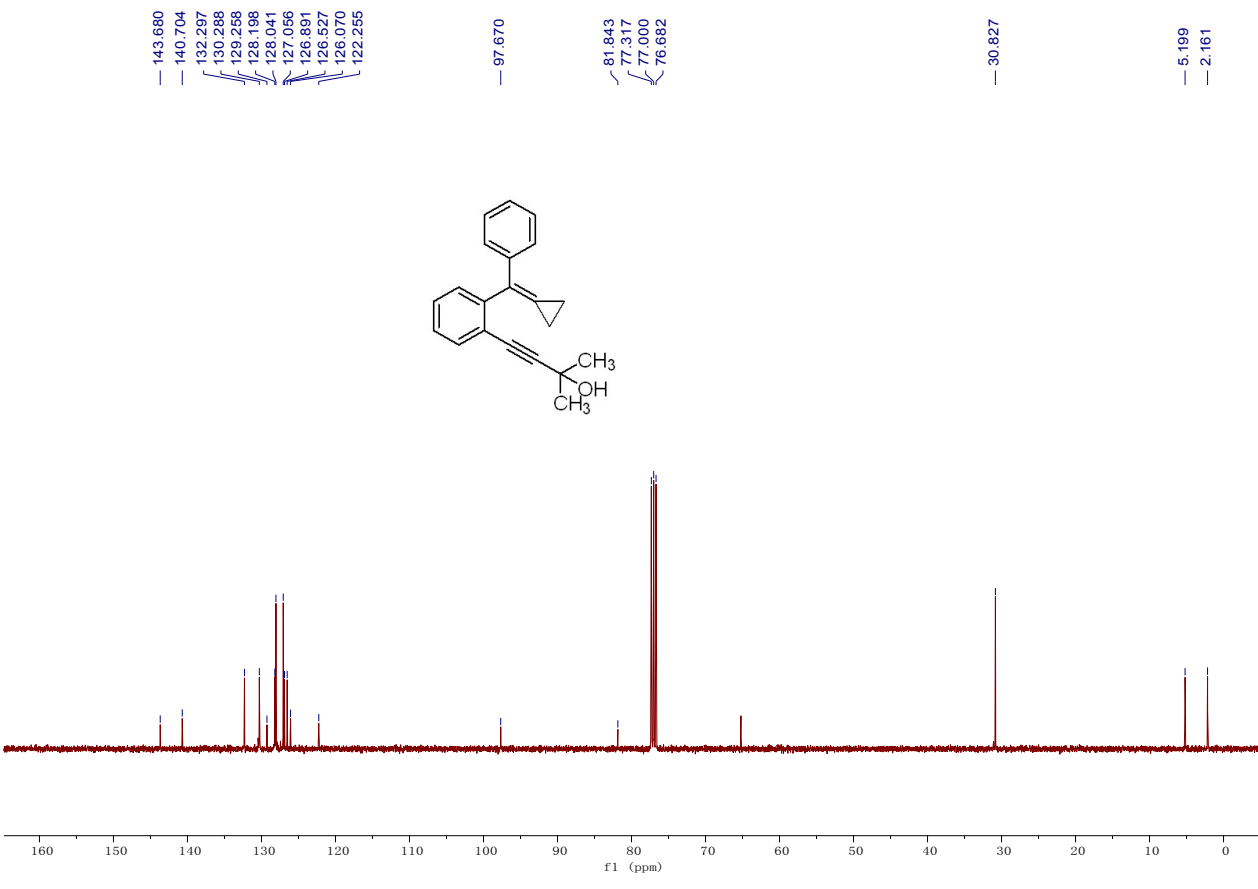
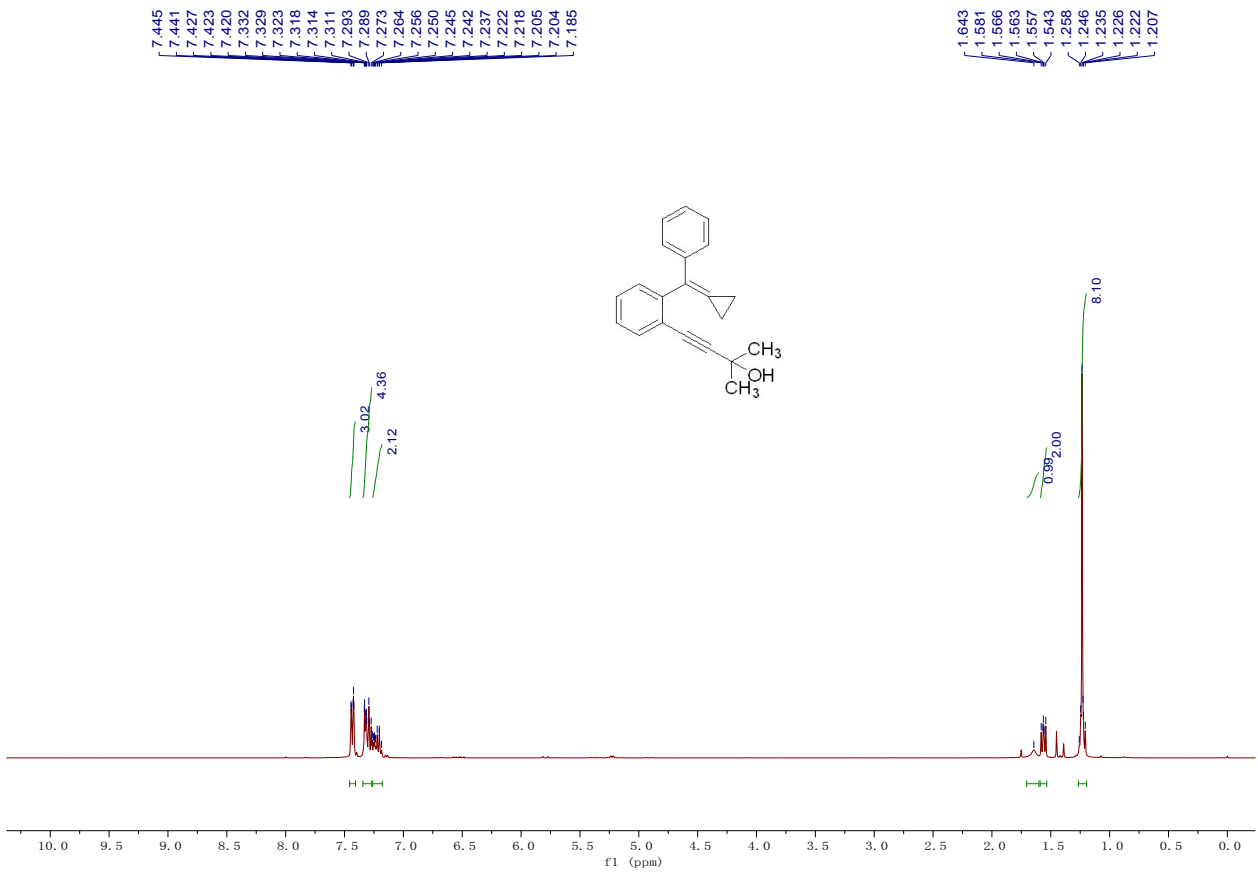


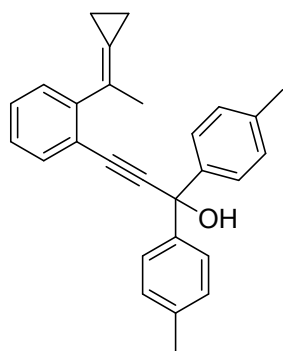
Compound 1o: Yield: 1.1 g, 70%; A faint yellow oil; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.49 (m, 1H), 7.43 – 7.32 (m, 6H), 7.30 – 7.24 (m, 3H), 7.23 – 7.17 (m, 4H), 1.96 (s, 1H), 1.55 – 1.49 (m, 5H), 1.22 – 1.16 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 145.4, 144.0, 140.4, 132.3, 130.2, 129.1, 128.4, 128.1, 128.0, 127.3, 126.9, 126.6, 125.9, 124.8, 122.3, 95.9, 84.4, 70.0, 32.8, 5.3, 1.9; IR (neat): ν 3372, 2965, 1483, 1089, 1034, 759 cm⁻¹; HRMS (DART) Calcd. for C₂₆H₂₂O [M+NH₄]⁺: 368.2009, Found: 368.2006.



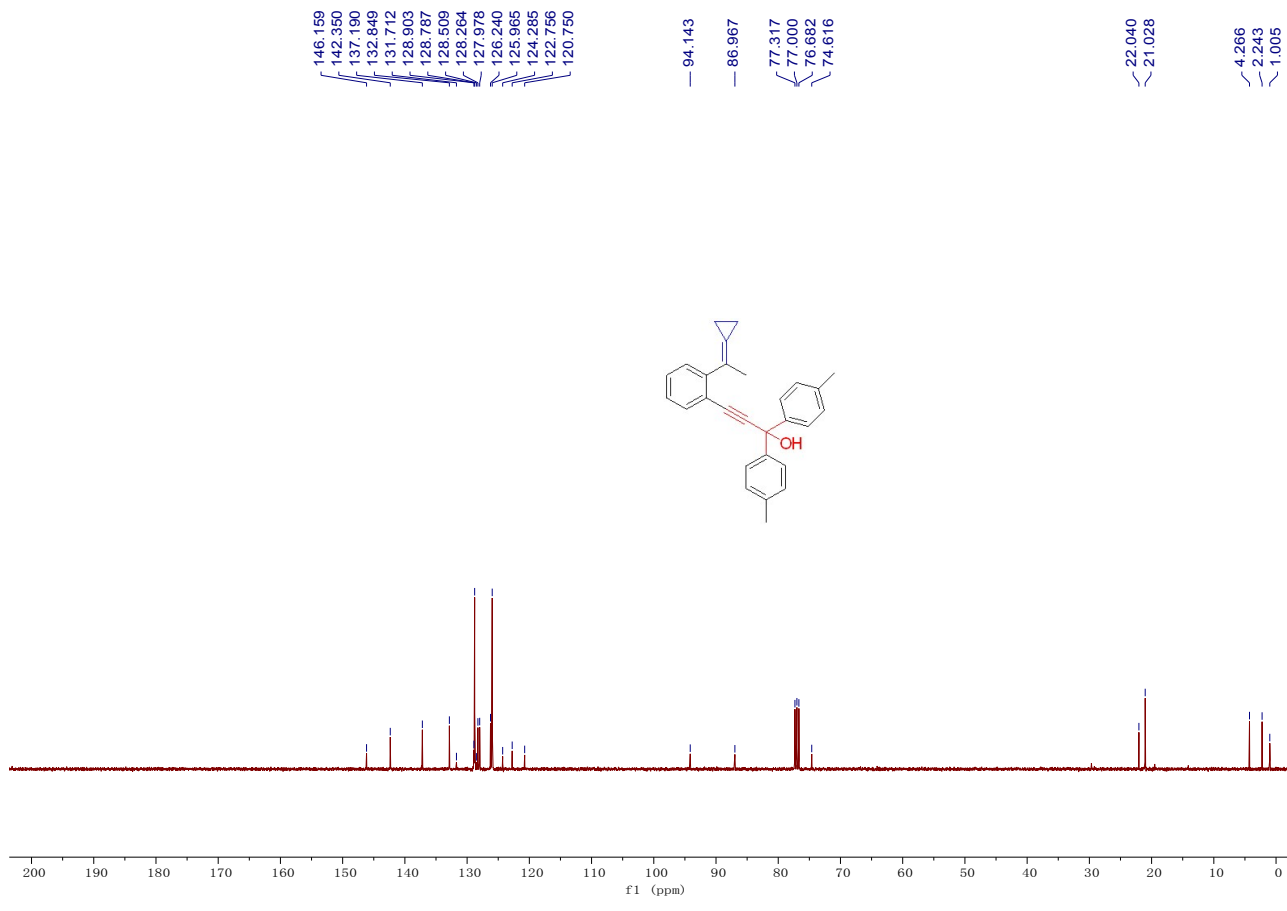
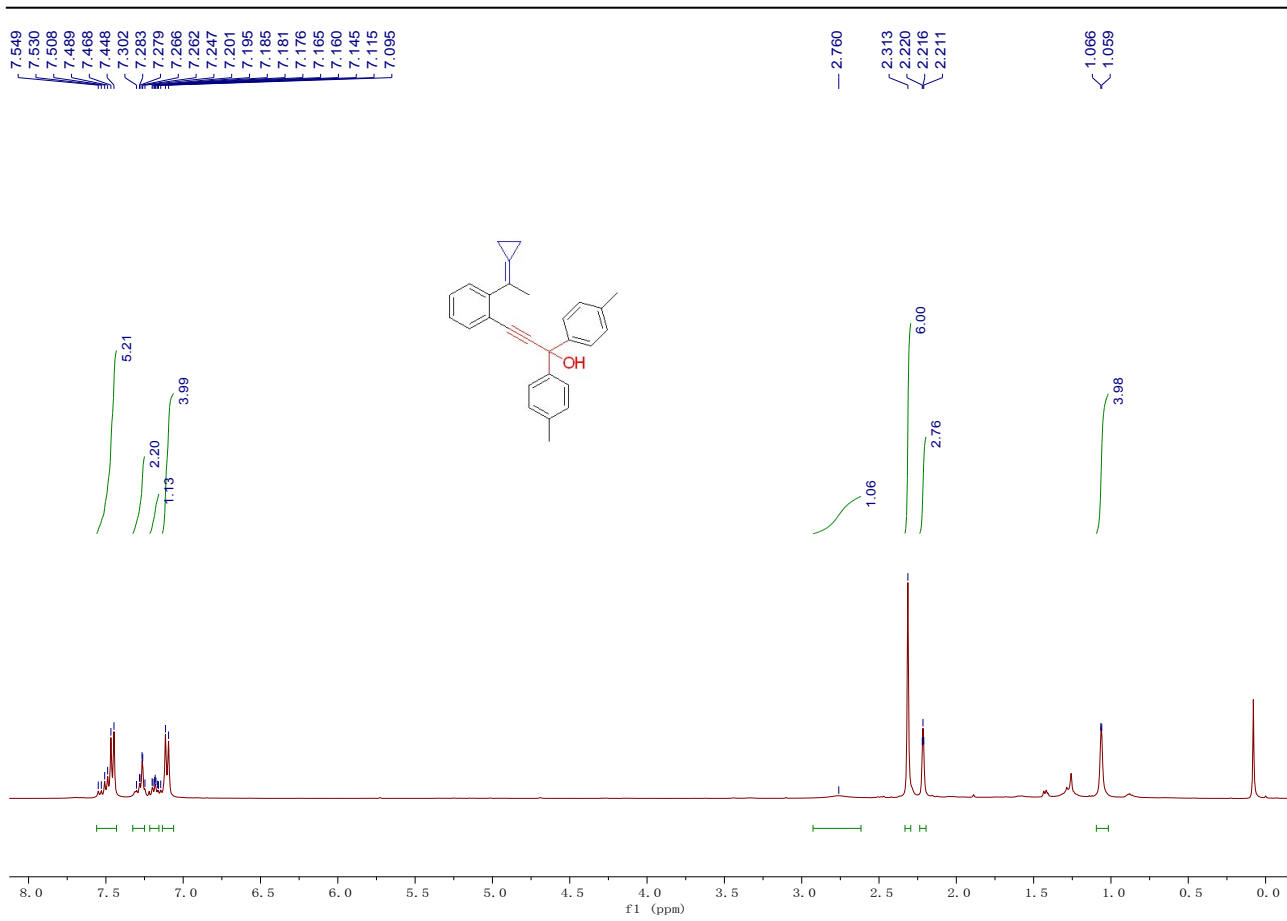


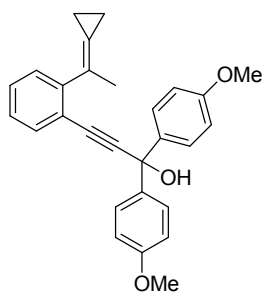
Compound 1p: Yield: 0.8 g, 65%; A faint yellow oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 3H), 7.34 – 7.27 (m, 4H), 7.26 – 7.18 (m, 2H), 1.64 (s, 1H), 1.59 – 1.53 (m, 2H), 1.26 – 1.20 (m, 8H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.7, 140.7, 132.3, 130.3, 129.3, 128.2, 128.0, 127.1, 126.9, 126.5, 126.1, 122.3, 97.7, 81.8, 30.8, 5.2, 2.2; IR (neat): ν 2925, 2857, 1501, 1089, 834, 757 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{21}\text{H}_{20}\text{O}$ $[\text{M}]^+$: 288.1509, Found: 288.1507.



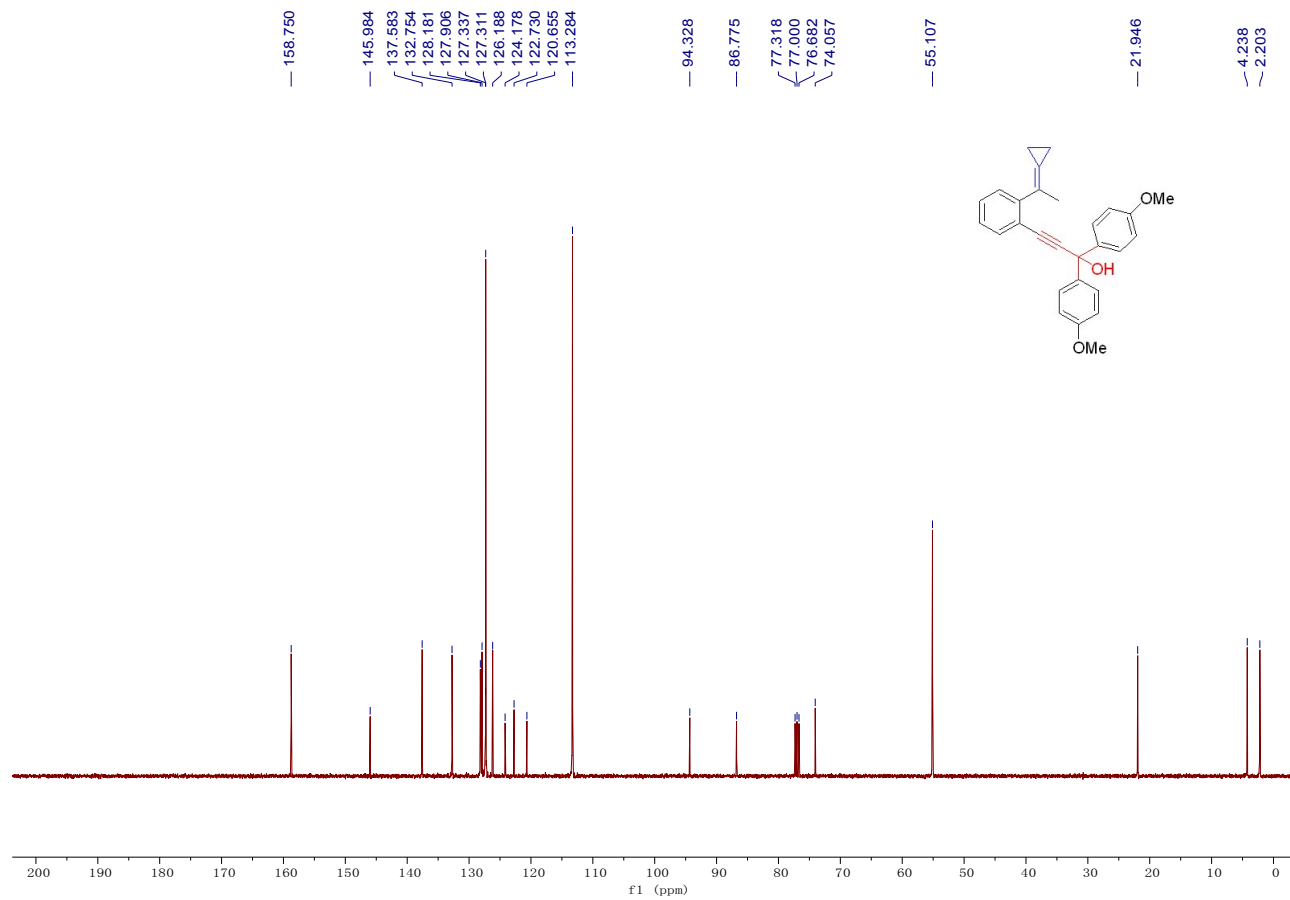
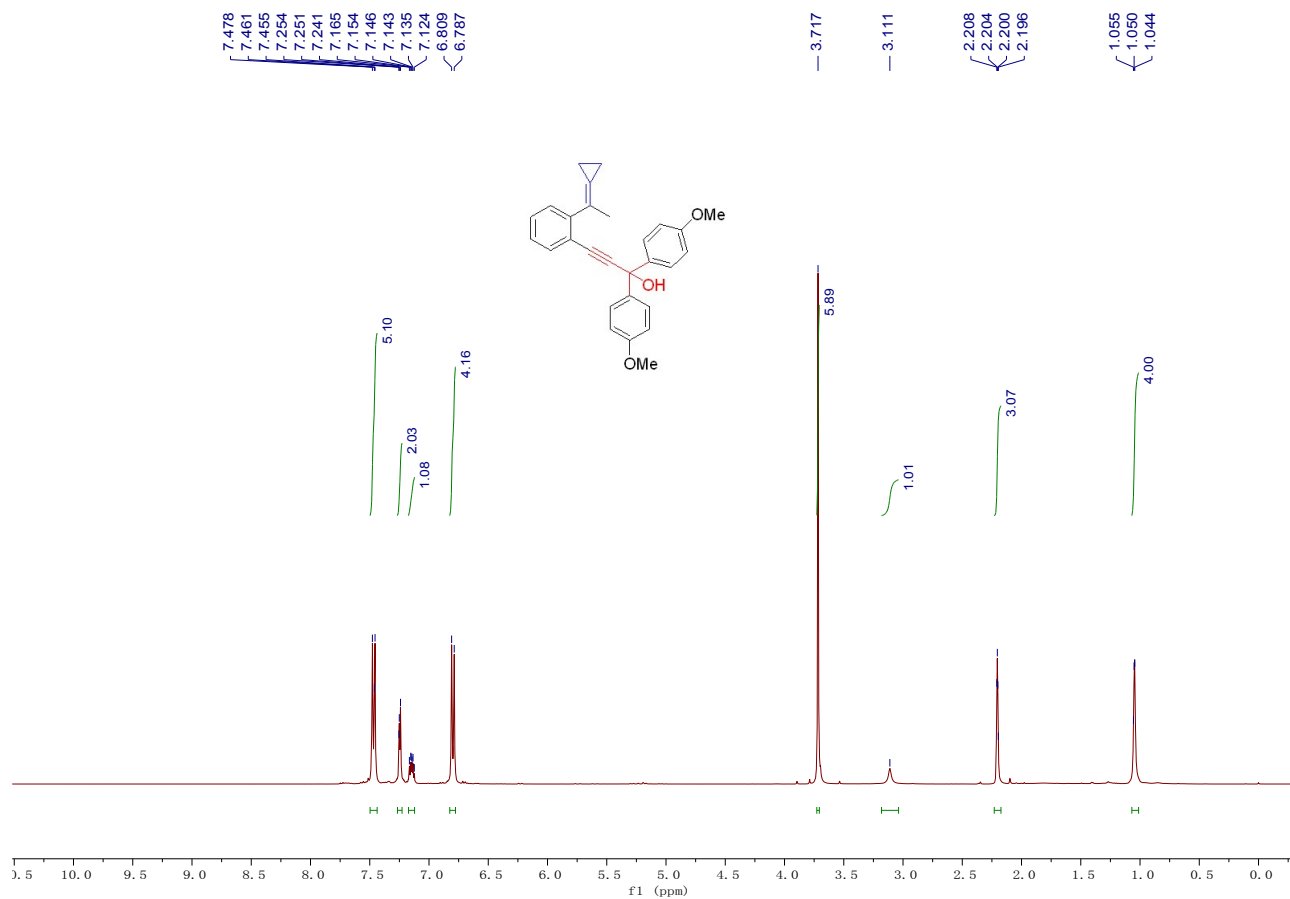


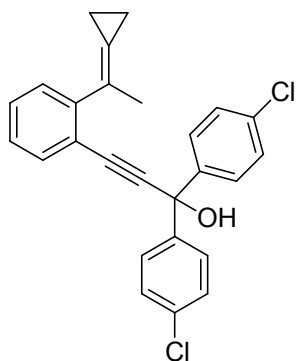
Compound 1r: Yield: 0.9 g, 48%; A faint yellow oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.43 (m, 5H), 7.33 – 7.25 (m, 2H), 7.22 – 7.16 (m, 1H), 7.10 (d, $J = 8.0$ Hz, 4H), 2.76 (s, 1H), 2.31 (s, 6H), 2.24 – 2.20 (m, 3H), 1.09 – 1.02 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.2, 142.3, 137.2, 132.8, 131.7, 128.9, 128.8, 128.5, 128.3, 128.0, 126.2, 126.0, 124.3, 122.8, 120.7, 94.1, 87.0, 74.6, 22.0, 21.0, 4.3, 2.2, 1.0; IR (neat): ν 3423, 2969, 2912, 1508, 989, 754, 754, 806 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{28}\text{H}_{26}\text{O}$ $[\text{M}]^+$: 378.1978, Found: 378.1979.



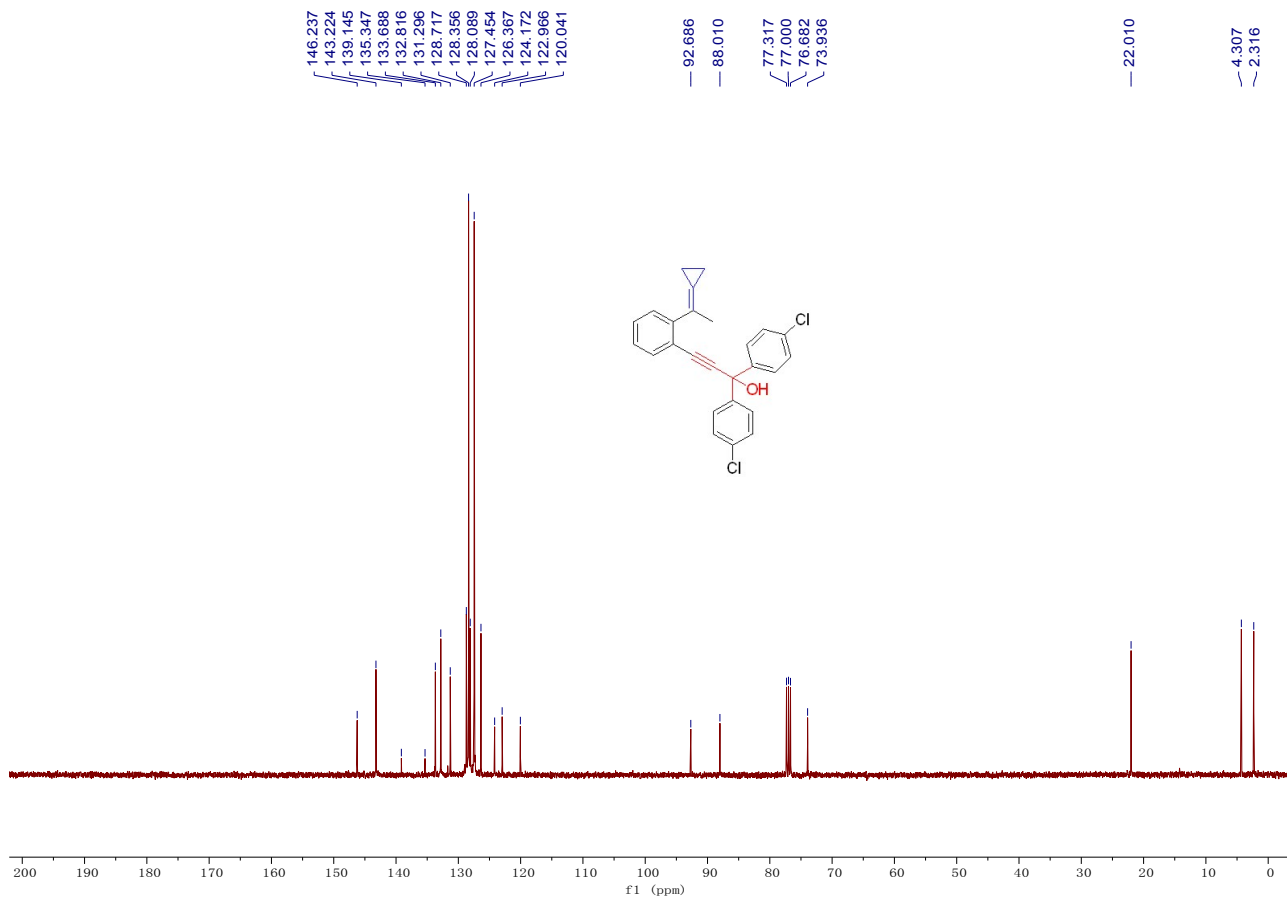
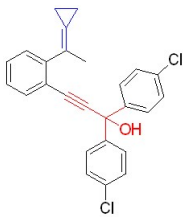
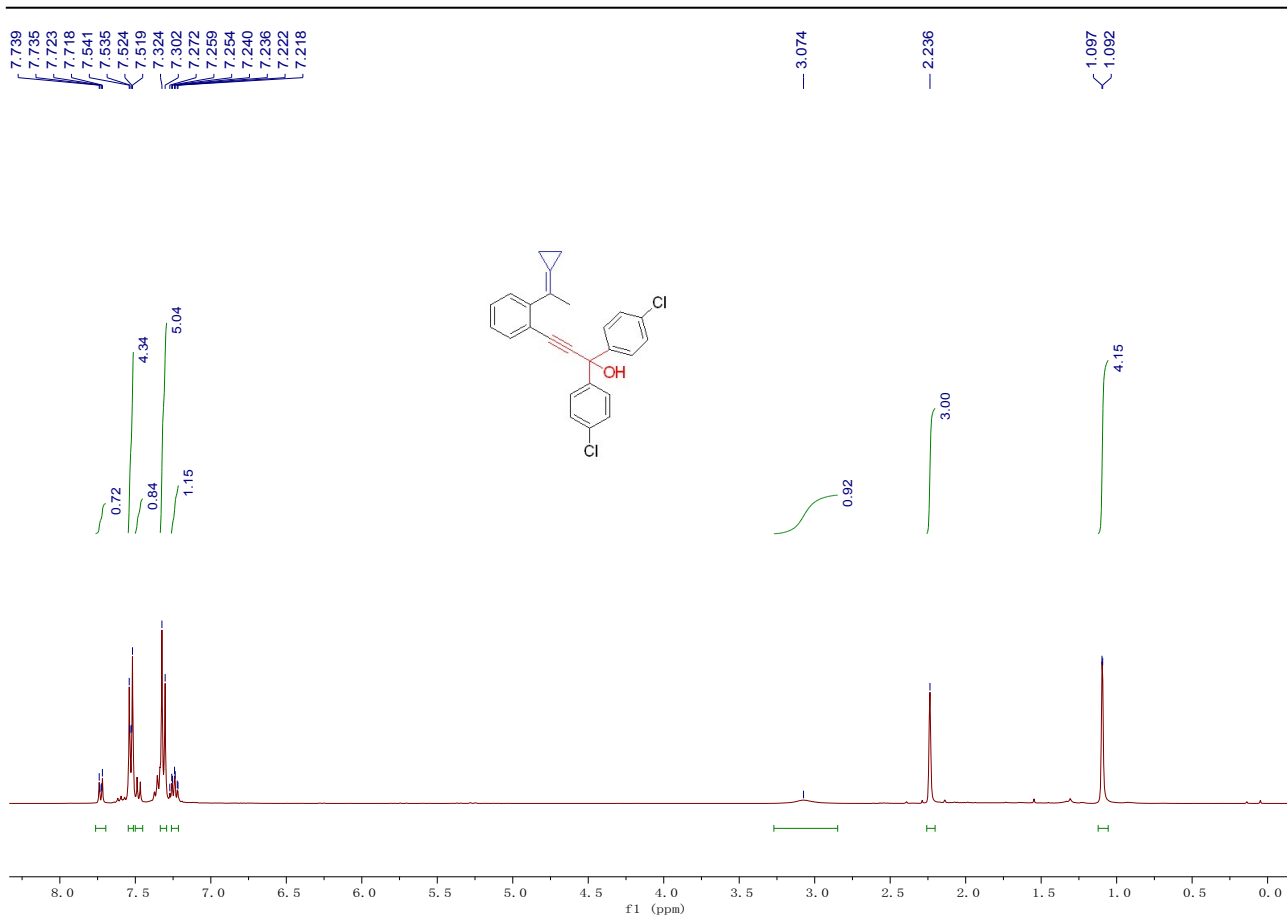


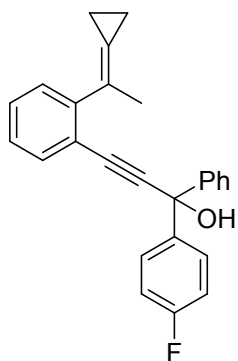
Compound 1s: Yield: 2.3 g, 69%; A faint yellow oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.43 (m, 5H), 7.28 – 7.22 (m, 2H), 7.19 – 7.10 (m, 1H), 6.83 – 6.76 (m, 4H), 3.72 (s, 6H), 2.23 – 2.17 (m, 3H), 1.05 (s, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.7, 146.0, 137.6, 132.8, 128.2, 127.9, 127.3, 126.2, 124.2, 122.7, 120.7, 113.3, 94.3, 86.8, 74.1, 55.1, 21.9, 4.2, 2.2; IR (neat): ν 2831, 1604, 1505, 1247, 1163, 1030, 827, 756 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{28}\text{H}_{26}\text{O}_3$ $[\text{M}]^+$: 410.1876, Found: 410.1876.



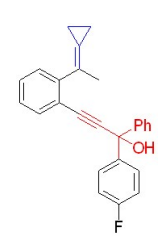
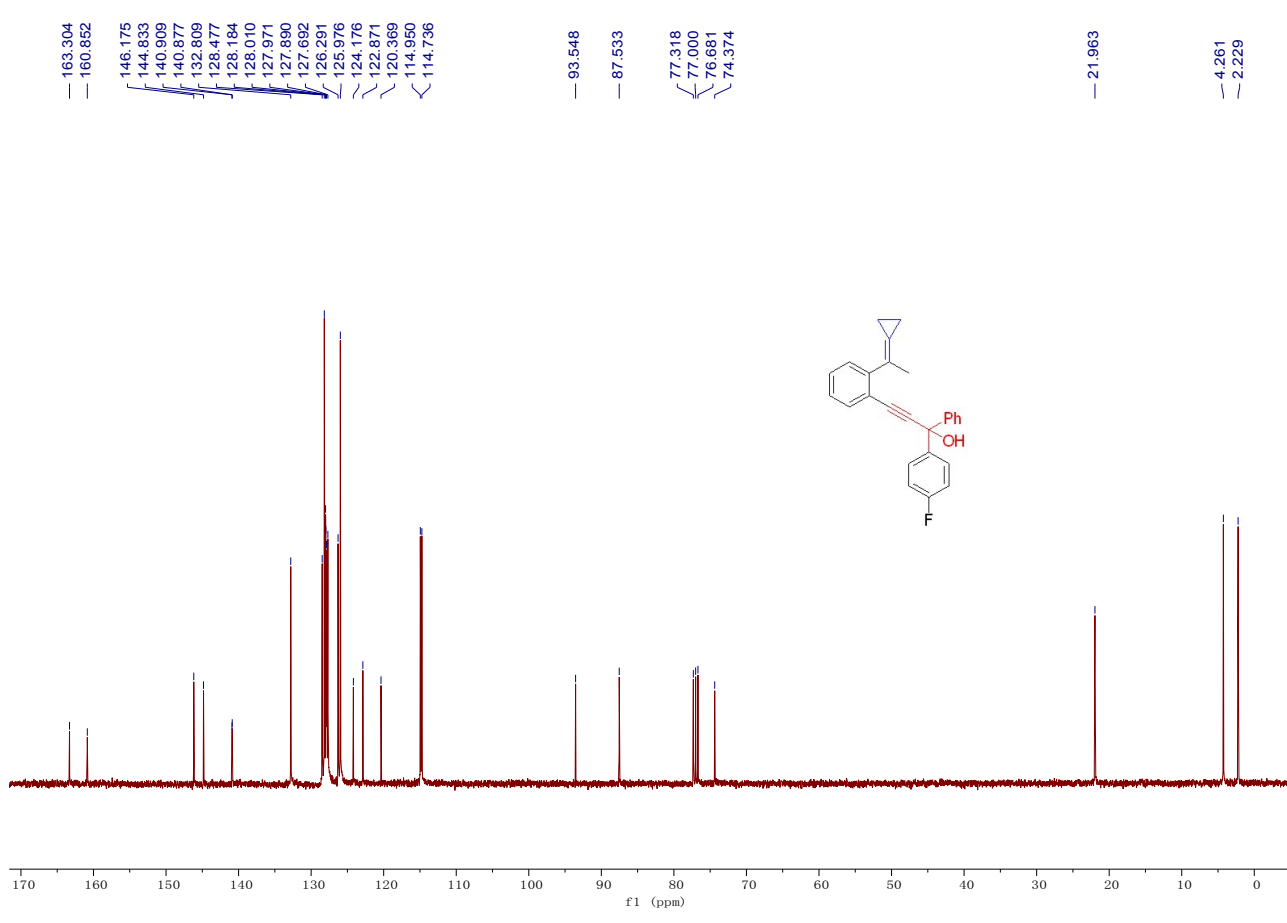
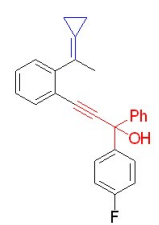
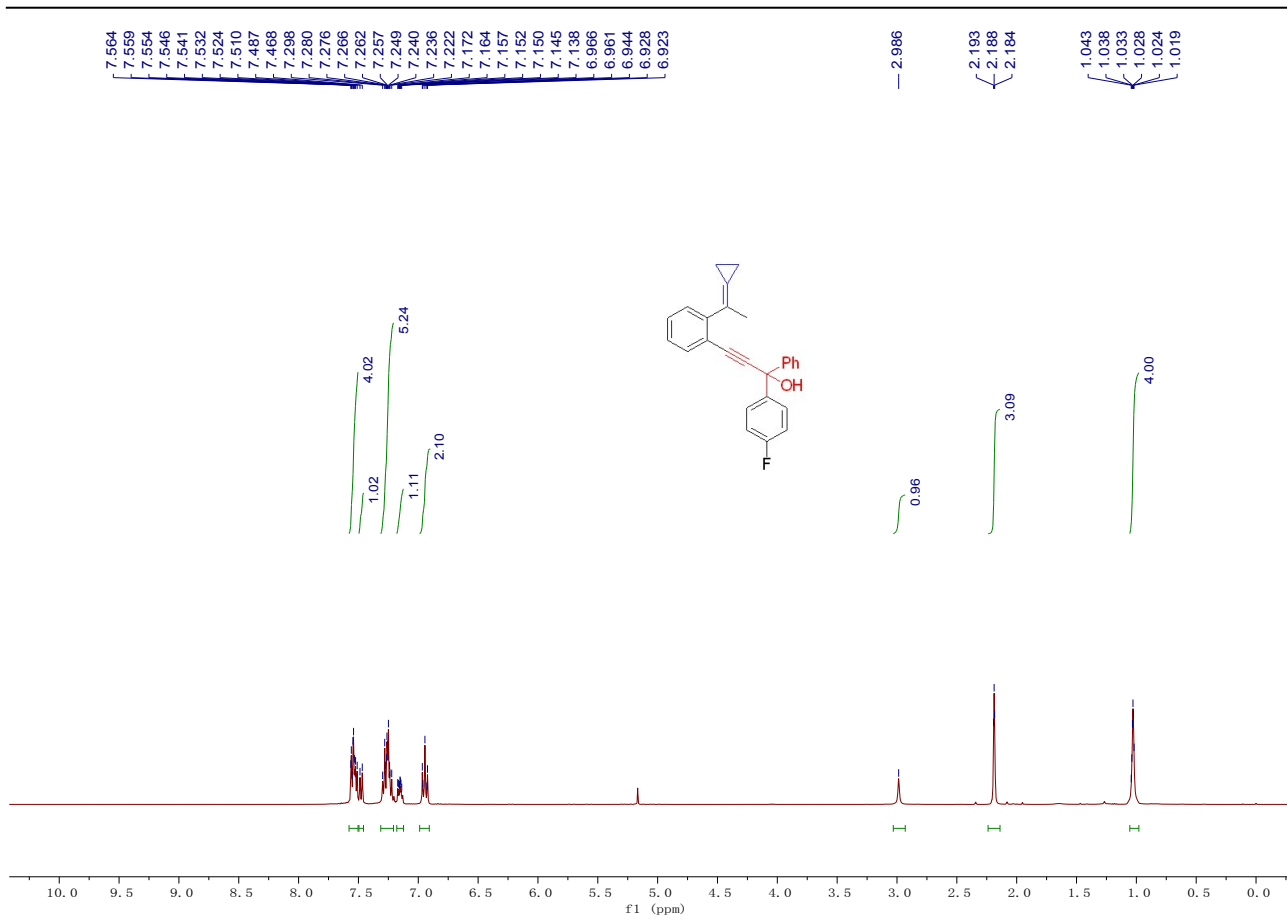


Compound 1t: Yield: 0.6 g, 53%; A faint yellow oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.70 (m, 1H), 7.55 – 7.51 (m, 4H), 7.50 – 7.45 (m, 1H), 7.33 – 7.29 (m, 5H), 7.26 – 7.21 (m, 1H), 3.02 (s, 1H), 2.26 – 2.20 (m, 3H), 1.12 – 1.06 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.2, 143.2, 139.1, 133.7, 132.8, 131.3, 128.7, 128.4, 128.1, 127.5, 126.4, 124.2, 123.0, 120.0, 92.7, 88.0, 73.9, 22.0, 4.3, 2.3; IR (neat): ν 3420, 2972, 1487, 1090, 1015, 816, 759 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{26}\text{H}_{20}\text{Cl}_2\text{O}$ $[\text{M}]^+$: 418.0886, Found: 418.0887.

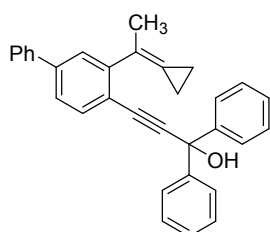
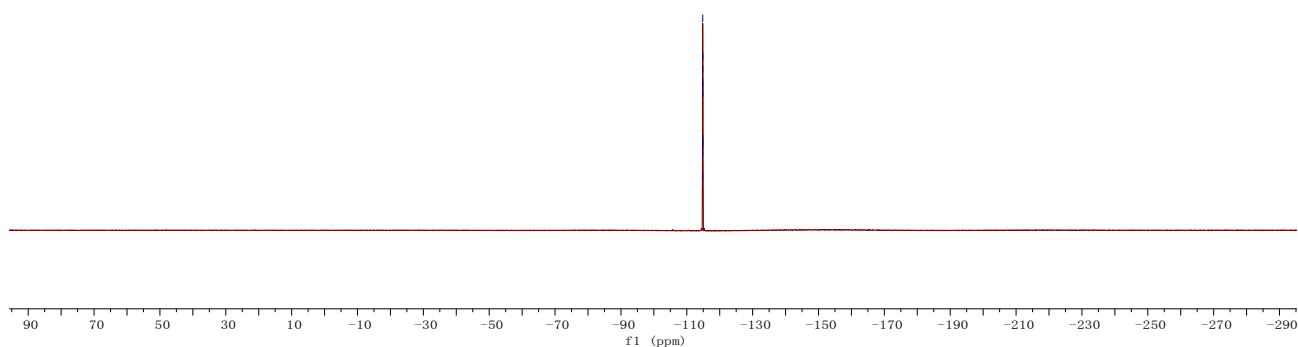
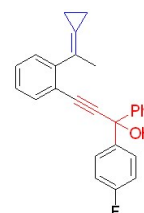




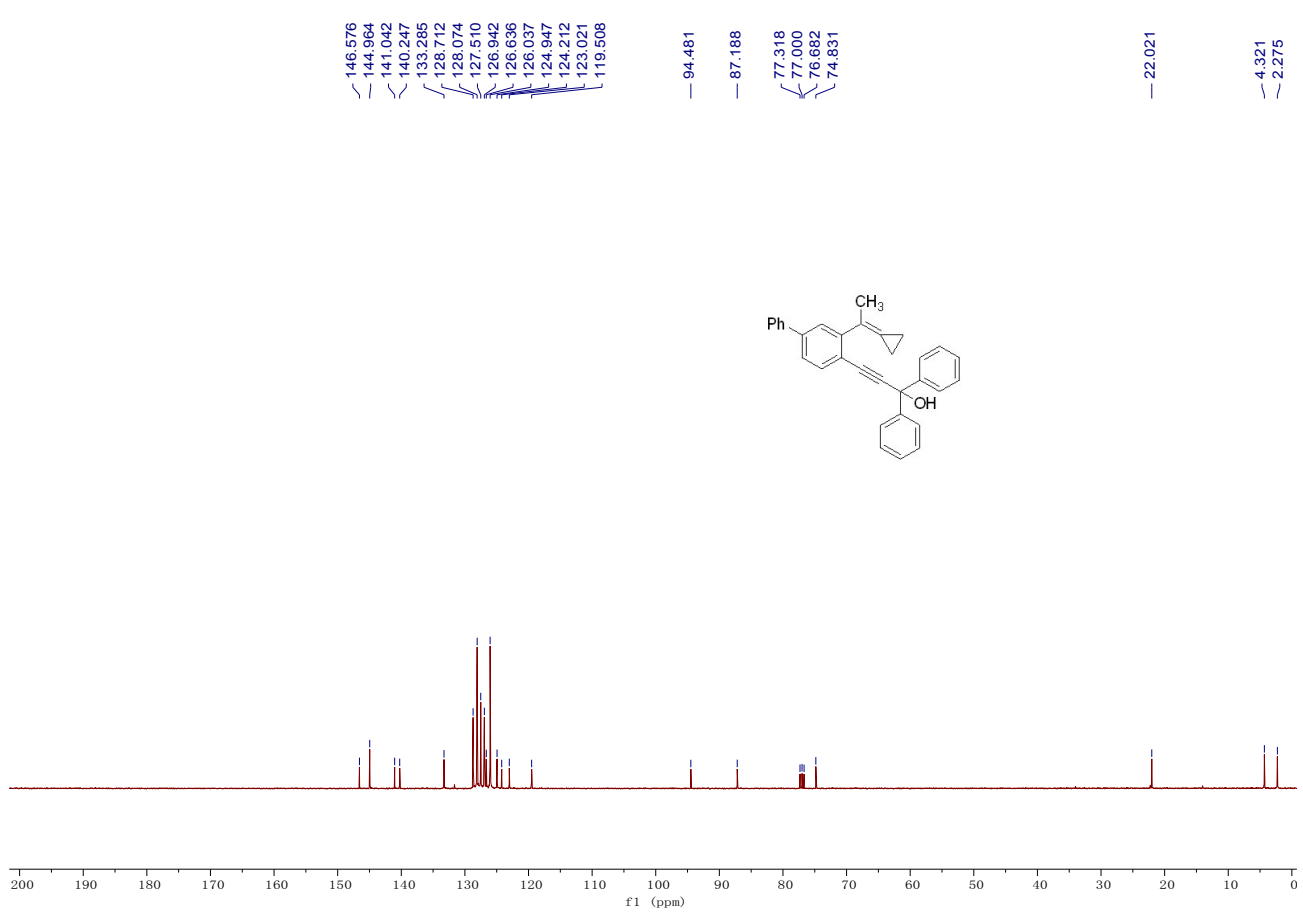
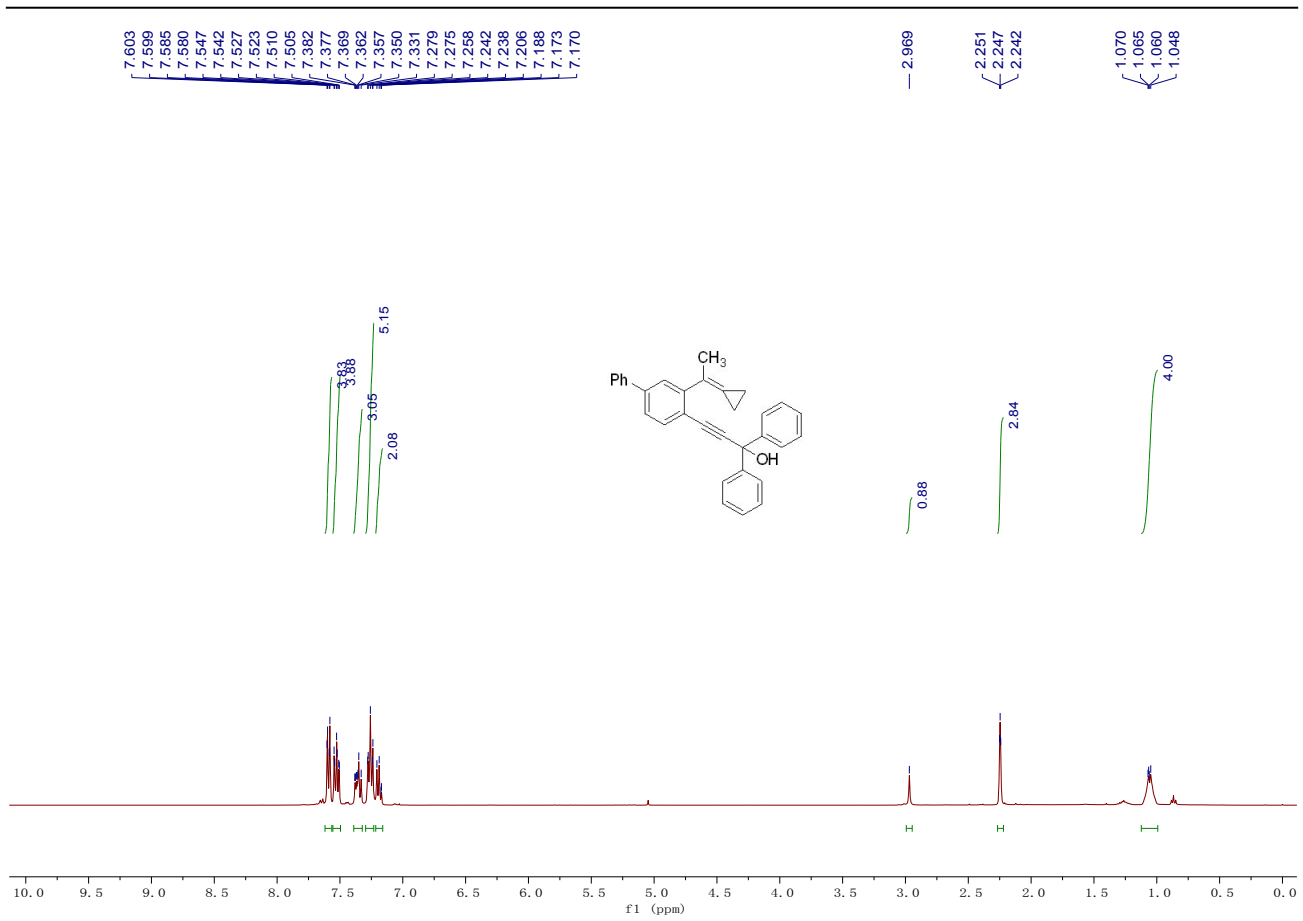
Compound 1u: Yield: 1.2 g, 59%; A faint yellow oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.50 (m, 4H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.31 – 7.21 (m, 5H), 7.18 – 7.12 (m, 1H), 6.99 – 6.91 (m, 2H), 2.99 (s, 1H), 2.24 – 2.14 (m, 3H), 1.05 – 0.98 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.1 (d, $J = 246.5$ Hz), 146.2, 144.8, 140.9 (d, $J = 3.2$ Hz), 132.8, 128.5, 128.2, 128.0, 127.9 (d, $J = 8.2$ Hz), 127.7, 126.3, 126.0, 124.2, 122.9, 120.4, 114.8 (d, $J = 21.5$ Hz), 93.5, 87.5, 74.4, 22.0, 4.3, 2.2; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.77 – -114.90 (m); IR (neat): ν 3380, 2989, 1496, 1040, 759, 696 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{26}\text{H}_{21}\text{FO}$ $[\text{M}]^+$: 368.1571, Found: 368.1574.

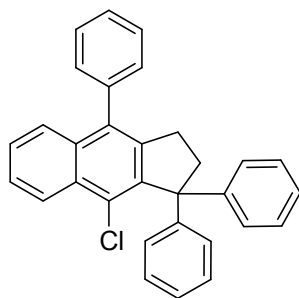


-114.798
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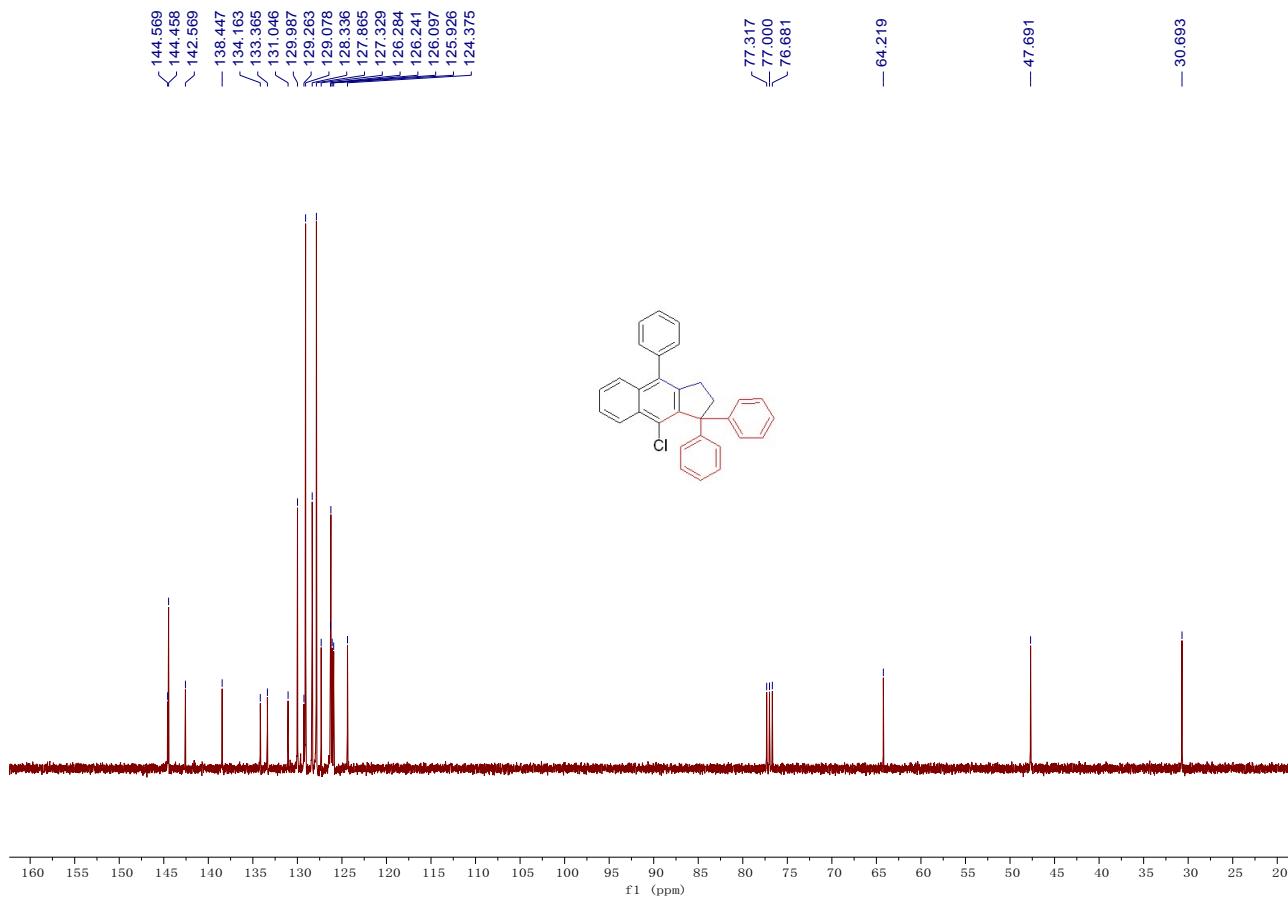
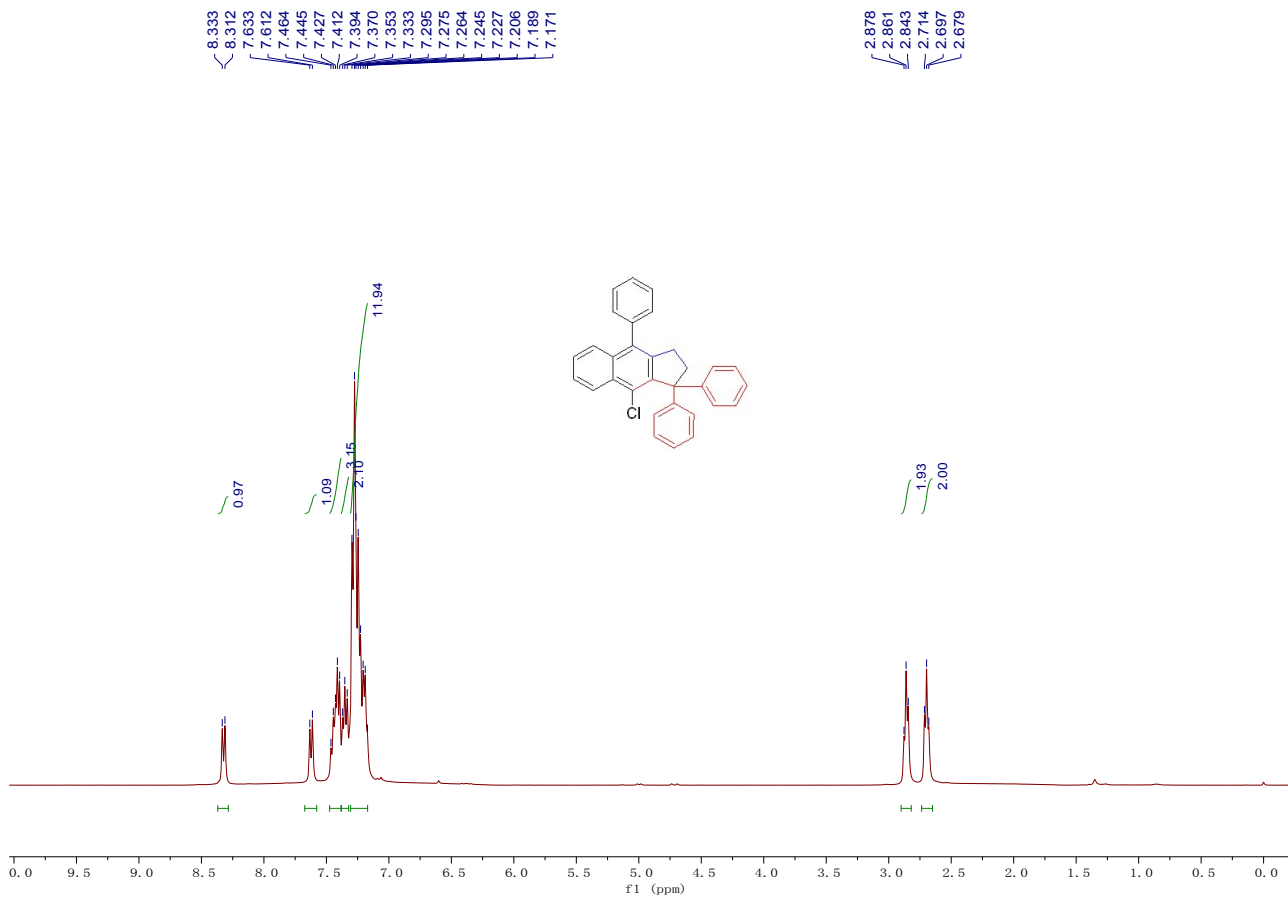


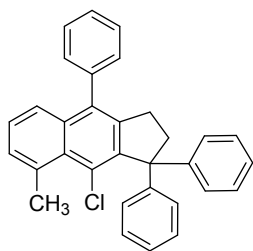
Compound 1v: Yield: 1.2 g, 89%; A faint yellow oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.56 (m, 4H), 7.56 – 7.50 (m, 4H), 7.39 – 7.32 (m, 3H), 7.30 – 7.23 (m, 5H), 7.22 – 7.16 (m, 2H), 2.97 (s, 1H), 2.27 – 2.22 (m, 3H), 1.12 – 0.99 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.6, 145.0, 141.0, 140.2, 133.3, 128.7, 128.1, 127.5, 126.9, 126.6, 126.0, 124.9, 124.2, 123.0, 119.5, 94.5, 87.2, 74.8, 22.0, 4.3, 2.3; IR (neat): ν 3371, 2966, 1482, 1445, 1033, 759, 696 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{32}\text{H}_{26}\text{O}$ $[\text{M}]^+$: 426.1978, Found: 426.1980.



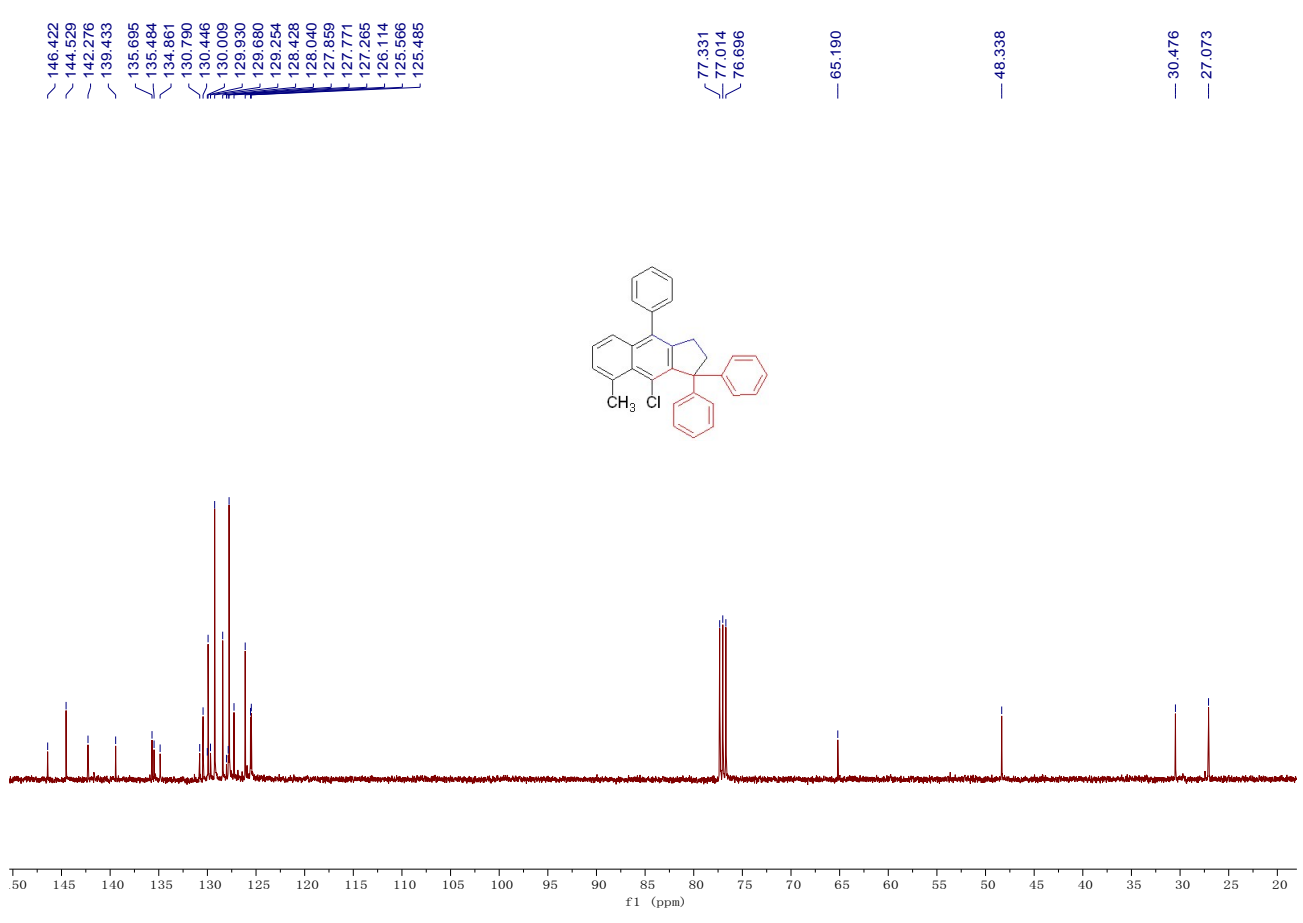
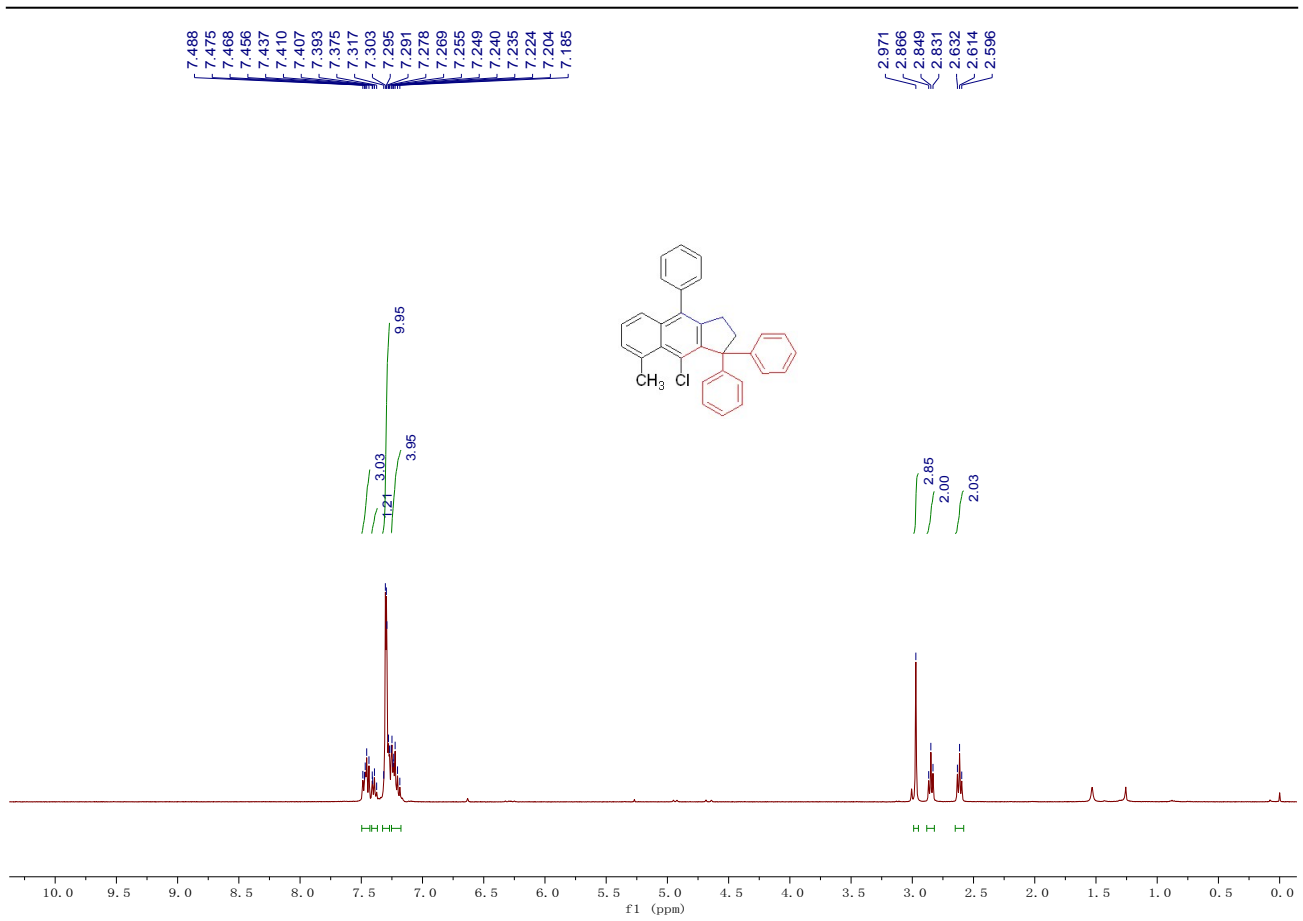


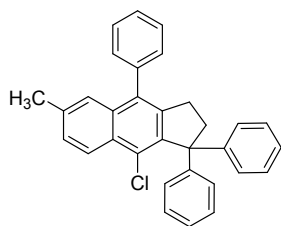
Compound 2a: Yield: 69 mg, 81%; A white solid; Mp: >200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, $J = 8.6$ Hz, 1H), 7.62 (d, $J = 8.6$ Hz, 1H), 7.42 (dd, $J = 13.2, 7.1$ Hz, 3H), 7.38 – 7.32 (m, 2H), 7.31 – 7.17 (m, 12H), 2.86 (t, $J = 7.0$ Hz, 2H), 2.70 (t, $J = 7.0$ Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.6, 144.5, 142.6, 138.4, 134.2, 133.4, 131.0, 130.0, 129.3, 129.1, 128.3, 127.9, 127.3, 126.28, 126.24, 126.1, 125.9, 124.4, 64.2, 47.7, 30.7; IR (neat): ν 2980, 1592, 1490, 1434, 1011, 765 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{31}\text{H}_{23}\text{Cl}$ $[\text{M}]^+$: 430.1483, Found: 430.1486.



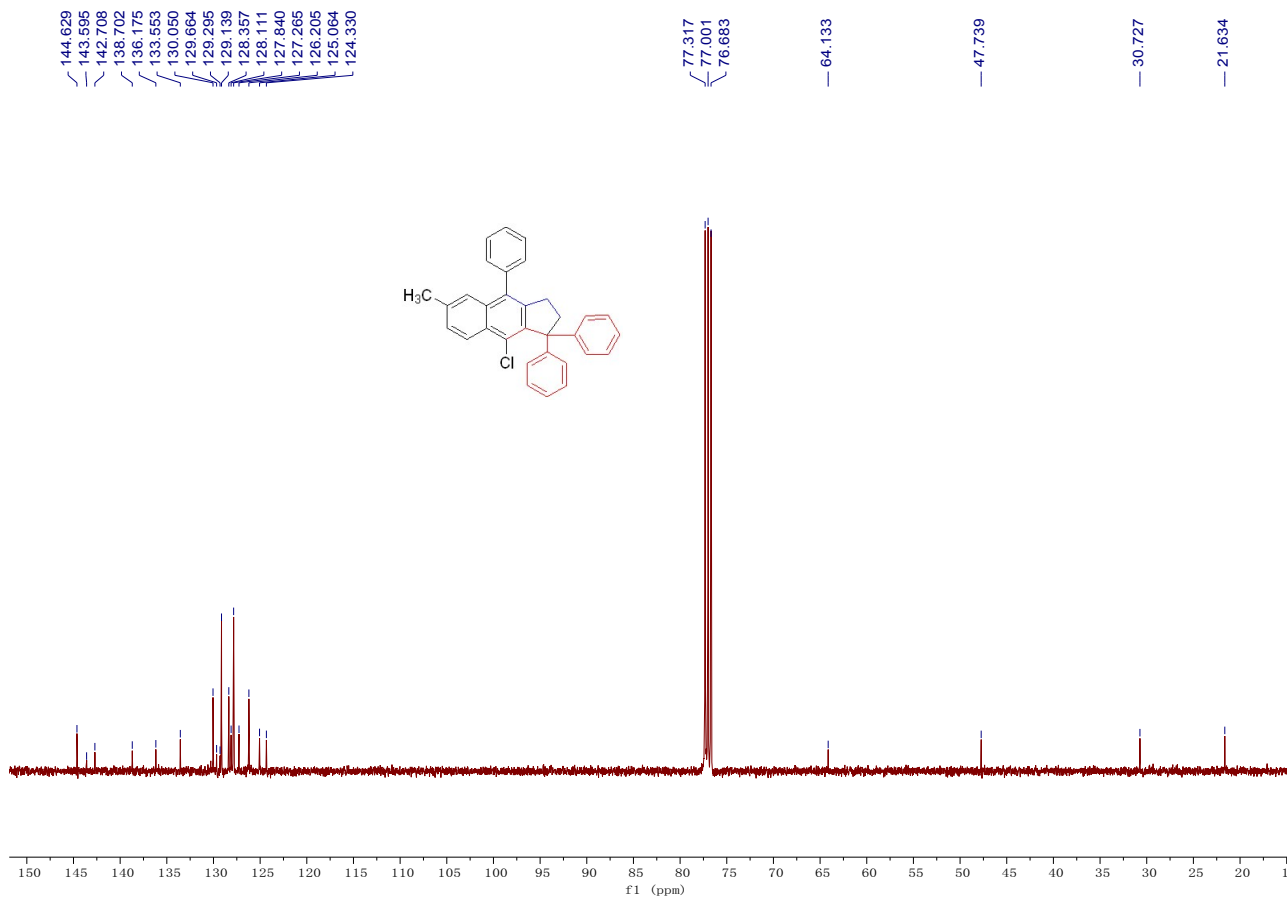
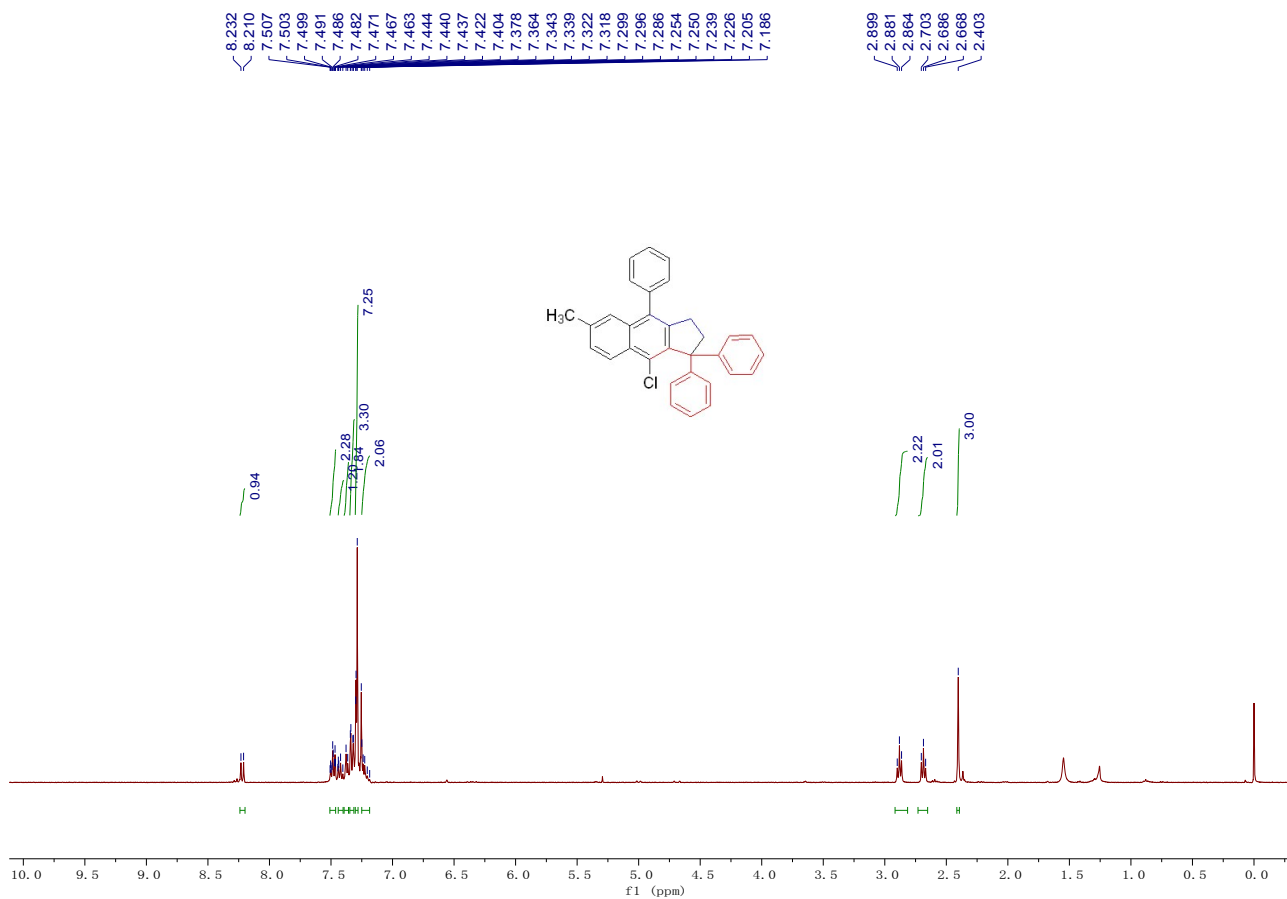


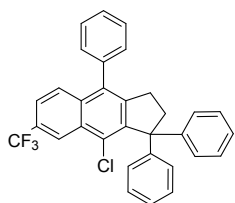
Compound 2b: Yield: 62 mg, 70%; A white solid; Mp: >200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.41 (m, 3H), 7.44 – 7.35 (m, 1H), 7.34 – 7.27 (m, 10H), 7.27 – 7.16 (m, 4H), 2.97 (s, 3H), 2.84 (t, $J = 7.0$ Hz, 2H), 2.61 (t, $J = 7.0$ Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.4, 144.5, 142.3, 139.4, 135.7, 135.5, 134.9, 130.8, 130.4, 130.0, 129.9, 129.7, 129.3, 128.4, 128.0, 127.9, 127.8, 127.3, 126.1, 125.6, 125.5, 48.3, 30.5, 27.1; IR (neat): ν 2979, 1591, 1492, 1437, 1025, 767, 699 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{32}\text{H}_{25}\text{Cl}$ $[\text{M}]^+$: 444.1639, Found: 444.1640.



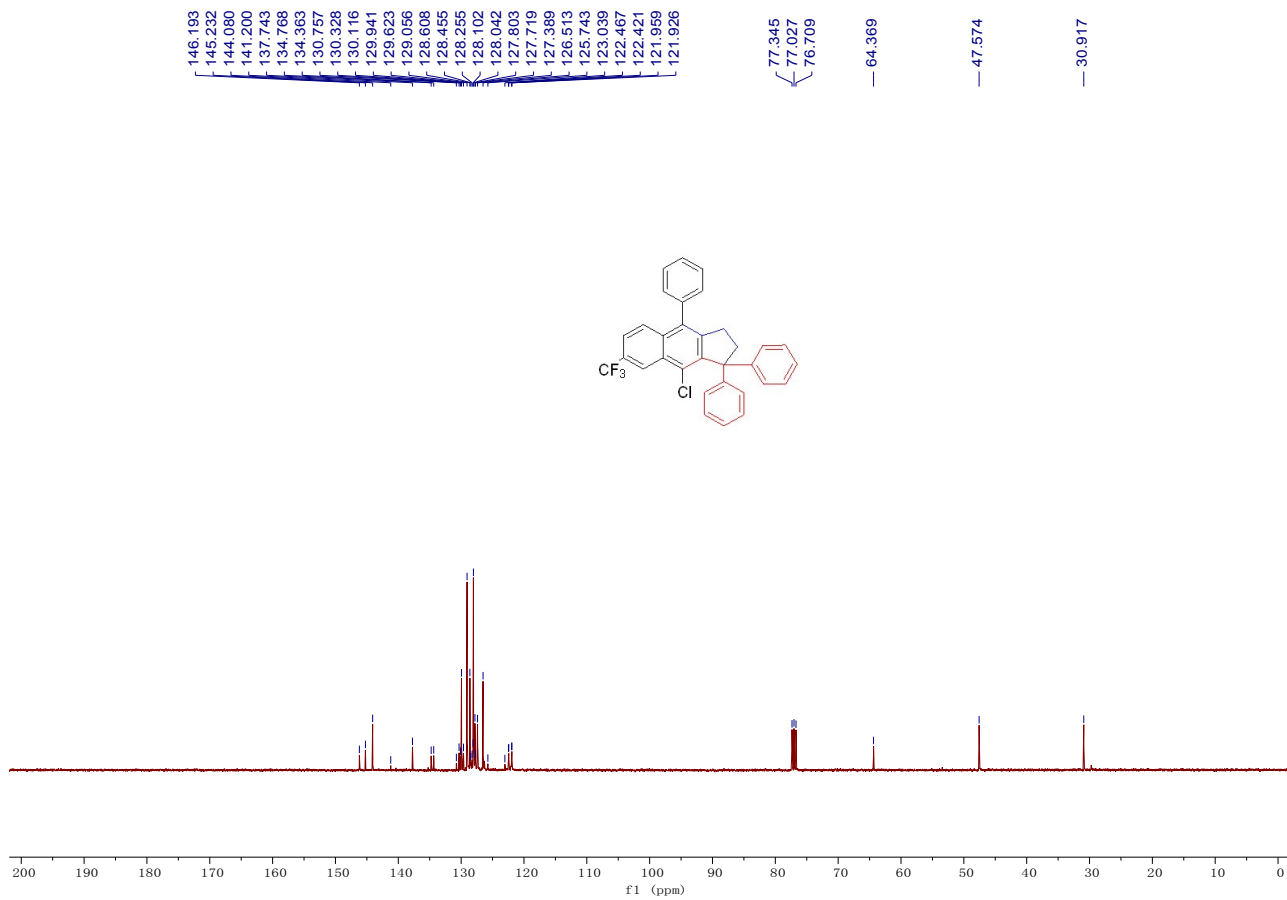
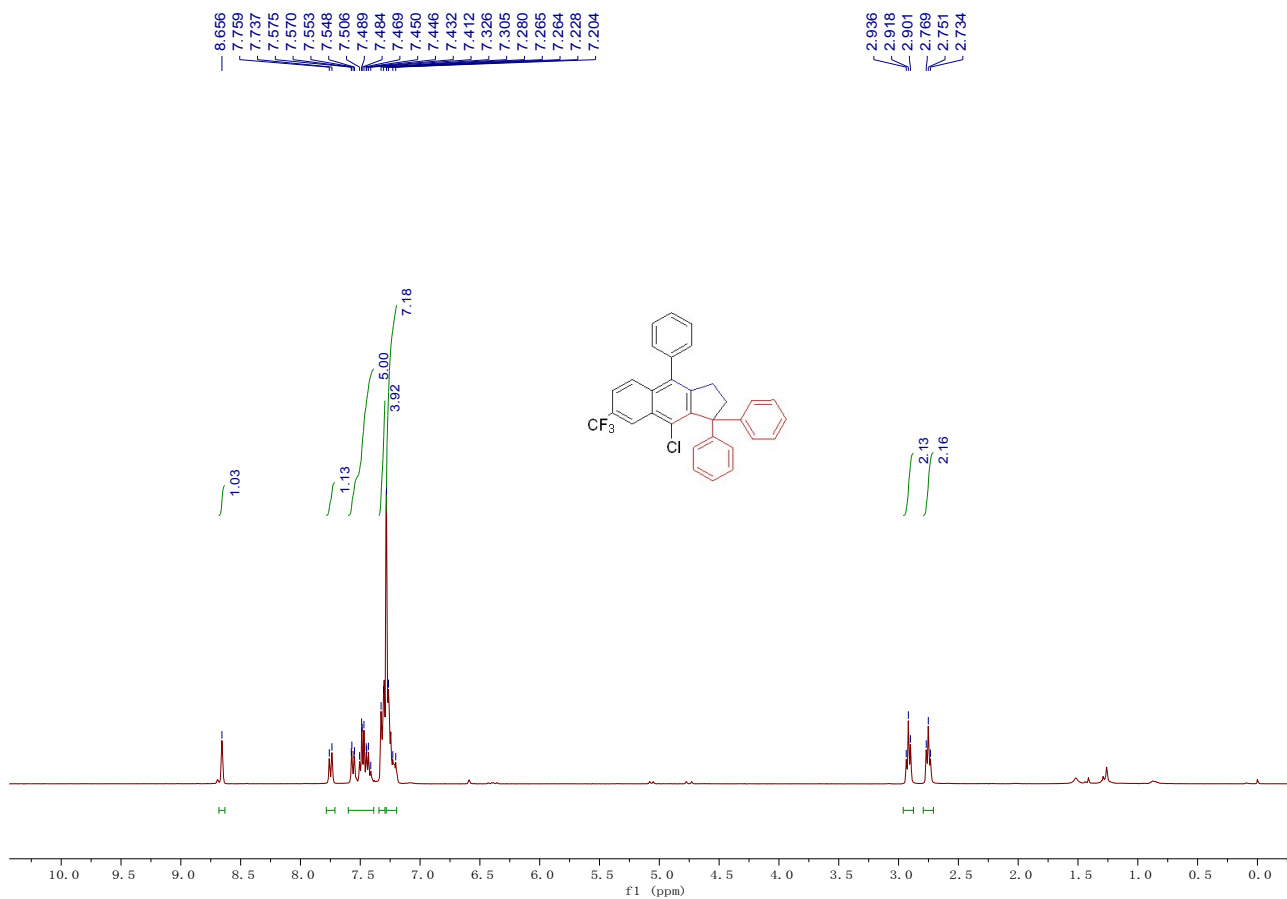


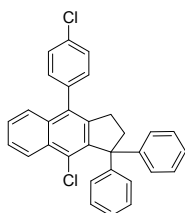
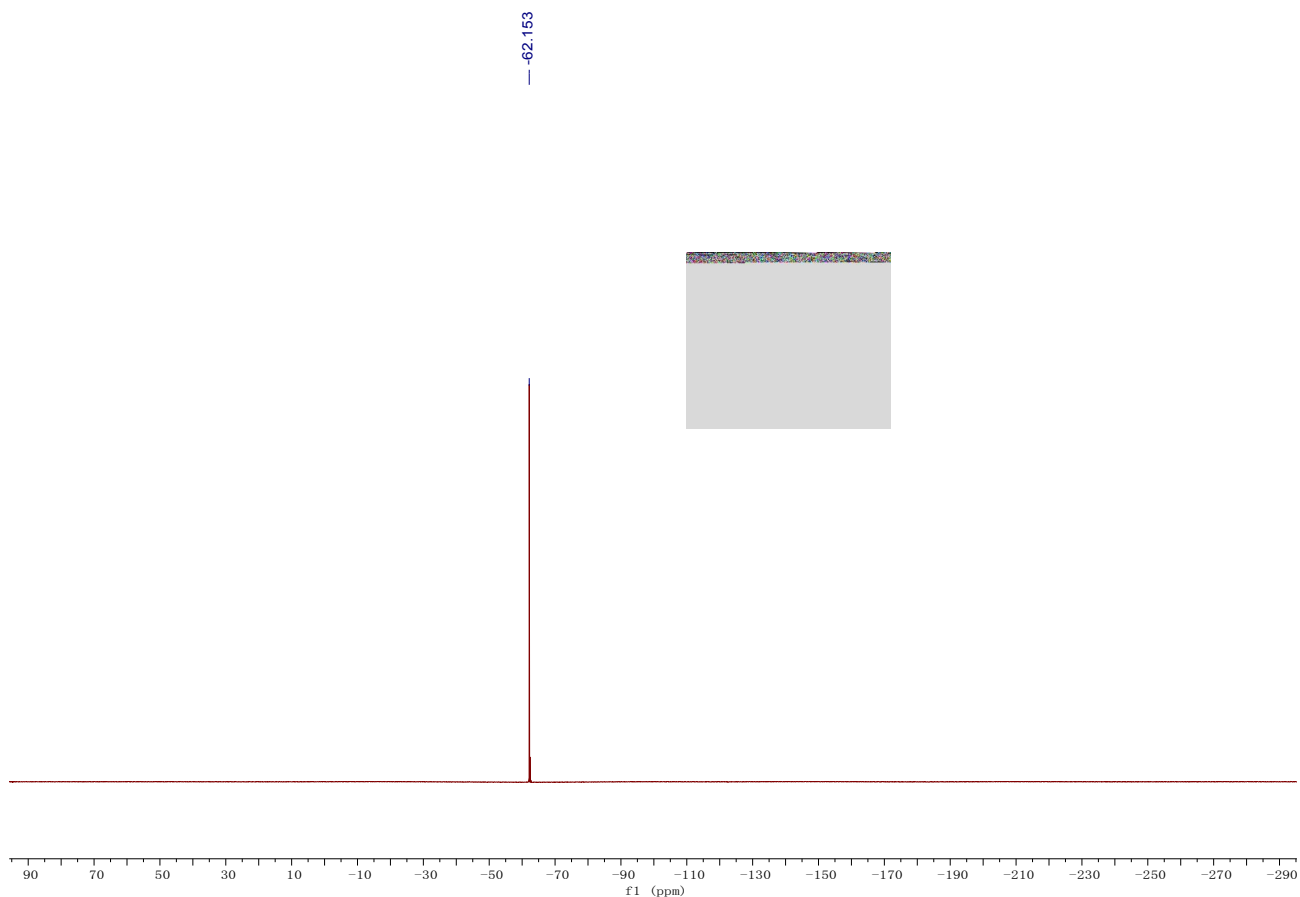
Compound 2c: Yield: 60 mg, 68%; A white solid; Mp: >200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, $J = 8.6$ Hz, 1H), 7.51 – 7.46 (m, 2H), 7.44 – 7.40 (m, 1H), 7.39 – 7.36 (m, 2H), 7.35 – 7.31 (m, 3H), 7.30 – 7.28 (m, 7H), 7.25 – 7.19 (m, 2H), 2.88 (t, $J = 7.0$ Hz, 2H), 2.69 (t, $J = 7.0$ Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.6, 143.6, 142.7, 138.7, 136.2, 133.6, 130.1, 129.7, 129.3, 129.1, 128.4, 128.1, 127.8, 127.3, 126.2, 125.1, 124.3, 64.1, 47.7, 30.7, 21.6; IR (neat): ν 2922, 1490, 1028, 816, 756, 699 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{32}\text{H}_{25}\text{Cl}$ $[\text{M}]^+$: 444.1639, Found: 444.1645.



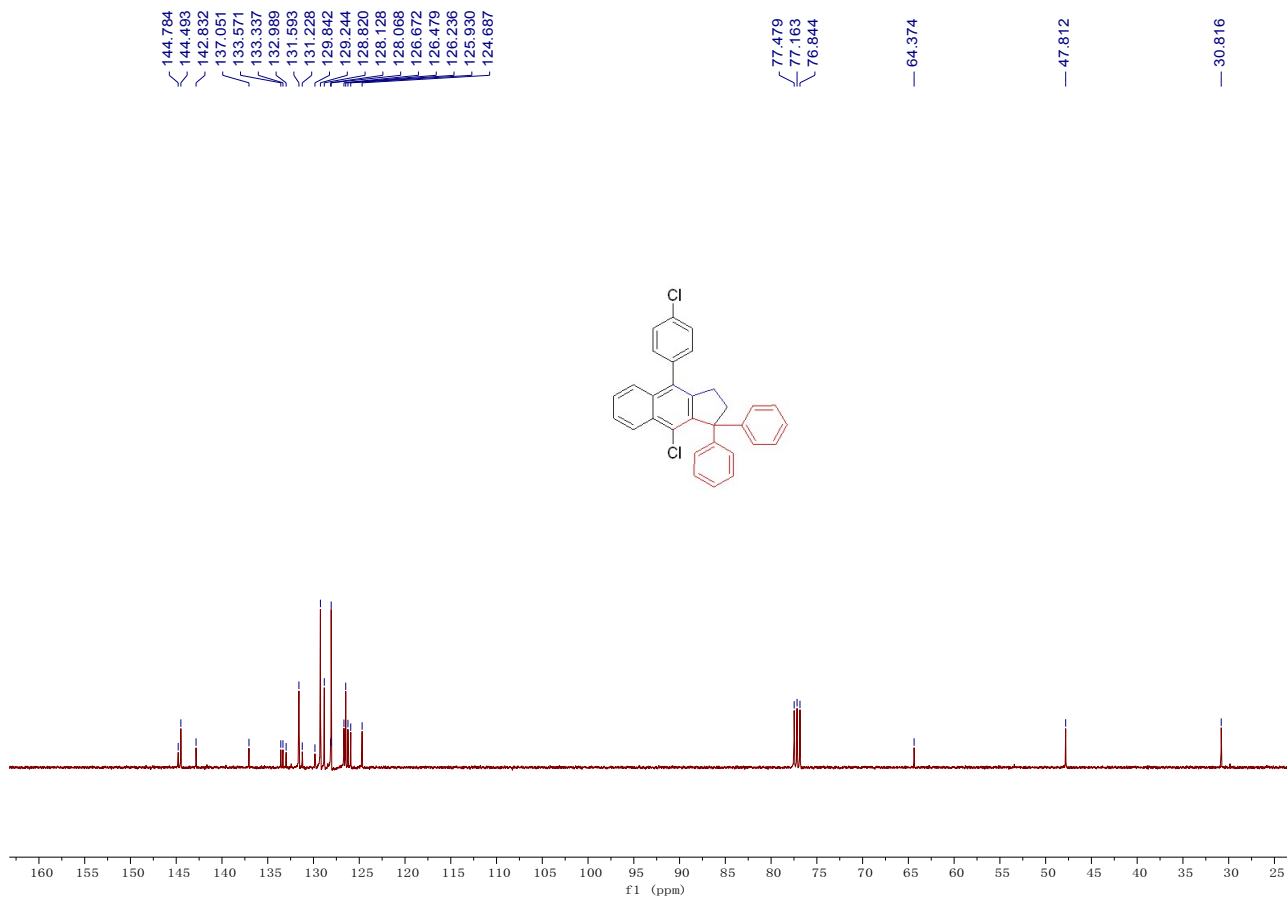
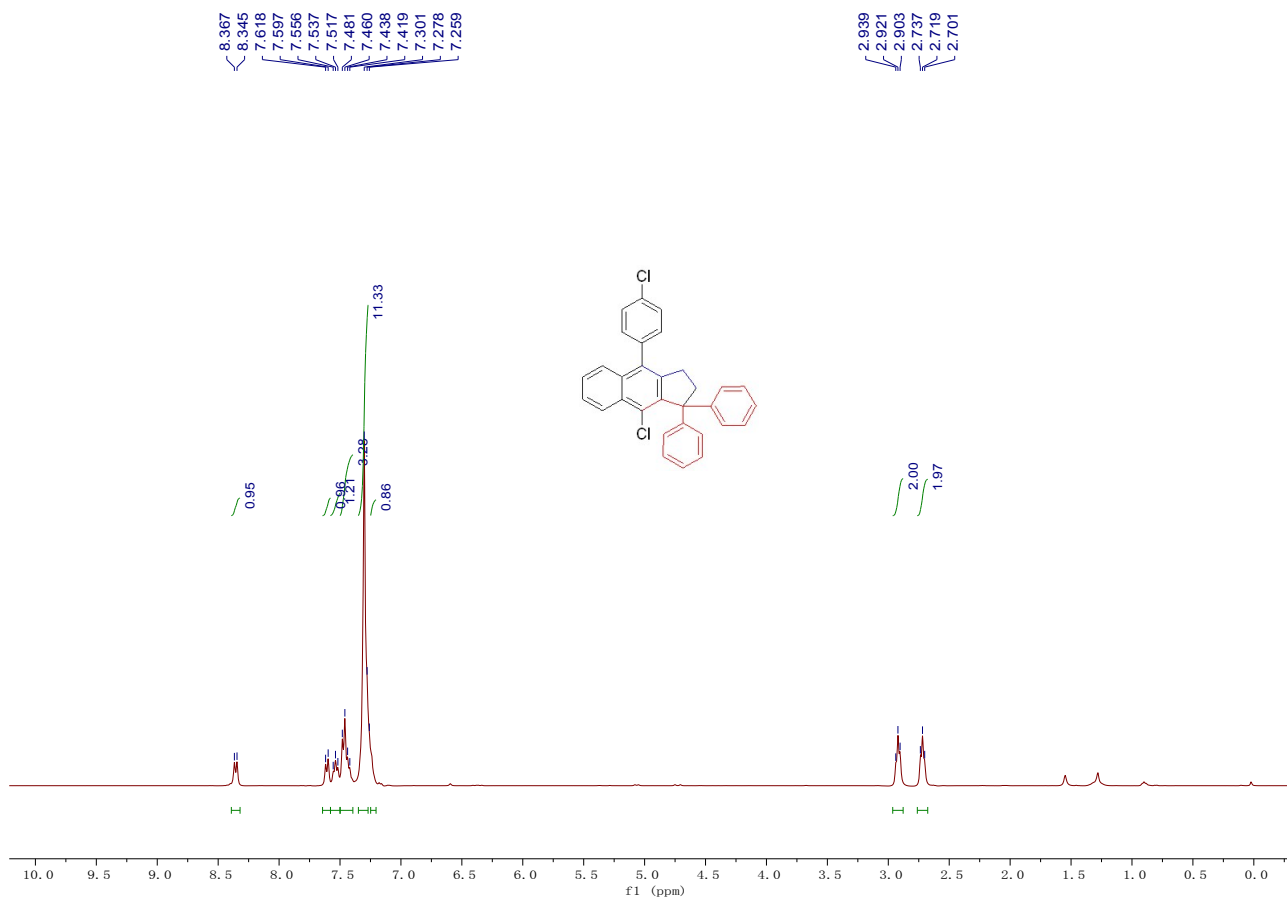


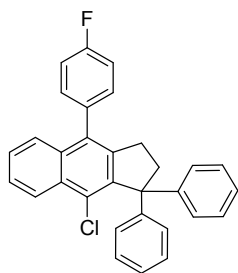
Compound 2d: Yield: 79 mg, 80%; A white solid; Mp: >200 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.60 – 7.39 (m, 5H), 7.32 (d, *J* = 8.4 Hz, 4H), 7.28 – 7.20 (m, 7H), 2.92 (t, *J* = 7.0 Hz, 2H), 2.75 (t, *J* = 7.0 Hz, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 146.2, 145.2, 144.1, 141.2, 137.7, 134.8, 134.4, 130.8, 130.3, 130.1, 129.9, 129.6, 129.1, 128.6, 128.0, 127.8, 127.4, 126.9 (q, *J* = 270.4 Hz), 126.5, 122.4 (q, *J* = 4.7 Hz), 121.9 (q, *J* = 3.3 Hz), 64.4, 47.6, 30.9; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.15; IR (neat): ν 2980, 1346, 1289, 1167, 1116, 1078, 702 cm⁻¹; HRMS (EI) Calcd. for C₃₂H₂₂ClF₃ [M]⁺: 498.1357, Found: 498.1368.



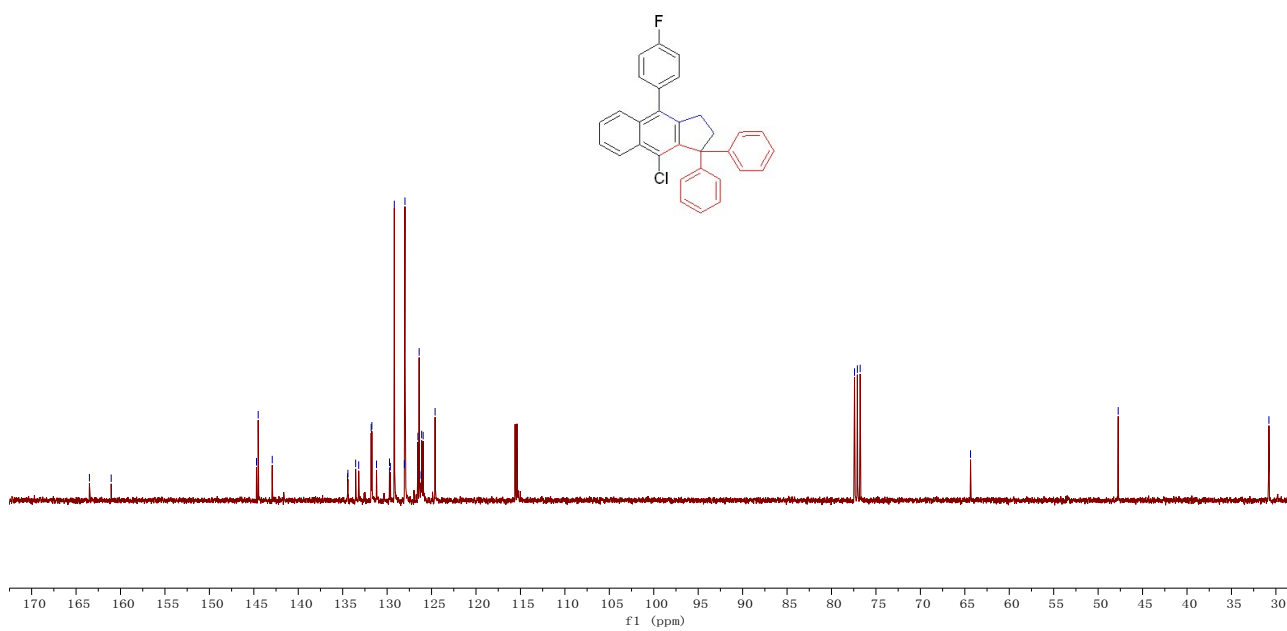
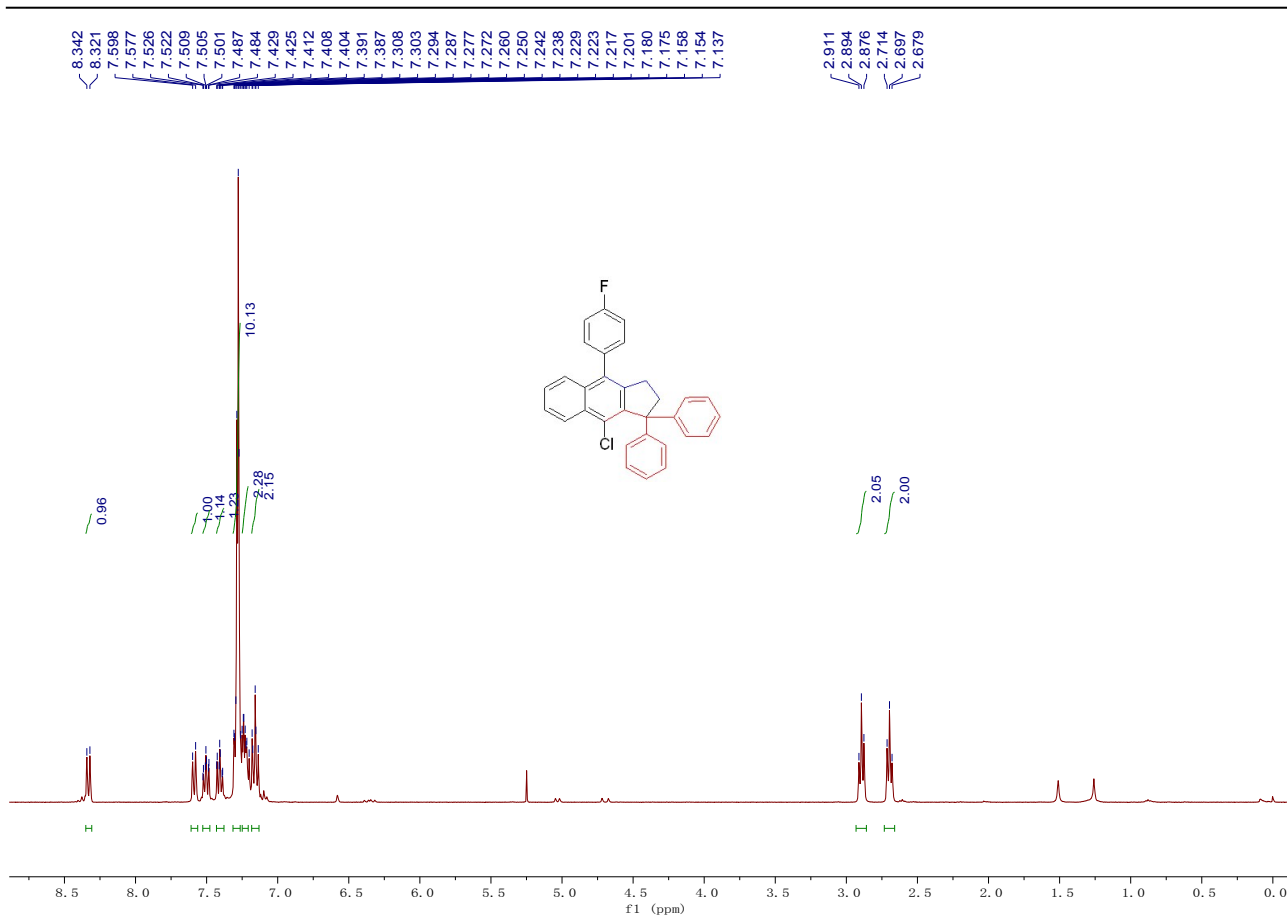


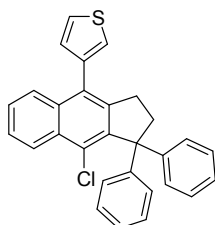
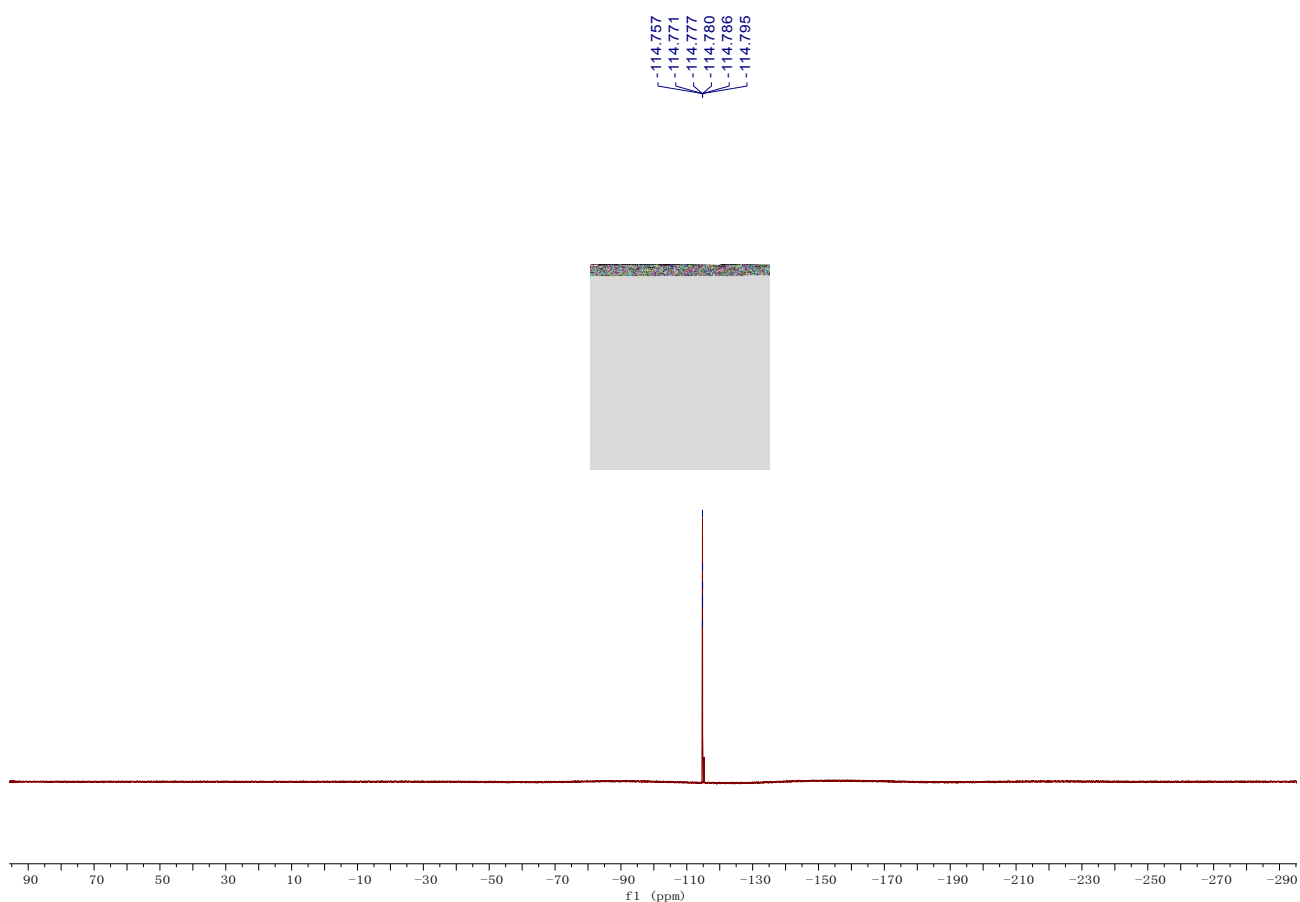
Compound 2e: Yield: 67 mg, 73%; A white solid; Mp: >200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, $J = 8.5$ Hz, 1H), 7.61 (d, $J = 8.5$ Hz, 1H), 7.54 (t, $J = 7.7$ Hz, 1H), 7.50 – 7.39 (m, 3H), 7.35 – 7.27 (m, 11H), 7.25 – 7.20 (m, 1H), 2.91 (t, $J = 7.1$ Hz, 2H), 2.72 (t, $J = 7.1$ Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.8, 144.5, 142.8, 137.1, 133.6, 133.3, 133.0, 131.6, 131.2, 129.8, 129.2, 128.8, 128.1, 126.7, 126.5, 126.2, 125.9, 124.7, 64.4, 47.8, 30.8; IR (neat): ν 2818, 1487, 1088, 1009, 822, 759, 696 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{31}\text{H}_{22}\text{Cl}_2$ $[\text{M}]^+$: 464.1093, Found: 464.1092.



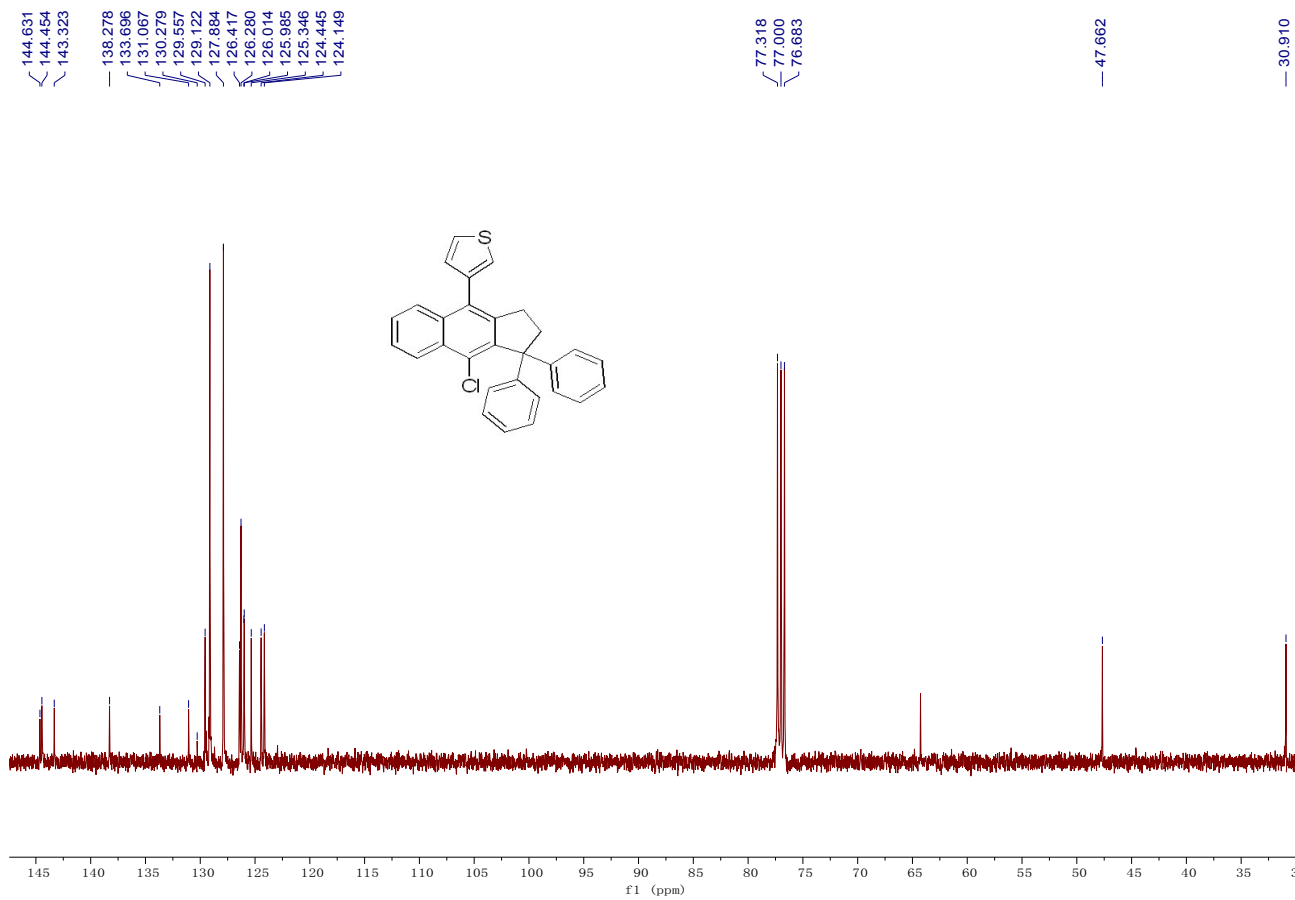
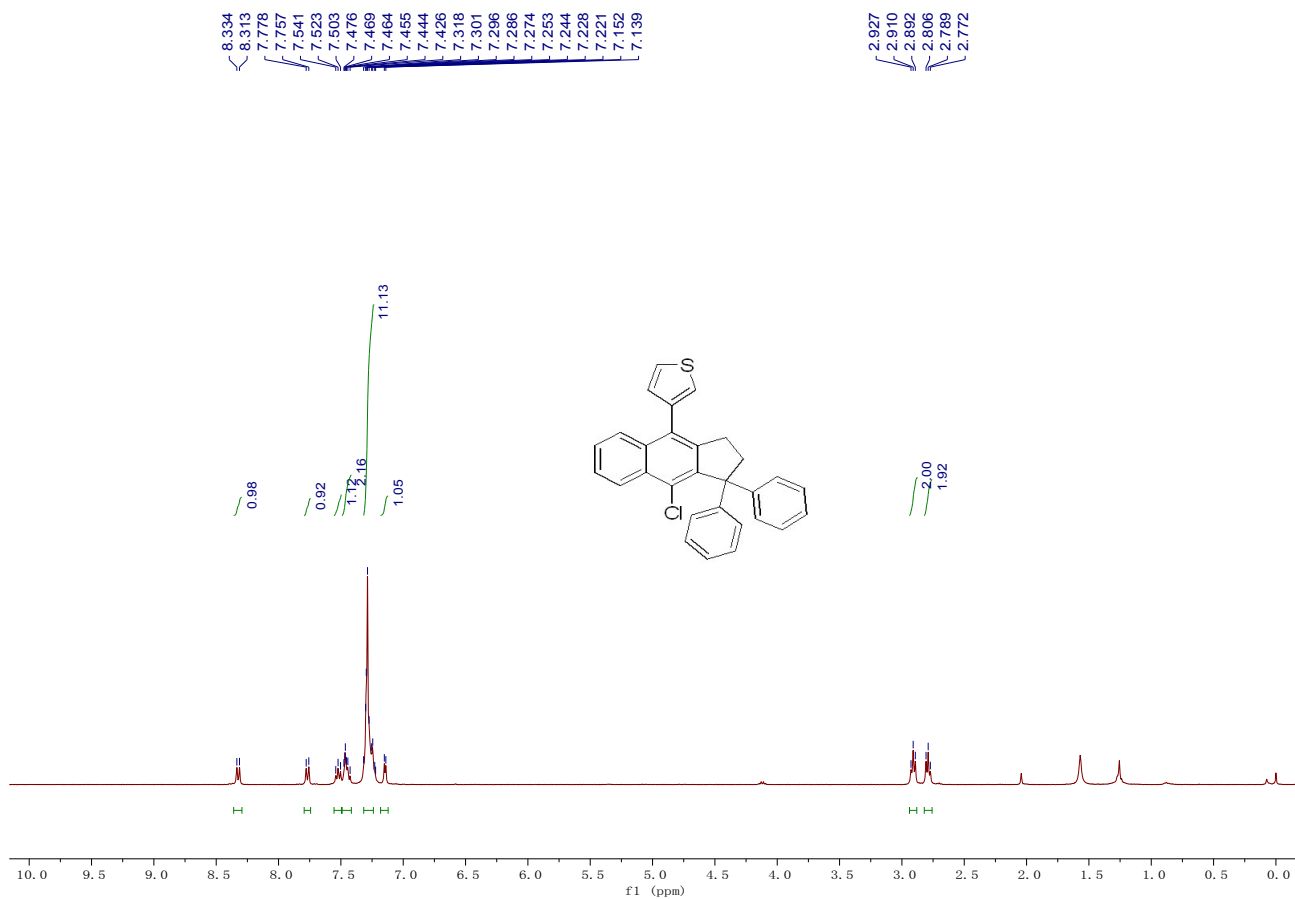


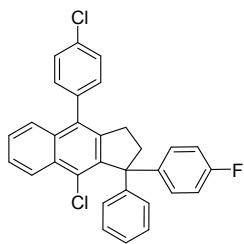
Compound 2f: Yield: 62 mg, 70%; A white solid; Mp: >200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, $J = 8.5$ Hz, 1H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.53 – 7.48 (m, 1H), 7.43 – 7.38 (m, 1H), 7.31 – 7.26 (m, 10H), 7.25 – 7.21 (m, 2H), 7.18 – 7.13 (m, 2H), 2.89 (t, $J = 7.0$ Hz, 2H), 2.70 (t, $J = 7.0$ Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.3 (d, $J = 246.4$ Hz), 144.7, 144.5, 142.9, 134.4, 134.3, 133.5, 133.2, 131.8 (d, $J = 8.0$ Hz), 131.2, 129.7, 129.6, 129.2, 128.1, 128.0, 126.5, 126.4, 126.2, 126.1, 125.9, 124.6, 115.5 (d, $J = 21.3$ Hz), 64.4, 47.7, 30.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.74 – -114.81 (m); IR (neat): ν 2919, 2844, 1505, 1223, 1153, 832, 696 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{31}\text{H}_{22}\text{ClF}$ $[\text{M}]^+$: 448.1389, Found: 448.1389.



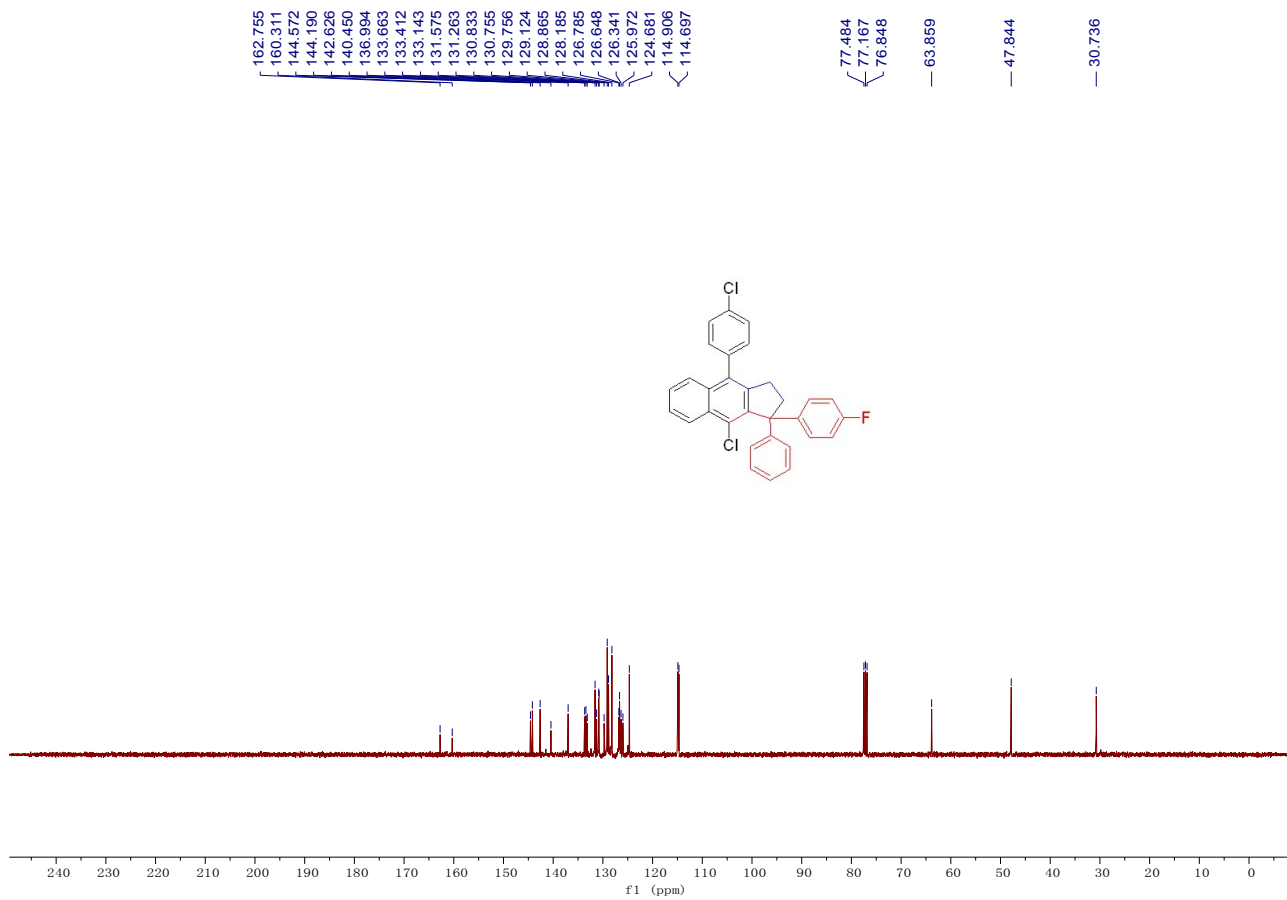
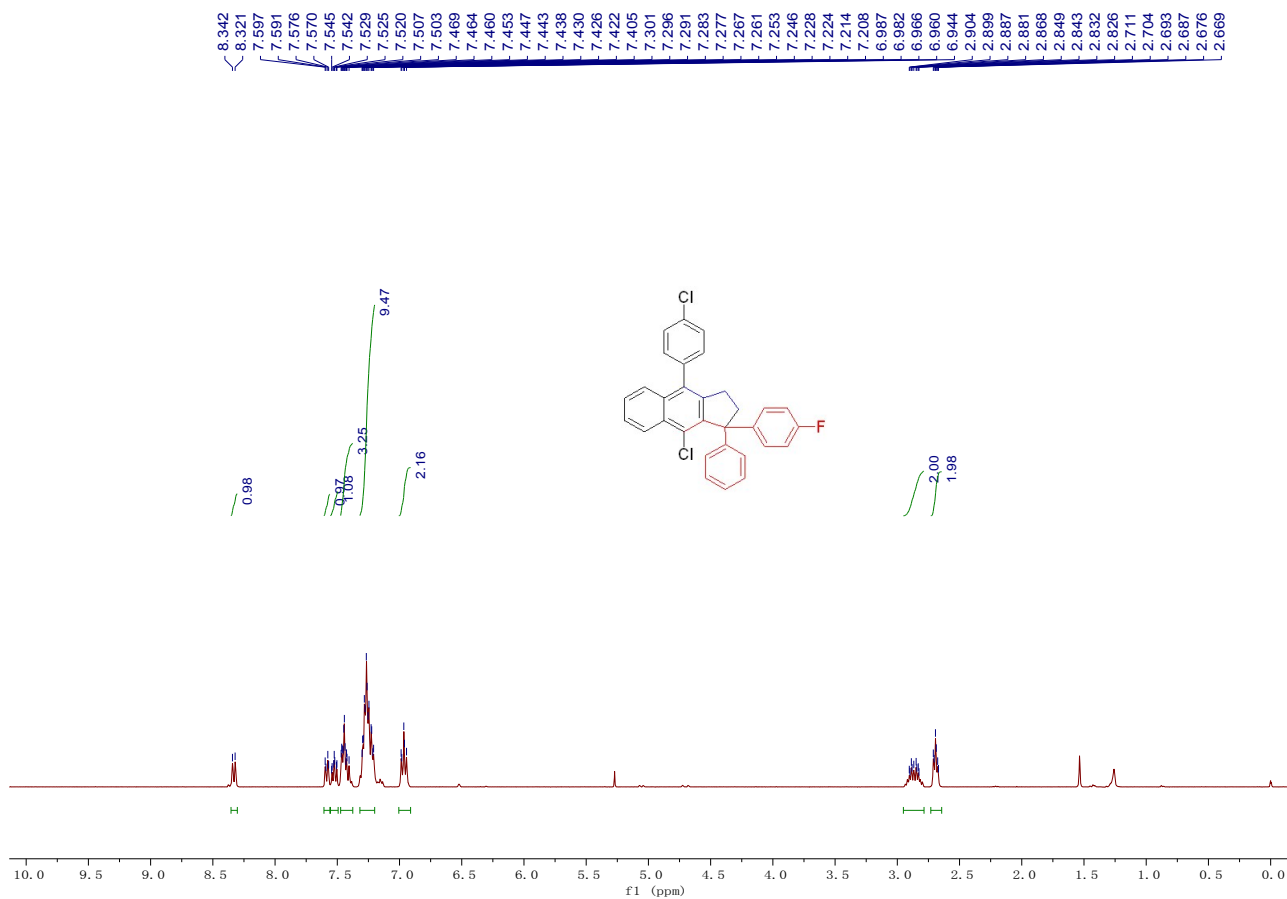


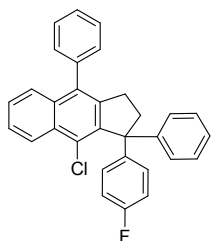
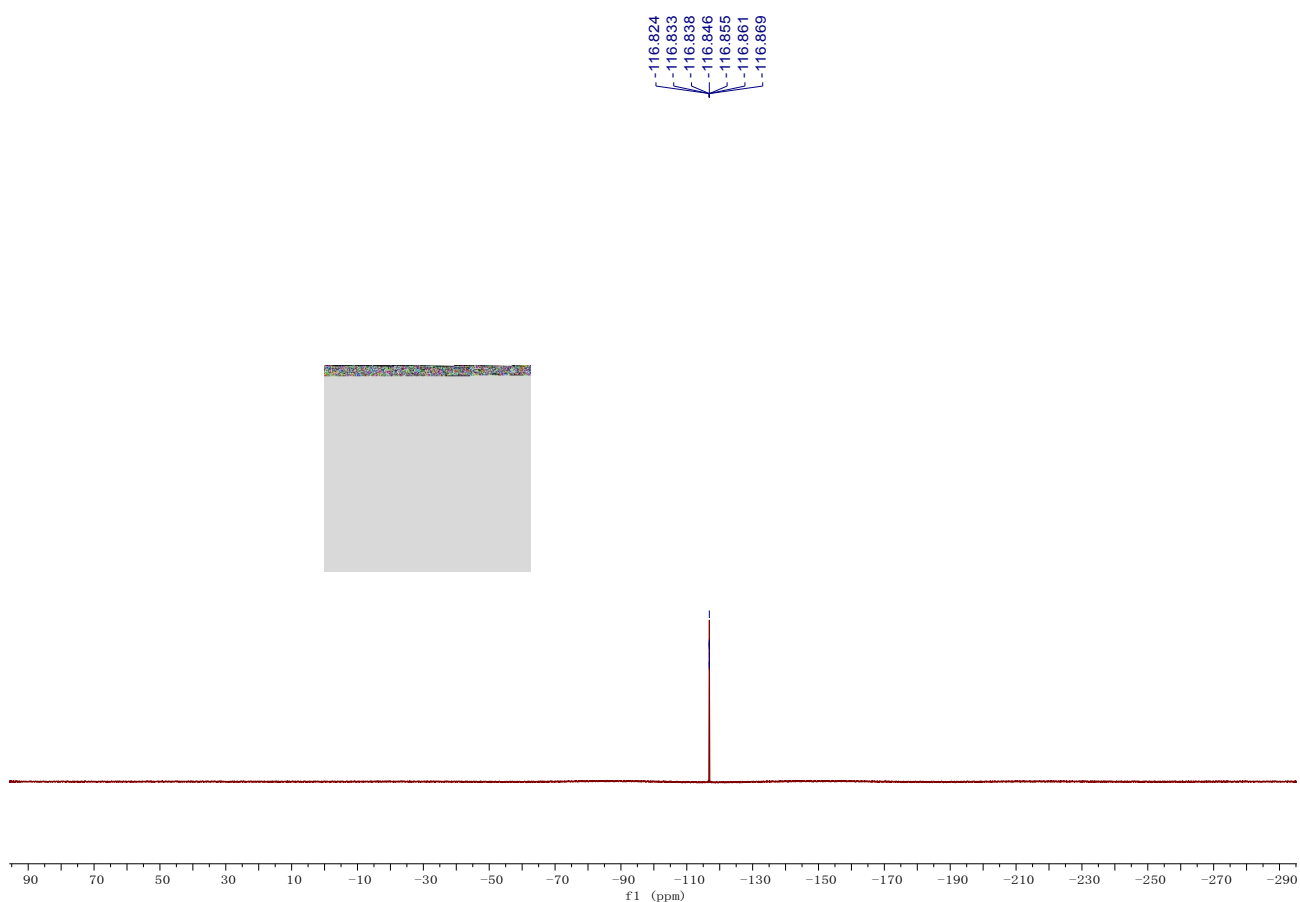
Compound 2j: Yield: 27 mg, 30%; A white solid; Mp: 162 - 164 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.32 – 7.24 (m, 11H), 7.15 (d, *J* = 4.9 Hz, 1H), 2.91 (t, *J* = 6.9 Hz, 2H), 2.79 (t, *J* = 6.9 Hz, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 144.5 (d, *J* = 17.8 Hz), 143.3, 138.3, 133.7, 131.1, 129.6, 129.1, 127.9, 126.4, 126.3, 126.0, 126.0, 125.3, 124.4, 124.1, 47.7, 30.9; IR (neat): ν 2989, 2898, 1507, 1080, 1024, 837, 769, 701 cm⁻¹; HRMS (DART) Calcd. for C₂₉H₂₁ClS [M+NH₄]⁺: 454.1391, Found: 454.1386.



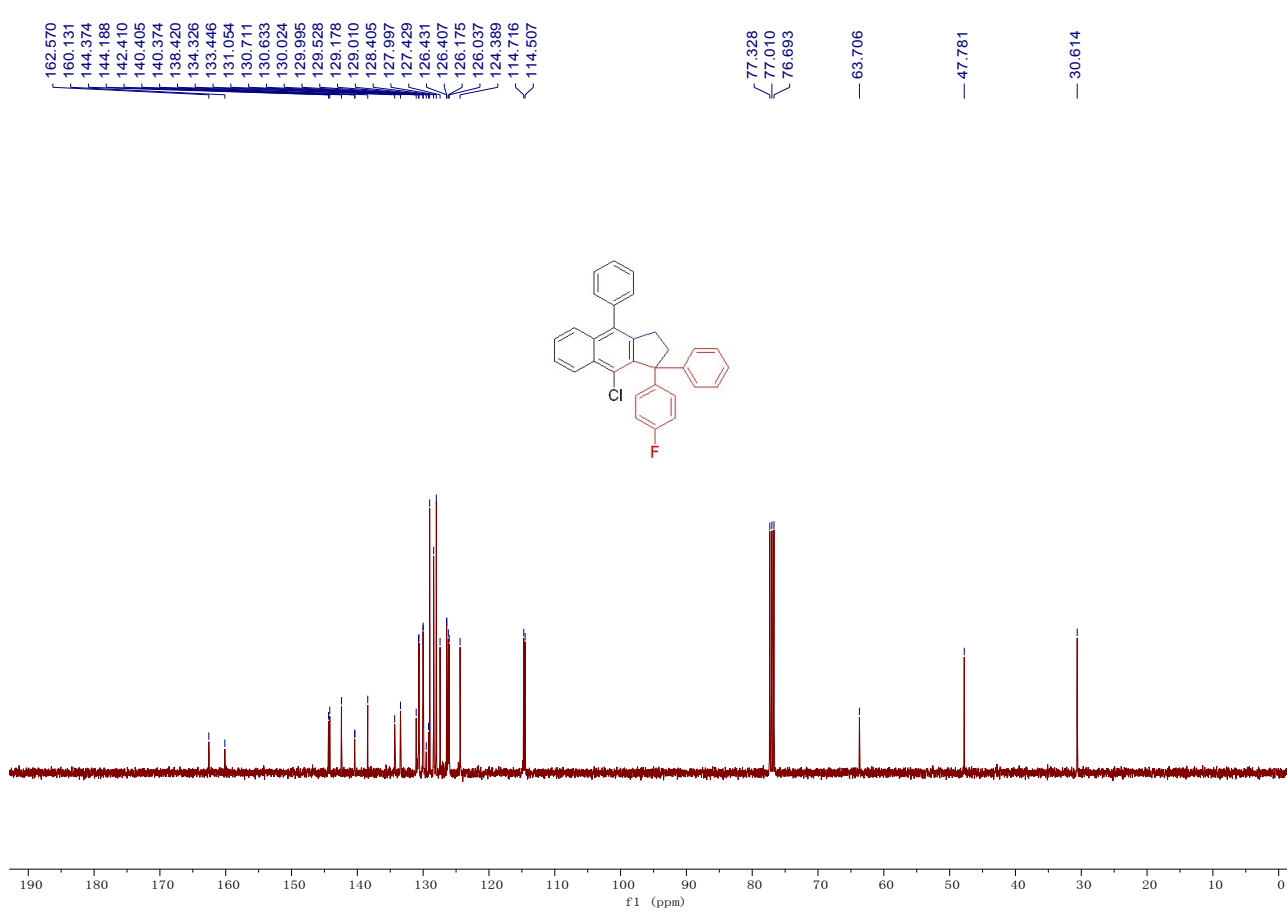
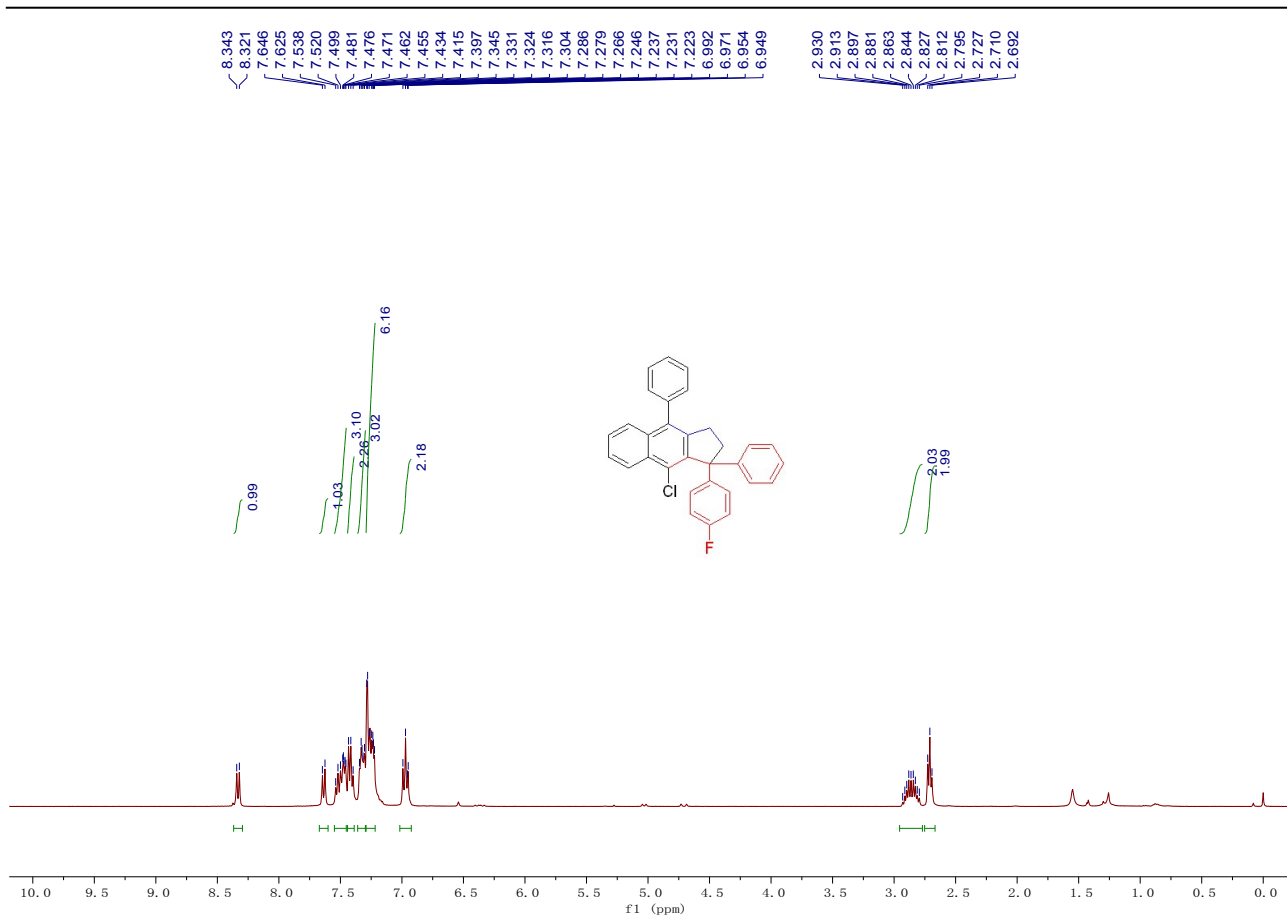


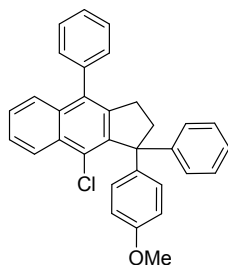
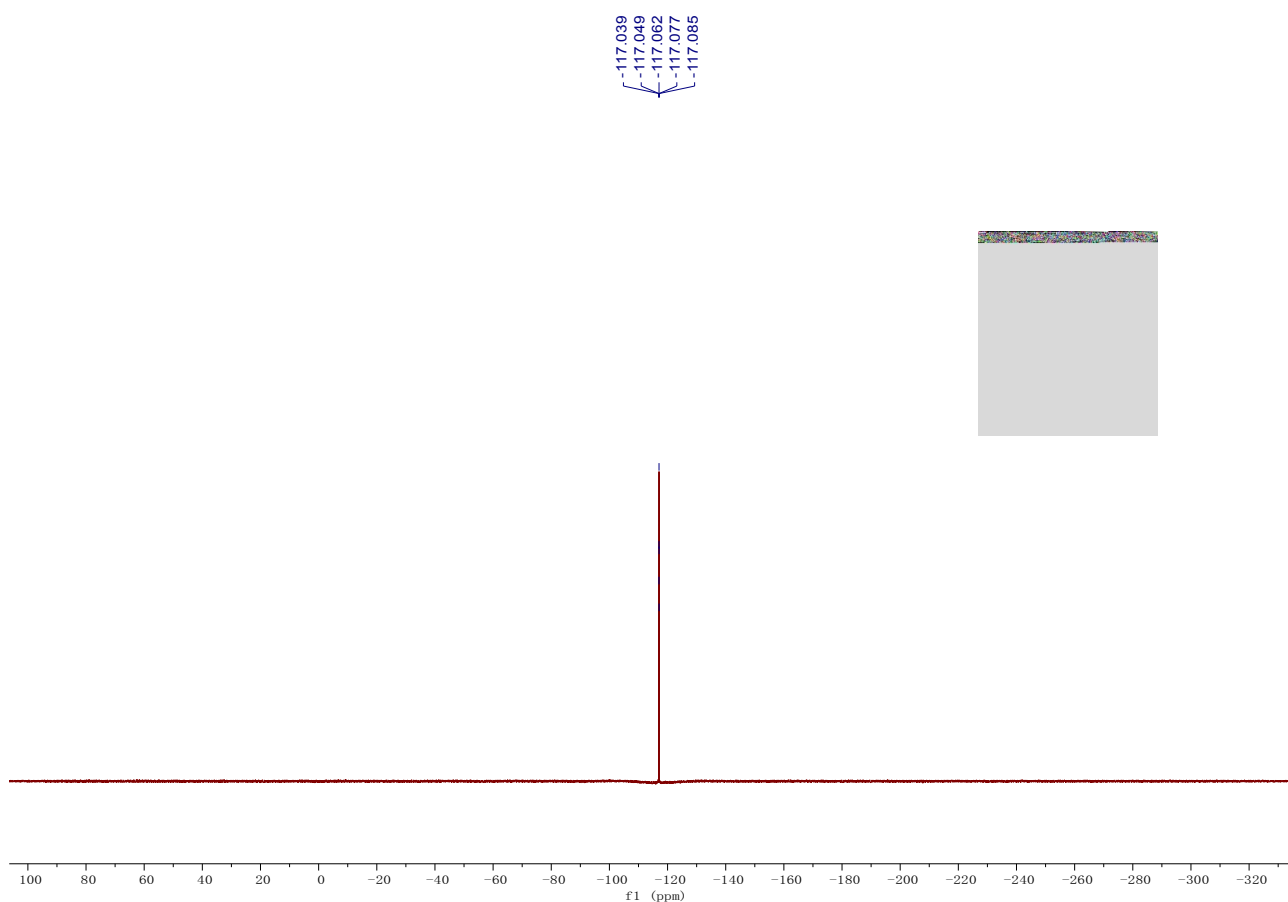
Compound 2k: Yield: 71 mg, 74%; A white solid; Mp: 169 - 171 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, $J = 8.5$ Hz, 1H), 7.61 – 7.56 (m, 1H), 7.56 – 7.49 (m, 1H), 7.47 – 7.38 (m, 3H), 7.32 – 7.20 (m, 9H), 7.01 – 6.91 (m, 2H), 2.95 – 2.79 (m, 2H), 2.73 – 2.64 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.5 (d, $J = 245.6$ Hz), 144.6, 144.2, 142.6, 140.5, 137.0, 133.7, 133.4, 133.1, 131.6, 131.3, 130.8 (d, $J = 7.8$ Hz), 129.8, 129.1, 128.9, 128.2, 126.8, 126.6, 126.3, 126.0, 124.7, 114.8 (d, $J = 21.1$ Hz), 63.9, 47.8, 30.7; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.80 – -116.90 (m); IR (neat): ν 3042, 2852, 1505, 1090, 1012, 827, 756, 702 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{31}\text{H}_{21}\text{Cl}_2\text{F}$ $[\text{M}]^+$: 482.0999, Found: 482.1011.



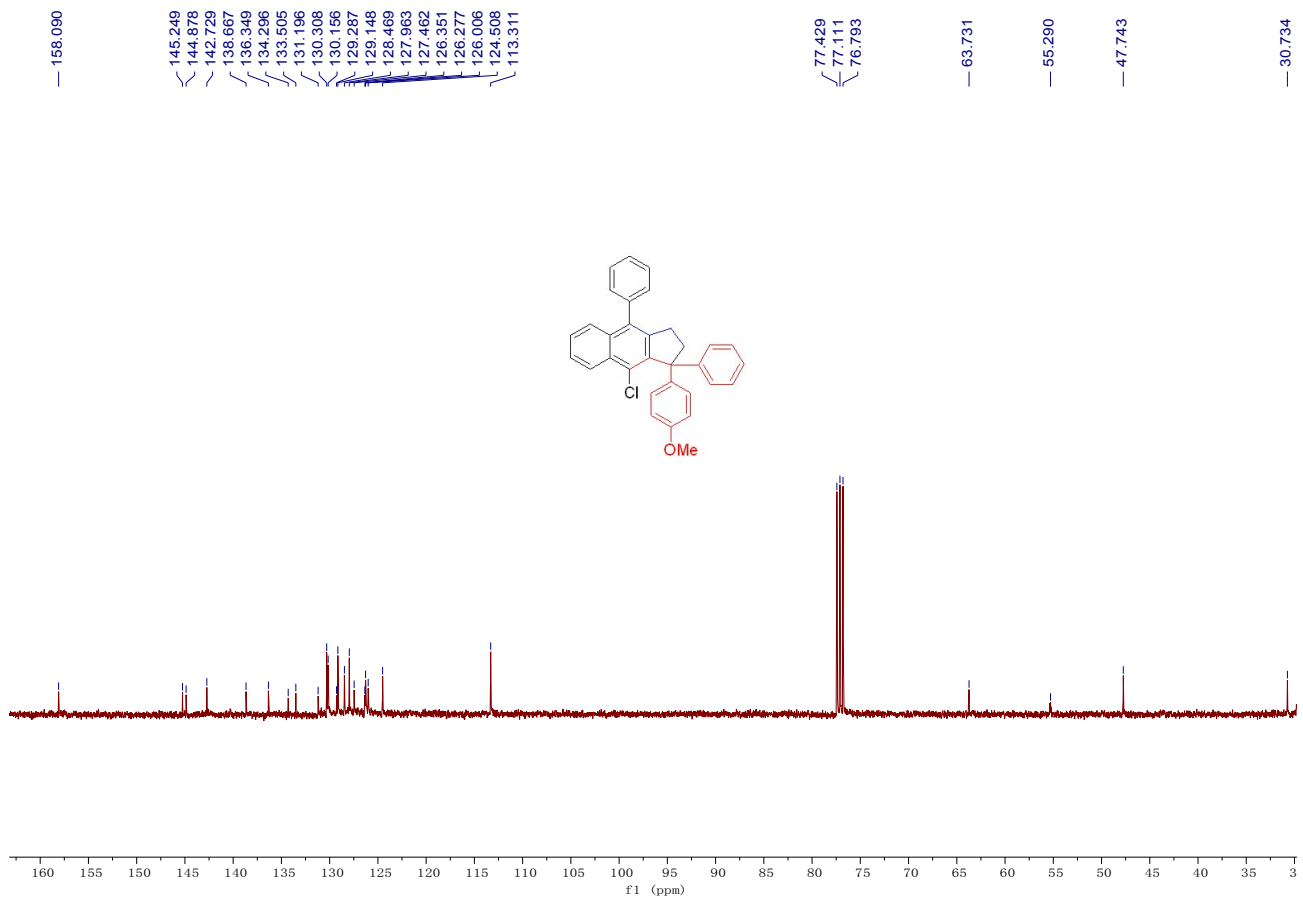
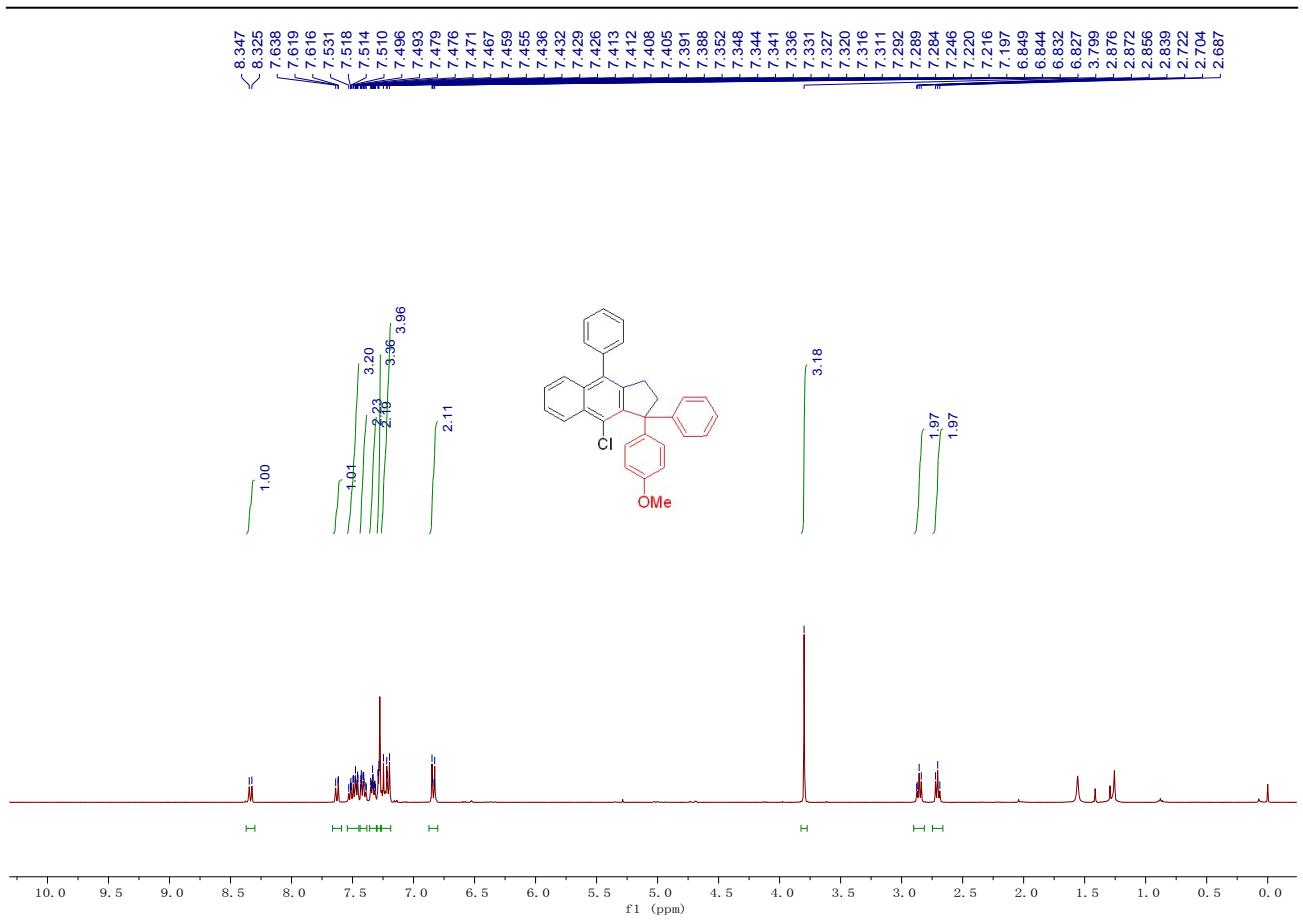


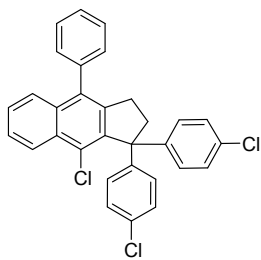
Compound 2l: Yield: 65 mg, 73%; A white solid; Mp: >200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, $J = 8.5$ Hz, 1H), 7.64 (d, $J = 8.5$ Hz, 1H), 7.55 – 7.45 (m, 3H), 7.44 – 7.39 (m, 2H), 7.36 – 7.30 (m, 3H), 7.29 – 7.22 (m, 6H), 7.02 – 6.92 (m, 2H), 2.96 – 2.77 (m, 2H), 2.71 (t, $J = 6.9$ Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.4 (d, $J = 245.3$ Hz), 144.4, 144.2, 142.4, 140.4, 140.3, 138.4, 134.3, 133.4, 131.1, 130.7 (d, $J = 7.8$ Hz), 130.0, 129.9, 129.5, 129.2, 129.0, 128.4, 128.0, 127.4, 126.4, 126.3, 126.2, 126.0, 124.4, 114.6 (d, $J = 21.1$ Hz), 63.7, 47.8, 30.6; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.00 – -117.12 (m); IR (neat): ν 2919, 1594, 1484, 1437, 900, 728, 699 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{31}\text{H}_{22}\text{ClF}$ $[\text{M}]^+$: 448.1389, Found: 448.1393.



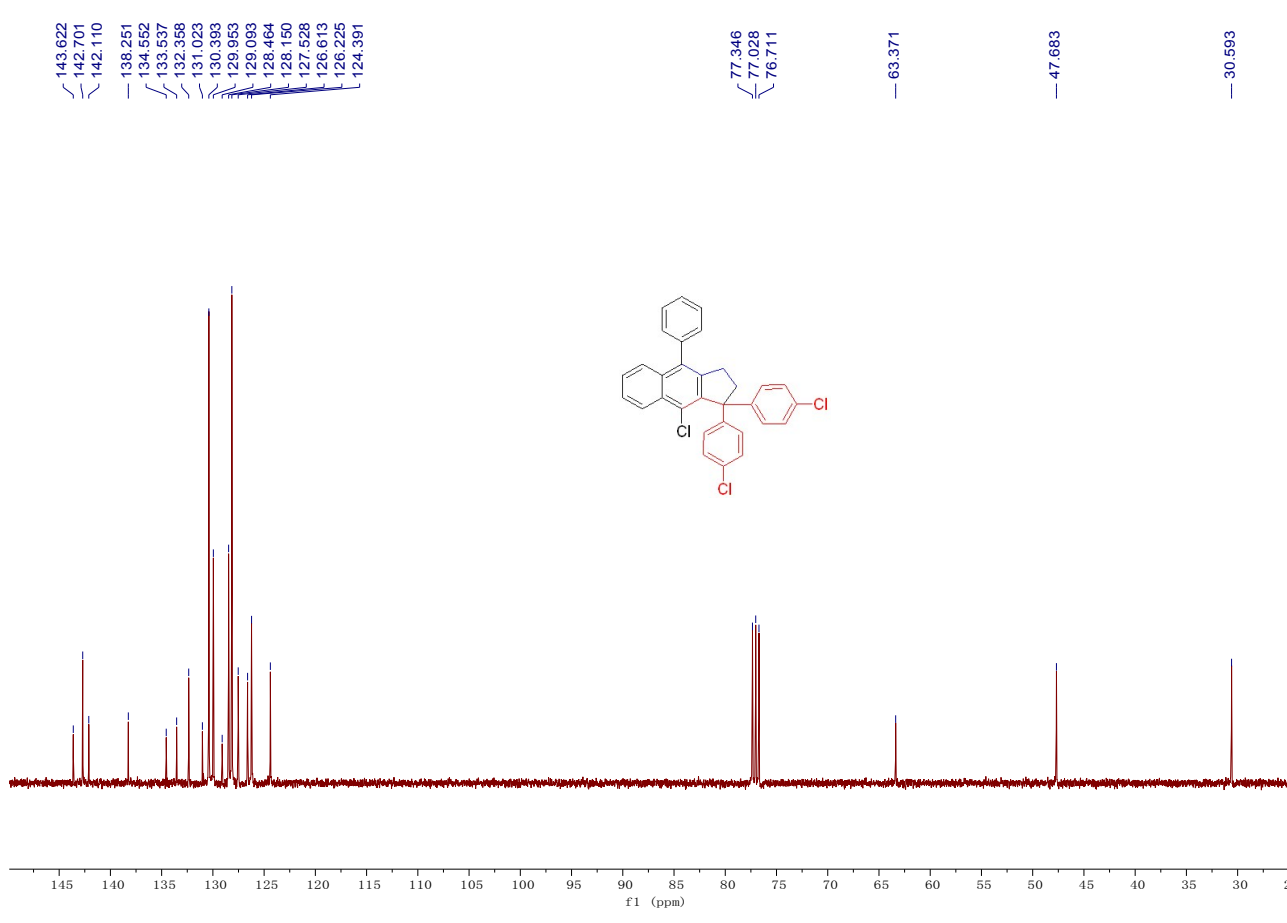
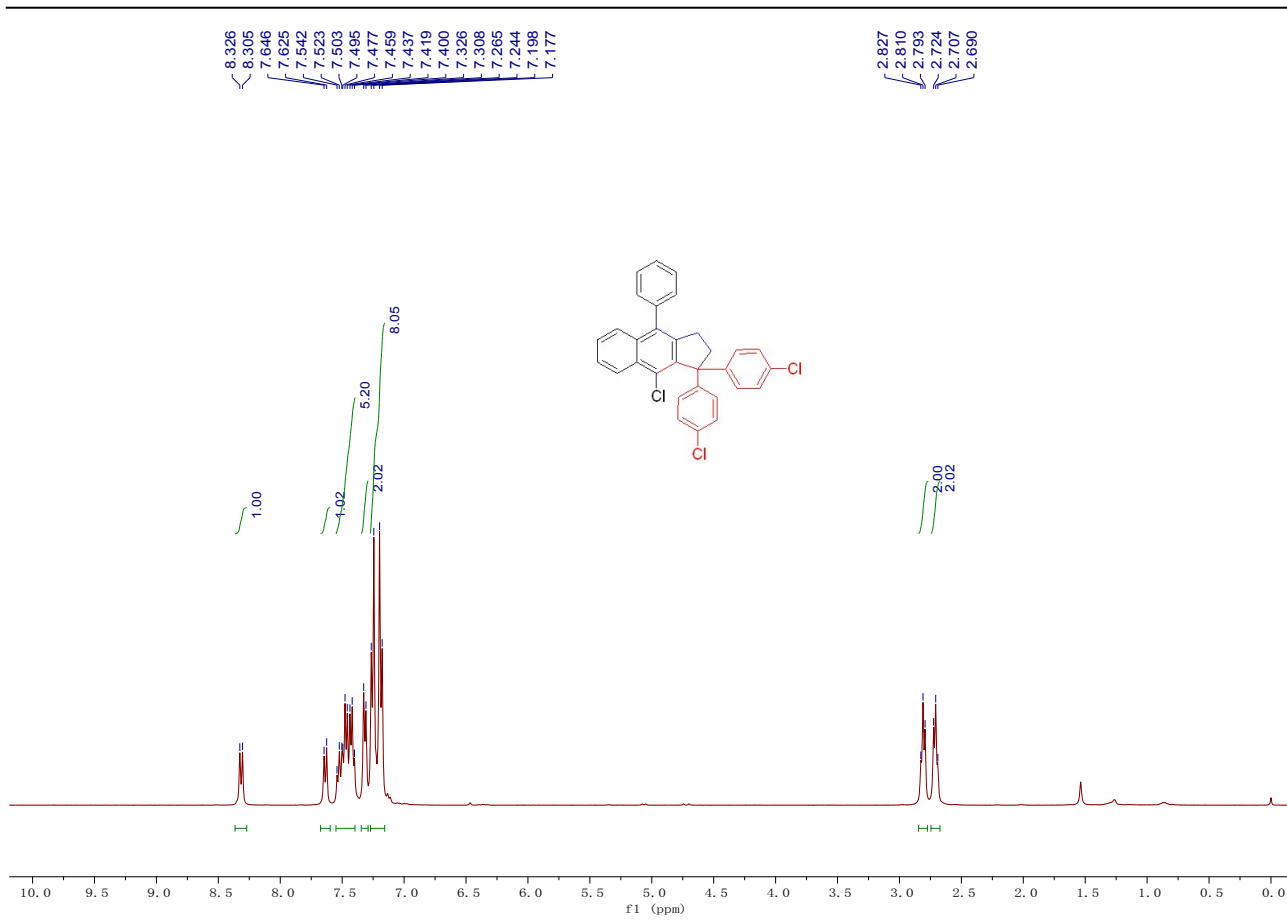


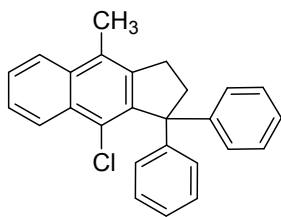
Compound 2m: Yield: 27 mg, 30%; A white solid; Mp: 181 - 183 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, $J = 8.5$ Hz, 1H), 7.66 – 7.59 (m, 1H), 7.54 – 7.45 (m, 3H), 7.44 – 7.38 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.27 (m, 3H), 7.26 – 7.19 (m, 4H), 6.87 – 6.80 (m, 2H), 3.80 (s, 3H), 2.86 (t, $J = 6.8$ Hz, 2H), 2.70 (t, $J = 6.8$ Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.1, 145.2, 144.9, 142.7, 138.7, 136.3, 134.3, 133.5, 131.2, 130.3, 130.2, 129.3, 129.1, 128.5, 128.0, 127.5, 126.4, 126.3, 126.0, 124.5, 113.3, 63.7, 55.3, 47.7, 30.7; IR (neat): ν 2919, 2849, 1510, 1247, 1041, 759, 694 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{32}\text{H}_{25}\text{ClO}$ $[\text{M}]^+$: 460.1588, Found: 460.1601.



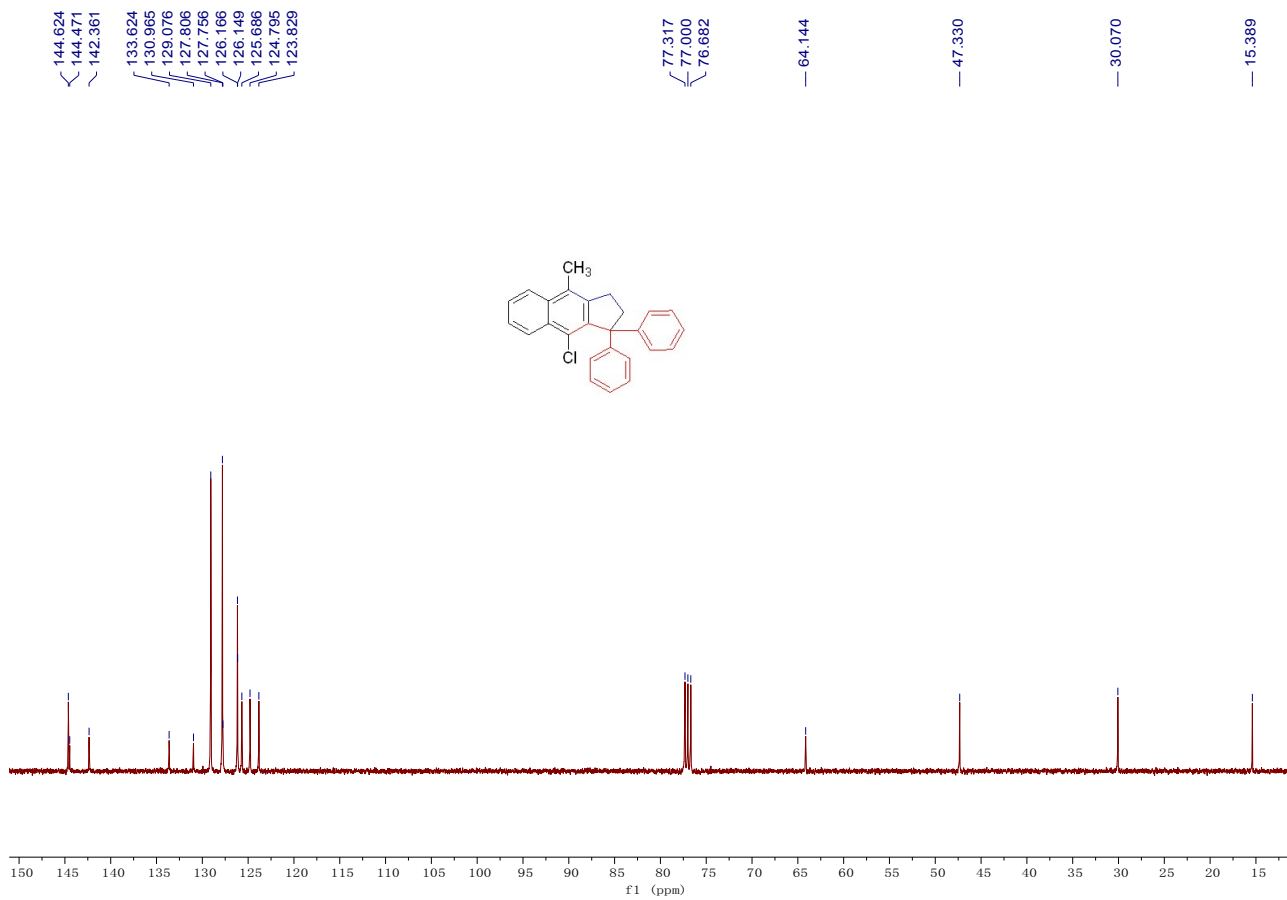
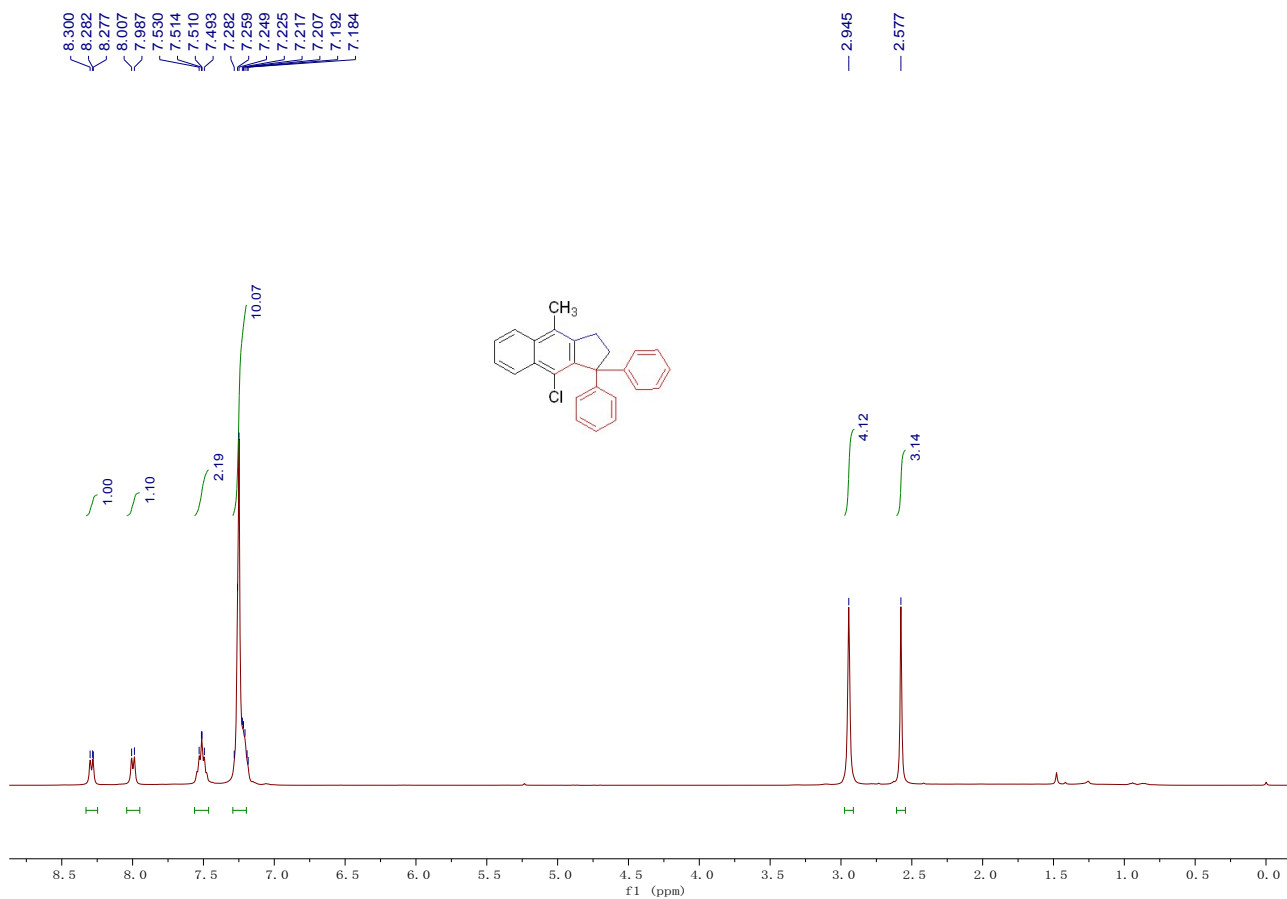


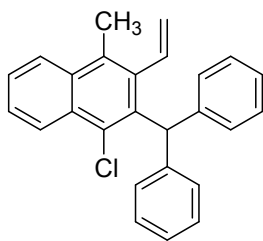
Compound 2n: Yield: 74 mg, 75%; A white solid; Mp: >200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, $J = 8.5$ Hz, 1H), 7.64 (d, $J = 8.5$ Hz, 1H), 7.55 – 7.40 (m, 5H), 7.32 (d, $J = 7.3$ Hz, 2H), 7.27 – 7.16 (m, 8H), 2.81 (t, $J = 6.9$ Hz, 2H), 2.71 (t, $J = 6.9$ Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.6, 142.7, 142.1, 138.3, 134.6, 133.5, 132.4, 131.0, 130.4, 130.0, 129.1, 128.5, 128.1, 127.5, 126.6, 126.2, 124.4, 63.4, 47.7, 30.6; IR (neat): ν 2919, 2849, 1488, 1092, 1013, 823, 757 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{31}\text{H}_{21}\text{Cl}_3$ $[\text{M}]^+$: 498.0703, Found: 498.0716.



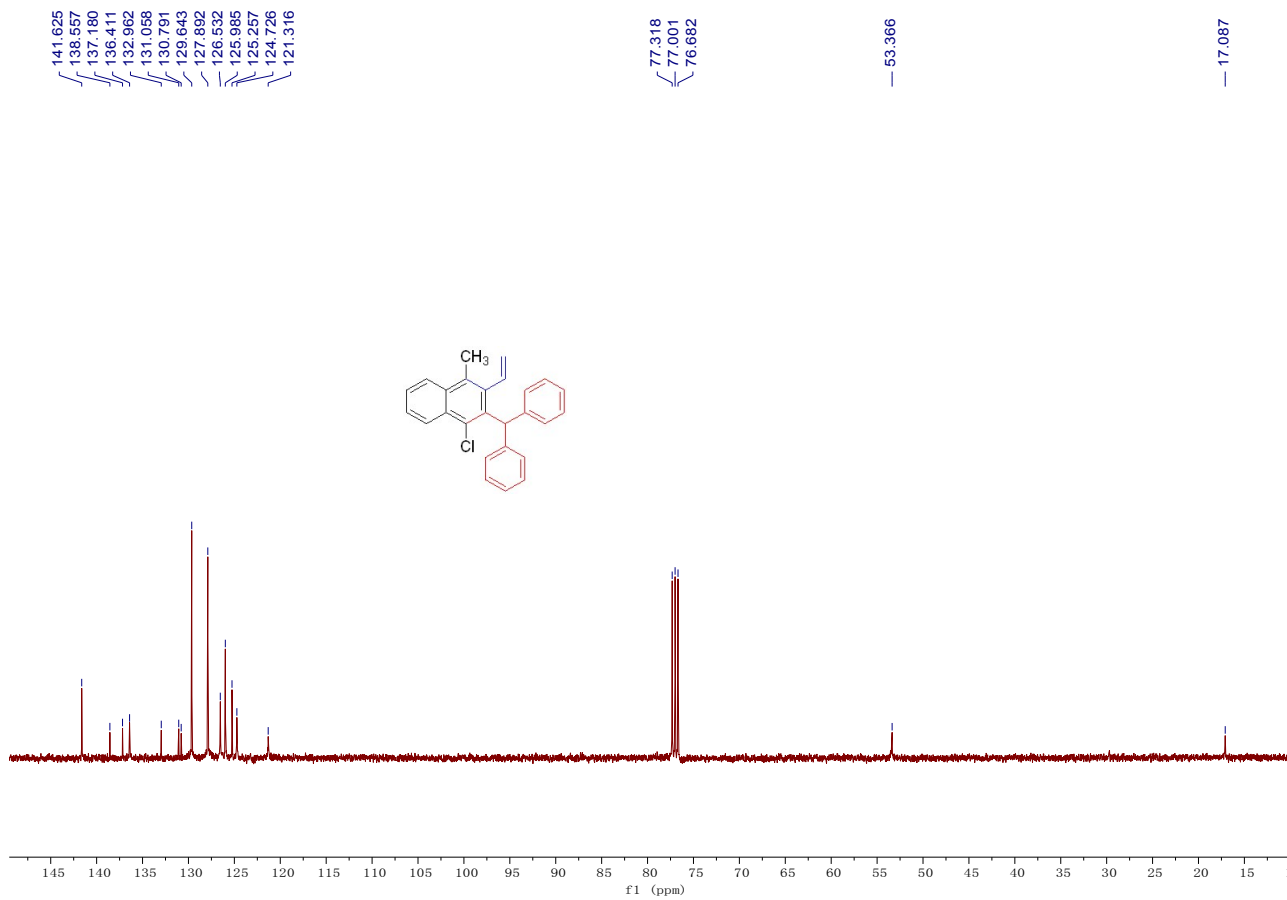
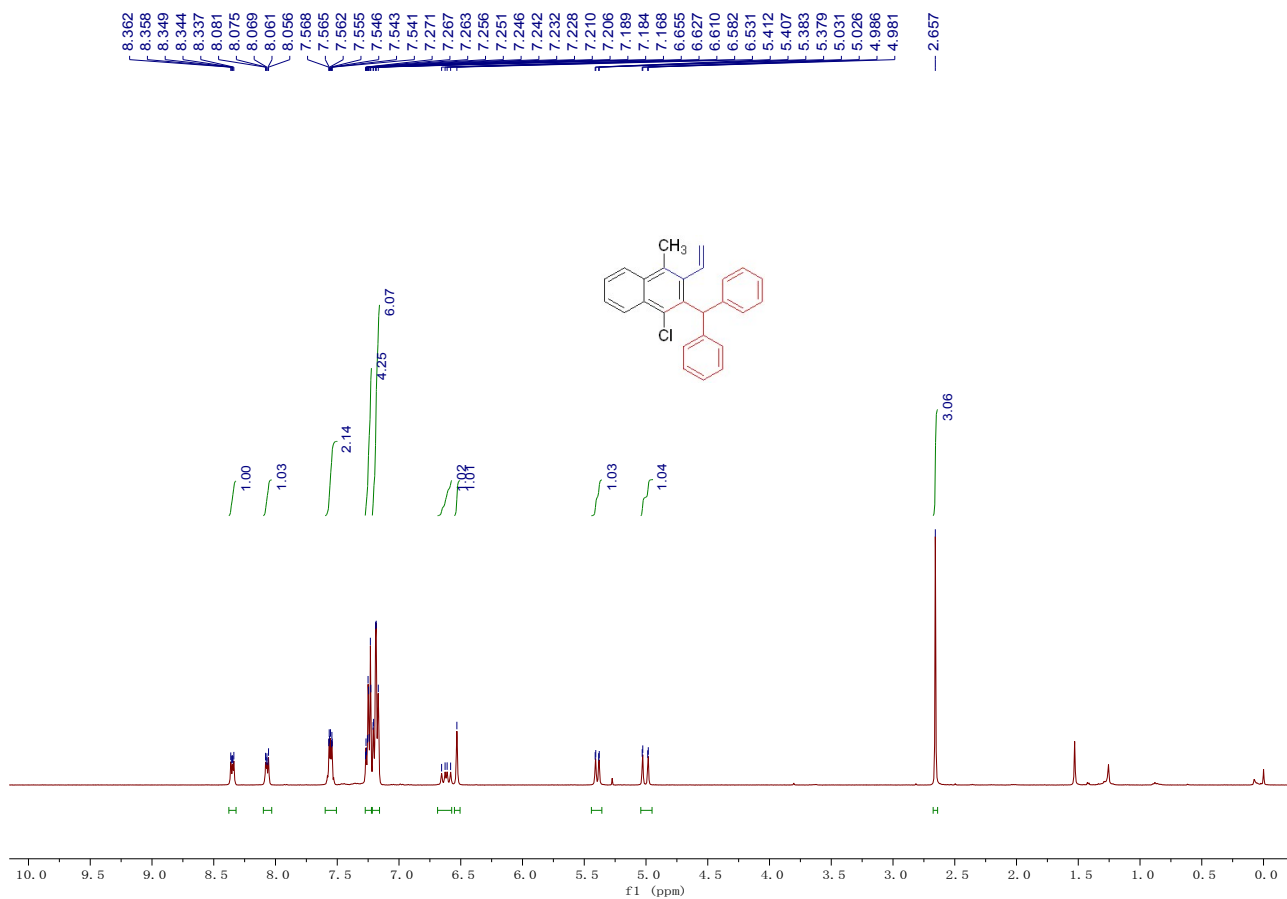


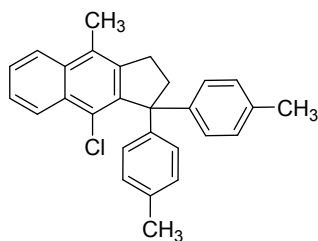
Compound 2q: Yield: 36 mg, 50%; A white solid; Mp: >200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.29 (d, $J = 7.4$ Hz, 1H), 8.00 (d, $J = 7.9$ Hz, 1H), 7.56 – 7.46 (m, 2H), 7.28 – 7.18 (m, 10H), 2.95 - 2.87 (m, 4H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.6, 144.5, 142.4, 133.6, 131.0, 129.1, 127.8, 126.2, 126.1, 125.7, 124.8, 123.8, 64.1, 47.3, 30.1, 15.4; IR (neat): ν 2920, 1598, 1490, 1442, 1033, 911, 759, 727, 697 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{26}\text{H}_{21}\text{Cl}$ $[\text{M}]^+$: 368.1326, Found: 368.1344.



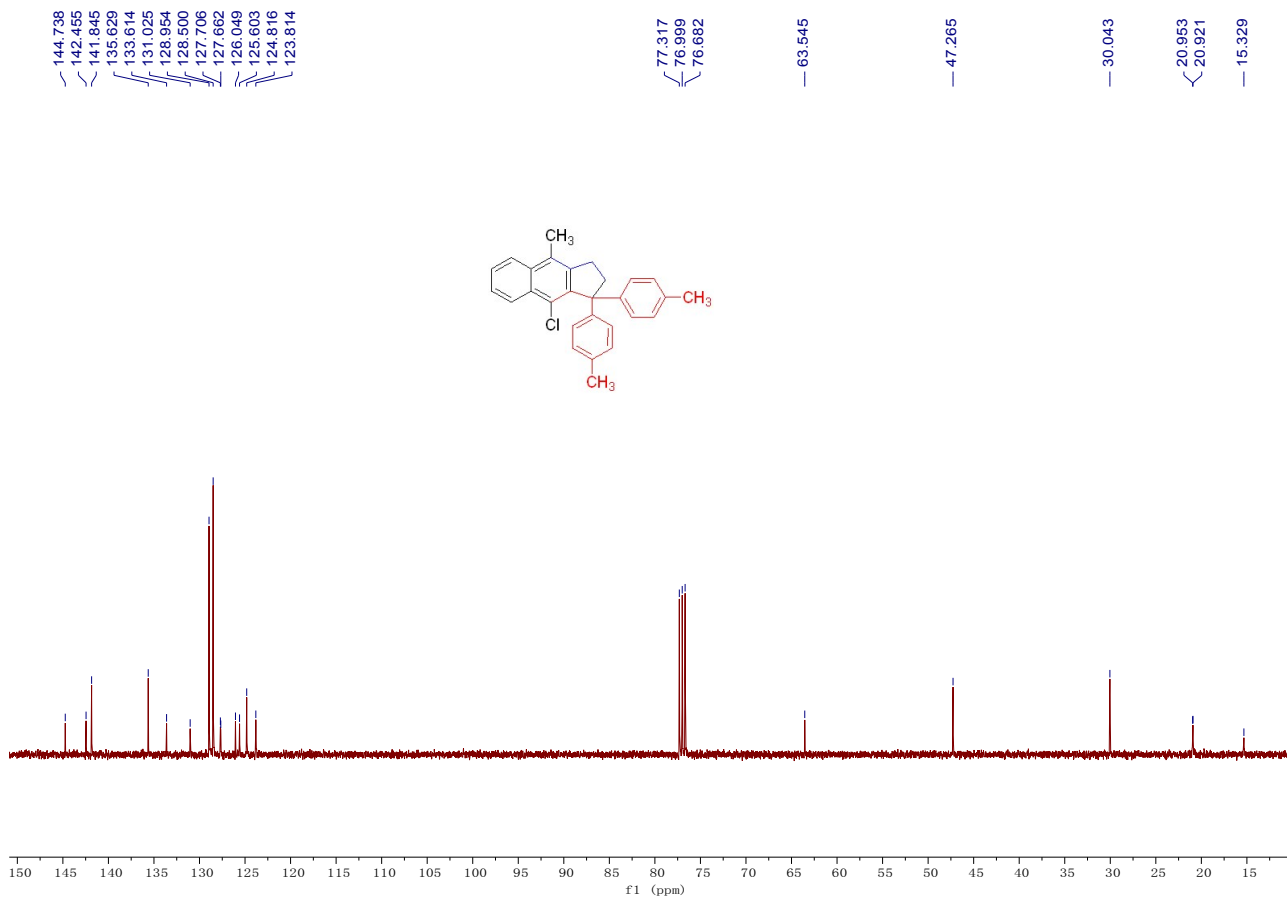
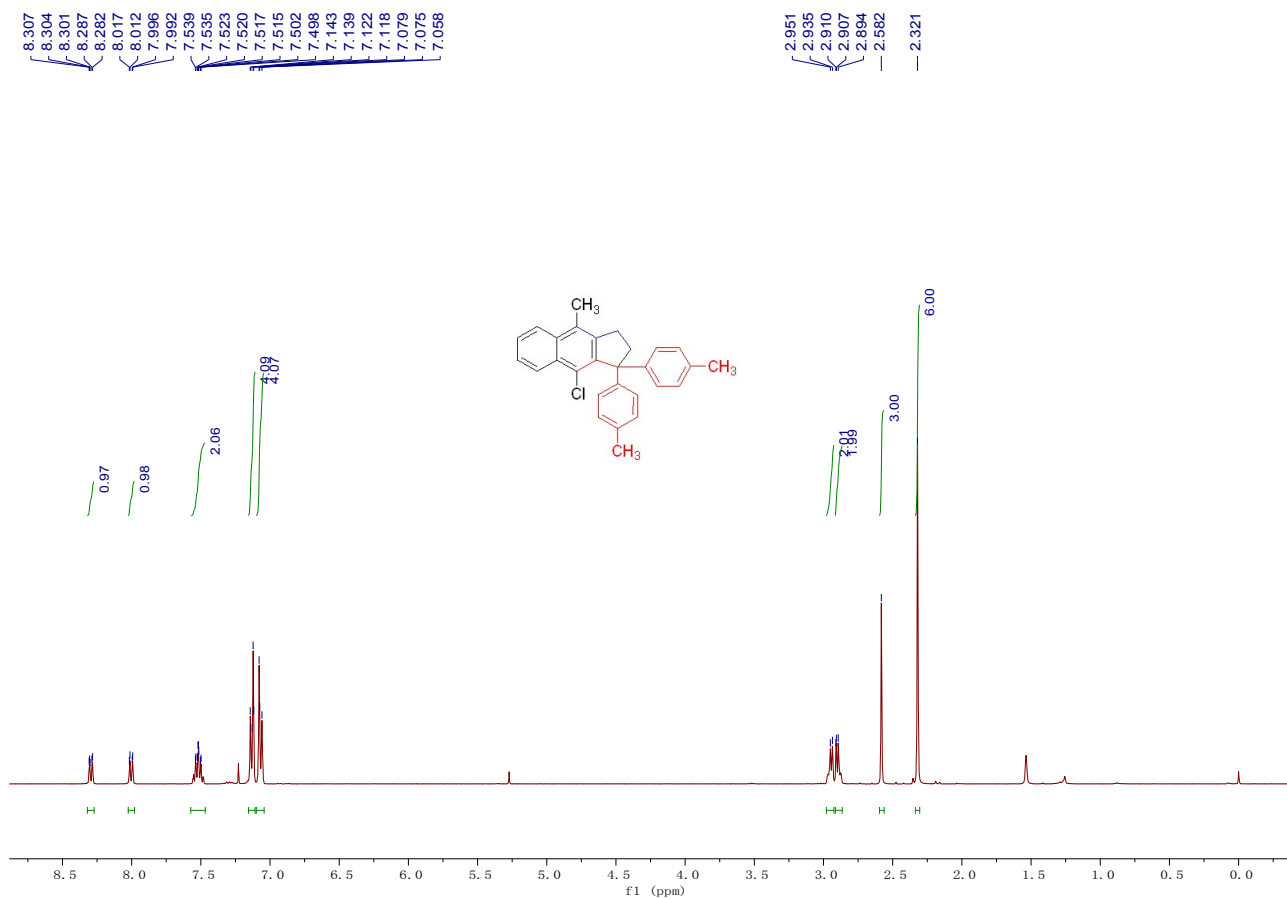


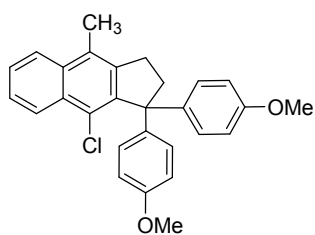
Compound 2q': Yield: 40 mg, 55%; A white solid; Mp: 139 - 141 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.38 – 8.32 (m, 1H), 8.10 – 8.03 (m, 1H), 7.60 – 7.51 (m, 2H), 7.27 – 7.22 (m, 4H), 7.22 – 7.16 (m, 6H), 6.62 (dd, *J* = 17.9, 11.3 Hz, 1H), 6.53 (s, 1H), 5.40 (dd, *J* = 11.3, 1.9 Hz, 1H), 5.01 (dd, *J* = 17.9, 1.9 Hz, 1H), 2.66 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 141.6, 138.6, 137.2, 136.4, 133.0, 131.1, 130.8, 129.6, 127.9, 126.5, 126.0, 125.3, 124.7, 121.3, 53.4, 17.1; IR (neat): ν 3055, 3024, 2922, 2846, 1492, 929, 749, 694 cm⁻¹; HRMS (EI) Calcd. for C₂₆H₂₁Cl [M]⁺: 368.1326, Found: 368.1329.



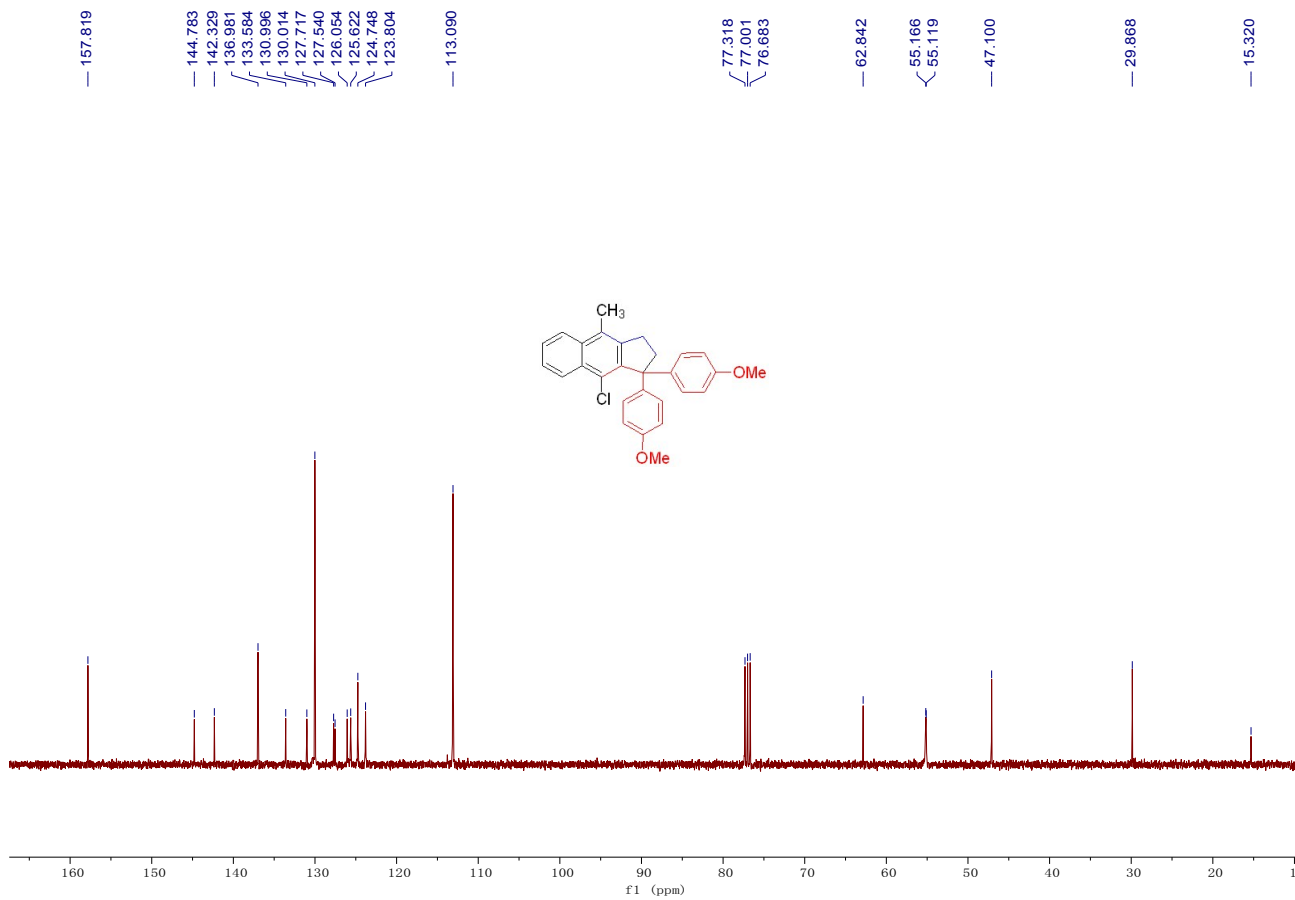
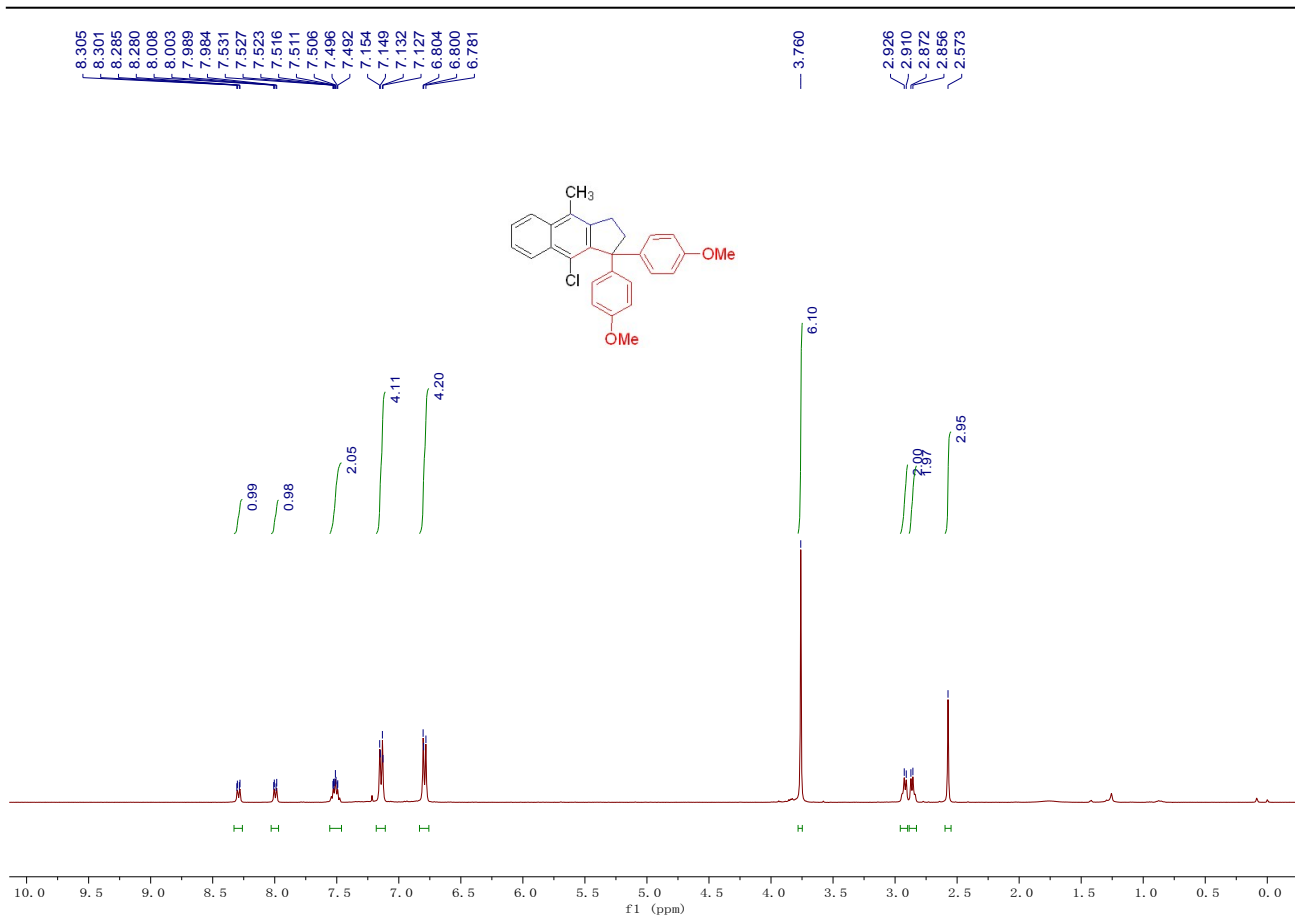


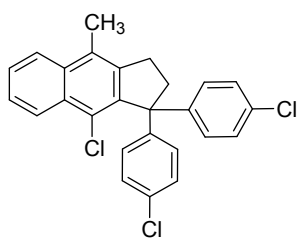
Compound 2r: Yield: 43 mg, 55%; A white solid; Mp: 179 - 181 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.32 – 8.27 (m, 1H), 8.02 – 7.98 (m, 1H), 7.57 – 7.47 (m, 2H), 7.15 – 7.11 (m, 4H), 7.10 – 7.04 (m, 4H), 2.95 – 2.92 (m, 2H), 2.91 – 2.86 (m, 2H), 2.58 (s, 3H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.7, 142.5, 141.8, 135.6, 133.6, 131.0, 129.0, 128.5, 127.7, 127.6, 126.0, 125.6, 124.8, 123.8, 63.5, 47.3, 30.0, 21.0, 20.9, 15.3; IR (neat): ν 2925, 2852, 1508, 1450, 1187, 811, 754 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{28}\text{H}_{25}\text{Cl}$ $[\text{M}]^+$: 396.1639, Found: 396.1648.



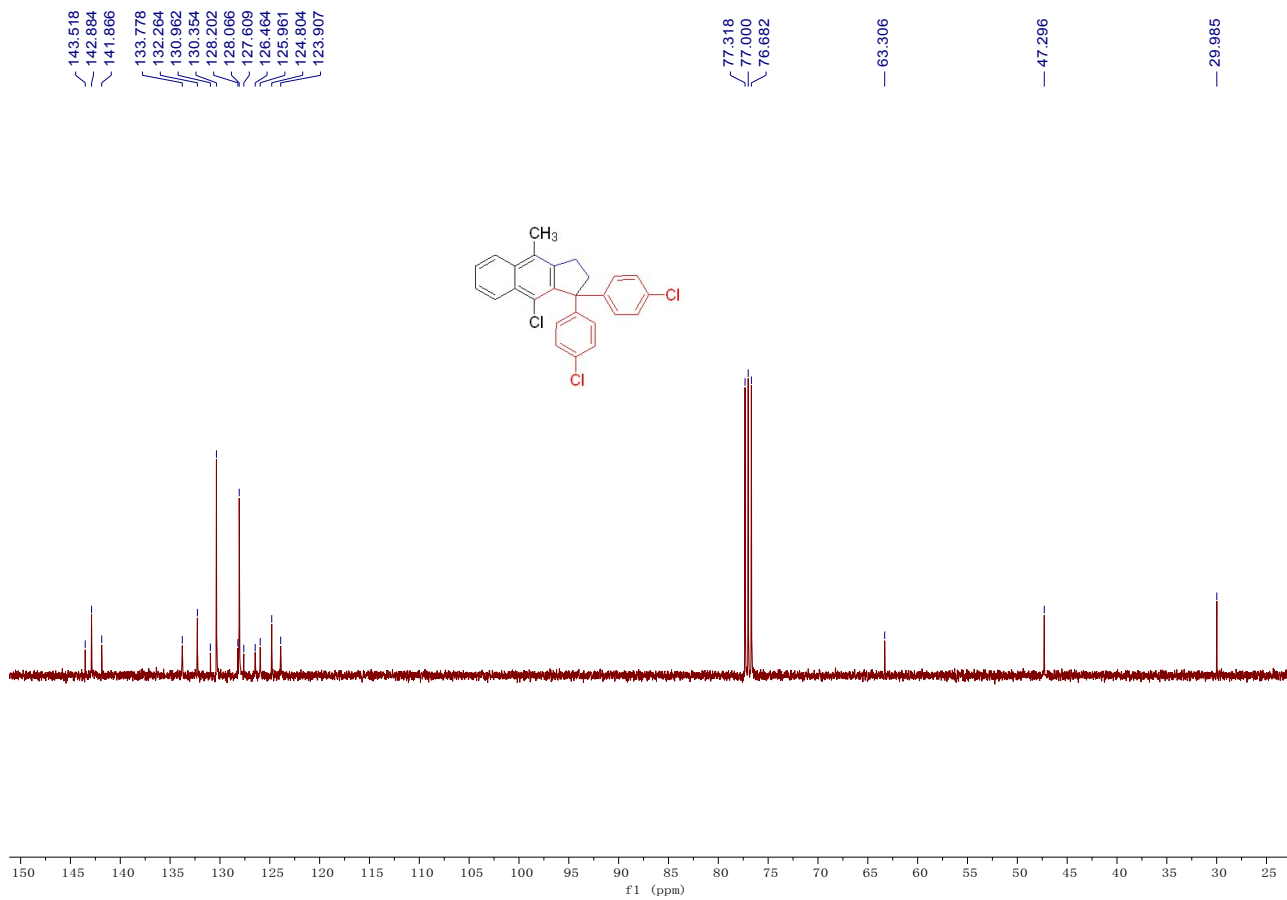
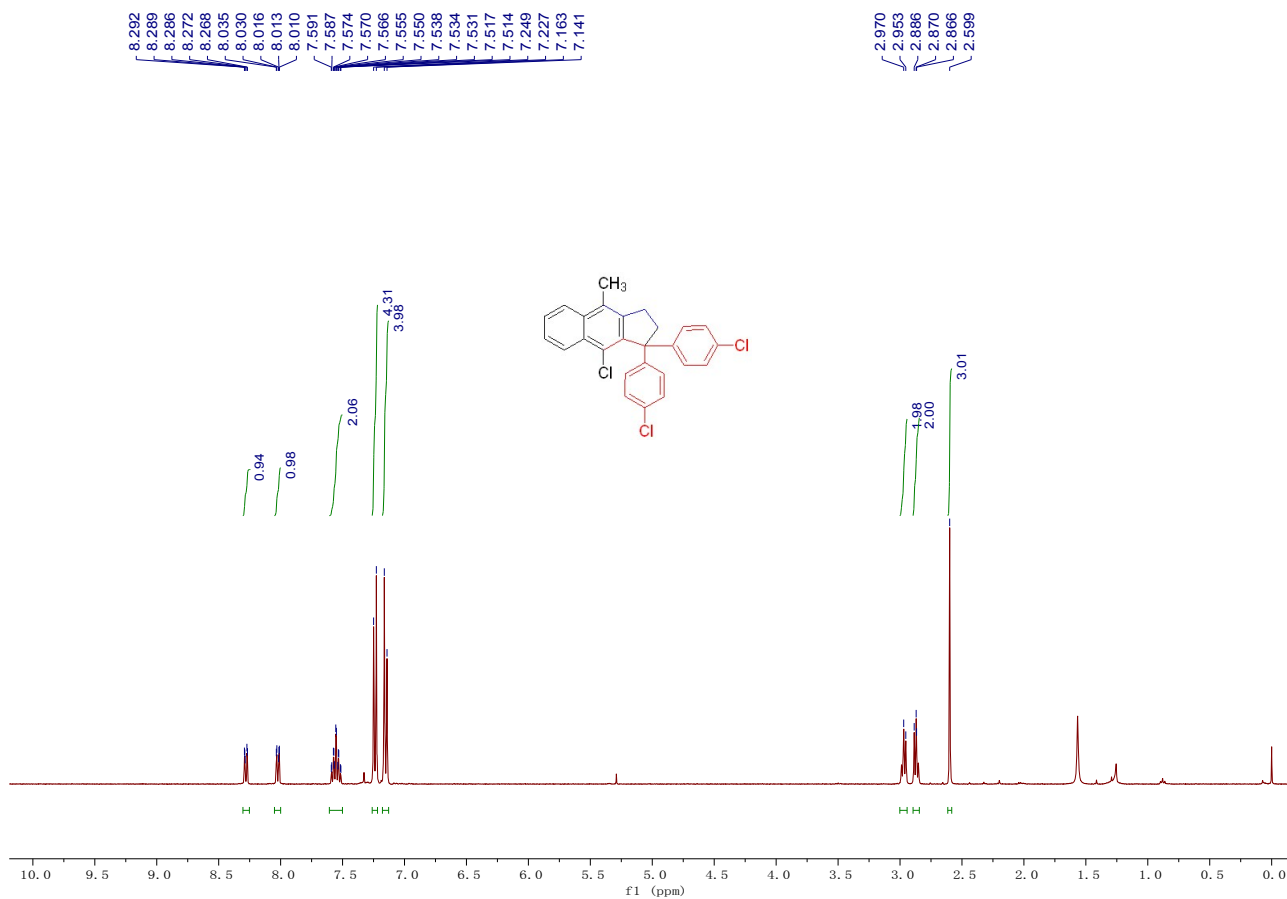


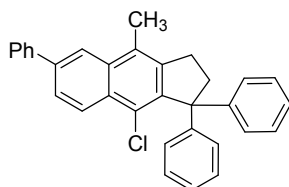
Compound 2s: Yield: 51 mg, 60%; A white solid; Mp: 76 - 78 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.33 – 8.26 (m, 1H), 8.00 (dd, $J = 7.6, 2.0$ Hz, 1H), 7.56 – 7.46 (m, 2H), 7.18 – 7.11 (m, 4H), 6.83 – 6.76 (m, 4H), 3.76 (s, 6H), 2.94 - 2.90 (m, 2H), 2.90 – 2.80 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.8, 144.8, 142.3, 137.0, 133.6, 131.0, 129.9, 127.7, 127.5, 126.1, 125.6, 124.7, 123.8, 113.1, 62.8, 55.2, 55.1, 47.1, 29.9, 15.3; IR (neat): ν 2951, 2828, 1604, 1508, 1247, 1179, 1033, 824 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{28}\text{H}_{25}\text{ClO}_2$ $[\text{M}]^+$: 428.1538, Found: 428.1539.



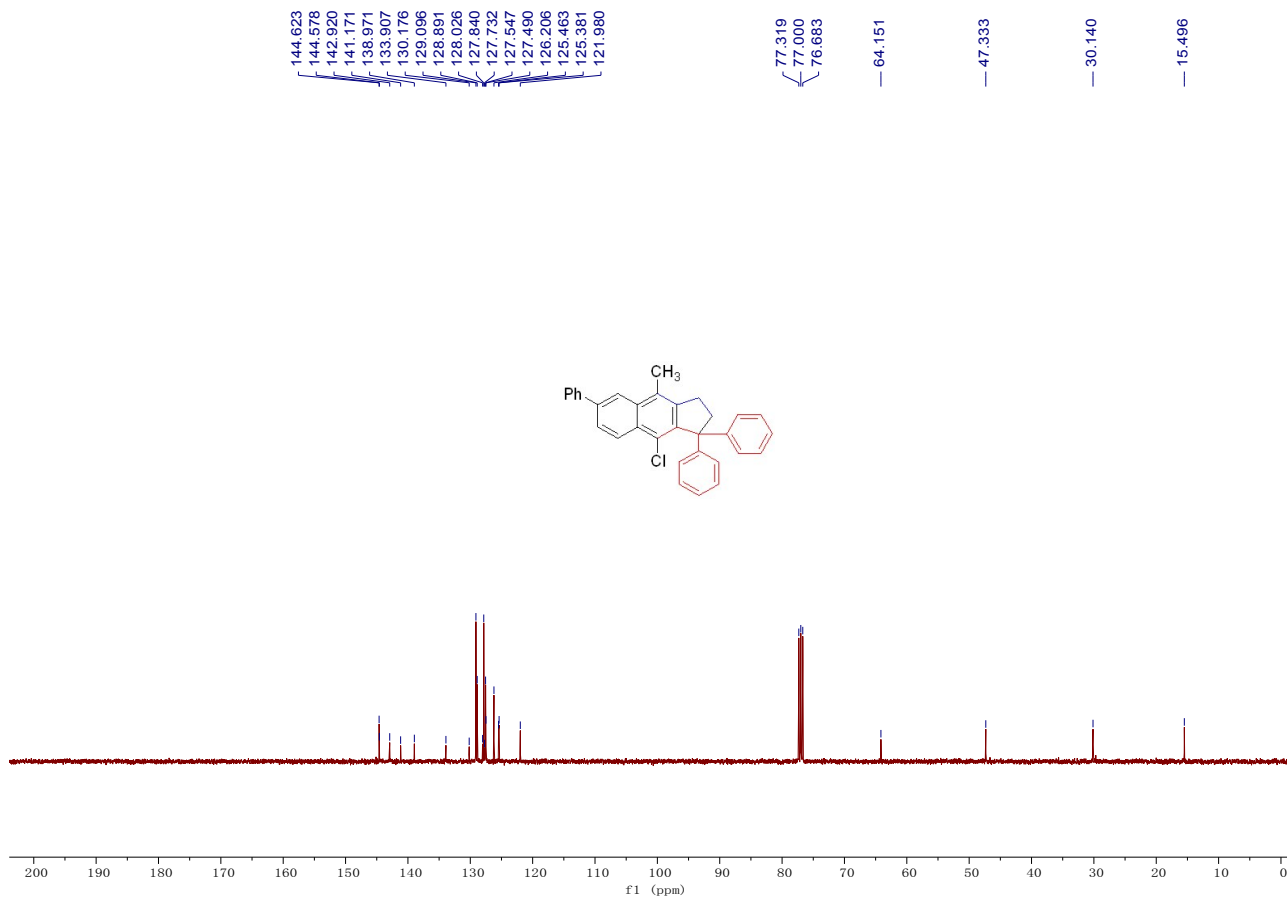
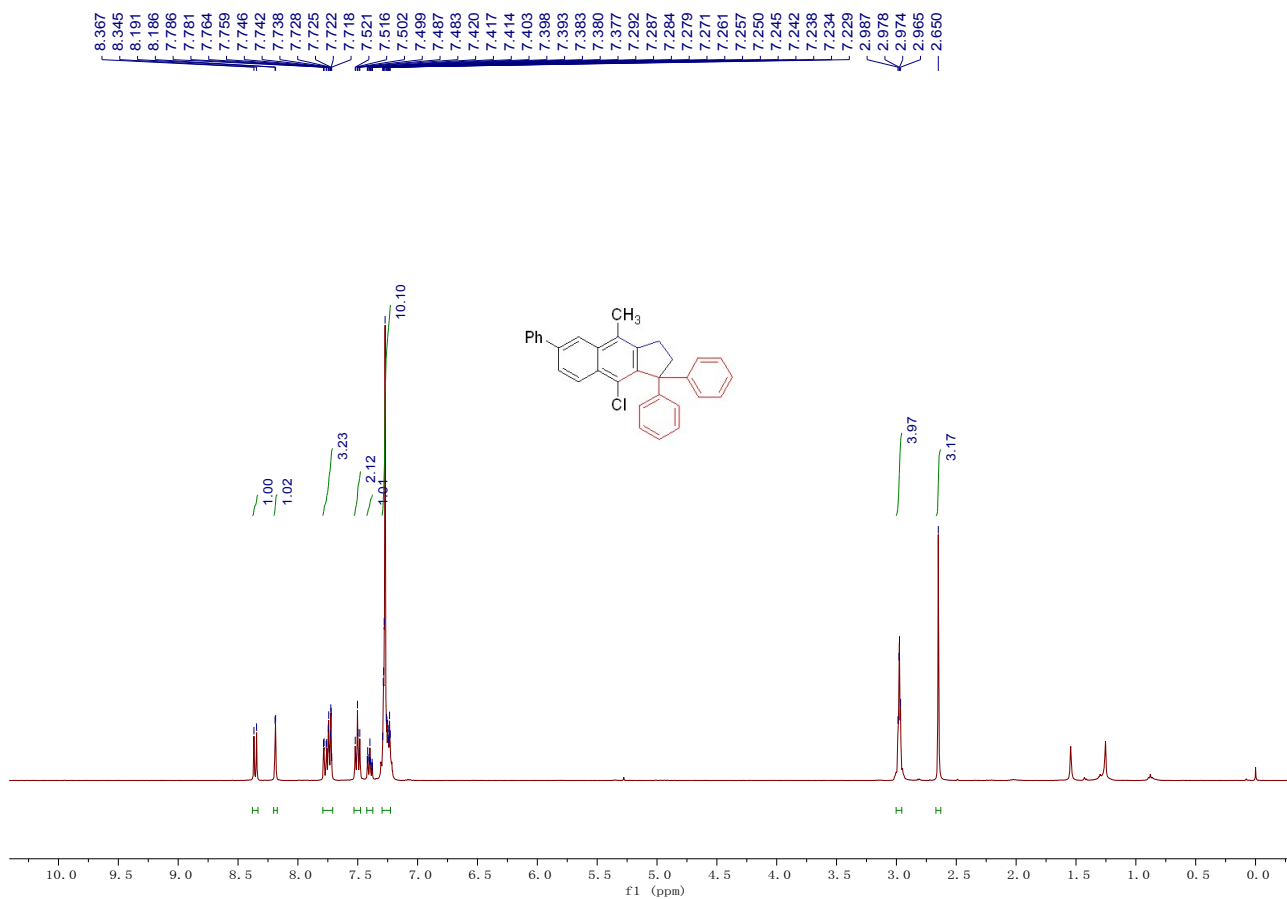


Compound 2t: Yield: 30 mg, 35%; A white solid; Mp: 198 - 200 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.30 – 8.25 (m, 1H), 8.05 – 8.00 (m, 1H), 7.61 – 7.50 (m, 2H), 7.26 – 7.22 (m, 4H), 7.18 – 7.13 (m, 4H), 3.00 – 2.94 (m, 2H), 2.89 – 2.84 (m, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.5, 142.9, 141.9, 133.8, 132.3, 131.0, 130.4, 128.2, 128.1, 127.6, 126.5, 126.0, 124.8, 123.9, 63.3, 47.3, 30.0; IR (neat): ν 2980, 2870, 1511, 1448, 1180, 755 cm^{-1} ; HRMS (EI) Calcd. for $\text{C}_{26}\text{H}_{19}\text{Cl}_3$ $[\text{M}]^+$: 436.0547, Found: 436.0555.

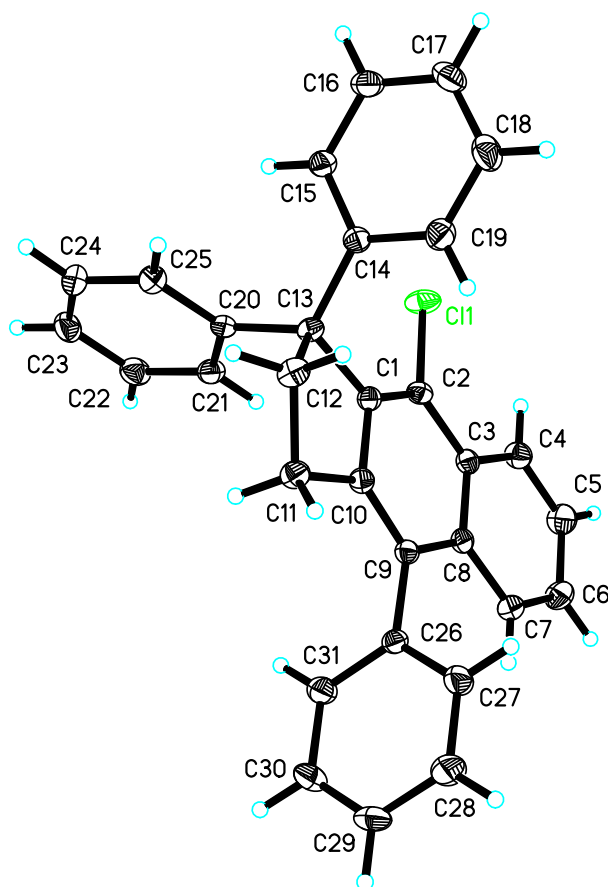




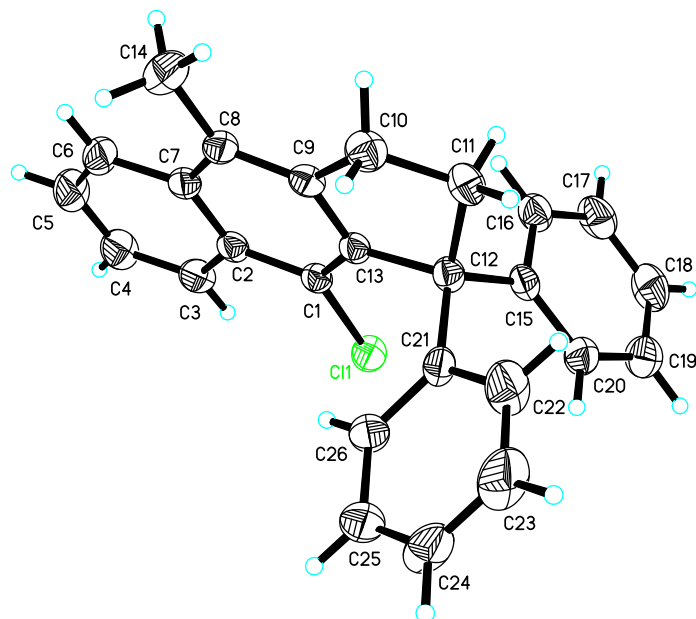
Compound 2v: Yield: 26 mg, 30%; A white solid; Mp: 190 - 192 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 8.8 Hz, 1H), 8.19 (d, *J* = 1.8 Hz, 1H), 7.79 – 7.71 (m, 3H), 7.50 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.30 – 7.23 (m, 10H), 3.00 – 2.90 (m, 4H), 2.65 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 144.6, 144.5, 142.9, 141.2, 139.0, 133.9, 130.2, 129.1, 128.9, 128.0, 127.8, 127.7, 127.54, 127.49, 126.2, 125.5, 125.4, 122.0, 64.2, 47.3, 30.1, 15.5; IR (neat): ν 2914, 2849, 1594, 1488, 1448, 1029, 933, 755 cm⁻¹; HRMS (EI) Calcd. for C₃₂H₂₅Cl [M]⁺: 444.4639, Found: 444.4642.



7. X-ray crystal data



The crystal data of **2a** have been deposited in CCDC with number 1949824. Empirical Formula: $C_{31}H_{23}Cl$; Formula Weight: 430.94; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.160 x 0.130 mm³; Crystal System: Monoclinic; Lattice Parameters: $a = 12.1573(13)\text{\AA}$, $b = 12.3663(13)\text{\AA}$, $c = 15.5243(14)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 107.422(3)^\circ$, $\gamma = 90^\circ$, $V = 2226.9(4)\text{\AA}^3$; Space group: P 21/n; $Z = 4$; $D_{calc} = 1.285\text{ g/cm}^3$; $F_{000} = 904$; Final R indices [$I > 2\sigma(I)$] $R1 = 0.0350$, $wR2 = 0.0828$.



The crystal data of **2q** have been deposited in CCDC with number 1975359. Empirical Formula: $C_{26}H_{21}Cl$; Formula Weight: 368.88; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.160 x 0.130 mm³; Crystal System: Orthorhombic; Lattice Parameters: $a = 20.7442(6) \text{ \AA}$, $b = 12.3960(3) \text{ \AA}$, $c = 7.5295(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 1936.17(9) \text{ \AA}^3$; Space group: $P n a 2_1$; $Z = 4$; $D_{calc} = 1.265 \text{ g/cm}^3$; $F_{000} = 776$; Final R indices [$I > 2\sigma(I)$] $R_1 = 0.0318$, $wR_2 = 0.0795$.