Electronic Supplementary Information (ESI)

Pd(0)-catalyzed chemoselective construction of spirocarbocycles via an alkyne insertion/β-naphthol dearomatization cascade

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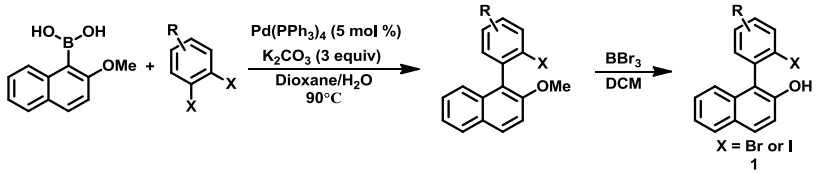
A. General information:

All reactions were carried out under an argon atmosphere using standard Schlenk-Lines or a glovebox (Innovative Technology). All reagents were used as received unless otherwise noted. CH_3CN and DMF were dried over CaH_2. Toluene, DME and THF were dried over sodium. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. Flash chromatography was performed with silica gel (300-400 mesh). Proton nuclear magnetic resonance (^{1}H NMR) data were acquired on Varian Unity Inova-400 (400 MHz) or Bruker Ascend 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet, br, broad. Coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on Varian Unity Inova-400 or Bruker Ascend 400 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-*d*. Infrared (IR) data were recorded as films on potassium bromide plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Mass spectra were acquired on a Bruker Daltonics

MicroTof-Q II mass spectrometer. Microwave irradiations were performed on a Smith Synthesizer from Biotage, and the temperature was monitored by a built-in, on-line IR-sensor. 2-Methoxynaphthalen-1-ylboronic acid,[1] 2-(methoxymethoxy)- naphthalen-1-ylboronic acid,[2] *ortho*-dihalogenated aryls,[3-9] **1k**[10] and alkynes[11-13] were prepared according to literature methods.

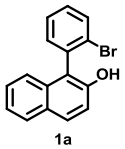
B. Preparation of substrates:

The following naphthol substrates were prepared by Suzuki-Miyaura reaction between 2-methoxynaphthalen-1-ylboronic acid and corresponding dihalogenated aryl derivatives, followed by demethylation with BBr_3.



A 25 mL round bottom flask with a stirring bar is fitted with a rubber septum and flame dried under high vacuum. The flask is purged with argon and charged with $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol), K_2CO_3 (0.83 g, 6.0 mmol), 2-methoxynaphthalen-1-ylboronic acid (0.61 g, 3.0 mmol), dihalogenated aryl (2.0 mmol), 8.0 mL deoxygenated 1,4-dioxane and 2.0 mL deoxygenated water. The reaction mixture was then heated at 90 ℃ for 4 days. After the reaction cooled down to room temperature, extracted with ethyl acetate (15.0 mL × 3), dried over $MgSO_4$ and concentrated. The residue was subjected to a plug of silica, eluted with hexane/EtOAc (100/1) to afford the desired compound.

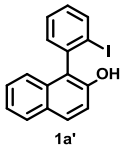
A solution of BBr_3 (3.0 equiv) in CH_2Cl_2 was slowly added to a solution of the above product in CH_2Cl_2 (10.0 mL) at 0 ℃ and the mixture was stirred for 3 h at room temperature. After cooled to 0 ℃, the reaction was quenched with ice cold H_2O and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel to afford the desired product **1**.



1a

1-(2-Bromophenyl)naphthalen-2-ol (**1a**)

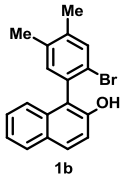
Starting material = 1-bromo-2-iodobenzene. White solid (0.42 g, 70% yield). Mp: 83-84 ℃.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.75 (m, 3H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.39-7.30 (m, 4H), 7.25 (d, *J* = 8.9 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 1H), 4.88 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 135.5, 133.9, 133.5, 133.0, 130.6, 130.4, 129.1, 128.6, 128.4, 127.0, 126.4, 124.5, 123.8, 120.6, 117.8. IR (KBr): 3515, 3057, 1622, 1597, 1463, 1391, 816, 754 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{11}BrONa$ $[M+Na]^+$ 320.9891, found 320.9887.



1a'

1-(2-Iodophenyl)naphthalen-2-ol (**1a'**)

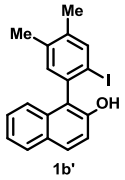
Starting material = 1,2-diiodobenzene. Light yellow solid (0.48 g, 70% yield). Mp: 99-100 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.9 Hz, 1H), 7.84 (t, *J* = 8.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.40-7.31 (m, 3H), 7.25 (d, *J* = 9.0 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 4.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 140.3, 139.8, 132.9, 132.5, 130.5, 130.4, 129.4, 129.1, 128.3, 127.0, 124.5, 123.9, 123.8, 117.8, 102.7. IR (KBr): 3511, 3056, 1621, 1596, 1460, 1390, 1176, 1146, 863, 754 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{11}IONa$ $[M+Na]^+$ 368.9752, found 368.9749.



1b

1-(2-Bromo-4,5-dimethylphenyl)naphthalen-2-ol (**1b**)

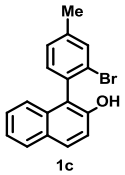
Starting material = 1,2-dibromo-4,5-dimethylbenzene. Yellow solid (0.38 g, 58% yield). Mp: 46-47 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.83 (m, 2H), 7.65 (s, 1H), 7.39 (d, *J* = 6.4 Hz, 2H), 7.31 (t, *J* = 7.0 Hz, 2H), 7.20 (s, 1H), 5.08 (s, 1H), 2.39 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 139.8, 137.4, 134.5, 134.2, 133.1, 132.2, 130.1, 129.0, 128.3, 126.8, 124.7, 123.6, 122.8, 120.6, 117.6, 19.7, 19.6. IR (KBr): 3533, 3056, 2919, 1622, 1597, 1465, 1383, 1209, 1178, 1146, 816, 749 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{15}BrONa$ $[M+Na]^+$ 349.0204, found 349.0204.



1b'

1-(2-Iodo-4,5-dimethylphenyl)naphthalen-2-ol (**1b'**)

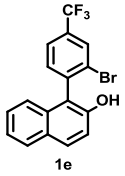
Starting material = 1,2-diiodo-4,5-dimethylbenzene. White solid (0.52 g, 70% yield). Mp: 131-132 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 11.0 Hz, 3H), 7.42-7.32 (m, 2H), 7.27 (d, *J* = 8.9 Hz, 1H), 7.21 (d, *J* = 6.5 Hz, 1H), 7.15 (s, 1H), 4.91 (s, 1H), 2.35 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 140.9, 139.8, 138.4, 136.7, 133.4, 133.0, 130.1, 129.0, 128.3, 126.8, 124.7, 123.8, 123.7, 117.6, 98.6, 19.7, 19.4. IR (KBr): 3531, 3058, 2923, 1621, 1596, 1514, 1346, 1177, 1144, 1117, 816, 748 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{15}IONa$ $[M+Na]^+$ 397.0065, found 397.0062.



1c

1-(2-Bromo-4-methylphenyl)naphthalen-2-ol (**1c**)

Starting material = 2-bromo-1-iodo-4-methylbenzene. Yellow oil (0.39 g, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 2H), 7.66 (s, 1H), 7.38-7.29 (m, 3H), 7.28-7.23 (m, 2H), 7.22-7.17 (m, 1H), 4.86 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 141.0, 134.4, 133.2, 133.1, 132.2, 130.3, 129.5, 129.1, 128.4, 126.9, 126.1, 124.6, 123.7, 120.5, 117.7, 21.3. IR (KBr): 3535, 3058, 2925, 1620, 1597, 1514, 1391, 1310, 1269, 1174, 1144, 816, 746 cm^{-1}. HRMS (ESI) m/z calculated for $C_{17}H_{13}BrONa$ $[M+Na]^+$ 335.0047, found 335.0049.

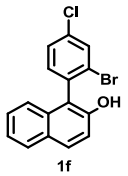


1e

1-(2-Bromo-4-(trifluoromethyl)phenyl)naphthalen-2-ol (**1e**)

Starting material = 2-bromo-1-iodo-4-(trifluoromethyl)benzene. White solid (0.50 g, 68% yield). Mp: 101-102 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.90-7.82 (m, 2H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.42-7.34 (m, 2H), 7.24 (d, *J* = 9.0 Hz, 1H), 7.16-7.08 (m, 1H), 4.77 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 140.2, 133.9, 132.6, 132.4, 130.9, 130.8, 130.8, 129.1, 128.5, 127.4, 126.7, 125.3, 125.2, 124.7, 124.2, 124.1, 122.0, 119.7, 117.9. IR (KBr): 3422, 3059, 2925, 1623, 1514, 1388, 1322,

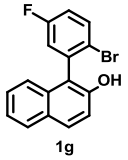
1174, 1134, 814, 749 cm^{-1}. HRMS (ESI) m/z calculated for $C_{17}H_{10}BrF_3ONa$ $[M+Na]^+$ 388.9765, found 388.9768.



1f

1-(2-Bromo-4-chlorophenyl)naphthalen-2-ol (**1f**)

Starting material = 2-bromo-4-chloro-1-iodobenzene. Yellow oil (0.47 g, 71% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.93-7.77 (m, 3H), 7.47 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.40-7.27 (m, 3H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.18-7.09 (m, 1H), 4.80 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 135.6, 134.5, 134.2, 133.6, 133.1, 130.8, 129.2, 128.9, 128.6, 127.3, 126.9, 124.4, 124.1, 119.8, 117.9. IR (KBr): 3540, 3059, 2925, 1623, 1512, 1466, 1392, 1343, 1270, 1174, 1148, 816, 748 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{10}BrClONa$ $[M+Na]^+$ 354.9501, found 354.9496.



1g

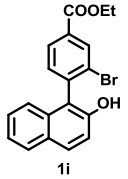
1-(2-Bromo-5-fluorophenyl)naphthalen-2-ol (**1g**)

Starting material = 1-bromo-4-fluoro-2-iodobenzene. White solid (0.41 g, 65% yield). Mp: 94-95 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.89-7.76 (m, 3H), 7.41-7.33 (m, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.20-7.10 (m, 3H), 4.80 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 161.3, 150.2, 137.9, 135.2, 135.1, 132.8, 130.8, 129.2, 128.6, 127.4, 124.4, 124.1, 120.6, 120.4, 119.9, 117.9, 117.7. IR (KBr): 3431, 3063, 2924, 1623, 1513, 1462, 1345, 1306, 1195, 882, 825 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{10}BrFONa$ $[M+Na]^+$ 338.9797, found 338.9801.

1h

1-(2-Bromo-4,5-difluorophenyl)naphthalen-2-ol (**1h**)

Starting material = 1,2-dibromo-4,5-difluorobenzene. White solid (0.46 g, 69% yield). Mp: 84-85 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.90-7.81 (m, 2H), 7.67 (dd, *J* = 9.6, 7.5 Hz, 1H), 7.42-7.34 (m, 2H), 7.27-7.21 (m, 2H), 7.19-7.12 (m, 1H), 4.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 151.7, 151.6, 151.5, 150.3, 149.3, 149.2, 149.0, 132.9, 131.0, 129.2, 128.6, 127.5, 124.2, 122.8, 122.6, 121.9, 121.7, 120.1, 119.2, 117.8. IR (KBr): 3430, 3060, 1625, 1596, 1496, 1436, 1209, 1183, 1147, 818, 749 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_9BrF_2ONa$ $[M+Na]^+$ 356.9703, found 356.9707.

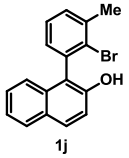


1i

Ethyl 3-bromo-4-(2-hydroxynaphthalen-1-yl)benzoate (**1i**)

Starting material = ethyl 3-bromo-4-iodobenzoate. White solid (0.38 g, 52% yield). Mp: 160-161 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 1.6 Hz, 1H), 8.15 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.89-7.82 (m, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.39-7.33 (m, 2H), 7.28-7.23 (m, 1H), 7.16-7.10 (m, 1H), 4.92 (s, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 150.2, 141.0, 134.7, 133.5,

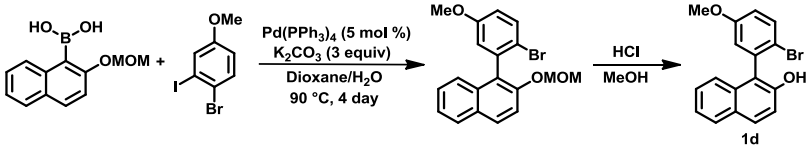
132.7, 132.4, 130.7, 129.3, 129.0, 128.4, 127.2, 126.4, 124.2, 123.9, 120.0, 118.0, 62.0, 14.6. IR (KBr): 3422, 3061, 2926, 1705, 1623, 1599, 1437, 1284, 1245, 818, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{19}H_{15}BrO_3Na$ $[M+Na]^+$ 393.0102, found 393.0099.



1j

1-(2-Bromo-3-methylphenyl)naphthalen-2-ol (**1j**)

Starting material = 2-bromo-1-iodo-3-methylbenzene. White solid (0.35 g, 56% yield). Mp: 99-100 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87-7.80 (m, 2H), 7.40 (d, *J* = 5.0 Hz, 2H), 7.36-7.32 (m, 2H), 7.28-7.24 (m, 1H), 7.22-7.16 (m, 2H), 4.84 (s, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 140.1, 135.6, 132.8, 131.3, 130.5, 129.9, 128.8, 128.5, 128.1, 128.0, 126.7, 124.4, 123.5, 121.2, 117.5, 24.1. IR (KBr): 3520, 3488, 3422, 1619, 1592, 1511, 1459, 1382, 1313, 1191, 1028, 813, 782 743 cm^{-1}. HRMS (ESI) m/z calculated for $C_{17}H_{13}BrONa$ $[M+Na]^+$ 335.0047, found 335.0044.

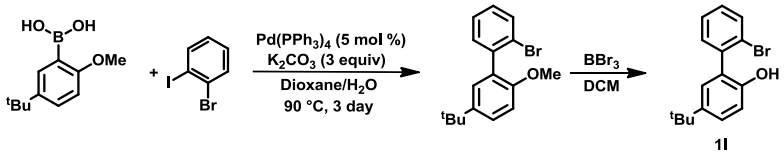


1d

1-(2-Bromo-5-methoxyphenyl)naphthalen-2-ol (**1d**)

A 25 mL round bottom flask with a stirring bar is fitted with a rubber septum and flame dried under high vacuum. The flask is purged with argon and charged with $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol), K_2CO_3 (0.83 g, 6.0 mmol), (2-(methoxymethoxy)naphthalen-1-yl)boronic acid (0.70 g, 3.0 mmol), 1-bromo-2-iodo-4-methoxybenzene (0.63 g, 2.0 mmol), 8.0 mL deoxygenated 1,4-dioxane, and 2.0 mL deoxygenated water. The reaction mixture was then heated at 90 ℃ for 4 days. After the reaction cooled down to room temperature, the organic layer was extracted with ethyl acetate (15.0 mL × 3), dried over $MgSO_4$ and concentrated. The residue was subjected to a plug of silica, eluted with hexane/EtOAc (100/1) to afford the desired compound.

The above compound was dissolved in MeOH (20.0 mL), warmed to 60 ℃ and conc. HCl aq. (35%, 3 drops) was added. After stirring for 3.0 h, 40.0 mL of distilled water was added and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to give a crude mixture, which was purified by column chromatography (PE/EtOAc = 20/1) to afford **1d** as a white solid (0.40 g, 61% yield). Mp: 94-95 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (t, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.40-7.31 (m, 2H), 7.30-7.20 (m, 2H), 7.01-6.89 (m, 2H), 4.87 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 150.2, 136.3, 134.6, 132.9, 130.4, 129.0, 128.4, 127.1, 124.6, 123.8, 120.6, 118.2, 117.8, 117.0, 116.4, 55.9. IR (KBr): 3468, 3051, 2938, 1745, 1651, 1619, 1512, 1460, 1207, 1020, 810, 744, 616 cm^{-1}. HRMS (ESI) m/z calculated for $C_{17}H_{13}BrO_2Na$ $[M+Na]^+$ 350.9997, found 351.0000.



1l

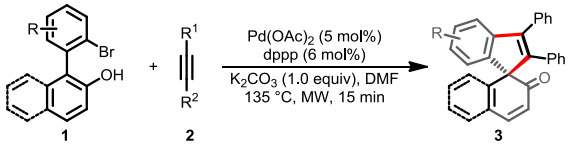
2'-Bromo-5-(tert-butyl)-[1,1'-biphenyl]-2-ol (**1l**)

A 25 mL round bottom flask with a stirring bar is fitted with a rubber septum and flame dried under high vacuum. The flask is purged with argon and charged with $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol), K_2CO_3 (0.83 g, 6.0 mmol), (5-(tert-butyl)-2-methoxyphenyl)boronic acid (0.62 g, 3.0 mmol), 1-bromo-2-iodobenzene (0.57 g, 2.0 mmol), 8.0 mL deoxygenated 1,4-dioxane, and 2.0 mL deoxygenated water. The reaction mixture was then heated at 90 ℃ for 3 days. After the reaction cooled down to room temperature, extracted with ethyl acetate

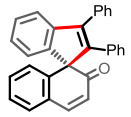
(15.0 mL × 3), dried over $MgSO_4$ and concentrated. The residue was subjected to a plug of silica, eluted with hexane/EtOAc (100/1) to afford the desired compound.

A solution of BBr_3 (3.0 equiv) in CH_2Cl_2 (1.0 mL) was slowly added to a solution of the above compound in CH_2Cl_2 (10.0 mL) at 0 ℃ and the mixture was stirred for 3 h at room temperature. After cooled to 0 ℃, the reaction was quenched with ice cold H_2O and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel to afford the desired product **1l** as Yellow oil (0.48 g, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.44-7.35 (m, 2H), 7.33 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.30-7.24 (m, 1H), 7.16 (d, *J* = 2.5 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 4.62 (s, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 143.2, 138.2, 133.4, 132.1, 129.7, 127.9, 127.7, 126.9, 126.6, 124.5, 115.2, 34.2, 31.6. IR (KBr): 3533, 3435, 3056, 2960, 2868, 1502, 1469, 1228, 1175, 1021, 822, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{17}BrONa$ $[M+Na]^+$ 327.0360, found 327.0359.

C. Catalytic results:



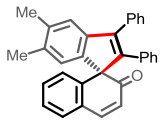
Microwave irradiation conditions (Method A): In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), dppp (4.9 mg, 0.012 mmol), K_2CO_3 (27.6 mg, 0.20 mmol) and DMF (1.2 mL). After the mixture was stirred for 5 min, alkyne (0.30 mmol) and 1-aryl-2-naphthol (0.20 mmol) were sequentially added. The vial was sealed with a Teflon screw cap and exposed to microwave irradiation at 135 ℃ for 15 min. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product.



3a

2,3-Diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (3a)

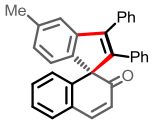
White solid (74.5 mg, 94% yield for **1a**; 73.0 mg, 92% yield for **1a'**). The spectroscopic data is consistent with that reported in the literature.[14]



3b

5,6-Dimethyl-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (3b)

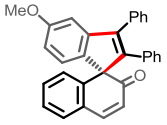
Yellow solid (76.4 mg, 90% yield for **1b**; 67.9 mg, 80% yield for **1b'**). Mp: 169-170 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 9.9 Hz, 1H), 7.52 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.4-7.34 (m, 4H), 7.25 (td, *J* = 7.5, 1.2 Hz, 1H), 7.15 (td, *J* = 7.6, 1.3 Hz, 1H), 7.04 (s, 1H), 7.01-6.90 (m, 4H), 6.84-6.78 (m, 2H), 6.76 (s, 1H), 6.39 (d, *J* = 9.9 Hz, 1H), 2.19 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 146.4, 145.7, 144.9, 144.5, 143.5, 141.8, 136.4, 135.7, 135.1, 134.7, 130.9, 130.1, 129.7, 129.2, 129.1, 128.1, 128.0, 127.6, 127.2, 127.02, 126.8, 123.2, 123.1, 71.6, 20.3, 20.3. IR (KBr): 3046, 2923, 1663, 1446, 1393, 872, 757, 760, 699 cm^{-1}. HRMS (ESI) m/z calculated for $C_{32}H_{24}ONa$ $[M+Na]^+$ 447.1725, found 447.1730.



3c

5-Methyl-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3c**)

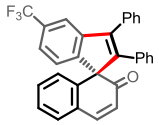
Yellow solid (74.7 mg, 91% yield). Mp: 84-85 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 9.9 Hz, 1H), 7.55-7.50 (m, 2H), 7.49-7.37 (m, 4H), 7.28-7.22 (m, 2H), 7.16 (td, *J* = 7.6, 1.3 Hz, 1H), 7.08 (s, 1H), 7.01-6.94 (m, 4H), 6.90-6.86 (m, 2H), 6.84-6.80 (m, 2H), 6.39 (d, *J* = 9.9 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8, 145.1, 144.5, 144.1, 143.8, 143.6, 140.3, 136.6, 134.2, 133.3, 129.6, 128.8, 128.5, 128.5, 128.0, 127.8, 126.8, 126.7, 126.4, 126.0, 125.9, 125.8, 125.5, 121.5, 120.3, 70.3, 20.5. IR (KBr): 3056, 2918, 1664, 1470, 1394, 1263, 1236, 872, 744, 699 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{22}ONa$ $[M+Na]^+$ 433.1568, found 433.1565.



3d

5-Methoxy-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3d**)

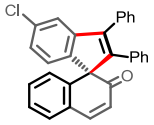
Yellow solid (75.9 mg, 89% yield). Mp: 90-91 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 9.9 Hz, 1H), 7.55-7.49 (m, 2H), 7.47-7.35 (m, 4H), 7.31-7.24 (m, 1H), 7.22-7.13 (m, 2H), 7.03-6.92 (m, 4H), 6.86-6.72 (m, 3H), 6.58 (d, *J* = 2.3 Hz, 1H), 6.39 (d, *J* = 9.9 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 158.9, 149.5, 146.5, 144.5, 143.3, 141.5, 138.5, 135.6, 134.7, 131.0, 130.2, 129.8, 129.7, 129.1, 129.0, 128.1, 128.0, 127.8, 127.2, 127.0, 126.7, 122.6, 112.7, 109.0, 71.6, 55.7. IR (KBr): 3053, 2934, 1664, 1597, 1482, 1306, 1280, 912, 742 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{22}O_2Na$ $[M+Na]^+$ 449.1517, found 449.1515.



3e

2,3-Diphenyl-5-(trifluoromethyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3e**)

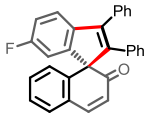
Yellow solid (83.6 mg, 90% yield). Mp: 191-192 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 9.9 Hz, 1H), 7.55-7.42 (m, 7H), 7.35-7.28 (m, 2H), 7.20 (td, *J* = 7.6, 1.3 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 7.06-6.97 (m, 3H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.87-6.76 (m, 2H), 6.41 (d, *J* = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 151.2, 147.2, 146.8, 146.5, 143.9, 140.0, 134.6, 133.9, 131.1, 130.5, 129.9, 129.6, 129.3, 129.3, 128.5, 128.3, 127.8, 127.1, 126.6, 125.8, 123.6, 122.2, 118.8, 118.7, 71.8. IR (KBr): 3050, 2925, 1666, 1433, 1350, 1165, 746, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{19}F_3ONa$ $[M+Na]^+$ 487.1286, found 487.1294.



3f

5-Chloro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3f**)

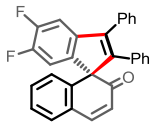
Yellow solid (73.2 mg, 85% yield). Mp: 147-148 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 9.9 Hz, 1H), 7.52-7.38 (m, 6H), 7.29 (td, *J* = 7.5, 1.1 Hz, 1H), 7.24 (d, *J* = 1.9 Hz, 1H), 7.19 (td, *J* = 7.6, 1.3 Hz, 1H), 7.06-6.88 (m, 6H), 6.85-6.76 (m, 2H), 6.39 (d, *J* = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 147.6, 147.0, 146.6, 146.1, 144.0, 140.6, 134.7, 134.1, 134.1, 131.1, 130.3, 129.8, 129.6, 129.3, 129.2, 128.4, 128.3, 128.1, 127.6, 127.1, 126.6, 126.4, 122.9, 122.2, 71.4. IR (KBr): 3056, 2927, 1666, 1457, 1395, 1165, 747, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{19}ClONa$ $[M+Na]^+$ 453.1022, found 453.1020.



3g

6-Fluoro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3g**)

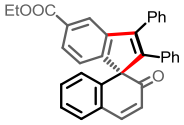
Yellow solid (72.9 mg, 88% yield). Mp: 53-54 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 9.9 Hz, 1H), 7.52-7.47 (m, 2H), 7.47-7.36 (m, 4H), 7.30 (td, *J* = 7.5, 1.1 Hz, 1H), 7.24-7.16 (m, 2H), 7.03-6.89 (m, 5H), 6.85-6.77 (m, 2H), 6.72 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.39 (d, *J* = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 163.1, 160.6, 149.5, 146.6, 145.0, 144.0, 141.6, 140.6, 135.1, 134.3, 131.1, 130.4, 129.8, 129.7, 129.2, 129.1, 128.2, 128.1, 127.3, 127.1, 126.6, 122.9, 122.9, 115.0, 114.7, 110.1, 109.9, 71.6. IR (KBr): 3057, 2925, 1666, 1596, 1474, 1306, 1258, 1200, 867, 810 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{19}FONa$ $[M+Na]^+$ 437.1318, found 437.1325.



3h

5,6-Difluoro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3h**)

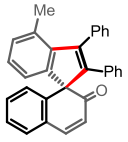
White solid (73.2 mg, 84% yield). Mp: 159-160 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 9.9 Hz, 1H), 7.52-7.37 (m, 6H), 7.31 (td, *J* = 7.5, 1.2 Hz, 1H), 7.21 (td, *J* = 7.6, 1.3 Hz, 1H), 7.10-6.92 (m, 5H), 6.88-6.76 (m, 3H), 6.38 (d, *J* = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 152.1, 150.6, 150.5, 149.6, 148.1, 148.0, 146.7, 143.3, 142.2, 140.2, 134.6, 134.0, 131.1, 130.5, 129.8, 129.5, 129.3, 129.2, 128.5, 128.3, 127.6, 127.1, 126.5, 111.6, 111.4, 110.8, 110.6, 71.3. IR (KBr): 3056, 2927, 1663, 1482, 1361, 1237, 875, 743, 700 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{18}F_2ONa$ $[M+Na]^+$ 455.1223, found 455.1218.



3i

Ethyl 2'-oxo-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalene]-5-carboxylate (**3i**)

Yellow solid (76.8 mg, 82% yield). Mp: 213-214 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.94 (d, *J* = 1.1 Hz, 1H), 7.78 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.69 (d, *J* = 9.9 Hz, 1H), 7.56-7.51 (m, 2H), 7.50-7.38 (m, 4H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 7.18 (td, *J* = 7.6, 1.3 Hz, 1H), 7.07-6.96 (m, 5H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.89-6.77 (m, 2H), 6.40 (d, *J* = 9.9 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 166.7, 152.5, 146.7, 146.4, 146.1, 144.3, 140.3, 134.8, 134.2, 131.1, 130.6, 130.4, 129.9, 129.7, 129.3, 129.2, 128.3, 128.3, 128.2, 127.6, 127.1, 126.7, 123.0, 121.8, 71.9, 61.3, 14.6. IR (KBr): 3055, 2925, 1716, 1665, 1444, 1247, 1098, 1025, 746, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{33}H_{24}O_3Na$ $[M+Na]^+$ 491.1623, found 491.1619.

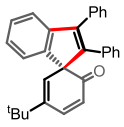


3j

4-Methyl-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (3j)

Yellow solid (57.5 mg, 70% yield). Mp: 183-184 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 9.9 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.48-7.36 (m, 6H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.98-6.88 (m, 3H), 6.86-6.81 (m, 1H), 6.77-6.73 (m, 2H), 6.39 (d, *J* = 9.9 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 147.7, 146.6, 146.1, 142.6, 141.5, 138.1, 134.3, 133.3, 131.1,

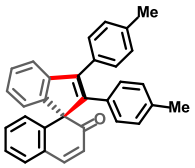
130.7, 130.0, 129.9, 129.6, 129.0, 128.8, 128.5, 127.8, 127.6, 127.5, 126.9, 126.8, 126.6, 126.2, 119.5, 71.2, 20.2. IR (KBr): 3056, 2955, 2922, 1661, 1443, 1234, 1194, 1026, 781, 753, 724, 684 cm^{-1}. HRMS (ESI) m/z calculated for $C_{31}H_{22}ONa$ $[M+Na]^+$ 433.1568, found 433.1568.



3l

3-(Tert-butyl)-2',3'-diphenylspiro[cyclohexa[2,4]diene-1,1'-inden]-6-one (3l)

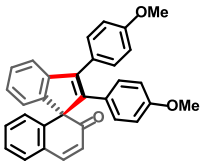
Yellow solid (6.4 mg, 8% yield). Mp: 83-84 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.35 (m, 6H), 7.30-7.27 (m, 2H), 7.19-7.07 (m, 5H), 7.02 (dd, *J* = 6.6, 3.2 Hz, 2H), 6.31 (d, *J* = 10.2 Hz, 1H), 5.96 (d, *J* = 2.4 Hz, 1H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 146.8, 144.5, 144.4, 144.1, 143.7, 142.4, 135.2, 135.0, 133.7, 129.7, 129.0, 128.9, 128.3, 128.2, 128.0, 127.8, 127.5, 126.5, 122.0, 121.9, 70.5, 34.7, 29.1. IR: 3054, 2958, 2925, 1665, 1635, 1480, 1221, 785. HRMS (ESI) m/z calculated for $C_{30}H_{26}ONa$ $[M+Na]^+$ 425.1881, found 425.1875.



3b'

2,3-Di-p-tolyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (3b')

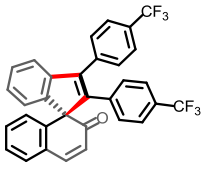
Yellow solid (78.9 mg, 93% yield). Mp: 79-80 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 9.9 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 3H), 7.29-7.12 (m, 6H), 6.99 (dt, *J* = 17.0, 7.8 Hz, 3H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.1 Hz, 2H), 6.40 (d, *J* = 9.9 Hz, 1H), 2.42 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 146.3, 145.1, 144.6, 143.5, 142.9, 140.3, 136.4, 135.6, 131.2, 130.4, 129.6, 128.8, 128.5, 128.3, 127.8, 127.7, 126.6, 126.4, 125.7, 125.5, 125.0, 120.7, 120.4, 76.3, 76.0, 75.7, 70.5, 20.4, 20.0. IR (KBr): 3057, 2926, 2854, 1666, 1617, 1596, 1474, 1444, 1260, 1200, 810, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{32}H_{24}ONa$ $[M+Na]^+$ 447.1725, found 447.1714.



3c'

2,3-Bis(4-methoxyphenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (3c')

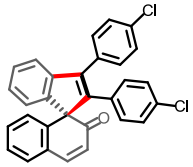
Yellow solid (73.0 mg, 80% yield). Mp: 64-65 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 9.9 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.32-7.09 (m, 4H), 7.04-6.93 (m, 5H), 6.83-6.76 (m, 2H), 6.53 (d, *J* = 8.9 Hz, 2H), 6.40 (d, *J* = 9.9 Hz, 1H), 3.87 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 159.4, 158.6, 147.6, 146.4, 146.0, 144.4, 143.1, 141.8, 131.0, 130.9, 130.6, 130.2, 129.9, 128.0, 127.8, 127.8, 127.3, 127.1, 126.8, 126.2, 121.8, 114.6, 113.7, 71.8, 55.5, 55.2. IR (KBr): 3062, 2958, 2837, 1664, 1612, 1509, 1461, 1250, 1180, 1032, 827, 741 cm^{-1}. HRMS (ESI) m/z calculated for $C_{32}H_{24}O_3Na$ $[M+Na]^+$ 479.1623, found 479.1631.



3d'

2,3-Bis(4-(trifluoromethyl)phenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3d'**)

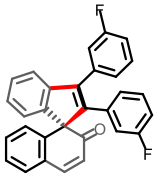
Yellow solid (100.1 mg, 94% yield). Mp: 183-184 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (t, *J* = 9.6 Hz, 3H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.49-7.45 (m, 1H), 7.35-7.24 (m, 5H), 7.20 (td, *J* = 7.6, 1.3 Hz, 1H), 7.15-7.10 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 3H), 6.41 (d, *J* = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 147.9, 146.8, 145.5, 144.9, 144.4, 140.2, 138.6, 137.8, 131.1, 130.5, 130.1, 129.9, 129.4, 128.34, 127.5, 127.0, 126.6, 126.3, 125.4, 122.2, 72.2. IR (KBr): 3068, 2930, 1666, 1617, 1327, 1169, 1125, 1070, 860, 824, 746 cm^{-1}. HRMS (ESI) m/z calculated for $C_{32}H_{18}F_6ONa$ $[M+Na]^+$ 555.1160, found 555.1171.



3e'

2,3-Bis(4-chlorophenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3e'**)

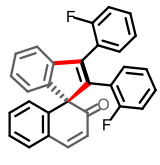
Yellow solid (80.9 mg, 87% yield). Mp: 108-109 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 9.9 Hz, 1H), 7.49-7.39 (m, 5H), 7.33-7.23 (m, 3H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.10-7.05 (m, 1H), 7.03-6.95 (m, 3H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 2H), 6.37 (d, *J* = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 147.8, 146.7, 144.9, 144.6, 144.3, 140.6, 134.2, 133.4, 133.3, 132.9, 131.1, 131.0, 130.5, 130.4, 129.9, 129.5, 128.6, 128.2, 128.1, 127.1, 127.0, 126.68, 122.1, 122.0, 72.0. IR (KBr): 3063, 2930, 1665, 1489, 1396, 1265, 1236, 1092, 820, 744 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{18}Cl_2ONa$ $[M+Na]^+$ 487.0632, found 487.0640.



3f'

2,3-Bis(3-fluorophenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3f'**)

Yellow solid (79.0 mg, 92% yield). Mp: 158-159 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 9.7 Hz, 1H), 7.50-7.39 (m, 2H), 7.35-7.23 (m, 4H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.15-7.07 (m, 2H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 6.8 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 7.0 Hz, 1H), 6.64 (d, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 10.3 Hz, 1H), 6.41 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 164.6, 163.7, 162.1, 161.3, 147.8, 146.7, 144.7, 144.6, 140.5, 137.0, 136.5, 131.1, 130.9, 130.8, 130.4, 129.9, 129.8, 128.2, 128.1, 127.1, 127.0, 126.7, 125.5, 125.1, 122.1, 122.1, 116.7, 116.5, 116.0, 115.8, 115.5, 115.3, 114.6, 114.4, 72.0. IR (KBr): 3067, 1664, 1613, 1581, 1482, 1436, 1225, 950, 823, 700 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{18}F_2ONa$ $[M+Na]^+$ 455.1223, found 455.1226.

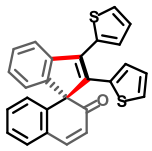


3g'

(R)-2,3-Bis(2-fluorophenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3g'**)

Yellow solid (77.3 mg, 90% yield). Mp: 70-71 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 9.9 Hz, 1H), 7.37-7.29 (m, 3H), 7.29-7.20 (m, 3H), 7.20-7.14 (m, 2H), 7.14-7.08 (m, 2H), 7.07-6.98 (m, 3H), 6.95 (td, *J* = 7.6, 1.7 Hz, 1H), 6.86-6.79 (m, 1H), 6.77-6.69 (m, 1H), 6.37 (d, *J* = 9.9 Hz, 1H). ^{13}C NMR (100

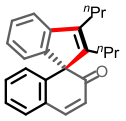
MHz, $CDCl_3$): δ 196.7, 161.6, 161.0, 159.1, 158.5, 148.1, 146.4, 144.4, 139.8, 130.7, 130.5, 130.2, 130.2, 129.9, 129.7, 129.6, 128.1, 127.9, 127.7, 126.9, 126.7, 124.4, 123.8, 123.8, 122.8, 122.6, 122.2, 116.0, 115.8, 73.0. IR (KBr): 3065, 1665, 1486, 1452, 1265, 1226, 822 and 757 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{18}F_2ONa$ $[M+Na]^+$ 455.1223, found 455.1227.



3h'

2,3-Di(thiophen-2-yl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (3h')

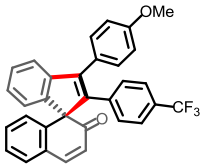
Yellow solid (74.3 mg, 91% yield). Mp: 82-83 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 9.9 Hz, 1H), 7.58 (d, *J* = 4.3 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.38-7.16 (m, 6H), 7.09-6.92 (m, 4H), 6.72 (dd, *J* = 4.9, 3.9 Hz, 1H), 6.49-6.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1, 146.5, 145.4, 142.0, 141.3, 136.8, 136.4, 134.5, 131.2, 130.3, 129.6, 128.9, 128.4, 128.2, 128.1, 127.7, 127.1, 127.0, 126.9, 126.7, 126.5, 122.1, 121.6, 71.8. IR (KBr): 3067, 2926, 1457, 1395, 1236, 1118, 831, 743, 703 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{16}OS_2Na$ $[M+Na]^+$ 431.0540, found 431.0544.



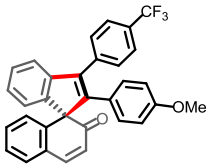
3i'

2,3-Dipropyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (3i')

Yellow solid (55.2 mg, 84% yield). Mp: 88-89 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 9.9 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 10.1 Hz, 3H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.97 (q, *J* = 7.0 Hz, 1H), 6.83 (d, *J* = 7.1 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 6.35 (d, *J* = 10.1 Hz, 1H), 2.62 (t, *J* = 6.9 Hz, 2H), 2.29-2.17 (m, 1H), 2.04 (d, *J* = 7.1 Hz, 1H), 1.73 (dd, *J* = 13.0, 6.1 Hz, 2H), 1.14 (d, *J* = 7.5 Hz, 2H), 1.05 (t, *J* = 6.6 Hz, 3H), 0.76 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 149.0, 147.3, 146.5, 146.0, 142.5, 141.3, 130.2, 129.77, 127.6, 127.0, 125.5, 121.9, 119.9, 71.2, 30.0, 27.9, 22.4, 14.9, 14.6. IR (KBr): 3064, 2956, 2932, 2870, 1664, 1463, 1237, 1203, 825, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{24}ONa$ $[M+Na]^+$ 351.1725, found 351.1716.



3j'-1



3j'-2

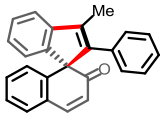
Compounds **3j'** was isolated as a regioisomeric mixture of **3j'-1** and **3j'-2** (rr = 1:1) in 90% yield (87.1 mg) by silica gel column chromatography with hexane/EtOAc (20/1). The pure analytical samples of **3j'-1** and **3j'-2** were obtained by preparative TLC on silica gel**.**

3-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (3j'-1)

White solid. Mp: 102-103 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 9.9 Hz, 1H), 7.48-7.39 (m, 3H), 7.34-7.22 (m, 6H), 7.20-7.15 (m, 1H), 7.08 (td, *J* = 7.4, 1.1 Hz, 1H), 7.02-6.91 (m, 5H), 6.40 (d, *J* = 9.9 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 159.6, 147.6, 146.4, 145.0, 142.6, 140.7, 138.3, 130.9, 130.7, 130.4, 130.2, 129.6, 129.2, 128.0, 127.9, 126.9, 126.7, 126.7, 126.5, 125.0, 124.9, 122.3, 121.7, 114.5, 71.6, 55.3. IR (KBr): 3063, 2925, 2847, 1665, 1613, 1507, 1459, 1325, 1245, 1168, 1117, 1070, 847, 820, 753 cm^{-1}. HRMS (ESI) m/z calculated for $C_{33}H_{21}F_3O_2Na$ $[M+Na]^+$ 517.1391, found 517.1400.

2-(4-Methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (3j'-2)

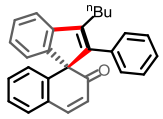
White solid. Mp: 92-93 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.60 (m, 5H), 7.47-7.39 (m, 1H), 7.28 (td, *J* = 7.5, 1.1 Hz, 1H), 7.25-7.15 (m, 3H), 7.08-7.03 (m, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.96-6.90 (m, 1H), 6.78-6.69 (m, 2H), 6.59-6.50 (m, 2H), 6.39 (d, *J* = 9.9 Hz, 1H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 158.7, 147.4, 146.4, 146.2, 144.9, 141.8, 140.9, 139.3, 130.8, 130.4, 130.1, 129.7, 127.9, 127.8, 126.9, 126.5, 126.3, 126.2, 125.9, 125.9, 125.9, 121.8, 121.3, 113.7, 71.8, 55.1. IR (KBr): 3065, 2927, 2844, 1664, 1610, 1510, 1459, 1323, 1251, 1170, 1122, 1065, 1027, 909, 827, 735 cm^{-1}. HRMS (ESI) m/z calculated for $C_{33}H_{21}F_3O_2Na$ $[M+Na]^+$ 517.1391, found 517.1401.



3k'

3-Methyl-2-phenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3k'**)

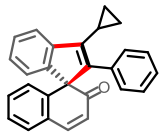
Compounds **3k'** was isolated as a regioisomeric mixture (rr = 3:1) in 95% yield (63.5 mg) by silica gel column chromatography with hexane/EtOAc (20/1). The spectroscopic data of the major regioisomer is consistent with that reported in the literature.[14]



3l'

3-Butyl-2-phenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (3l')

Compounds **3l'** was isolated as a regioisomeric mixture (rr = 3:1) in 93% yield (70.0 mg) by silica gel column chromatography with hexane/EtOAc (20/1). The pure analytical sample of the major regioisomer of **3l'** was obtained by preparative TLC on silica gel**.** Yellow solid. Mp: 162-163 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 9.9 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.35-7.21 (m, 4H), 7.20-7.11 (m, 3H), 7.06 (td, *J* = 7.5, 0.7 Hz, 1H), 6.99-6.91 (m, 3H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.27 (d, *J* = 9.9 Hz, 1H), 2.72 (t, *J* = 7.9 Hz, 1H), 1.82-1.65 (m, 1H), 1.44 (dd, *J* = 14.7, 7.4 Hz, 1H), 0.92 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 147.4, 145.0, 144.9, 144.0, 143.4, 139.7, 134.2, 129.3, 129.0, 128.6, 127.7, 127.0, 126.6, 126.4, 126.2, 126.1, 125.6, 125.0, 120.9, 119.7, 71.1, 30.1, 25.1, 21.8, 12.9. IR (KBr): 3055, 2952, 2922, 2857, 1660, 1444, 1393, 1235, 1198, 1025, 755, 732, 693 cm^{-1}. HRMS (ESI) m/z calculated for $C_{28}H_{24}ONa$ $[M+Na]^+$ 399.1725, found 399.1729.



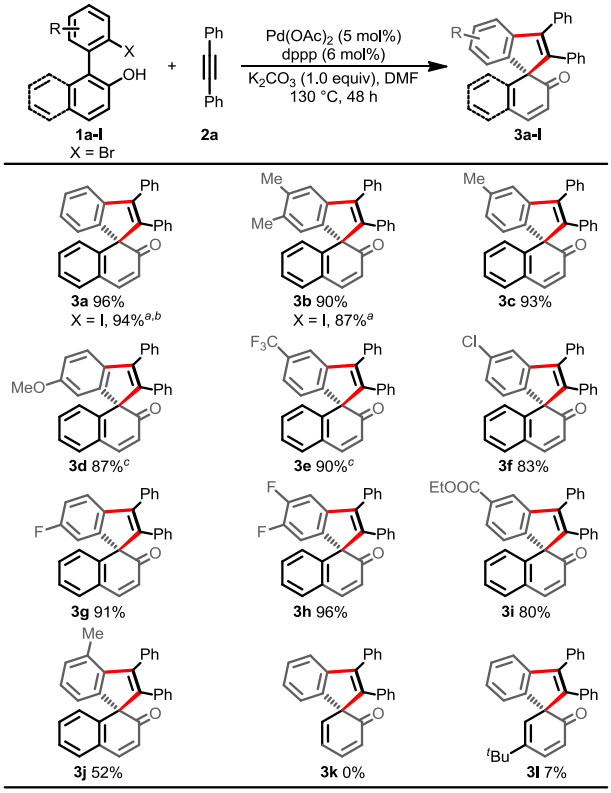
3m'

3-Cyclopropyl-2-phenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (3m')

Compounds **3m'** was isolated as a regioisomeric mixture (rr = 3:1) in 84% yield (60.5 mg) by silica gel column chromatography with hexane/EtOAc (20/1). The pure analytical sample of the major regioisomer of **3m'** was obtained by preparative TLC on silica gel**.** Yellow solid (43.2 mg, 60% yield). Mp: 158-159 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 8.7, 6.0 Hz, 2H), 7.37 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.28 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.20-7.09 (m, 6H), 7.02 (td, *J* = 7.5, 1.0 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.30 (d, *J* = 9.9 Hz, 1H), 2.06-1.97 (m, 1H), 1.03-0.93 (m, 2H), 0.71-0.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 147.8, 146.1, 146.1, 145.7, 144.6, 141.3, 134.8, 130.5, 129.8, 129.1, 127.8, 127.7, 127.4, 127.1, 126.9, 126.6, 126.0, 121.5, 121.42, 71.6, 9.0, 7.5. IR (KBr): 3062, 3004, 1657, 1617, 1592, 1556, 1457, 1391, 1200, 1024, 817, 750, 690 cm^{-1}. HRMS (ESI) m/z calculated for $C_{27}H_{20}ONa$ $[M+Na]^+$ 383.1412, found 383.1410.

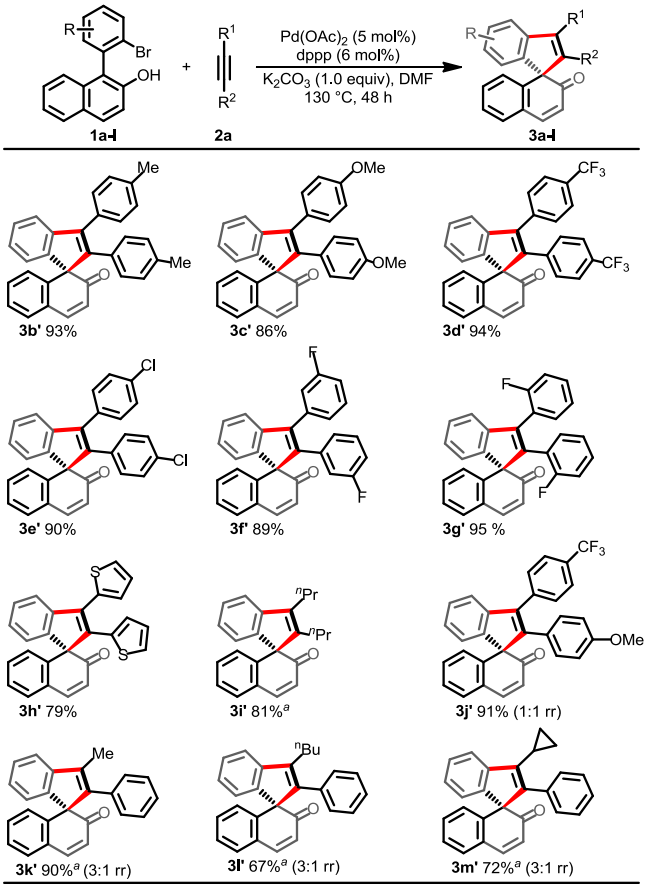
Thermal conditions (Method B): In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), dppp (4.9 mg, 0.012 mmol), K_2CO_3 (27.6 mg, 0.20 mmol) and DMF (1.2 mL). After the mixture was stirred for 5 min, alkyne (0.30 mmol) and 1-aryl-2-naphthol (0.20 mmol) were sequentially added. The vial was sealed with a Teflon screw cap and was heated at 130 ℃ for 48 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product.

Table S1 Survey of the scope of the naphthol coupling partner

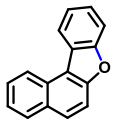


[a]1.0 equiv of $^nBu_4NCl$ was added. [b]2.0 equiv of K_2CO_3 was used.
[c]3.0 equiv of **2a** was used.

Table S2 Survey of the scope of the alkynes coupling partner



[a]3.0 equiv. of alkyne was used.

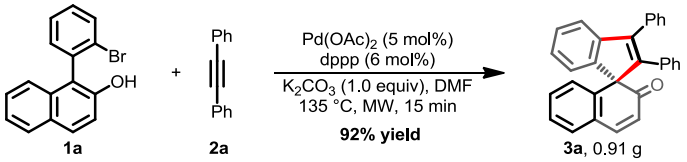


4a

Naphtho[2,1-b]benzofuran (**4a**)

The spectroscopic data is consistent with that reported in the literature.[15]

D. Gram-scale preparation of 3a:



In a glovebox, a 20.0 mL vial equipped with a stirring bar was charged with $Pd(OAc)_2$ (28.0 mg, 0.13 mmol), dppp (62.4 mg, 0.15 mmol), K_2CO_3 (0.35 g, 2.5 mmol) and DMF (10.0 mL). After the mixture was stirred for 5 minutes, alkyne **2a** (0.67 g, 3.8 mmol) and 2-naphthol **1a** (0.75 g, 2.5 mmol) were sequentially added. The vial was sealed with a Teflon screw cap and exposed to microwave irradiation at 135 ℃ for 15 min. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel to afford 0.91 g of **3a** (92% yield).

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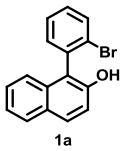
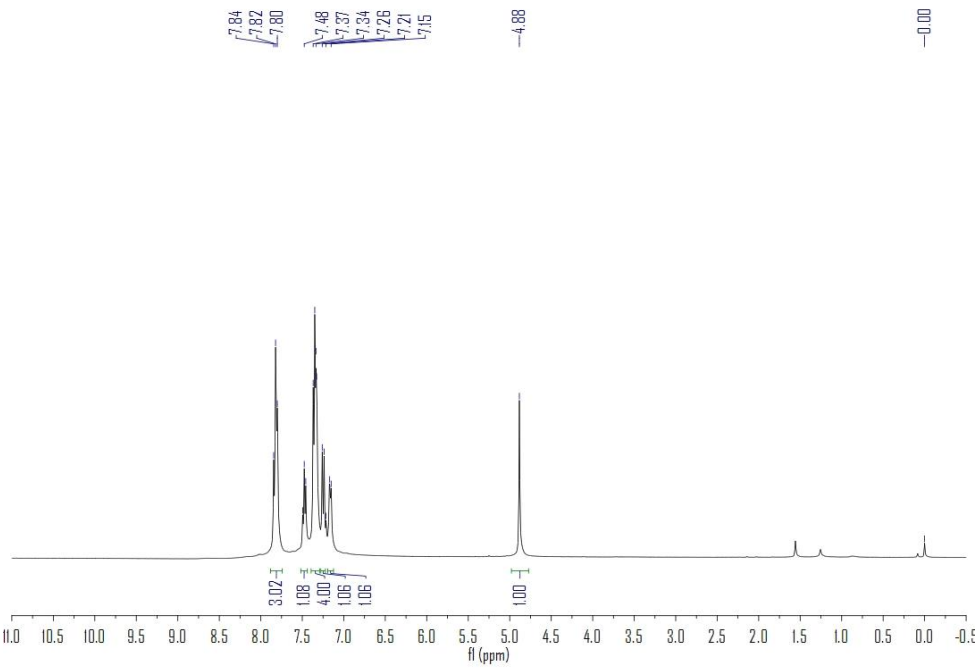
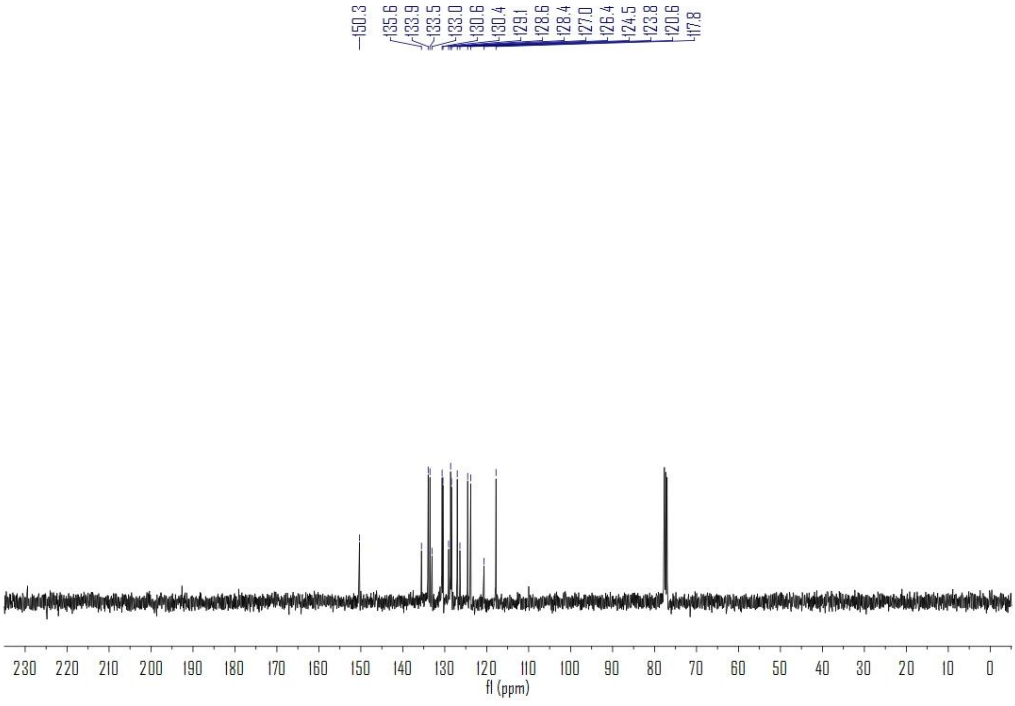
(15) C. S. Nervig, P. J. Waller and D. Kalyani, *Org. Lett.*, 2012, **14**, 4838.

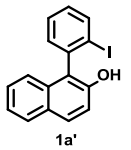
NMR spectra:



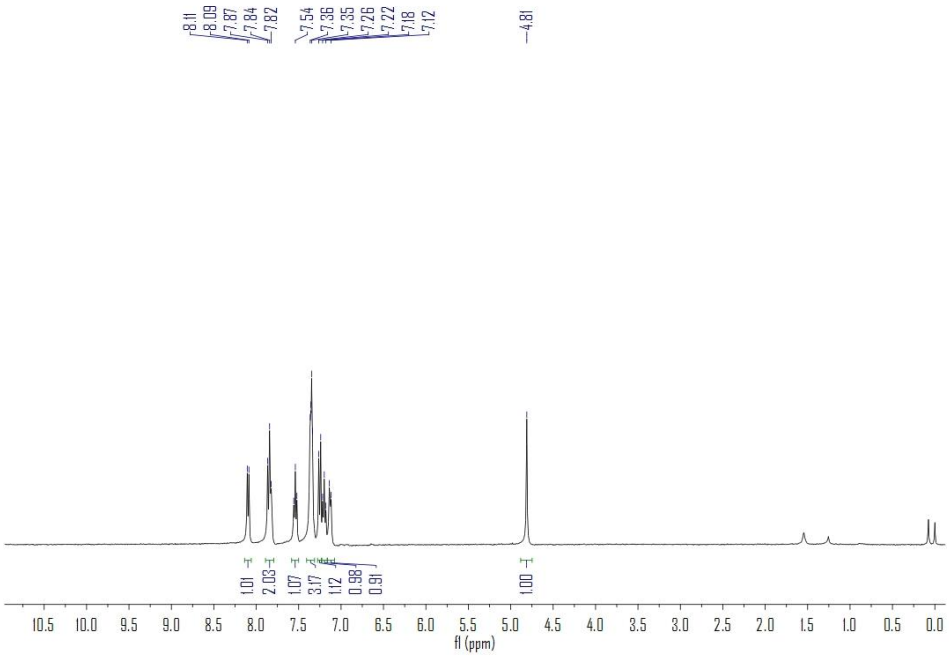
1a






I
OH

1a'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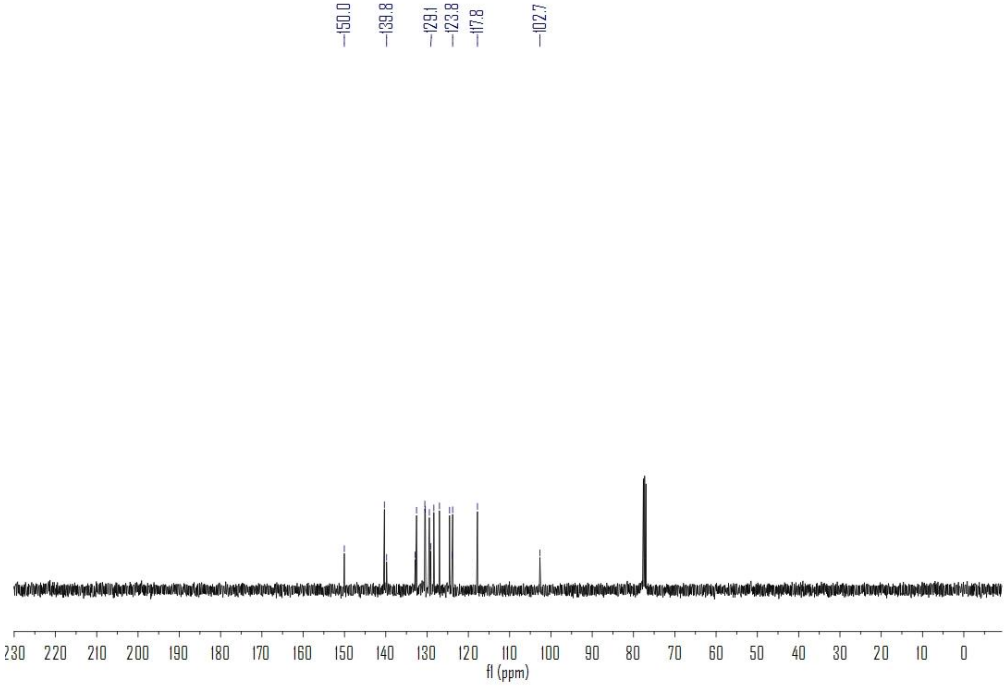
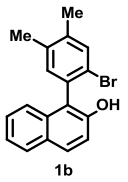
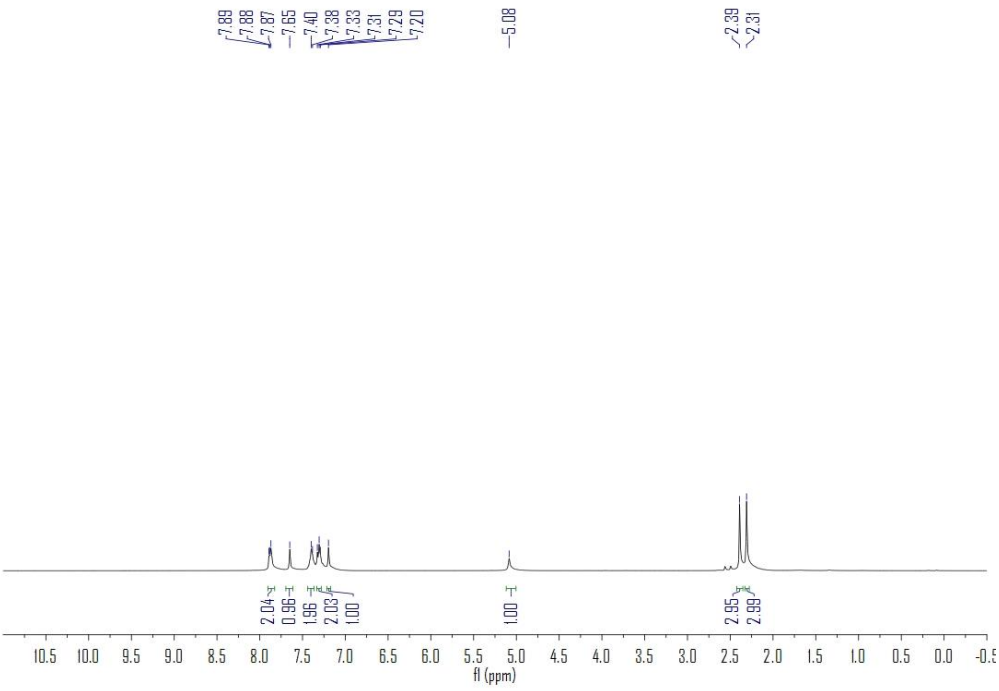
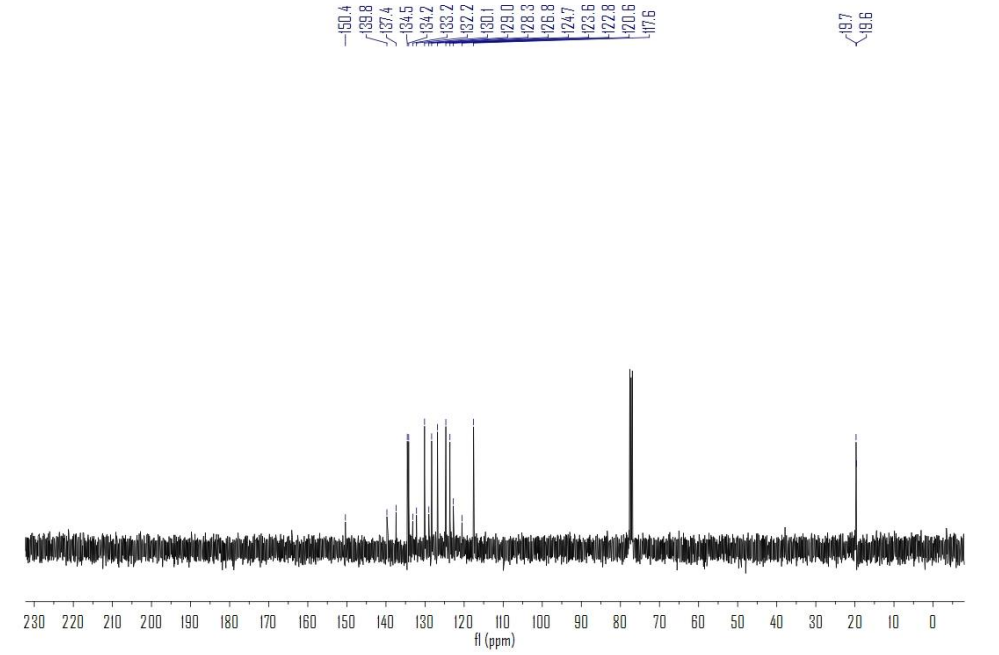
8.09
7.87
7.84
7.82
7.54
7.38
7.35
7.26
7.22
7.18
7.12
4.81
1.01
2.03
1.07
3.17
1.12
0.98
0.91
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

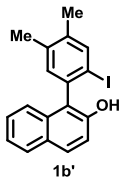

150.0
139.8
129.1
123.8
117.8
102.7
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
Me
Br
OH

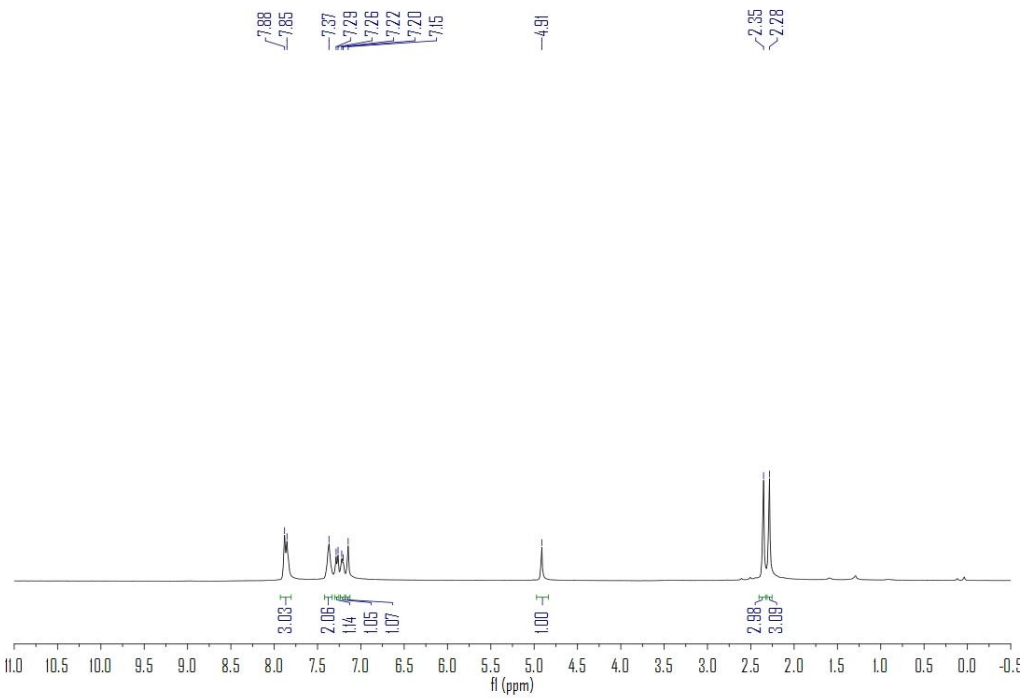
1b


7.89
7.88
7.87
7.65
7.40
7.38
7.33
7.31
7.29
7.20
5.08
2.39
2.31
2.04
0.96
1.96
2.03
1.00
1.00
2.95
2.99
f1 (ppm)


150.4
139.8
137.4
134.5
134.2
133.2
132.2
130.1
129.0
128.3
126.8
124.7
123.6
122.8
120.6
117.6
19.7
19.6
f1 (ppm)


Me
Me
I
OH

1b'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7.85
7.37
7.29
7.26
7.22
7.20
7.15
4.91
2.35
2.28
3.03
2.06
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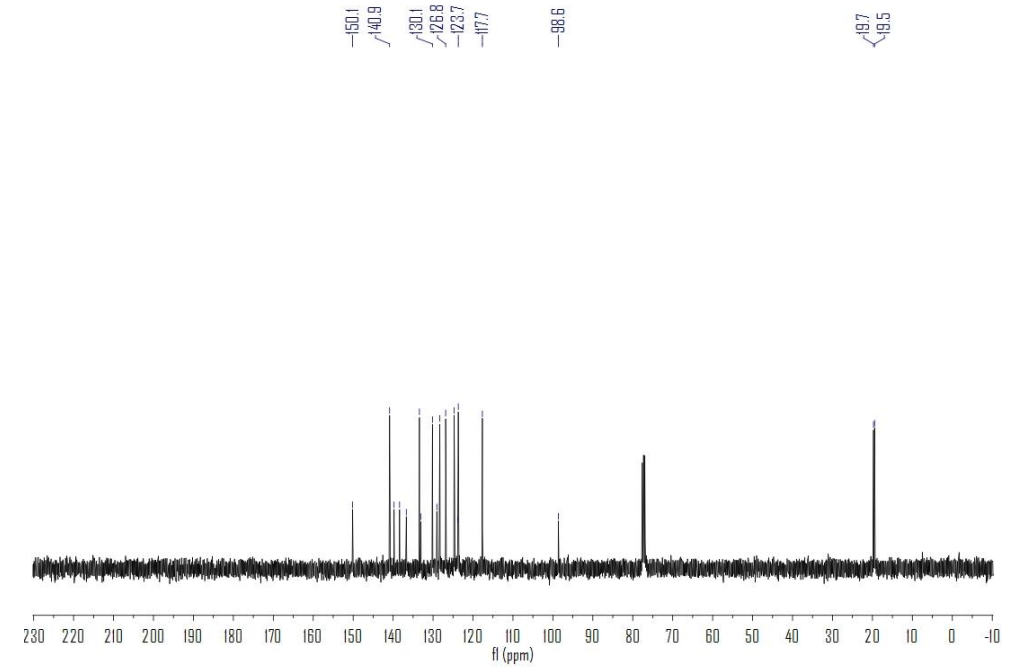
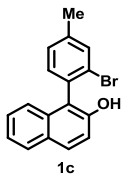
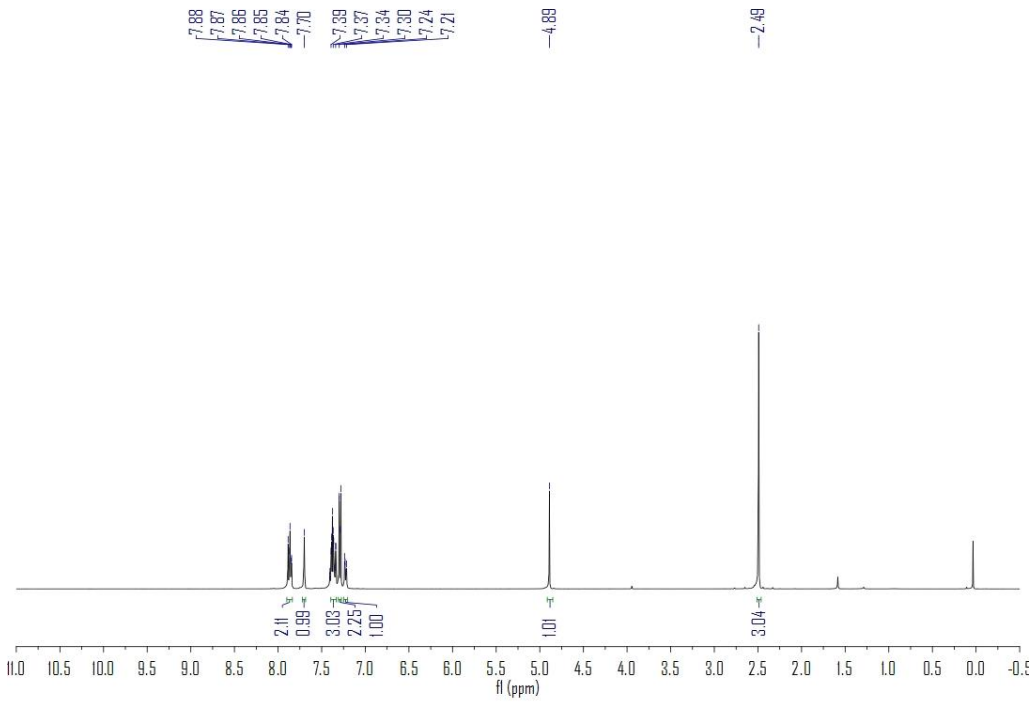
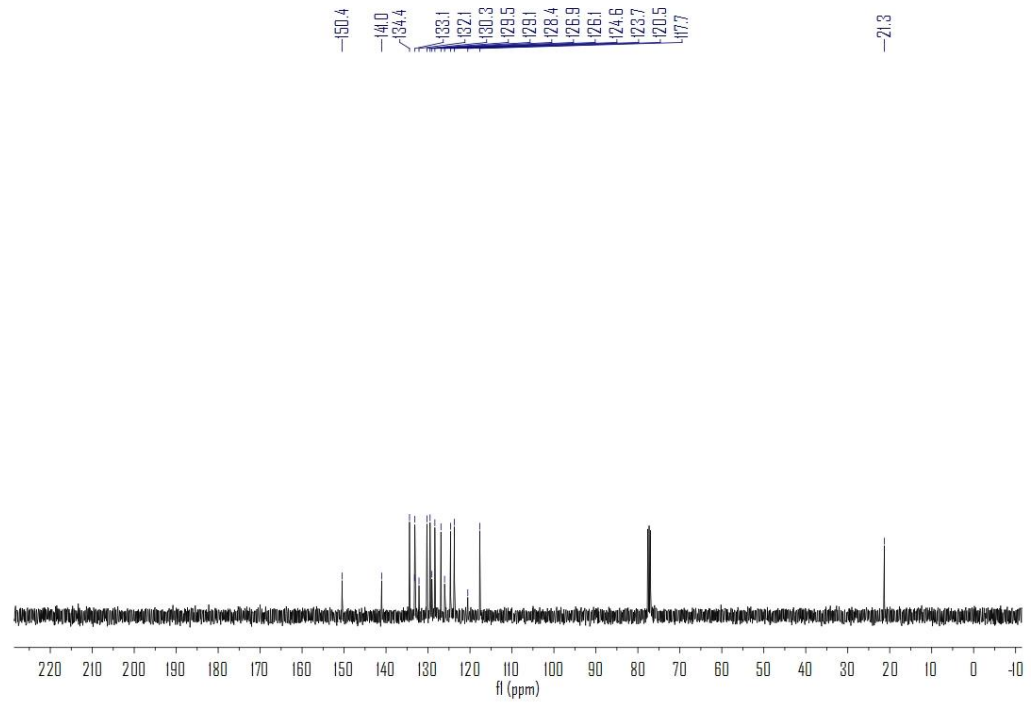
1.07
1.00
2.98
3.09
f1 (ppm)

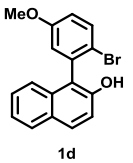

150.1
140.9
130.1
126.8
123.7
117.7
98.6
19.7
19.5
f1 (ppm)


Me
Br
OH

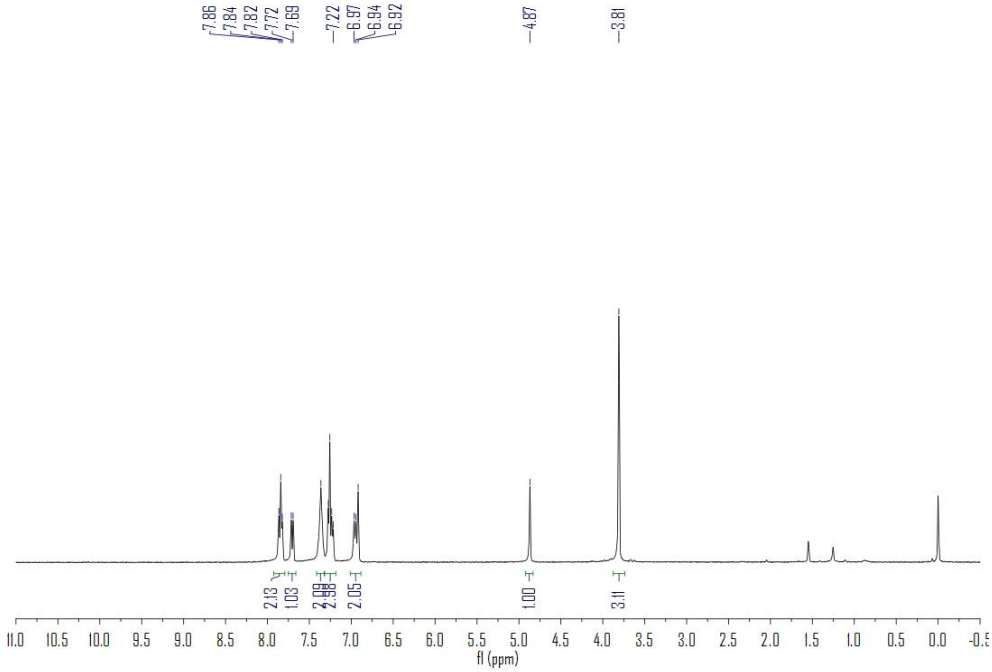
1c

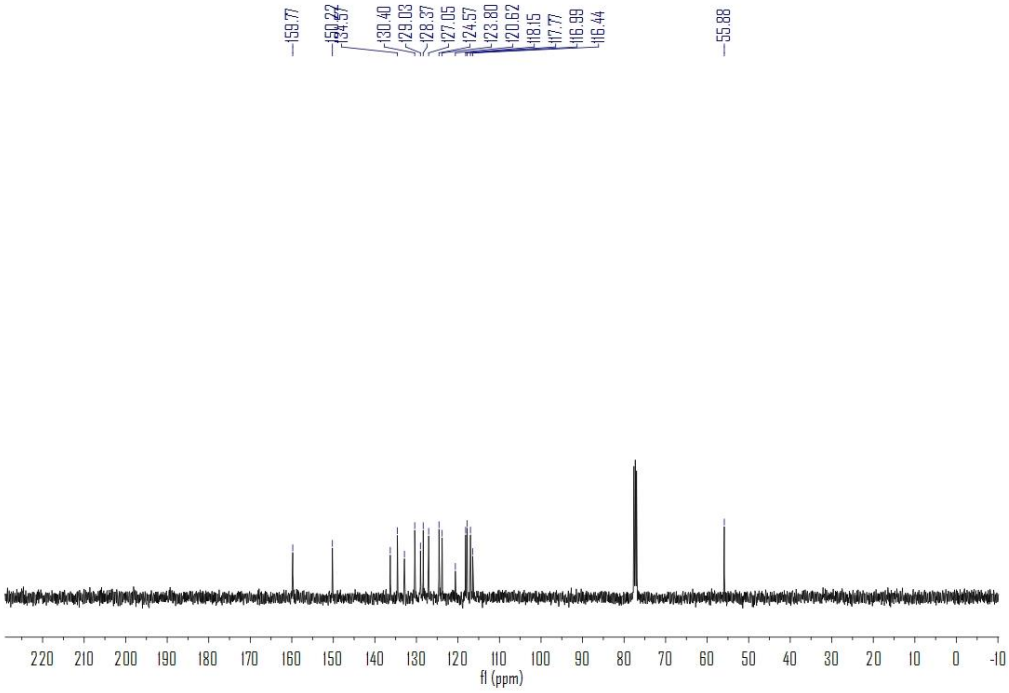

7.88
7.87
7.86
7.85
7.84
7.70
7.39
7.37
7.34
7.30
7.24
7.21
4.89
2.49
2.11
0.99
3.03
2.25
1.00
1.01
3.04
f1 (ppm)

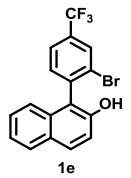

150.4
141.0
134.4
133.1
132.1
130.3
129.5
129.1
128.4
126.9
126.1
124.6
123.7
120.5
117.7
21.3
f1 (ppm)


MeO
Br
OH

1d

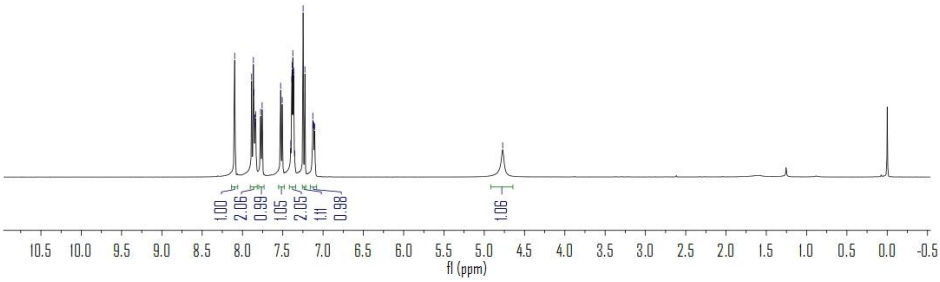

7.86
7.84
7.82
7.72
7.69
7.22
6.97
6.94
6.92
4.87
3.81
2.13
1.03
2.99
2.98
2.05
1.00
3.11
f1 (ppm)


159.77
150.22
134.37
130.40
129.03
128.37
127.05
124.57
123.80
120.62
118.15
117.77
116.99
116.44
55.88
f1 (ppm)

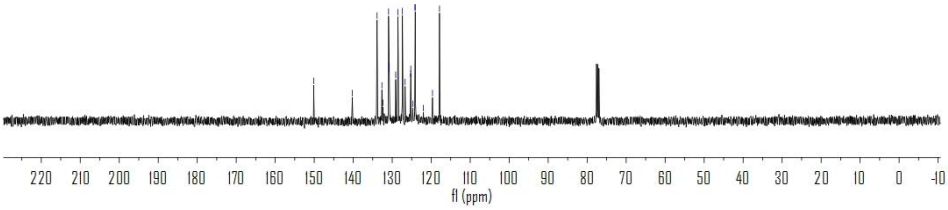

CF3
Br
OH

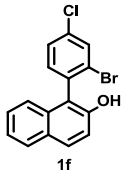
1e


7.84
7.84
7.78
7.76
7.53
7.51
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.25
7.22
7.13
7.12
7.12
7.12
7.10
4.77


1.00
2.06
0.99
1.05
2.05
1.11
0.98
1.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

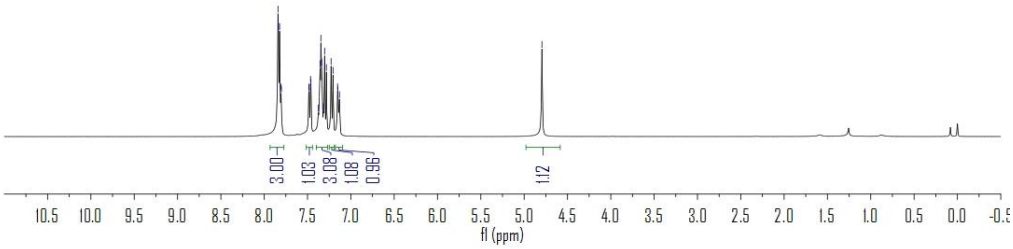

150.1
140.2
133.9
132.6
132.4
130.9
130.8
130.8
129.1
128.5
127.4
126.7
125.3
125.2
124.7
124.2
124.1
122.0
119.7
117.9


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

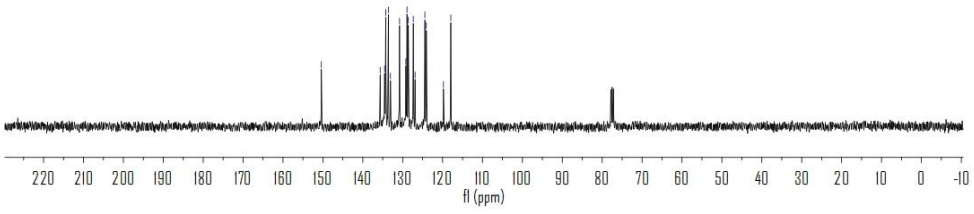

Cl
Br
OH

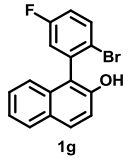
1f


7.84
7.84
7.82
7.81
7.80
7.46
7.35
7.34
7.30
7.23
7.15
7.13
4.80


3.00
1.03
3.08
1.08
0.96
1.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

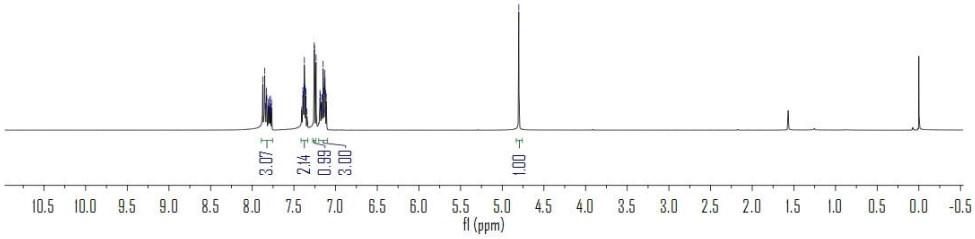

150.4
135.6
134.5
134.3
133.6
133.1
130.8
129.2
128.9
128.6
127.3
126.9
124.4
124.1
119.8
117.9


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

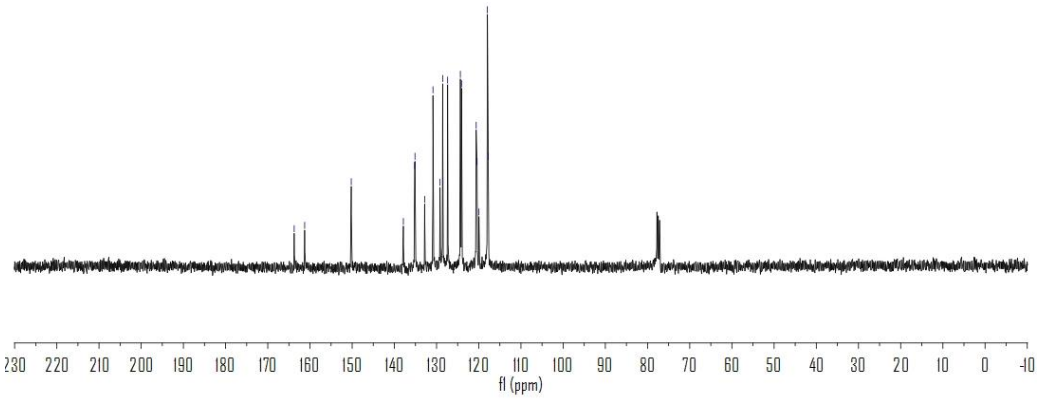

F
Br
OH

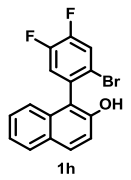
1g


7.85
7.83
7.83
7.81
7.81
7.80
7.79
7.79
7.79
7.78
7.78
7.78
7.77
7.39
7.36
7.19
7.17
7.14
7.13
4.80


3.07
2.14
0.99
3.00
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

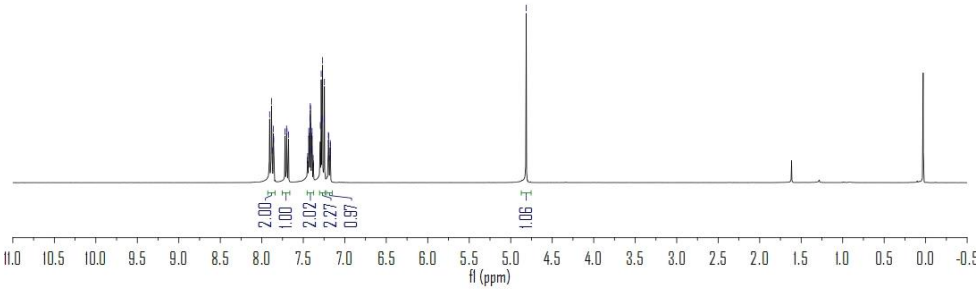

163.7
161.3
150.2
137.9
135.2
135.1
132.8
130.9
129.2
128.6
127.4
124.4
124.1
120.6
120.4
120.0
117.9
117.7

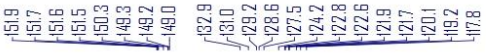

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

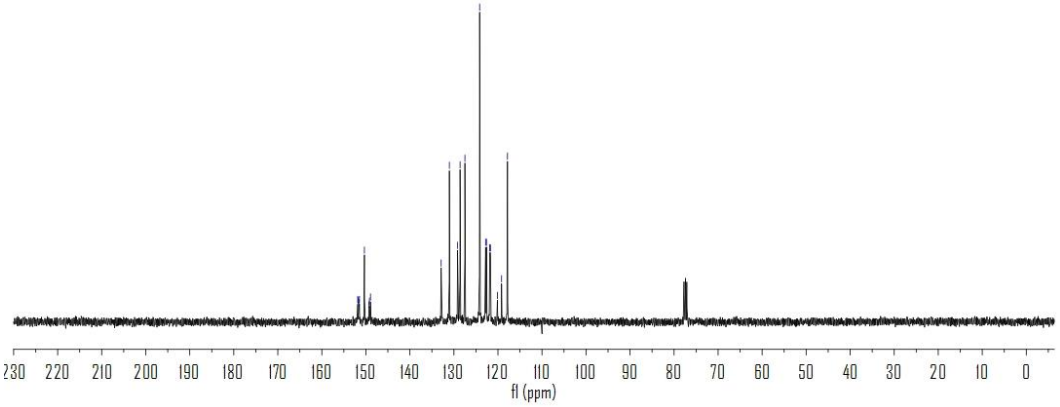

F
F
Br
OH

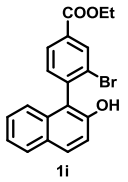
1h


7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.29
7.28
7.27
7.27
7.25
7.25
7.20
7.19
7.18
7.18
7.17
7.17
4.81

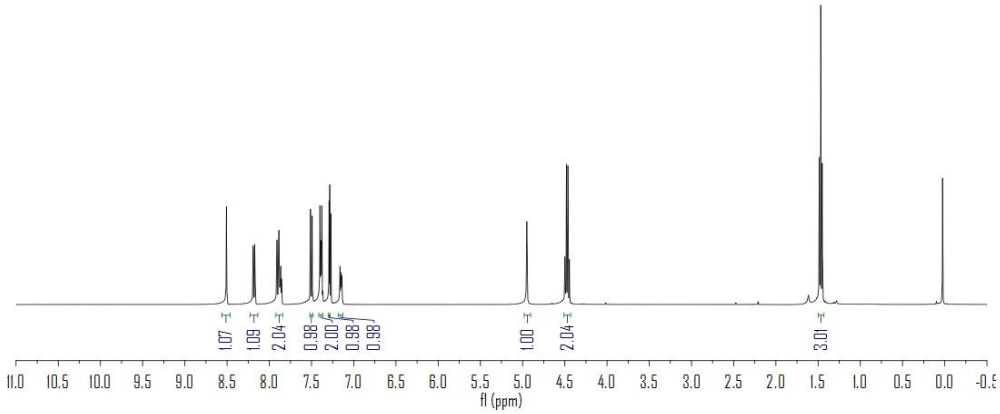

2.00
1.00
2.02
2.27
0.97
1.06
f1 (ppm)


151.9
151.7
151.6
151.5
150.3
149.3
149.2
149.0
132.9
131.0
129.2
128.6
127.5
124.2
122.8
122.6
121.9
121.7
120.1
119.2
117.8

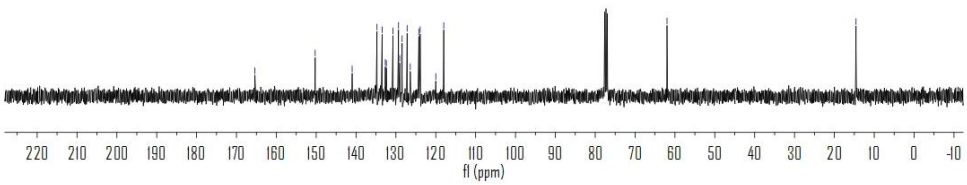

f1 (ppm)

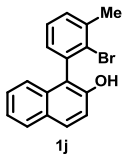

COOEt
Br
OH

1i

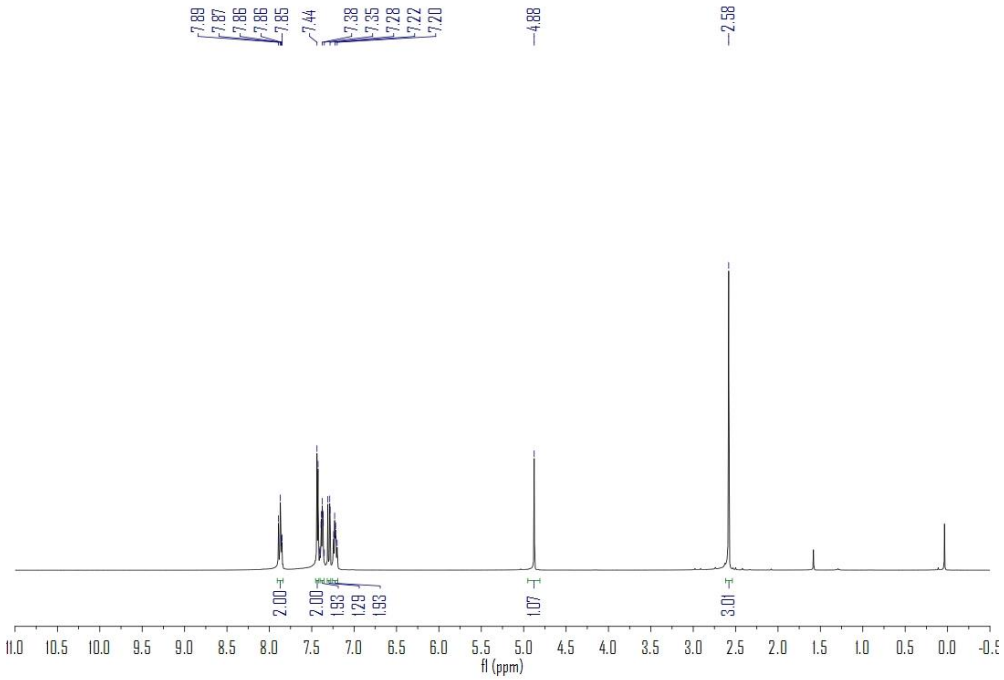

1.07
1.09
2.04
0.98
2.00
0.98
0.98
1.00
2.04
3.01
f1 (ppm)

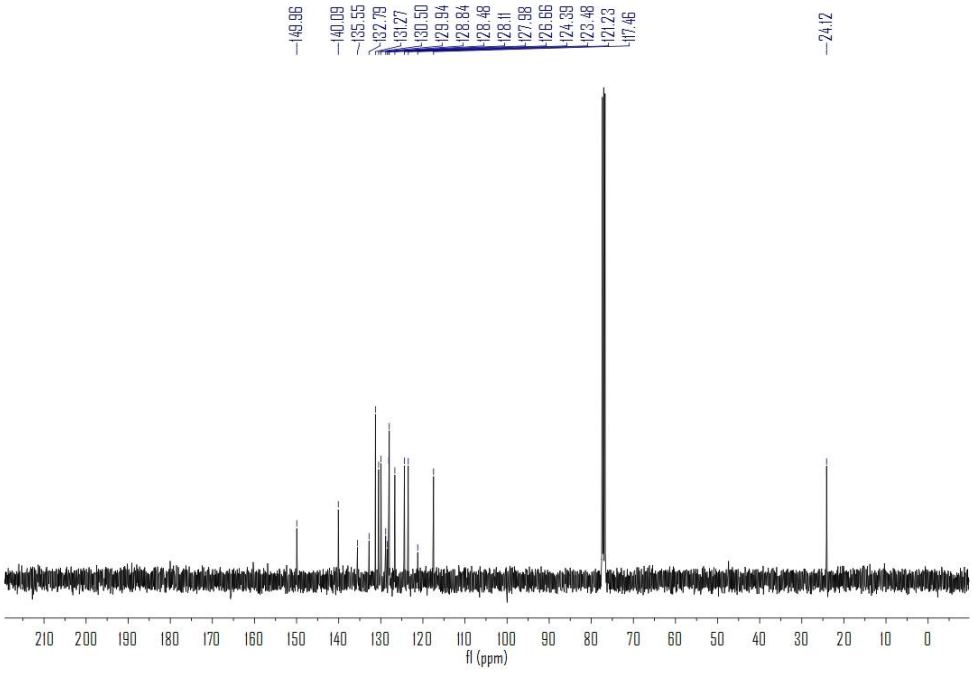

165.4
150.3
144.0
129.3
129.0
128.4
127.2
126.4
124.2
123.9
120.0
118.0
62.0
14.6

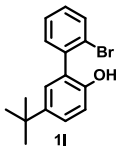

f1 (ppm)


Me
Br
OH

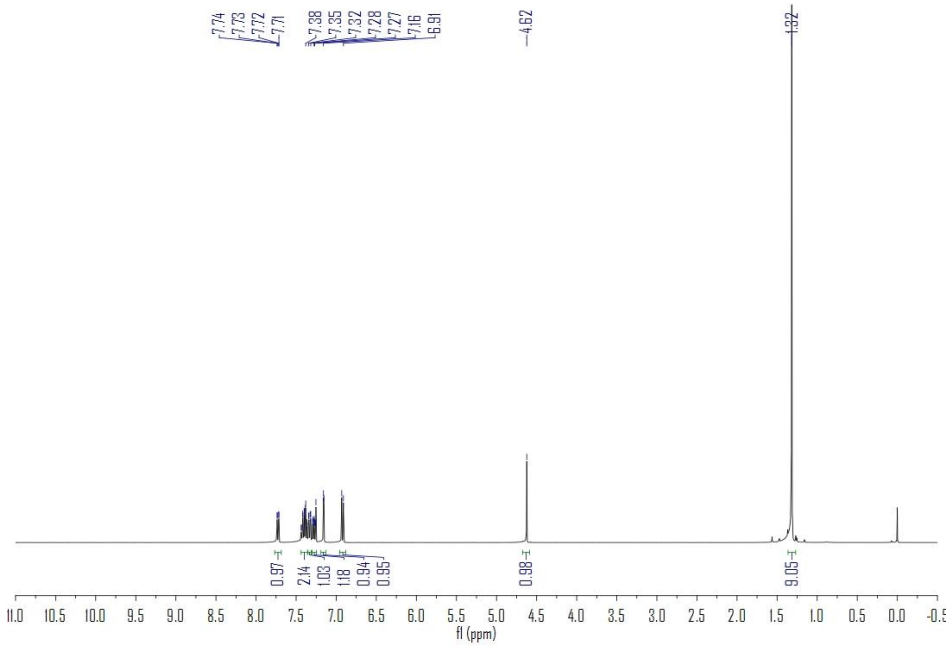
1j

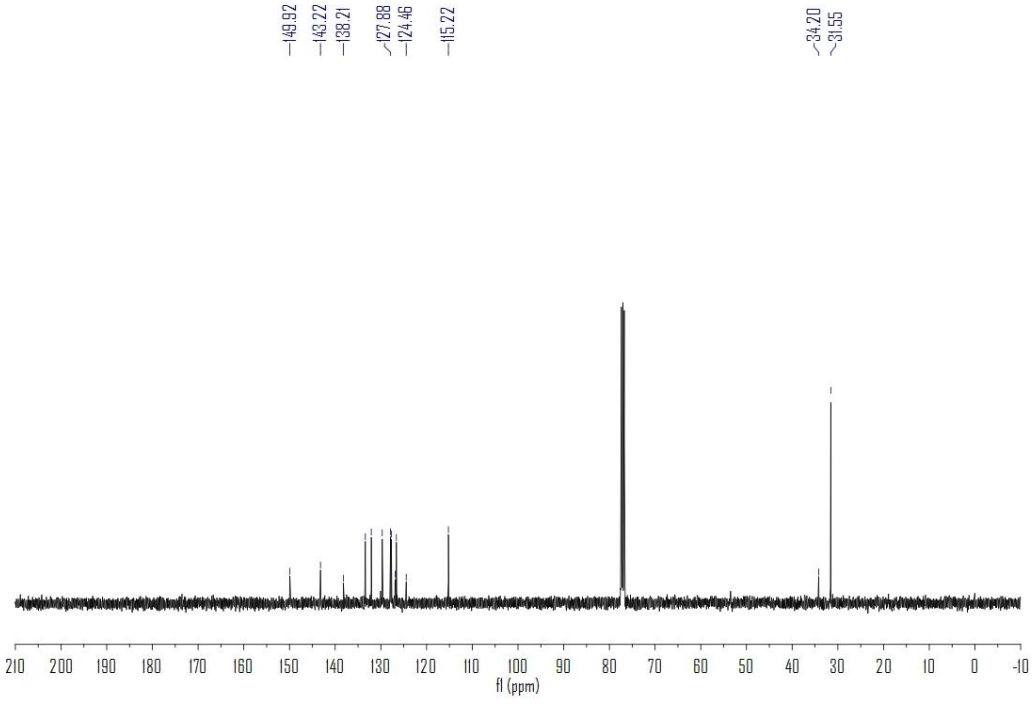

7.89
7.87
7.86
7.86
7.85
7.44
7.38
7.35
7.28
7.22
7.20
4.88
2.58
2.00
2.00
1.93
1.29
1.93
1.07
3.01
f1 (ppm)

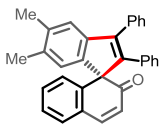

149.96
140.09
135.55
132.79
131.27
130.50
129.94
128.84
128.48
128.11
127.98
126.66
124.39
123.48
121.23
117.46
24.12
f1 (ppm)


Br
OH

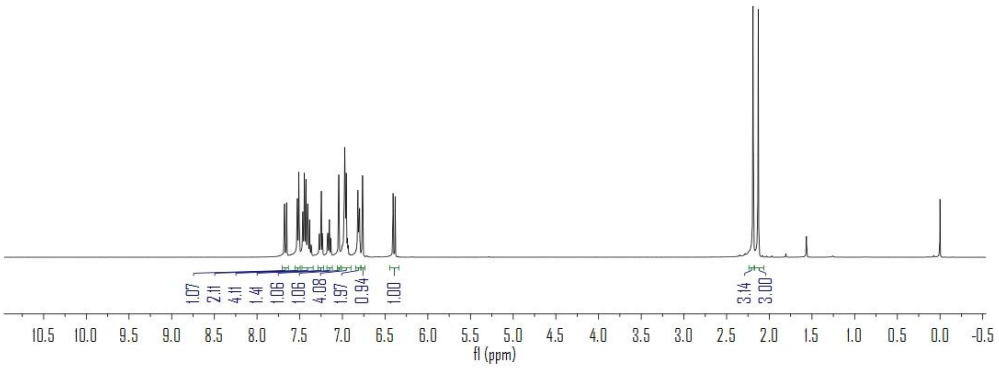
1l


7.74
7.73
7.72
7.71
7.38
7.35
7.32
7.28
7.27
7.16
6.91
4.62
1.32
0.97
2.14
1.03
1.18
0.94
0.95
0.98
9.05
f1 (ppm)

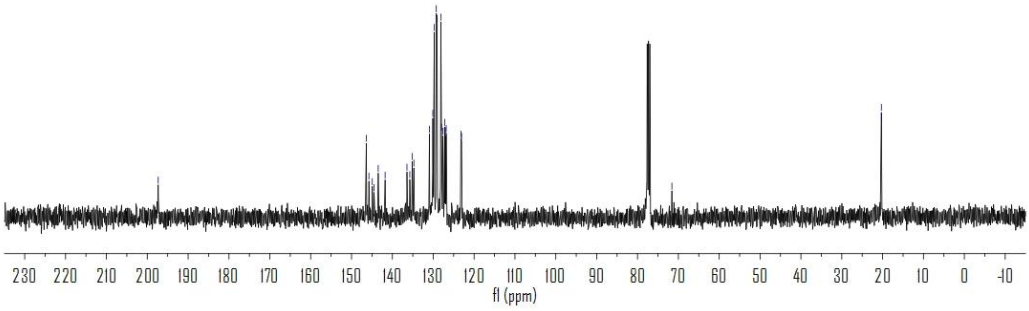

149.92
143.22
138.21
127.88
124.46
115.22
34.20
31.55
f1 (ppm)

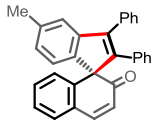

Me
Me
Ph
Ph
O

3b

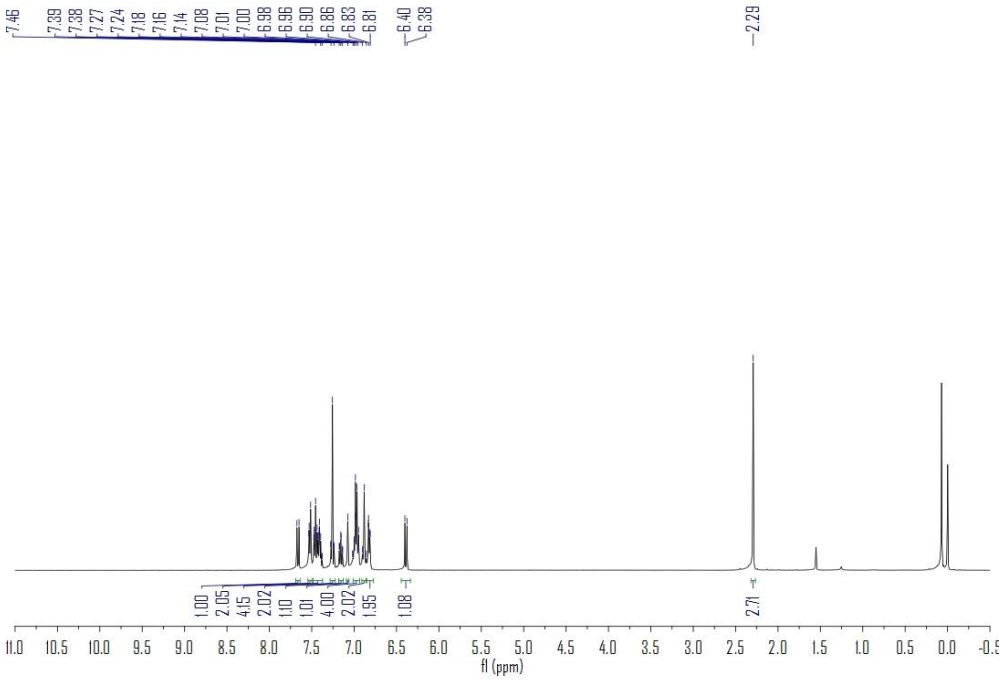

1.07
2.11
4.11
1.41
1.06
1.06
4.08
1.97
0.94
1.00
3.14
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

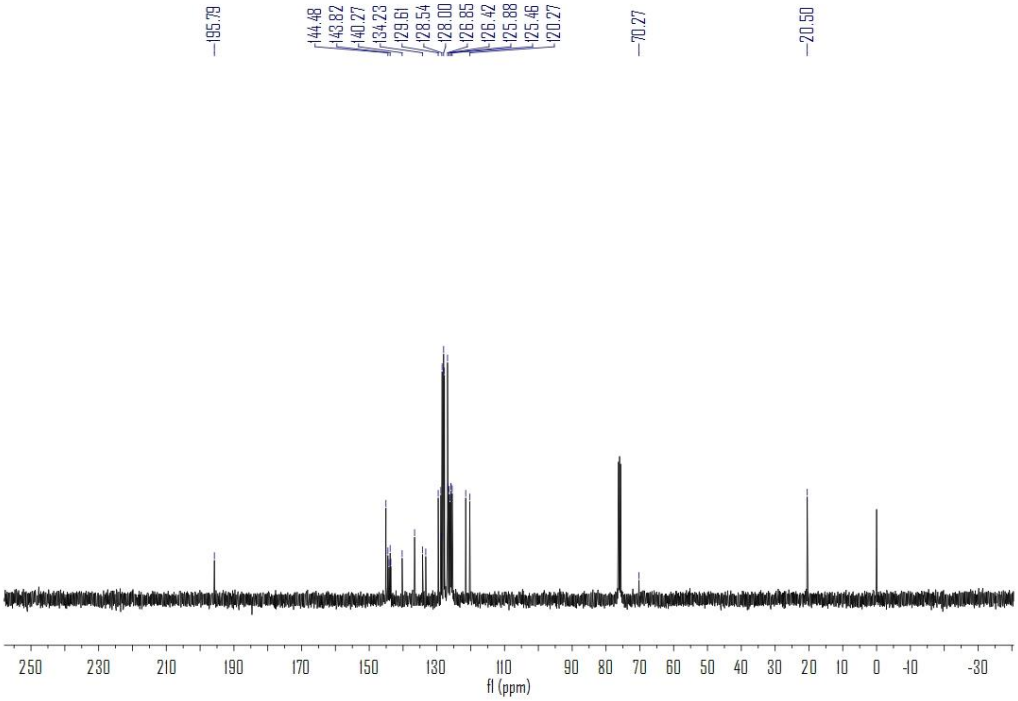

197.32
146.38
130.93
130.11
129.75
129.25
129.05
128.13
127.99
127.65
127.20
127.02
126.83
123.23
123.06
71.58
20.30
20.28

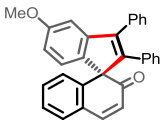

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Ph
Ph
O

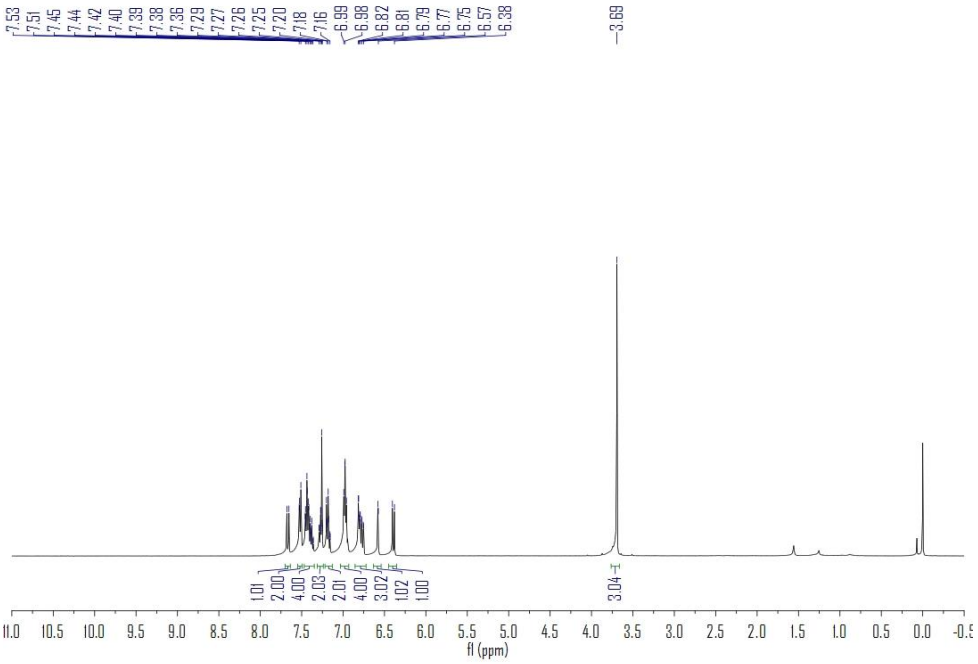
3c


7.46
7.39
7.38
7.27
7.24
7.18
7.16
7.14
7.08
7.01
7.00
6.98
6.96
6.90
6.86
6.83
6.81
6.40
6.38
2.29
1.00
2.05
4.15
2.02
1.10
1.01
4.00
2.02
1.95
1.08
2.71
f1 (ppm)


195.79
144.48
143.82
140.27
134.23
129.61
128.54
128.00
126.85
126.42
125.88
125.46
120.27
70.27
20.50
f1 (ppm)


MeO
Ph
Ph
O

3d


7.53
7.51
7.45
7.44
7.42
7.40
7.39
7.38
7.36
7.29
7.27
7.26
7.25
7.20
7.18
7.16
6.99
6.98
6.82
6.81
6.79
6.77
6.75
6.57
6.38
3.69
1.01
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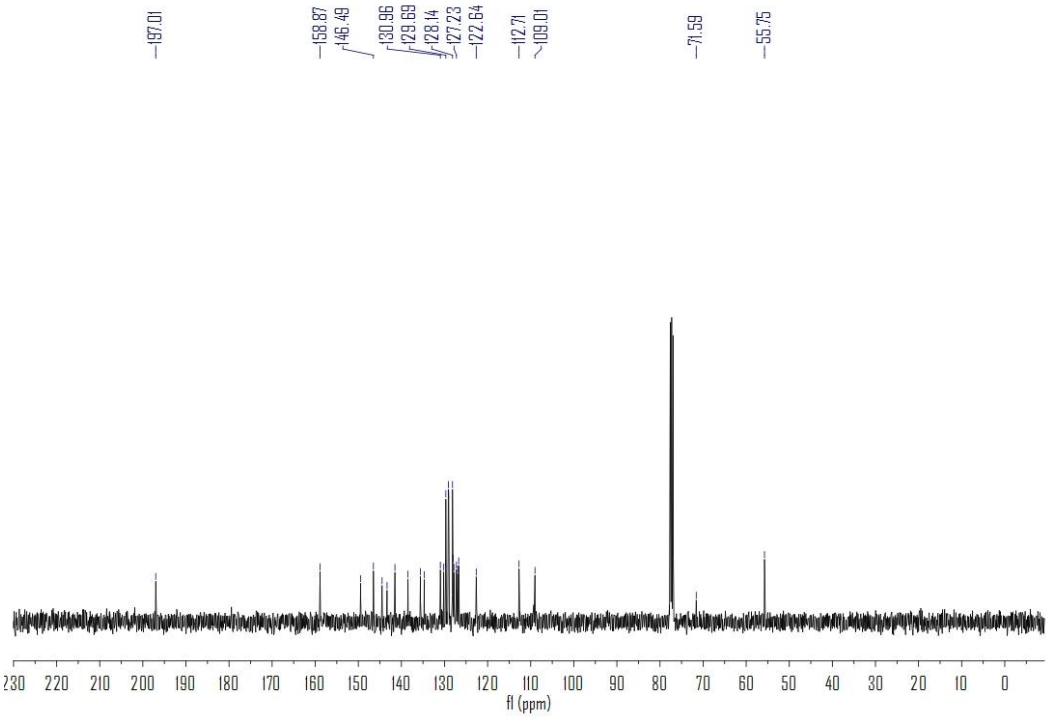
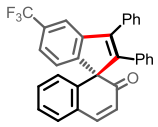
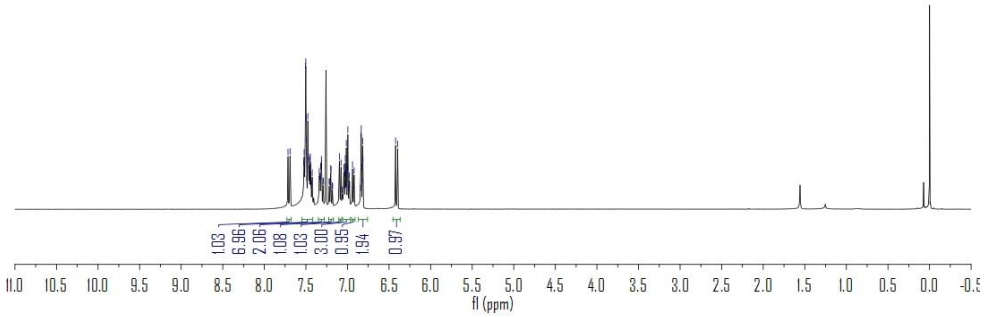
4.00
2.03
2.01
4.00
3.02
1.02
1.00
3.04
f1 (ppm)


197.01
158.87
146.49
130.96
129.69
128.14
127.23
122.64
112.71
109.01
71.59
55.75
f1 (ppm)

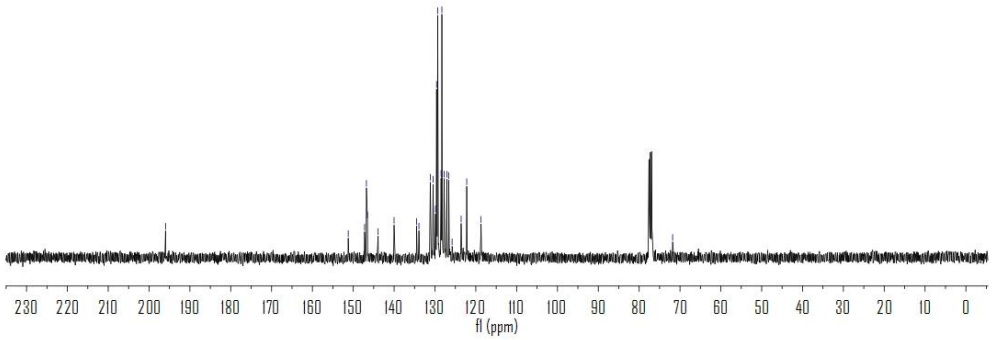

F3C
Ph
Ph
O

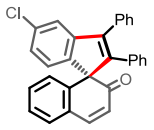
3e


7.50
7.47
7.45
7.44
7.33
7.32
7.29
7.22
7.18
7.08
7.04
7.02
7.00
6.97
6.84
6.83
6.81
6.42
6.40

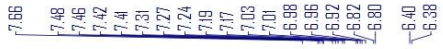

1.03
6.96
2.06
1.08
1.03
3.00
0.95
1.94
0.97
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

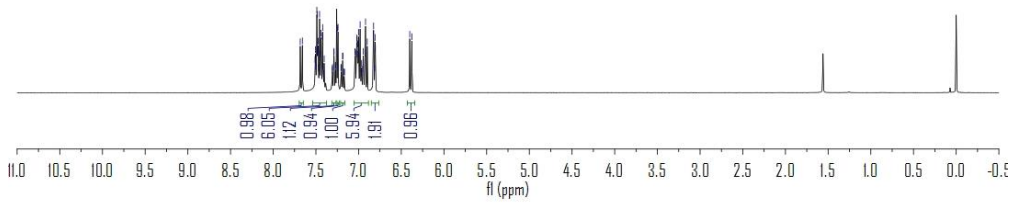

195.96
151.23
147.23
146.78
146.52
143.91
140.01
131.13
129.88
129.34
128.50
127.76
126.62
123.59
118.71
71.80

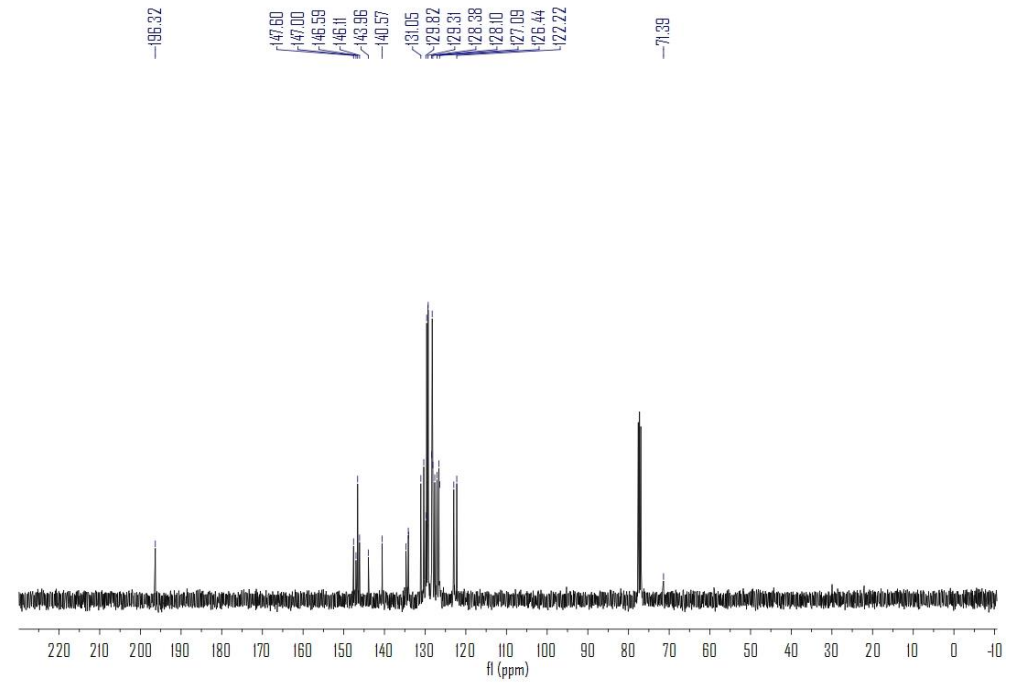

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

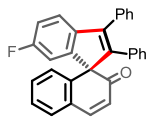

Cl
Ph
Ph
O

3f


7.66
7.48
7.46
7.42
7.41
7.31
7.27
7.24
7.19
7.17
7.03
7.01
6.98
6.96
6.92
6.82
6.80
6.40
6.38

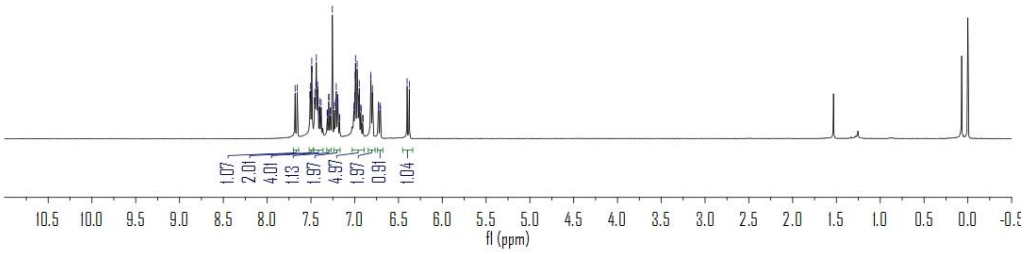

0.98
6.05
1.12
0.94
1.00
5.94
1.91
0.96
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.32
147.60
147.00
146.59
146.11
143.96
140.57
131.05
129.82
129.31
128.38
128.10
127.09
126.44
122.22
71.39
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

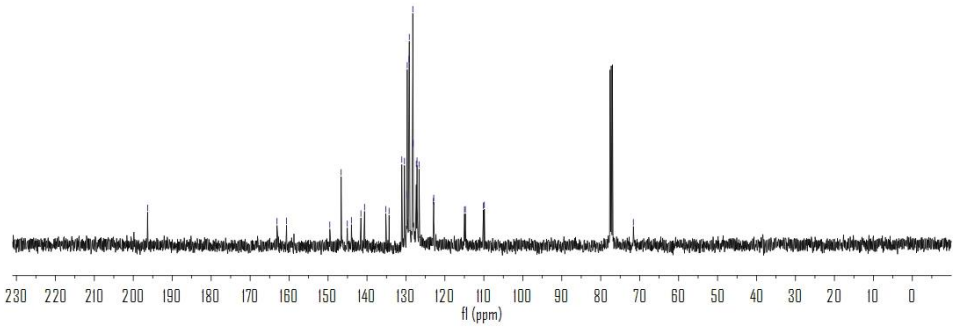

Ph
F
Ph
O

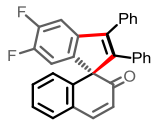
3g


7.30
7.28
7.25
7.22
7.20
7.19
7.17
7.00
6.99
6.97
6.95
6.93
6.90
6.81
6.79
6.73
6.70
6.40
6.38

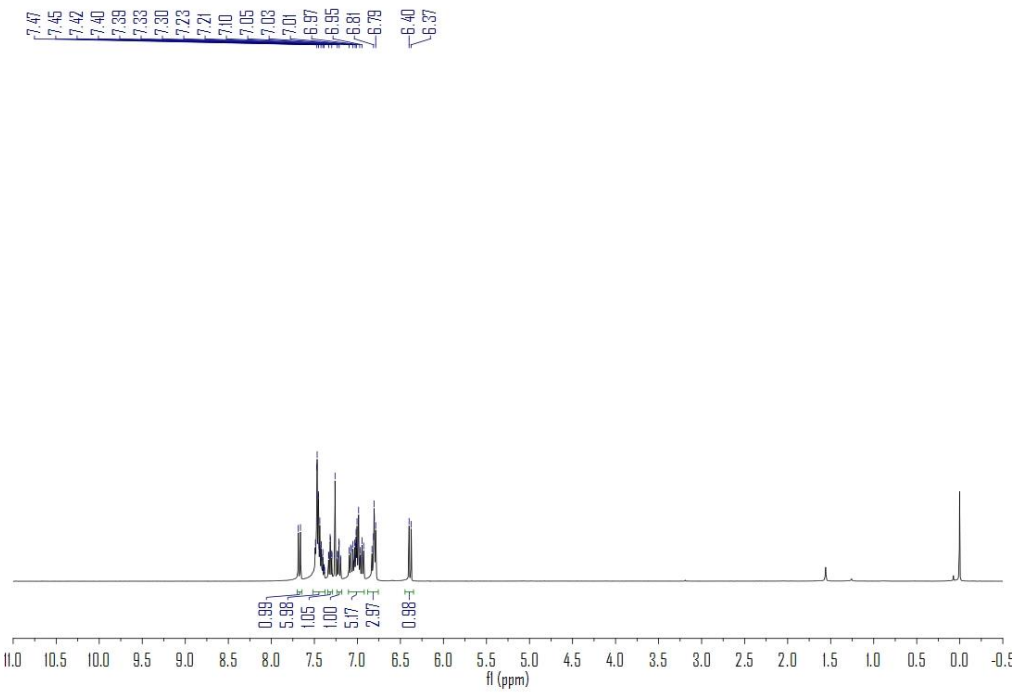

1.07
2.01
4.01
1.13
1.97
4.97
1.97
0.91
1.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.33
163.10
160.65
146.63
144.01
140.63
129.80
128.14
122.87
114.97
114.75
110.10
109.86
71.62


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


F
F
Ph
Ph
O

3h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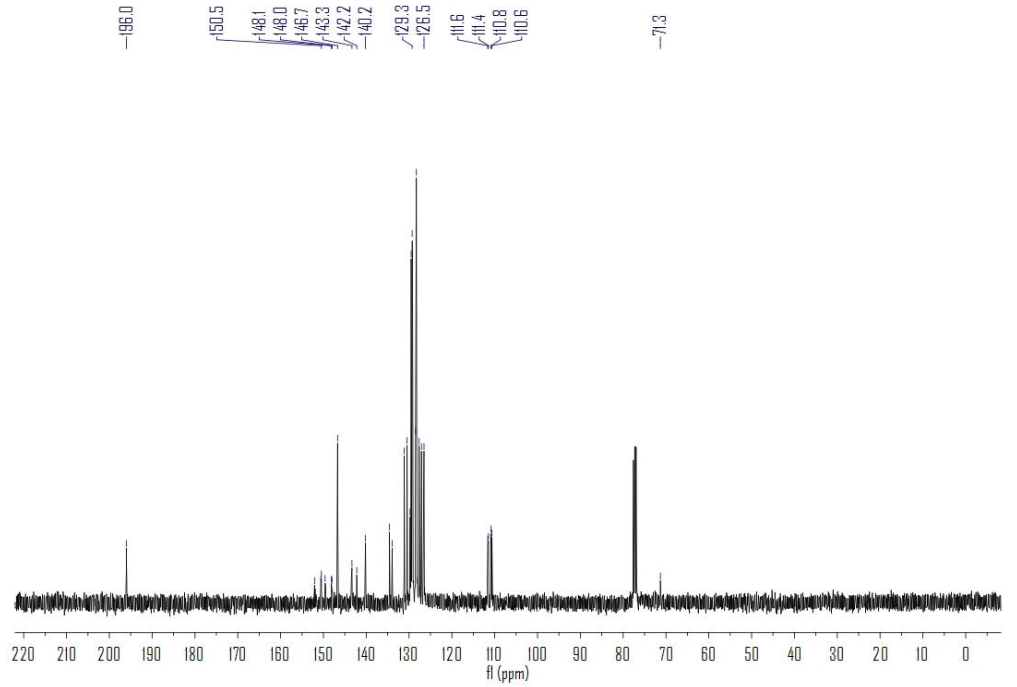
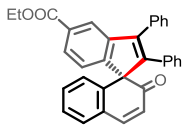
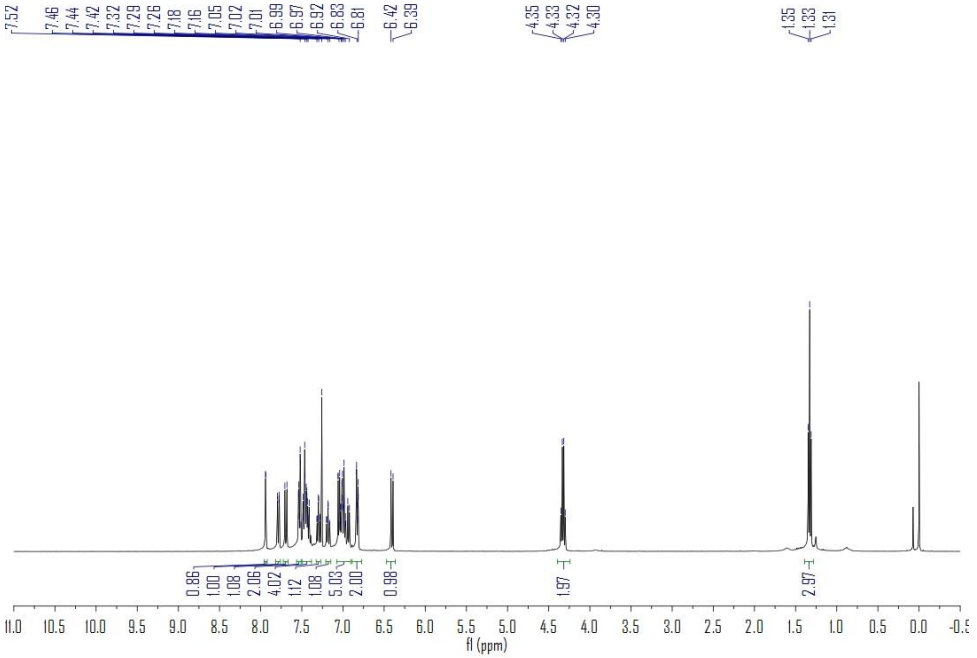
7.45
7.42
7.40
7.39
7.33
7.30
7.23
7.21
7.10
7.05
7.03
7.01
6.97
6.95
6.81
6.79
6.40
6.37
0.99
5.98
1.05
1.00
5.17
2.97
0.98
f1 (ppm)


196.0
150.5
148.1
148.0
146.7
143.3
142.2
140.2
129.3
126.5
111.6
111.4
110.8
110.6
71.3
f1 (ppm)


EtOOC
Ph
Ph
O

3i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7.42
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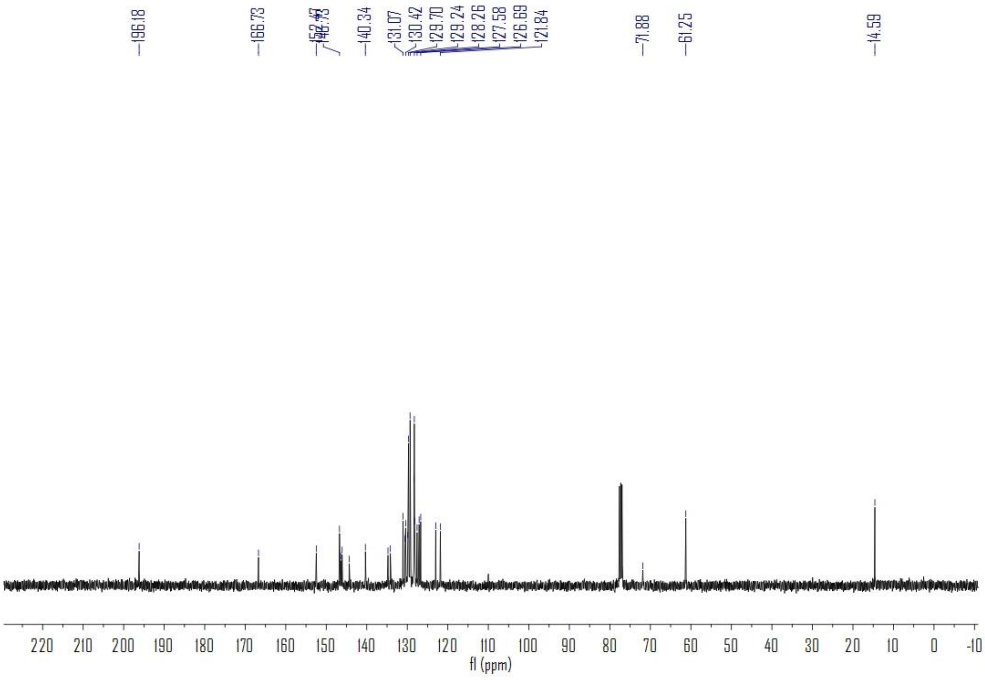
7.29
7.26
7.18
7.16
7.05
7.02
7.01
6.99
6.97
6.92
6.83
6.81
6.42
6.39
4.35
4.33
4.32
4.30
1.35
1.33
1.31
0.86
1.00
1.08
2.06
4.02
1.12
1.08
5.03
2.00
0.98
1.97
2.97
f1 (ppm)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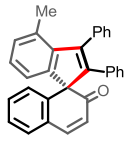
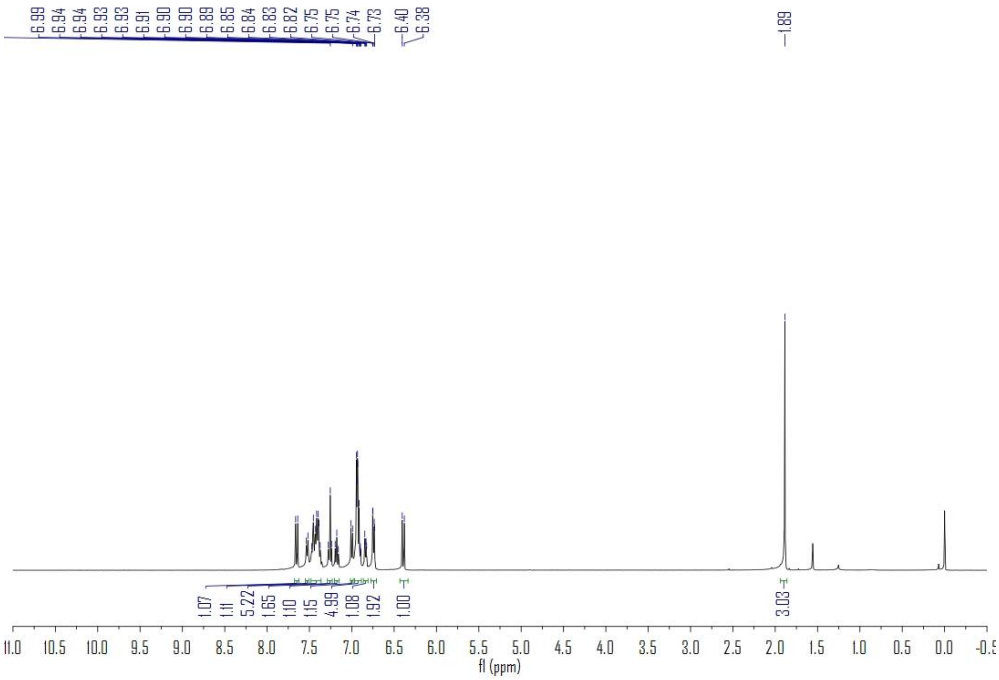
166.73
152.47
148.73
140.34
131.07
130.42
129.70
129.24
128.26
127.58
126.69
121.84
71.88
61.25
14.59
f1 (ppm)


Me
Ph
Ph
O

3j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6.94
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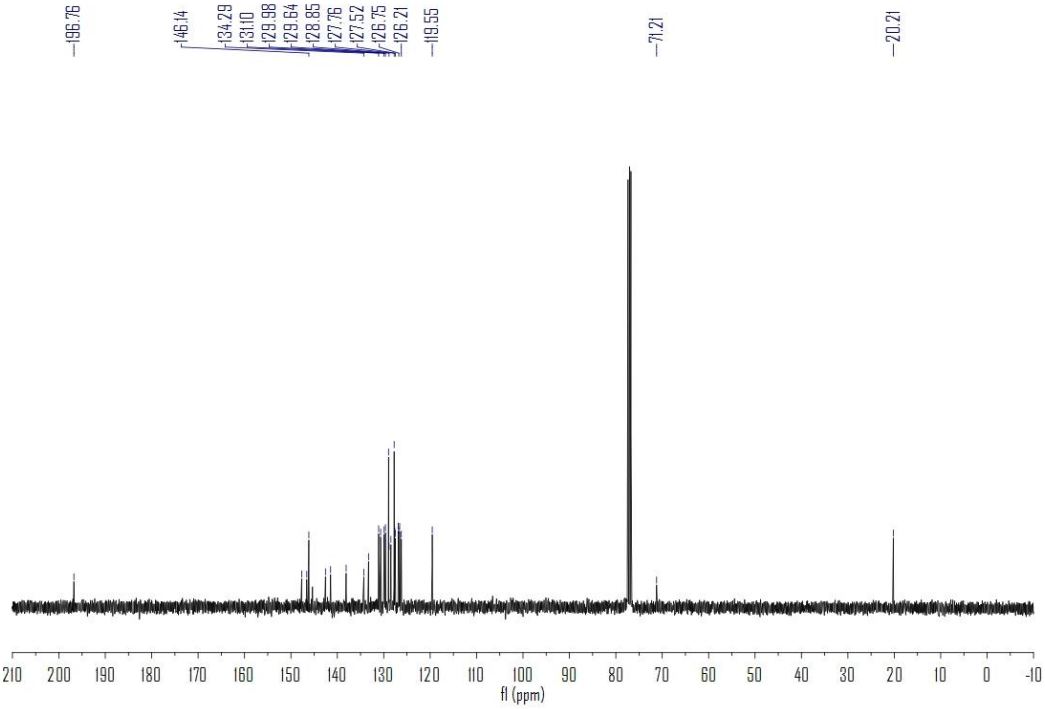
6.91
6.90
6.90
6.89
6.85
6.84
6.83
6.82
6.75
6.75
6.74
6.73
6.40
6.38
1.89
1.07
1.11
5.22
1.65
1.10
1.15
4.99
1.08
1.92
1.00
3.03
f1 (ppm)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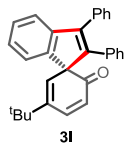
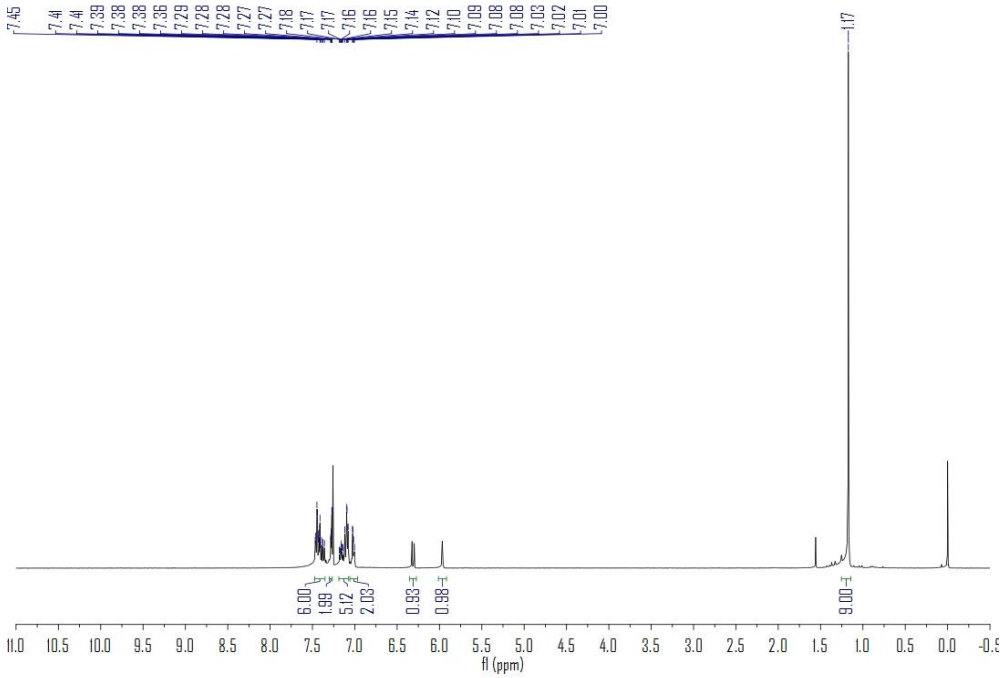
128.85
127.76
127.52
126.75
126.21
119.55
71.21
20.21
f1 (ppm)


Ph
Ph
O
tBu

3l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7.41
7.40
7.39
7.38
7.38
7.36
7.29
7.28
7.28
7.27
7.27
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.12
7.10
7.09
7.08
7.08
7.03
7.02
7.01
7.00
1.17
6.00
1.99
5.12
2.03
0.93
0.98
9.00
f1 (ppm)


198.12
146.81
144.46
144.36
144.10
143.74
142.43
128.93
128.17
128.01
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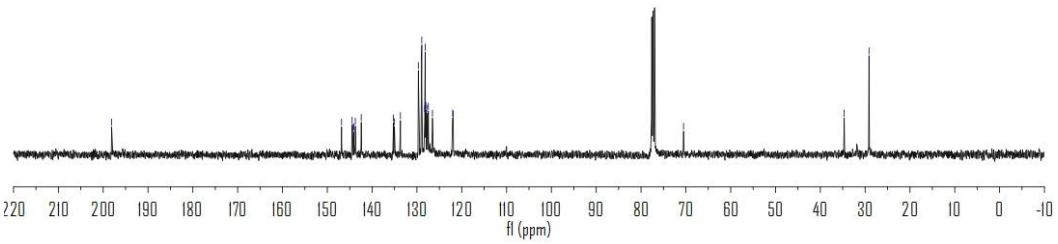
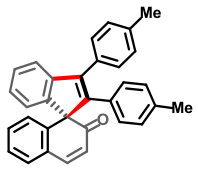
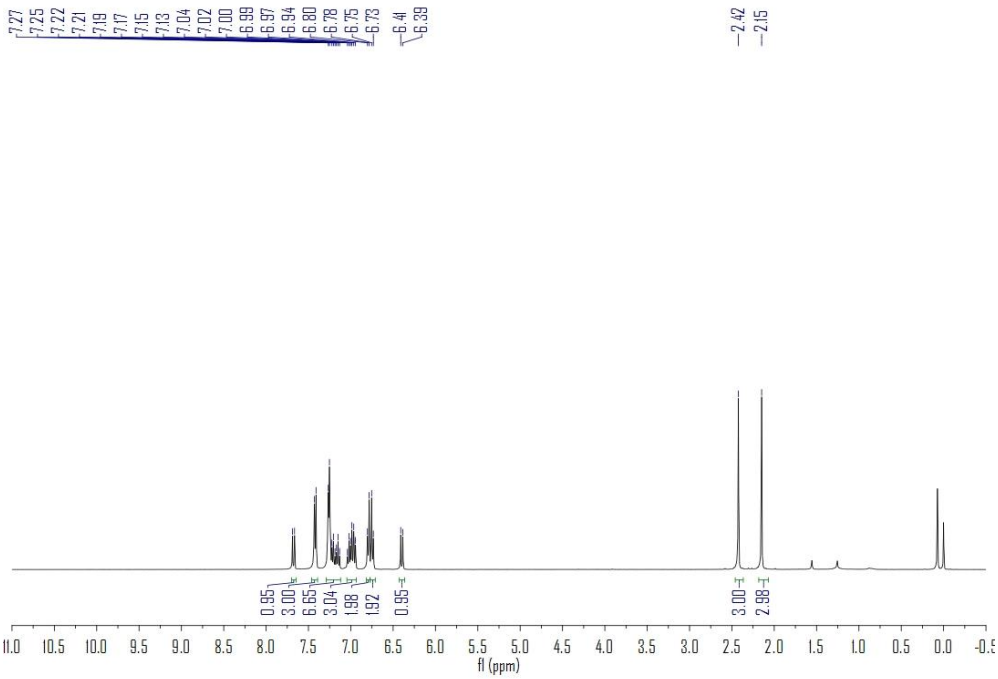
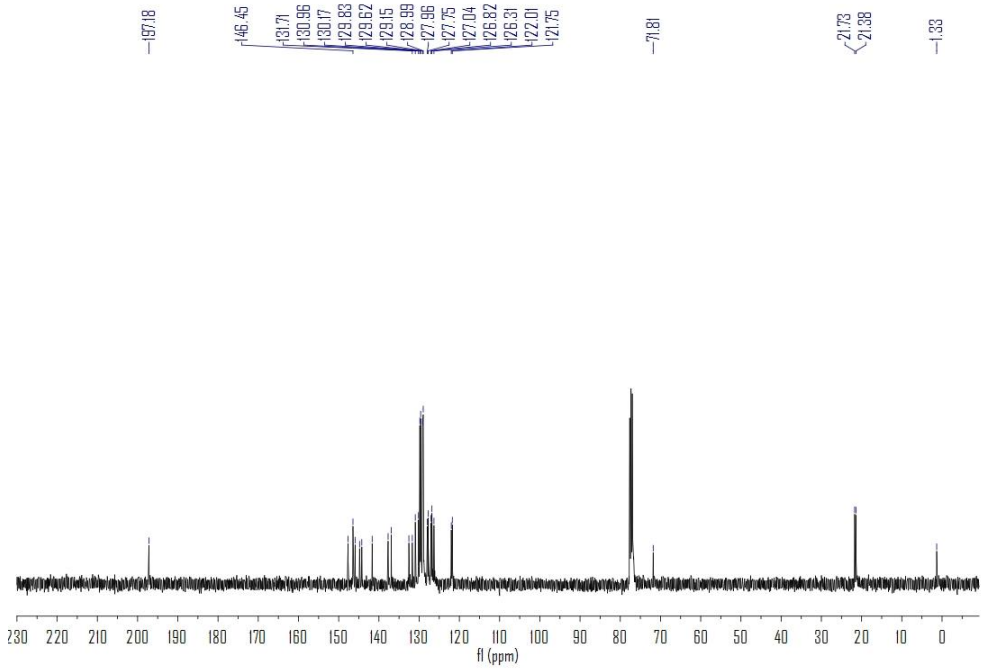
127.45
126.54
122.04
121.89
70.52
34.67
29.14

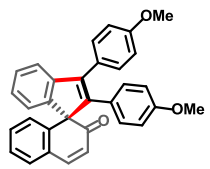

f1 (ppm)


Me
Me

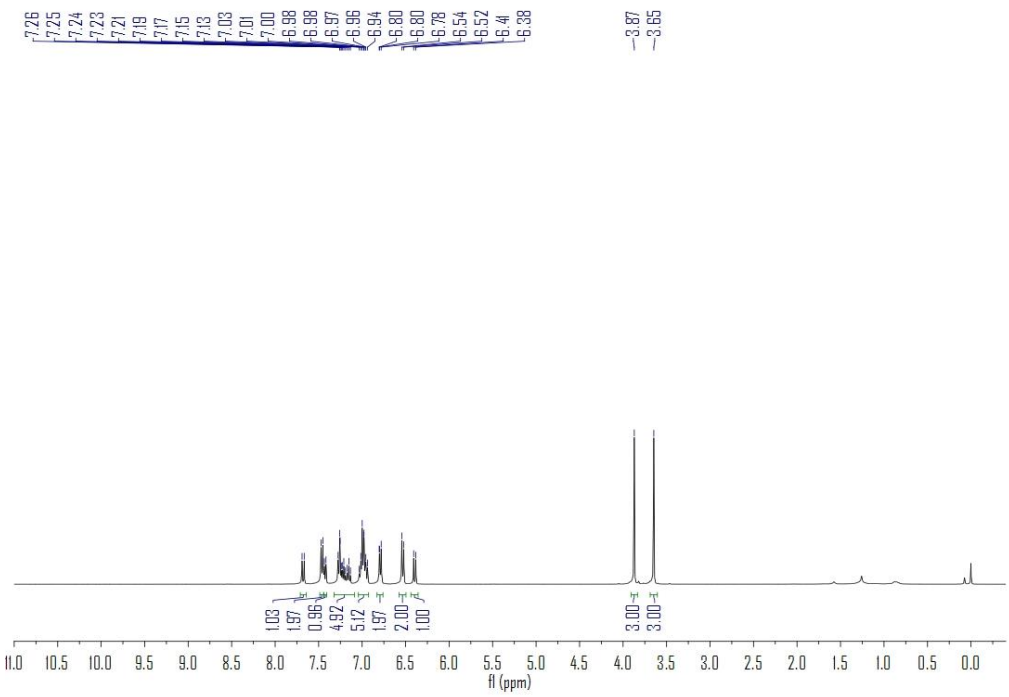
3b'


7.27
7.25
7.22
7.21
7.19
7.17
7.15
7.13
7.04
7.02
7.00
6.99
6.97
6.94
6.80
6.78
6.75
6.73
6.41
6.39
2.42
2.15
0.95
3.00
6.65
3.04
1.98
1.92
0.95
3.00
2.98
f1 (ppm)


197.18
146.45
131.71
130.96
130.17
129.83
129.62
129.15
128.99
127.96
127.75
127.04
126.82
126.31
122.01
121.75
71.81
21.73
21.38
1.33
f1 (ppm)


OMe
OMe
O

3c'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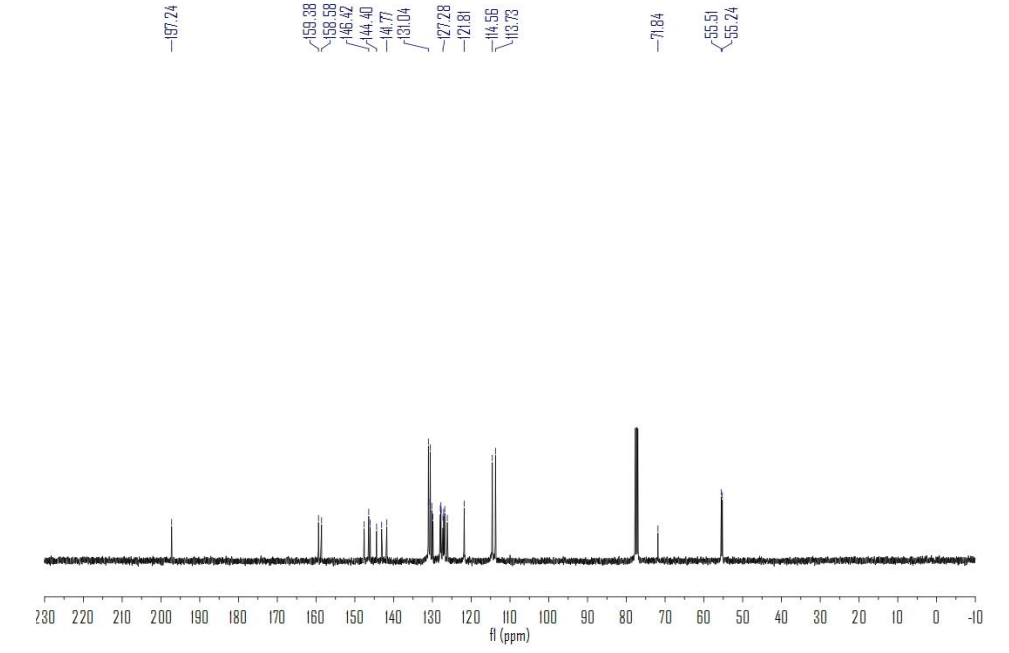
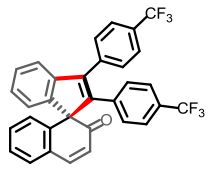
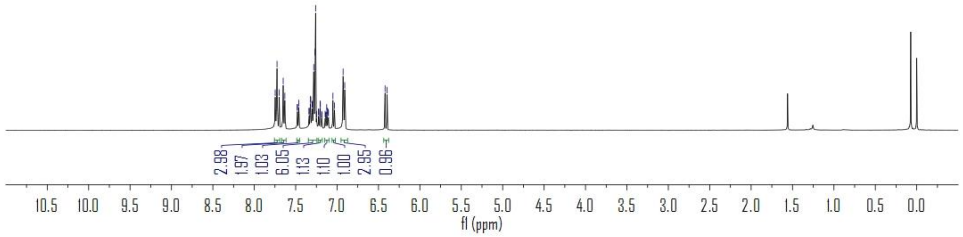
7.23
7.21
7.19
7.17
7.15
7.13
7.03
7.01
7.00
6.98
6.98
6.97
6.96
6.94
6.80
6.80
6.78
6.54
6.52
6.4
6.38
3.87
3.65
1.03
1.97
0.96
4.92
5.12
1.97
2.00
1.00
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


197.24
159.38
158.58
146.42
144.40
141.77
131.04
127.28
121.81
114.56
113.73
71.84
55.51
55.24
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

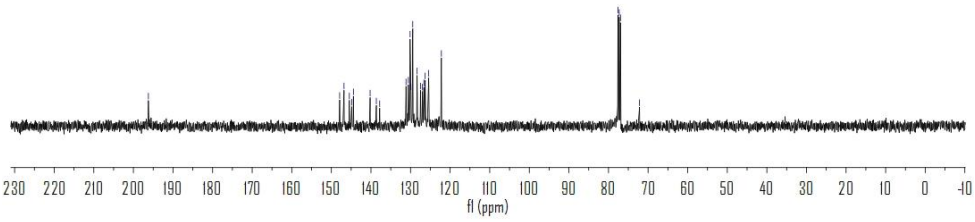

CF3
CF3
O

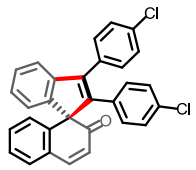
3d'


7.73
7.65
7.48
7.46
7.34
7.32
7.30
7.27
7.25
7.22
7.20
7.18
7.14
7.12
7.10
7.03
6.91
6.42
6.40


2.98
1.97
1.03
6.05
1.13
1.10
1.00
2.95
0.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

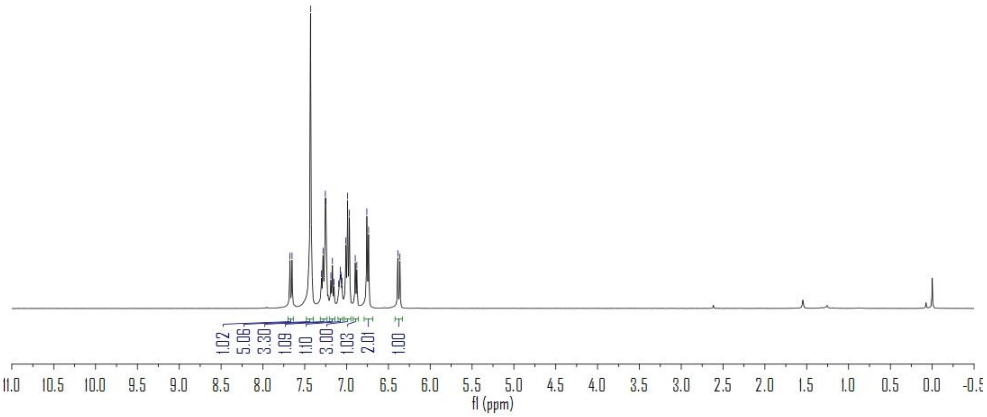

196.21
146.80
145.46
144.88
144.43
140.21
138.64
137.80
130.55
129.91
128.35
127.02
126.31
122.22
77.61
77.29
76.97
72.16


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

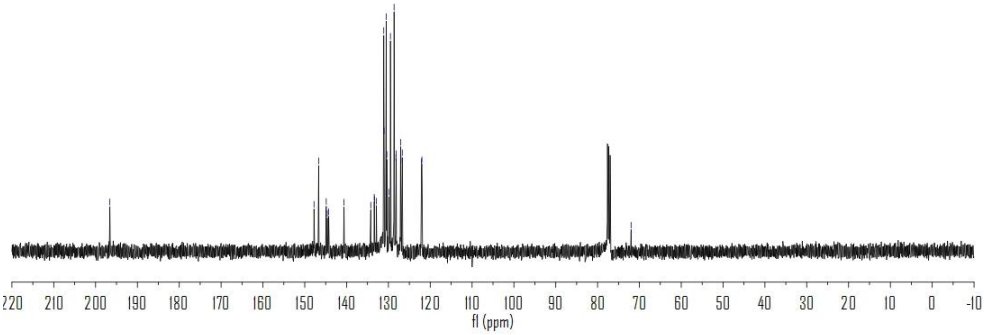

Cl
Cl
O

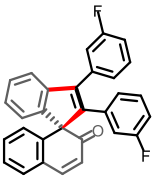
3e'


7.25
7.25
7.19
7.17
7.15
7.09
7.08
7.07
7.06
7.06
7.01
6.99
6.97
6.90
6.88
6.76
6.74
6.39
6.36


1.02
5.06
3.30
1.09
1.10
3.00
1.03
2.01
1.00
f1 (ppm)

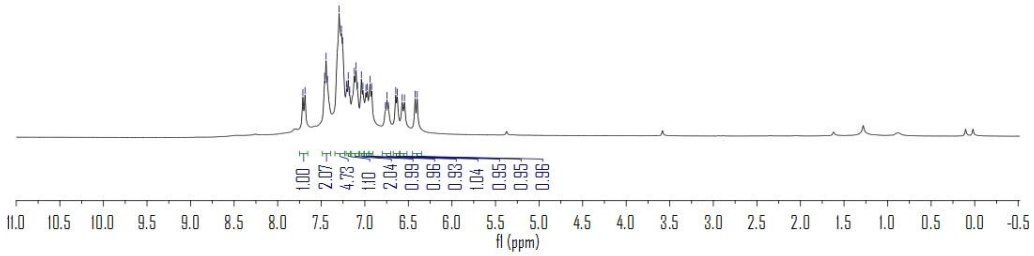

196.59
147.79
146.67
144.86
144.62
144.27
140.61
133.39
131.04
130.38
129.52
128.20
127.08
126.69
121.99
71.99


f1 (ppm)

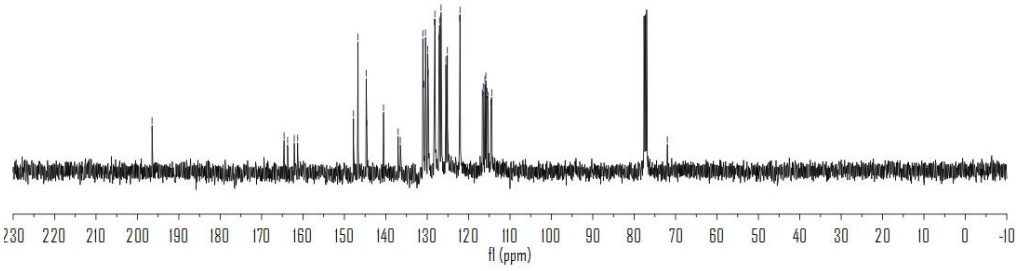


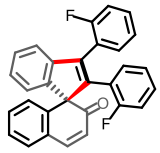
3f'


7.71
7.69
7.46
7.44
7.43
7.30
7.27
7.26
7.21
7.19
7.17
7.12
7.10
7.08
7.04
7.02
6.99
6.97
6.94
6.92
6.76
6.75
6.73
6.64
6.63
6.57
6.55
6.42
6.40


1.00
2.07
4.73
1.10
2.04
0.99
0.96
0.93
1.04
0.95
0.95
0.96
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

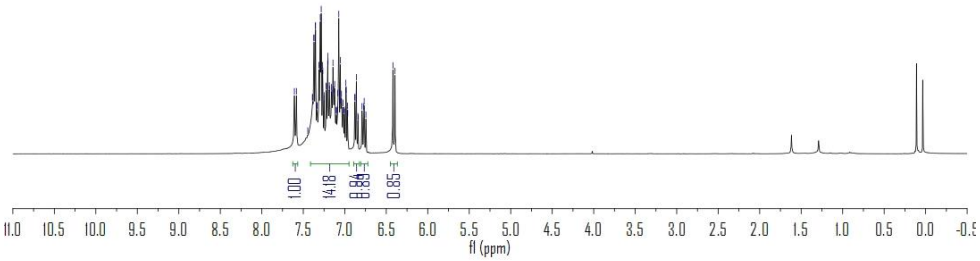

196.46
164.57
163.72
162.47
161.28
140.55
137.01
136.90
128.14
122.07
115.82
115.54
115.33
114.64
114.43
72.00

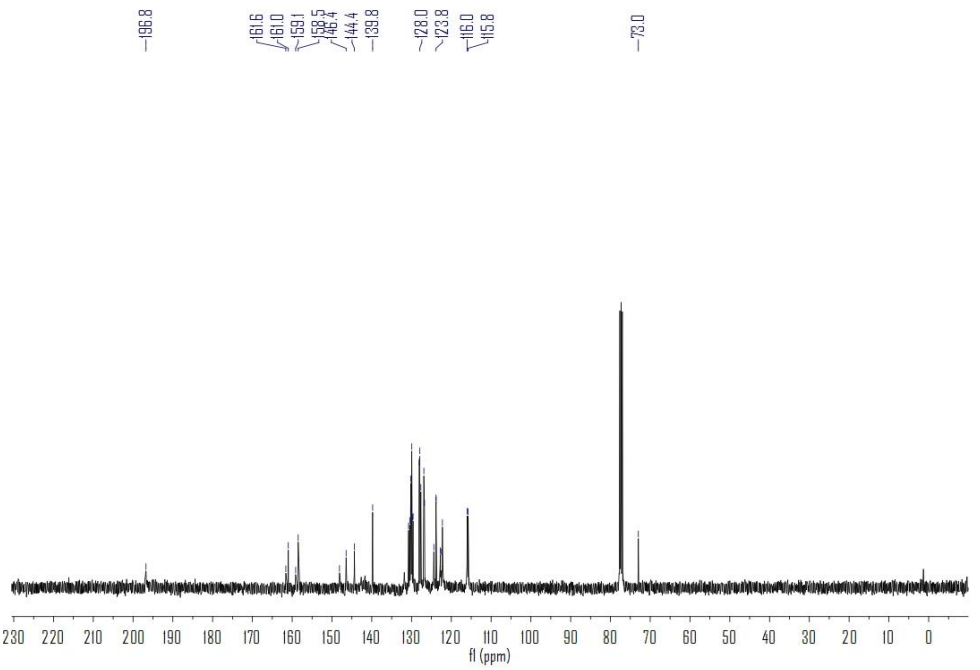

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

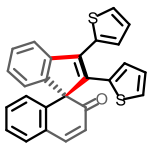

F
O
F

3g'


7.37
7.34
7.30
7.26
7.22
7.20
7.16
7.13
7.10
7.07
7.05
7.02
6.99
6.96
6.86
6.79
6.75
6.42
6.39

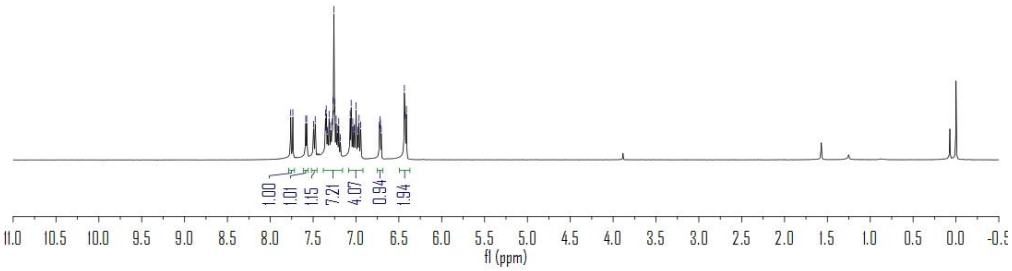

1.00
14.18
0.85
f1 (ppm)


196.8
161.6
161.0
159.1
158.5
146.4
144.4
139.8
128.0
123.8
116.0
115.8
73.0
f1 (ppm)

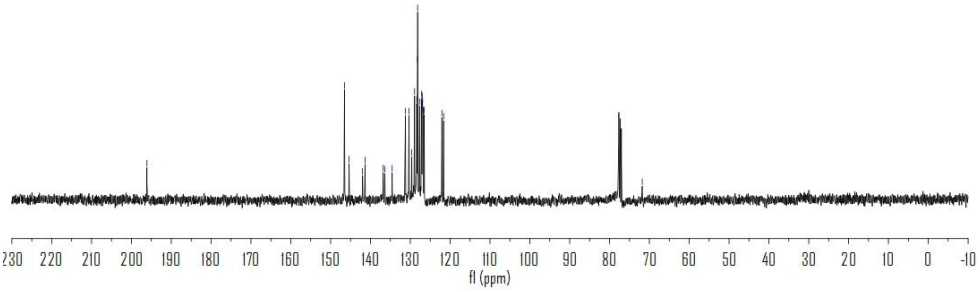


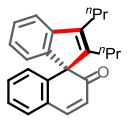
3h'


7.23
7.22
7.20
7.18
7.07
7.06
7.04
7.02
7.02
7.00
6.98
6.96
6.95
6.73
6.72
6.72
6.71
6.44
6.42
6.41

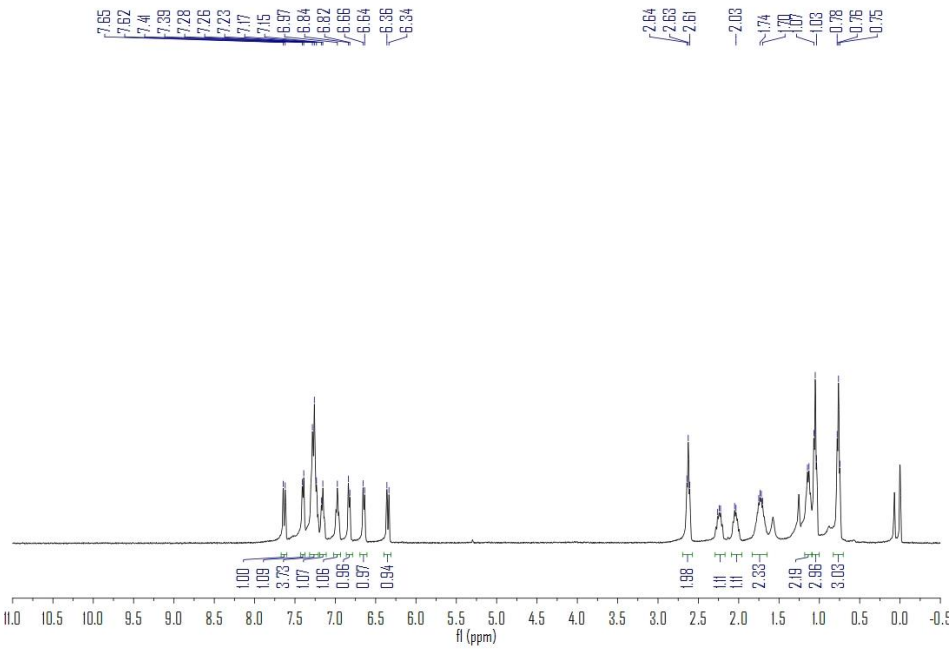

1.00
1.01
1.15
7.21
4.07
0.94
1.94
f1 (ppm)

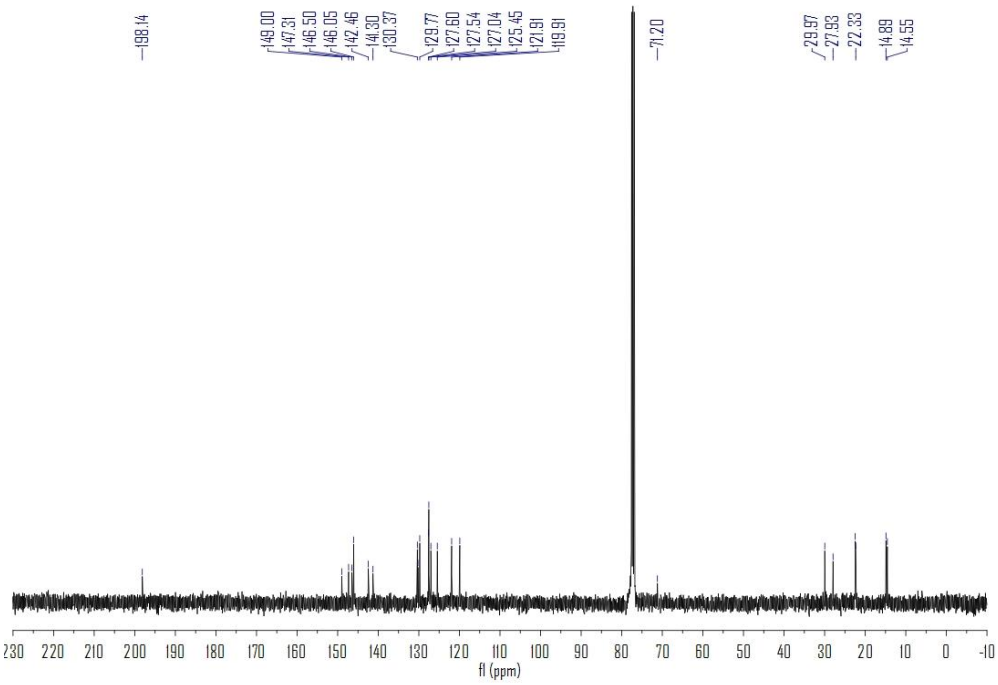

196.11
146.52
130.32
129.63
128.93
128.38
128.19
128.15
127.67
127.16
127.01
126.90
126.73
126.51
122.07
121.64
71.79

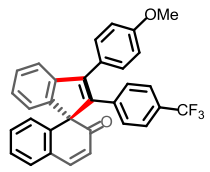

f1 (ppm)


nPr
nPr
O

3i'

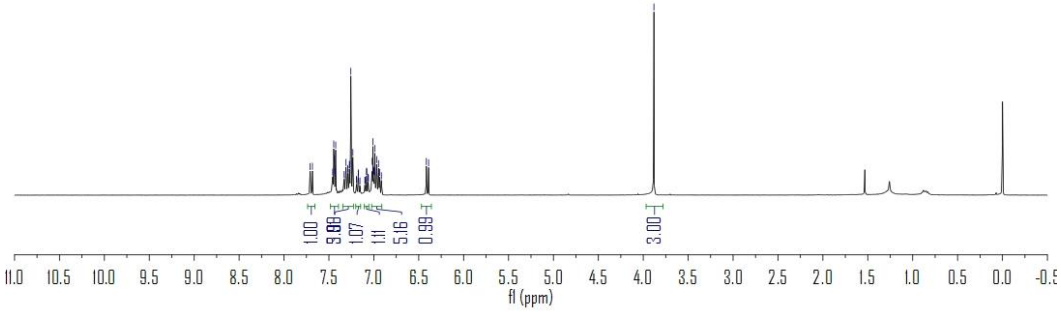

7.65
7.62
7.41
7.39
7.28
7.26
7.23
7.17
7.15
6.97
6.84
6.82
6.66
6.64
6.36
6.34
2.64
2.63
2.61
2.03
1.74
1.73
1.71
1.07
1.03
0.78
0.76
0.75
1.00
1.09
3.73
1.07
1.06
0.96
0.97
0.94
1.98
1.11
1.11
2.33
2.19
2.96
3.03
f1 (ppm)

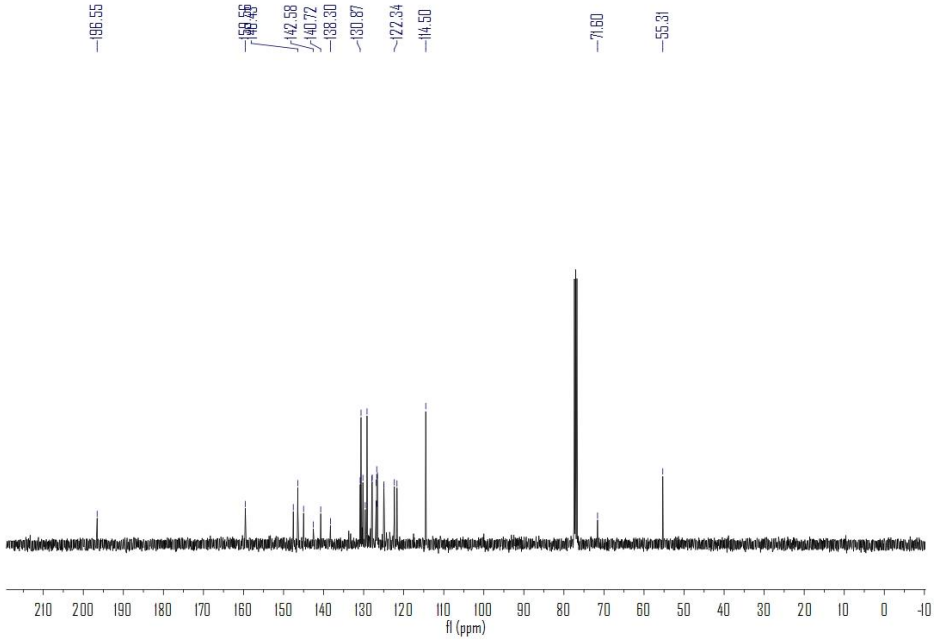

198.14
149.00
147.31
146.50
146.05
142.46
141.30
130.37
129.77
127.60
127.54
127.04
125.45
121.91
119.91
71.20
29.97
27.93
22.33
14.89
14.55
f1 (ppm)

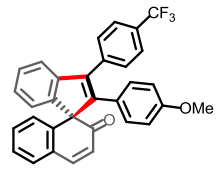

OMe
CF3
O

3j'

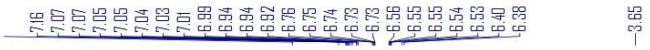

7.45
7.43
7.33
7.29
7.27
7.26
7.19
7.17
7.15
7.10
7.08
7.06
7.01
7.00
6.99
6.95
6.92
6.42
6.39
3.88


1.00
9.86
1.07
1.11
5.16
0.99
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.55
142.58
140.72
138.30
130.87
122.34
114.50
71.60
55.31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CF3
OMe
O

3j'''


7.16
7.07
7.07
7.05
7.05
7.04
7.03
7.01
6.99
6.94
6.94
6.92
6.76
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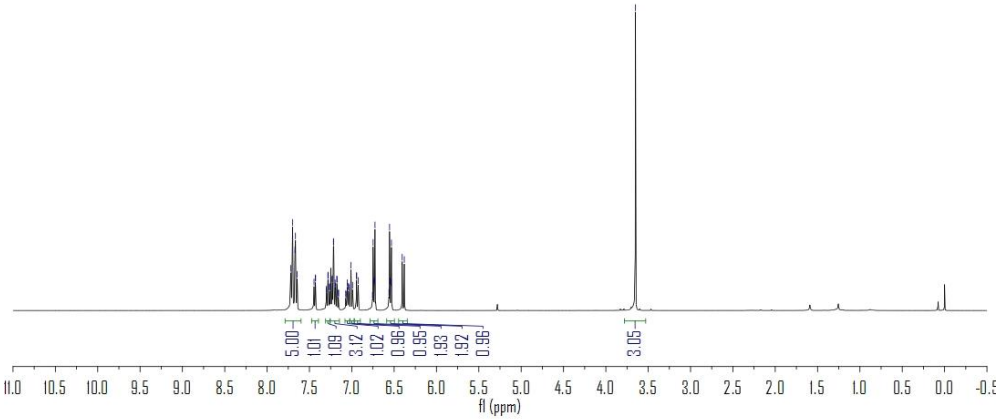
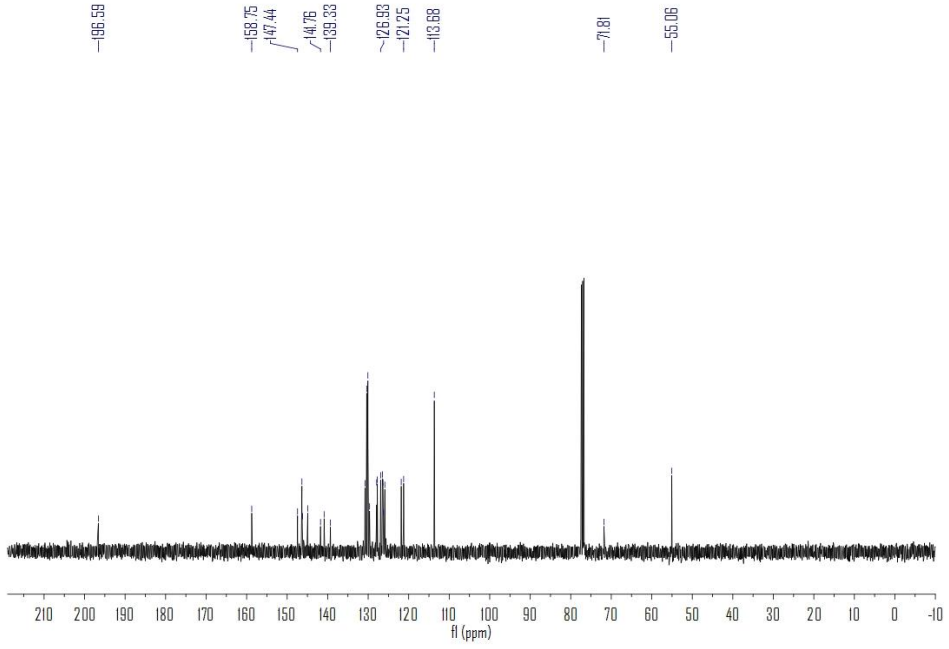
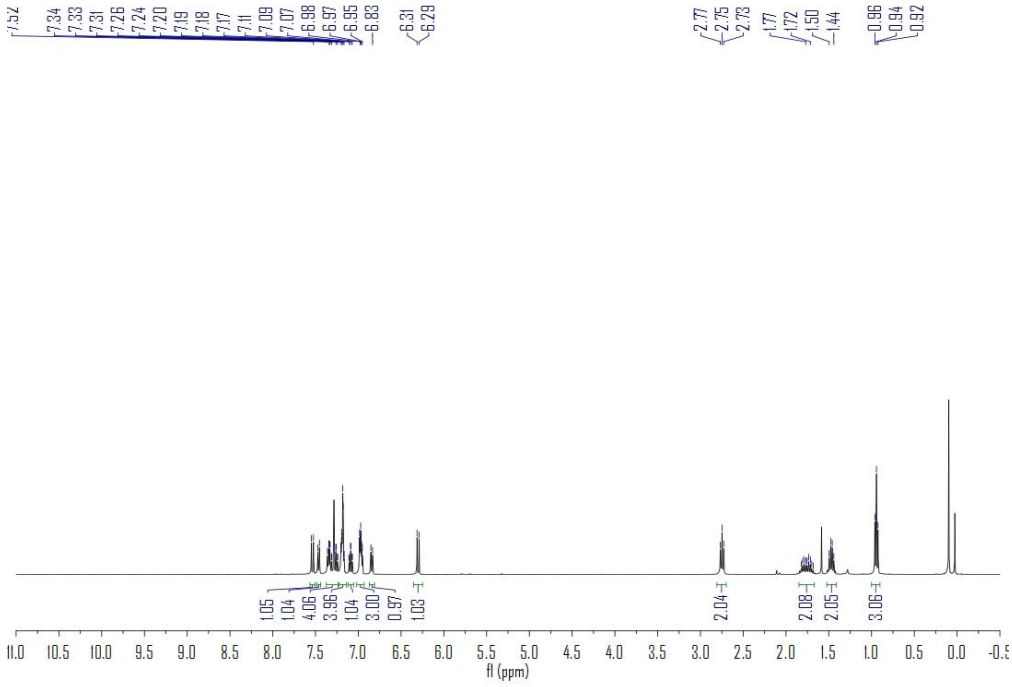
6.55
6.54
6.53
6.40
6.38
3.65

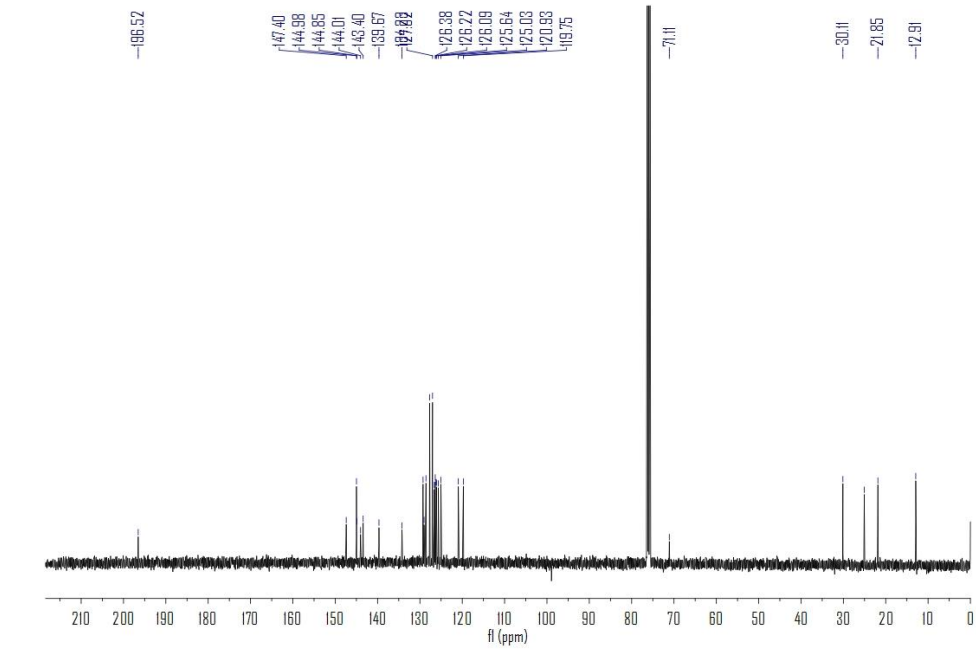

5.00
1.01
1.09
3.12
1.02
0.96
0.95
1.93
1.92
0.96
3.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

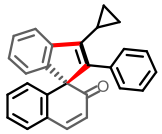

196.59
158.75
147.44
141.76
139.33
126.93
121.25
113.68
71.81
55.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


nBu
O

3l'


7.34
7.33
7.31
7.26
7.24
7.20
7.19
7.18
7.17
7.11
7.09
7.07
6.98
6.97
6.95
6.83
6.31
6.29
2.77
2.75
2.73
1.77
1.72
1.50
1.44
0.96
0.94
0.92
1.05
1.04
4.06
3.96
1.04
3.00
0.97
1.03
2.04
2.08
2.05
3.06
f1 (ppm)


196.52
147.40
144.98
144.85
144.01
143.40
139.67
126.38
126.22
126.09
125.64
125.03
120.93
119.75
71.11
30.11
21.85
12.91
f1 (ppm)



3m'