Highly Chemo- and Regioselective Construction of Spirocarbocycles by a Pd(0)-Catalyzed Dearomatization of Phenol-Based Biaryls with 1,3-Dienes

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Supporting Information

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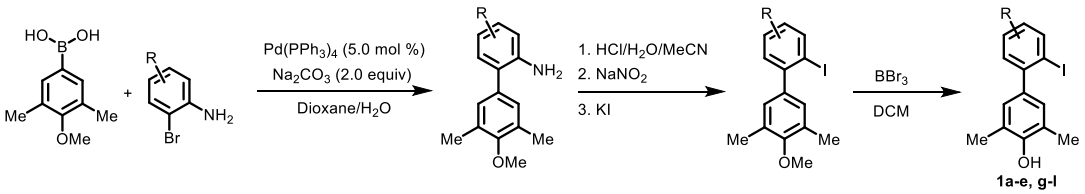
A. General information:

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. DME, MeCN and DMF were dried over CaH_2. Toluene, 1,4-dioxane 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 a WNMR-I 400 (400 MHz) or Bruker Ascend 400 (400 MHz) spectrometer, and 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; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet, coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on a WNMR-I 400 (400 MHz) or Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-*d* and a heptet at 40.0 ppm for dimethyl sulfoxide-d_6. Infrared spectra were recorded on a TENSOR 27 FT-IR spectrophotometer and reported in wave numbers (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. HPLC analyses were performed on an Agilent Technologies 1260 Series using Daicel Chiralpak columns (IA, IB, IC,) in *n*-hexane/*i*-PrOH. Optical rotations were measured on a Rudolph Research Analytical Autopol II automatic polarimeter. Substrate **1p**[1] and conjugated dienes and triene **2a-g**[2], **2i**[3] and **2j**[4] were prepared according to literature methods.

B. Preparation of substrates:

General procedure for the preparation of phenol substrates 1a-e, g-l:

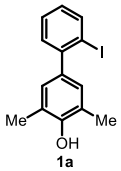
The following phenol substrates **1a-e, g-l** were prepared by Suzuki-Miyaura coupling reaction between (4-methoxy-3,5-dimethylphenyl)boronic acid and corresponding *ortho*-bromoaniline derivatives, followed by Sandmeyer reaction[5] and demethylation with BBr_3.



A 25 mL round bottom flask with a stir bar was fitted with a rubber septum and flame dried under high vacuum. The flask was purged with argon and charged with $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol), Na_2CO_3 (0.53 g, 5.0 mmol), (4-methoxy-3,5-dimethylphenyl)boronic acid (0.54 g, 3.0 mmol), *ortho*-bromoanilin derivatives (2.5 mmol), 10.0 mL deoxygenated dioxane and 2.0 mL deoxygenated water. The mixture was stirred at 80 ℃ until the reaction was judged to be completed by TLC analysis. Water was added and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired compound.

To a solution of the above product dissolved in MeCN (8.0 mL) was added aq. HCl (1.5 mL conc. HCl in 5.0 mL water), then the mixture was cooled to 0 ℃, and it was added a solution of $NaNO_2$ (0.24 g in 5.0 mL water). After addition, the reaction was kept at the temperature lower than 5 ℃ for 1.0 h and it was added a solution of KI (0.73 g in 5.0 mL water). The reaction was kept at room temperature overnight. Water was added and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired compound.

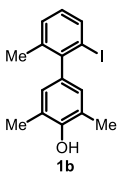
Under an argon atmosphere, a solution of BBr_3 (2.0 equiv) in DCM (1.0 mL) was slowly added to a solution of the above product in DCM (20.0 mL) at 0 ℃ and the mixture was stirred at room temperature for 3 h. After cooling to 0 ℃, the reaction was quenched with cold water and extracted with DCM. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product.



1a

2'-Iodo-3,5-dimethyl-[1,1'-biphenyl]-4-ol (**1a**)

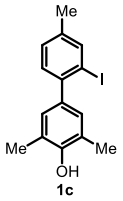
Starting material = 2-bromoaniline. White solid (0.66 g, 82% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.29-7.23 (m, 1H), 7.02-6.92 (m, 3H), 4.68 (s, 1H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 146.5, 139.4, 136.4, 130.2, 129.6, 128.4, 128.1, 122.5, 99.2, 16.0. IR (KBr): 3447, 3020, 2920, 1606, 1491, 1461, 1385, 878, 754, 722 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{13}IONa$ $[M+Na]^+$ 346.9909, found 346.9901.



1b

2'-Iodo-3,5,6'-trimethyl-[1,1'-biphenyl]-4-ol (**1b**)

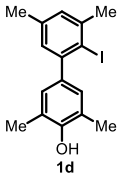
Starting material = 2-bromo-3-methylaniline. Yellow solid (0.54 g, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.74 (t, *J* = 7.7 Hz, 1H), 6.60 (s, 2H), 4.67 (s, 1H), 2.14 (s, 6H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 146.2, 138.0, 136.5, 136.4, 129.7, 129.1, 128.7, 122.8, 102.0, 22.5, 16.1. IR (KBr): 3463, 3023, 2921, 2857, 1604, 1553, 1490, 1442, 877, 768, 742 cm^{-1}. HRMS (ESI) m/z calculated for $C_{15}H_{15}IONa$ $[M+Na]^+$ 361.0065, found 361.0050.



1c

2'-Iodo-3,5,5'-trimethyl-[1,1'-biphenyl]-4-ol (**1c**)

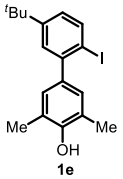
Starting material = 2-bromo-5-methylaniline. White solid (0.63 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.15 (s, 2H), 6.95 (s, 2H), 4.66 (s, 1H), 2.33 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 143.6, 139.9, 138.4, 136.2, 129.9, 129.7, 128.9, 122.4, 99.1, 20.5, 16.0. IR (KBr): 3450, 3025, 2920, 2859, 1598, 1499, 1474, 1384, 878, 821, 764 cm^{-1}. HRMS (ESI) m/z calculated for $C_{15}H_{15}IONa$ $[M+Na]^+$ 361.0065, found 361.0051.



1d

2'-Iodo-3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4-ol (**1d**)

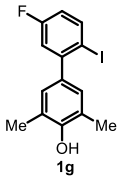
Starting material = 2-bromo-4,6-dimethylaniline. White solid (0.64 g, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (d, *J* = 1.5 Hz, 1H), 6.92 (s, 2H), 6.89 (s, 1H), 4.65 (s, 1H), 2.49 (s, 3H), 2.29 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 147.5, 142.0, 137.8, 137.3, 129.6, 129.2, 128.4, 122.4, 102.6, 30.0, 20.7, 16.1. IR (KBr): 3422, 3022, 2923, 2861, 1605, 1528, 1453, 1385, 895, 863, 764 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{17}IONa$ $[M+Na]^+$ 375.0222, found 375.0211.



1e

5'-(*Tert*-butyl)-2'-iodo-3,5-dimethyl-[1,1'-biphenyl]-4-ol (**1e**)

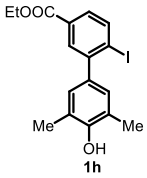
Starting material = 2-bromo-4-(*tert*-butyl)aniline. Yellow solid (0.63 g, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 2.5 Hz, 1H), 7.02-6.98 (m, 1H), 6.97 (s, 2H), 4.77 (s, 1H), 2.28 (s, 6H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 151.4, 145.9, 139.0, 136.8, 129.6, 127.6, 125.9, 122.5, 95.4, 34.6, 31.3, 16.1. IR (KBr): 3444, 3026, 2963, 2867, 1606, 1523, 1489, 1460, 1383, 1362, 875, 818, 772, 734 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{21}IONa$ $[M+Na]^+$ 403.0535, found 403.0518.



1g

5'-Fluoro-2'-iodo-3,5-dimethyl-[1,1'-biphenyl]-4-ol (**1g**)

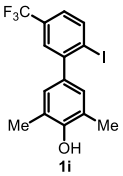
Starting material = 2-bromo-4-fluoroaniline. Yellow solid (0.60 g, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.81 (m, 1H), 7.04-6.99 (m, 1H), 6.95 (s, 2H), 6.79-6.71 (m, 1H), 4.72 (s, 1H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, *J* = 246.6 Hz), 152.1, 148.4 (d, *J* = 7.7 Hz), 140.5 (d, *J* = 7.8 Hz), 135.4 (d, *J* = 2.3 Hz), 129.4, 122.7, 117.4 (d, *J* = 21.8 Hz), 115.7 (d, *J* = 21.5 Hz), 92.0, 16.0. IR (KBr): 3448, 3021, 2921, 1596, 1569, 1491, 1386, 1261, 869, 808, 764 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{12}IFONa$ $[M+Na]^+$ 364.9815, found 364.9802.



1h

Ethyl 4'-hydroxy-6-iodo-3',5'-dimethyl-[1,1'-biphenyl]-3-carboxylate (**1h**)

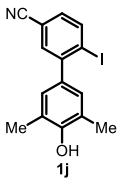
Starting material = ethyl 4-amino-3-bromobenzoate. White solid (0.66 g, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 2.1 Hz, 1H), 7.65-7.60 (m, 1H), 6.97 (s, 2H), 4.82 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 6H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 152.1, 146.9, 139.7, 135.5, 130.7, 130.4, 129.5, 128.9, 122.7, 105.5, 61.3, 16.0, 14.3. IR (KBr): 3454, 3026, 2984, 1701, 1587, 1559, 1490, 1458, 1386, 1315, 877, 849, 762 cm^{-1}. HRMS (ESI) m/z calculated for $C_{17}H_{17}IO_3Na$ $[M+Na]^+$ 419.0120, found 419.0106.



1i

2'-Iodo-3,5-dimethyl-5'-(trifluoromethyl)-[1,1'-biphenyl]-4-ol (**1i**)

Starting material = 2-bromo-4-(trifluoromethyl)aniline. Yellow solid (0.70 g, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 2.1 Hz, 1H), 7.26-7.18 (m, 1H), 6.97 (s, 2H), 4.77 (s, 1H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 147.4, 140.1, 135.1, 130.6 (q, *J* = 32.5 Hz), 129.4, 126.5 (q, *J* = 3.7 Hz), 124.7 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 270.8 Hz), 122.8, 103.6, 16.0. IR (KBr): 3373, 3027, 2912, 2858, 1599, 1570, 1489, 1463, 1167, 870, 823, 798 cm^{-1}. HRMS (ESI) m/z calculated for $C_{15}H_{12}IF_3ONa$ $[M+Na]^+$ 414.9783, found 414.9772.

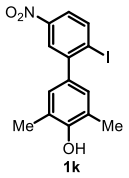


1j

4'-Hydroxy-6-iodo-3',5'-dimethyl-[1,1'-biphenyl]-3-carbonitrile (**1j**)

Starting material = 4-amino-3-bromobenzonitrile. Yellow solid (0.51 g, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.16-7.12 (m, 1H), 6.85 (s, 2H), 4.90 (s, 1H), 2.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 148.0, 140.5, 134.2, 132.8, 130.9, 129.3, 123.1,

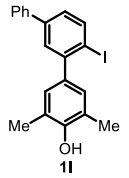
118.3, 112.1, 105.7, 16.1. IR (KBr): 3443, 3027, 2919, 2232, 1636, 1490, 1458, 1385, 1317, 873, 820, 764 cm^{-1}. HRMS (ESI) m/z calculated for $C_{15}H_{12}INONa$ $[M+Na]^+$ 371.9861, found 371.9845.



1k

2'-Iodo-3,5-dimethyl-5'-nitro-[1,1'-biphenyl]-4-ol (1k)

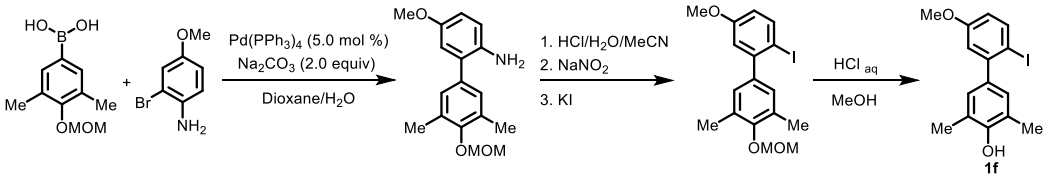
Starting material = 2-bromo-4-nitroaniline. Yellow solid (0.52 g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.11 (m, 2H), 7.86-7.82 (m, 1H), 7.01 (s, 2H), 4.85 (s, 1H), 2.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 148.3, 148.1, 140.5, 134.3, 129.3, 124.2, 123.0, 122.4, 107.5, 15.9. IR (KBr): 3443, 3030, 2918, 1636, 1516, 1488, 1456, 1384, 1275, 871, 824, 764 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{12}INO_3Na$ $[M+Na]^+$ 391.9760, found 391.9742.



1l

6'-Iodo-3,5-dimethyl-[1,1':3',1''-terphenyl]-4-ol (1l)

Starting material = 3-bromo-[1,1'-biphenyl]-4-amine. White solid (0.78 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.55-7.50 (m, 2H), 7.49 (d, *J* = 2.3 Hz, 1H), 7.38-7.32 (m, 2H), 7.31-7.27 (m, 1H), 7.17-7.12 (m, 1H), 6.99 (s, 2H), 4.75 (s, 1H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 147.1, 141.3, 140.1, 140.0, 136.5, 129.8, 129.1, 129.0, 127.9, 127.2, 127.1, 122.8, 98.1, 16.2. IR (KBr): 3446, 3030, 2922, 1604, 1491, 1462, 1379, 878, 825, 790, 762, 699 cm^{-1}. HRMS (ESI) m/z calculated for $C_{20}H_{17}IONa$ $[M+Na]^+$ 423.0222, found 423.0204.



1f

2'-Iodo-5'-methoxy-3,5-dimethyl-[1,1'-biphenyl]-4-ol (**1f**)

A 25 mL round bottom flask with a stir bar was fitted with a rubber septum and flame dried under high vacuum. The flask was purged with argon and charged with $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol), Na_2CO_3 (0.53 g, 5.0 mmol), (4-(methoxymethoxy)-3,5-dimethylphenyl)boronic acid (0.63 g, 3.0 mmol), 2-bromo-4-methoxyaniline (0.50 g, 2.5 mmol), 10.0 mL deoxygenated dioxane and 2.0 mL deoxygenated water. The mixture was stirred at 80 ℃ until the reaction was judged to be completed by TLC analysis. Water was added and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired compound.

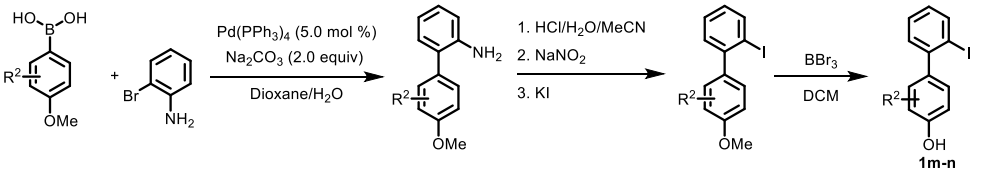
To a solution of the above product dissolved in MeCN (8.0 mL) was added aq. HCl (1.5 mL conc. HCl in 5.0 mL water), then the mixture was cooled to 0 ℃, and it was added a solution of $NaNO_2$ (0.24 g in 5.0 mL water). After addition, the reaction was kept at the temperature lower than 5 ℃ for 1.0 h and it was added a solution of KI (0.73 g in 5.0 mL water). The reaction was kept at room temperature overnight. Water was added and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and

concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired compound.

The above product was dissolved in 30.0 mL MeOH in a 100 mL round bottom flask, warmed to 70 ℃ and conc. HCl aq. (35%, 3 drops) was added. After stirring for 3 h, the flask was removed from the oil bath and cooled to room temperature, 40.0 mL of distilled water was added and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give a crude product of **1f**, which was purified by column chromatography to afford **1f** as a brown solid (0.51 g, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.7 Hz, 1H), 6.97 (s, 2H), 6.85 (d, *J* = 2.9 Hz, 1H), 6.64-6.58 (m, 1H), 4.70 (s, 1H), 3.79 (s, 3H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 151.8, 147.4, 139.9, 136.2, 129.4, 122.5, 115.9, 114.9, 87.7, 55.4, 16.0. IR (KBr): 3445, 3025, 2920, 2908, 1587, 1563, 1492, 1464, 1387, 1263, 877, 814, 766 cm^{-1}. HRMS (ESI) m/z calculated for $C_{15}H_{15}IO_2Na$ $[M+Na]^+$ 377.0014, found 377.0004.

General procedure for the preparation of phenol substrates 1m-n:

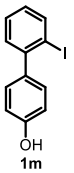
The following phenol substrates were prepared by Suzuki-Miyaura reaction between substituted (4-methoxyphenyl)boronic acid and 2-bromoaniline, followed by Sandmeyer reaction and demethylation with BBr_3.



A 25 mL round bottom flask with a stir bar was fitted with a rubber septum and flame dried under high vacuum. The flask was purged with argon and charged with $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol), Na_2CO_3 (0.53 g, 5.0 mmol), substituted (4-methoxyphenyl)boronic acid (3.0 mmol), 2-bromoaniline (0.43 g, 2.5 mmol), 10.0 mL deoxygenated dioxane and 2.0 mL deoxygenated water. The mixture was stirred at 80 ℃ until the reaction was judged to be completed by TLC analysis. Water was added and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired compound.

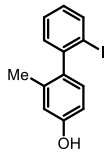
To a solution of the above product dissolved in MeCN (8.0 mL) was added aq. HCl (1.5 mL conc. HCl in 5.0 mL water), then the mixture was cooled to 0 ℃, and it was added a solution of $NaNO_2$ (0.24 g in 5.0 mL water). After addition, the reaction was kept at the temperature lower than 5 ℃ for 1.0 h and it was added a solution of KI (0.73 g in 5.0 mL water). The reaction was kept at room temperature overnight. Water was added and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired compound.

Under an argon atmosphere, a solution of BBr_3 (2.0 equiv) in DCM (1.0 mL) was slowly added to a solution of the above product in DCM (20.0 mL) at 0 ℃ and the mixture was stirred at room temperature for 3 h. After cooling to 0 ℃, the reaction was quenched with cold water and extracted with DCM. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **1m-n**.



2'-Iodo-[1,1'-biphenyl]-4-ol (1m)

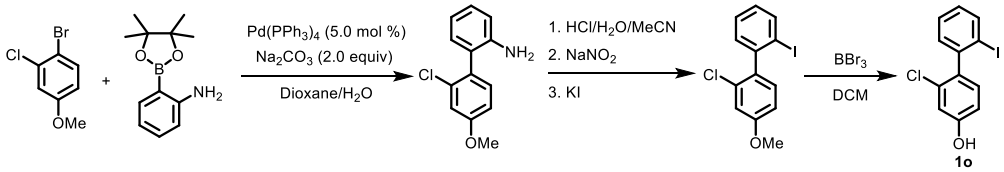
Starting material = (4-methoxyphenyl)boronic acid. White solid (0.56 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.92 (m, 1H), 7.39-7.34 (m, 1H), 7.30-7.27 (m, 1H), 7.25-7.24 (m, 1H), 7.23-7.21 (m, 1H), 7.04-6.98 (m, 1H), 6.93-6.85 (m, 2H), 4.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 146.2, 139.5, 137.1, 130.7, 130.2, 128.6, 128.2, 114.9, 99.2. IR (KBr): 3160, 1896, 1609, 1591, 1515, 1459, 835, 820, 760 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_9IONa$ $[M+Na]^+$ 318.9596, found 318.9583.



1n

2'-Iodo-2-methyl-[1,1'-biphenyl]-4-ol (**1n**)

Starting material = (4-methoxy-2-methylphenyl)boronic acid. White solid (0.56 g, 72% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.40 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.67 (s, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.3, 146.7, 138.9, 136.5, 135.6, 130.7, 130.4, 129.3, 128.7, 116.8, 113.0, 102.0, 20.3. IR (KBr): 2426, 3054, 2921, 1610, 1585, 1505, 1457, 1384, 896, 813, 763, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{11}IONa$ $[M+Na]^+$ 332.9752, found 332.9737.



1o

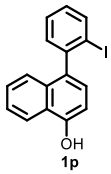
2-Chloro-2'-iodo-[1,1'-biphenyl]-4-ol (1o)

A 25 mL round bottom flask with a stir bar was fitted with a rubber septum and flame dried under high vacuum. The flask was purged with argon and charged with $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol), Na_2CO_3 (0.53 g, 5.0 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (0.66 g, 3.0 mmol), 1-bromo-2-chloro-4-methoxybenzene (0.55 g, 2.5 mmol), 10.0 mL deoxygenated dioxane and 2.0 mL deoxygenated water. The mixture was stirred at 80 ℃ until the reaction was judged to be completed by TLC analysis. Water was added and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired compound.

To a solution of the above product dissolved in MeCN (8.0 mL) was added aq. HCl (1.5 mL conc. HCl in 5.0 mL water), then the mixture was cooled to 0 ℃, and it was added a solution of $NaNO_2$ (0.24 g in 5.0 mL water). After addition, the reaction was kept at the temperature lower than 5 ℃ for 1.0 h and it was added a solution of KI (0.73 g in 5.0 mL water). The reaction was kept at room temperature overnight. Water was added and extracted with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired compound.

Under an argon atmosphere, a solution of BBr_3 (2.0 equiv) in DCM (1.0 mL) was slowly added to a solution of the above product in DCM (20.0 mL) at 0 ℃ and the mixture was stirred at room temperature for 3 h. After cooling to 0 ℃, the reaction was quenched with cold water and extracted with DCM. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **1o** as a white solid (0.46 g, 56% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.03 (s, 1H), 7.95-7.91 (m, 1H), 7.46-7.41 (m, 1H), 7.26-7.21 (m, 1H), 7.14-7.08 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 6.83-6.78 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.2, 149.3, 143.7, 138.7, 137.5, 137.0, 135.7, 134.7, 133.4, 120.8, 119.5, 106.4. IR

(KBr): 3405, 3028, 2994, 1770, 1758, 1655, 1460, 1246, 902, 852, 758 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_8IClONa$ $[M+Na]^+$ 352.9206, found 352.9194.



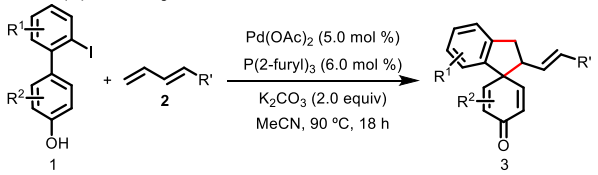
1p

4-(2-Iodophenyl)naphthalen-1-ol (1p)

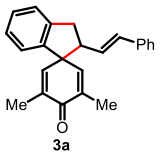
White solid (0.55 g, 63% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.52-7.48 (m, 1H), 7.45-7.41 (m, 2H), 7.38-7.32 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.13-7.09 (m, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 5.35 (s, 1H). Analytical data are in accordance with the literature values.[1]

C. Catalytic results:

General procedure for the Pd(0)-Catalyzed Dearomatization:



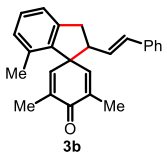
In a glovebox, a 5.0 mL vial equipped with a stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), tri(2-furyl)phosphine (2.8 mg, 0.012 mmol), K_2CO_3 (55.2 mg, 0.4 mmol) and MeCN (1.6 mL) was then added. After the catalyst mixture was stirred at room temperature for 10 min, substrate **1** (0.2 mmol) and 1,3-diene **2** (0.4 mmol) were sequentially added. The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 90 ℃ for 18 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired product **3**.



3a

(*E*)-3,5-Dimethyl-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3a)

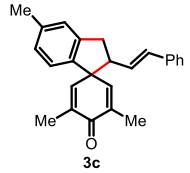
Yellow solid (55.5 mg, 85% yield). PE/EA = 20:1, R_f = 0.46. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.4 Hz, 1H), 7.31-7.27 (m, 4H), 7.25-7.15 (m, 3H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 1.3 Hz, 1H), 6.66 (d, *J* = 1.3 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.11 (dd, *J* = 15.8, 7.4 Hz, 1H), 3.49-3.39 (m, 1H), 3.35-3.19 (m, 2H), 2.02 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 147.6, 144.4, 143.6, 142.6, 136.9, 136.7, 133.8, 131.8, 128.6, 128.1, 127.7, 127.6, 127.1, 126.3, 125.3, 124.1, 57.4, 54.9, 37.0, 16.4, 16.3. IR (KBr): 3062, 3026, 2924, 2852, 1638, 1602, 1496, 1476, 1449, 1461, 1375, 1264, 966, 761, 751, 696 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{22}ONa$ $[M+Na]^+$ 349.1568, found 349.1553.



3b

(*E*)-3,5,7'-Trimethyl-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3b)

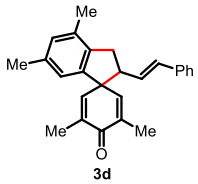
Yellow solid (57.2 mg, 84% yield). PE/EA = 20:1, R_f = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.25 (m, 4H), 7.24-7.15 (m, 3H), 7.00-6.91 (m, 1H), 6.82-6.77 (m, 1H), 6.63-6.59 (m, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.00 (dd, *J* = 15.8, 7.4 Hz, 1H), 3.41-3.12 (m, 3H), 2.01 (s, 6H), 1.90 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 148.9, 143.2, 143.0, 140.9, 136.9, 136.1, 135.7, 135.2, 131.9, 129.3, 128.6, 128.2, 127.5, 127.3, 126.3, 122.9, 57.8, 54.8, 37.2, 18.2, 16.3, 16.2. IR (KBr): 3056, 3026, 2923, 2852, 1633, 1495, 1460, 1447, 1398, 1264, 964, 753, 748, 704 cm^{-1}. HRMS (ESI) m/z calculated for $C_{25}H_{24}ONa$ $[M+Na]^+$ 363.1725, found 363.1713.



3c

(*E*)-3,5,5'-Trimethyl-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3c)

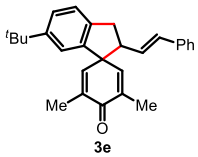
Yellow solid (51.7 mg, 76% yield). PE/EA = 20:1, R_f = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.28 (m, 3H), 7.27-7.15 (m, 3H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.73-6.69 (m, 1H), 6.66-6.62 (m, 1H), 6.48-6.40 (m, 1H), 6.10 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.48-3.36 (m, 1H), 3.30-3.14 (m, 2H), 2.36 (s, 3H), 2.00 (d, *J* = 1.2 Hz, 3H), 1.85 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8, 147.8, 144.6, 142.8, 140.5, 138.0, 136.9, 136.6, 133.6, 131.7, 128.6, 127.9, 127.8, 127.5, 126.3, 126.0, 123.8, 57.0, 55.0, 36.8, 21.4, 16.4, 16.3. IR (KBr): 3057, 3025, 2923, 2855, 1634, 1481, 1447, 1399, 1374, 1317, 965, 879, 849, 748, 694 cm^{-1}. HRMS (ESI) m/z calculated for $C_{25}H_{24}ONa$ $[M+Na]^+$ 363.1725, found 363.1711.



3d

(*E*)-3,4',5,6'-Tetramethyl-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3d)

Light yellow solid (58.1 mg, 82% yield). PE/EA = 20:1, R_f = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 4H), 7.25-7.19 (m, 1H), 6.92 (s, 1H), 6.73 (s, 1H), 6.65 (s, 1H), 6.56 (s, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.13 (dd, *J* = 15.8, 7.4 Hz, 1H), 3.47-3.36 (m, 1H), 3.29-3.20 (m, 1H), 3.12-3.02 (m, 1H), 2.32 (s, 3H), 2.27 (s, 3H), 2.03 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8, 148.0, 144.8, 143.4, 138.5, 137.2, 137.0, 136.5, 134.6, 133.5, 131.7, 129.9, 128.6, 127.9, 127.5, 126.3, 121.9, 57.6, 54.6, 35.1, 21.2, 19.2, 16.4, 16.3. IR (KBr): 3060, 3026, 2923, 2853, 1636, 1595, 1494, 1477, 1447, 1397, 1373, 1264, 963, 746, 694 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{26}ONa$ $[M+Na]^+$ 377.1881, found 377.1867.

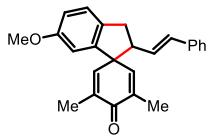


3e

(*E*)-6'-(*Tert*-butyl)-3,5-dimethyl-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3e)

Light yellow solid (49.7 mg, 65% yield). PE/EA = 20:1, R_f = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.15 (m, 7H), 6.88 (d, *J* = 1.4 Hz, 1H), 6.77-6.73 (m, 1H), 6.69-6.65 (m, 1H), 6.46-6.39 (m, 1H), 6.09 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.51-3.37 (m, 1H), 3.30-3.12 (m, 2H), 2.03 (d, *J* = 1.2 Hz, 3H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.9, 150.6, 147.8, 144.8, 143.5, 139.7, 136.9, 136.7, 133.6, 131.7, 128.6, 127.8, 127.5, 126.3, 125.3, 124.8, 120.7, 57.6, 55.2, 36.5, 34.8, 31.5, 16.4, 16.3.

IR (KBr): 3059, 3026, 2961, 2925, 2868, 1636, 1492, 1448, 1397, 1384, 1375, 1262, 964, 897, 825, 750, 695 cm^{-1}. HRMS (ESI) m/z calculated for $C_{28}H_{30}ONa$ $[M+Na]^+$ 405.2194, found 405.2180.



3f

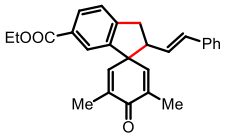
(*E*)-6'-Methoxy-3,5-dimethyl-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (**3f**)

Yellow solid (29.9 mg, 42% yield). PE/EA = 20:1, R_f = 0.36. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23-7.19 (m, 4H), 7.18-7.10 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 6.57 (s, 1H), 6.43-6.28 (m, 2H), 6.16 (dd, *J* = 16.0, 7.6 Hz, 1H), 3.67 (s, 3H), 3.43-3.28 (m, 1H), 3.22-3.01 (m, 2H), 1.94 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 159.2, 147.5, 145.0, 144.3, 136.9, 136.8, 134.4, 133.8, 131.7, 128.6, 127.6, 127.5, 126.3, 125.9, 114.1, 109.1, 57.5, 55.5, 55.4, 36.1, 16.4, 16.3. IR (KBr): 3058, 3025, 2953, 2924, 2854, 1636, 1609, 1489, 1464, 1448, 1374, 1350, 1214, 964, 871, 814, 746, 694 cm^{-1}. HRMS (ESI) m/z calculated for $C_{25}H_{24}O_2Na$ $[M+Na]^+$ 379.1674, found 379.1662.

3g

(*E*)-6'-Fluoro-3,5-dimethyl-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3g)

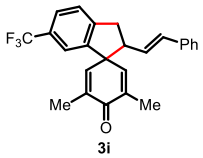
Light yellow solid (61.3 mg, 89% yield). PE/EA = 20:1, R_f = 0.44. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.19 (m, 6H), 6.98-6.91 (m, 1H), 6.73-6.68 (m, 1H), 6.66-6.57 (m, 2H), 6.48-6.40 (m, 1H), 6.08 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.51-3.40 (m, 1H), 3.30-3.13 (m, 2H), 2.01 (d, *J* = 1.3 Hz, 3H), 1.87 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 162.3 (d, *J* = 246.3 Hz), 146.7, 145.8 (d, *J* = 7.3 Hz), 143.6, 137.8 (d, *J* = 2.6 Hz), 137.1, 136.7, 134.2, 132.0, 128.6, 127.6, 127.2, 126.3, 126.2 (d, *J* = 8.6 Hz), 115.0 (d, *J* = 22.3 Hz), 111.2 (d, *J* = 22.5 Hz), 57.3, 55.4, 36.2, 16.4, 16.3. IR (KBr): 3059, 3026, 2924, 2853, 1635, 1483, 1448, 1375, 1317, 1262, 965, 870, 815, 749, 696 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{21}FONa$ $[M+Na]^+$ 367.1474, found 367.1462.



3h

(*E*)-Ethyl 3,5-dimethyl-4-oxo-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-indene]-6'-carboxylate (3h)

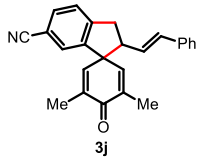
Light yellow solid (69.3 mg, 87% yield). PE/EA = 20:1, R_f = 0.34. ^1H NMR (400 MHz, $CDCl_3$): δ 7.99-7.95 (m, 1H), 7.55 (d, *J* = 1.2 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.31-7.28 (m, 3H), 7.26 (s, 1H), 7.25-7.20 (m, 1H), 6.74-6.70 (m, 1H), 6.63-6.59 (m, 1H), 6.49-6.42 (m, 1H), 6.08 (dd, *J* = 15.8, 7.5 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.49-3.42 (m, 1H), 3.38-3.22 (m, 2H), 2.03 (d, *J* = 1.3 Hz, 3H), 1.88 (d, *J* = 1.3 Hz, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5, 166.4, 147.8, 146.7, 144.2, 143.5, 137.2, 136.7, 134.3, 132.1, 129.9, 129.7, 128.6, 127.7, 127.0, 126.3, 125.2, 125.1, 61.1, 57.0, 54.9, 36.9, 16.4, 16.3, 14.4. IR (KBr): 3058, 3027, 2924, 2853, 1715, 1637, 1610, 1578, 1494, 1447, 1397, 1368, 1281, 964, 906, 845, 747, 695 cm^{-1}. HRMS (ESI) m/z calculated for $C_{27}H_{26}O_3Na$ $[M+Na]^+$ 421.1780, found 421.1763.



3i

(*E*)-3,5-Dimethyl-2'-styryl-6'-(trifluoromethyl)-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3i)

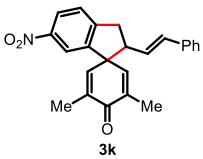
Light yellow solid (59.2 mg, 75% yield). PE/EA = 20:1, R_f = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.50 (m, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.31-7.20 (m, 5H), 7.15 (s, 1H), 6.73-6.69 (m, 1H), 6.62-6.59 (m, 1H), 6.49-6.42 (m, 1H), 6.08 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.52-3.42 (m, 1H), 3.39-3.22 (m, 2H), 2.04 (d, *J* = 1.3 Hz, 3H), 1.89 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.3, 146.6, 146.3, 144.8, 143.1, 137.4, 136.6, 134.5, 132.3, 129.8 (q, *J* = 32.0 Hz), 128.6, 127.7, 126.8, 126.3, 125.6, 125.2 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 270.6 Hz), 121.0 (q, *J* = 3.7 Hz), 57.0, 55.0, 36.8, 16.4, 16.3. IR (KBr): 3057, 3027, 2924, 2853, 1637, 1495, 1447, 1425, 1374, 1274, 1239, 965, 893, 832, 747, 694 cm^{-1}. HRMS (ESI) m/z calculated for $C_{25}H_{21}F_3ONa$ $[M+Na]^+$ 417.1442, found 417.1430.



3j

(*E*)-3,5-Dimethyl-4-oxo-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-indene]-6'-carbonitrile (3j)

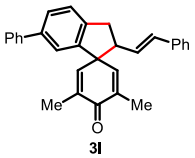
Yellow solid (32.3 mg, 46% yield). PE/EA = 20:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.30-7.26 (m, 5H), 7.21 (s, 1H), 6.67 (s, 1H), 6.58 (s, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.06 (dd, *J* = 15.8, 7.4 Hz, 1H), 3.48-3.42 (m, 1H), 3.39-3.24 (m, 2H), 2.03 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.1, 148.0, 145.7, 145.3, 142.5, 137.7, 136.5, 134.8, 132.6, 132.1, 128.6, 127.9, 127.8, 126.3, 126.2, 118.7, 111.1, 56.9, 54.7, 37.1, 16.4, 16.3. IR (KBr): 3059, 3028, 2924, 2854, 2228, 1636, 1495, 1482, 1448, 1375, 1266, 966, 902, 829, 740, 696 cm^{-1}. HRMS (ESI) m/z calculated for $C_{25}H_{21}NONa$ $[M+Na]^+$ 374.1521, found 374.1507.



3k

(*E*)-3,5-Dimethyl-6'-nitro-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3k)

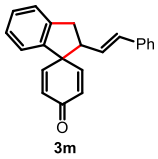
Yellow solid (36.4 mg, 49% yield). PE/EA = 20:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17-8.13 (m, 1H), 7.76 (d, *J* = 2.1 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.33-7.27 (m, 4H), 7.25-7.20 (m, 1H), 6.70 (d, *J* = 1.4 Hz, 1H), 6.58 (d, *J* = 1.4 Hz, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.07 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.56-3.46 (m, 1H), 3.44-3.24 (m, 2H), 2.05 (d, *J* = 1.0 Hz, 3H), 1.89 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.0, 149.9, 147.8, 145.9, 145.4, 142.2, 137.9, 136.4, 135.0, 132.6, 128.6, 127.8, 126.3, 126.2, 125.8, 123.7, 119.5, 56.8, 55.0, 36.8, 16.4, 16.3. IR (KBr): 3062, 3029, 2923, 2853, 1637, 1520, 1495, 1447, 1375, 1345, 1262, 964, 899, 842, 749, 695 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{21}NO_3Na$ $[M+Na]^+$ 394.1419, found 394.1408.



3l

(*E*)-3,5-Dimethyl-6'-phenyl-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (**3l**)

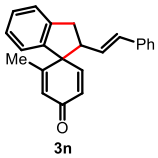
Yellow solid (66.7 mg, 83% yield). PE/EA = 20:1, R_f = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.49 (m, 3H), 7.46-7.40 (m, 3H), 7.35 (d, *J* = 7.1 Hz, 1H), 7.33-7.29 (m, 4H), 7.25-7.18 (m, 1H), 7.12 (s, 1H), 6.78 (d, *J* = 1.3 Hz, 1H), 6.72 (s, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.14 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.54-3.45 (m, 1H), 3.39-3.23 (m, 2H), 2.04 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 147.5, 144.4, 144.3, 141.7, 140.8, 140.7, 136.9, 136.8, 133.9, 131.9, 128.8, 128.6, 127.6, 127.5, 127.4, 127.2, 127.1, 126.3, 125.6, 122.8, 57.4, 55.1, 36.6, 16.5, 16.3. IR (KBr): 3058, 3027, 2924, 2853, 1634, 1495, 1477, 1448, 1374, 1264, 964, 890, 814, 750, 697 cm^{-1}. HRMS (ESI) m/z calculated for $C_{30}H_{26}ONa$ $[M+Na]^+$ 425.1881, found 425.1866.



3m

(*E*)-2'-Styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (**3m**)

Yellow solid (39.9 mg, 67% yield). PE/EA = 20:1, R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.4 Hz, 1H), 7.32-7.27 (m, 5H), 7.25-7.18 (m, 2H), 7.01-6.94 (m, 2H), 6.91-6.86 (m, 1H), 6.55-6.45 (m, 2H), 6.26-6.21 (m, 1H), 6.13 (dd, *J* = 15.8, 7.6 Hz, 1H), 3.55-3.46 (m, 1H), 3.38-3.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 152.3, 149.5, 142.7, 142.3, 136.5, 132.4, 130.7, 128.6, 128.5, 127.8, 127.7, 127.4, 126.8, 126.3, 125.5, 124.3, 58.1, 54.9, 37.0. IR (KBr): 3060, 3026, 2925, 2852, 1663, 1611, 1494, 1475, 1449, 1263, 965, 753, 745, 693 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{18}ONa$ $[M+Na]^+$ 321.1255, found 321.1243.

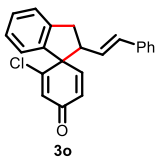


3n

(*E*)-2-methyl-2'-styryl-2',3'-dihydrospiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (**3n**)

Compound **3n** was isolated by silica gel column chromatography as a diastereomeric mixture (dr = 2.6:1) in 70% yield (43.7 mg). The pure major diastereomer was obtained by preparative TLC on silica gel.

White solid. PE/EA = 20:1, R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.4 Hz, 1H), 7.23-7.10 (m, 7H), 6.80-6.74 (m, 2H), 6.41-6.33 (m, 2H), 6.15-6.10 (m, 1H), 6.02 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.67-3.54 (m, 1H), 3.31-3.16 (m, 2H), 1.89 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.6, 159.8, 149.9, 143.2, 142.9, 136.6, 132.2, 131.2, 128.6, 128.3, 127.7, 127.6, 127.1, 126.9, 126.3, 125.4, 123.8, 61.1, 52.9, 36.7, 20.3. IR (KBr): 3060, 3026, 2923, 2851, 1663, 1625, 1494, 1475, 1456, 1351, 965, 753, 731, 694 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{20}ONa$ $[M+Na]^+$ 335.1412, found 335.1404.

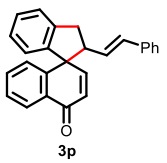


3o

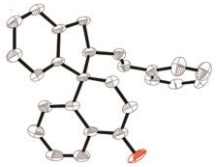
(*E*)-2-Chloro-2'-styryl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3o)

Compound **3o** was isolated by silica gel column chromatography as a diastereomeric mixture (dr = 1.8:1) in 45% yield (30.0 mg). The pure major diastereomer was obtained by preparative TLC on silica gel.

White solid. PE/EA = 20:1, R_f = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.4 Hz, 1H), 7.29-7.26 (m, 1H), 7.26-7.16 (m, 6H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 10.0 Hz, 1H), 6.72 (d, *J* = 1.7 Hz, 1H), 6.49-6.43 (m, 1H), 6.20-6.15 (m, 1H), 6.04 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.03-3.90 (m, 1H), 3.37-3.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.9, 157.7, 148.9, 142.6, 141.7, 136.4, 133.2, 132.2, 128.8, 128.6, 127.9, 127.7, 126.4, 126.2, 125.4, 124.0, 63.3, 54.2, 36.7. IR (KBr): 3061, 3026, 2924, 2852, 1699, 1657, 1595, 1521, 1495, 753, 729, 694 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{17}ClONa$ $[M+Na]^+$ 355.0866, found 355.0870.



3p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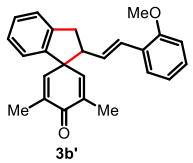
(*E*)-2-styryl-2,3-dihydro-4'H-spiro[indene-1,1'-naphthalen]-4'-one (3p)

Compound **3p** was isolated by silica gel column chromatography as a diastereomeric mixture (dr = 4.5:1) in 92% yield (64.1 mg). The pure major diastereomer was obtained by preparative TLC on silica gel and unambiguously assigned by X-ray studies.

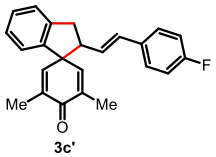
Yellow solid. PE/EA = 20:1, R_f = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.21 (m, 1H), 7.59-7.52 (m, 1H), 7.47-7.39 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.30-7.26 (m, 1H), 7.25-7.11 (m, 6H), 6.92 (d, *J* = 10.2 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 10.2 Hz, 1H), 6.20 (d, *J* = 15.9 Hz, 1H), 6.06 (dd, *J* = 15.8, 7.2 Hz, 1H), 3.85-3.79 (m, 1H), 3.44-3.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.0, 149.7, 147.0, 146.4, 142.7, 136.7, 133.1, 132.8, 132.0, 128.5, 128.3, 128.0, 127.6, 127.5, 127.4, 127.2, 127.0, 126.4, 126.3, 125.1, 125.0, 59.7, 58.6, 36.7. IR (KBr): 3061, 3027, 2924, 2852, 1662, 1621, 1495, 1475, 1455, 1265, 965, 756, 737, 696 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{20}ONa$ $[M+Na]^+$ 371.1412, found 371.1403.



3b'

(*E*)-2'-(2-Methoxystyryl)-3,5-dimethyl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3b')

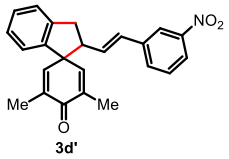
Light yellow solid (49.9 mg, 70% yield). PE/EA = 10:1, R_f = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.25-7.15 (m, 2H), 6.95-6.88 (m, 2H), 6.88-6.83 (m, 1H), 6.76 (d, *J* = 15.9 Hz, 2H), 6.67 (d, *J* = 1.1 Hz, 1H), 6.09 (dd, *J* = 15.9, 7.4 Hz, 1H), 3.83 (s, 3H), 3.52-3.42 (m, 1H), 3.37-3.21 (m, 2H), 2.02 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8, 156.5, 147.8, 144.6, 143.7, 142.8, 136.6, 133.6, 128.6, 128.2, 128.0, 127.1, 126.7, 126.4, 126.0, 125.3, 124.1, 120.7, 110.9, 57.5, 55.5, 55.2, 37.0, 16.4, 16.2. IR (KBr): 3058, 3027, 2923, 2838, 1633, 1599, 1489, 1463, 1374, 1275, 972, 751 cm^{-1}. HRMS (ESI) m/z calculated for $C_{25}H_{24}O_2Na$ $[M+Na]^+$ 379.1674, found 379.1664.



3c'

(*E*)-2'-(4-Fluorostyryl)-3,5-dimethyl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (**3c'**)

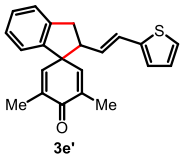
Light yellow solid (59.8 mg, 87% yield). PE/EA = 20:1, R_f = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.4 Hz, 1H), 7.28-7.22 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.01-6.94 (m, 2H), 6.91 (d, *J* = 7.4 Hz, 1H), 6.75-6.71 (m, 1H), 6.66-6.62 (m, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.01 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.46-3.37 (m, 1H), 3.33-3.18 (m, 2H), 2.01 (d, *J* = 1.3 Hz, 3H), 1.87 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 162.3 (d, *J* = 249.0 Hz), 147.5, 144.3, 143.5, 142.5, 136.8, 133.8, 133.0 (d, *J* = 3.3 Hz), 130.6, 128.1, 127.8 (d, *J* = 8.0 Hz), 127.4 (d, *J* = 2.1 Hz), 127.2, 125.3, 124.1, 115.5 (d, *J* = 21.5 Hz), 57.4, 54.8, 36.9, 16.4, 16.3. IR (KBr): 3054, 3028, 2923, 2851, 1636, 1601, 1508, 1457, 1374, 1264, 966, 815, 749 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{21}FONa$ $[M+Na]^+$ 367.1474, found 367.1462.



3d'

(*E*)-3,5-Dimethyl-2'-(3-nitrostyryl)-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3d')

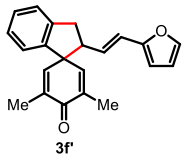
Yellow solid (37.1 mg, 50% yield). PE/EA = 20:1, R_f = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 8.09-8.04 (m, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.74 (s, 1H), 6.66 (s, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.25 (dd, *J* = 15.8, 7.7 Hz, 1H), 3.52-3.41 (m, 1H), 3.35-3.23 (m, 2H), 2.02 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5, 148.6, 147.2, 143.8, 143.3, 142.2, 138.6, 137.0, 134.0, 132.0, 131.1, 129.8, 129.5, 128.2, 127.3, 125.4, 124.1, 122.2, 121.0, 57.4, 54.8, 36.8, 16.4, 16.3. IR (KBr): 3061, 3030, 2924, 2853, 1636, 1528, 1475, 1457, 1374, 1265, 965, 875, 803, 761 cm^{-1}. HRMS (ESI) m/z calculated for $C_{24}H_{21}NO_3Na$ $[M+Na]^+$ 394.1419, found 394.1406.



3e'

(*E*)-3,5-Dimethyl-2'-(2-(thiophen-2-yl)vinyl)-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3e')

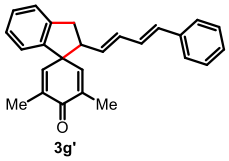
Yellow solid (53.8 mg, 81% yield). PE/EA = 20:1, R_f = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.4 Hz, 1H), 7.29-7.23 (m, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 5.0 Hz, 1H), 6.97-6.86 (m, 3H), , 6.71 (s, 1H), 6.64 (s, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 5.95 (dd, *J* = 15.6, 7.6 Hz, 1H), 3.46-3.34 (m, 1H), 3.33-3.15 (m, 2H), 2.02 (d, *J* = 0.9 Hz, 3H), 1.88 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 147.4, 144.1, 143.5, 142.5, 141.9, 136.8, 133.9, 128.1, 127.4, 127.3, 127.2, 125.4, 125.3, 124.9, 124.1, 57.4, 54.8, 36.9, 16.4, 16.2. IR (KBr): 3068, 3035, 2923, 2850, 1636, 1601, 1475, 1456, 1398, 1374, 1265, 954, 933, 874, 760, 738, 700 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{20}SONa$ $[M+Na]^+$ 355.1133, found 355.1119.



3f'

(*E*)-2'-(2-(Furan-2-yl)vinyl)-3,5-dimethyl-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3f')

Yellow solid (50.1 mg, 79% yield). PE/EA = 20:1, R_f = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.30 (m, 2H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 6.64 (s, 1H), 6.37-6.32 (m, 1H), 6.25 (d, *J* = 15.9 Hz, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 6.04 (dd, *J* = 15.8, 7.7 Hz, 1H), 3.42-3.36 (m, 1H), 3.29-3.17 (m, 2H), 2.01 (d, *J* = 0.9 Hz, 3H), 1.87 (d, *J* = 0.9 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8, 152.2, 147.5, 144.2, 143.6, 142.5, 141.8, 136.7, 133.8, 128.0, 127.1, 126.3, 125.3, 124.0, 120.3, 111.2, 107.6, 57.3, 54.9, 37.0, 16.4, 16.3. IR (KBr): 3065, 3033, 2923, 2851, 1635, 1489, 1474, 1457, 1398, 1374, 1261, 960, 933, 883, 763, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{20}O_2Na$ $[M+Na]^+$ 339.1361, found 339.1349.

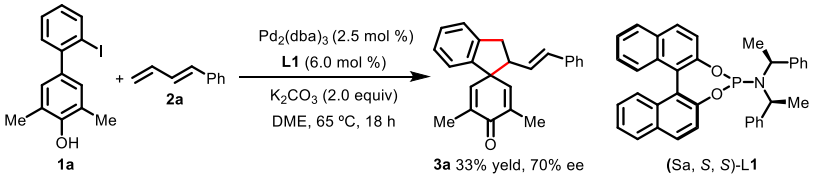


3g'

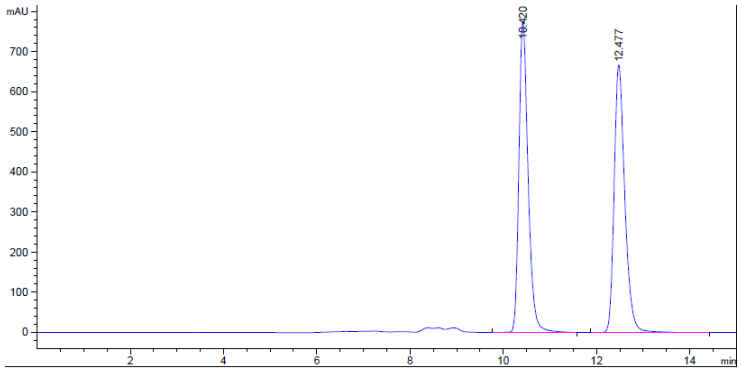
3,5-Dimethyl-2'-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)-2',3'-dihydrospiro[cyclohexa[2,5]diene-1,1'-inden]-4-one (3g')

Light yellow solid (46.5 mg, 66% yield). PE/EA = 20:1, R_f = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.28 (m, 6H), 7.24−7.14 (m, 2H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.73-6.59 (m, 2H), 6.62 (s, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 6.31-6.22 (m, 1H), 5.72 (dd, J = 15.1, 7.4 Hz, 1H), 3.45-3.33 (m, 1H), 3.31-3.13 (m, 2H), 2.02 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8, 147.6, 144.4, 143.6, 142.6, 137.2, 136.7, 133.7, 132.3, 131.9, 131.8, 128.6, 128.5, 128.0, 127.5, 127.1, 126.3, 125.3, 124.0, 57.3, 54.8, 36.9, 16.4, 16.3. IR (KBr): 3055, 3023, 2923, 2851, 1633, 1498, 1477, 1447, 1375, 1262, 966, 753, 749, 692 cm^{-1}. HRMS (ESI) m/z calculated for $C_{26}H_{24}ONa$ $[M+Na]^+$ 375.1725, found 375.1712.

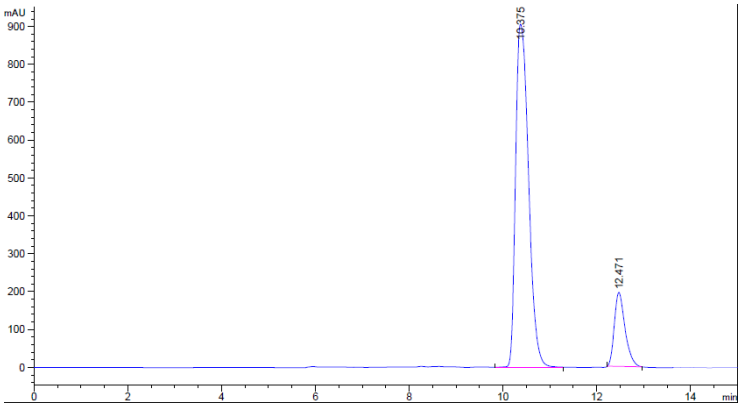
D. Preliminary asymmetric studies:



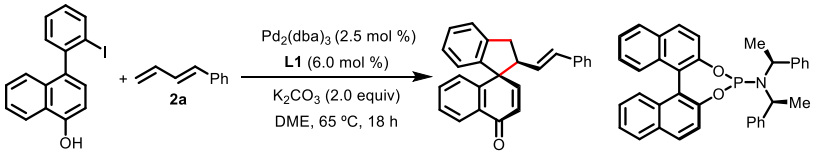
In a glovebox, a 5.0 mL vial equipped with a stir bar was charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), phosphoramidite ligand **L1** (3.2 mg, 0.006 mmol), K_2CO_3 (27.6 mg, 0.2 mmol) and DME (0.6 mL) was then added. After the catalyst mixture was stirred at room temperature for 10 min, substrate **1a** (32.4 mg, 0.1 mmol) and 1,3-diene **2a** (26.0 mg, 0.2 mmol) were sequentially added. The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 65 ℃ for 18 h. The crude reaction mixture was then subjected to a silica gel column to afford the desired product **3a**. 33% yield. 70% ee, $[\alpha]_D^{20}$ = +11.9 (c = 0.5, $CHCl_3$). The ee of compound **3a** was determined by HPLC using an IB column (*n*-hexane/*i*-PrOH = 85/15, flow rate = 0.5 mL/min, t_{major} = 10.4 min, t_{minor} = 12.5 min).



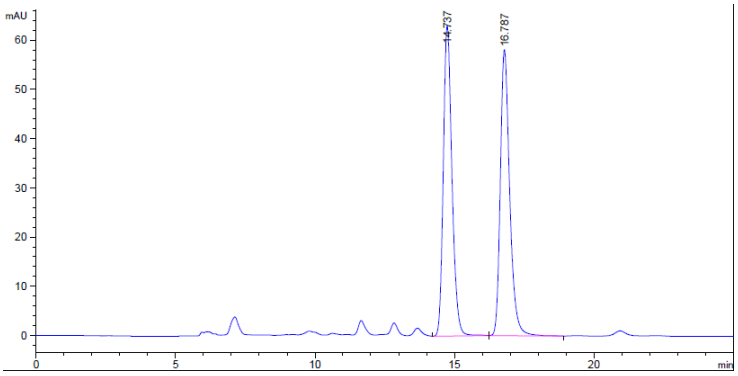
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.420	BB	0.2076	1.06125e4	775.87927	50.0771
2	12.477	BB	0.2411	1.05798e4	666.73328	49.9229



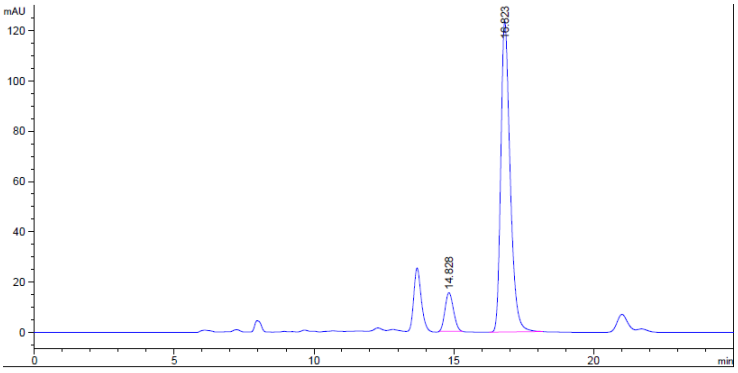
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.375	BBA	0.3046	1.73614e4	906.01648	84.8395
2	12.471	BBA	0.2390	3102.42310	195.63242	15.1605



In a glovebox, a 5.0 mL vial equipped with a stir bar was charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol), phosphoramidite ligand **L1** (3.2 mg, 0.006 mmol), K_2CO_3 (27.6 mg, 0.2 mmol) and DME (0.6 mL) was then added. After the catalyst mixture was stirred at room temperature for 10 min, substrate **1p** (34.6 mg, 0.1 mmol) and 1,3-diene **2a** (26.0 mg, 0.2 mmol) were sequentially added. The vial was sealed with a Teflon screw cap and the reaction mixture was heated at 65 ℃ for 18 h. The crude reaction mixture was then subjected to a silica gel column to afford the desired product **3p** as a diastereomeric mixture (dr = 2.5:1) in 76% yield. The pure major diastereomer **3p'** was obtained by preparative TLC on silica gel. 80% ee, $[\alpha]_D^{13}$ = +33.1 (c = 0.5, $CHCl_3$). The ee of the major diastereomer **3p'** was determined by HPLC using an IB column (*n*-hexane/*i*-PrOH = 85/15, flow rate = 0.5 mL/min, t_{major} = 16.8 min, t_{minor} = 14.8 min).



#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.737	BB	0.3280	1356.85754	63.05946	50.0368
2	16.787	BB	0.3531	1354.86353	58.10033	49.9632

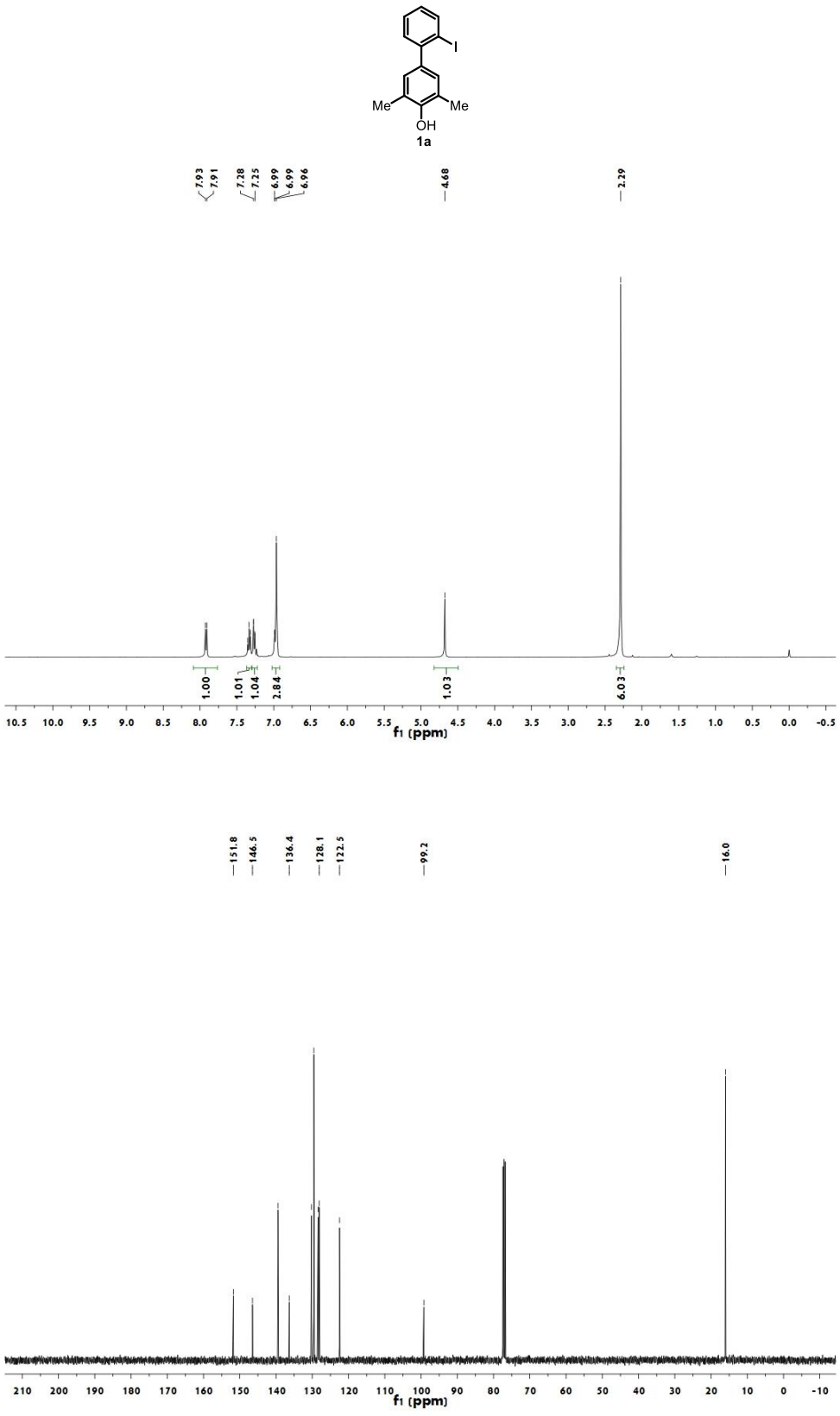


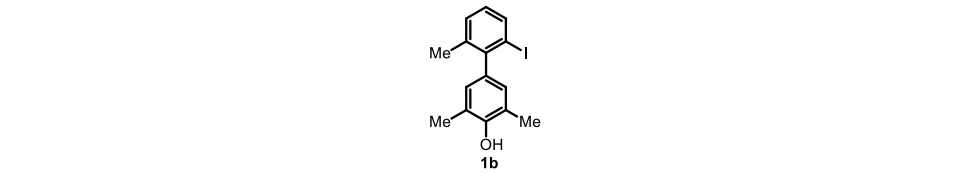
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.828	BBA	0.3259	316.34326	15.25459	9.9520
2	16.823	BBA	0.3524	2862.35327	123.51563	90.0480

E. References:

(1) Yang, L.; Zheng, H.; Luo, L.; Nan, J.; Liu, J.; Wang, Y.; Luan, X. *J. Am. Chem. Soc.* **2015**, *137*, 4876.
(2) Anton, L.; Kilian, M. *Chem. Eur. J.* **2012**, *18*, 2212.
(3) Timsina, Y. N.; Souvagya, B.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **2014,** *136*, 6215.
(4) Yildizhan, S.; Schulz, S. *Synlett* **2011,** 2831.
(5) Lv, J.; Liu, Q.; Tang, J.; Franc, P.; Kristof, K. *Tetrahedron Lett.*, **2012**, *53*, 5248.

F. NMR spectra:

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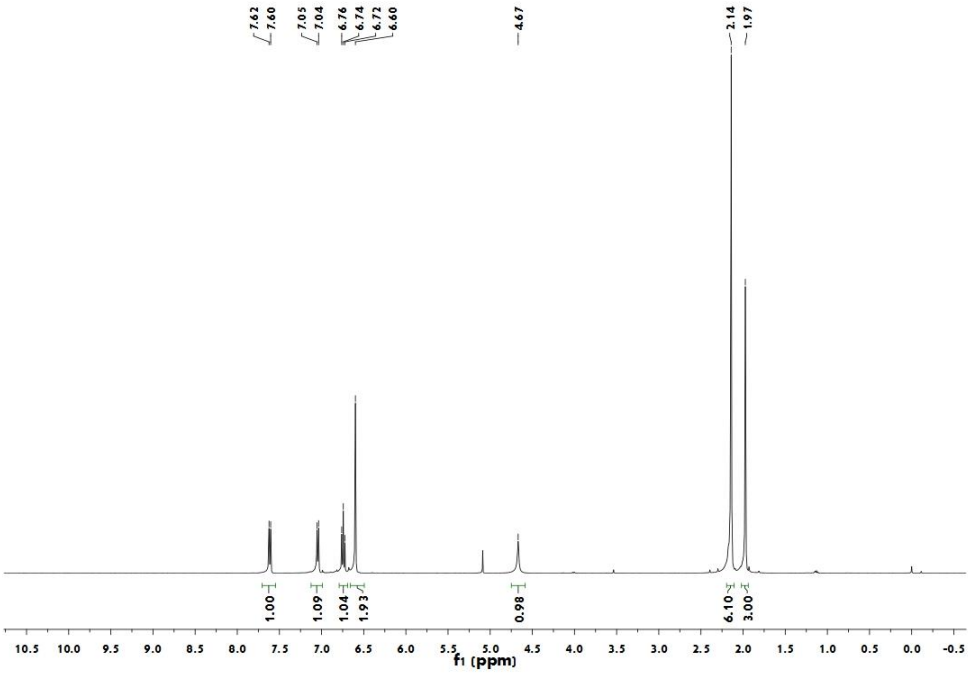
I
Me
Me
OH

1b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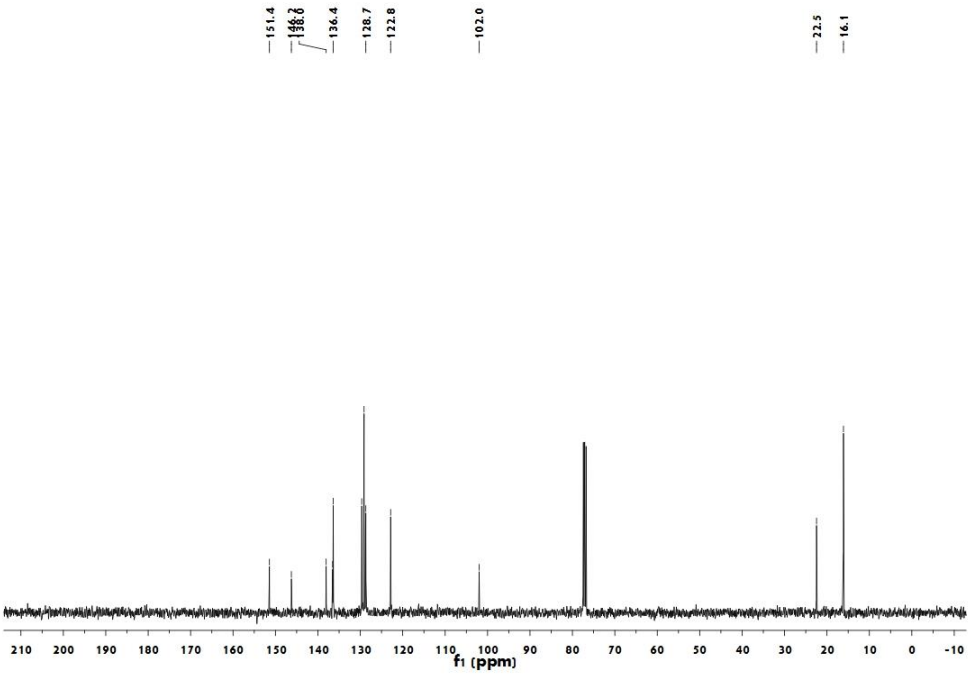
1.09
1.04
1.93
0.98
6.10
3.00
f1 (ppm)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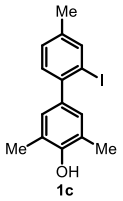
136.4
128.7
122.8
102.0
22.5
16.1
f1 (ppm)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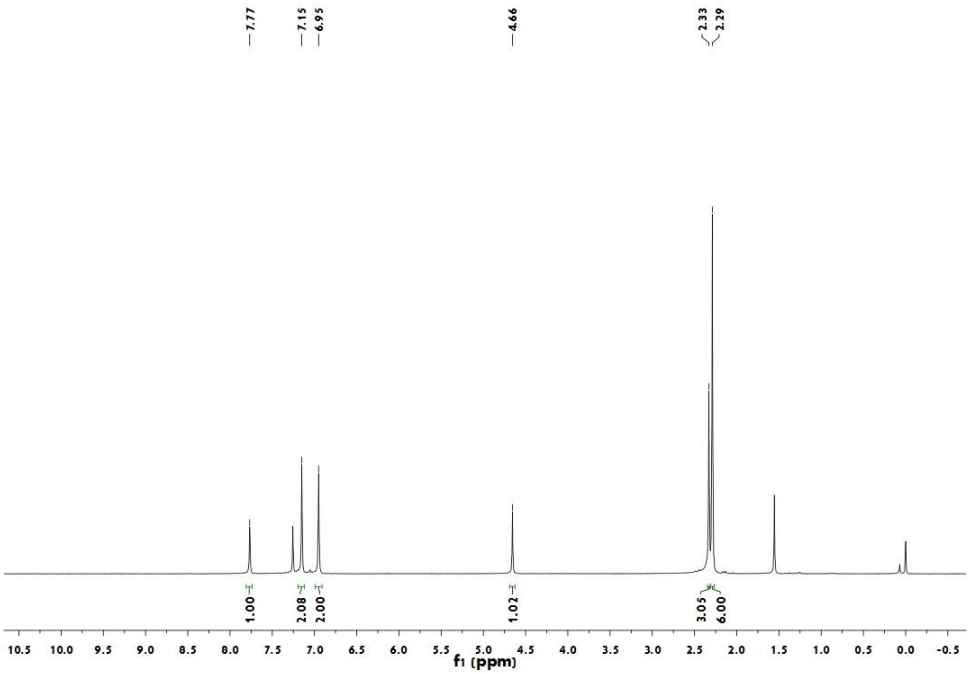
I
Me
Me
OH

1c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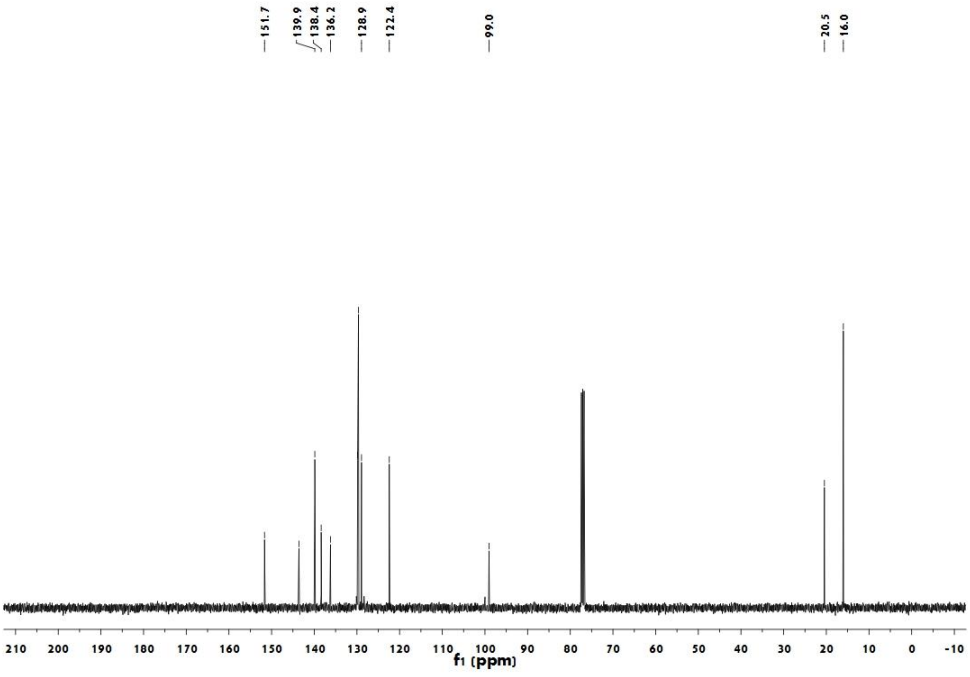
6.00
f1 (ppm)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122.4
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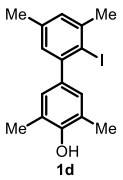
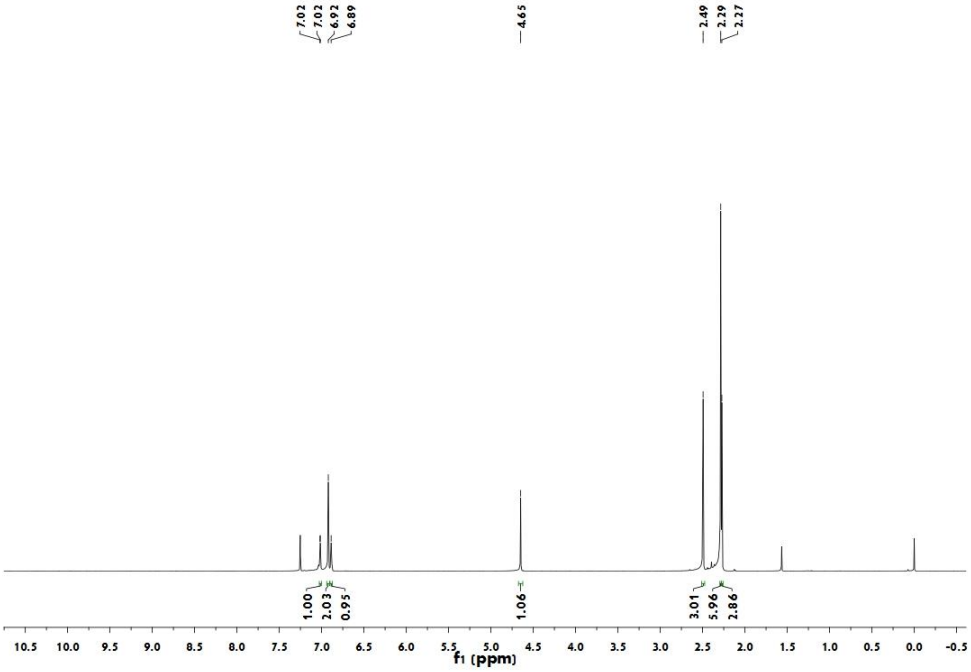
20.5
16.0
f1 (ppm)


Me
Me
I
Me
Me
OH

1d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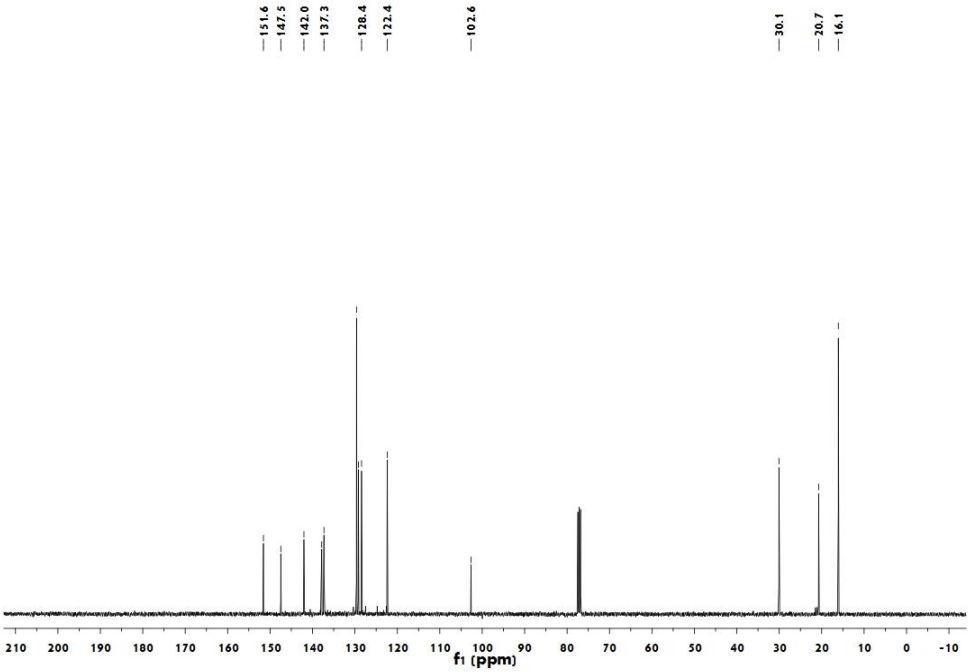
2.86
f1 (ppm)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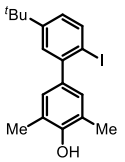
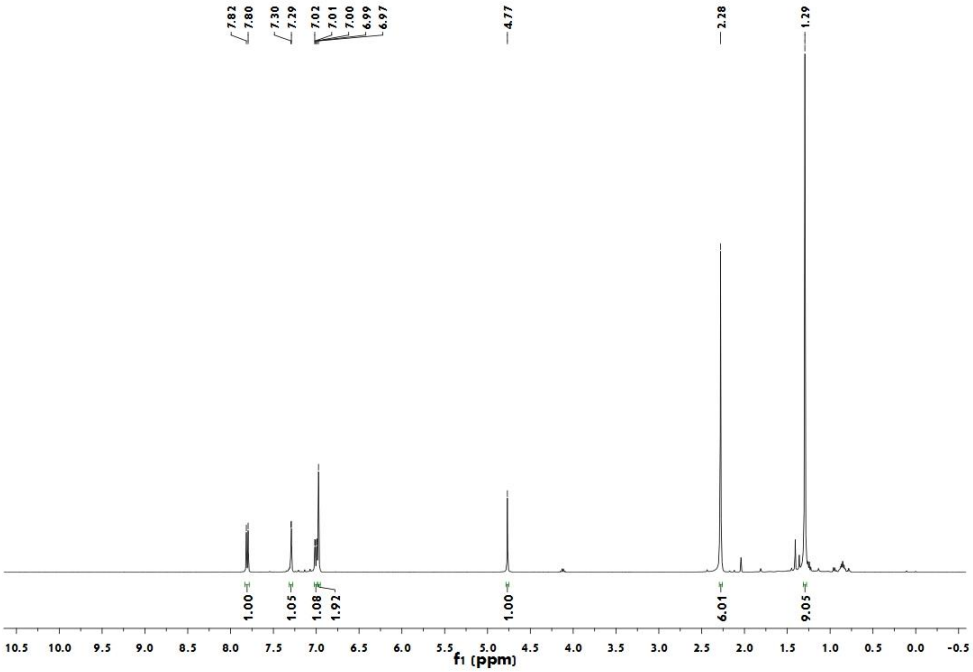
f1 (ppm)


tBu
I
Me
Me
OH

1e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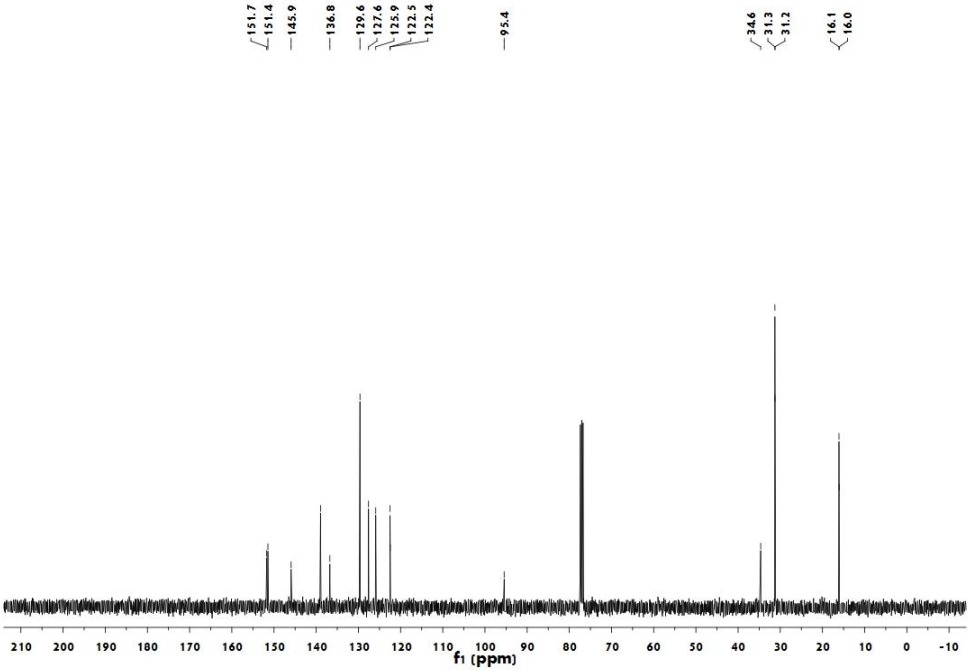
9.05
f1 (ppm)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31.2
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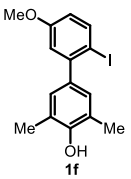
16.0
f1 (ppm)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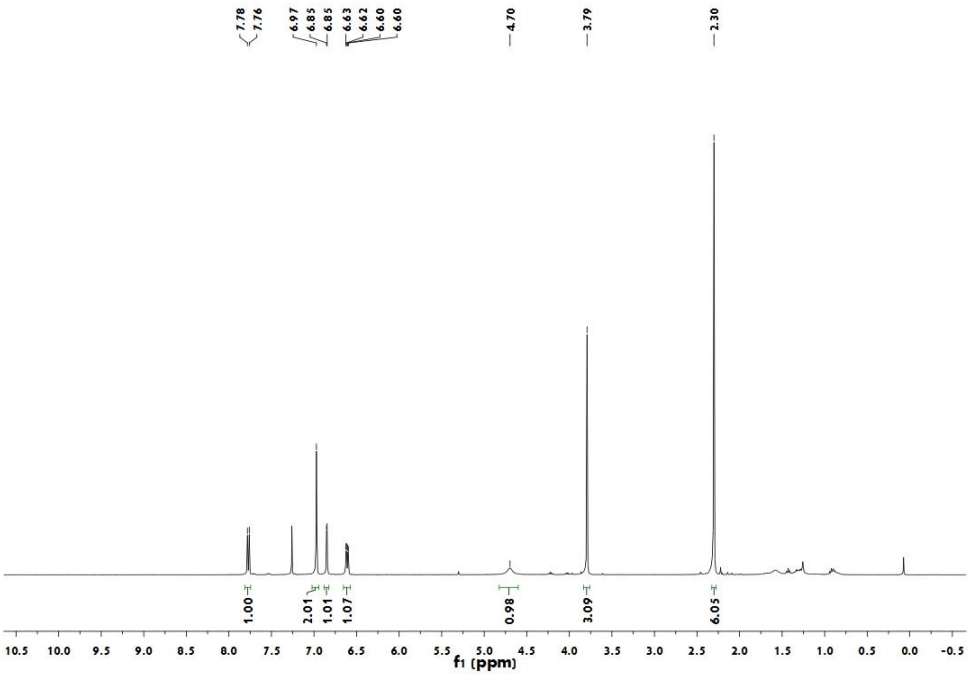
Me
OH

1f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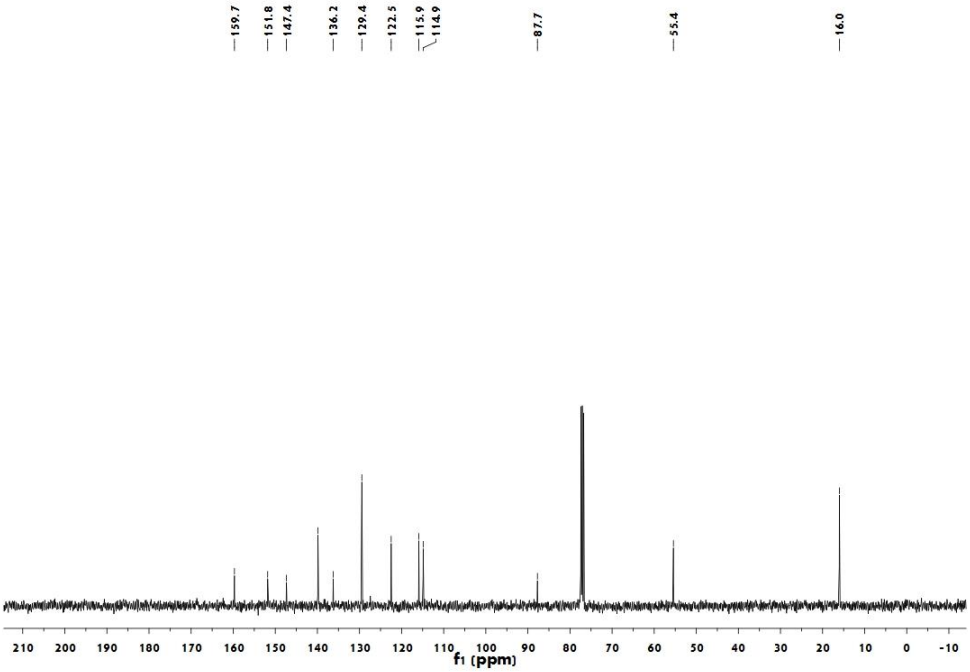
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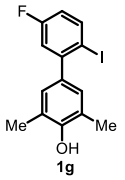
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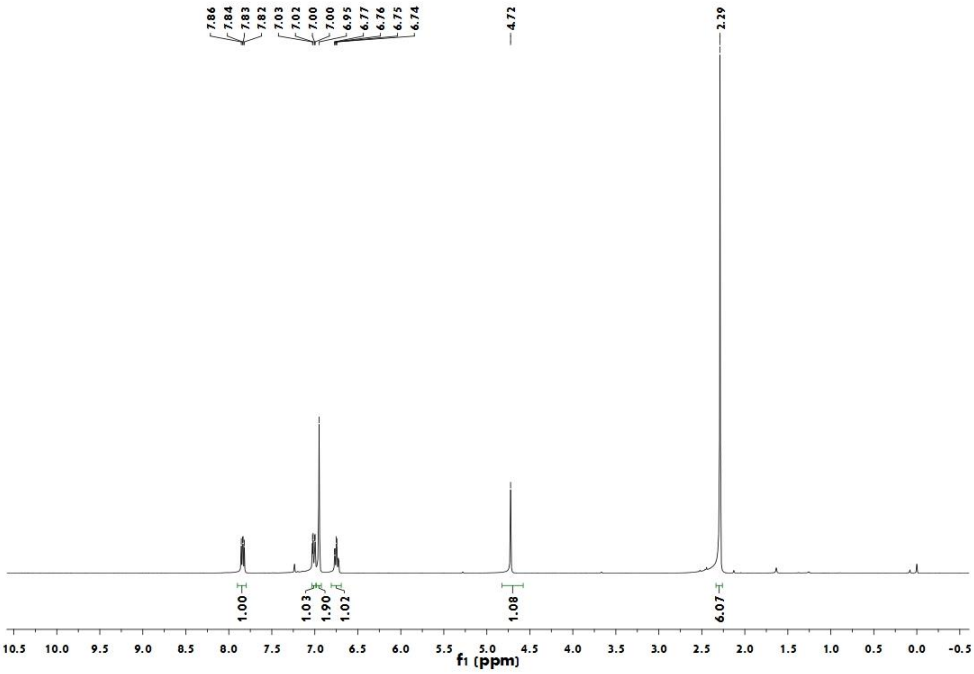
I
Me
Me
OH

1g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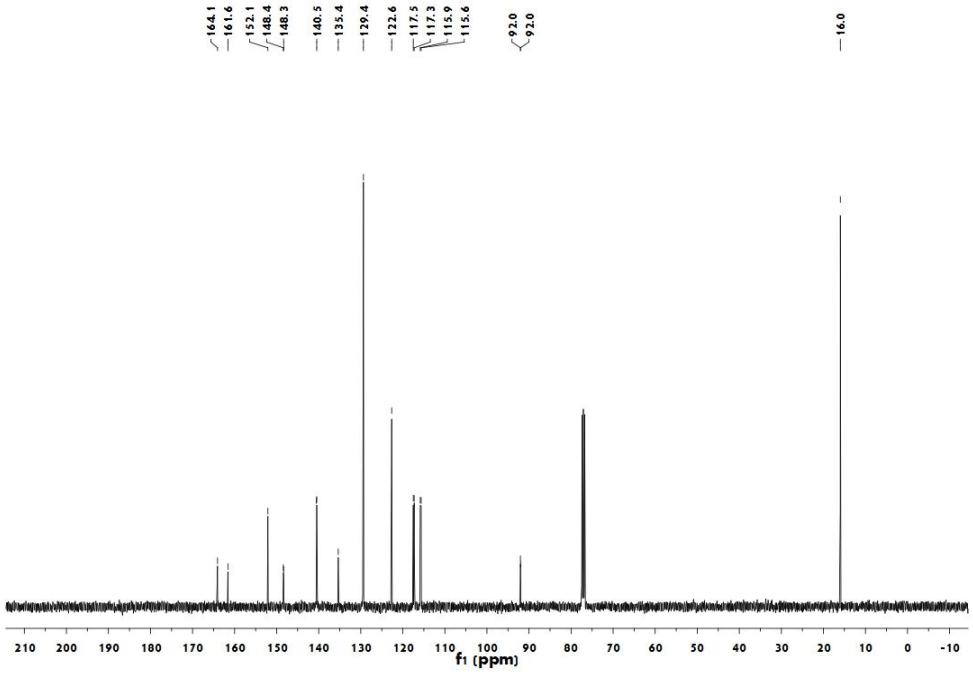
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115.6
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92.0
16.0
f1 (ppm)


EtOOC
I
Me
Me
OH
1h
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6.97
4.82
4.39
4.38
4.36
4.34
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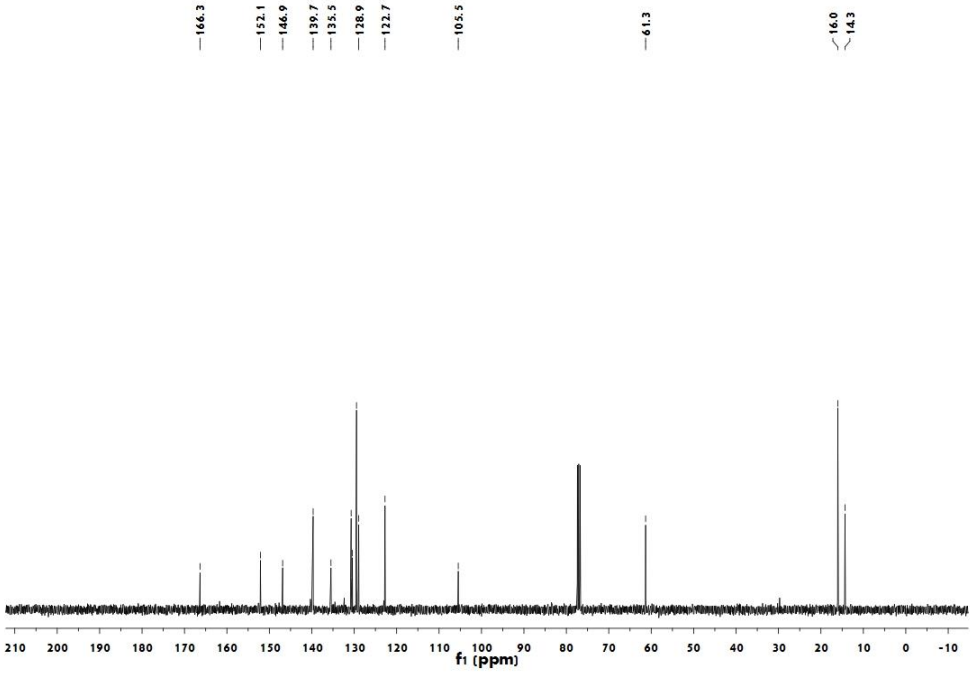
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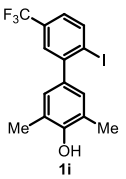
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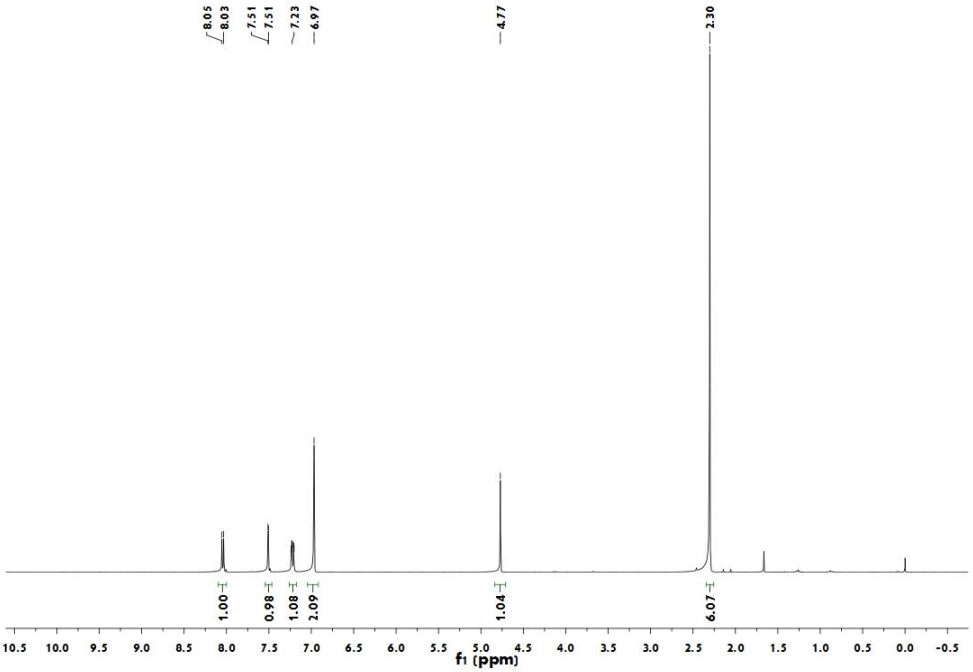
1i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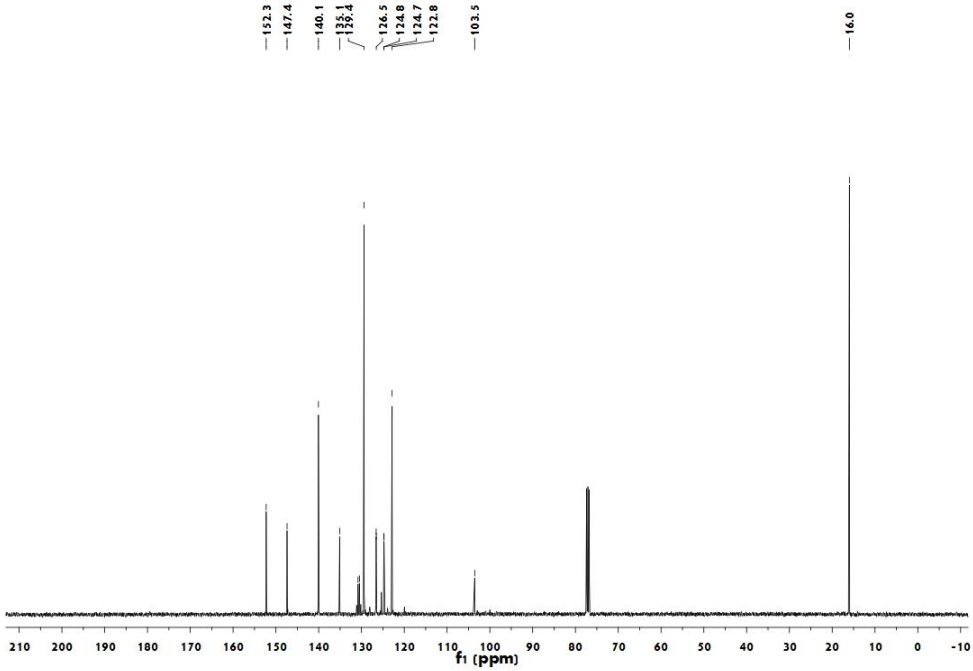
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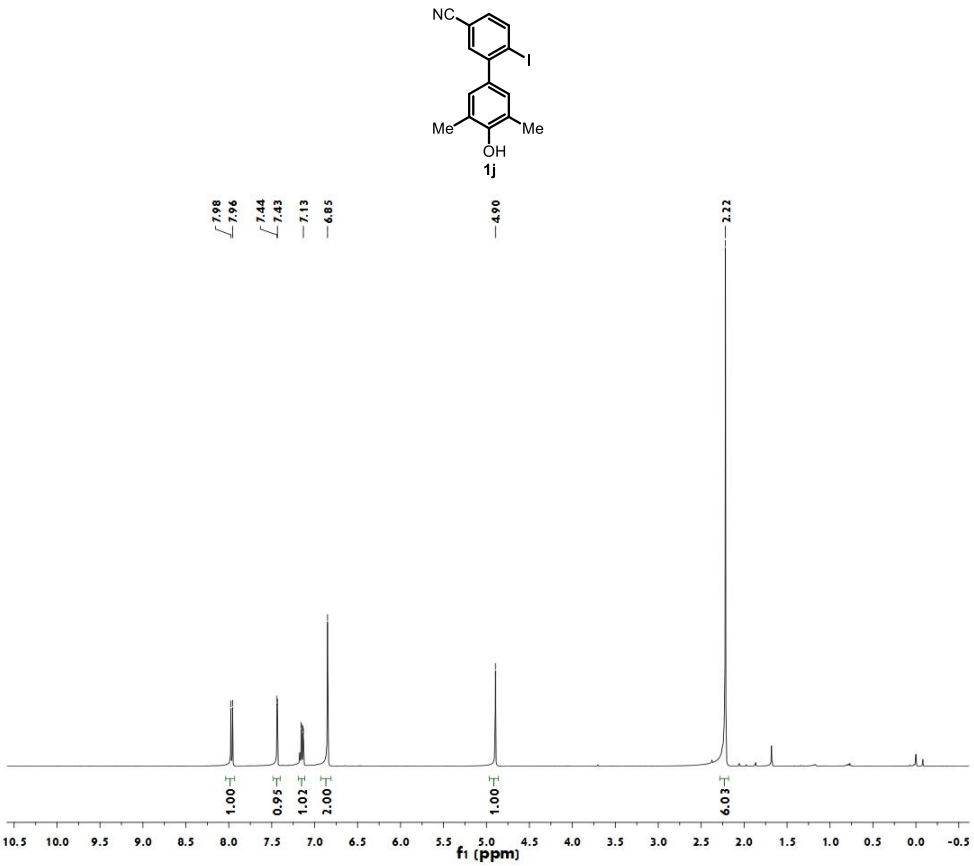
16.0
f1 (ppm)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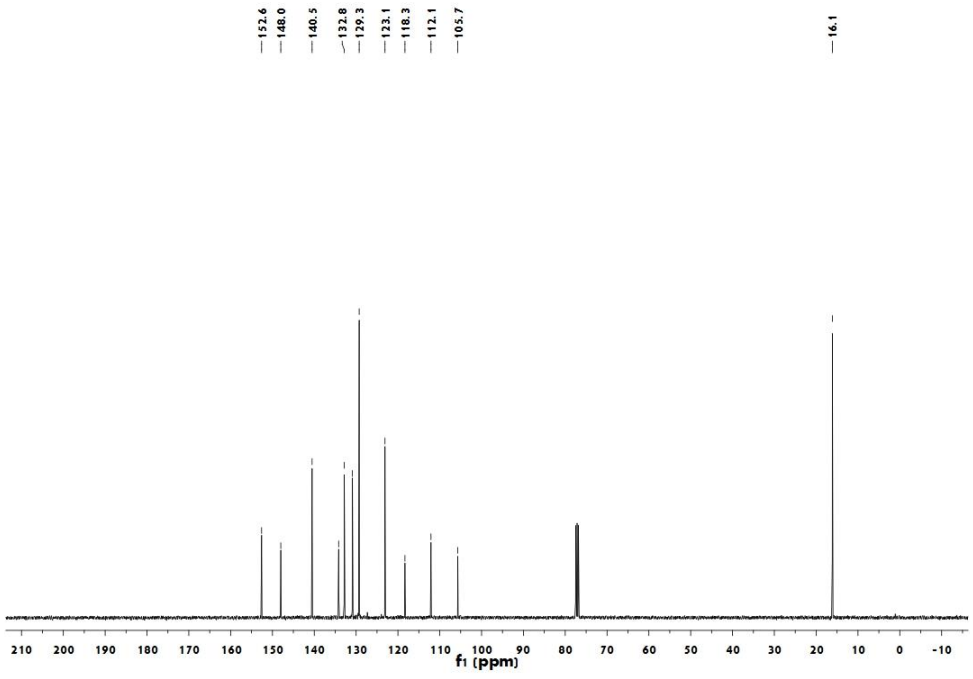
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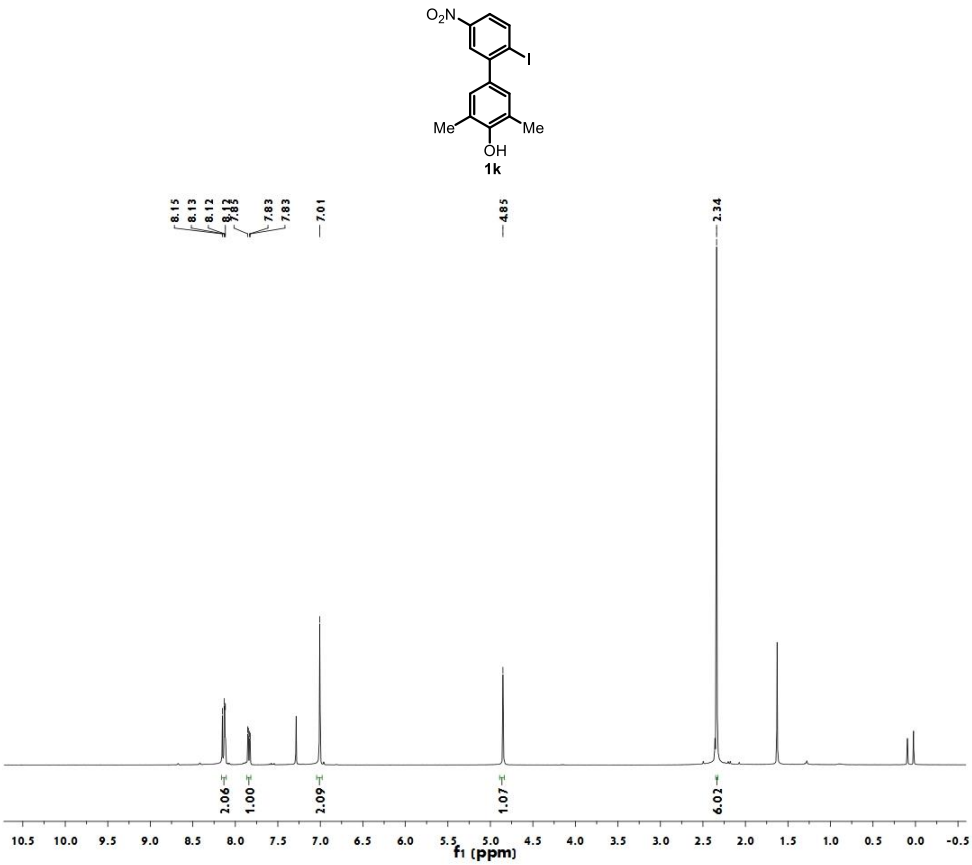
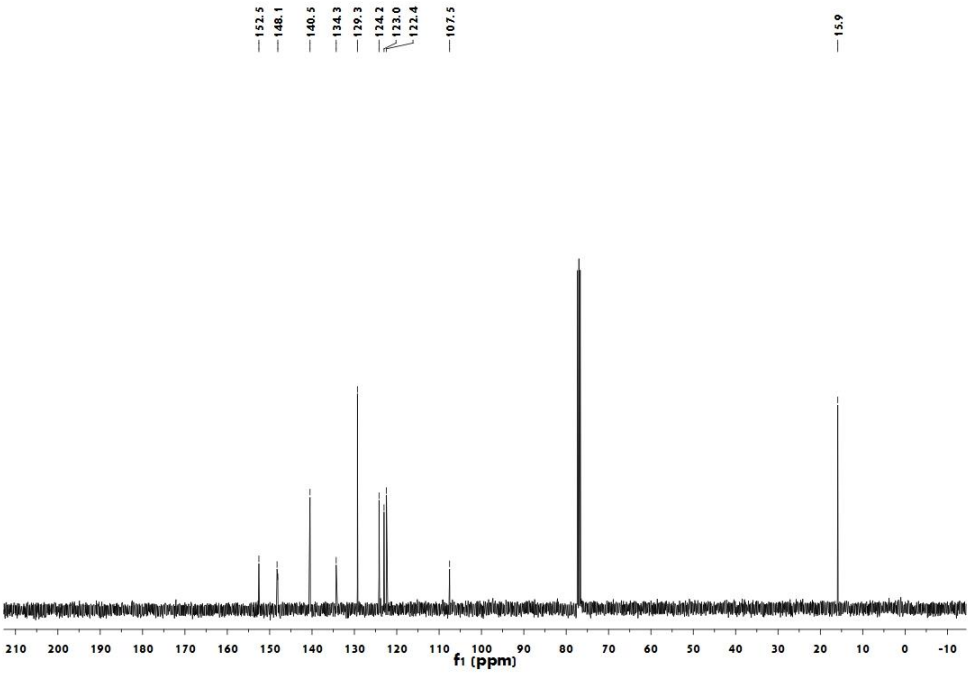
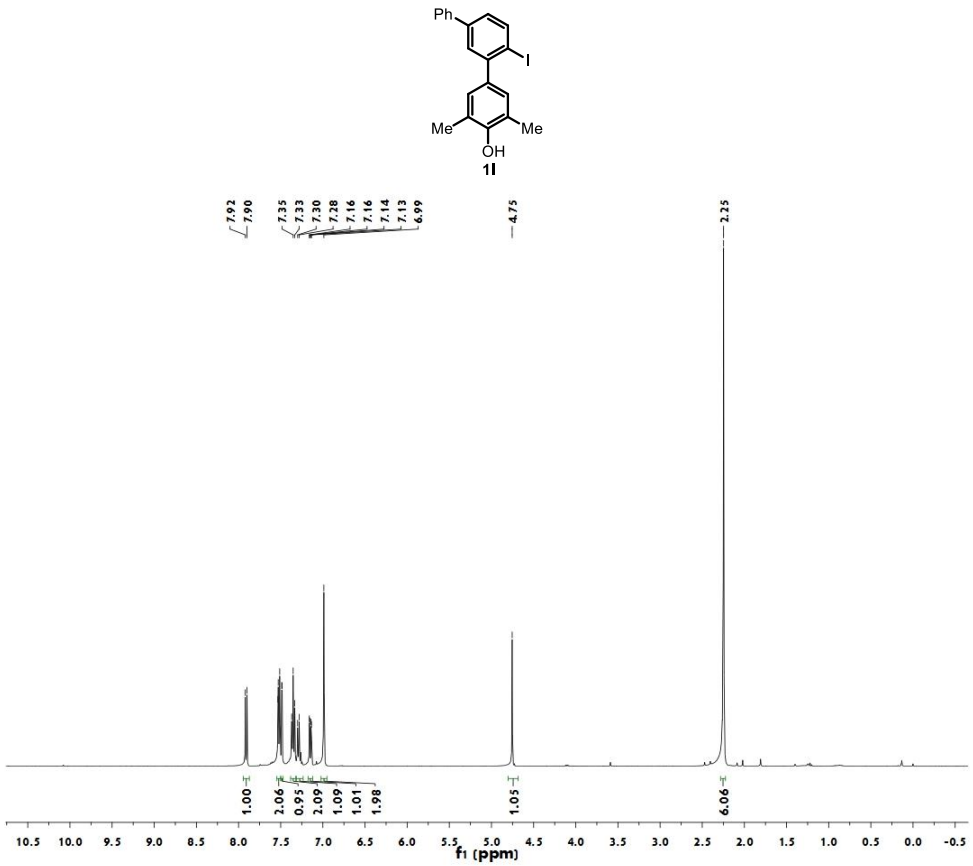
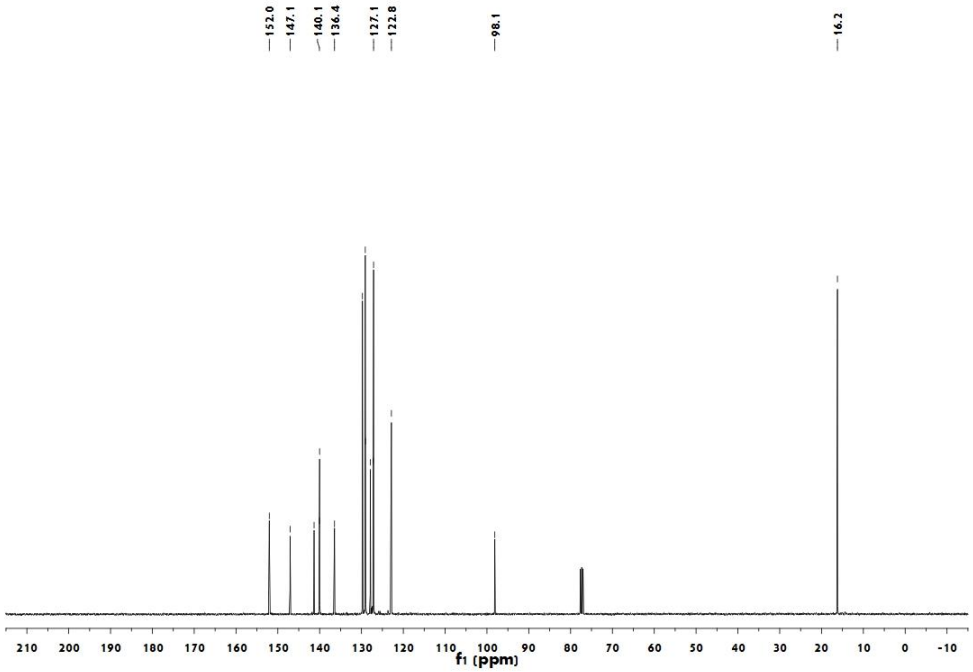
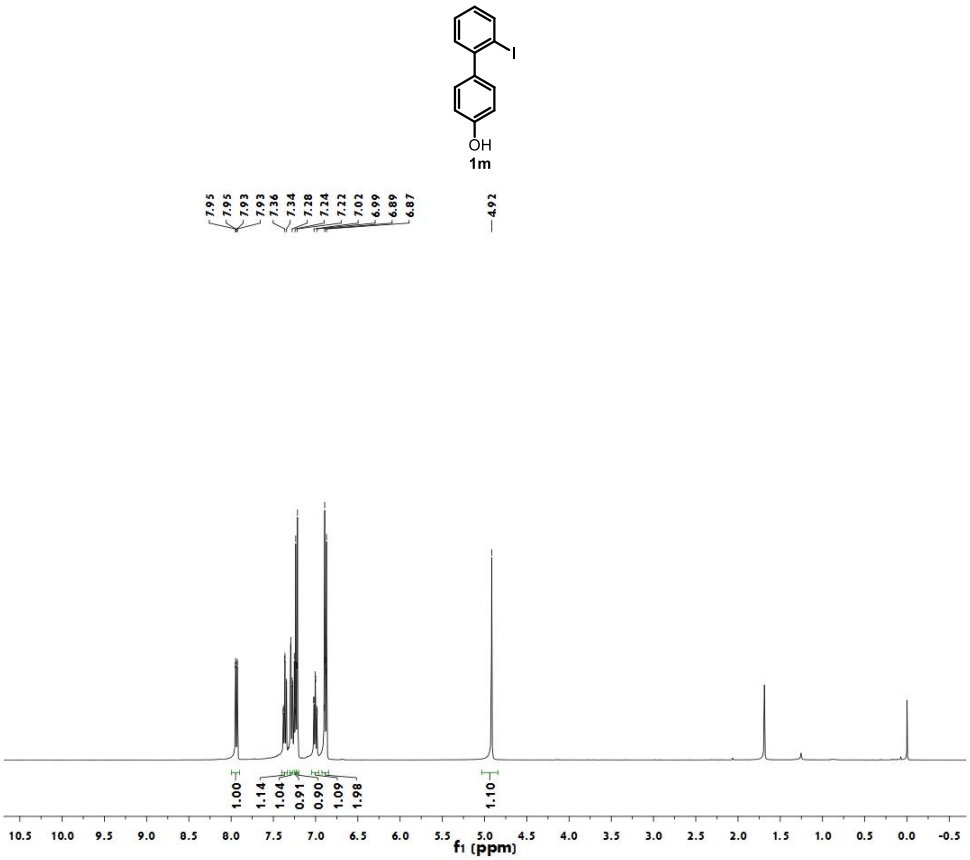
16.1
f1 (ppm)

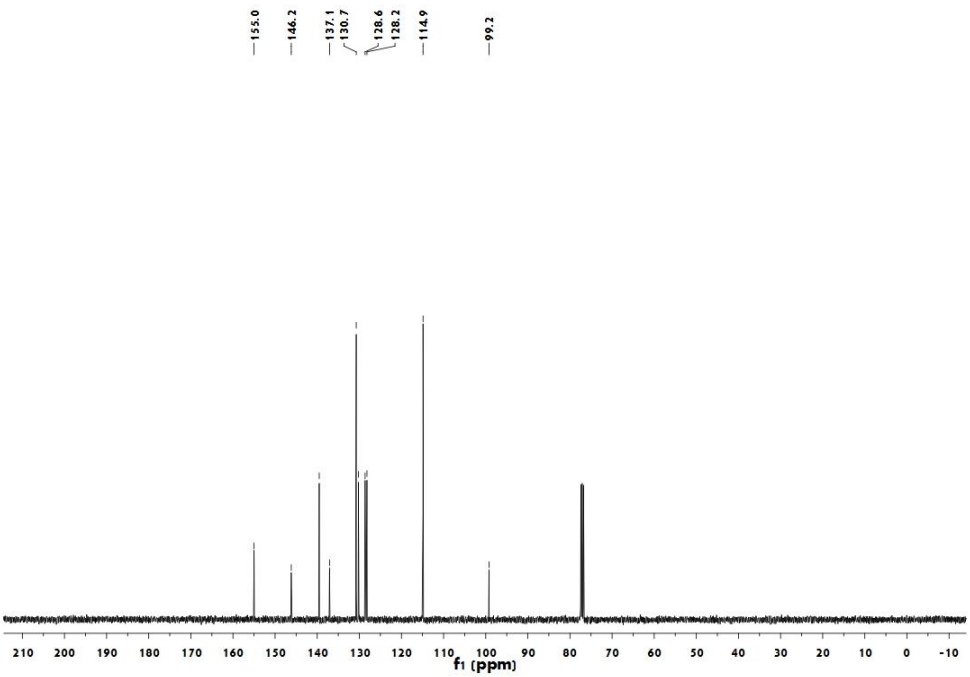

O2N
I
Me
Me
OH
1k
8.15
8.13
8.12
7.85
7.83
7.83
7.01
4.85
2.34
2.06
1.00
2.09
1.07
6.02
f1 (ppm)

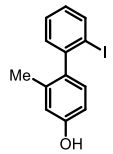

152.5
148.1
140.5
134.3
129.3
124.2
123.0
122.4
107.5
15.9
f1 (ppm)


Ph
I
Me
Me
OH
1l
7.92
7.90
7.35
7.33
7.30
7.28
7.16
7.16
7.14
7.13
6.99
4.75
2.25
1.00
2.06
0.95
2.09
1.09
1.01
1.98
1.05
6.06
f1 (ppm)

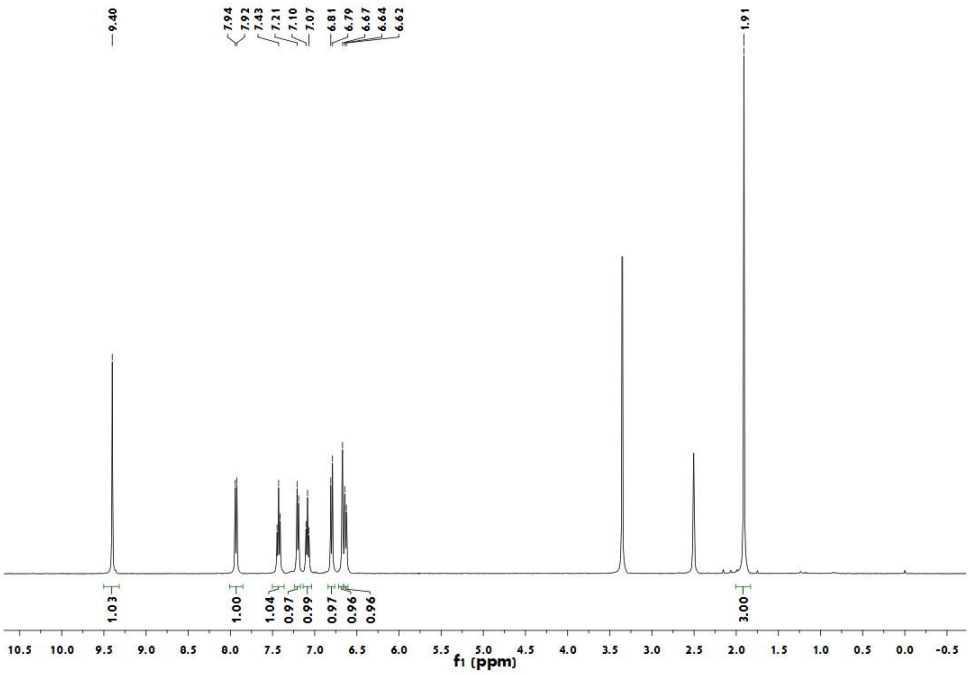

152.0
147.1
140.1
136.4
127.1
122.8
98.1
16.2
f1 (ppm)

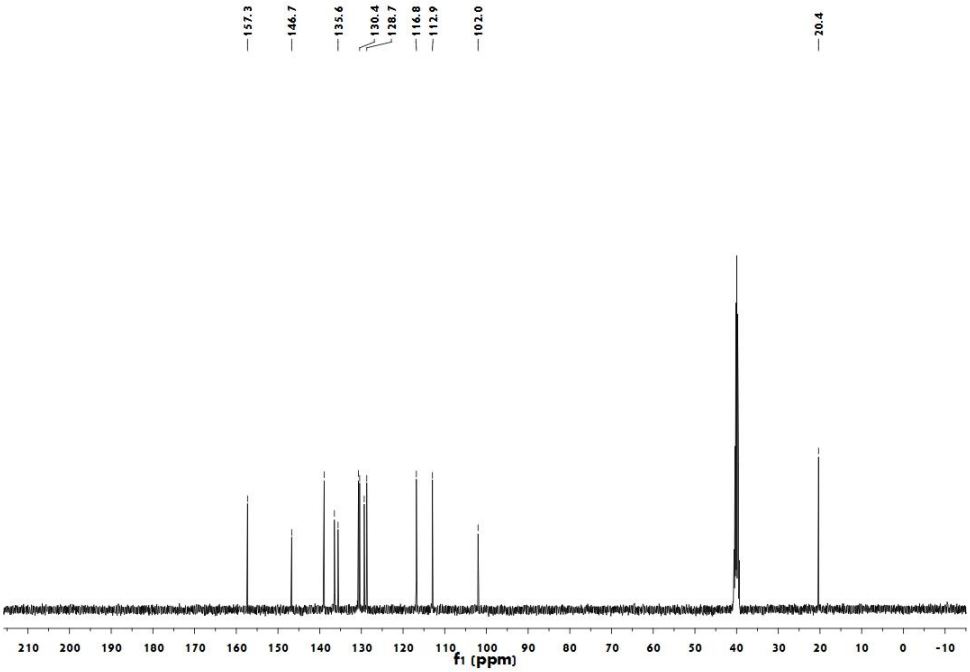

I
OH
1m
7.95
7.95
7.93
7.93
7.36
7.34
7.28
7.24
7.22
7.02
6.99
6.89
6.87
4.92
1.00
1.14
1.04
0.91
0.90
1.09
1.98
1.10
f1 (ppm)

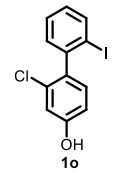

155.0
146.2
137.1
130.7
128.6
128.2
114.9
99.2
f1 (ppm)


I
Me
OH

1n

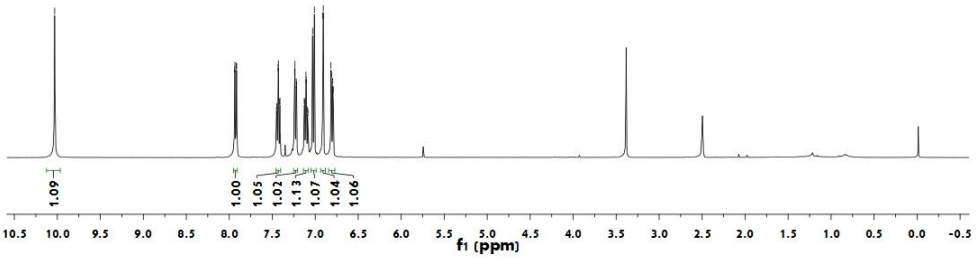

9.40
7.94
7.92
7.43
7.21
7.10
7.07
6.81
6.79
6.67
6.64
6.62
1.91
1.03
1.00
1.04
0.97
0.99
0.97
0.96
0.96
3.00
f1 (ppm)

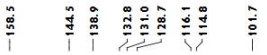

157.3
146.7
135.6
130.4
128.7
116.8
112.9
102.0
20.4
f1 (ppm)

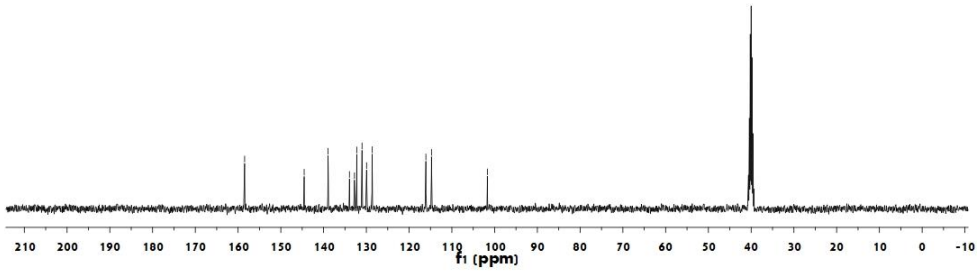

I
Cl
OH

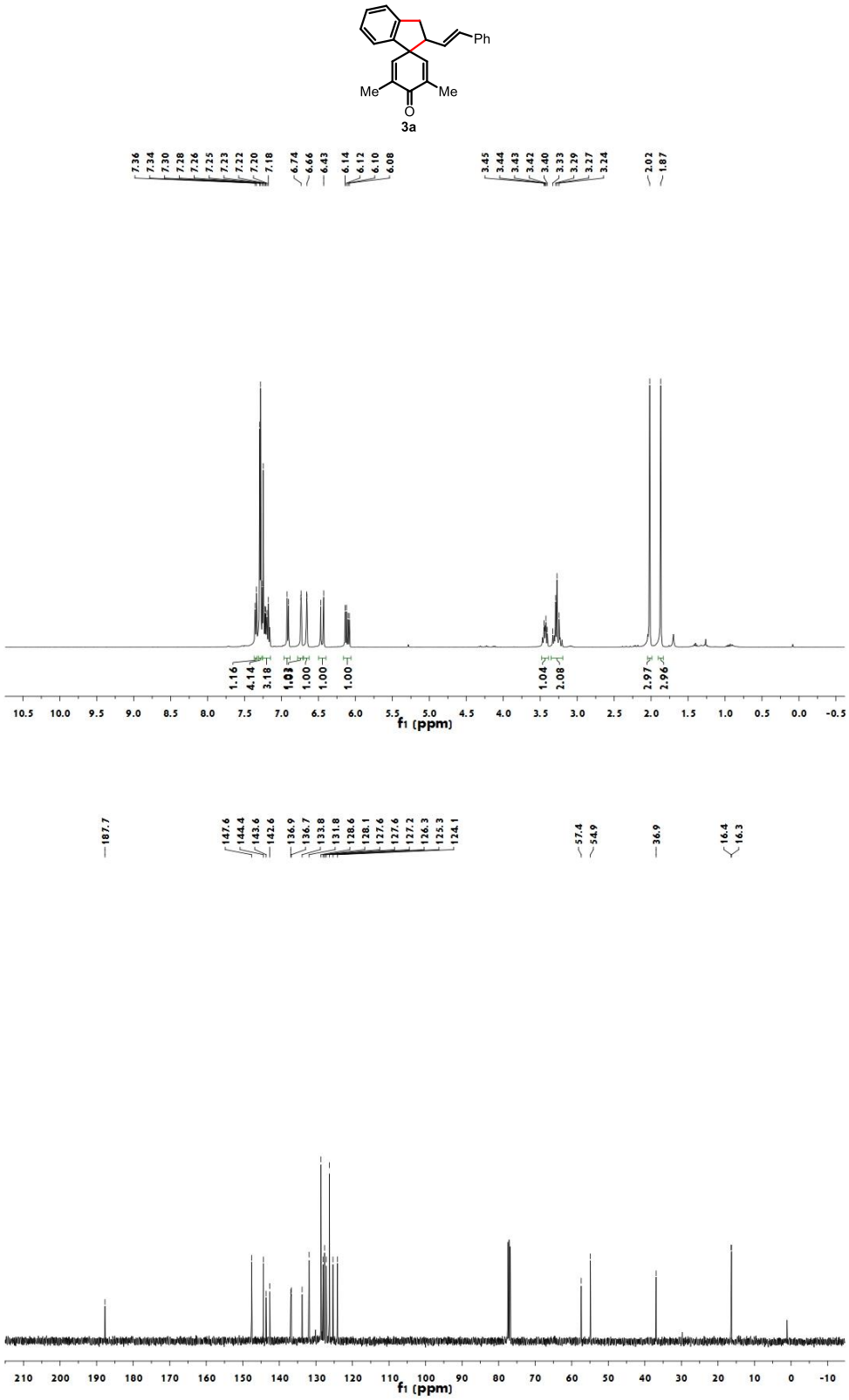
1o

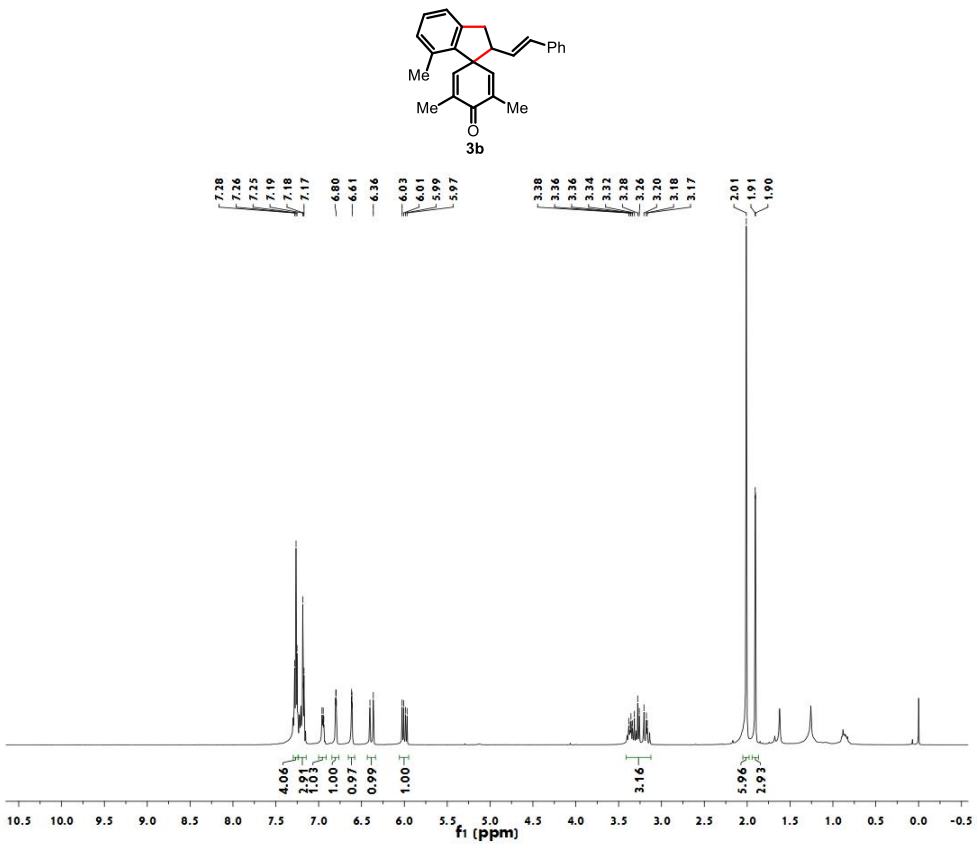

10.03
7.94
7.93
7.92
7.91
7.45
7.45
7.43
7.43
7.41
7.41
7.24
7.24
7.22
7.22
7.13
7.12
7.11
7.10
7.09
7.09
7.03
7.01
6.91
6.91
6.82
6.81
6.80
6.79

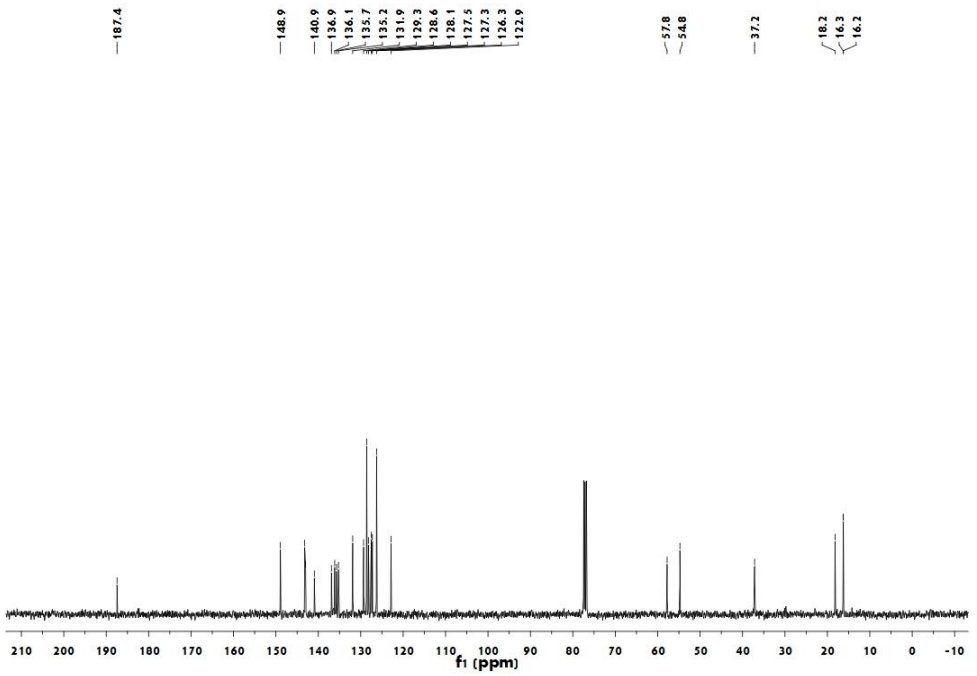

1.09
1.00
1.05
1.02
1.13
1.07
1.04
1.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.5
144.5
138.9
132.8
131.0
128.7
116.1
114.8
101.7


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
Me
Me
O
3a
7.36
7.34
7.30
7.28
7.26
7.25
7.23
7.22
7.20
7.18
6.74
6.66
6.43
6.14
6.12
6.10
6.08
3.45
3.44
3.43
3.42
3.40
3.33
3.29
3.27
3.24
2.02
1.87
1.16
4.14
3.18
1.03
1.00
1.00
1.00
1.04
2.08
2.97
2.96
f1 (ppm)
187.7
147.6
144.4
143.6
142.6
136.9
136.7
133.8
131.8
128.6
128.1
127.6
127.6
127.2
126.3
125.3
124.1
57.4
54.9
36.9
16.4
16.3
f1 (ppm)

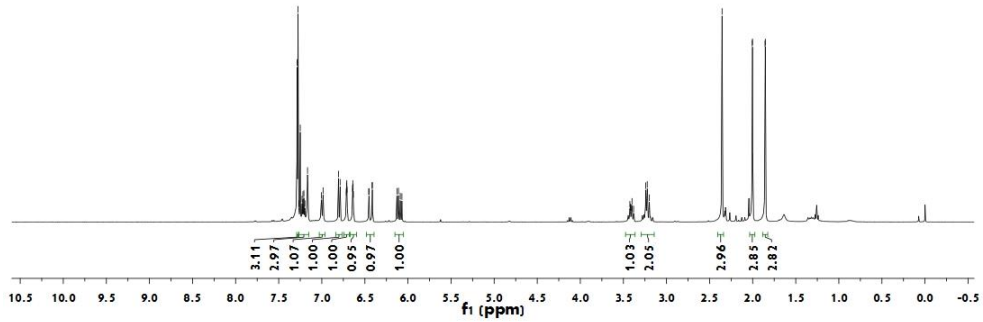

Ph
Me
Me
Me
O
3b
7.28
7.26
7.25
7.19
7.18
7.17
6.80
6.61
6.36
6.03
6.01
5.99
5.97
3.38
3.36
3.36
3.34
3.32
3.28
3.26
3.20
3.18
3.17
2.01
1.91
1.90
4.06
2.01
1.03
1.00
0.97
0.99
1.00
3.16
5.96
2.93
f1 (ppm)


187.4
148.9
140.9
136.9
136.1
135.7
135.2
131.9
129.3
128.6
128.1
127.5
127.3
126.3
122.9
57.8
54.8
37.2
18.2
16.3
16.2
f1 (ppm)

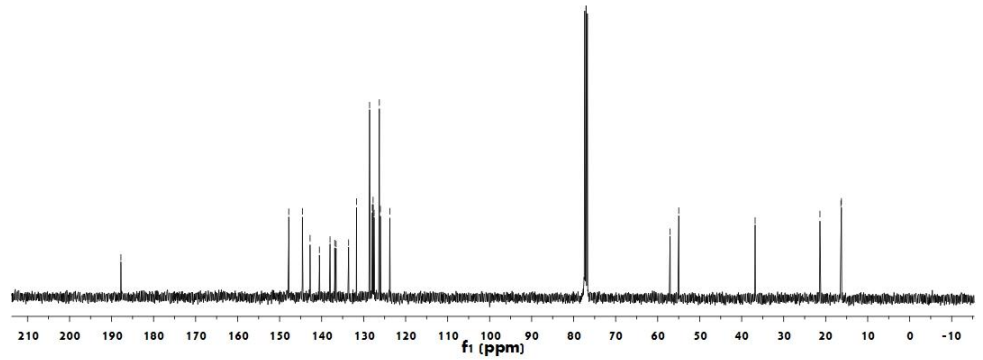

Me
Ph
Me
Me
O

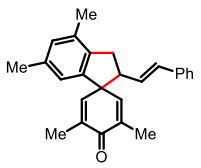
3c


7.23
7.22
7.21
7.20
7.17
7.00
6.99
6.81
6.79
6.72
6.71
6.71
6.71
6.64
6.64
6.64
6.63
6.46
6.45
6.42
6.41
6.13
6.11
6.09
6.07
3.42
3.42
3.42
3.41
3.40
3.38
3.24
3.22
3.20
2.36
2.00
2.00
1.86
1.85


3.11
2.97
1.07
1.00
1.00
0.95
0.97
1.00
1.03
2.05
2.96
2.85
2.82
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)

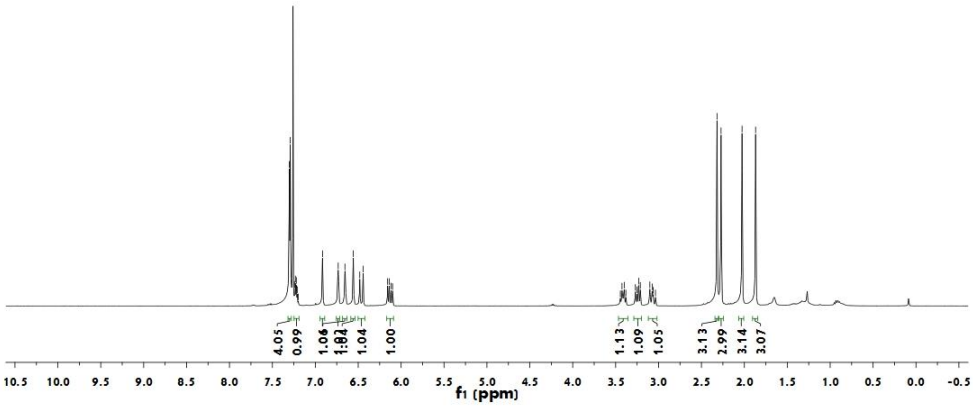

187.8
147.8
144.6
142.8
140.5
138.0
136.9
136.6
133.6
131.7
128.6
127.9
127.7
127.5
126.3
126.0
123.8
57.0
55.0
36.8
21.4
16.4
16.3


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)

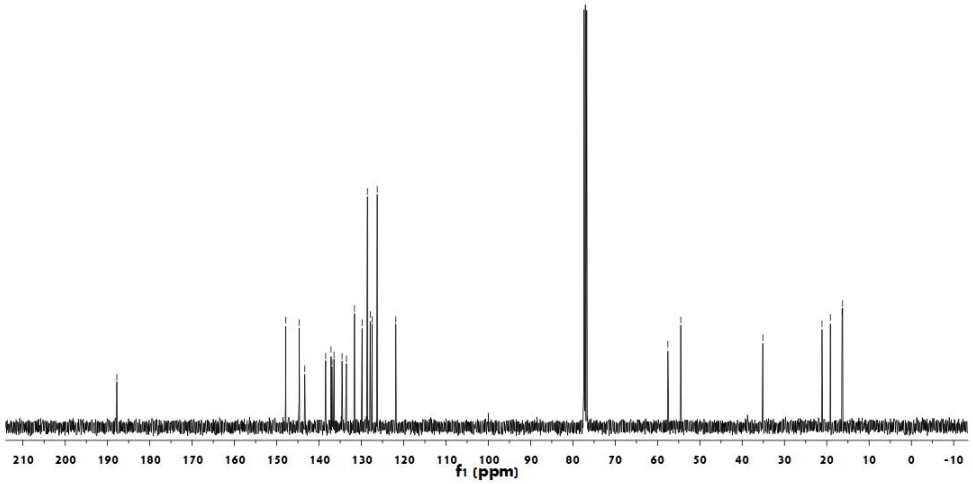

Me
Me
Ph
Me
Me
O

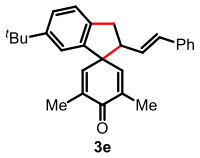
3d


7.30
7.29
7.24
7.23
7.22
7.21
7.20
6.73
6.56
6.44
6.16
6.14
6.12
6.10
3.43
3.40
3.38
3.27
3.25
3.23
3.21
3.10
3.07
3.06
3.04
2.32
2.27
2.03
1.87

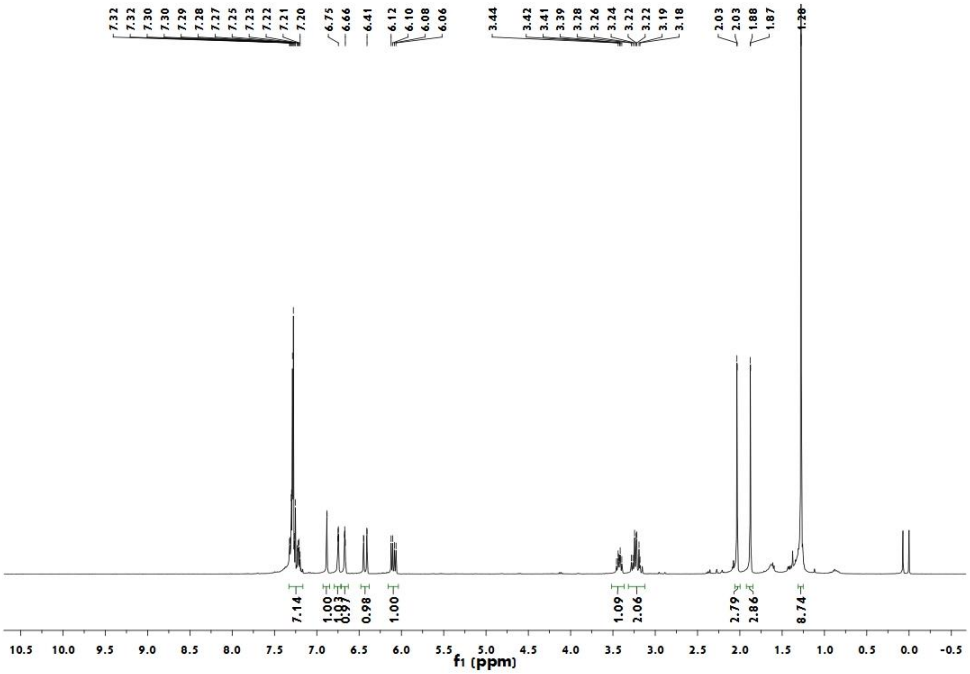

4.05
0.99
1.06
1.01
1.04
1.00
1.13
1.09
1.05
3.13
2.99
3.14
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

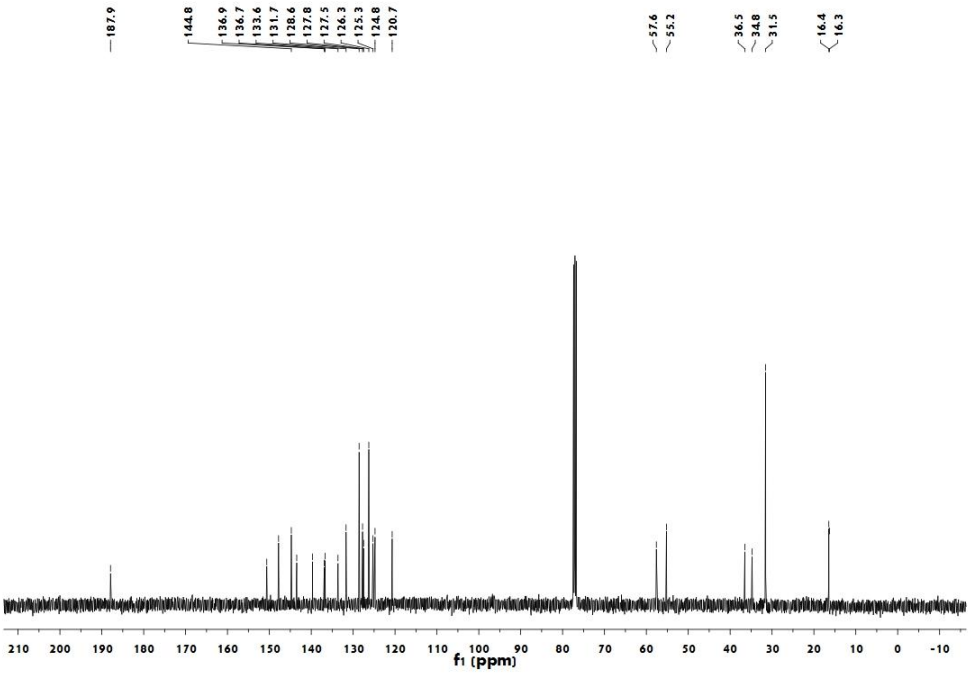

187.8
147.9
144.7
143.4
136.9
133.5
128.6
126.3
121.9
57.6
54.5
35.1
21.1
19.1
16.4
16.3

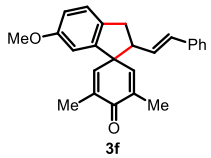

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


tBu
Ph
Me
Me
O

3e

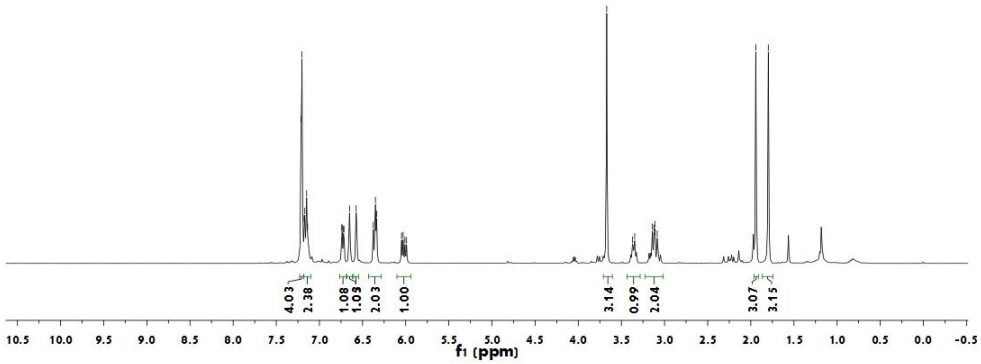

7.32 7.32 7.30 7.30 7.29 7.28 7.27 7.25 7.23 7.22 7.21 7.20
6.75 6.66 6.41 6.12 6.10 6.08 6.06
3.44 3.42 3.41 3.39 3.28 3.26 3.24 3.22 3.22 3.19 3.18
2.03 2.03 1.88 1.87 1.26
7.14 1.00 1.03 0.97 0.98 1.00 1.09 2.06 2.79 2.86 8.74
f1 (ppm)


187.9 144.8 136.9 136.7 133.6 131.7 128.6 127.8 127.5 126.3 125.3 124.8 120.7
57.6 55.2 36.5 34.8 31.5 16.4 16.3
f1 (ppm)

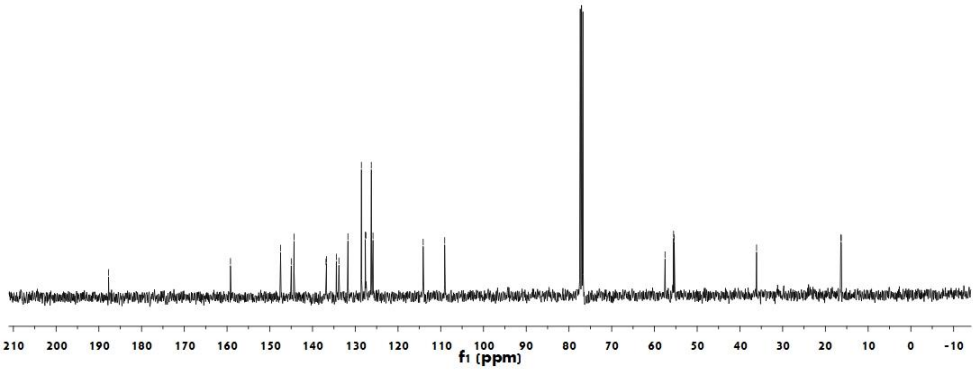

MeO
Ph
Me
Me
O

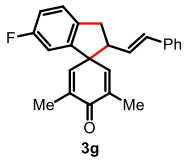
3f


7.21
7.20
7.18
7.17
7.15
7.14
6.72
6.57
6.34
6.05
6.03
6.01
5.99
3.67
3.35
3.14
3.12
3.11
3.08
1.94
1.80


4.03
2.38
1.08
1.03
2.03
1.00
3.14
0.99
2.04
3.07
3.15
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)

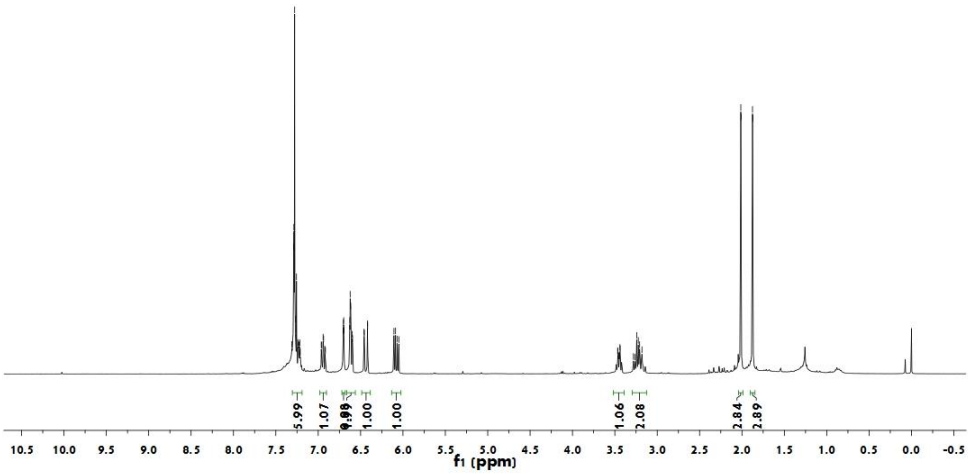

187.7
159.2
147.5
145.0
144.3
136.8
133.8
128.6
127.5
125.8
114.1
109.1
57.5
55.5
55.4
36.1
16.4
16.3


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)

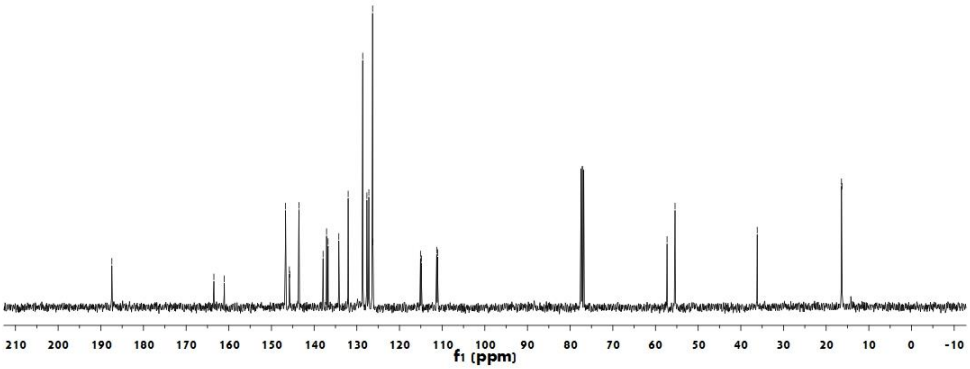

F
Ph
Me
Me
O

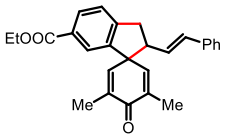
3g


7.31
7.29
7.29
7.28
7.27
7.26
7.24
7.23
7.23
7.22
7.21
6.91
6.62
6.42
6.11
6.09
6.07
6.05
3.46
3.46
3.45
3.44
3.44
3.28
3.26
3.24
3.22
3.21
3.18
2.01
2.01
1.88
1.87

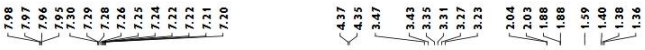

5.99
1.07
1.00
1.00
1.06
2.08
2.84
2.89
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

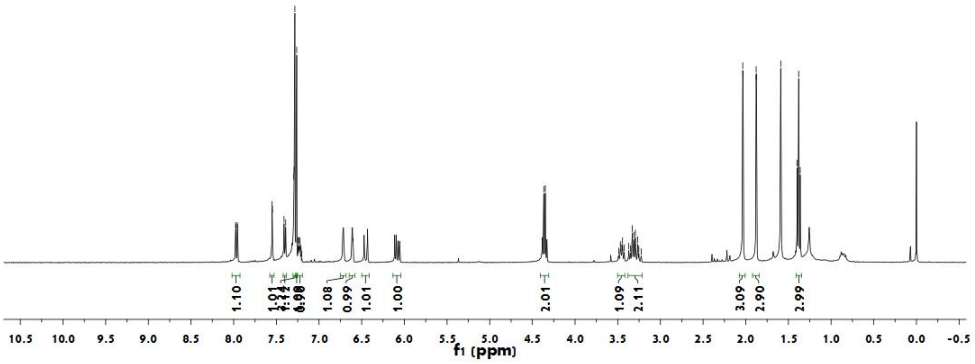

187.4
163.5
161.1
146.7
145.7
143.6
134.2
127.6
126.2
115.1
114.9
111.3
111.1
57.3
55.4
36.2
16.4
16.3

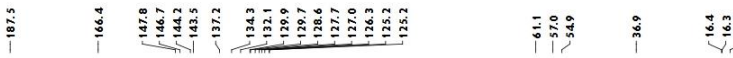

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

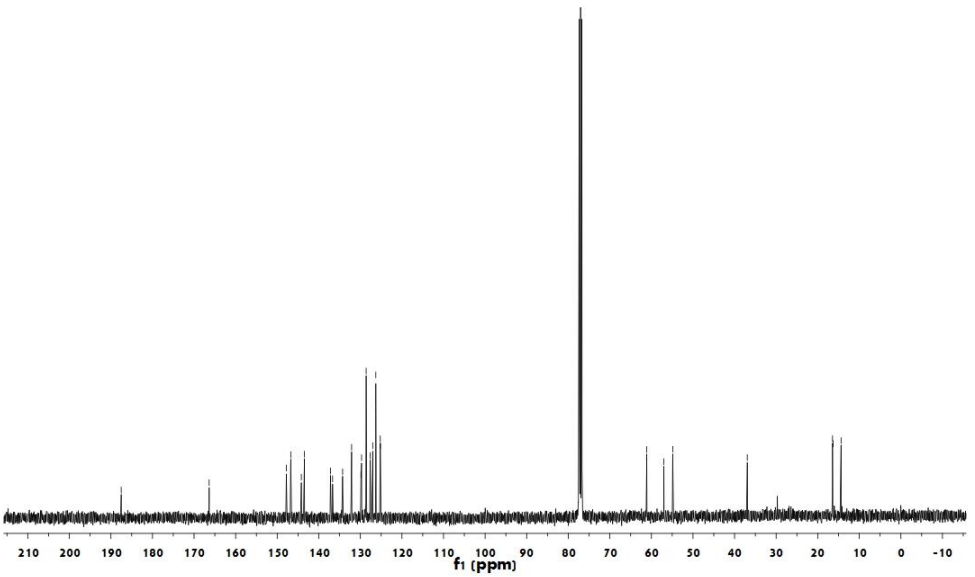

EtOOC
Ph
Me
Me
O

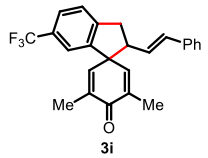
3h


7.98
7.97
7.96
7.95
7.30
7.29
7.28
7.26
7.25
7.24
7.22
7.22
7.21
7.20
4.37
4.35
3.47
3.43
3.35
3.31
3.27
3.23
2.04
2.03
1.88
1.88
1.59
1.40
1.38
1.36

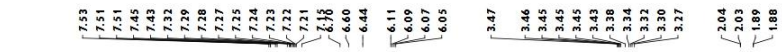

1.10
1.01
1.12
6.98
1.08
0.99
1.01
1.00
2.01
1.09
2.11
3.09
2.90
2.99
f1 (ppm)


187.5
166.4
147.8
146.7
144.2
143.5
137.2
134.3
132.1
129.9
129.7
128.6
127.7
127.0
126.3
125.2
125.2
61.1
57.0
54.9
36.9
16.4
16.3
14.4


f1 (ppm)


F3C
Ph
Me
Me
O

3i


7.53
7.51
7.51
7.45
7.43
7.32
7.29
7.28
7.27
7.25
7.24
7.23
7.22
7.21
7.15
6.70
6.60
6.44
6.11
6.09
6.07
6.05
3.47
3.46
3.45
3.45
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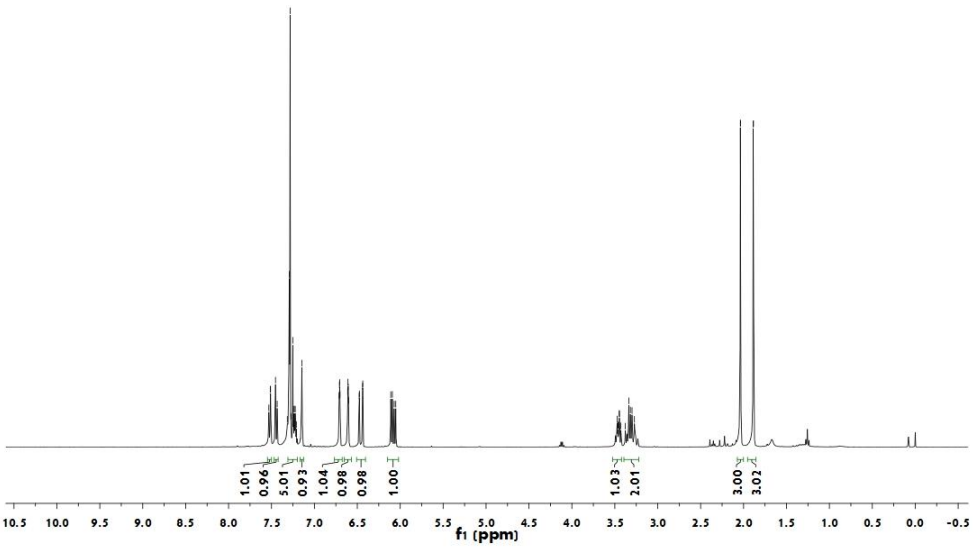
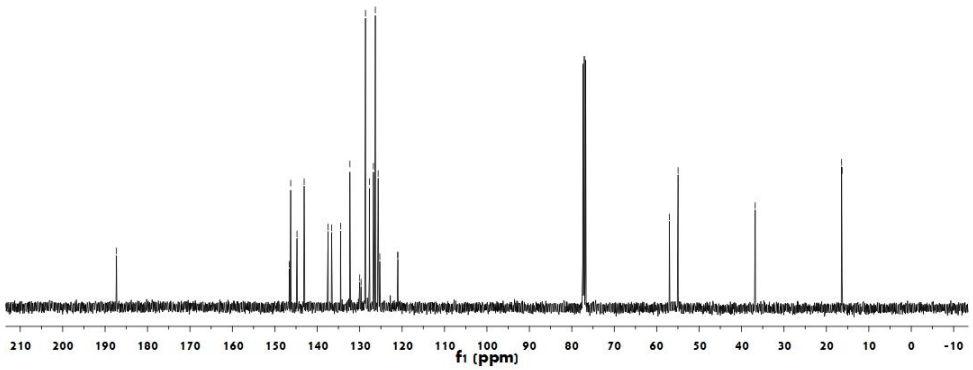
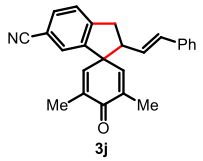
3.30
3.27
2.04
2.03
1.89
1.88


1.01
0.96
5.01
0.93
1.04
0.98
0.98
1.00
1.03
2.01
3.00
3.02
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)


187.3
146.6
146.3
144.8
143.1
134.5
129.7
126.8
125.3
121.0
121.0
57.0
54.9
36.8
16.4
16.3


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)


NC
Ph
Me
Me
O

3j


7.56
7.54
7.45
7.43
7.32
7.30
7.28
7.26
7.23
7.21
6.67
6.47
6.44
6.09
6.07
6.05
6.03
3.47
3.44
3.42
3.39
3.37
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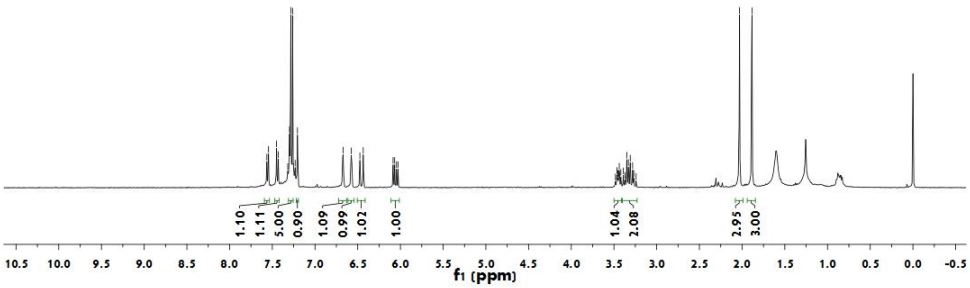
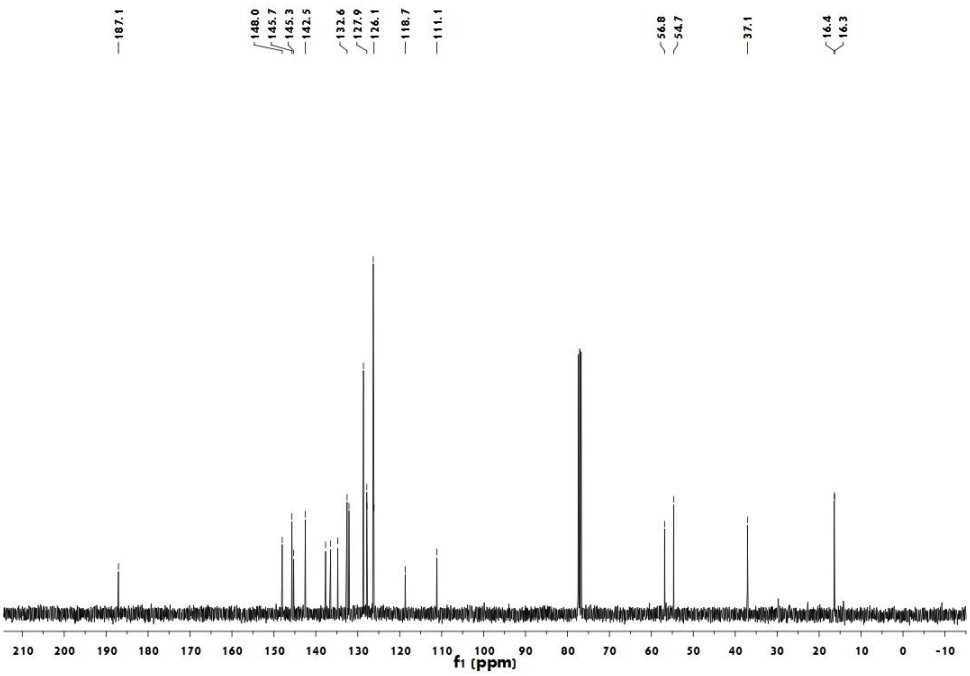
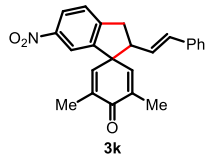
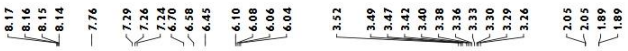
3.31
3.28
3.27
3.24
2.03
1.88

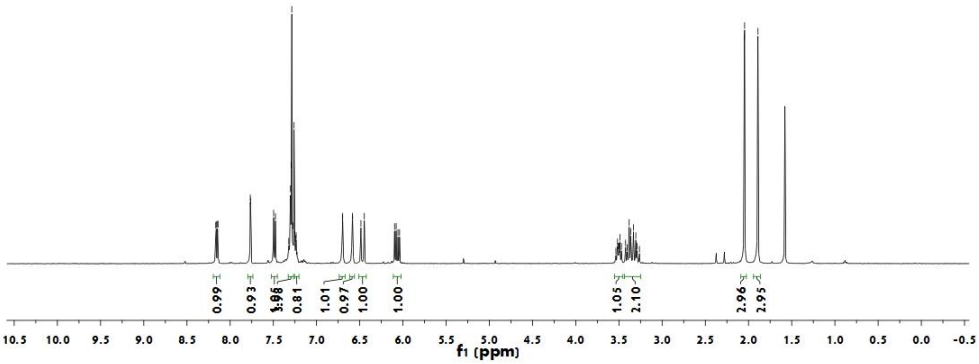

1.10
1.11
5.00
0.90
1.09
0.99
1.02
1.00
1.04
2.08
2.95
3.00
f1 (ppm)


187.1
148.0
145.7
145.3
142.5
132.6
127.9
126.1
118.7
111.1
56.8
54.7
37.1
16.4
16.3
f1 (ppm)

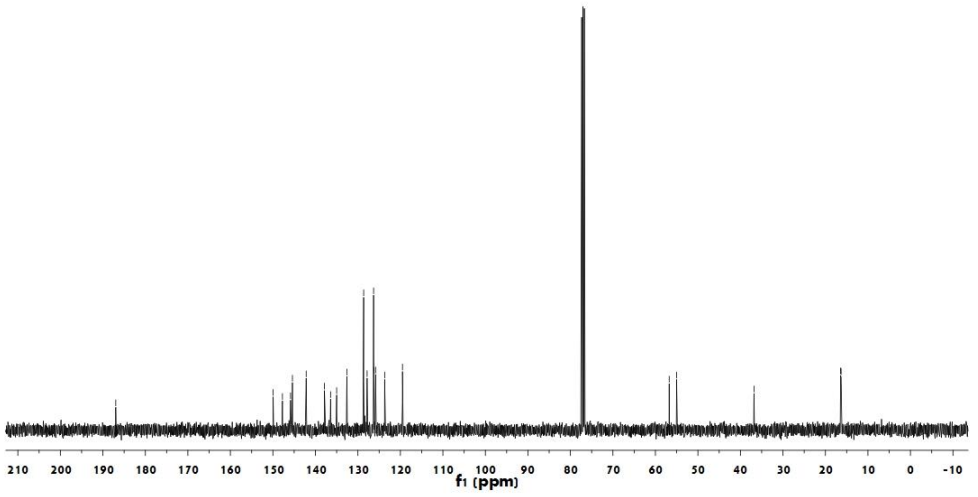

O2N
Ph
Me
Me
O

3k


8.17
8.16
8.15
8.14
7.76
7.29
7.26
7.24
6.70
6.58
6.45
6.10
6.08
6.06
6.04
3.52
3.49
3.47
3.42
3.40
3.38
3.36
3.33
3.30
3.29
3.26
2.05
2.05
1.89
1.89


0.99
0.93
1.98
0.81
1.01
0.97
1.00
1.00
1.05
2.10
2.96
2.95
f1 (ppm)

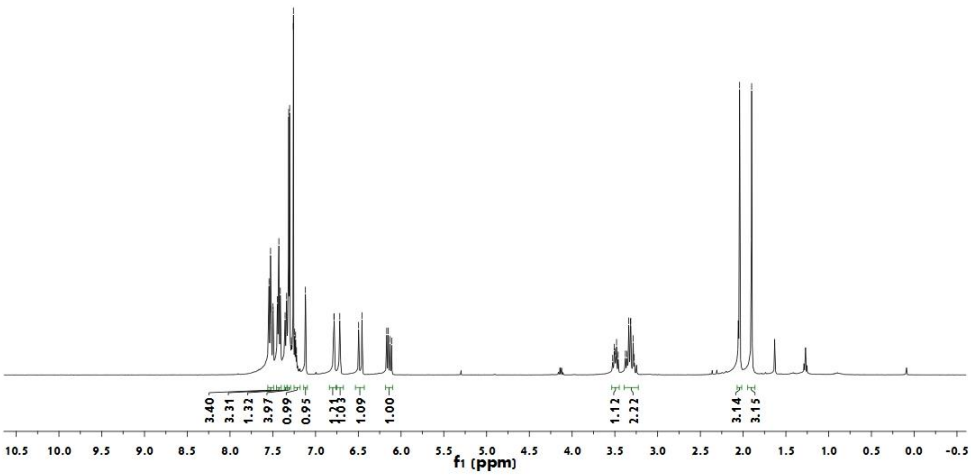

187.0
149.9
147.8
145.8
145.4
142.2
132.6
127.8
126.2
123.7
119.5
56.8
55.0
36.8
16.4
16.3


f1 (ppm)

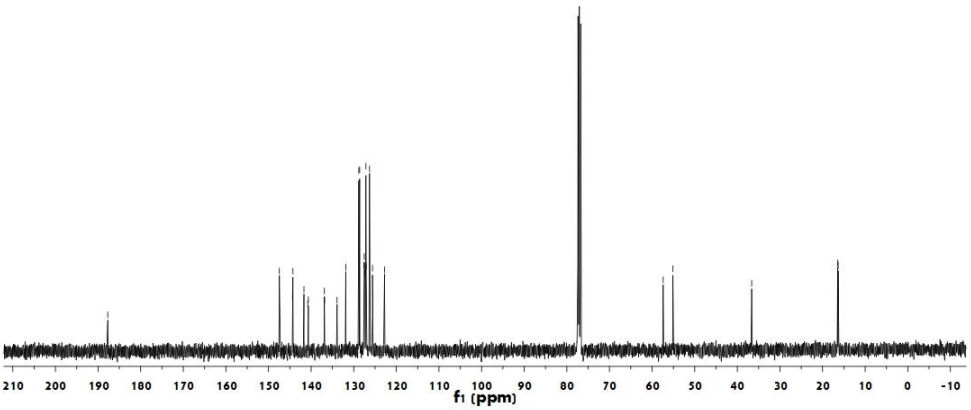

Ph
Ph
Me
Me
O

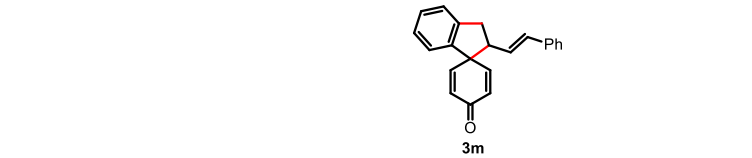
3l


7.53
7.52
7.50
7.50
7.45
7.43
7.41
7.36
7.34
7.31
7.30
7.28
7.26
7.26
7.24
7.23
7.22
7.12
6.72
6.46
6.17
6.15
6.13
6.11
3.51
3.50
3.48
3.46
3.38
3.36
3.34
3.32
3.31
3.29
3.27
2.04
1.90


3.40
3.31
1.32
3.97
0.99
0.95
1.03
1.09
1.00
1.12
2.22
3.14
3.15
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)

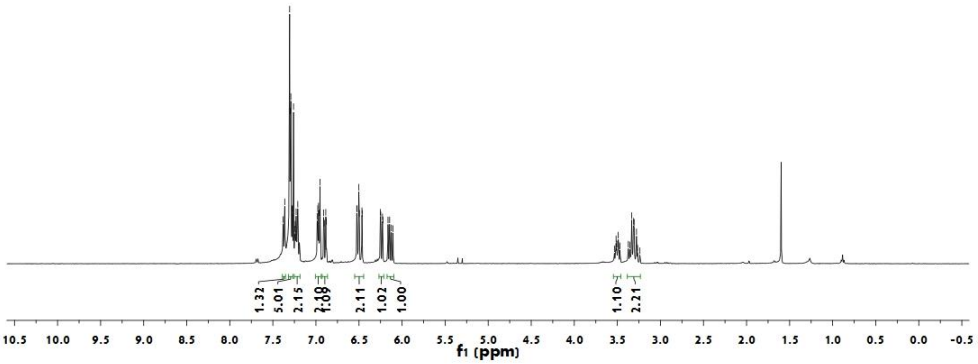

187.7
147.5
144.4
144.3
141.7
140.8
140.7
136.9
136.8
133.9
131.9
128.8
128.6
127.6
127.5
127.4
127.1
127.1
126.3
125.6
122.8
57.4
55.1
36.6
16.5
16.3

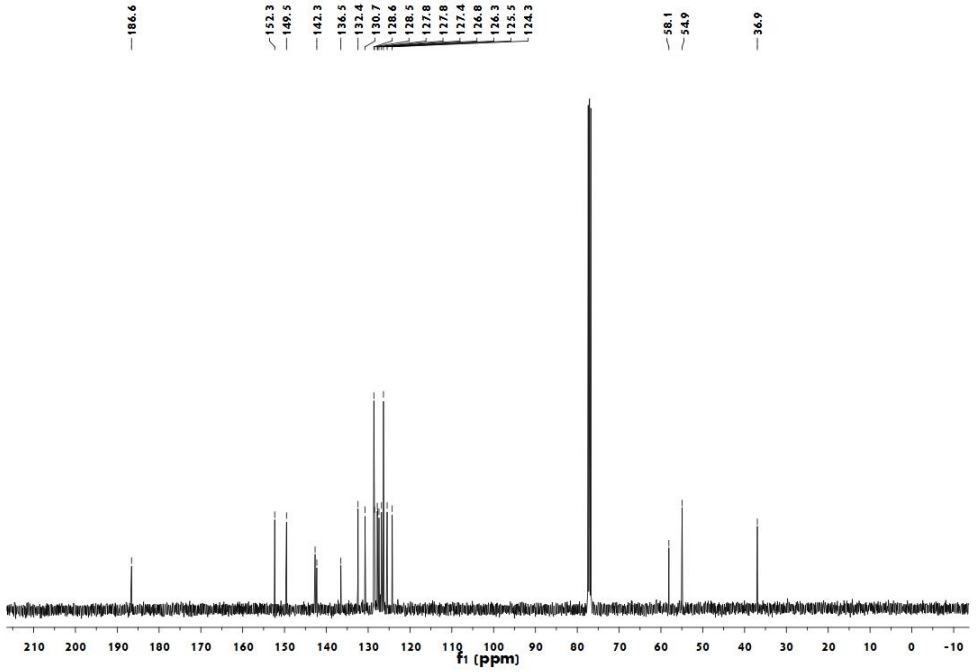

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

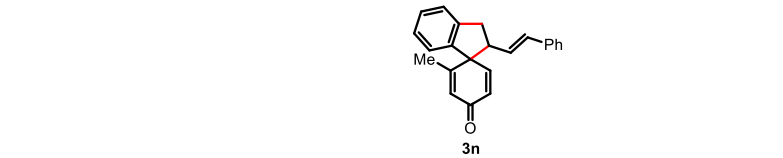

Ph
O

3m


7.38
7.36
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.21
6.88
6.46
6.45
6.16
6.14
6.12
6.10
3.53
3.51
3.51
3.50
3.49
3.47
3.37
3.35
3.33
3.31
3.30
3.28
3.27
3.24

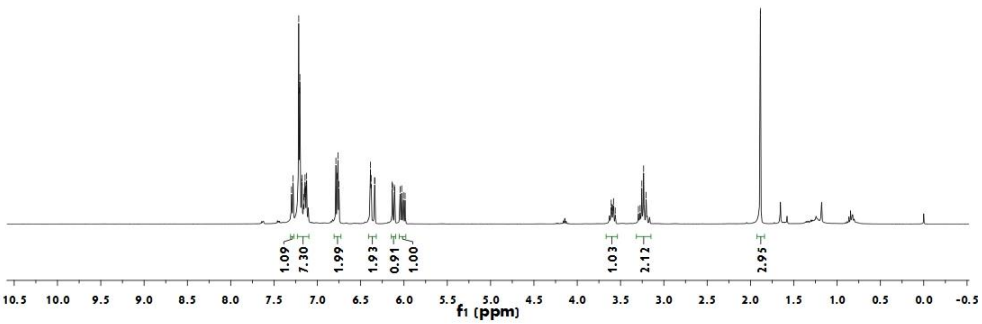

1.32
5.01
2.15
2.10
1.00
2.11
1.02
1.00
1.10
2.21
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


186.6
152.3
149.5
142.3
136.5
132.4
130.7
128.6
128.5
127.8
127.8
127.4
126.8
126.3
125.5
124.3
58.1
54.9
36.9
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
O

3n


7.30
7.28
7.21
7.21
7.20
7.18
7.18
7.16
7.15
7.14
7.14
7.12
6.75
6.34
6.14
6.05
6.03
6.01
5.99
3.61
3.60
3.59
3.58
3.56
3.27
3.25
3.23
3.20
1.89
1.88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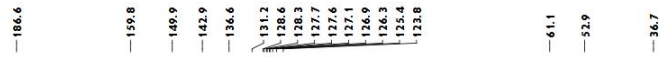
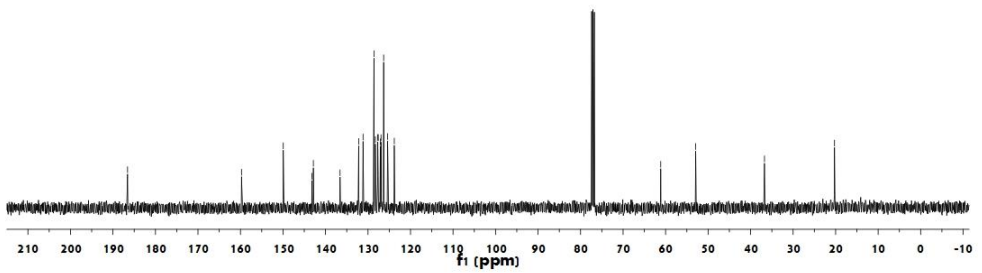
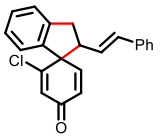
7.30
1.99
1.93
0.91
1.00
1.03
2.12
2.95
f1 (ppm)

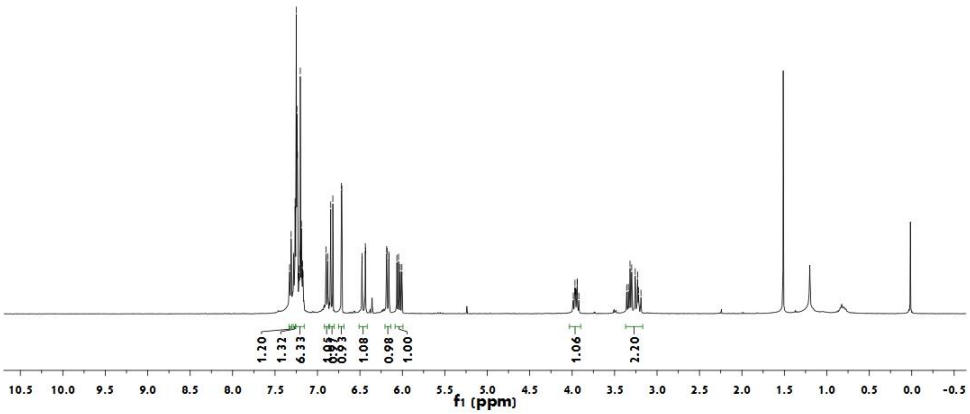

186.6
159.8
149.9
142.9
136.6
131.2
128.6
128.3
127.7
127.6
127.1
126.9
126.3
125.4
123.8
61.1
52.9
36.7
20.3

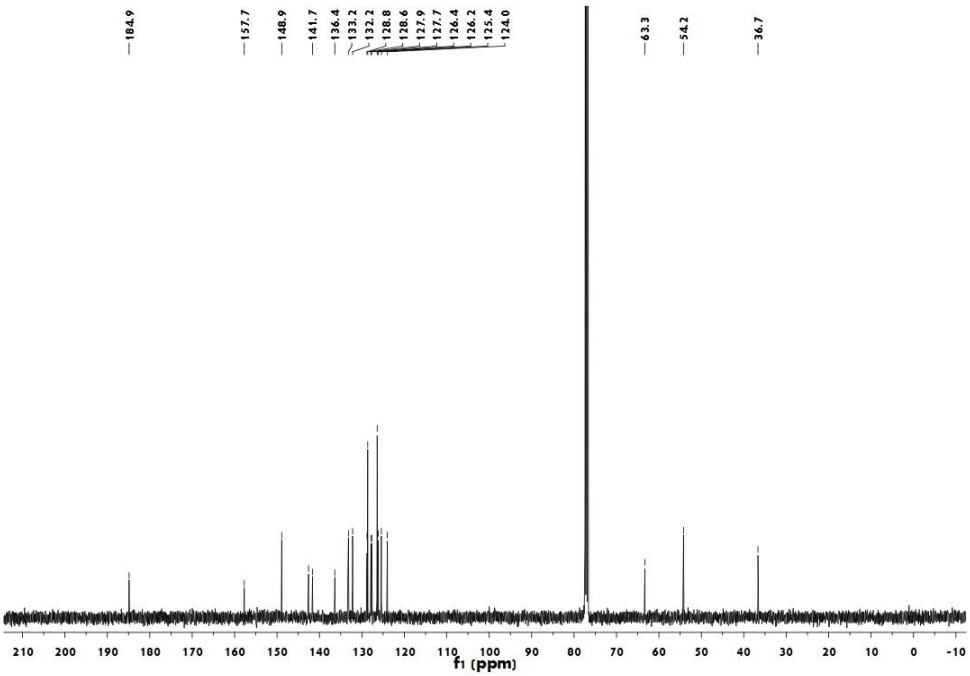

f1 (ppm)

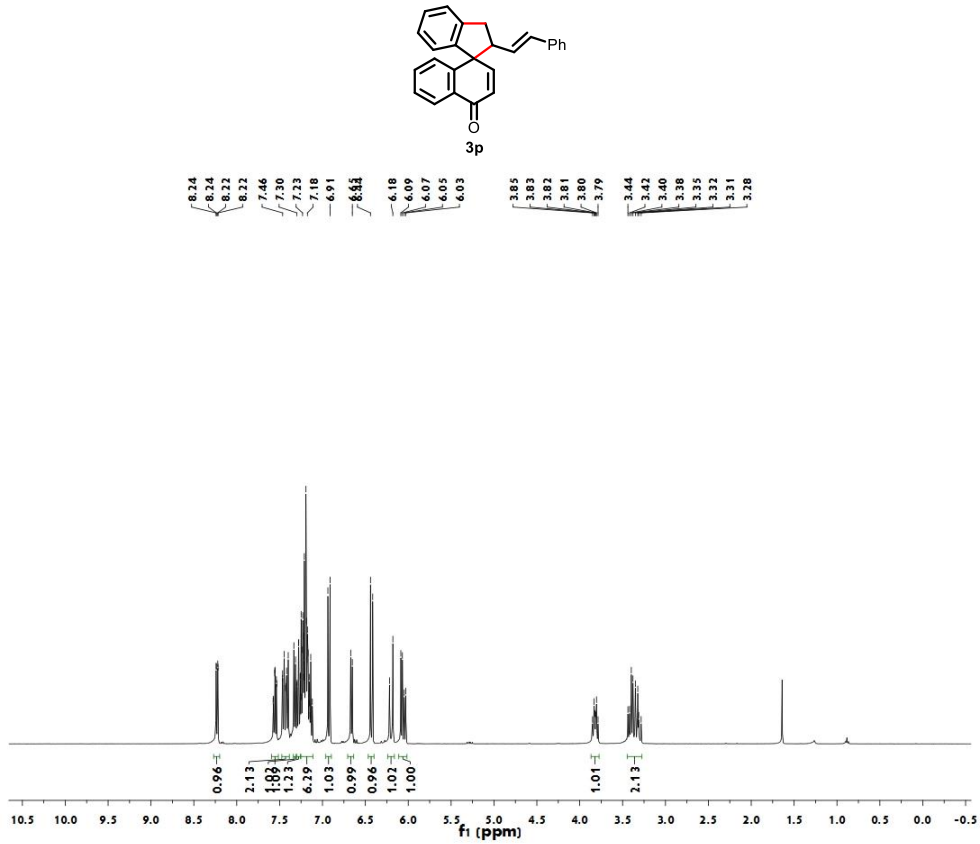

Ph
Cl
O

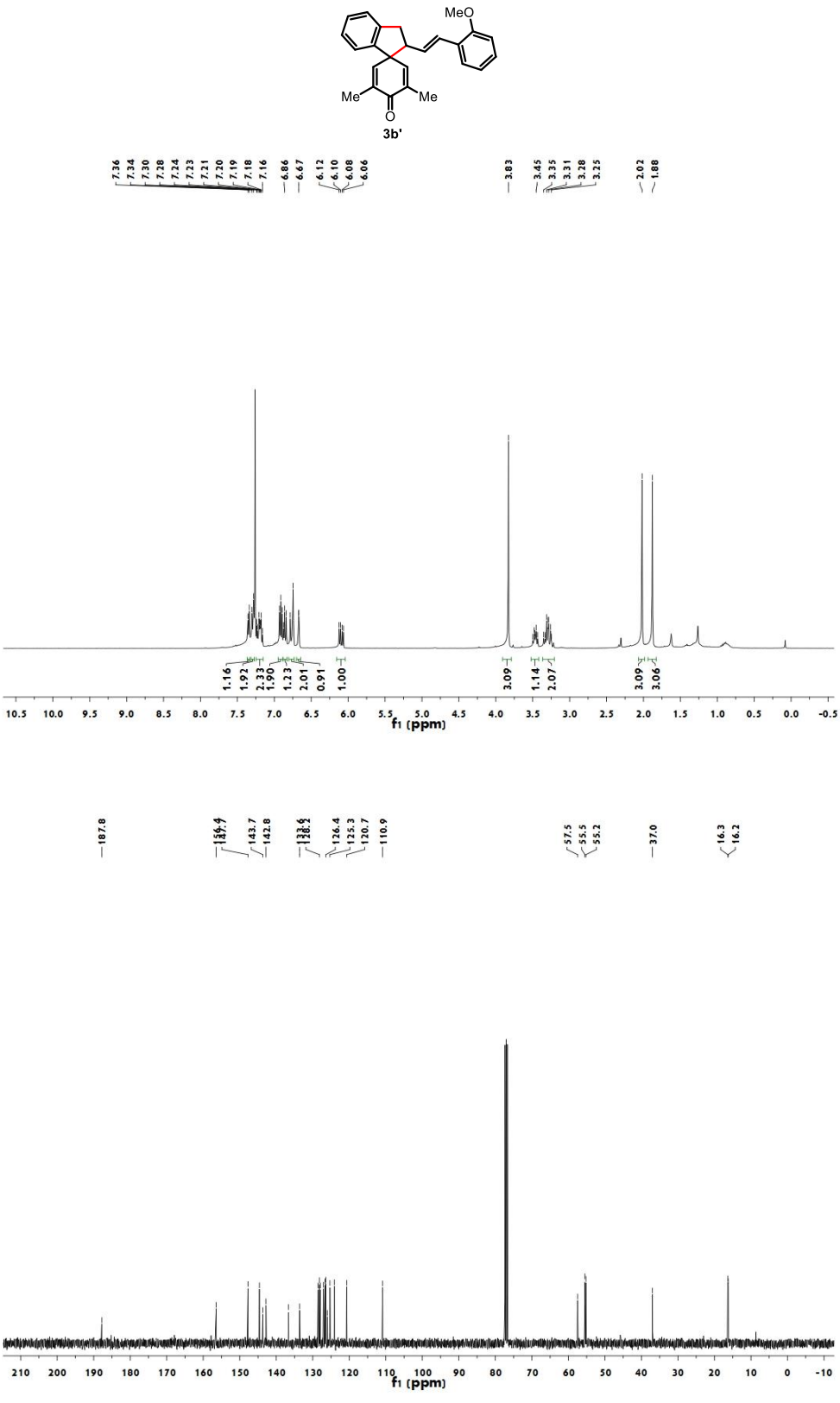
3o

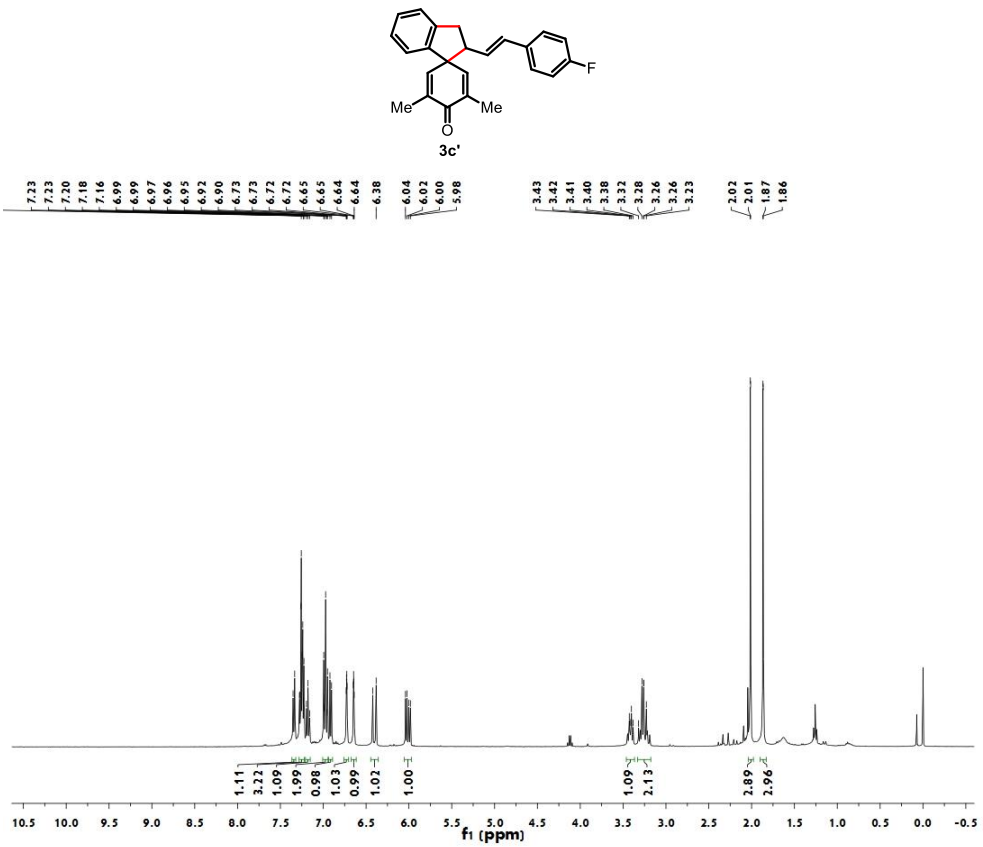

7.31 7.28 7.28 7.26 7.26 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.17 7.17
6.71 6.43 6.18 6.16 6.06 6.04 6.01 3.96 3.95 3.94 3.94 3.92
3.36 3.34 3.32 3.30 3.26 3.23 3.22 3.19

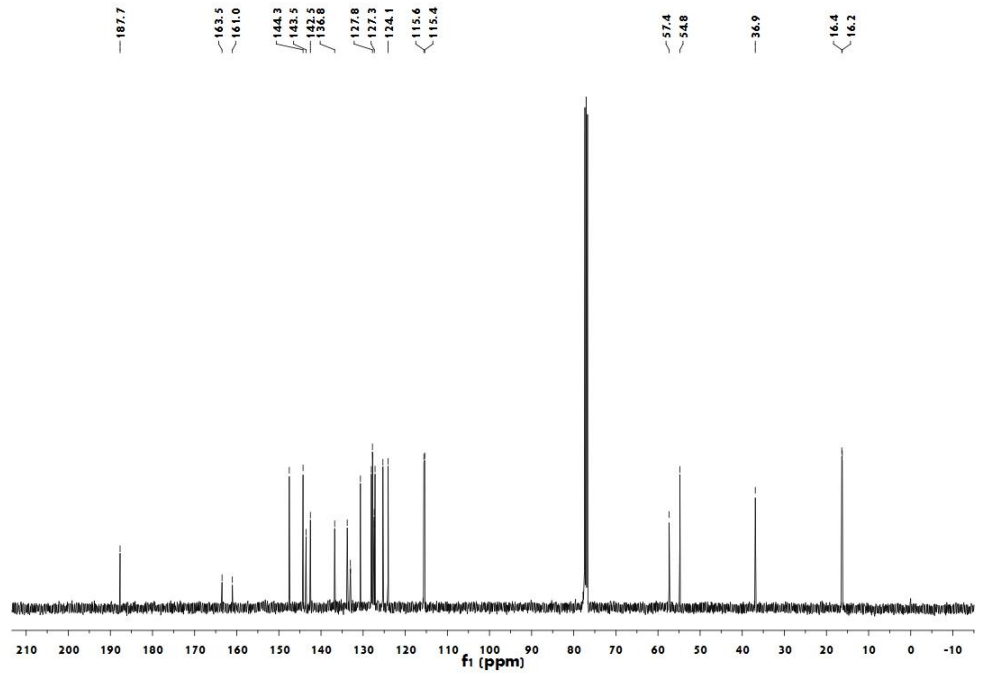

1.20 1.32 6.33 1.95 0.93 1.08 0.98 1.00 1.06 2.20
f1 (ppm)

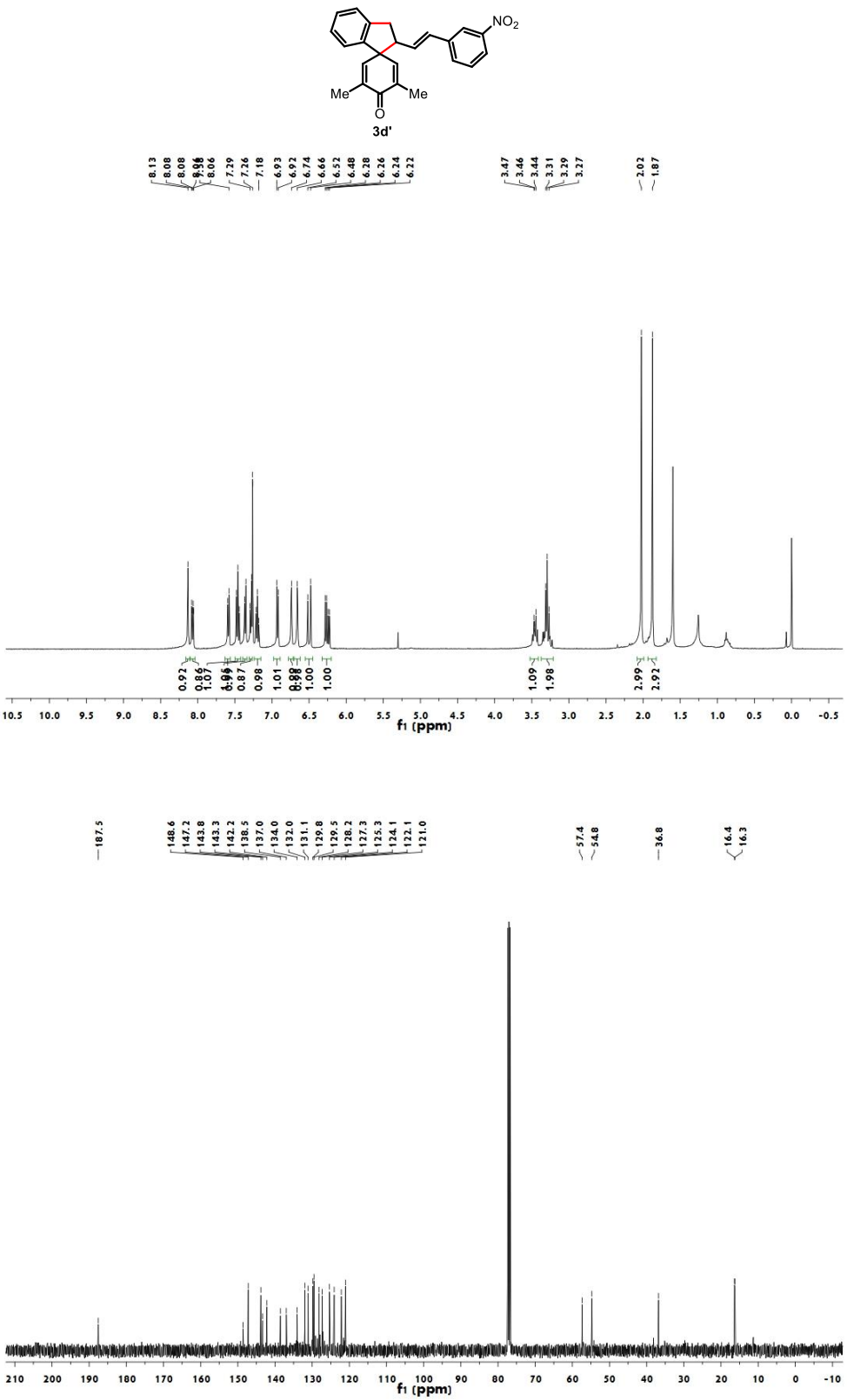

184.9 157.7 148.9 141.7 136.4 133.2 132.2 128.8 128.6 127.9 127.7 126.4 126.2 125.4 124.0
63.3 54.2 36.7
f1 (ppm)

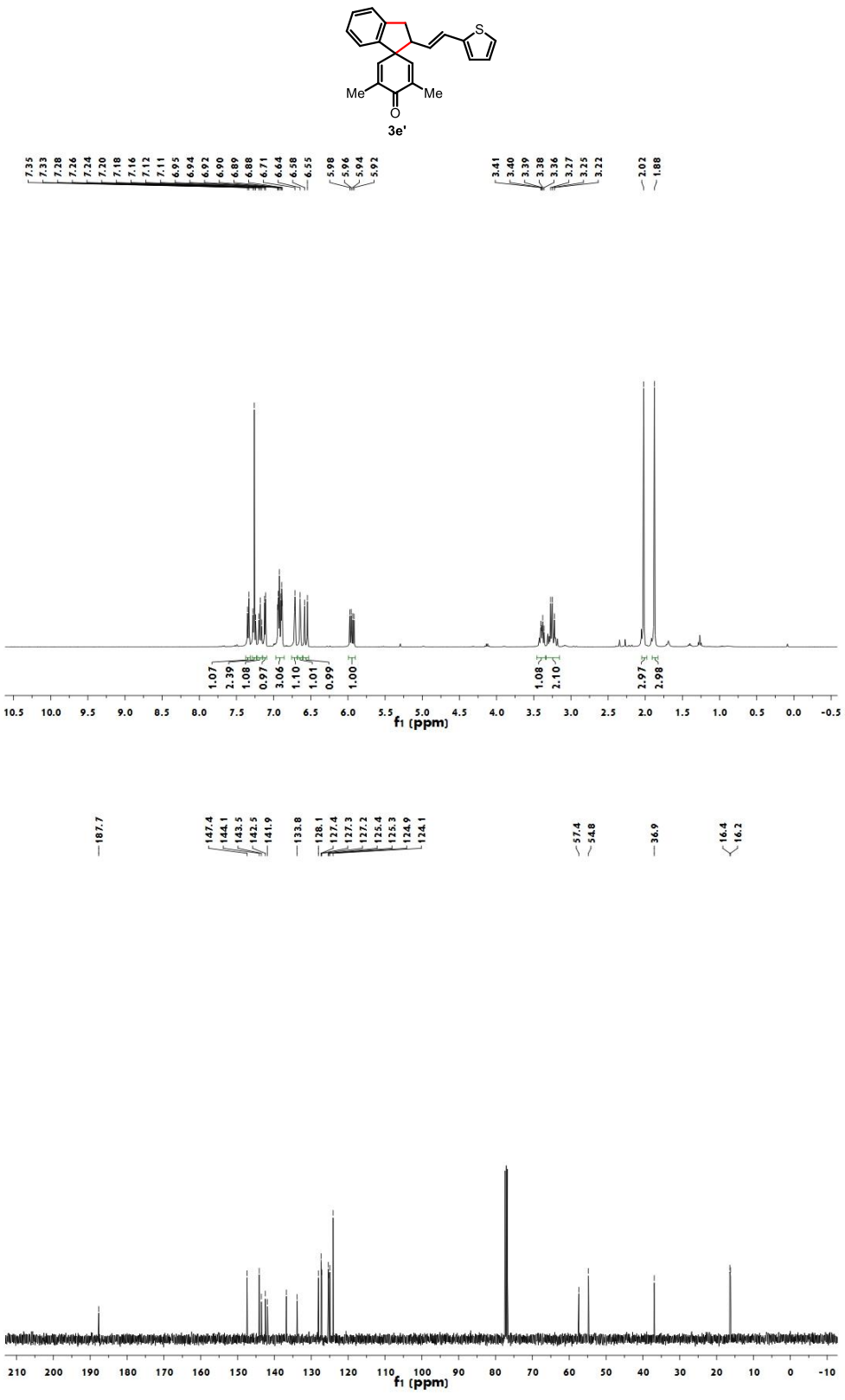

Ph
O
3p
8.24
8.24
8.22
8.22
7.46
7.30
7.23
7.18
6.91
6.18
6.09
6.07
6.05
6.03
3.85
3.83
3.82
3.81
3.80
3.79
3.44
3.42
3.40
3.38
3.35
3.32
3.31
3.28
0.96
2.13
1.23
6.29
1.03
0.99
0.96
1.02
1.00
1.01
2.13
f1 (ppm)
185.0
149.7
147.0
146.4
142.7
128.5
128.3
128.0
127.6
127.5
127.4
127.2
127.0
126.3
125.1
125.0
59.7
58.6
36.7
f1 (ppm)

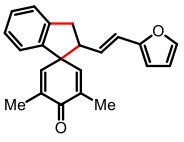

MeO
Me
Me
O
3b'
7.36
7.34
7.30
7.28
7.24
7.23
7.21
7.20
7.19
7.18
7.16
6.86
6.67
6.12
6.10
6.08
6.06
3.83
3.45
3.35
3.31
3.28
3.25
2.02
1.88
1.16
1.92
2.33
1.90
1.23
2.01
0.91
1.00
3.09
1.14
2.07
3.09
3.06
f1 (ppm)
187.8
154.4
147.7
143.7
142.8
133.6
128.1
126.4
125.3
120.7
110.9
57.5
55.5
55.2
37.0
16.3
16.2
f1 (ppm)


F
Me
Me
O
3c'
7.23
7.23
7.20
7.18
7.16
6.99
6.99
6.97
6.96
6.95
6.92
6.90
6.73
6.73
6.72
6.72
6.65
6.65
6.64
6.64
6.38
6.04
6.02
6.00
5.98
3.43
3.42
3.41
3.40
3.38
3.32
3.28
3.26
3.26
3.23
2.02
2.01
1.87
1.86
1.11
3.22
1.09
1.99
0.98
1.03
0.99
1.02
1.00
1.09
2.13
2.89
2.96
f1 (ppm)

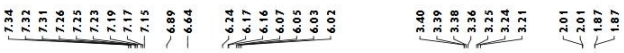

187.7
163.5
161.0
144.3
143.5
142.5
136.8
127.8
127.3
124.1
115.6
115.4
57.4
54.8
36.9
16.4
16.2
f1 (ppm)


NO2
Me
Me
O
3d'
8.13
8.08
8.08
8.06
7.29
7.26
7.18
6.93
6.92
6.74
6.66
6.52
6.48
6.28
6.26
6.24
6.22
3.47
3.46
3.44
3.31
3.29
3.27
2.02
1.87
0.92
0.86
1.07
0.87
0.98
1.01
1.00
1.00
1.09
1.98
2.99
2.92
f1 (ppm)
187.5
148.6
147.2
143.8
143.3
142.2
138.5
137.0
134.0
132.0
131.1
129.8
129.5
128.2
127.3
125.3
124.1
122.1
121.0
57.4
54.8
36.8
16.4
16.3
f1 (ppm)


Me
Me
O
S
3e'
7.35
7.33
7.28
7.26
7.24
7.20
7.18
7.16
7.12
7.11
6.95
6.94
6.92
6.90
6.89
6.88
6.71
6.64
6.58
6.55
5.98
5.96
5.94
5.92
3.41
3.40
3.39
3.38
3.36
3.27
3.25
3.22
2.02
1.88
1.07
2.39
1.08
0.97
3.06
1.10
1.01
0.99
1.00
1.08
2.10
2.97
2.98
f1 (ppm)
187.7
147.4
144.1
143.5
142.5
141.9
133.8
128.1
127.4
127.3
127.2
125.4
125.3
124.9
124.1
57.4
54.8
36.9
16.4
16.2
f1 (ppm)


Me
Me
O
O

3f'


7.34
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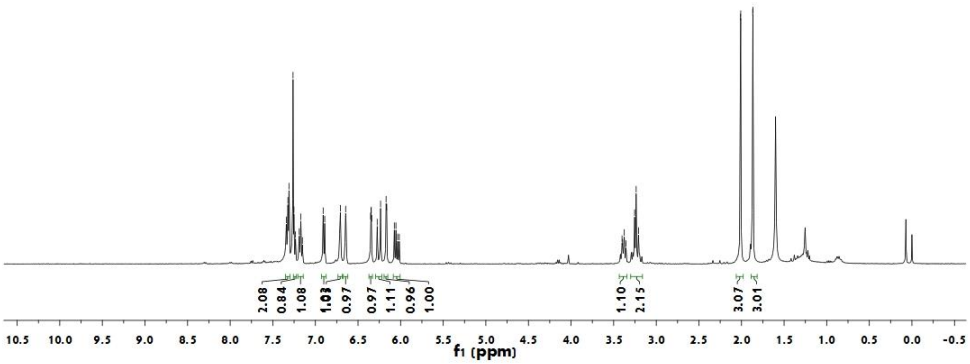
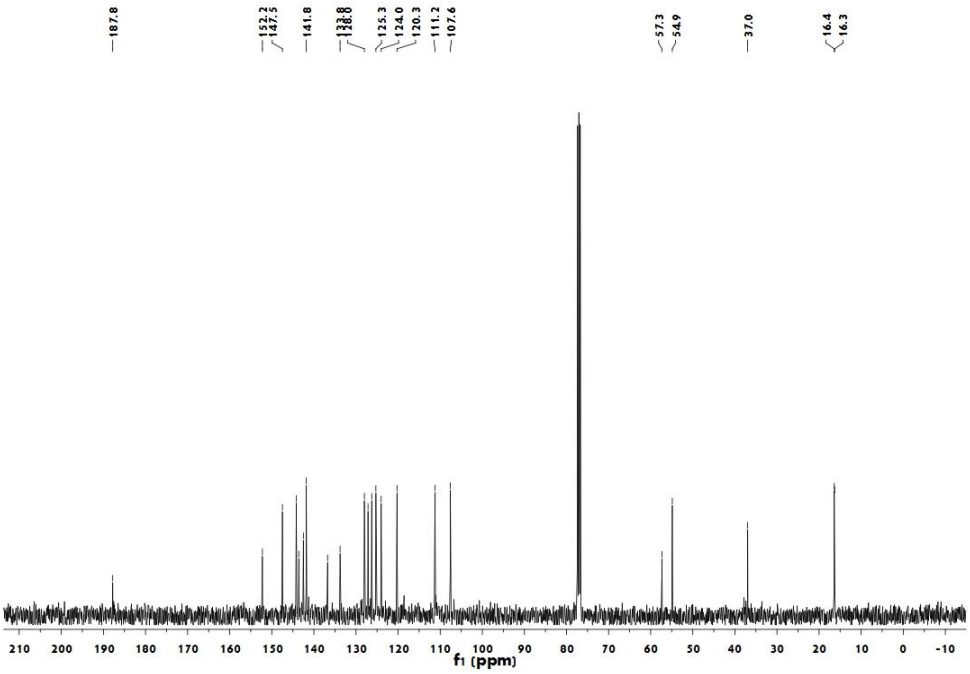
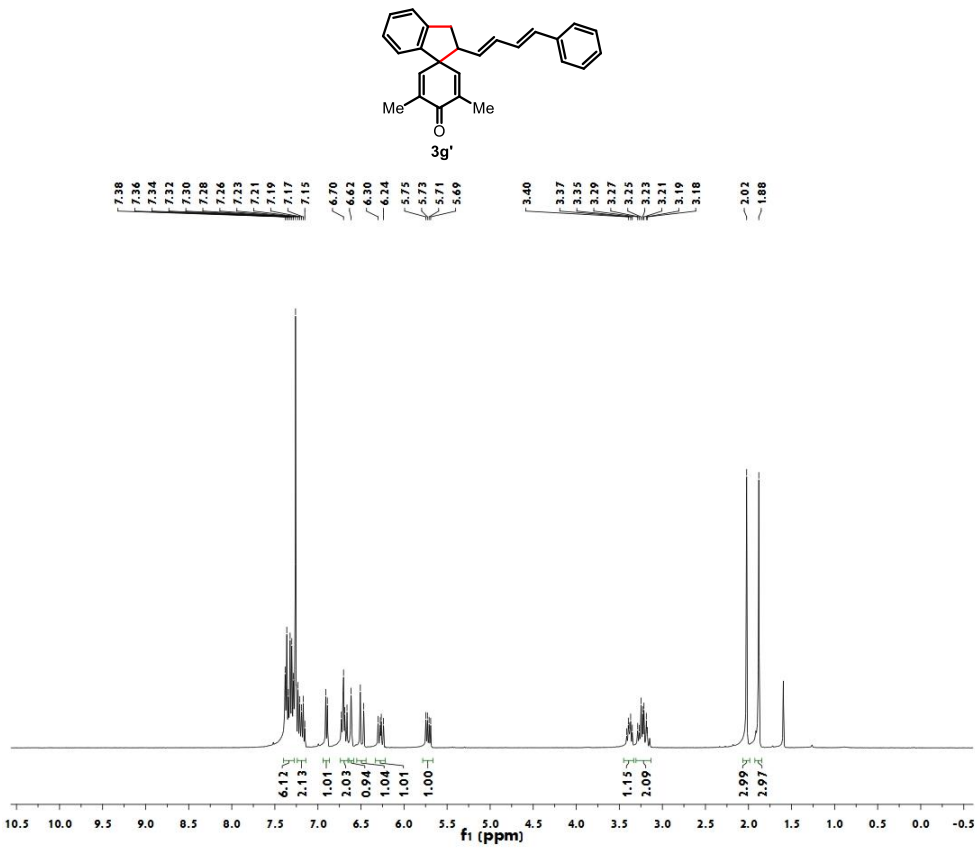
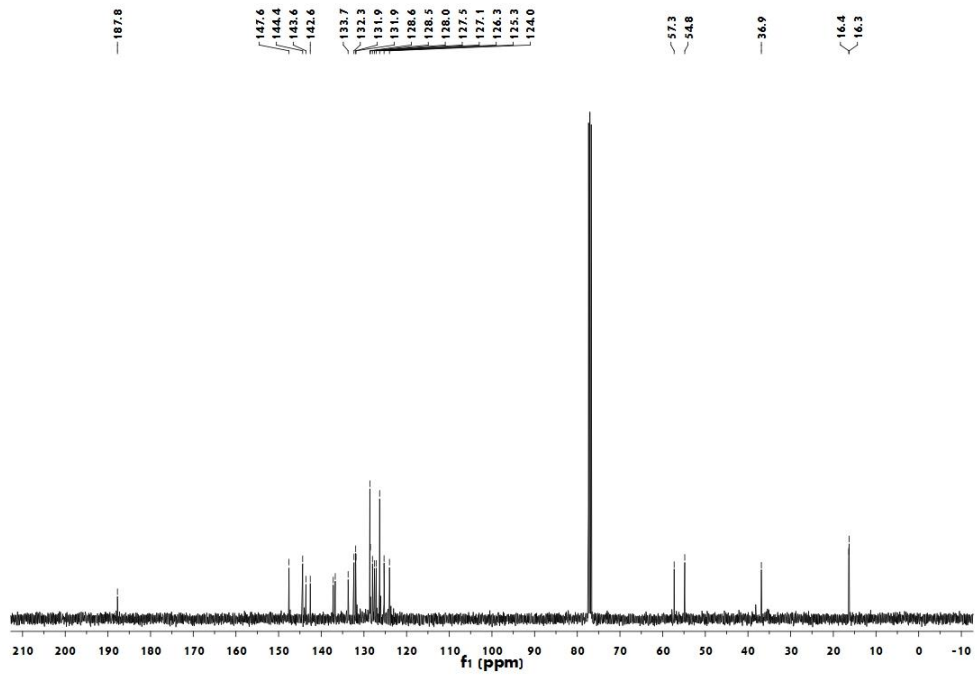
7.31
7.26
7.25
7.23
7.19
7.17
7.15
6.89
6.64
6.24
6.17
6.16
6.07
6.05
6.03
6.02
3.40
3.39
3.38
3.36
3.25
3.24
3.21
2.01
2.01
1.87
1.87


2.08
0.84
1.08
1.03
0.97
0.97
1.11
0.96
1.00
1.10
2.15
3.07
3.01
f1 (ppm)


187.8
152.2
147.5
141.8
133.8
128.0
125.3
124.0
120.3
111.2
107.6
57.3
54.9
37.0
16.4
16.3
f1 (ppm)


Me
Me
O
3g'
7.38
7.36
7.34
7.32
7.30
7.28
7.26
7.23
7.21
7.19
7.17
7.15
6.70
6.62
6.30
6.24
5.75
5.73
5.71
5.69
3.40
3.37
3.35
3.29
3.27
3.25
3.23
3.21
3.19
3.18
2.02
1.88
6.12
2.13
1.01
2.03
0.94
1.04
1.01
1.00
1.15
2.09
2.99
2.97
f1 (ppm)


187.8
147.6
144.4
143.6
142.6
133.7
132.3
131.9
131.9
128.6
128.5
128.0
127.5
127.1
126.3
125.3
124.0
57.3
54.8
36.9
16.4
16.3
f1 (ppm)