Supplementary information

Palladium-Catalyzed Alkynylative [5+1] Carboannualation of 1,3-Diarylprop-2-yn-1-yl acetates with Terminal Alkynes Enabled by C-H Functionalization

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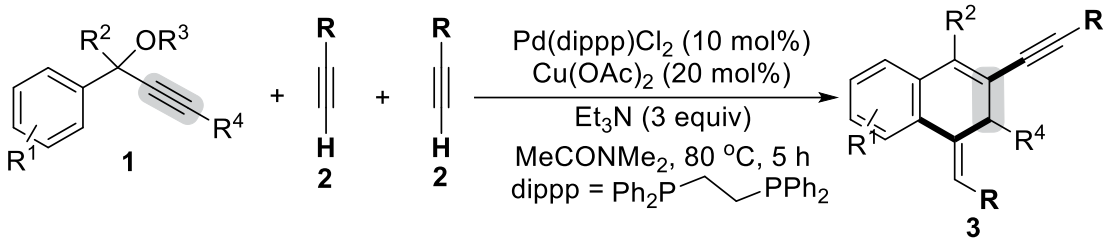
(A) General Experimental Procedure

(a) General Information

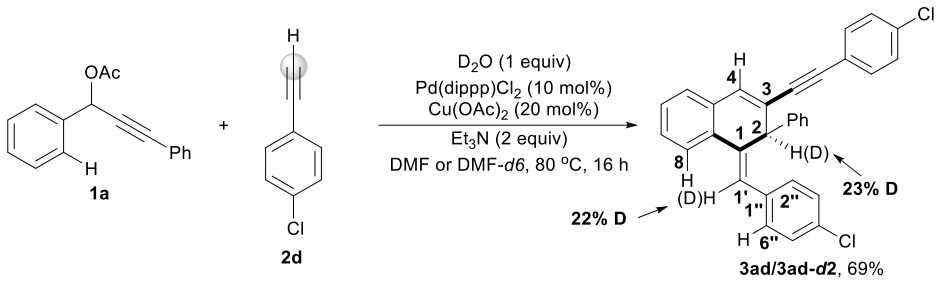
All ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer at room temperature in $CDCl_3$ with tetramethylsilane as internal standard. High-resolution mass spectra (HRMS) was recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Unless otherwise noted, all reactions were carried out using standard Schlenk techniques, and all starting materials and solvents were commercially available and were used without further purification. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA). 1-Arylprop-2-yn-1-yl acetates (**1**) were prepared according to reported literatures,[1] and terminal alkynes (**2**) were purchased from commercial sources and used as received.

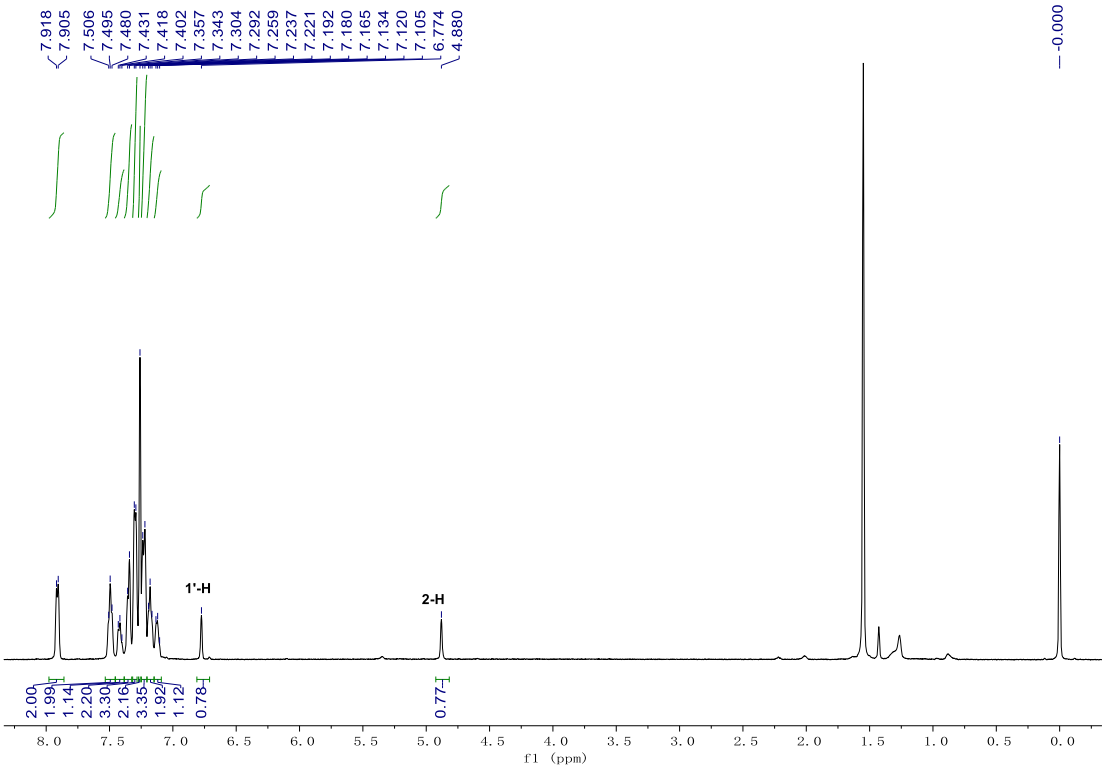
(b) Typical Experimental Procedure for the Synthesis of Products 3：

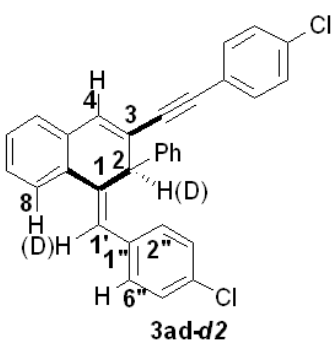


To a Schlenk tube were added **1** (0.2 mmol), alkynes **2** (0.4 mmol), $Pd(dippp)Cl_2$ (10 mol%; 0.02 mmol), $Cu(OAc)_2$ (20 mol%; 0.04 mmol), Et_3N (0.6 mmol) and $MeCONMe_2$ (DMF; 2 mL). Then the tube was charged with Ar and was stirred at 80 ^{o}C (oil bar temperature) for 5 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, quenched by water and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuum, the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product **3**.

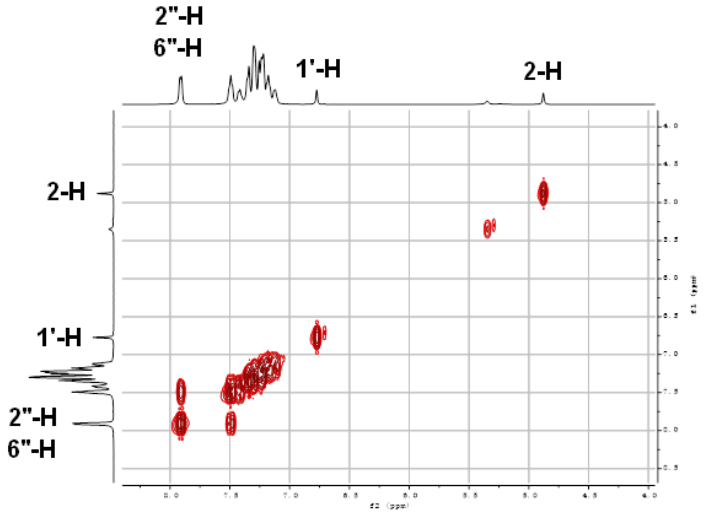
(c) The Deuterium-Labelled Experiments:



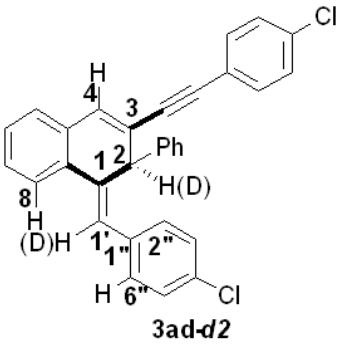




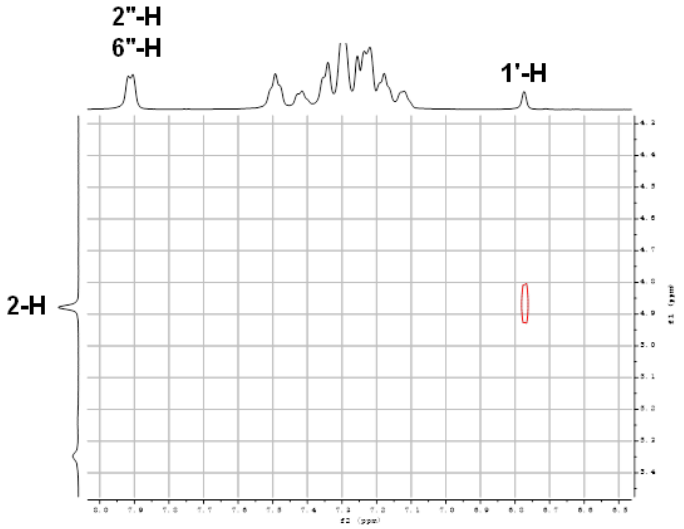
Weak H-H COSY between 2-H and 1'-H



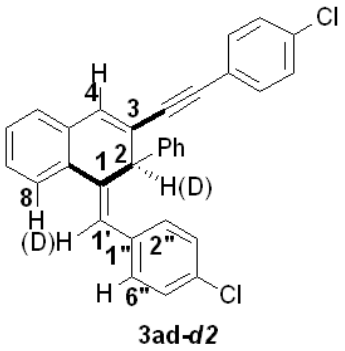
H-H COSY



3ad-*d2*



H-H COSY



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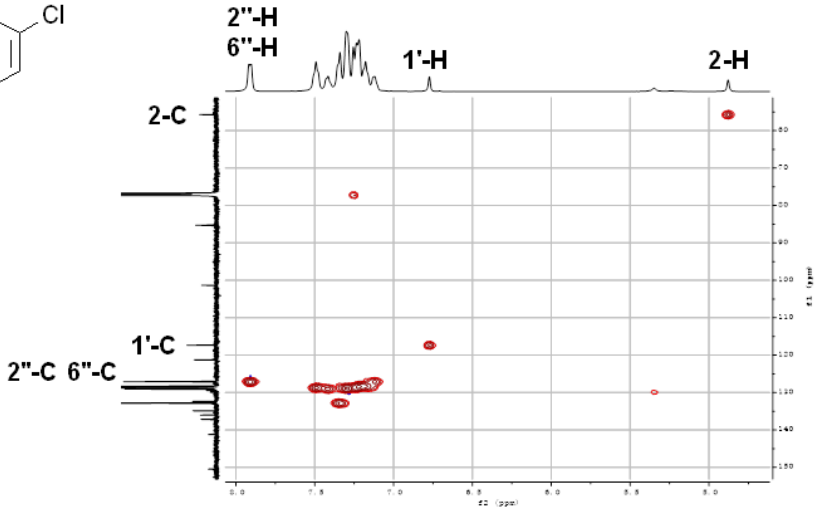
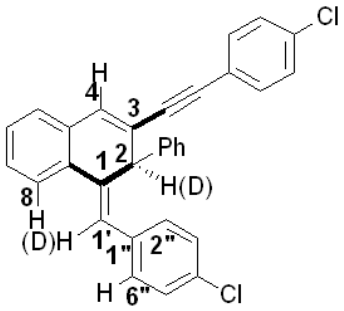


HSQC



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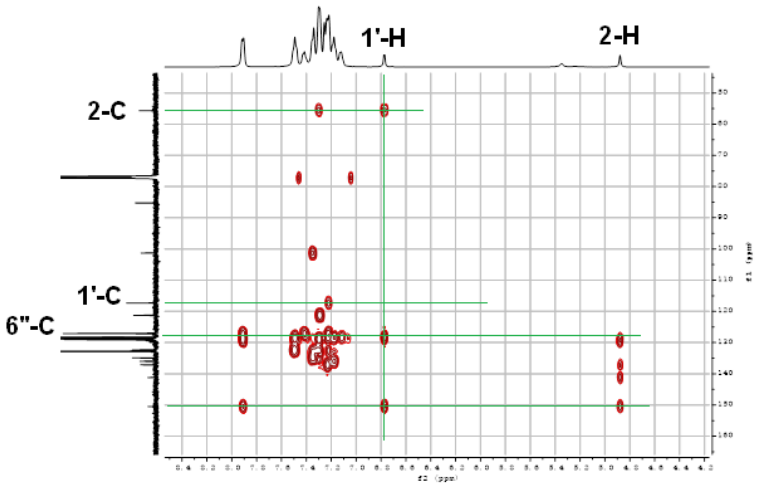
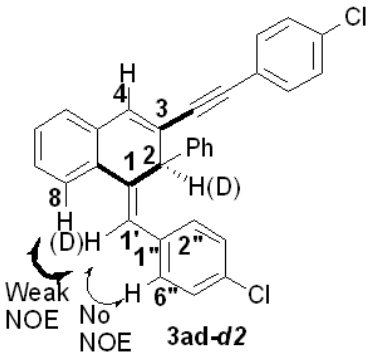
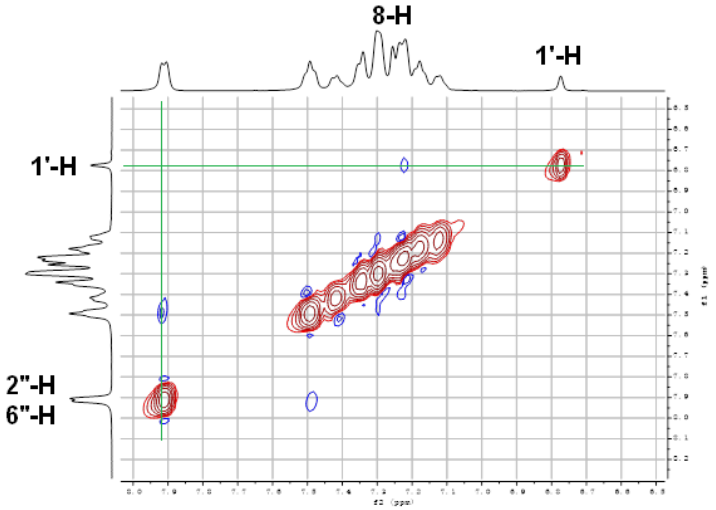


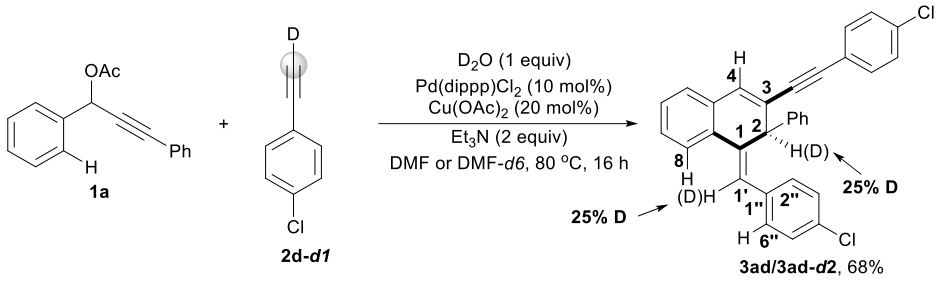
HMBC

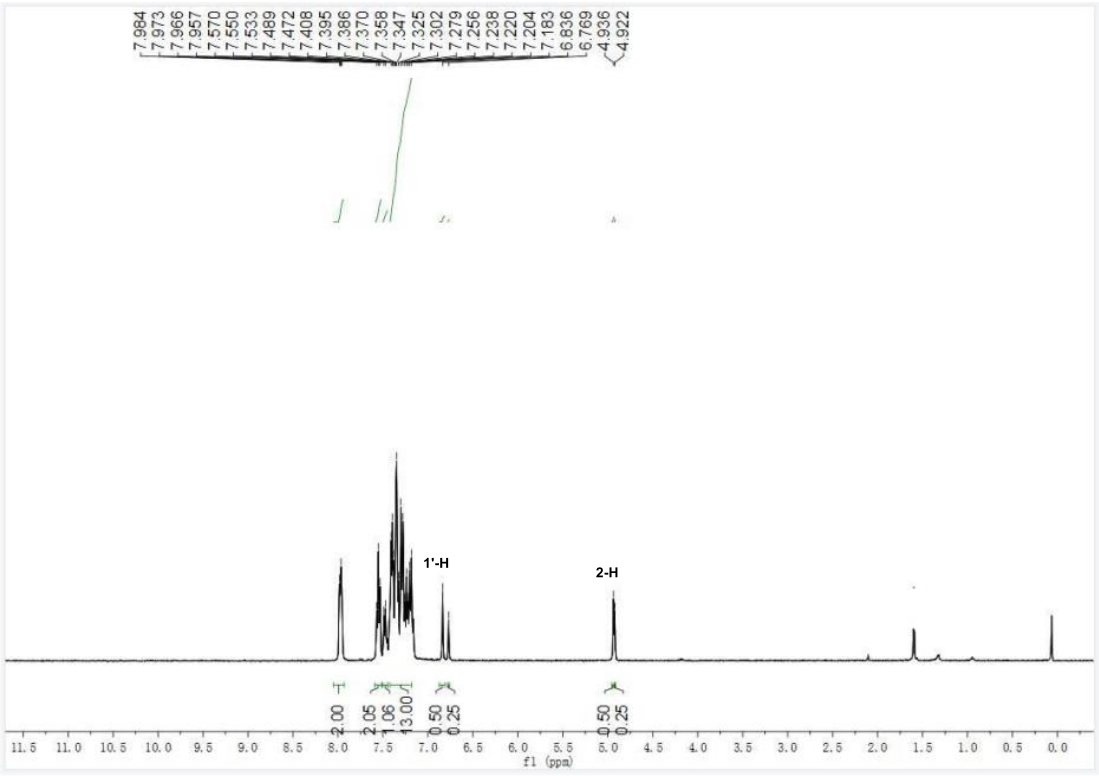


3ad-*d2*



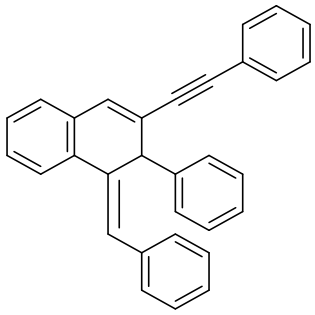
H-H NOE


OAc
Ph
H
1a
+
D
Cl
2d-d1
D2O (1 equiv)
Pd(dippp)Cl2 (10 mol%)
Cu(OAc)2 (20 mol%)
Et3N (2 equiv)
DMF or DMF-d6, 80 °C, 16 h
Cl
H
4
3
Ph
1
2
H(D)
25% D
8
H
(D)H
1'
1"
2"
25% D
H
6"
Cl
3ad/3ad-d2, 68%


7.984
7.973
7.966
7.957
7.570
7.550
7.533
7.489
7.472
7.408
7.395
7.386
7.370
7.358
7.347
7.325
7.302
7.279
7.256
7.238
7.220
7.204
7.183
6.836
6.769
4.936
4.922
1'-H
2-H
2.00
2.05
1.06
13.00
0.50
0.25
0.50
0.25
f1 (ppm)

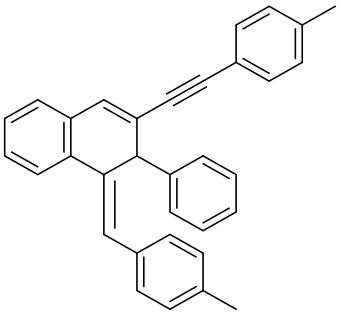
(B) Analytical Data

1-benzylidene-2-phenyl-3-(phenylethynyl)-1,2-dihydronaphthalene (3aa):



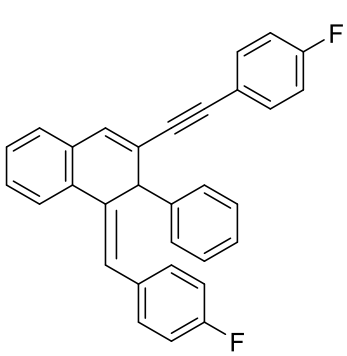
52.0 mg, 66%, *E/Z* > 99:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.42-7.3 (m, 5H), 7.27-7.23 (m, 7H), 7.18-7.12 (m, 3H), 7.08-7.04 (m, 1H), 6.76 (s, 1H), 4.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.8, 141.7, 138.6, 136.3, 132.6, 131.6, 130.4, 128.8, 128.7, 128.6, 128.5, 128.3, 128.3, 128.2, 127.7, 127.1, 126.9, 126.7, 122.9, 116.8, 102.5, 84.6, 56.5; HRMS m/z (ESI) calcd for $C_{31}H_{23}$ ($[M+H]^+$) 395.1794, found 395.1799.

1-(4-methylbenzylidene)-2-phenyl-3-(p-tolylethynyl)-1,2-dihydronaphthalene (3ab):



53.2 mg, 63%; *E/Z* = 3:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.41-7.24 (m, 8H), 7.20-7.07 (m, 5H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 1H), 4.88 (s, 0.75H), 4.87 (s, 0.25H), 2.34 (s, 3H), 2.27 (s, 0.75H), 2.24 (s, 2.25H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 142.1, 140.8, 138.9, 138.9, 136.5, 136.5, 136.3, 135.7, 133.6, 132.8, 132.7, 131.6, 131.5, 130.9, 130.2, 129.2, 129.1, 129.0, 128.7, 128.6, 128.5, 128.3, 128.2, 128.2, 127.8, 127.6, 127.1, 126.9, 126.6, 120.0, 116.5, 116.4, 102.9, 102.7, 84.5, 84.2, 56.5, 56.2, 21.6, 21.1; HRMS m/z (ESI) calcd for $C_{33}H_{27}$ ($[M+H]^+$) 423.2107, found 423.2116.

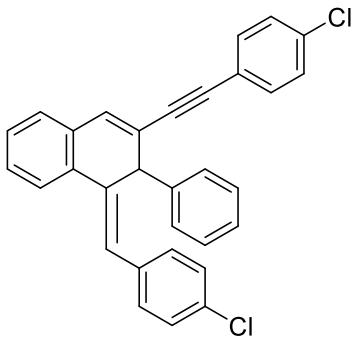
1-(4-fluorobenzylidene)-3-((4-fluorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3ac):



58.5 mg, 68%; *E:Z* = 1:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93-7.90 (m, 2H), 7.48 (m, 2H), 7.41-7.11 (m, 10H), 7.02-6.92 (m, 3H), 6.83 (t, *J* = 8.4 Hz, 1H), 6.76 (s, 0.5H), 6.71 (s, 0.5H), 4.87 (s, 0.5H), 4.85 (s, 0.5H); ^{19}F NMR (471 MHz, CDCl3) δ: -109.6, -109.7, -114.8, -115.7; ^{13}C NMR (100 MHz, $CDCl_3$) δ:

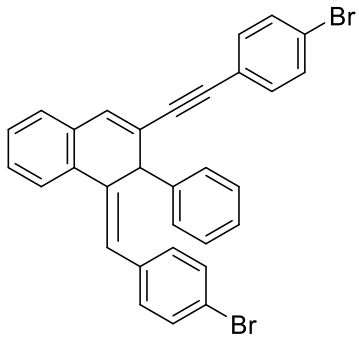
163.6 (d, *J* = 90.2 Hz), 163.5 (d, *J* = 103 Hz), 161.1 (d, *J* = 83.8 Hz), 161.0 (d, *J* = 99.4 Hz), 149.9, 149.9, 141.7, 141.4, 138.5, 136.1, 134.4, 134.4, 133.7, 133.6, 132.6, 132.5, 132.5, 130.2, 130.1, 129.9, 129.8, 129.3, 129.2, 129.0, 129.0, 128.7, 128.6, 128.4, 128.3, 127.7, 127.2, 127.1, 127.1, 127.0, 119.1, 119.1, 119.0, 117.0, 115.9, 115.9, 115.7, 115.7, 115.5, 115.4, 115.3, 115.1, 101.5, 101.4, 84.3, 84.2, 56.3, 55.7; HRMS m/z (ESI) calcd for $C_{31}H_{21}F_2$ ($[M+H]^+$) 431.1606, found 431.1613.

1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3ad):



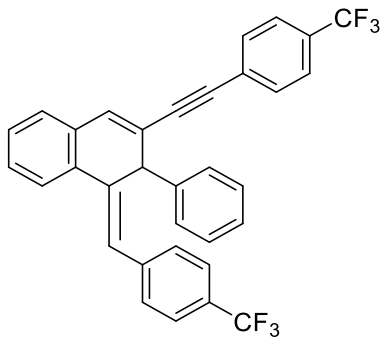
65.6 mg, 71%; *E/Z* = 1:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.47-7.45 (m, 1H), 7.39-7.32 (m, 7H), 7.29-7.15 (m, 7H), 6.81 (s, 0.9H), 6.74 (s, 0.1H), 4.92 (s, 0.9H), 4.90 (s, 0.1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.4, 150.2, 141.2, 137.2, 136.0, 134.9, 134.7, 133.7, 133.6, 132.8, 132.7, 132.6, 132.4, 129.6, 129.4, 129.1, 129.1, 128.9, 128.8, 128.8, 128.7, 128.7, 128.5, 128.3, 127.7, 127.3, 127.1, 127.1, 127.1, 121.4, 121.3, 117.5, 117.4, 115.8, 101.4, 101.2, 85.4, 85.3, 56.4, 55.7; HRMS m/z (ESI) calcd for $C_{31}H_{21}{}^{35}Cl_2$ ($[M+H]^+$) 463.1015, found 463.1021.

1-(4-bromobenzylidene)-3-((4-bromophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3ae):



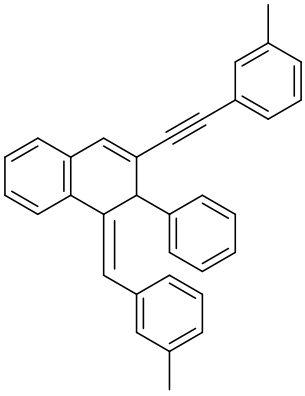
64.7 mg, 59%; *E/Z* = 3:2; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91-7.88 (m, 2H), 7.50-7.33 (m, 7H), 7.27-7.20 (m, 7H), 7.12-7.07 (m, 2H), 6.77 (s, 0.6H), 6.68 (s, 0.4H), 4.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.5, 150.2, 142.4, 141.1, 138.2, 137.6, 136.0, 135.1, 133.0, 132.3, 131.7, 131.6, 131.3, 130.3, 129.7, 129.4, 129.1, 129.0, 128.7, 128.6, 128.3, 128.3, 127.6, 127.2, 127.1, 127.1, 123.2, 123.1, 121.7, 121.7, 120.8, 120.8, 117.4, 115.8, 101.6, 101.4, 85.6, 85.4, 56.3, 55.7; HRMS m/z (ESI) calcd for $C_{31}H_{21}{}^{79}Br_2$ ($[M+H]^+$) 549.9932, found 549.9937.

2-phenyl-1-(4-(trifluoromethyl)benzylidene)-3-((4-(trifluoromethyl)phenyl)ethynyl)-1,2-dihydronaphthalene (3af):



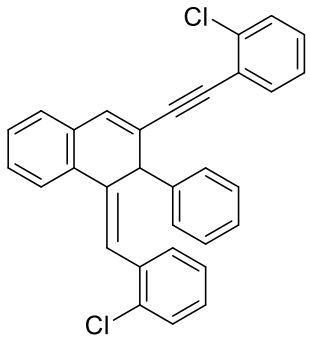
55.1 mg, 52%; *E/Z* = 3:2; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94-7.90 (m, 2H), 7.58-7.49 (m, 8H), 7.45-7.36 (m, 3H), 7.33-7.28 (m, 2H), 7.25-7.16 (m, 3H), 6.83 (s, 0.55H), 6.79 (s, 0.45H), 4.98 (s, 0.55H), 4.91 (s, 0.55H); ^{19}F NMR (471 MHz, CDCl3) δ: -62.7, -63.0; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.5, 151.0, 144.0, 142.6, 140.5, 139.5, 138.0, 135.8, 132.1, 132.1, 131.9, 131.8, 130.7, 130.4 (d, *J* = 32.5 Hz), 129.3 (d, *J* = 32.1 Hz), 129.4, 129.3, 128.8, 128.7, 128.6, 128.4, 128.3, 128.3, 128.0, 127.6, 127.4, 127.3, 127.2, 127.1, 126.4, 125.6 (q, *J* = 3.7 Hz), 125.3 (q, *J* = 3.6 Hz), 125.2 (q, *J* = 3.7 Hz), 122.6 (d, *J* = 4.3 Hz), 118.1, 116.0, 101.3, 100.8, 86.4, 86.3, 56.5, 55.9; HRMS m/z (ESI) calcd for $C_{33}H_{21}F_6$ ($[M+H]^+$) 531.1542, found 531.1540.

1-(3-methylbenzylidene)-2-phenyl-3-(m-tolylethynyl)-1,2-dihydronaphthalene (3ag):



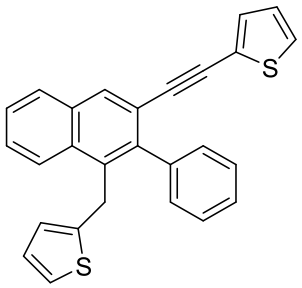
42.2 mg, 50%; *E/Z* = 1:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.29-6.98 (m, 12H), 6.75 (s, 0.5H), 6.72 (s, 0.5H), 4.89 (s, 0.5H), 4.86 (s, 0.5H), 2.30 (s, 3H), 2.27 (s, 1.5H), 2.19 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.8, 149.6, 141.9, 141.8, 138.9, 138.6, 138.0, 137.9, 137.6, 136.4, 136.2, 132.7, 132.1, 132.1, 130.6, 130.3, 129.6, 129.1, 128.8, 128.7, 128.6, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 127.7, 127.5, 127.1, 126.9, 126.7, 125.4, 124.9, 122.8, 122.8, 116.7, 116.7, 102.8, 102.6, 84.4, 84.4, 56.6, 56.5, 21.5, 21.3, 21.2; HRMS m/z (ESI) calcd for $C_{33}H_{21}F_6$ ($[M+H]^+$) 423.2107, found 423.2112.

1-(2-chlorobenzylidene)-3-((2-chlorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3ah):



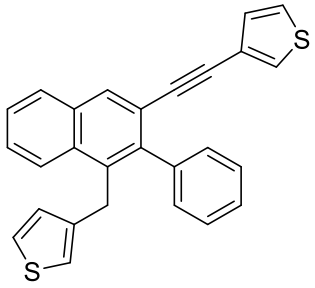
38.8 mg, 42%; *E*/*Z* = 3:2; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06-8.03 (m, 2H), 7.50-7.37 (m, 6H), 7.32-7.18 (m, 9H), 7.12-6.97 (m, 2H), 5.54 (s, 0.4H), 4.93 (s, 0.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.5, 150.4, 143.5, 140.6, 138.1, 136.0, 136.0, 134.2, 134.0, 133.4, 133.3, 133.3, 132.3, 132.2, 130.4, 129.7, 129.6, 129.6, 129.4, 129.3, 129.3, 129.2, 129.1, 129.1, 128.6, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 127.9, 127.7, 127.2, 127.2, 127.0, 127.0, 126.4, 126.2, 123.0, 122.8, 117.5, 113.3, 99.7, 99.5, 89.5, 89.4, 56.0, 52.8; HRMS m/z (ESI) calcd for $C_{33}H_{21}{}^{35}Cl_2$ ($[M+H]^+$) 463.1015, found 463.1017.

2-((2-phenyl-3-(thiophen-2-ylethynyl)naphthalen-1-yl)methyl)thiophene (3ai):



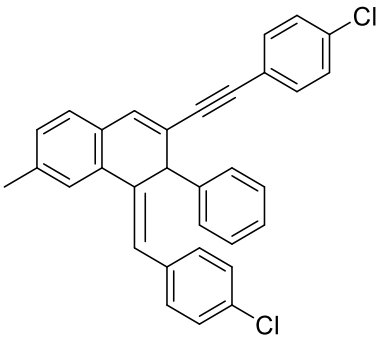
56.0 mg, 69%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (s, 1H), 7.42 (d, *J* = 5.6 Hz, 1H), 7.35-7.22 (m, 6H), 7.17-7.09 (m, 4H), 6.93 (d, *J* = 7.2 Hz, 2H), 6.86 (s, 2H), 4.20 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.7, 140.5, 139.7, 139.6, 138.9, 132.8, 131.3, 130.1, 128.3, 128.2, 128.0, 127.8, 127.2, 127.0, 126.9, 125.8, 123.9, 123.5, 123.4, 120.0, 93.7, 86.3, 37.1. HRMS m/z (ESI) calcd for $C_{27}H_{19}S_2$ ($[M+H]^+$) 407.0923, found 407.0925.

3-((2-phenyl-3-(thiophen-3-ylethynyl)naphthalen-1-yl)methyl)thiophene (3aj):



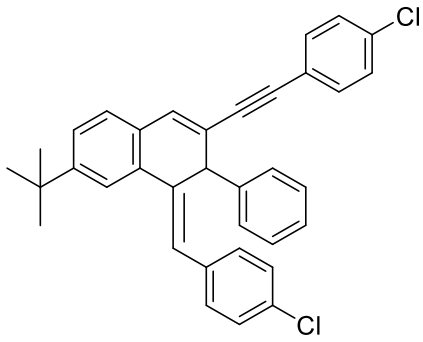
56.8 mg, 70%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (s, 1H), 7.35-7.28 (m, 8H), 7.16-7.07 (m, 4H), 6.98 (d, *J* = 6.8 Hz, 2H), 7.75 (d, *J* = 4.8 Hz, 1H), 4.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.1, 140.1, 139.7, 139.1, 138.7, 132.4, 130.2, 129.6, 128.5, 128.1, 127.9, 127.7, 127.4, 127.1, 126.0, 125.1, 125.0, 123.9, 122.5, 120.5, 89.4, 87.6, 38.7; HRMS m/z (ESI) calcd for $C_{27}H_{19}S_2$ ($[M+H]^+$) 407.0923, found 407.0929.

1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-7-methyl-2-phenyl-1,2-dihydronaphthalene (3bd):



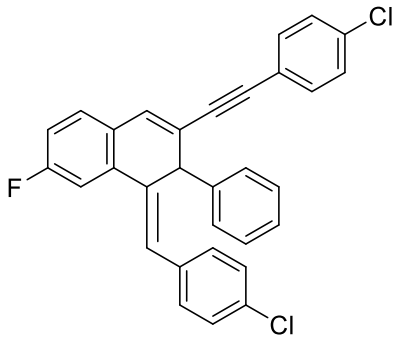
66.6 mg, 70%; *E/Z* = 2:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92-7.89 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.45-7.39 (m, 2H), 7.35-7.23 (m, 7H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.75 (s, 0.66H), 6.69 (s, 0.34H), 4.86 (s, 0.66H), 4.83 (s, 0.64H), 2.29 (s, 1H), 2.26 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.5, 150.1, 142.5, 140.2, 137.3, 137.0, 136.7, 135.2, 134.8, 133.2, 132.8, 132.8, 132.6, 132.4, 131.5, 129.4, 129.4, 129.1, 129.0, 129.0, 128.8, 128.7, 128.7, 128.7, 128.4, 128.2, 127.5, 127.1, 127.0, 121.3, 117.3, 115.6, 101.6, 101.1, 85.5, 85.4, 56.0, 55.7, 21.2; HRMS m/z (ESI) calcd for $C_{32}H_{23}{}^{35}Cl_2$ ($[M+H]^+$) 477.1171, found 477.1177.

7-(*tert*-butyl)-1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3cd):



74.6 mg, 72%; *E/Z* > 99:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 7.5 Hz, 2H), 7.47-7.16 (m, 15H), 6.75 (s, 1H), 4.84 (s, 1H), 1.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.6, 150.2, 140.3, 137.5, 134.8, 133.2, 132.8, 132.6, 132.4, 129.1, 128.8, 128.7, 128.7, 128.1, 127.1, 125.4, 121.3, 117.3, 101.1, 85.4, 55.7, 34.5, 31.2; HRMS m/z (ESI) calcd for $C_{35}H_{29}{}^{35}Cl_2$ ($[M+H]^+$) 519.1641, found 519.1644.

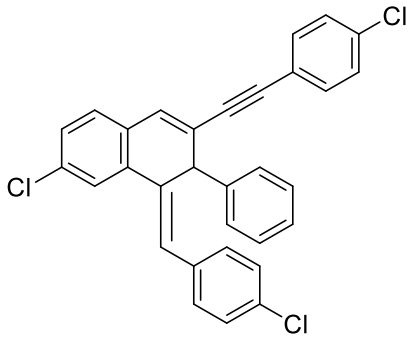
1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-7-fluoro-2-phenyl-1,2-dihydronaphthalene (3dd):



62.4 mg, 65%; *E/Z* = 1.5:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.97 (d, *J* = 7.2 Hz, 2H), 7.57-7.46 (m, 3H), 7.42-7.29 (m, 7H), 7.26-7.20 (m, 3H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 8.0 Hz, 1H), 6.80 (s, 0.6H), 6.78 (s, 0.4H), 4.90 (s, 1H); ^{19}F NMR

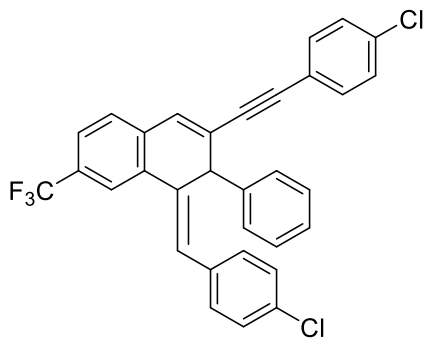
(471 MHz, CDCl3) δ: -114.3, -115.2; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.0 (d, *J* = 243.8 Hz), 161.8 (d, *J* = 246.4 Hz), 150.2, 150.1, 142.2, 140.8 (d, *J* = 2.3 Hz), 136.9, 134.9, 134.8, 134.5, 133.9 (d, *J* = 3.0 Hz), 132.8, 132.7, 132.3, 132.2, 132.1(d, *J* = 3.2 Hz), 129.8, 129.7, 129.5, 129.4, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.7, 128.6, 128.4, 127.0, 121.2, 116.0, 115.7 (d, *J* = 20.0 Hz), 115.4, 115.2, 101.6, 101.4, 85.2, 85.1, 55.5; HRMS m/z (ESI) calcd for $C_{31}H_{20}{}^{35}Cl_2F$ ($[M+H]^+$) 481.0921, found481.0934.

7-chloro-1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3ed):



67.5 mg, 65%; *E/Z* > 99:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 7.0 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.44-7.39 (m, 1H), 7.34-7.12 (m, 12H), 6.70 (s, 1H), 4.82 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.2, 141.8, 136.8, 135.0, 134.4, 133.7, 132.9, 132.8, 132.8, 132.2, 129.8, 129.4, 129.2, 129.0, 128.8, 128.8, 128.7, 128.5, 127.1, 121.1, 116.0, 101.7, 85.1, 55.6; HRMS m/z (ESI) calcd for $C_{31}H_{20}{}^{35}Cl_3$($[M+H]^+$) 497.0625, found 497.0639.

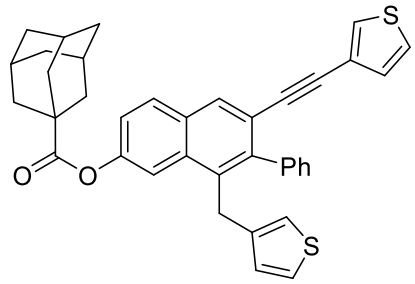
1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-phenyl-7-(trifluoromethyl)-1,2-dihydronaphthalene (3fd):



72 mg, 68%; *E/Z* > 3:2; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 7.5 Hz, 2H), 7.54-7.49 (m, 3H), 7.46-7.41 (m, 3H), 7.36-7.24 (m, 8H), 7.13 (s, 1H), 6.78 (s, 0.6H), 6.75 (s, 0.4H), 4.92 (s, 0.4H), 4.87 (s, 0.6H); ^{19}F NMR (471 MHz, CDCl3) δ: -62.4, -62.5; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.4, 150.1, 143.6, 142.4, 141.2, 139.4, 136.7, 135.5, 135.2, 134.7 (d, *J* = 90.3 Hz), 133.7, 133.1, 132.9, 132.9, 132.8, 132.1, 132.0, 130.8, 128.9 (q, *J* = 32.1 Hz), 129.3, 129.3, 129.0, 128.9, 128.8, 128.8, 128.8, 128.6, 128.2, 127.9, 127.1, 127.0, 125.7 (q, *J* = 3.6 Hz), 125.2 (q, *J* = 3.6 Hz), 123.1 (q, *J* = 4.5 Hz), 121.0, 120.9,

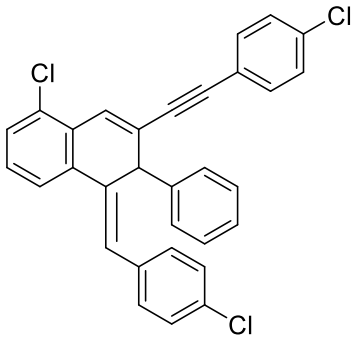
120.1, 116.3, 115.7, 102.2, 101.8, 84.9, 84.9, 55.8, 55.7; HRMS m/z (ESI) calcd for $C_{32}H_{20}{}^{35}Cl_2F_3$([M+H]$^+$) 531.0889, found 531.0895.

7-phenyl-6-(thiophen-3-ylethynyl)-8-(thiophen-3-ylmethyl)naphthalen-2-yl (3r,5r,7r)-adamantane-1-carboxylate (3gj):



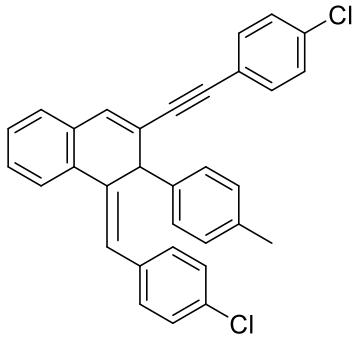
81.8 mg, 70%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00 (s, 1H), 7.42-7.28 (m, 4H), 7.33 (d, *J* = 10.5 Hz, 2H), 7.30-7.28 (m, 2H), 7.16-7.15 (m, 1H), 7.09-7.08 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 5.0 Hz, 2H), 4.14 (s, 2H), 2.05-2.01 (m, 9H), 1.77-1.71 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.2, 149.3, 141.0, 140.2, 139.6, 138.8, 136.3, 132.2, 130.1, 129.6, 129.3, 127.9, 127.8, 127.5, 127.2, 125.2, 125.0, 124.0, 122.5, 121.2, 120.6, 89.3, 87.6, 40.9, 38.7, 38.1, 36.4, 27.9; HRMS m/z (ESI) calcd for $C_{38}H_{33}O_2S_2$ ([M+H]$^+$) 585.1916, found 585.1918.

5-chloro-1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3hd):



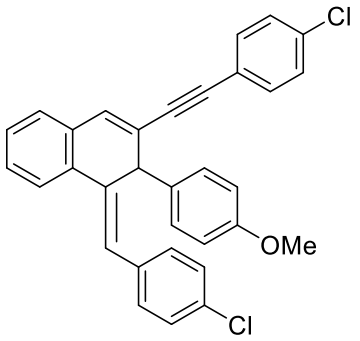
64.5 mg, 65%; *E/Z* = 4:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 7.0 Hz, 1.6H), 7.97 (d, *J* = 7.5 Hz, 0.4H), 7.58-7.54 (m, 2H), 7.50-7.32 (m, 8H), 7.29-7.24 (m, 3H), 7.18-7.05 (m, 2.8H), 6.80 (s, 0.2H), 5.52 (s, 0.2H), 4.91 (s, 0.8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.3, 145.0, 143.2, 141.2, 136.7, 135.6, 135.0, 134.9, 134.5, 134.1, 133.8, 133.7, 133.5, 132.8, 132.8, 132.7, 132.7, 132.3, 132.2, 130.1, 130.0, 129.5, 129.2, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.1, 127.3, 127.1, 127.0, 126.2, 121.3, 121.1, 115.9, 113.4, 101.8, 101.7, 85.40, 85.2, 55.3, 52.6; HRMS m/z (ESI) calcd for $C_{31}H_{20}{}^{35}Cl_3$ ([M+H]$^+$) 497.0625, found 497.0628.

1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-(p-tolyl)-1,2-dihydronaphthalene (3id):



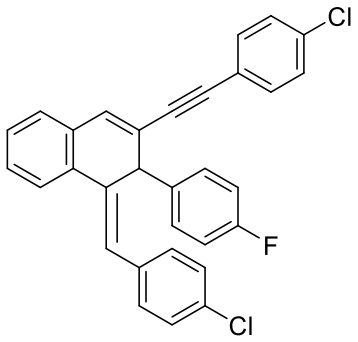
71.4 mg, 75%; *E/Z* = 2.3:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 7.0 Hz, 2H), 7.33-7.10 (m, 15H), 6.75 (s, 0.7H), 6.68 (s, 0.3H), 4.85 (s, 0.7H), 4.83 (s, 0.3H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.5, 150.2, 142.4, 141.4, 139.3, 139.2, 138.4, 137.3, 136.0, 134.8, 134.7, 133.6, 132.8, 132.6, 132.5, 129.6, 129.4, 129.1, 128.9, 128.7, 128.7, 128.6, 128.6, 128.4, 128.3, 127.7, 127.2, 127.0, 127.0, 126.9, 121.4, 121.3, 117.2, 115.7, 101.3, 101.1, 85.6, 85.5, 7 56.2, 55.6, 22.6, 21.5; HRMS m/z (ESI) calcd for $C_{32}H_{23}{}^{35}Cl_2$ ($[M+H]^+$) 477.1171, found 477.1183.

1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-(4-methoxyphenyl)-1,2-dihydronaphthalene (3jd):



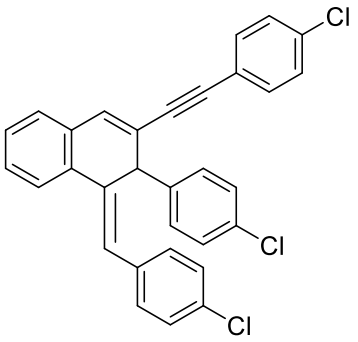
68.9 mg, 70%; *E/Z* = 9:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 8.0 Hz, 2H), 7.34-7.32 (m, 5H), 7.22-7.11 (m, 8H), 7.0 (d, *J* = 8.4 Hz, 2H), 6.74 (s, 0.9H), 6.67 (s, 0.1H), 4.85 (s, 0.9H), 4.83 (s, 0.1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2, 160.1, 150.0, 149.8, 142.4, 141.4, 138.6, 137.4, 136.1, 134.8, 134.7, 134.7, 132.7, 132.6, 132.5, 129.4, 129.0, 128.7, 128.7, 128.6, 128.6, 128.4, 128.3, 128.2, 127.6, 127.5, 127.1, 127.0, 125.4, 121.5, 121.4, 117.2, 117.1, 115.6, 114.1, 101.0, 100.8, 85.7, 85.6, 56.2, 55.5, 55.4; HRMS m/z (ESI) calcd for $C_{32}H_{23}{}^{35}Cl_2O$ ($[M+H]^+$) 493.1120, found 493.1126.

1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-(4-fluorophenyl)-1,2-dihydronaphthalene (3kd):



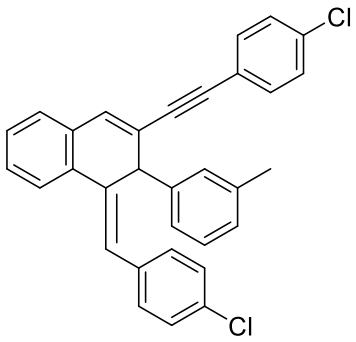
66.2 mg, 69%; *E/Z* = 1.5:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89-7.87 (m, 2H), 7.33-7.11 (m, 15H), 6.71 (s, 0.6H), 6.64 (s, 0.4H), 4.86 (s, 0.6H), 4.84 (s, 0.4H); ^{19}F NMR (471 MHz, CDCl3) δ: -110.4, -110.5; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.8 (d, *J* = 248.5 Hz), 149.2, 148.9, 142.0, 141.0, 138.1, 137.0, 135.8, 135.0, 134.9, 134.5, 132.8, 132.7, 132.6, 129.9 (d, *J* = 1.9 Hz), 129.4, 129.1, 129.1, 129.0, 129.0, 128.9, 128.9, 128.8, 128.6, 128.4, 128.3, 128.3, 127.6, 121.1 (d, *J* = 6.4 Hz), 117.3, 115.7 (d, *J* = 21.4 Hz), 115.7, 101.5, 101.4, 85.2, 85.0, 56.3, 55.7; HRMS m/z (ESI) calcd for $C_{31}H_{20}{}^{35}Cl_2F$ ($[M+H]^+$) 481.0921, found 481.0929.

1-(4-chlorobenzylidene)-2-(4-chlorophenyl)-3-((4-chlorophenyl)ethynyl)-1,2-dihydronaphthalene (3le):



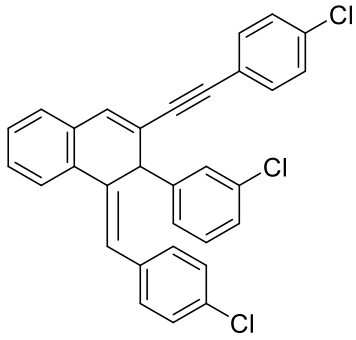
71.4 mg, 72%; *E/Z* = 9:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83-7.82 (m, 2H), 7.45-7.13 (m, 15H), 6.71 (s, 0.9H), 6.64 (s, 0.1H), 4.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 148.7, 141.8, 140.8, 138.0, 136.8, 135.8, 135.1, 135.0, 134.8, 134.7, 132.8, 132.8, 132.7, 130.7, 130.0, 129.4, 129.0, 128.9, 128.8, 128.7, 128.7, 128.4, 128.3, 128.3, 127.6, 127.3, 127.2, 121.1, 121.0, 117.4, 115.9, 102.0, 101.9, 85.1, 85.0, 56.4, 55.8; HRMS m/z (ESI) calcd for $C_{31}H_{20}{}^{35}Cl_3$ ($[M+H]^+$) 497.0625, found 497.0634.

1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-(m-tolyl)-1,2-dihydronaphthalene (3md):



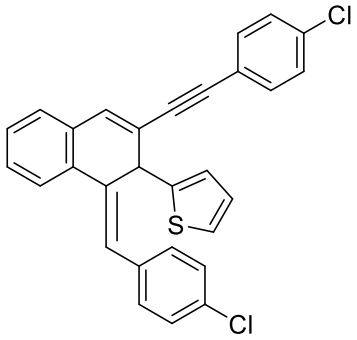
54.3 mg, 57%; *E/Z* = 4:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38-7.70 (m, 2H), 7.37-7.09 (m, 15H), 6.76 (s, 0.8H), 6.69 (s, 0.2H), 4.85 (s, 0.8H), 4.83 (s, 0.2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.6, 150.4, 142.4, 141.3, 138.3, 137.2, 136.0, 134.8, 134.7, 132.7, 132.6, 132.5, 132.3, 130.1, 129.9, 129.8, 129.4, 129.4, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 127.7, 127.7, 127.6, 127.2, 127.0, 124.2, 124.2, 121.4, 121.3, 117.3, 115.7, 101.4, 101.2, 85.5, 85.4, 56.3, 55.6, 21.6; HRMS m/z (ESI) calcd for $C_{32}H_{23}{}^{35}Cl_2$ ($[M+H]^+$) 477.1171, found 477.1174.

1-(4-chlorobenzylidene)-2-(3-chlorophenyl)-3-((4-chlorophenyl)ethynyl)-1,2-dihydronaphthalene (3nd):



54.6 mg, 55%; *E/Z* = 1.2:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (s, 1H), 7.76-7.75 (m, 1H), 7.37-7.12 (m, 15H), 6.73 (s, 0.55H), 6.66 (s, 0.45H), 4.86 (s, 0.55H), 4.85 (s, 0.45H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.7, 148.4, 141.7, 140.7, 137.9, 136.7, 135.7, 135.1, 135.1, 134.7, 134.4, 133.9, 132.8, 132.7, 131.5, 130.7, 130.0, 129.4, 129.0, 128.9, 128.9, 128.8, 128.8, 128.7, 128.7, 128.4, 128.3, 127.6, 127.3, 127.2, 127.1, 127.0, 121.0, 120.9, 117.5, 115.9, 102.5, 102.3, 85.1, 84.9, 56.5, 55.8; HRMS m/z (ESI) calcd for $C_{31}H_{20}{}^{35}Cl_3$ ($[M+H]^+$) 497.0625, found 497.0630.

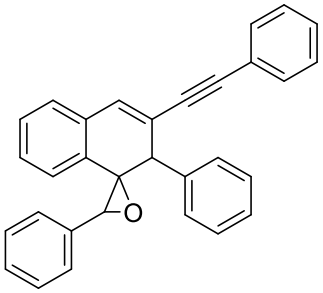
2-(1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-1,2-dihydronaphthalen-2-yl)thiophene (3od):



54.6 mg, 55%; *E/Z* > 99:1; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (s, 1H), 7.45-7.38 (m, 4H), 7.31-7.12 (m, 12H), 6.73 (s, 0.96H), 6.67 (s, 0.04H), 4.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.4, 140.1, 137.1, 135.7, 134.9, 134.0, 133.7, 132.8, 129.1, 128.9,

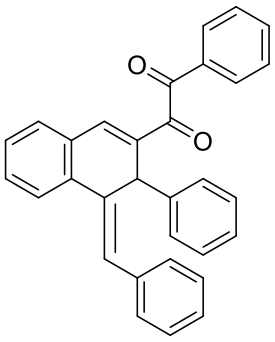
128.8, 128.7, 128.4, 128.3, 127.4, 127.2, 126.9, 126.9, 126.8, 121.3, 117.6, 102.8, 85.4, 55.8; HRMS m/z (ESI) calcd for $C_{29}H_{19}{}^{35}Cl_2S$ ($[M+H]^+$) 469.0579, found 469.0587.

2,3'-diphenyl-3-(phenylethynyl)-2H-spiro[naphthalene-1,2'-oxirane] (4aa):



48.0 mg, 72%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 6.5 Hz, 2H), 7.50-7.36 (m, 5H), 7.30 (s, 3H), 6.95 (s, 5H), 6.89 (s, 5H), 4.62 (s, 1H), 4.47 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.7, 136.5, 134.5, 132.3, 131.9, 129.1, 128.9, 128.8, 128.3, 128.1, 127.6, 127.6, 127.1, 126.5, 126.5, 126.3, 125.9, 122.6, 98.7, 83.8, 77.3, 77.0, 76.8, 73.9, 59.9, 57.9; HRMS m/z (ESI) calcd for $C_{31}H_{23}O$ ($[M+H]^+$) 411.1743, found 411.1752.

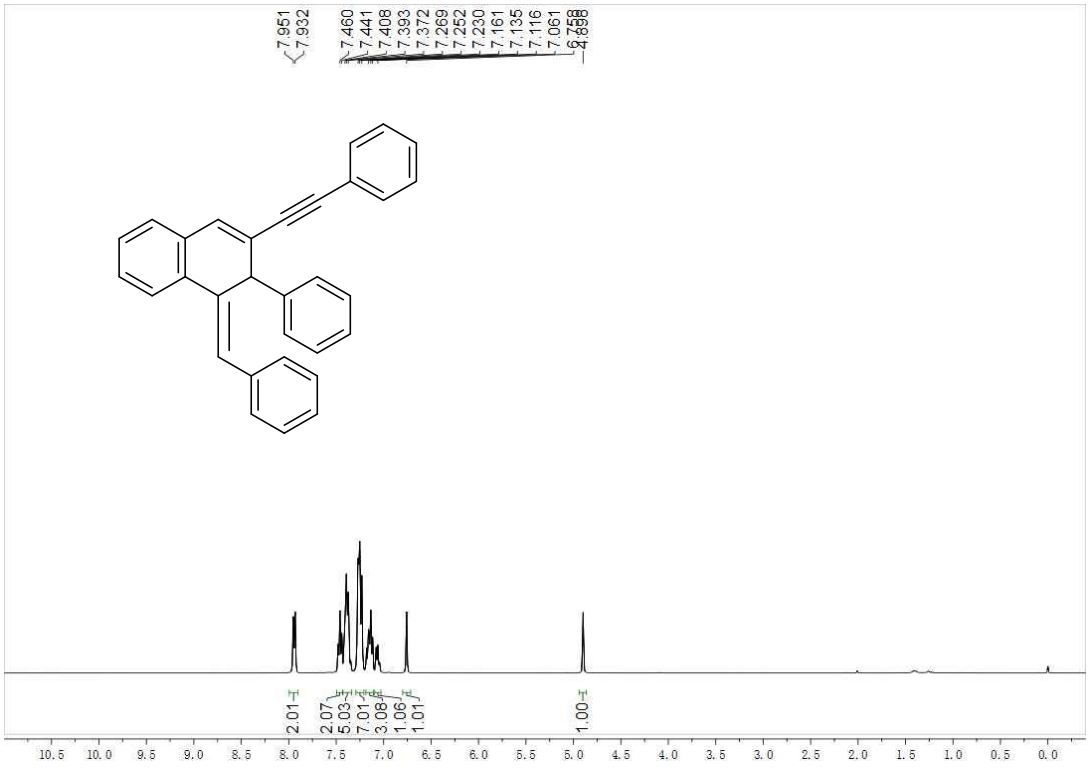
1-(4-benzylidene-3-phenyl-3,4-dihydronaphthalen-2-yl)-2-phenylethane-1,2-dione (5aa):

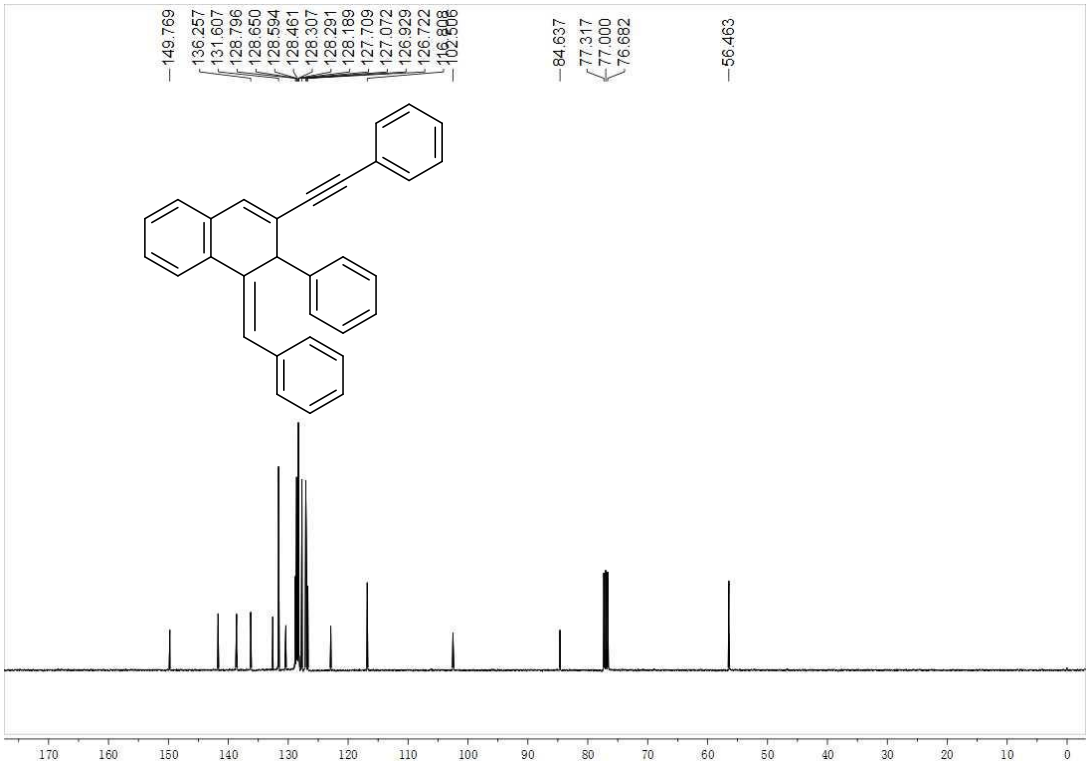


55.0 mg, 88%, *E/Z* > 99:1; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.9. (d, *J* = 4 Hz, 2H), 7.61 (d, *J* = 6.5 Hz, 2H), 7.47 (d, *J* = 7.0 Hz, 4H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.27 – 7.23 (m, 4H), 7.15 (s, 3H), 7.06 (t, *J* = 6.5 Hz, 2H), 6.97 (d, *J* = 7.5 Hz, 2H), 5.08 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.6, 189.0, 159.8, 142.7, 140.7, 137.9, 135.0, 134.1, 132.5, 130.8, 130.5, 129.7, 129.5, 129.1, 128.6, 128.5, 128.4, 128.4, 128.4, 128.0, 127.1, 125.0, 77.3, 77.0, 76.8, 53.2; HRMS m/z (ESI) calcd for $C_{31}H_{23}O_2$ ($[M+H]^+$) 427.1693, found 427.1698.

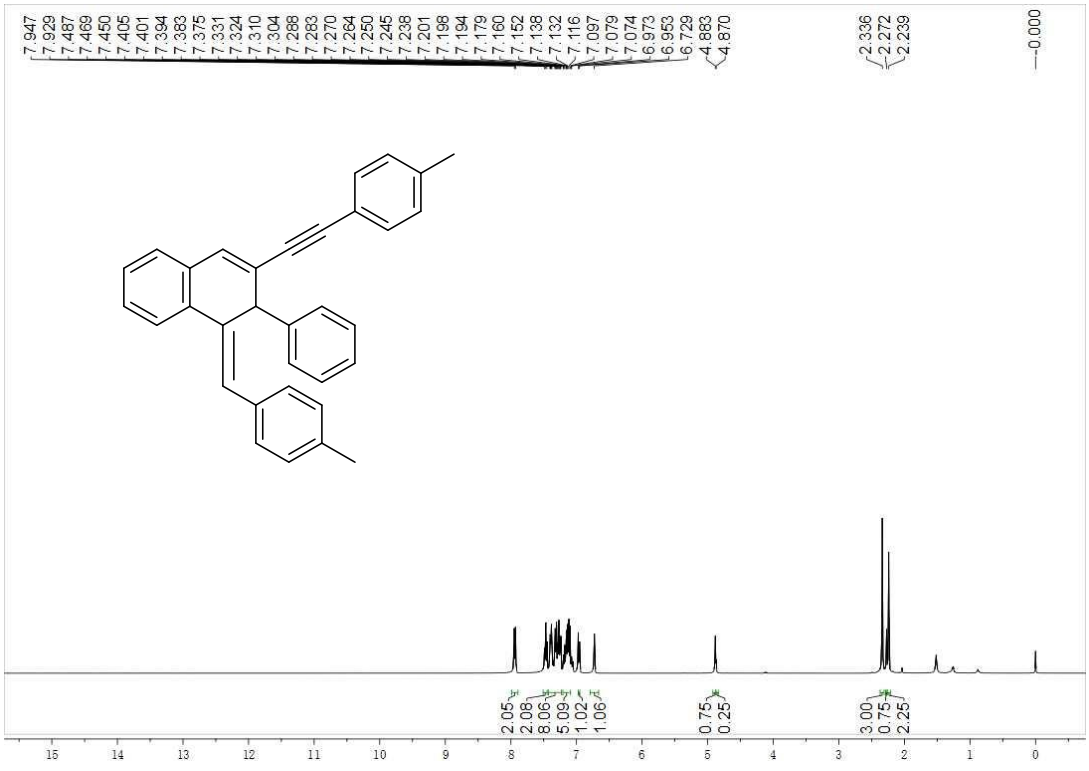
(C) Spectra

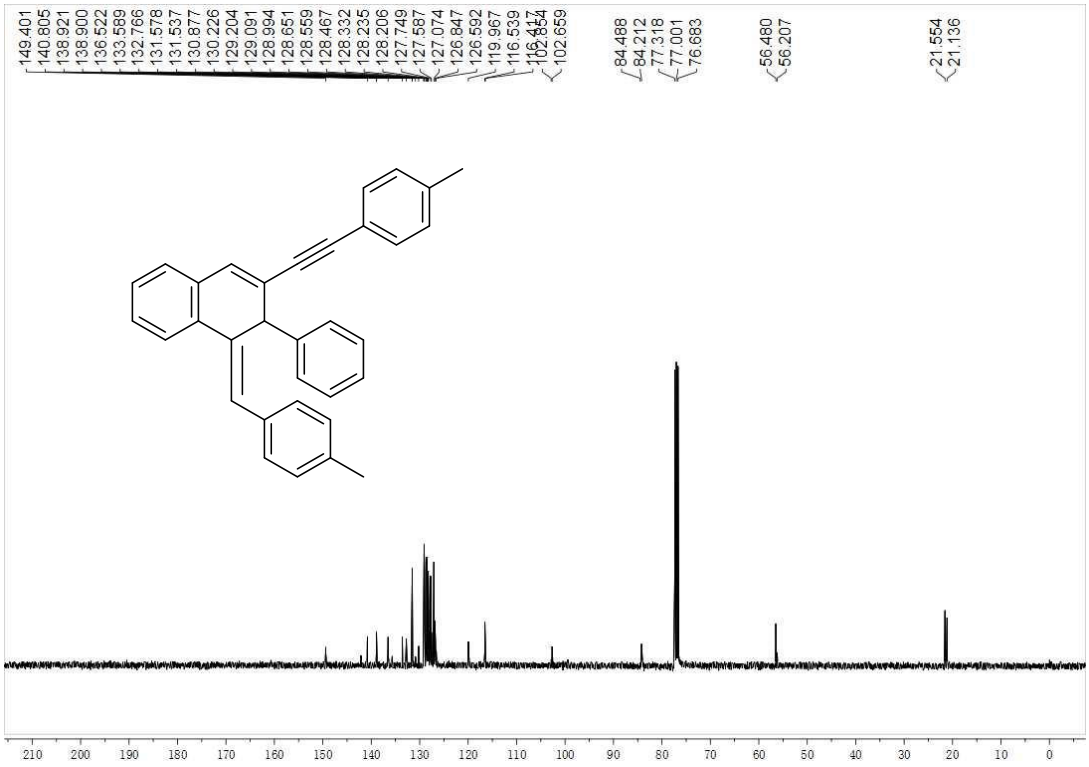
1-benzylidene-2-phenyl-3-(phenylethynyl)-1,2-dihydronaphthalene (3aa):



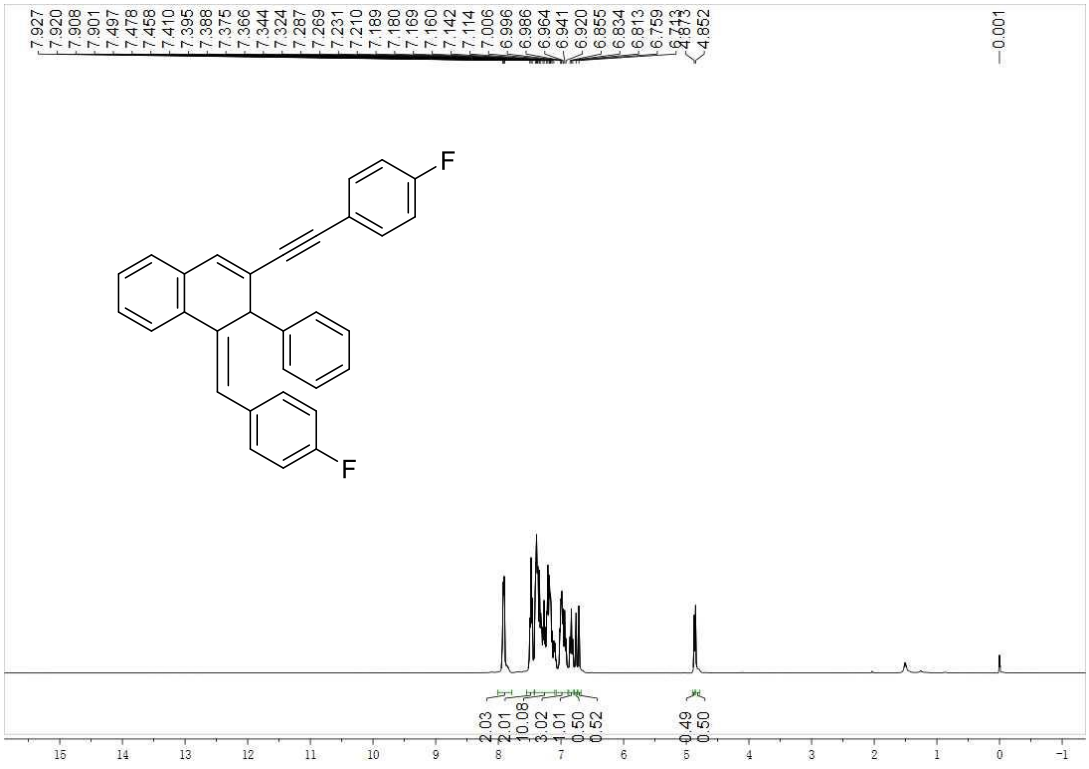


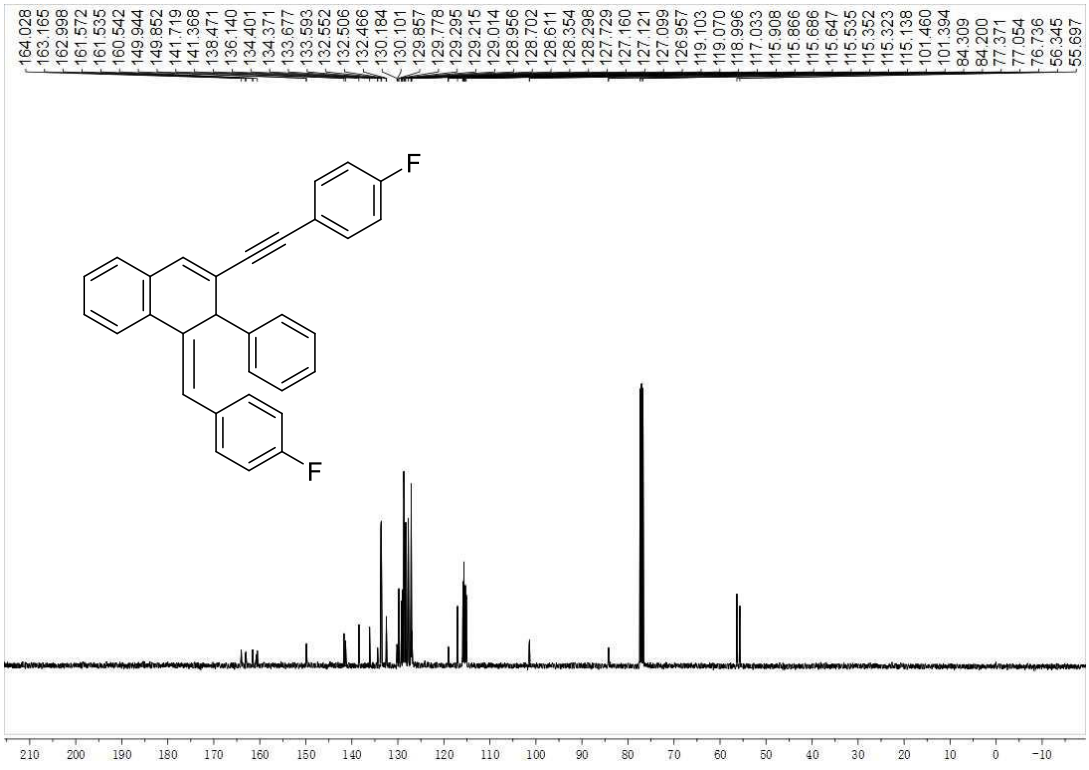
1-(4-methylbenzylidene)-2-phenyl-3-(p-tolylethynyl)-1,2-dihydronaphthalene (3ab):

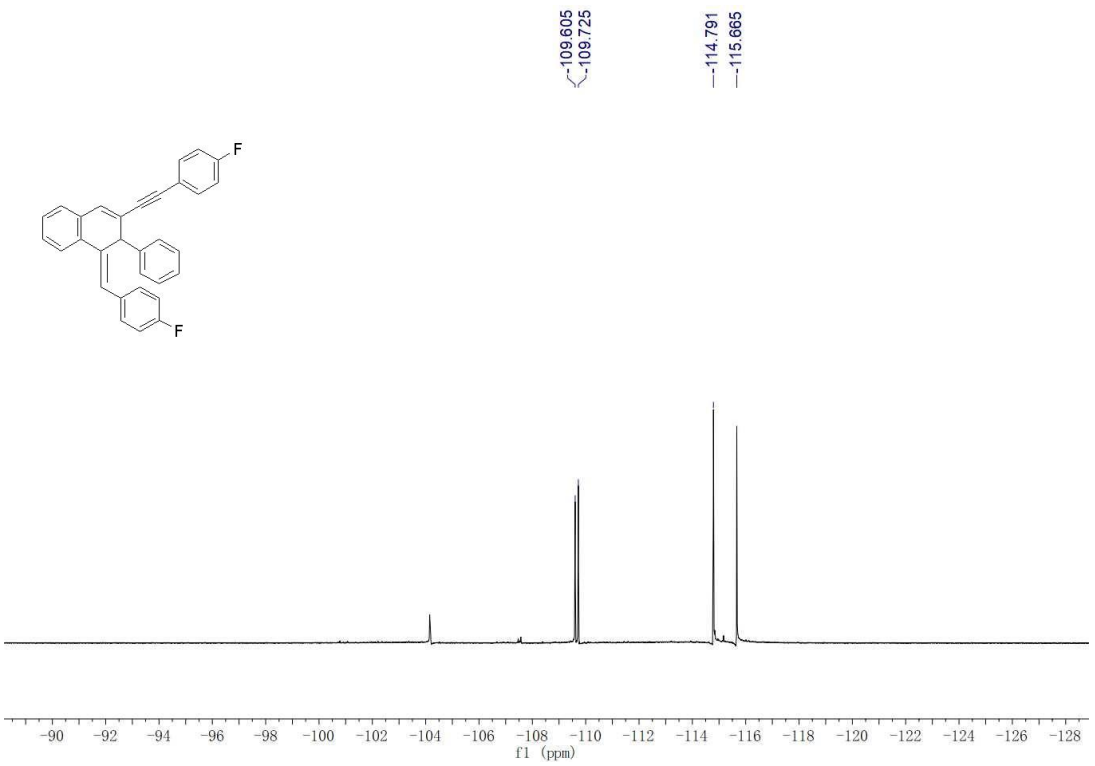




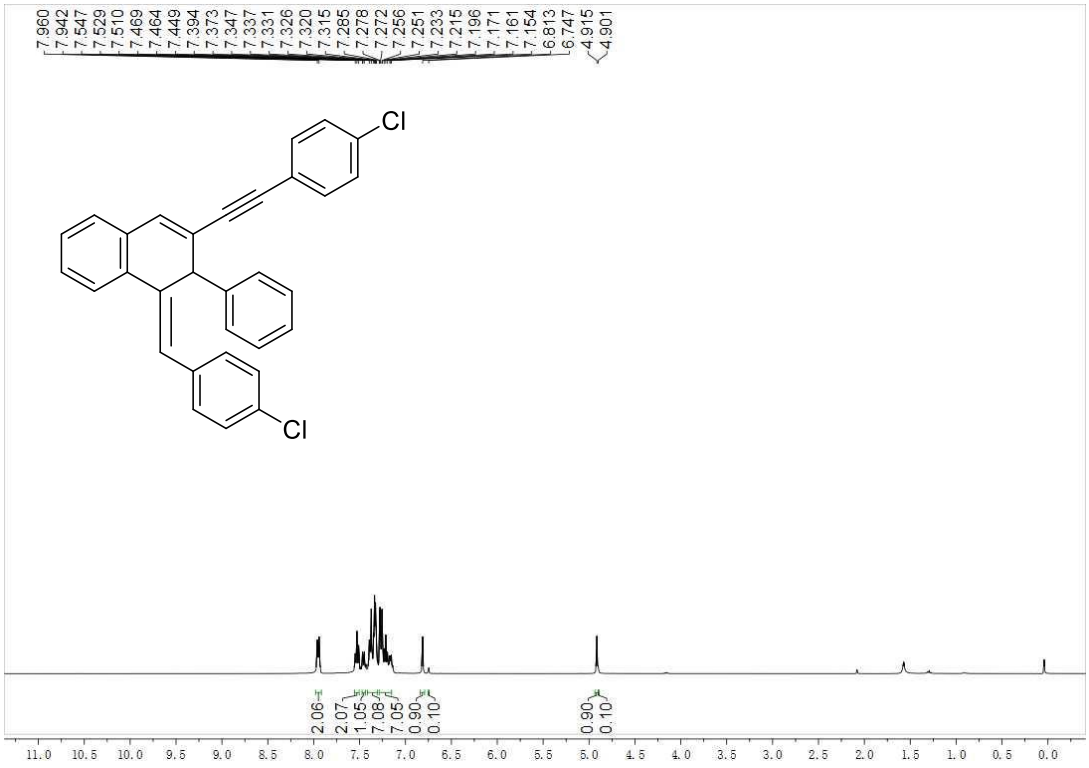
1-(4-fluorobenzylidene)-3-((4-fluorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3ac):

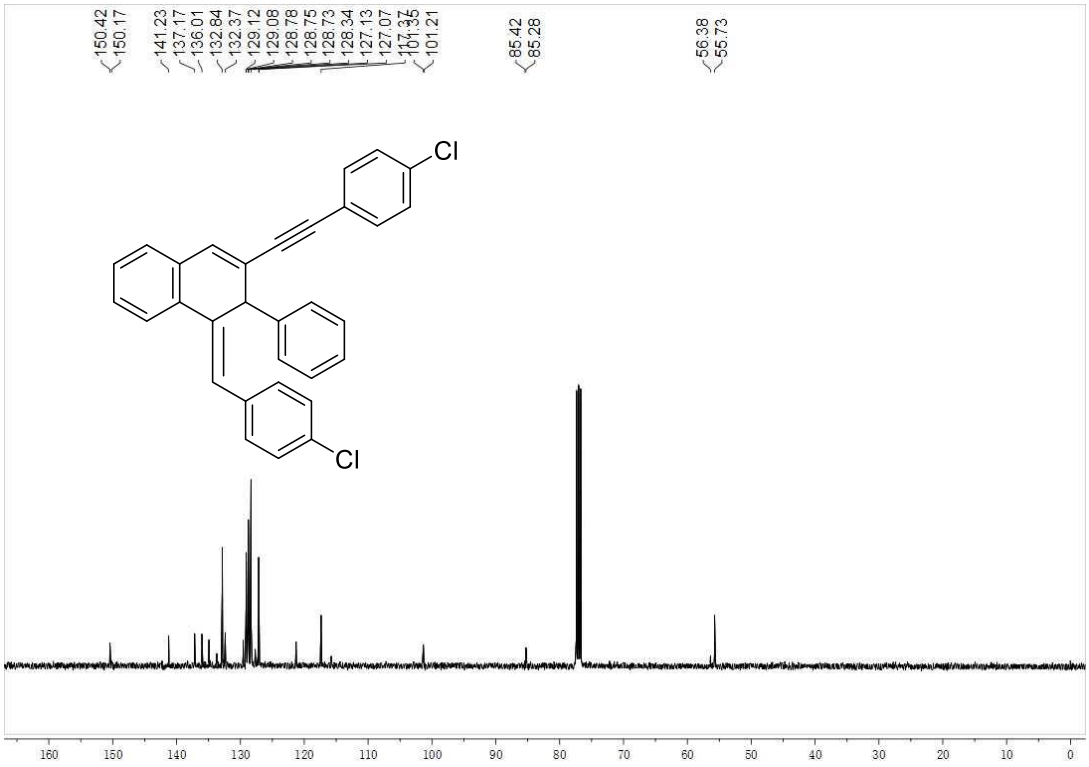


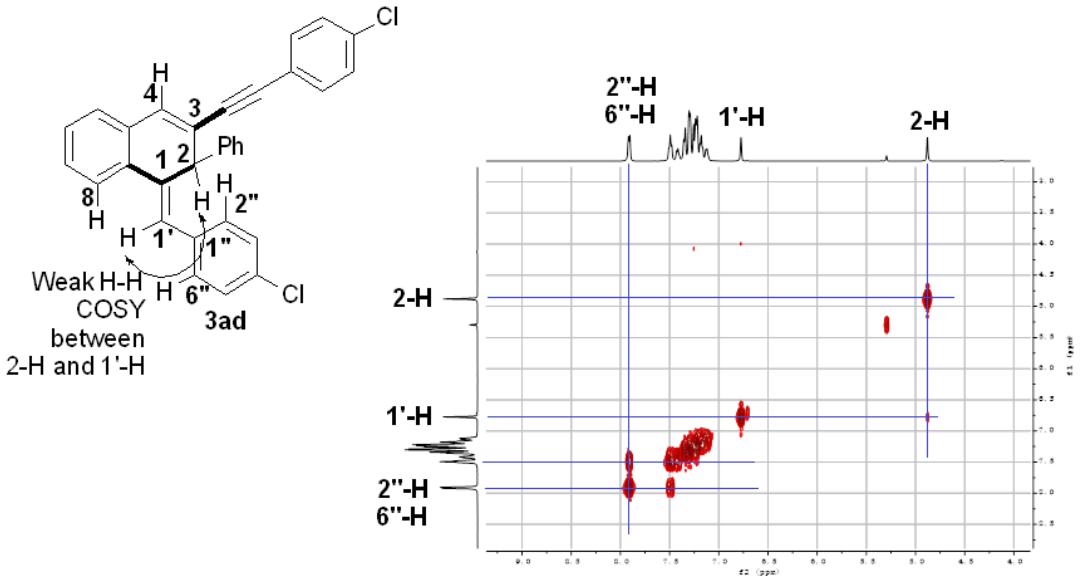



-109.605
-109.725
-114.791
-115.665
F
F
-90
-92
-94
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
f1 (ppm)

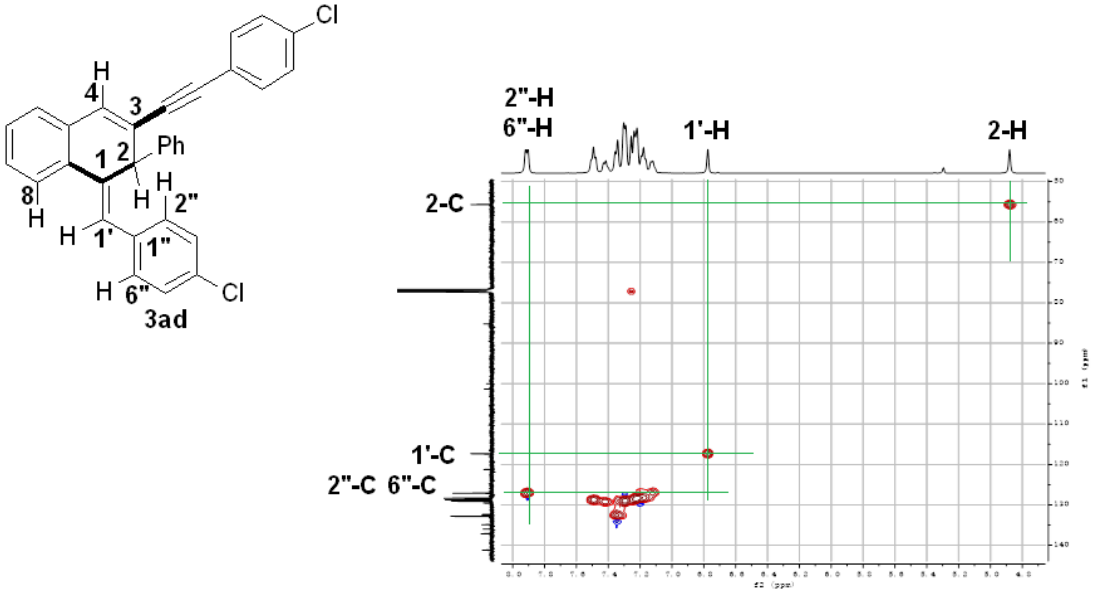
1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3ad):



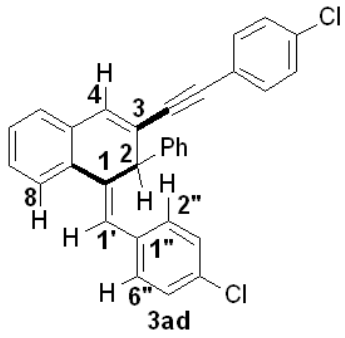


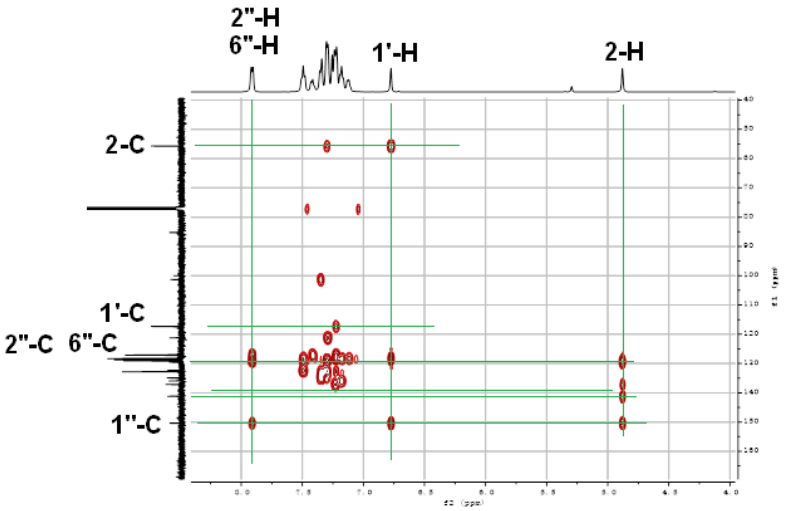

Cl
H
4
3
Ph
1
2
8
H
H
2"
H
1'
1"
Weak H-H
COSY
between
2-H and 1'-H
H
6"
Cl
3ad
2"-H
6"-H
1'-H
2-H
2-H
1'-H
2"-H
6"-H

H-H COSY

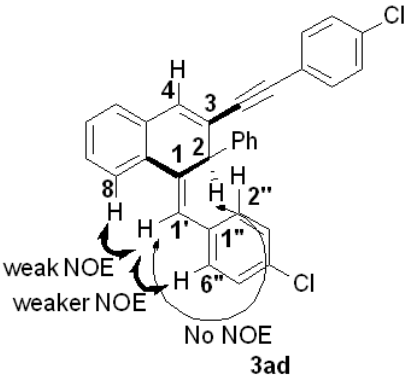

Cl
H
4
3
Ph
1
2
8
H
H
H
2"
H
1'
1"
H
6"
Cl
3ad
2"-H
6"-H
1'-H
2-H
2-C
1'-C
2"-C
6"-C

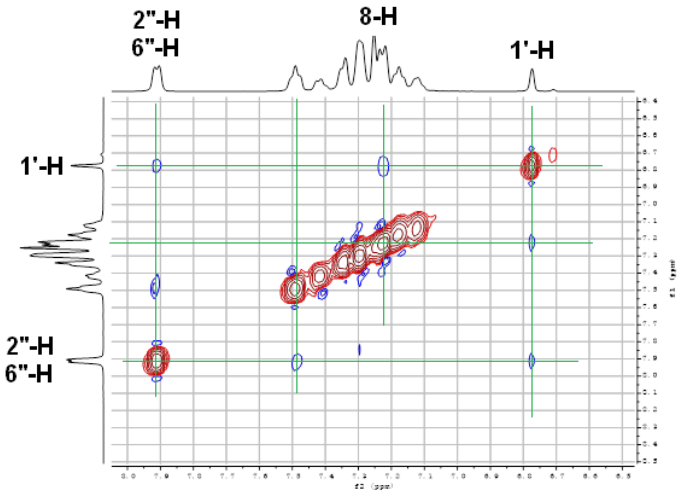
HSQC


Cl
H
4
3
Ph
1
2
H
8
H
H
2"
H
1'
1"
H
6"
Cl
3ad


2"-H
6"-H
1'-H
2-H
2-C
1'-C
2"-C
6"-C
1"-C

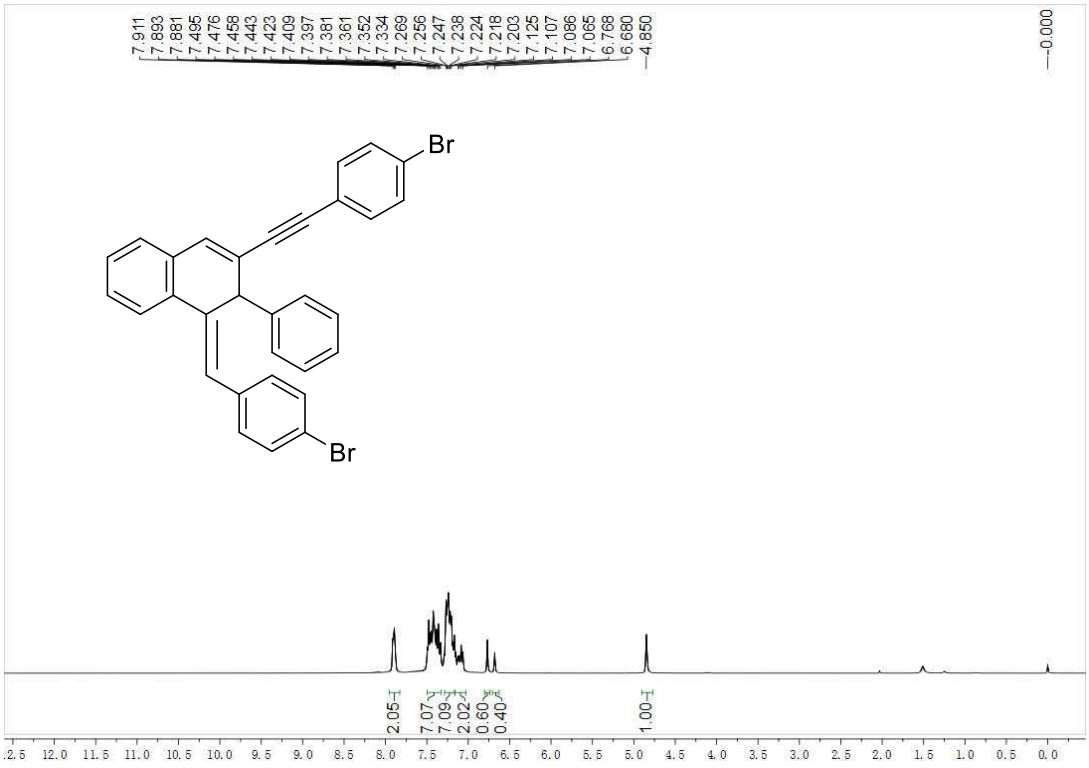
HMBC

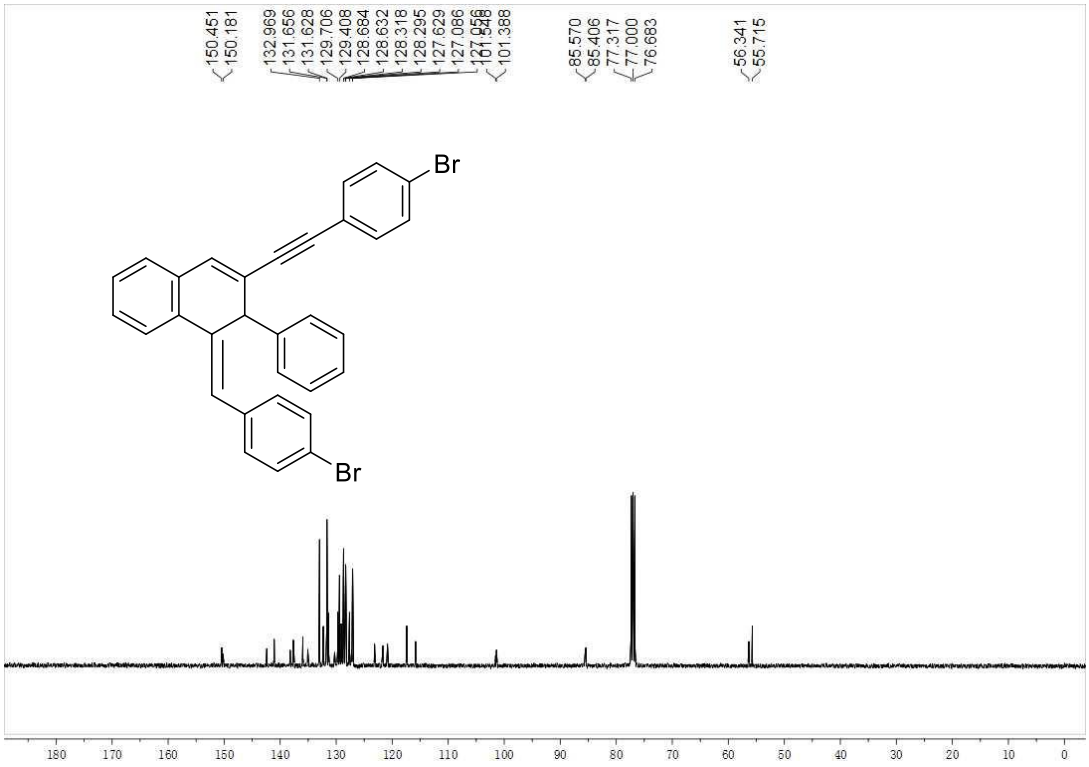

Cl
H
4
3
Ph
1
2
8
H
H
H
2"
H
1'
1"
H
6"
Cl
weak NOE
weaker NOE
No NOE
3ad


2"-H
6"-H
8-H
1'-H
1'-H
2"-H
6"-H

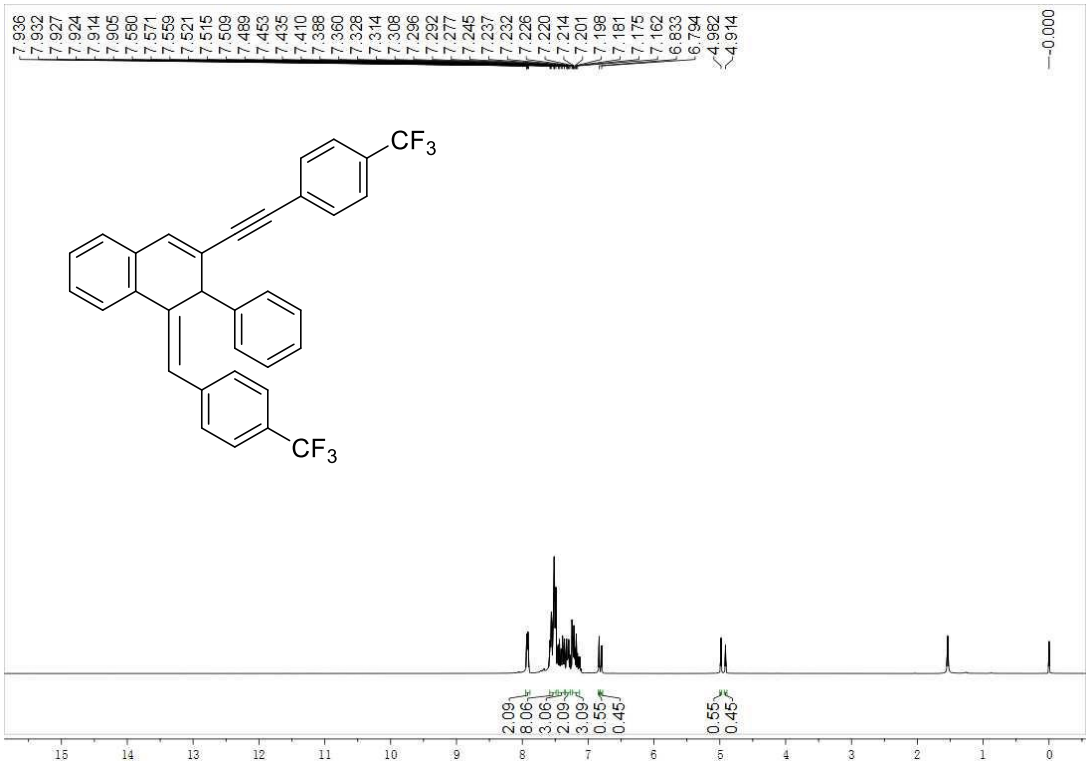
H-H NOE

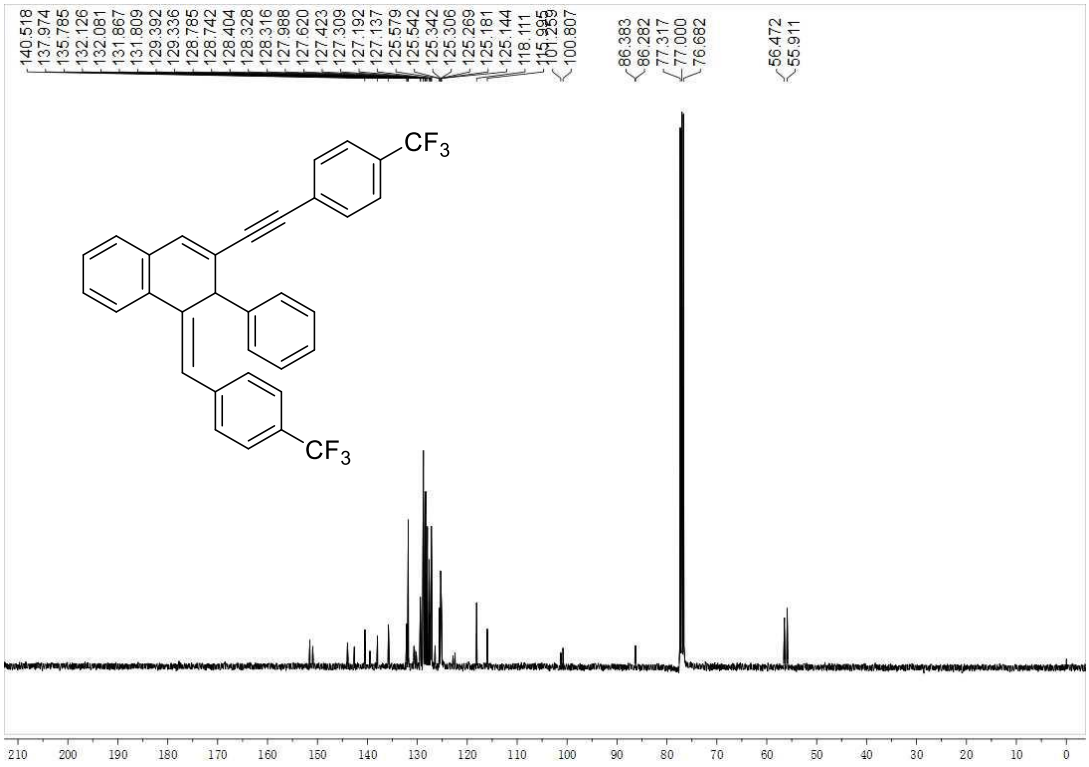
1-(4-bromobenzylidene)-3-((4-bromophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3ae):

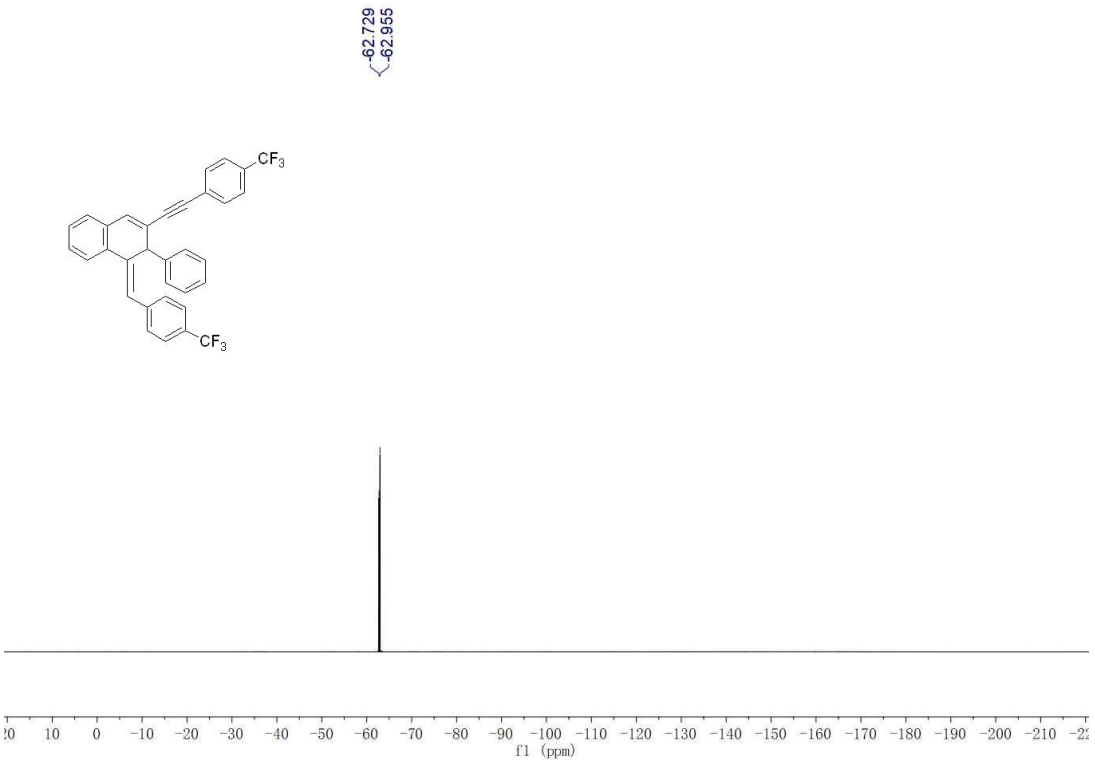




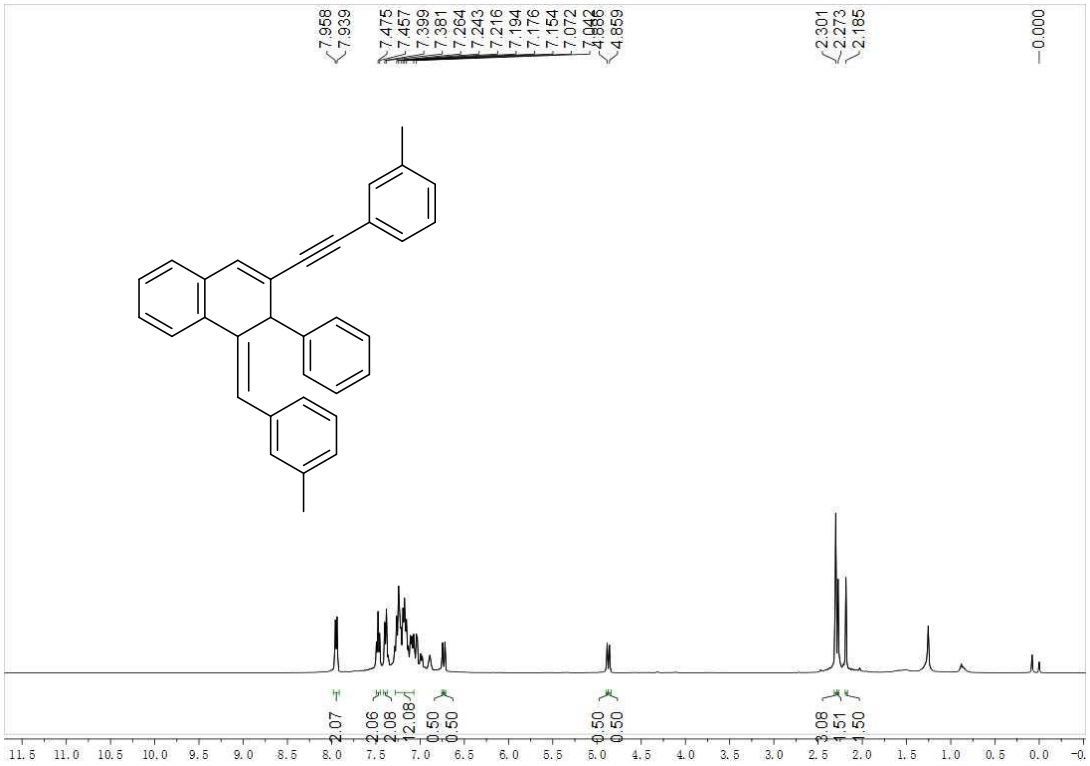
2-phenyl-1-(4-(trifluoromethyl)benzylidene)-3-((4-(trifluoromethyl)phenyl)ethynyl)-1,2-dihydronaphthalene (3af):

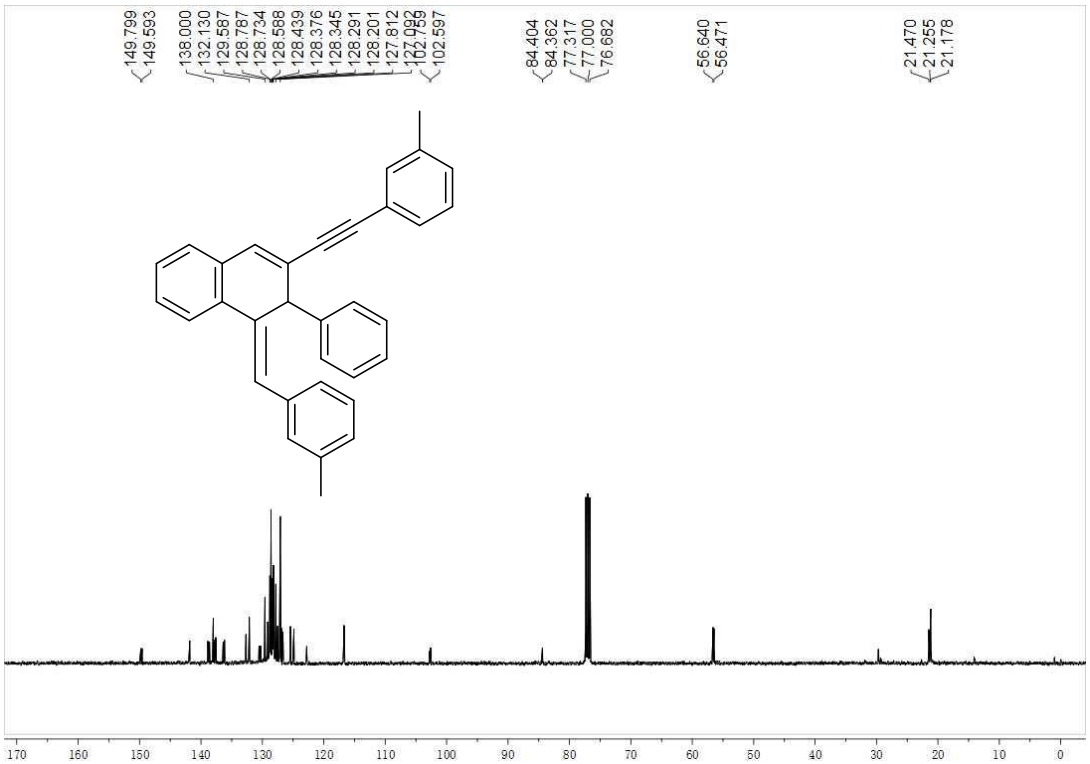




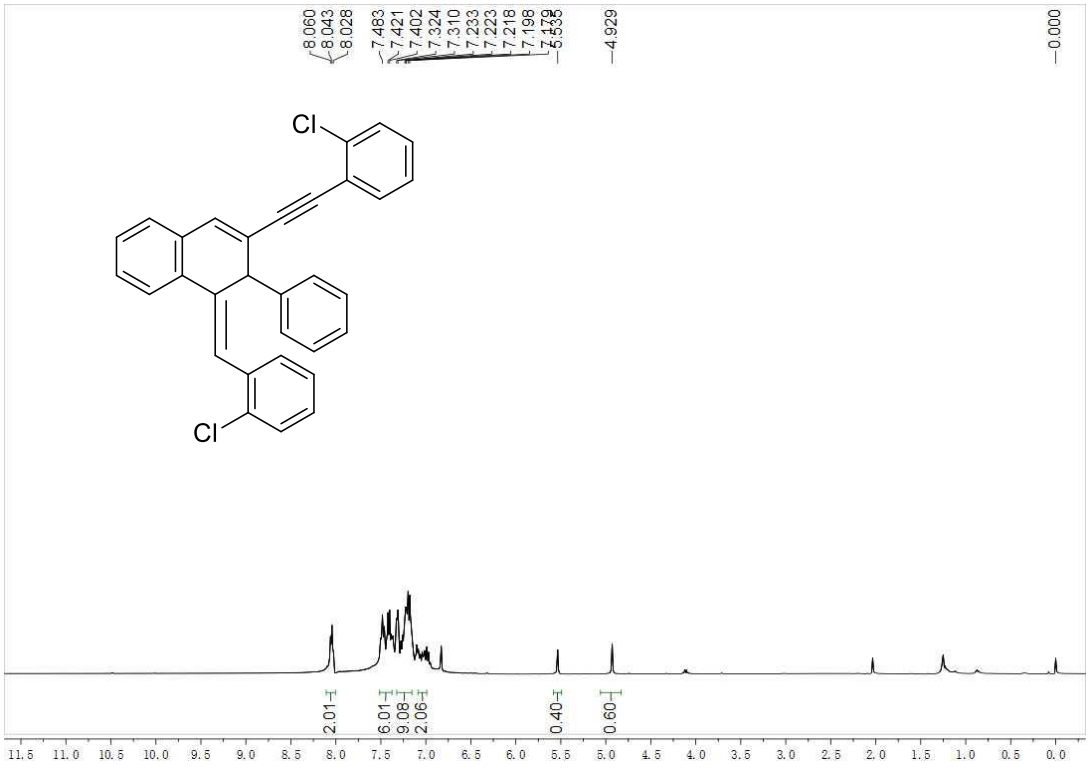

-62.729
-62.955
CF3
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

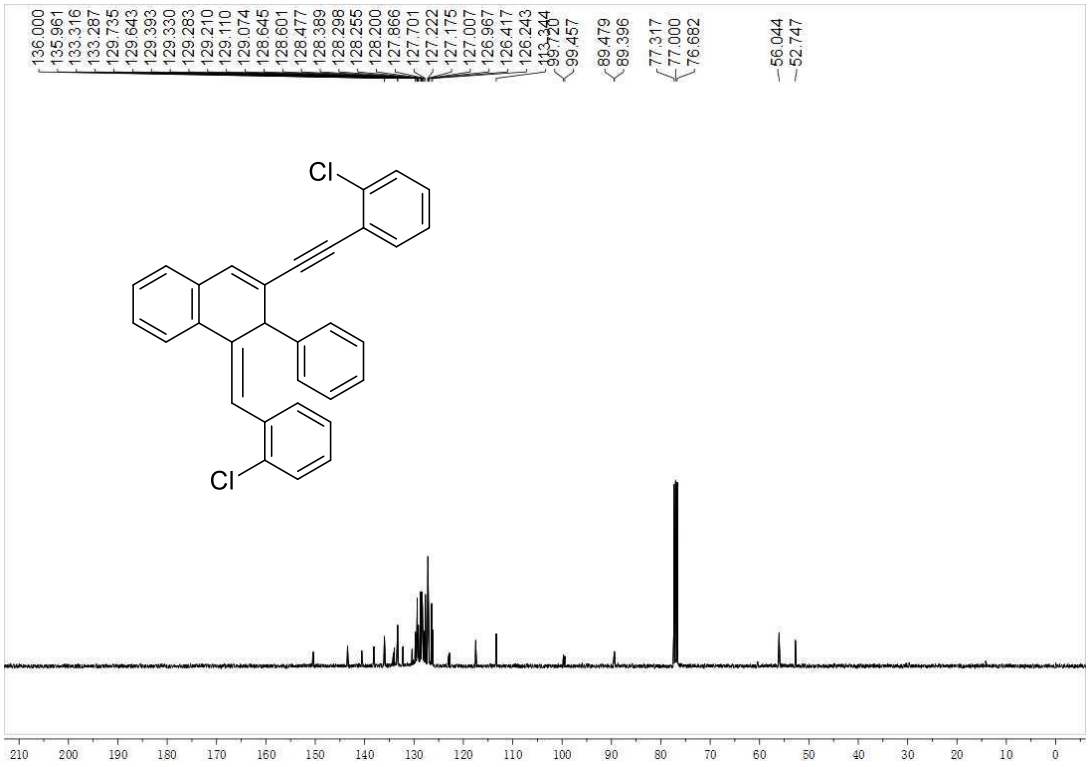
1-(3-methylbenzylidene)-2-phenyl-3-(m-tolylethynyl)-1,2-dihydronaphthalene (3ag):



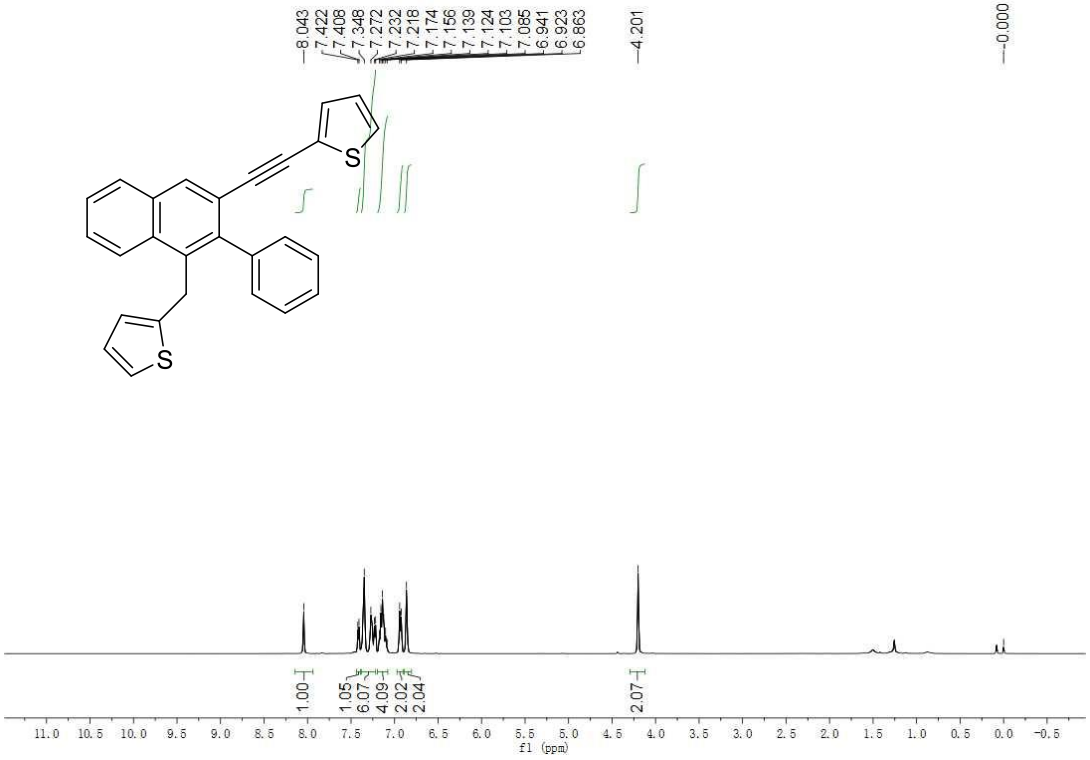


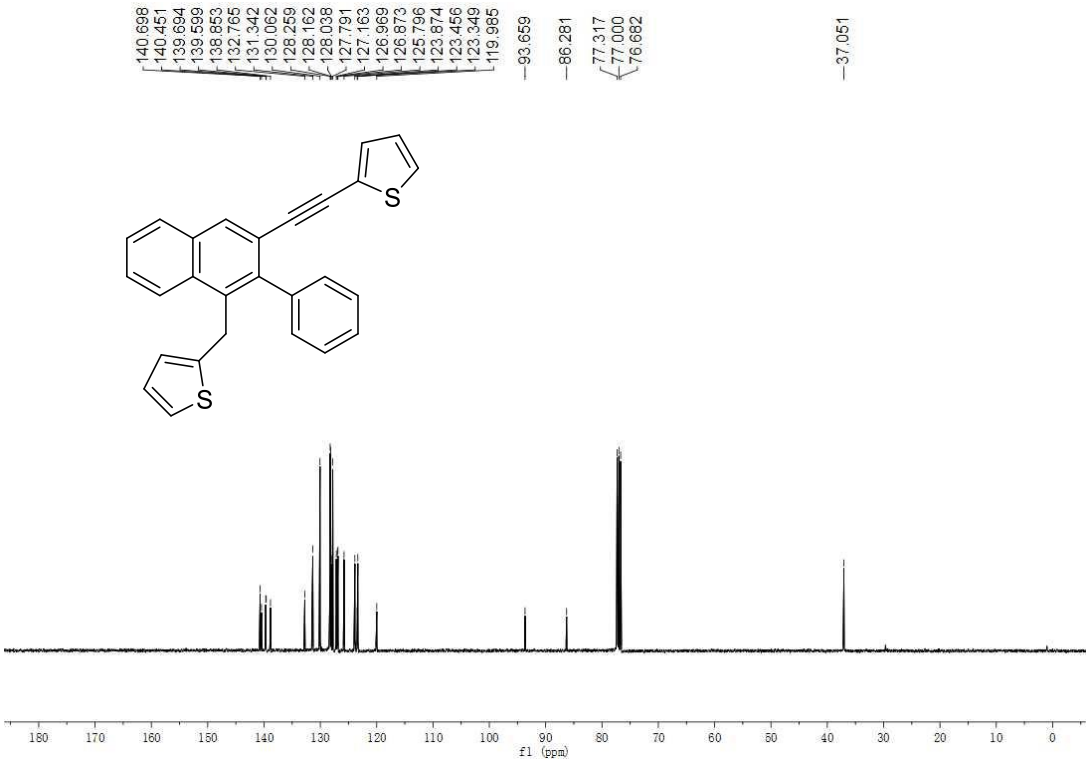
1-(2-chlorobenzylidene)-3-((2-chlorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3ah):



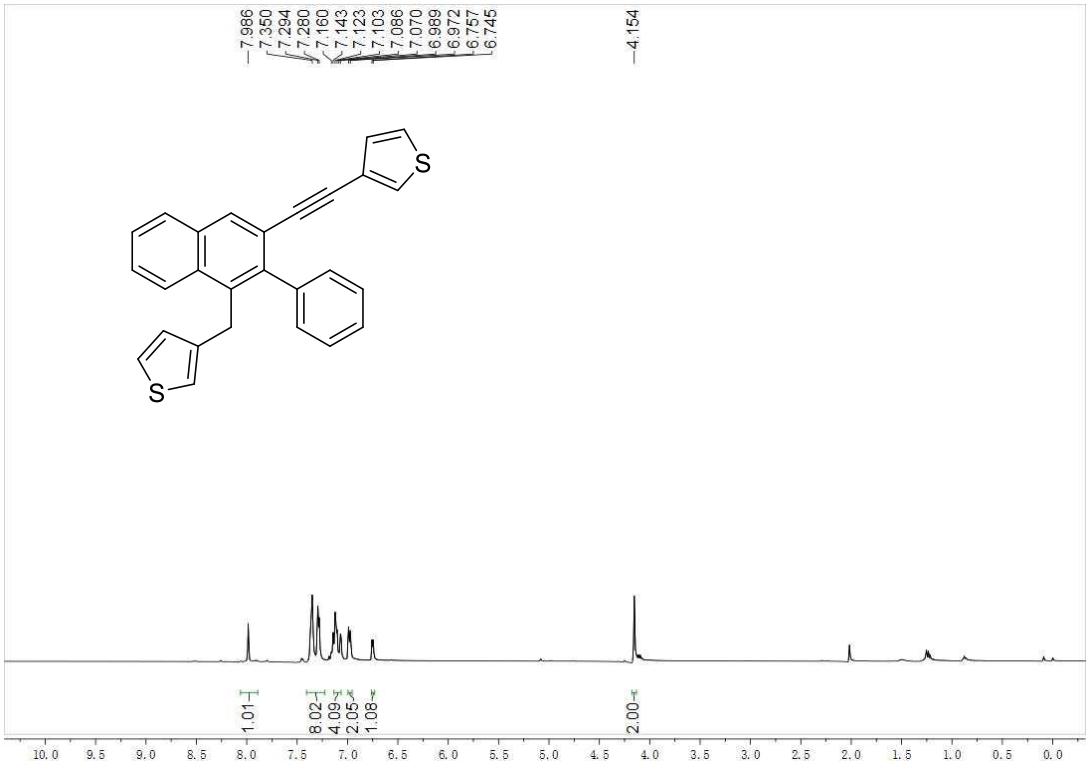


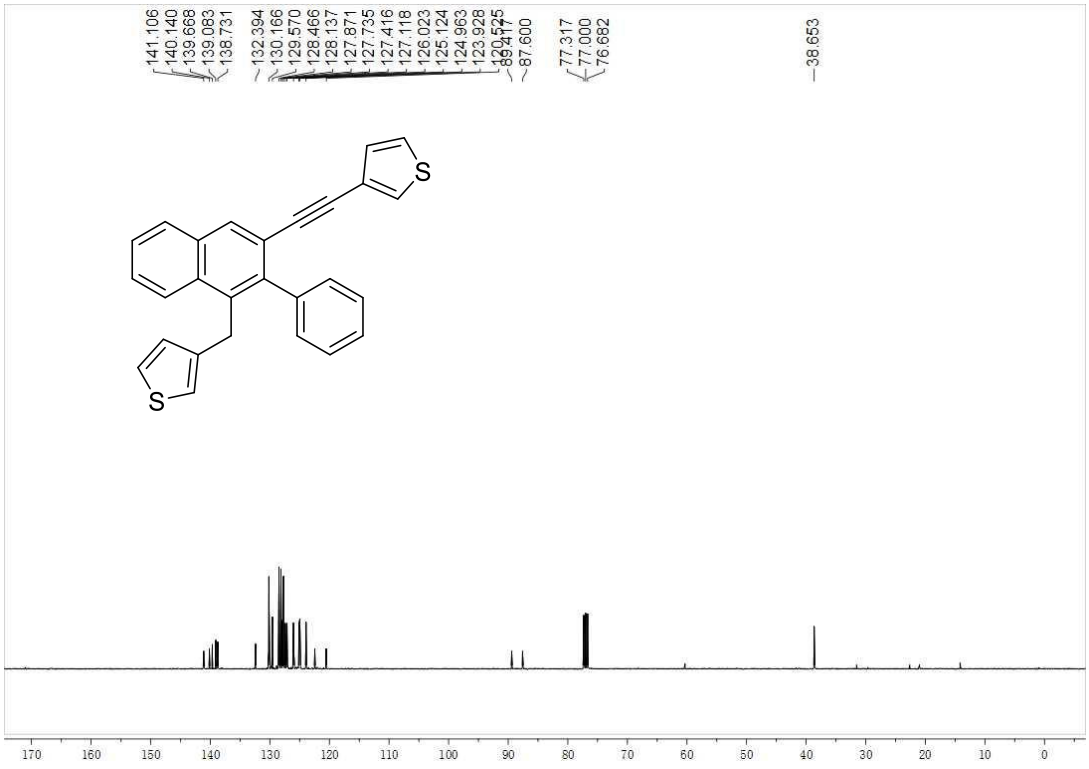
2-((2-phenyl-3-(thiophen-2-ylethynyl)naphthalen-1-yl)methyl)thiophene (3ai):



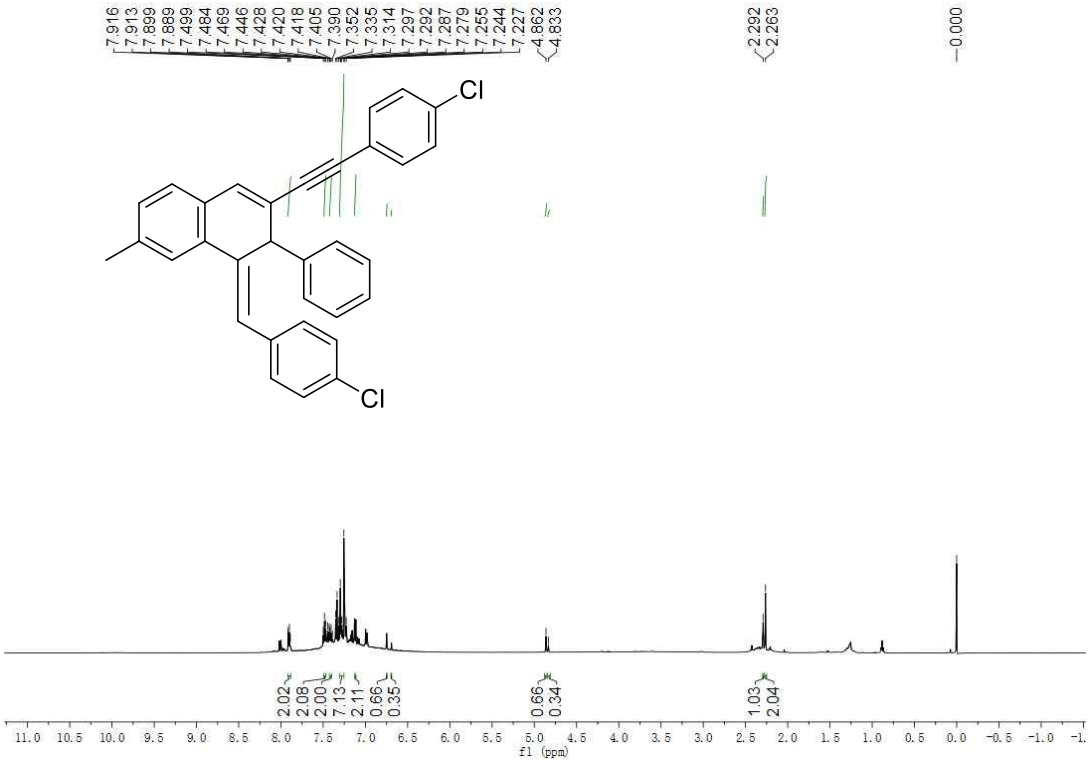


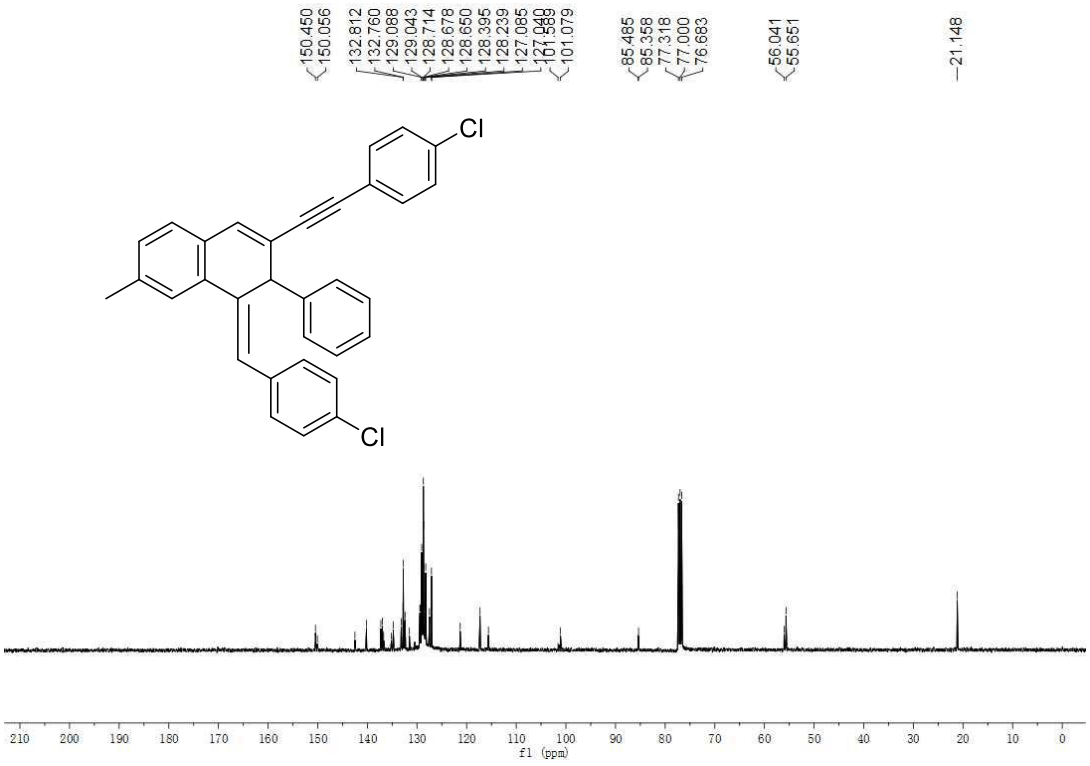
3-((2-phenyl-3-(thiophen-3-ylethynyl)naphthalen-1-yl)methyl)thiophene (3aj):



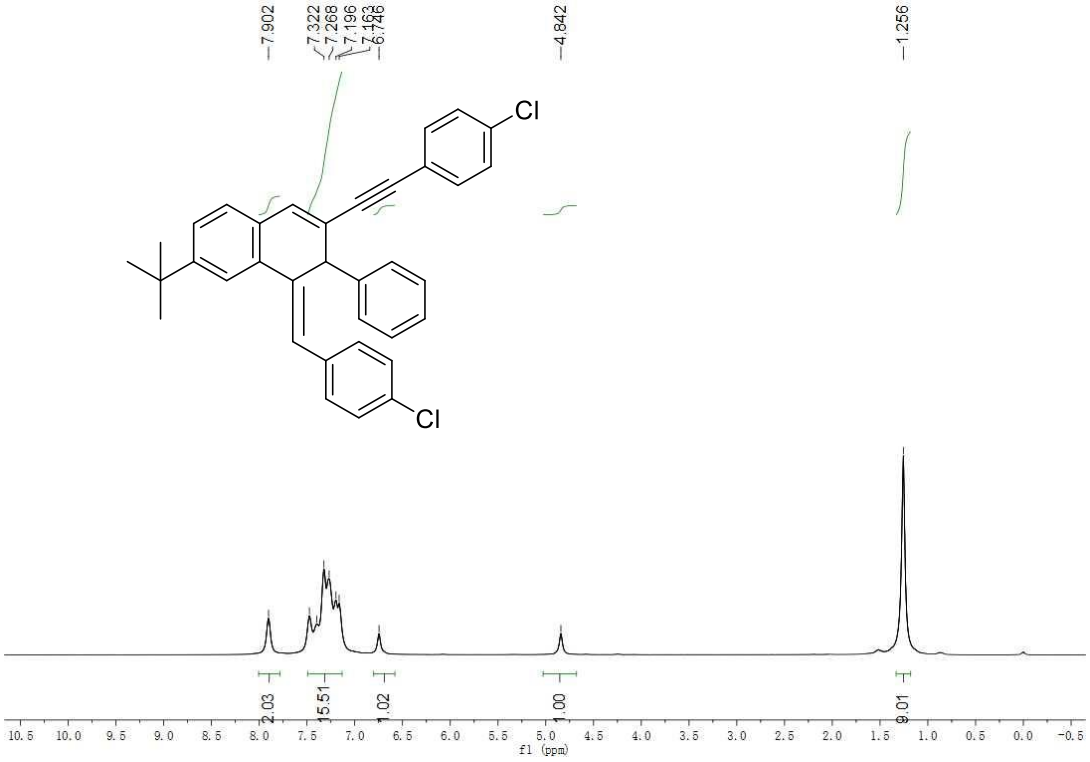


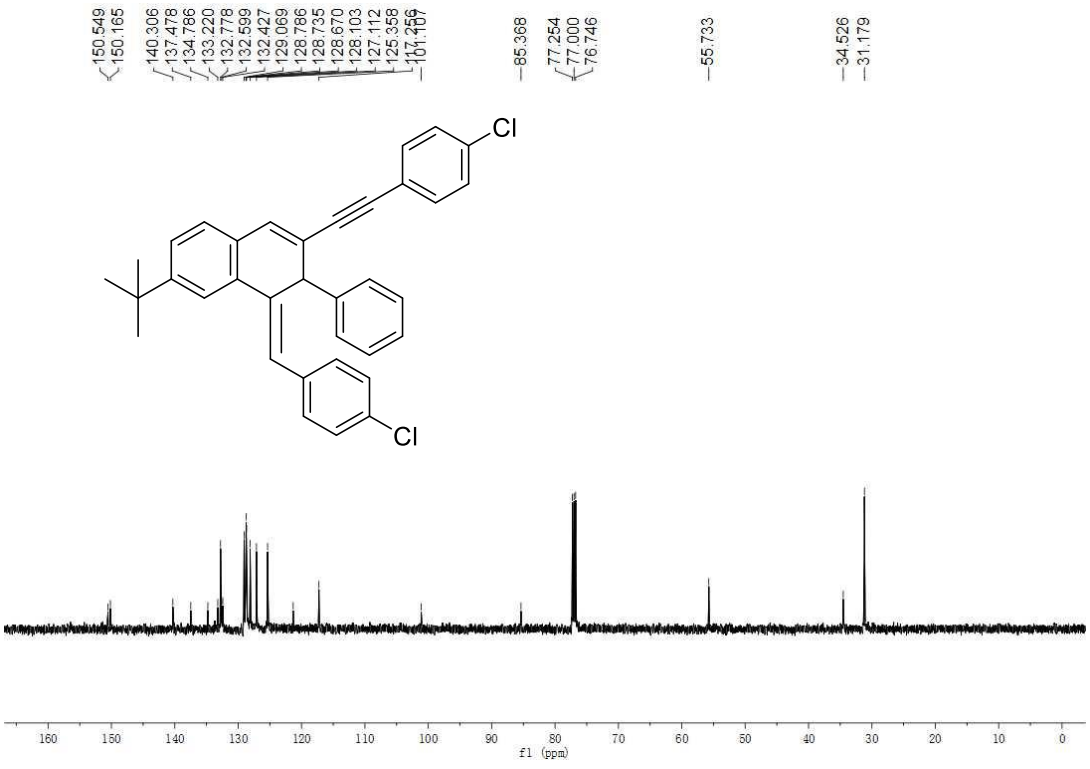
1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-7-methyl-2-phenyl-1,2-dihydronaphthalene (3bd):



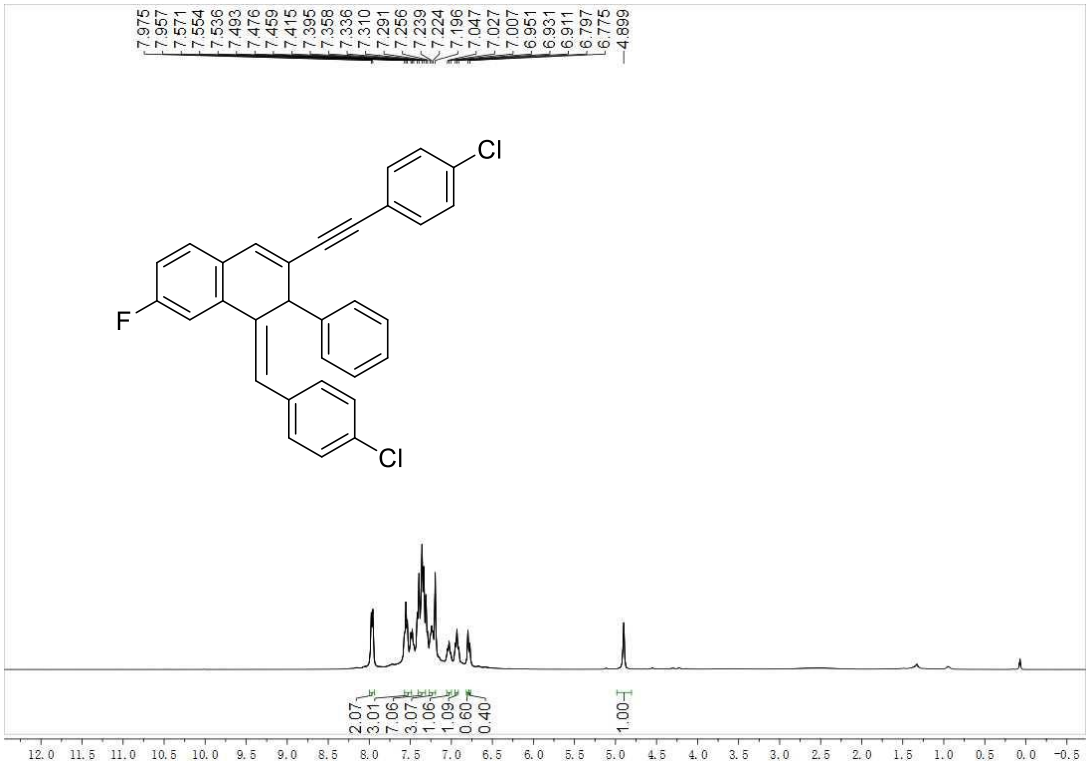


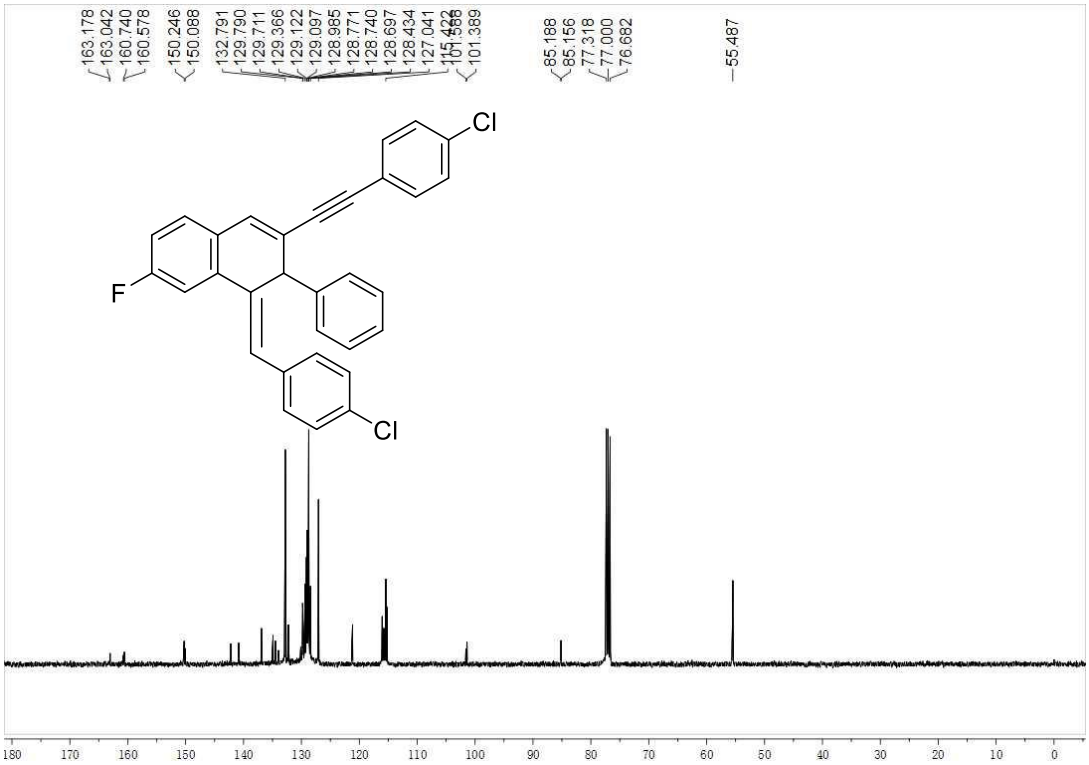
7-(tert-butyl)-1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3cd):

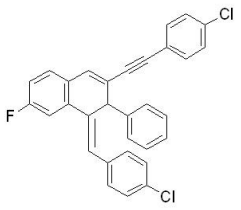




1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-7-fluoro-2-phenyl-1,2-dihydronaphthalene (3dd):

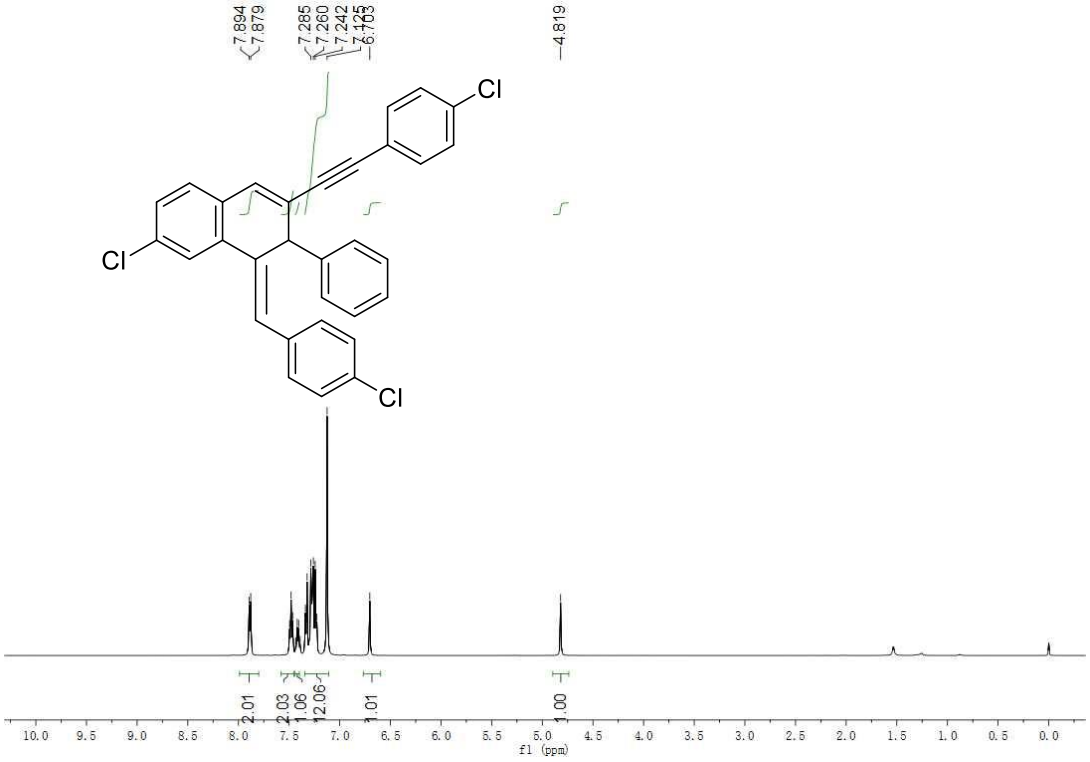


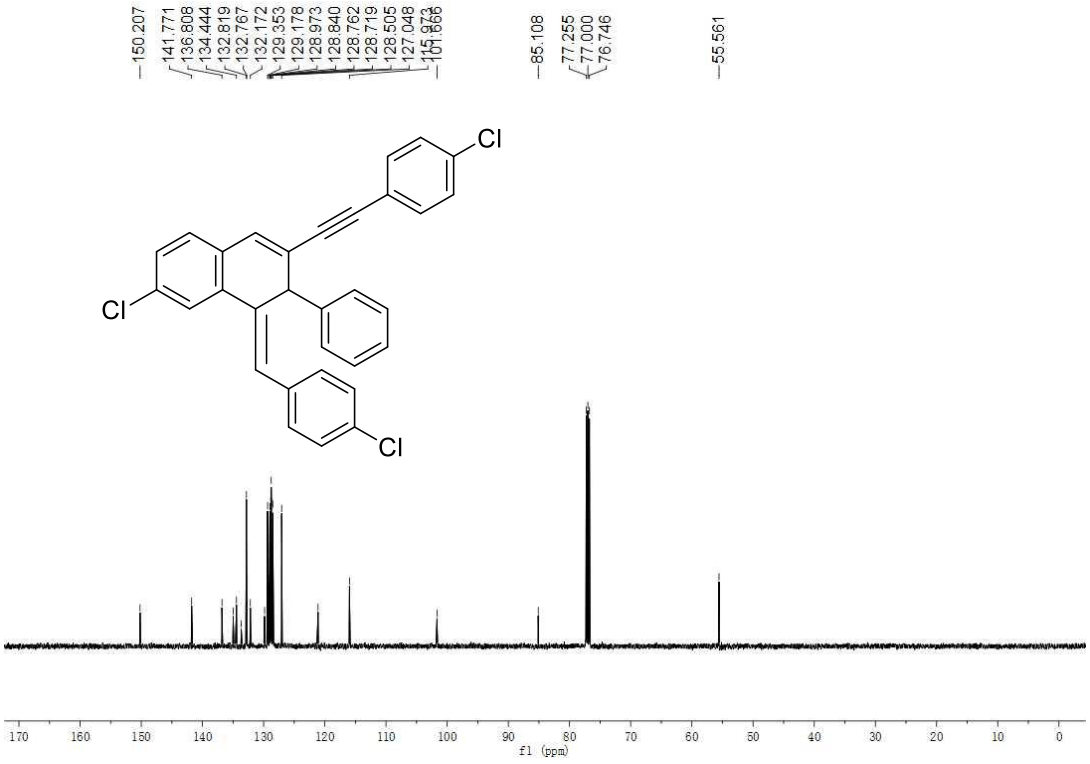



Cl
F
Cl

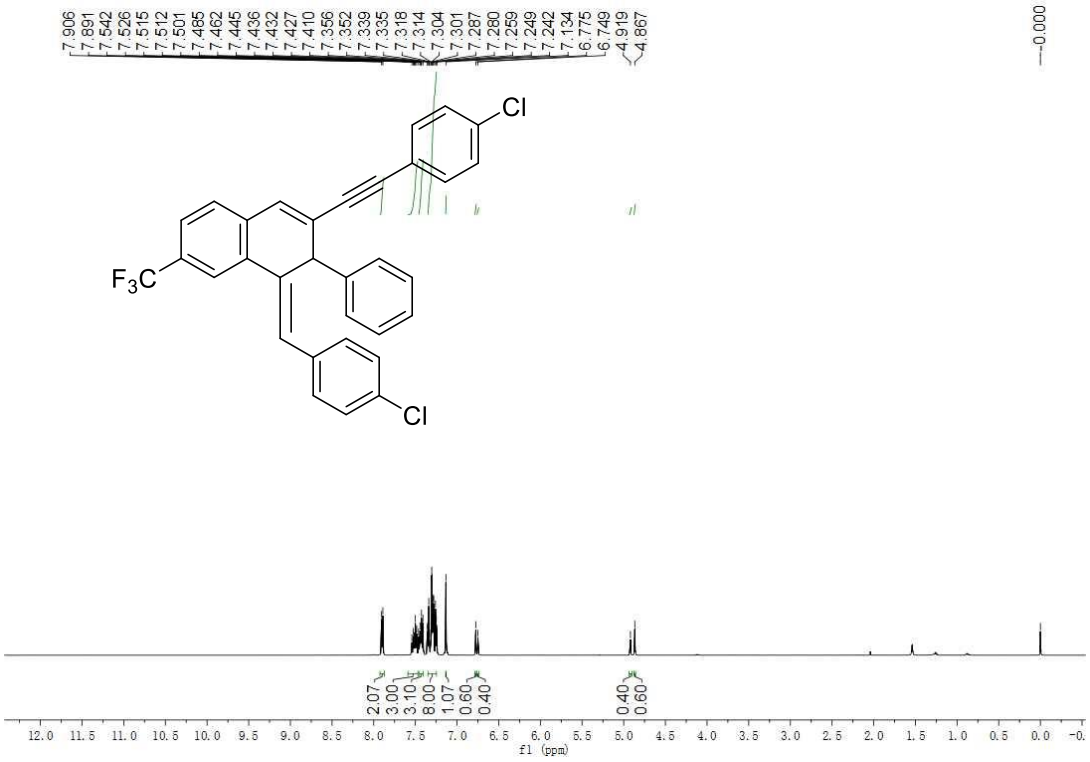
-114.279
-115.191
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

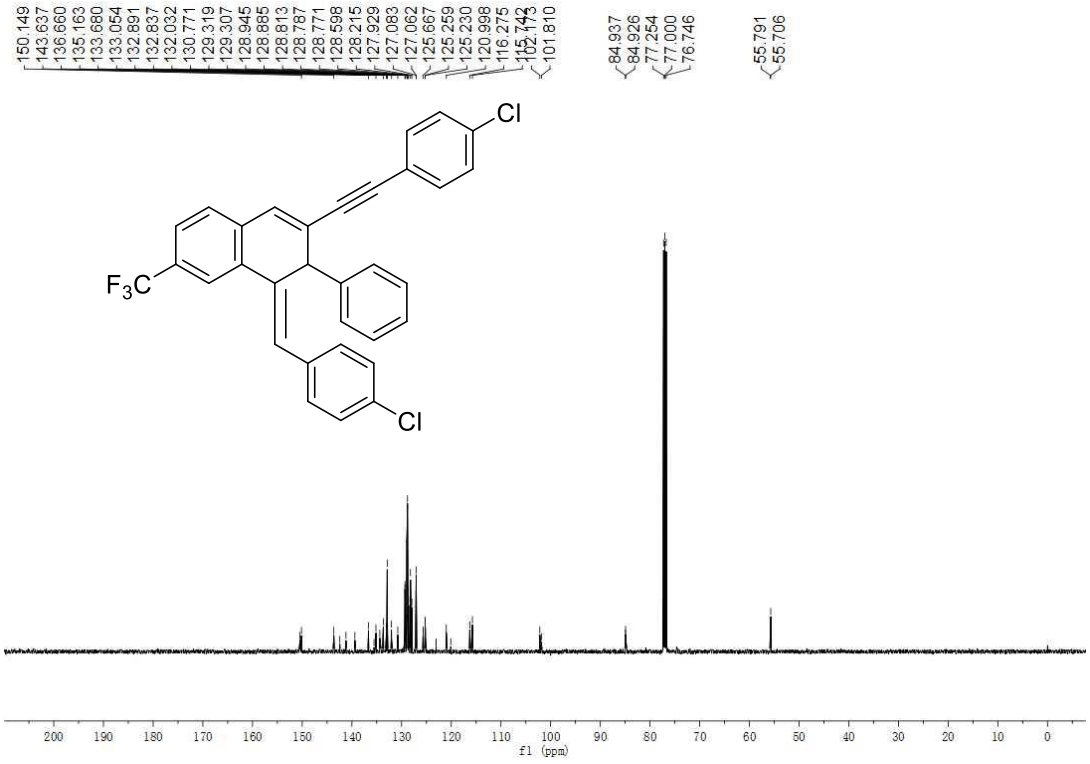
7-chloro-1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3ed):

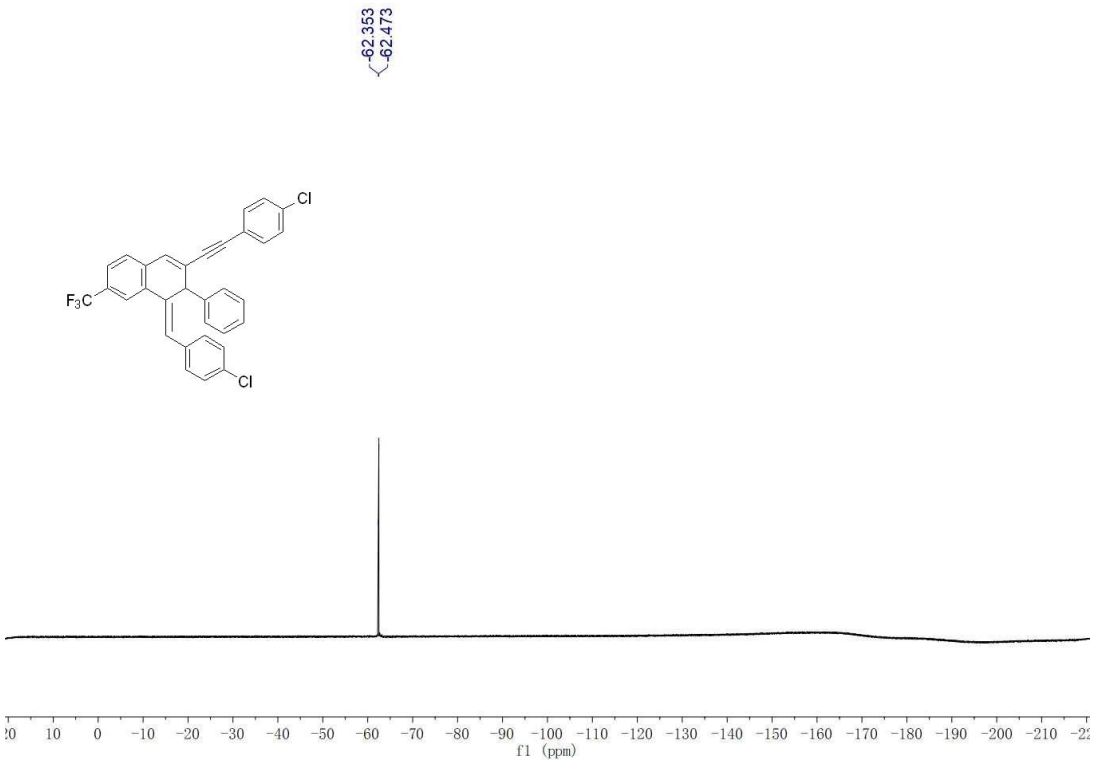




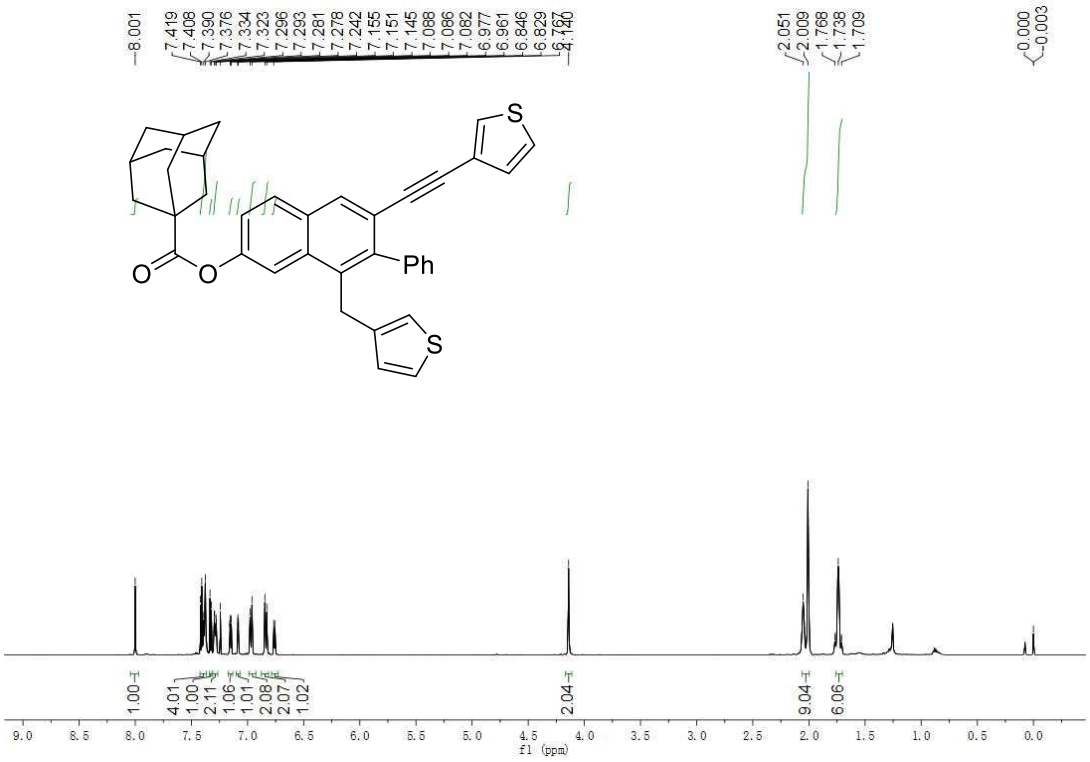
1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-phenyl-7-(trifluoromethyl)-1,2-dihydronaphthalene (3fd):

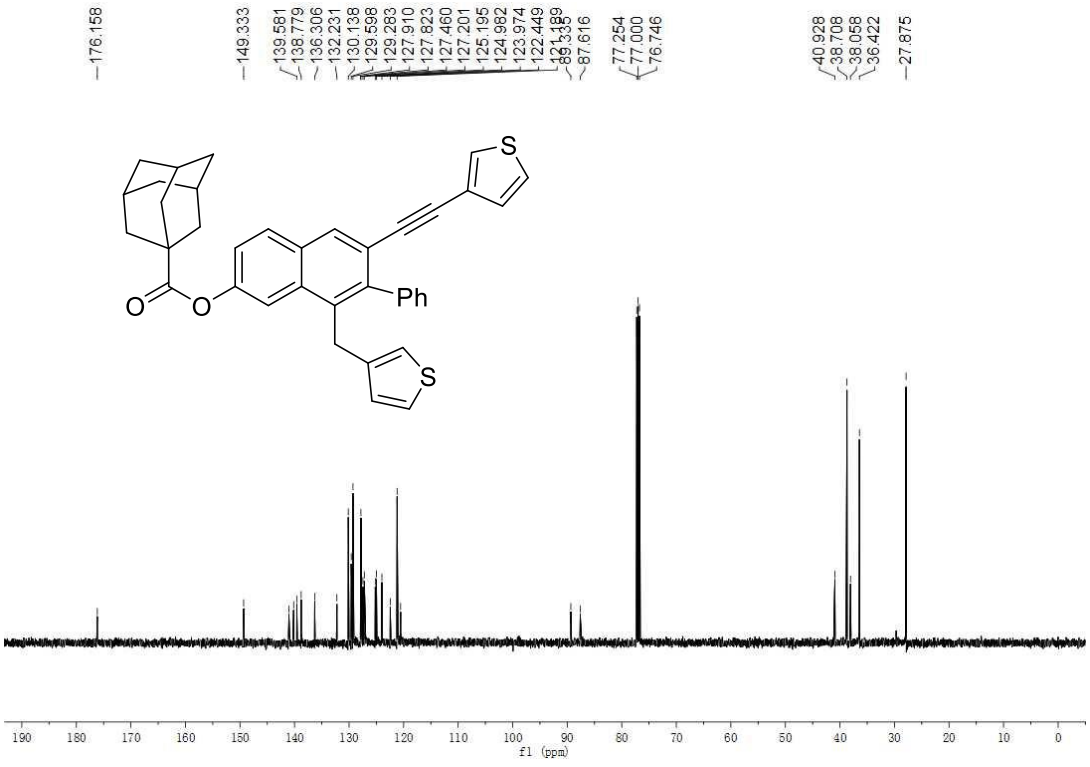




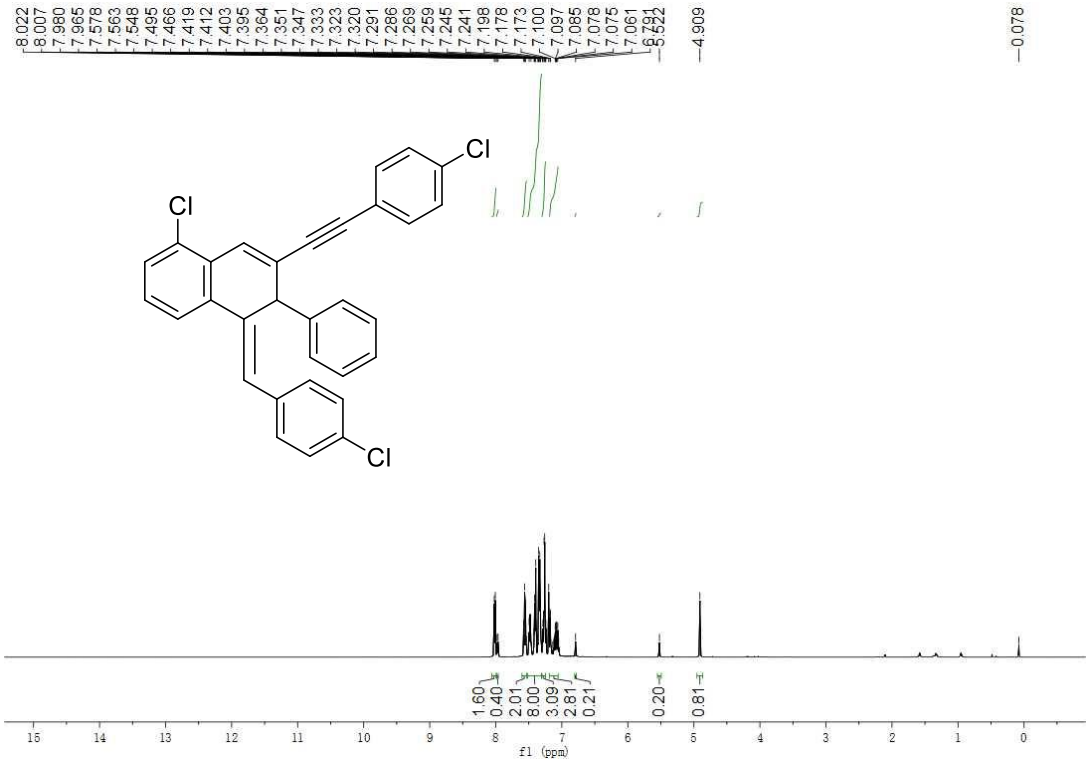

-62.353
-62.473
Cl
F3C
Cl
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

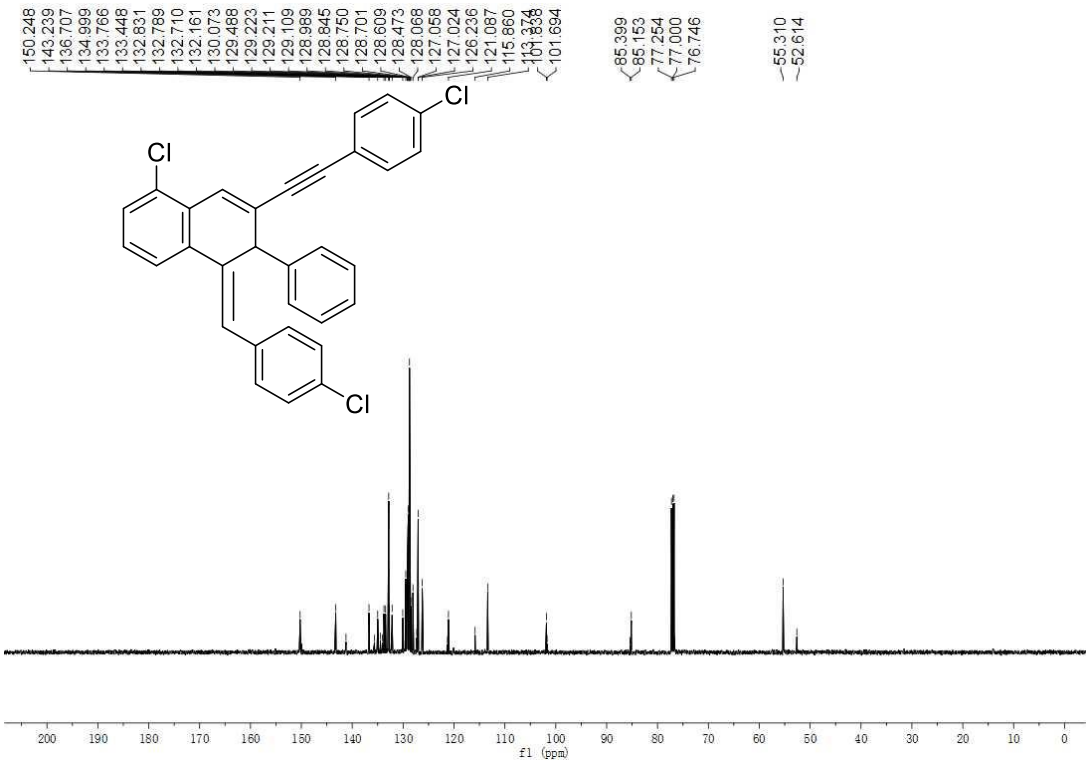
7-phenyl-6-(thiophen-3-ylethynyl)-8-(thiophen-3-ylmethyl)naphthalen-2-yl(3r,5r,7r)-adamantane-1-carboxylate (3gj):



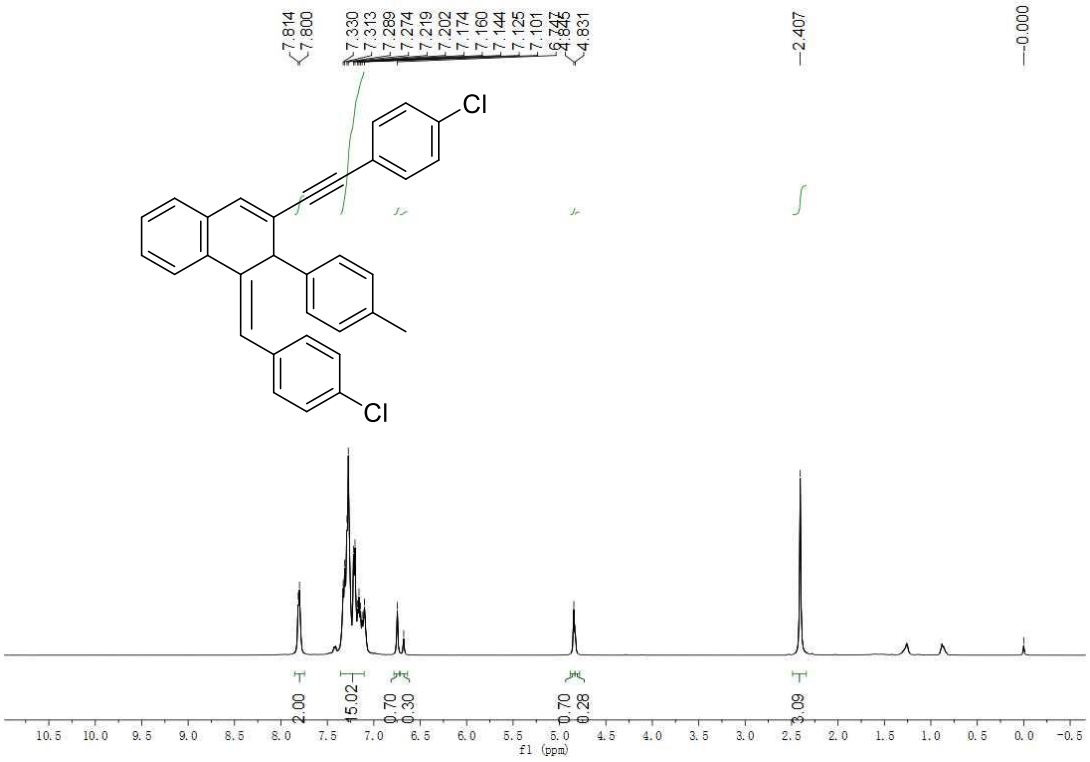


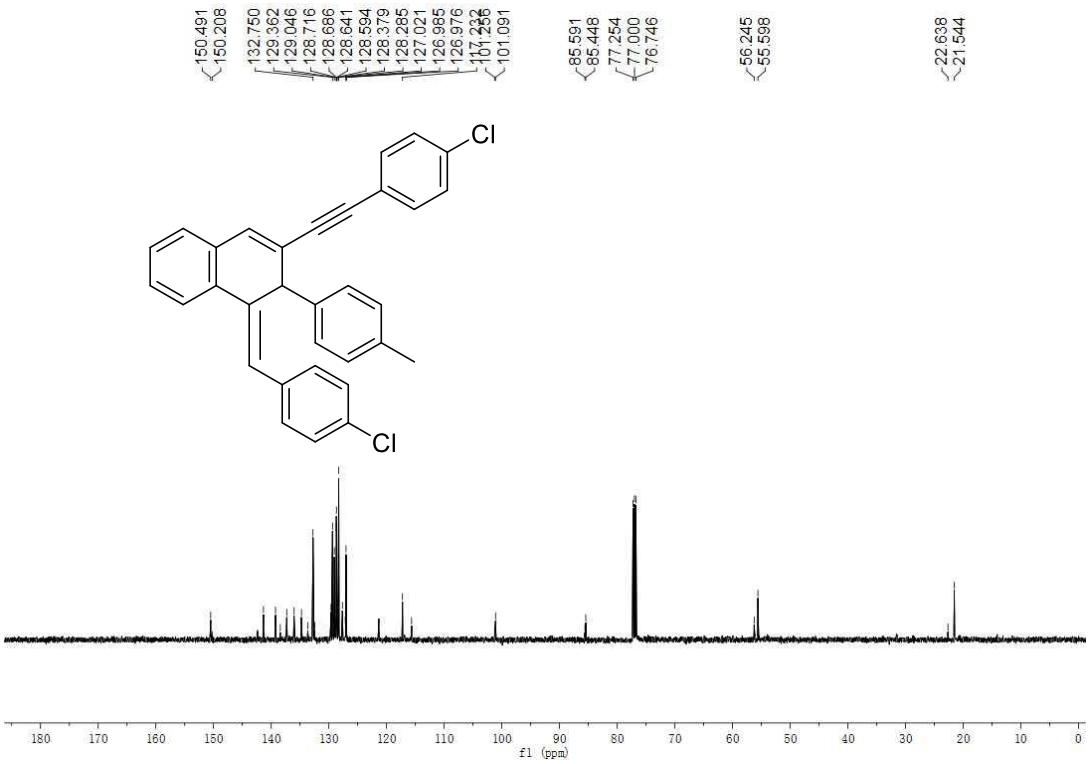
5-chloro-1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-phenyl-1,2-dihydronaphthalene (3hd):



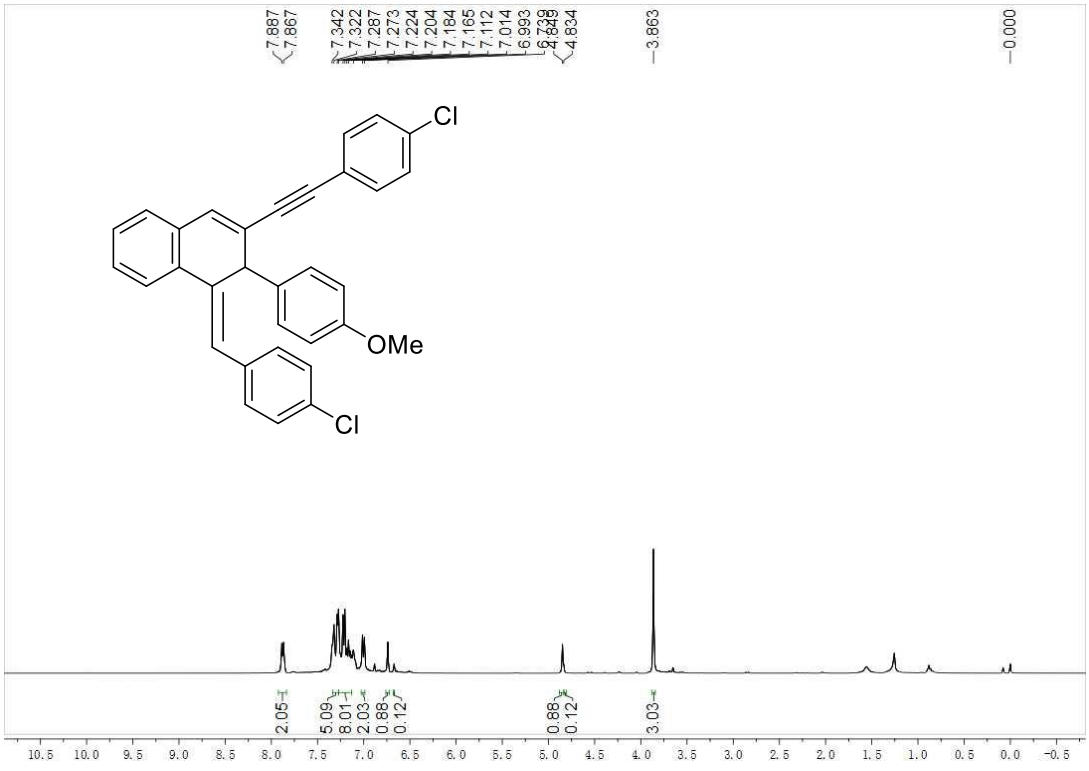


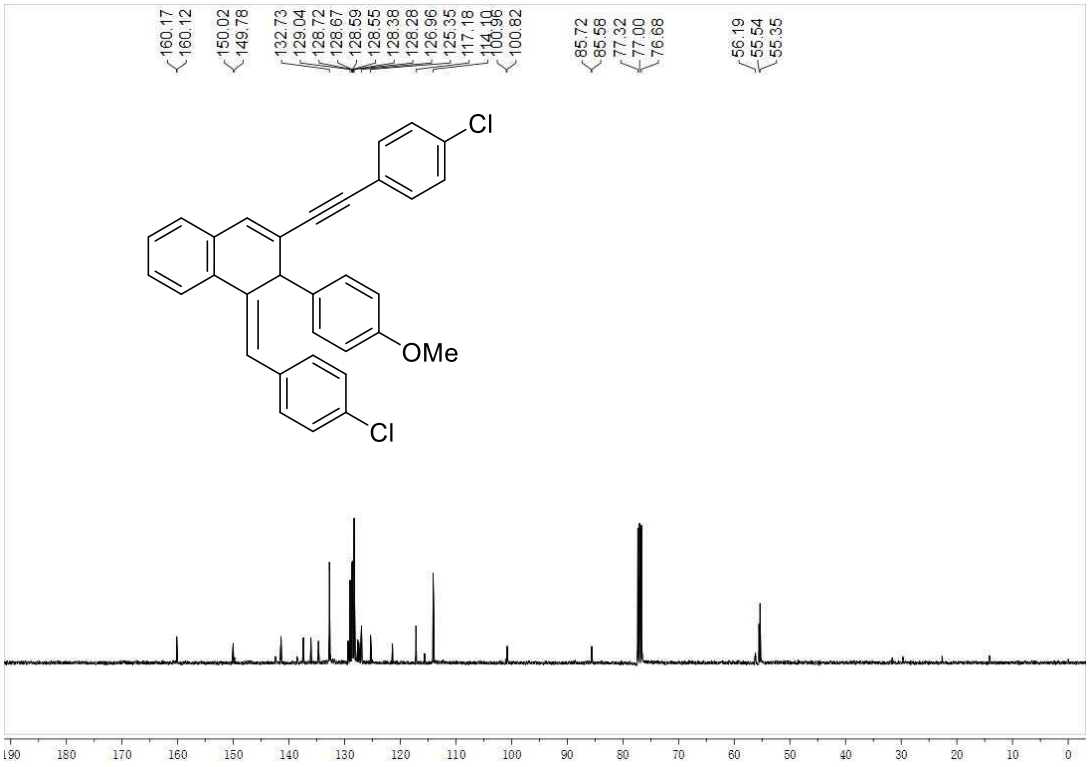
1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-(p-tolyl)-1,2-dihydronaphthalene (3id):



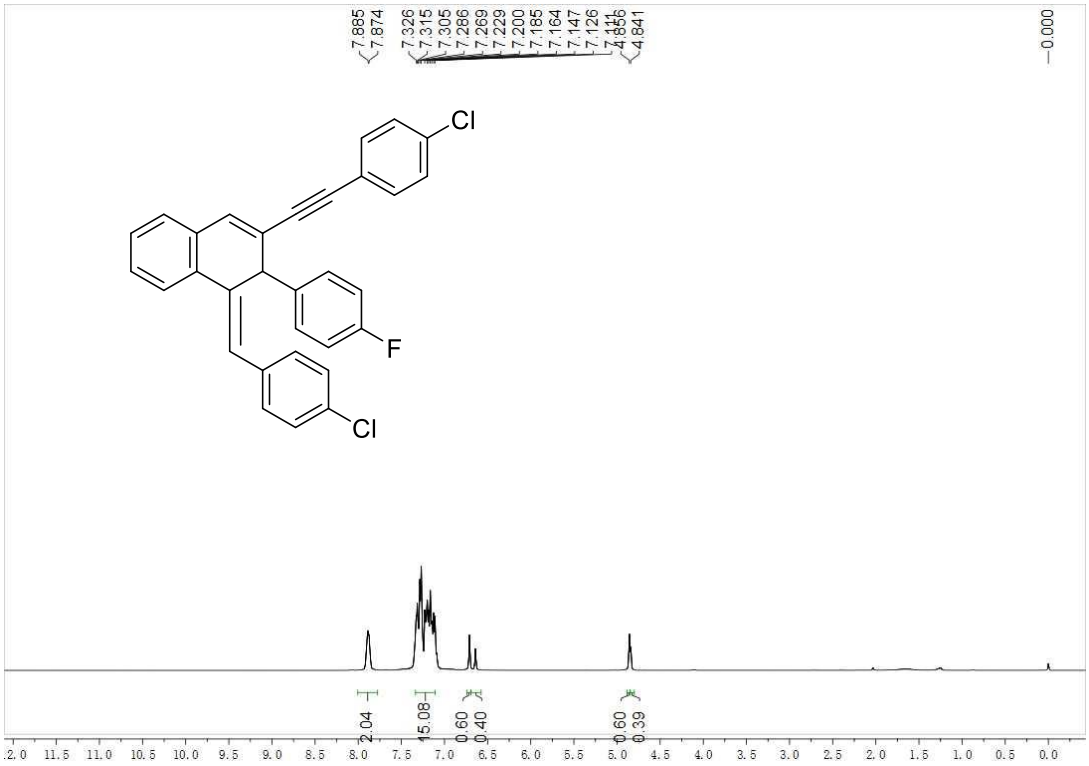


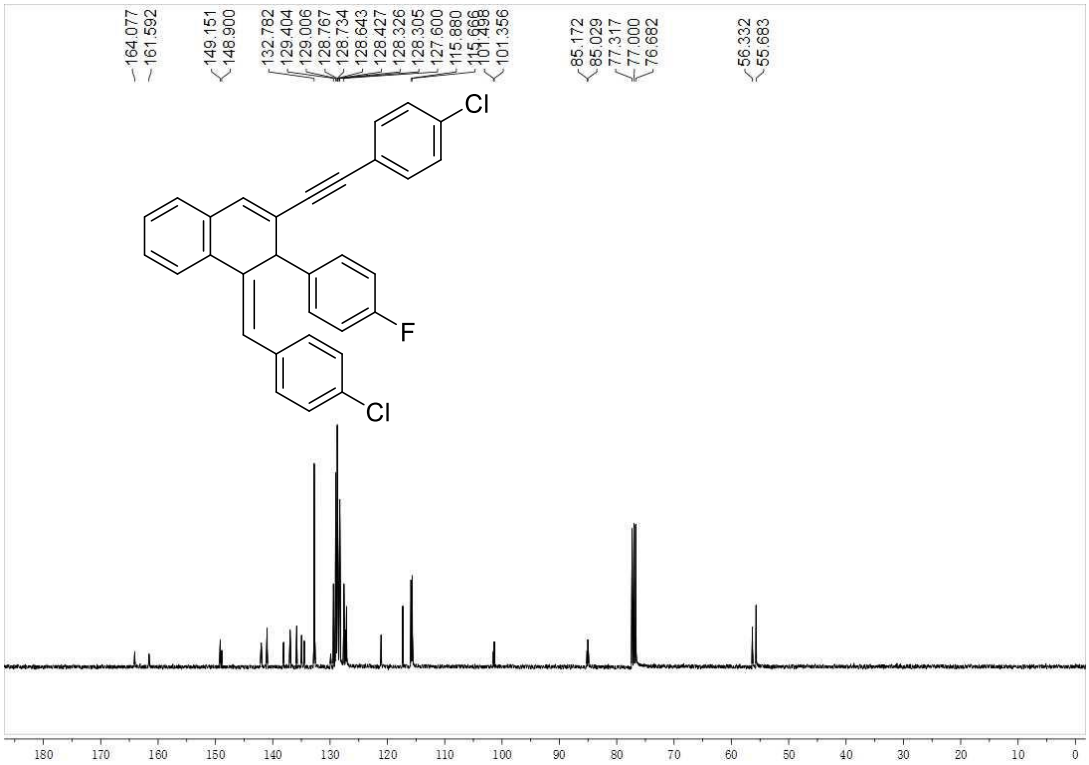
1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-(4-methoxyphenyl)-1,2-dihydronaphthalene (3jd):

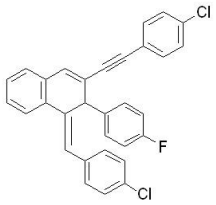




1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-(4-fluorophenyl)-1,2-dihydronaphthalene (3kd):

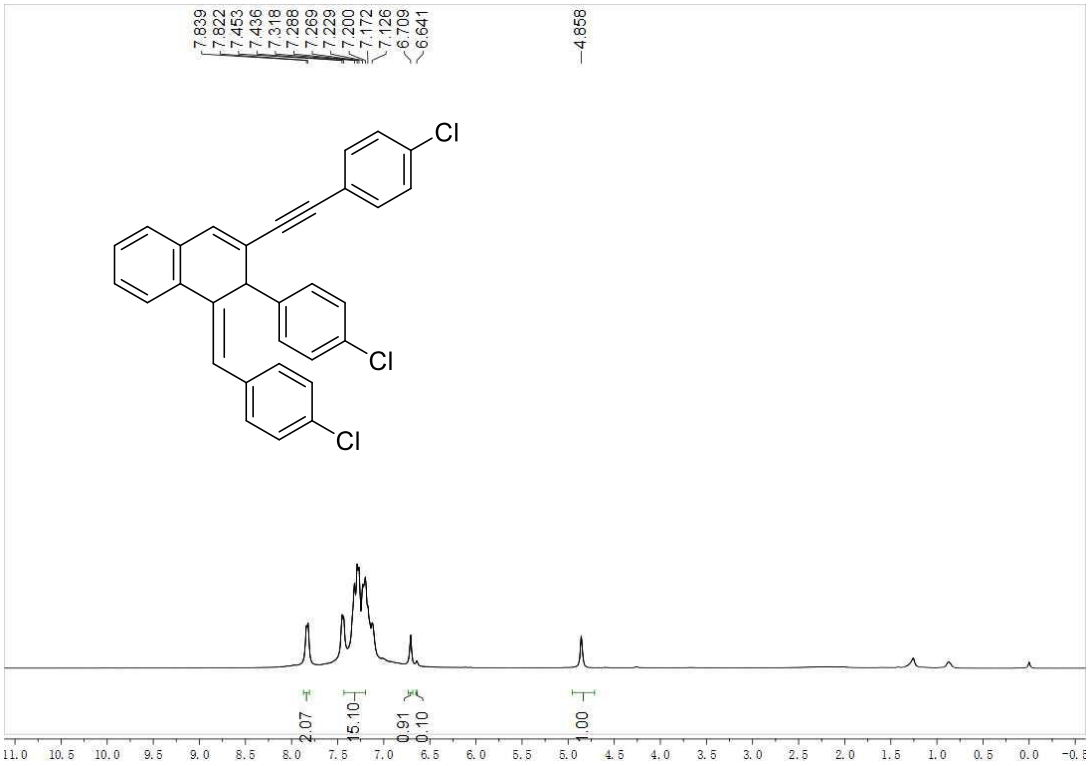


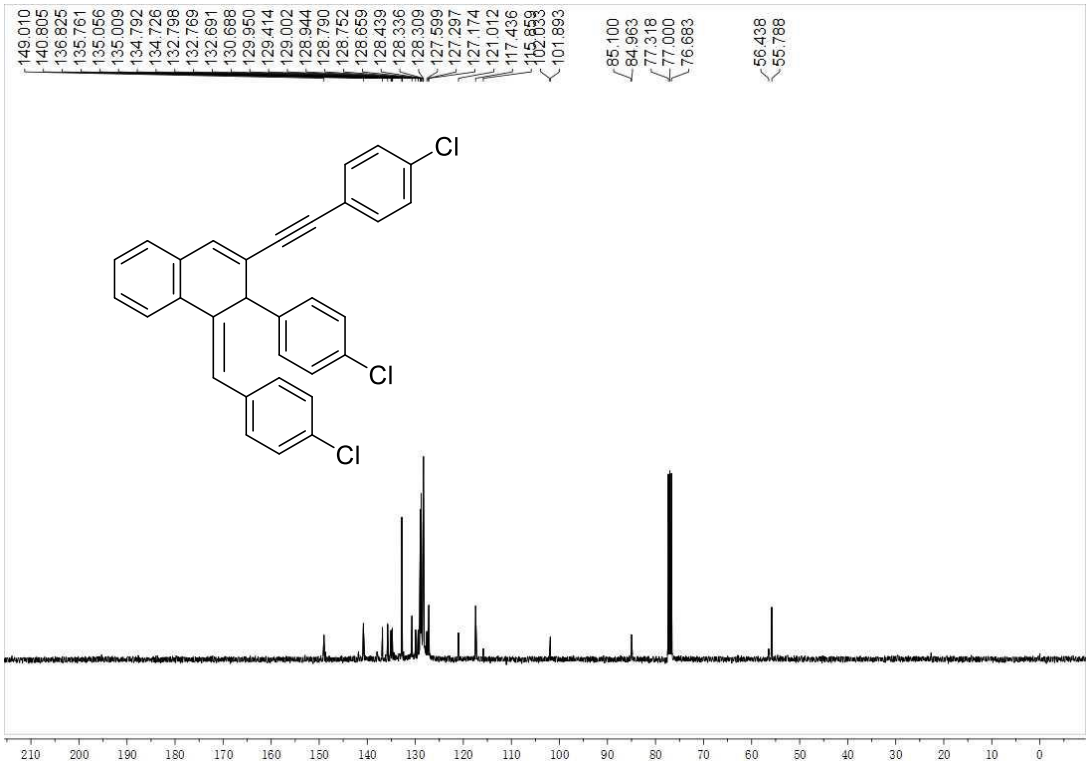



Cl
F
Cl

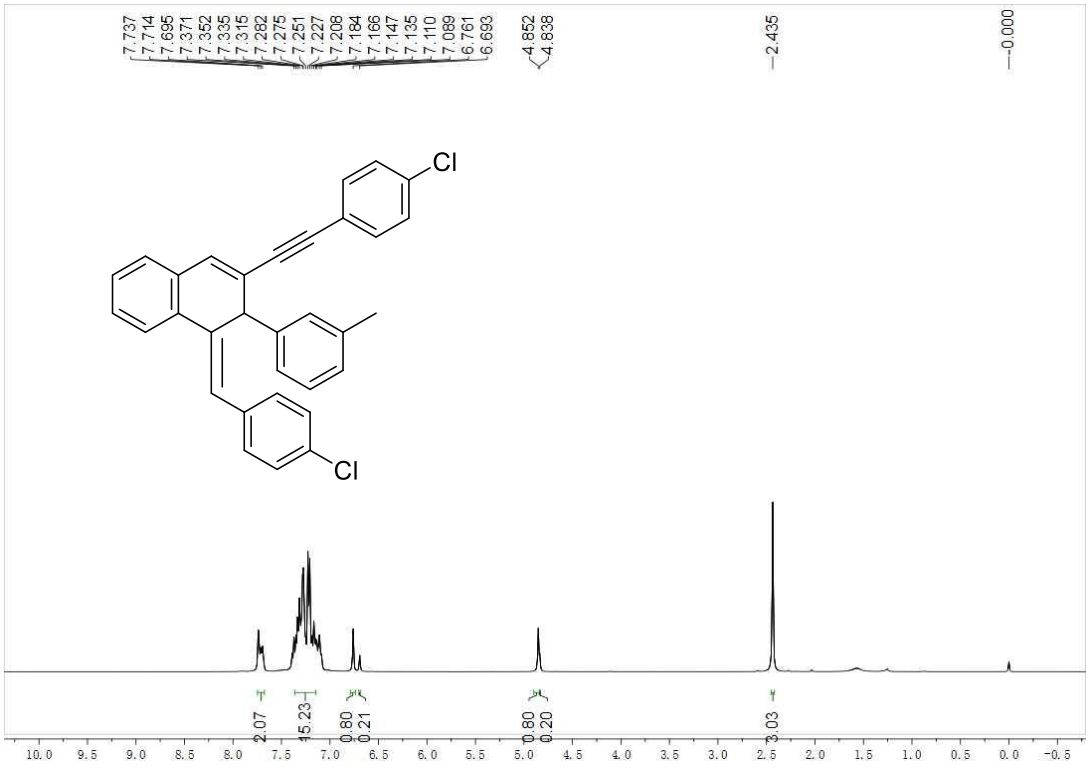
-110.371
-110.475
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

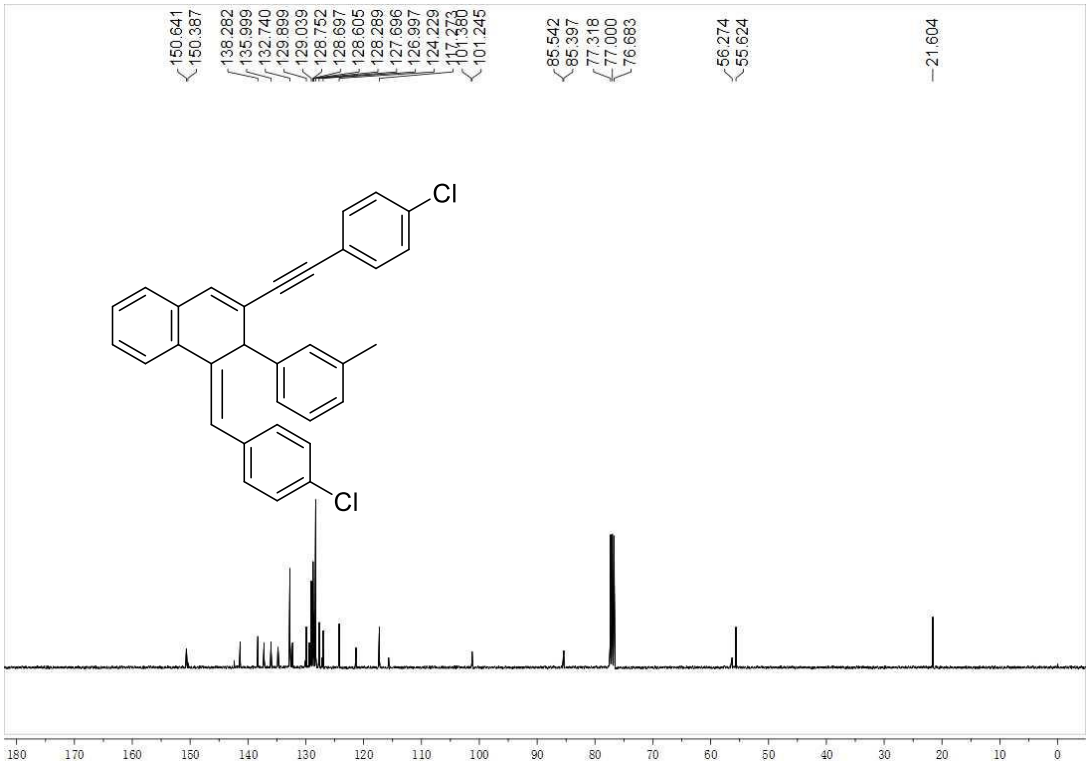
1-(4-chlorobenzylidene)-2-(4-chlorophenyl)-3-((4-chlorophenyl)ethynyl)-1,2-dihydronaphthalene (3ld):



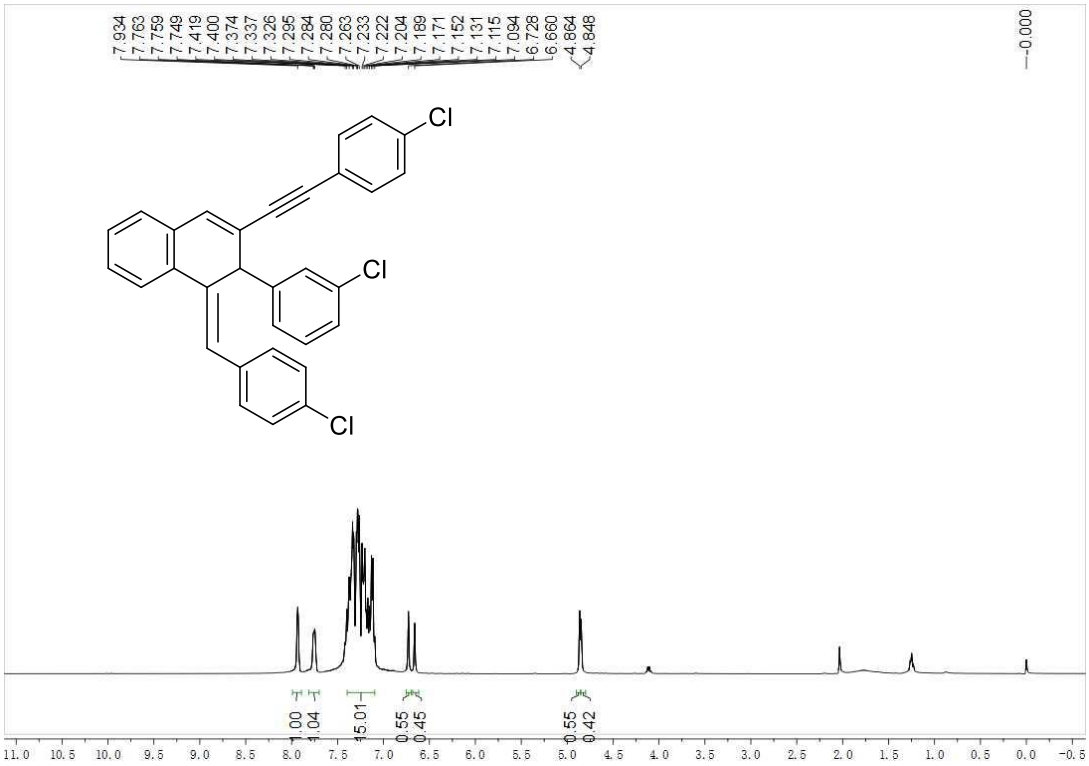


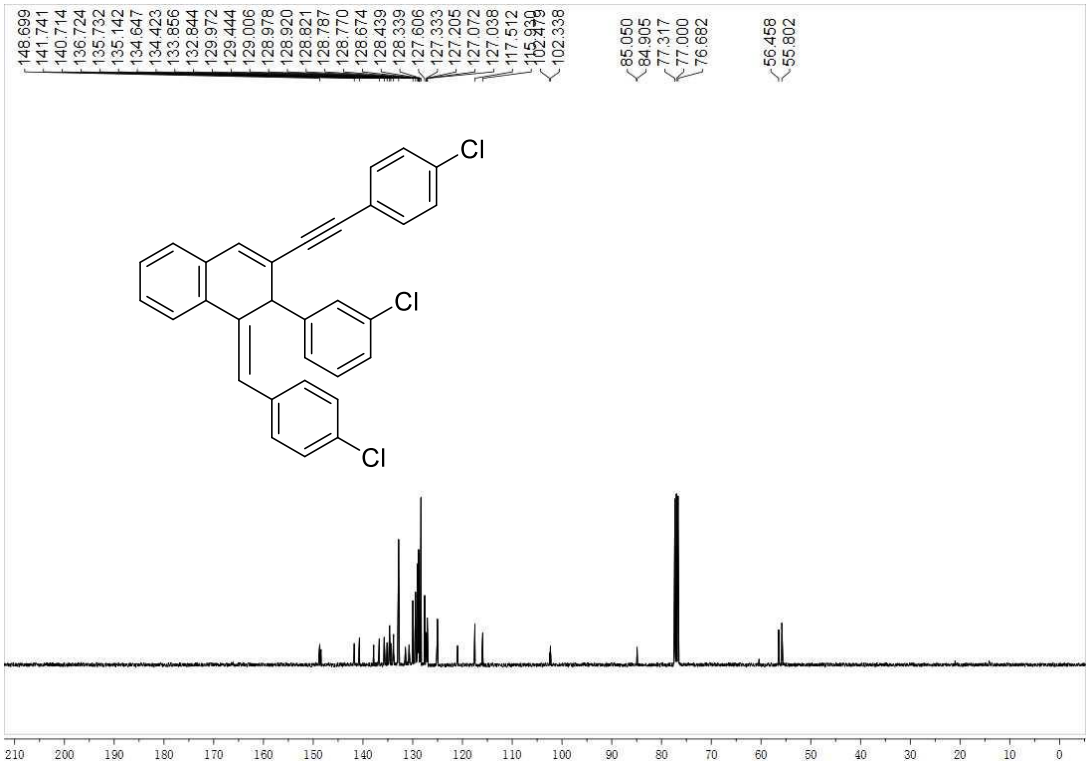
1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-2-(m-tolyl)-1,2-dihydronaphthalene (3md):



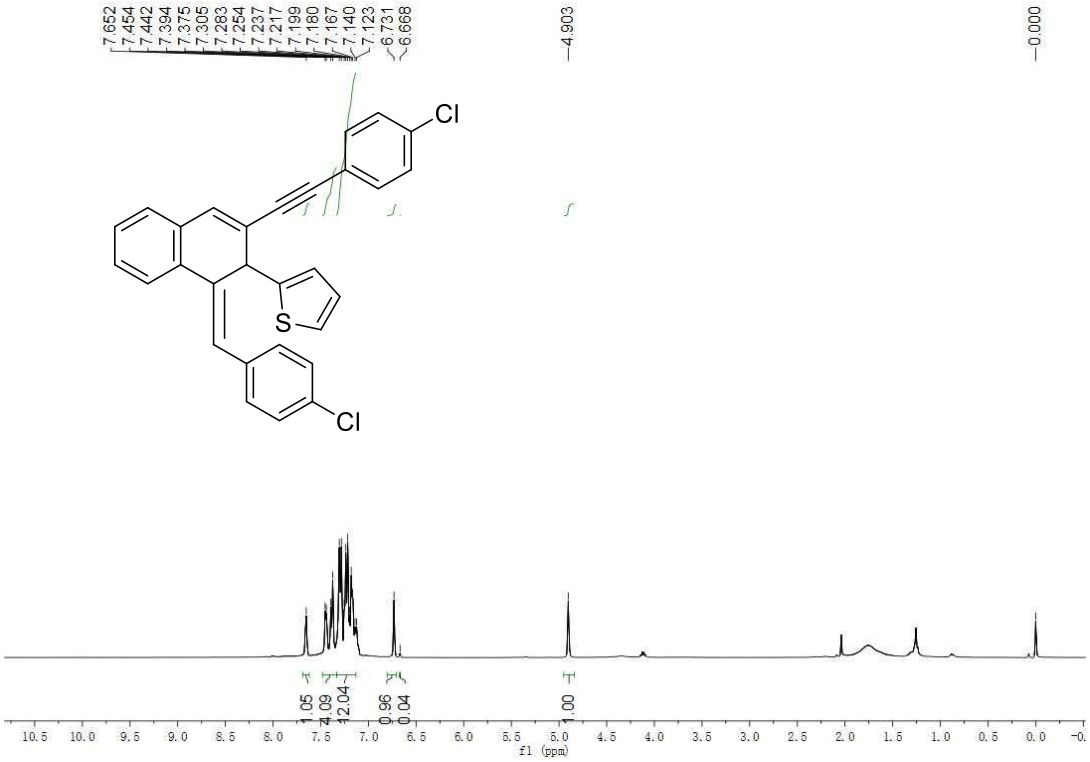


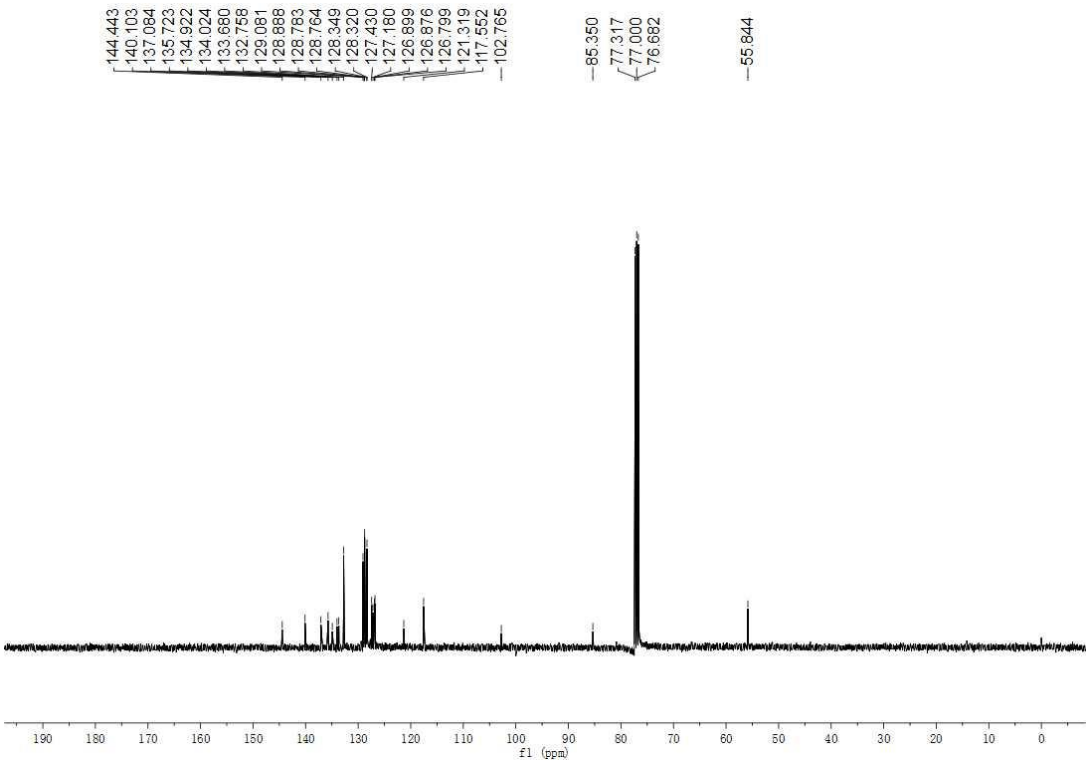
1-(4-chlorobenzylidene)-2-(3-chlorophenyl)-3-((4-chlorophenyl)ethynyl)-1,2-dihydronaphthalene (3nd):



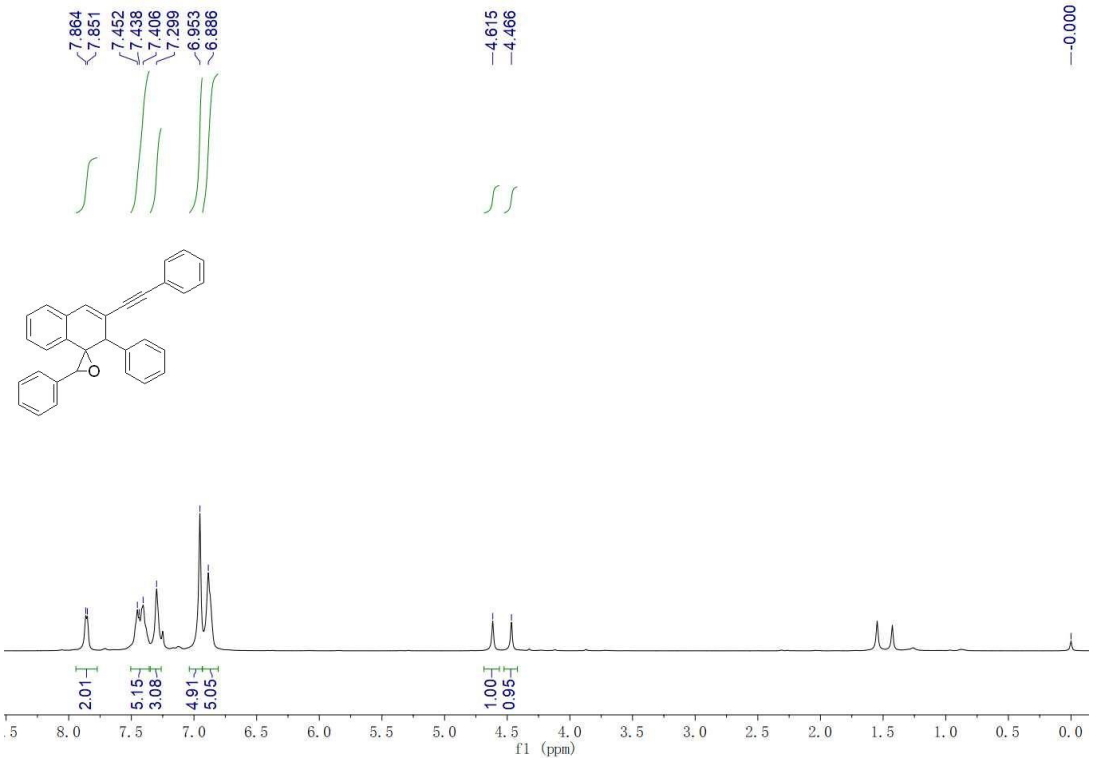


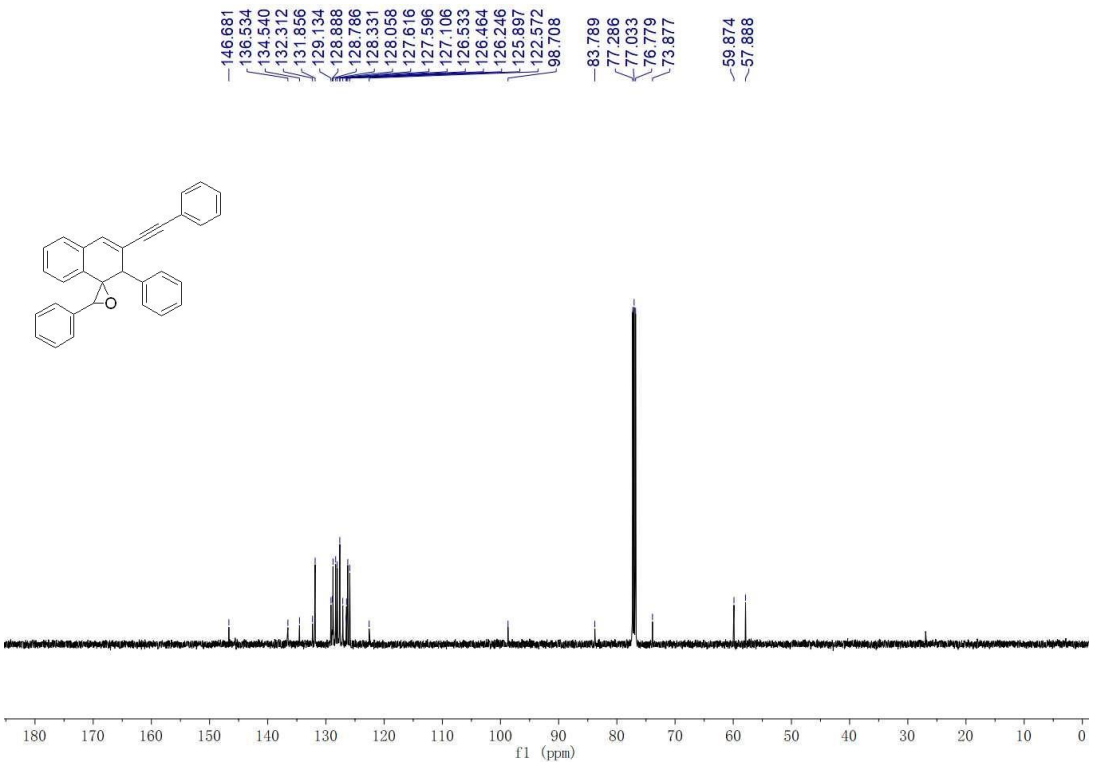
2-(1-(4-chlorobenzylidene)-3-((4-chlorophenyl)ethynyl)-1,2-dihydronaphthalen-2-yl)thiophene (3od):



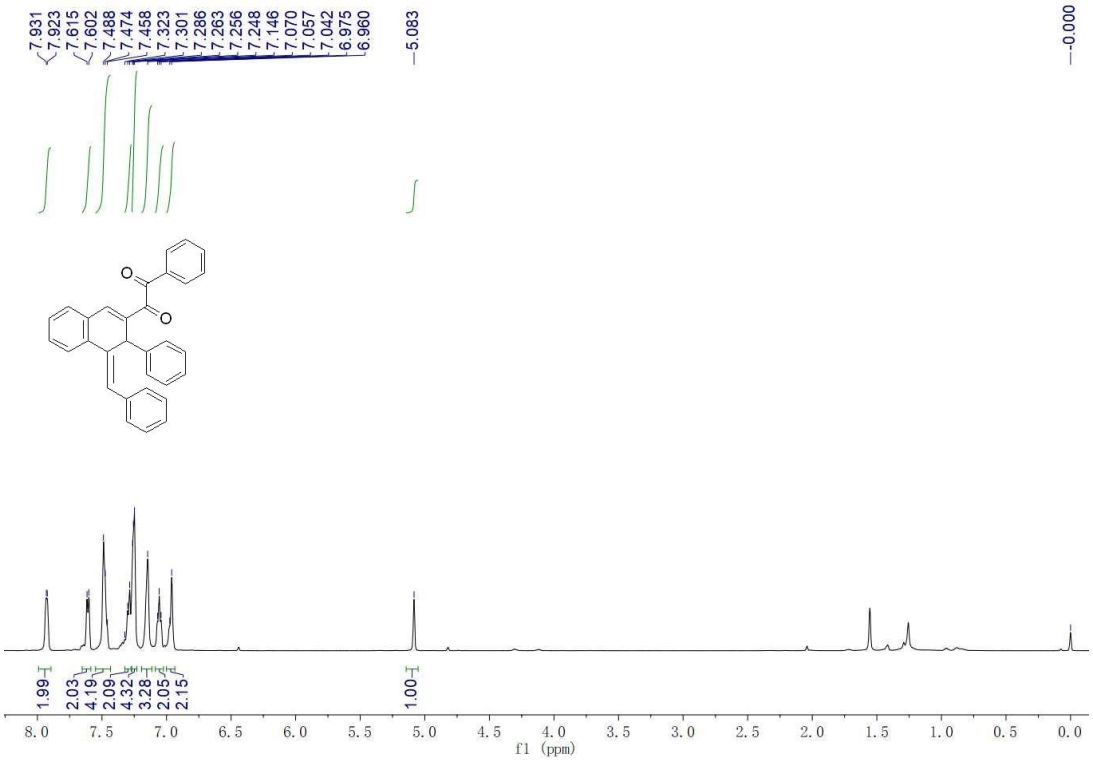


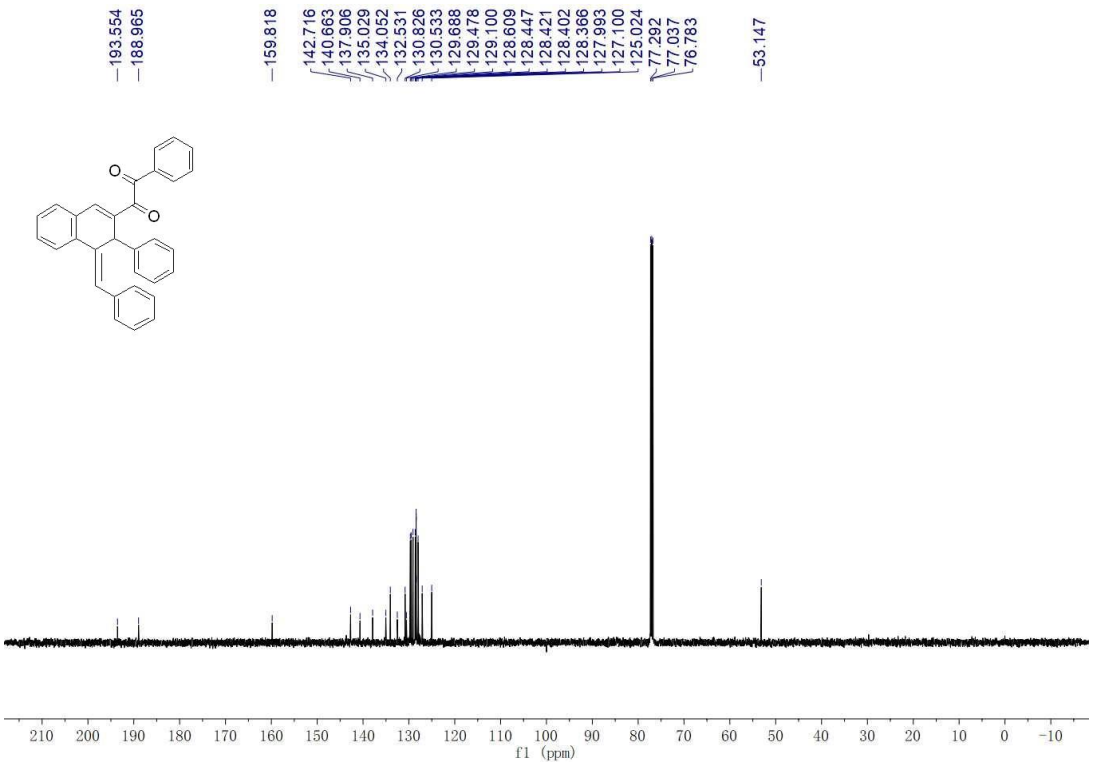
2,3'-diphenyl-3-(phenylethynyl)-2H-spiro[naphthalene-1,2'-oxirane] (4aa)





1-(4-benzylidene-3-phenyl-3,4-dihydronaphthalen-2-yl)-2-phenylethane-1,2-dione (5aa)





(D) References

1 (*a*) S.-C. Zhao, X.-Z. Shu, K.-G. Ji, A.-X. Zhou, T. He, X.-Y. Liu and Y.-M. Liang, Pd(0)-Catalyzed [1,5]-Sigmatropic Hydrogen Shift of Propargylic Esters toward Substituent Naphthylamines. *J. Org. Chem.*, 2011, **76**, 1941-1944; (*b*) M. Yoshida, S. Ohno and K. Namba, Synthesis of Substituted Tetrahydrocyclobuta[b]benzofurans by Palladium-Catalyzed Substitution/[2+2] Cycloaddition of Propargylic Carbonates with 2-Vinylphenols. *Angew. Chem. Int. Ed.*, 2013, **52**, 13597-13600.