$CuBr_2$-Promoted Cyclization And Bromination of Arene-Alkynes: C-Br Bond Formation via Reductive Elimination of Cu(III) Species

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Electronic Supplementary Information

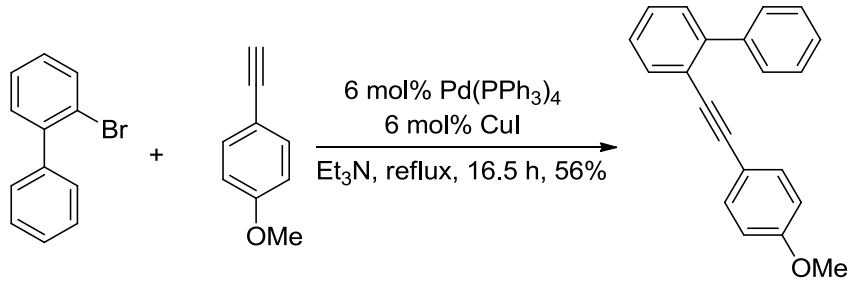
Experimental Section

General information

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of samples in $CDCl_3$ were recorded on an AVANCE III 400 spectrometer. IR spectra were recorded on a Avatar 360 FT-IR spectrometer. HRMS (EI) determinations were carried out on a Water GCT CA176 spectrometer. HRMS (ESI) determinations were carried out on a Bruker Daltonics APEXIII^{TM} ESI-FTICRMS spectrometer. Melting points were determined on a WRS-2 apparatus. X-ray crystal was carried out on a Bruker SMART CCD. Anhydrous $MeNO_2$ was distilled with $CaSO_4$.

Typical Procedure I for the synthesis of arene-alkynes.

Synthesis of 2-((4-methoxyphenyl)ethynyl)-1,1'-biphenyl (1a)[1]

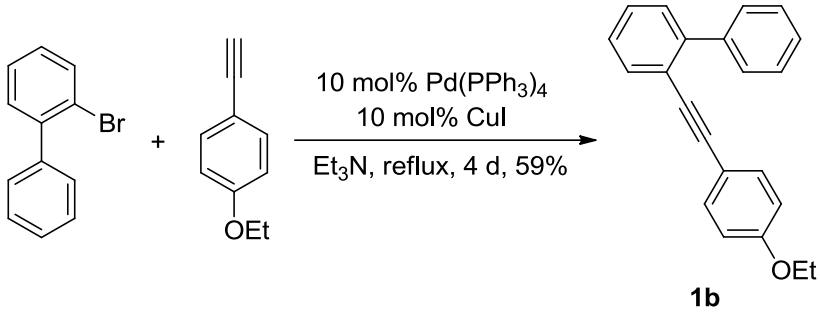


1a

2-Bromo-1,1'-biphenyl (10.35 mL, 60.0 mmol), 4-methoxyphenylacetylene (8.001 g, 60.5 mmol), $Pd(PPh_3)_4$ (4.193 g, 3.63 mmol), CuI (716 mg, 3.77 mmol), and Et_3N (160 mL) were added subsequently into a 250 mL of three-necked flask. The resulting mixture was refluxed and completed after 16.5 hours as monitored by TLC (eluent: petroleum ether). Then it was cooled to room temperature. The solvent was removed and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether) to afford **1a** as a liquid (9.491 g, 56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.2 Hz, 2 H), 7.62 (d, J = 8.0 Hz, 1 H), 7.51-7.20 (m, 8 H), 6.81 (d, J = 8.8 Hz, 2 H), 3.78 (s, 3 H).

The following compounds were prepared according to Typical Procedure I.

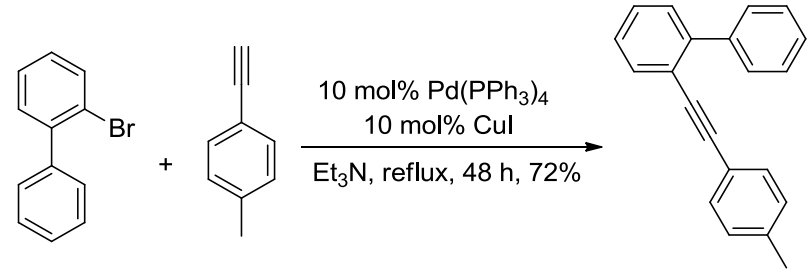
1) 2-((4-Ethoxyphenyl)ethynyl)-1,1'-biphenyl (1b)



1b

The reaction of 2-bromo-1,1'-biphenyl (3.4 mL, 19.8 mmol), 4-ethoxyphenylacetylene (4.304 g, 29.5 mmol), $Pd(PPh_3)_4$ (2.491 g, 2.15 mmol), CuI (381 mg, 2.00 mmol), and Et_3N (150 mL) afforded **1b** as a liquid (3.520 g, 59%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.2 Hz, 2 H), 7.61 (d, J = 8.8 Hz, 1 H), 7.49-7.20 (m, 8 H), 6.79 (d, J = 8.8 Hz, 2 H), 3.99 (q, J = 6.8 Hz, 2 H), 1.38 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 146.4, 143.4, 135.1, 134.9, 131.64, 131.62, 130.3, 130.0, 129.5, 129.1, 123.8, 117.0, 116.0, 93.0, 88.5, 62.8, 12.0; IR (neat) 1607, 1565, 1510, 1475, 1448, 1431 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{18}O$ 298.1358, found 298.1359.

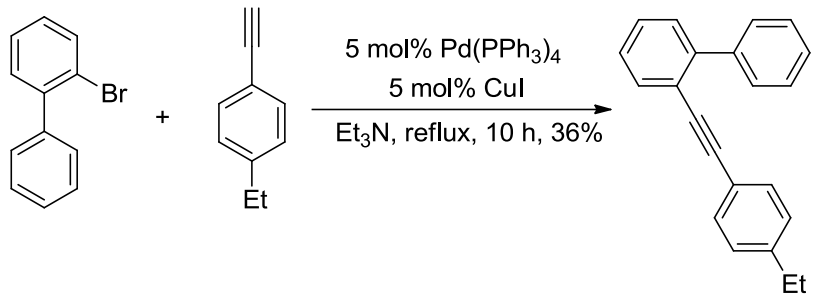
2) 2-(*p*-Tolylethynyl)-1,1'-biphenyl (1c)[1]



1c

The reaction of 2-bromo-1,1'-biphenyl (3.4 mL, 19.8 mmol), 4-methylphenylacetylene (2.811 g, 24.2 mmol), $Pd(PPh_3)_4$ (2.491 g, 2.15 mmol), CuI (380 mg, 2.00 mmol), and Et_3N (150 mL) afforded **1c** as a liquid (3.887 g, 72%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69-7.58 (m, 3 H), 7.48-7.26 (m, 6 H), 7.20 (d, J = 8.4 Hz, 2 H), 7.06 (d, J = 8.0 Hz, 2 H), 2.30 (s, 3 H).

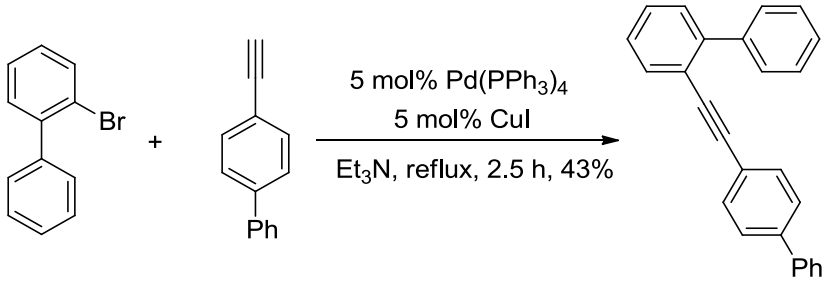
3) 2-((4-Ethylphenyl)ethynyl)-1,1'-biphenyl (1d)[2]



1d

The reaction of 2-bromo-1,1'-biphenyl (8.6 mL, 50.0 mmol), 4-ethylphenylacetylene (7.5 mL, 50.7 mmol), $Pd(PPh_3)_4$ (2.900 g, 2.50 mmol), CuI (480 mg, 2.50 mmol), and Et_3N (150 mL) afforded **1d** as a liquid (5.115 g, 36%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69-7.60 (m, 3 H), 7.50-7.20 (m, 8 H), 7.11 (d, J = 7.6 Hz, 2 H), 2.62 (q, J = 7.6 Hz, 2 H), 1.21 (t, J = 7.6 Hz, 3 H).

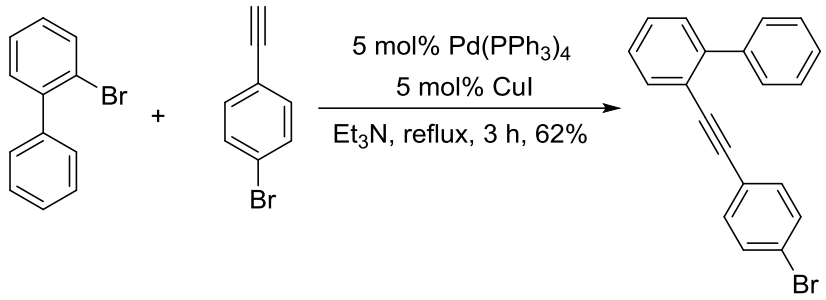
4) 2-((4-Phenylphenyl)ethynyl)-1,1'-biphenyl (1e)



1e

The reaction of 2-bromo-1,1'-biphenyl (4.6 mL, 26.7 mmol), 4-phenylphenylacetylene (4.700 g, 26.0 mmol), $Pd(PPh_3)_4$ (1.450 g, 1.25 mmol), CuI (237 mg, 1.25 mmol), and Et_3N (120 mL) afforded **1e** as a solid (3.553 g, 43%); mp 94.1-95.3 ^oC (dichloromethane/petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.28 (m, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 140.9, 140.7, 140.5, 133.0, 131.9, 129.63, 129.56, 129.0, 128.7, 128.0, 127.7, 127.6, 127.2, 127.12, 127.08, 122.5, 121.8, 92.3, 90.3; IR (neat) 1599, 1576, 1520, 1486, 1472, 1447, 1431, 1400 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{18}$ 330.1409, found 330.1401.

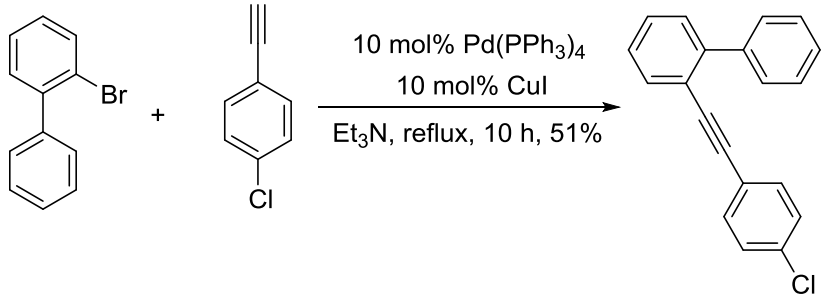
5) 2-((4-Bromophenyl)ethynyl)-1,1'-biphenyl (1g)



1g

The reaction of 2-bromo-1,1'-biphenyl (0.35 mL, 2.0 mmol), 4-bromophenylacetylene (362 mg, 2.0 mmol), $Pd(PPh_3)_4$ (120 mg, 0.10 mmol), CuI (19 mg, 0.10 mmol), and Et_3N (50 mL) afforded **1g** as a solid (0.412 g, 62%); mp 64.2-64.7 ^oC (dichloromethane/petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65-7.61 (m, 3 H), 7.49-7.28 (m, 8 H), 7.16 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 140.5, 132.8, 132.7, 131.5, 129.5, 129.3, 128.7, 127.9, 127.5, 127.1, 122.4, 122.3, 121.3, 91.1, 90.5; IR (neat) 1577, 1503, 1488, 1447, 1430 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{13}Br$ 332.0201, found 332.0199.

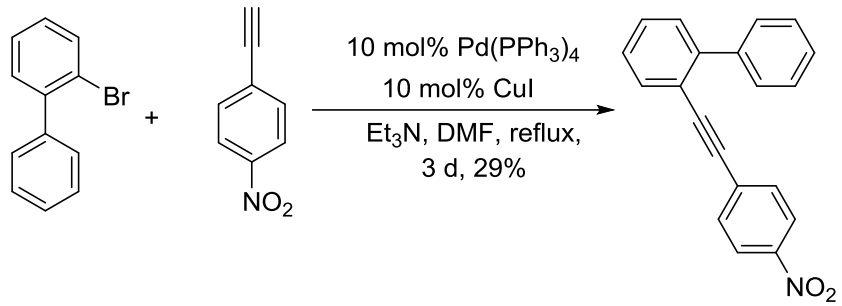
6) 2-((4-Chlorophenyl)ethynyl)-1,1'-biphenyl (1h)



1h

The reaction of 2-bromo-1,1'-biphenyl (3.4 mL, 19.8 mmol), 4-chlorophenylacetylene (3.801 g, 27.9 mmol), $Pd(PPh_3)_4$ (2.491 g, 2.15 mmol), CuI (380 mg, 2.00 mmol), and Et_3N (150 mL) afforded **1h** as a solid (2.907 g, 51%); mp 53.2-53.4 ^oC (dichloromethane/petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.68-7.55 (m, 3 H), 7.48-7.24 (m, 6 H), 7.21 (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 143.2, 136.5, 135.2, 134.9, 131.7, 131.6, 130.9, 130.8, 130.1, 129.7, 129.2, 123.9, 123.2, 91.7, 90.9; IR (neat) 1487, 1472, 1447, 1432, 1394 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{13}Cl$ 288.0706, found 288.0699.

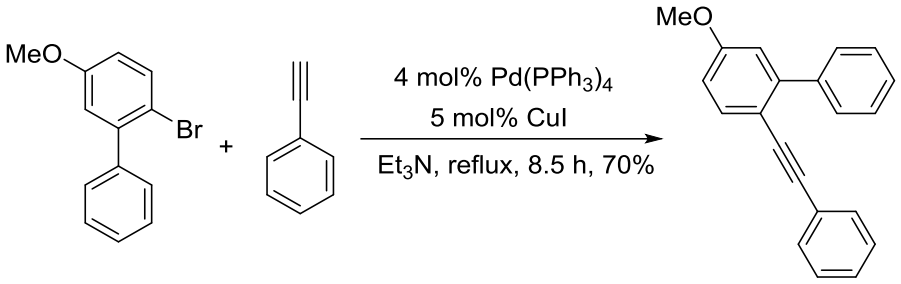
7) 2-((4-Nitrophenyl)ethynyl)-1,1'-biphenyl (1i)[1]



1i

The reaction of 2-bromo-1,1'-biphenyl (3.4 mL, 20.0 mmol), 4-nitrophenylacetylene (3.531 g, 24.0 mmol), $Pd(PPh_3)_4$ (2.490 g, 2.00 mmol), CuI (381 mg, 2.00 mmol), Et_3N (100 mL), and DMF (50 mL) afforded **1i** as a solid (1.700 g, 29%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.8 Hz, 2 H), 7.69-7.60 (m, 3 H), 7.52-7.34 (m, 8 H).

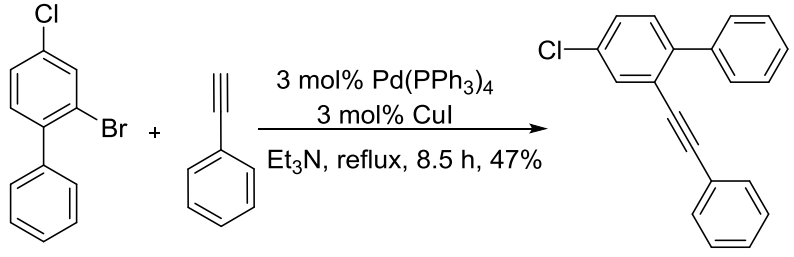
8) 5-Methoxy-2-(phenylethynyl)-1,1'-biphenyl (1j)[3]



1j

The reaction of 2-bromo-5-methoxy-1,1'-biphenyl (4.519 g, 17.2 mmol), phenylacetylene (2.8 mL, 25.5 mmol), $Pd(PPh_3)_4$ (770 mg, 0.67 mmol), CuI (170 mg, 0.89 mmol), and Et_3N (100 mL) afforded **1j** as a liquid (3.921 g, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.63 (m, 2 H), 7.55 (dd, J = 8.6, 1.4 Hz, 1 H), 7.47-7.19 (m, 8 H), 7.02-6.90 (m, 1 H), 6.88-6.81 (m, 1 H), 3.80 (s, 3 H).

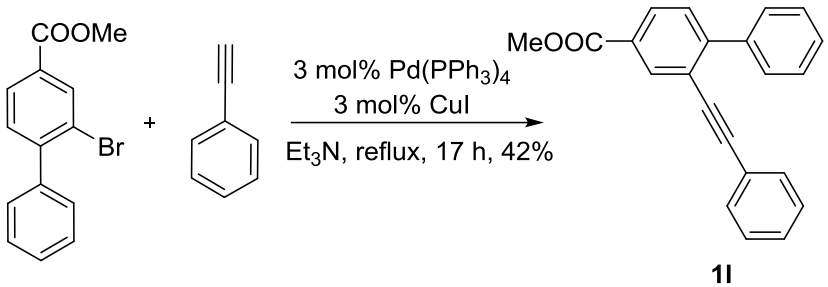
9) 4-Chloro-2-(phenylethynyl)-1,1'-biphenyl (1k)



1k

The reaction of 2-bromo-4-chloro-1,1'-biphenyl (5.424 g, 20.4 mmol), phenylacetylene (2.25 mL, 20.5 mmol), $Pd(PPh_3)_4$ (695 mg, 0.60 mmol), CuI (116 mg, 0.61 mmol), and Et_3N (60 mL) afforded **1k** as a liquid (2.771 g, 47%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.67-7.58 (m, 3 H), 7.51-7.23 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 142.0, 135.2, 134.6, 133.7, 132.9, 131.4, 130.8, 130.6, 130.4, 130.1, 129.9, 125.1, 124.8, 93.9, 88.6; IR (neat) 1601, 1586, 1546, 1491, 1473, 1442, 1389 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{13}Cl$ 288.0706, found 288.0710.

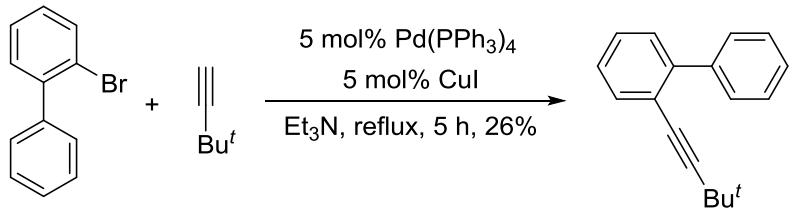
10) 4-Methoxycarbonyl-2-(phenylethynyl)-1,1'-biphenyl (1l)



1l

The reaction of 2-bromo-4-methoxycarbonyl-1,1'-biphenyl (3.287 g, 11.3 mmol), phenylacetylene (1.3 mL, 11.8 mmol), $Pd(PPh_3)_4$ (416 mg, 0.36 mmol), CuI (71 mg, 0.37 mmol), and Et_3N (40 mL) afforded **1l** as a solid (1.468 g, 42%); mp 60.6-61.3 ^oC (ethyl acetate/petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1 H), 8.04 (dd, J = 8.0, 1.6 Hz, 1 H), 7.73-7.65 (m, 2 H), 7.53-7.24 (m, 9 H), 3.96 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 148.0, 139.7, 134.3, 131.6, 129.8, 129.5, 129.4, 129.1, 128.55, 128.46, 128.3, 128.2, 123.2, 122.1, 93.1, 88.6, 52.5; IR (neat) 1728, 1596, 1579, 1567, 1553, 1485, 1471, 1441, 1427 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{17}O_2$ 313.1223, found 313.1216.

11) 2-(3,3-Dimethylbut-1-yn-1-yl)-1,1'-biphenyl (4a)[4]

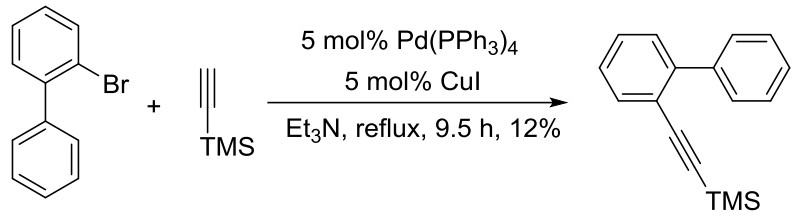


4a

The reaction of 2-bromo-1,1'-biphenyl (9.0 mL, 52.2 mmol), 3,3-dimethylbut-1-yne (6.2 mL, 50.4 mmol), $Pd(PPh_3)_4$ (2.890 g, 2.50 mmol), CuI (500 mg, 2.63 mmol), and

Et_3N (150 mL) afforded **4a** as a liquid (3.037 g, 26%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.2 Hz, 2 H), 7.48 (d, J = 8.4 Hz, 1 H), 7.42-7.15 (m, 6 H), 1.16 (s, 9 H).

12) 2-(Trimethylsilyleth-1-yn-1-yl)-1,1'-biphenyl (4b)

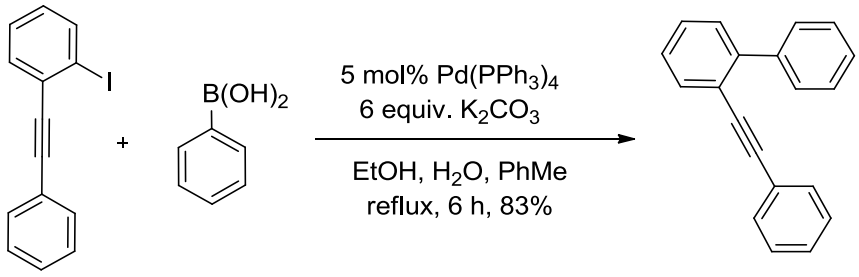


4b

The reaction of 2-bromo-1,1'-biphenyl (8.5 mL, 49.4 mmol), trimethylsilylethyne (8.0 mL, 56.4 mmol), $Pd(PPh_3)_4$ (2.500 g, 2.20 mmol), CuI (476 mg, 2.50 mmol), and Et_3N (130 mL) afforded **4b** as a liquid (1.468 g, 12%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.68-7.57 (m, 3 H), 7.47-7.24 (m, 6 H), 0.17 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 140.4, 133.4, 129.5, 128.8, 127.9, 127.5, 127.0, 121.6, 104.9, 97.7, -0.1; IR (neat) 1474, 1449, 1431, 1407 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{19}Si$ 251.1251, found 251.1253.

Typical Procedure II for the synyhesis of arene-alkynes.

Synthesis of 2-(phenylethynyl)-1,1'-biphenyl (1f)[5]



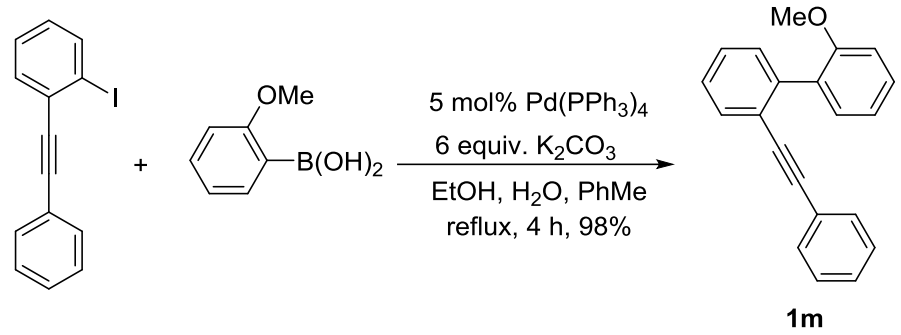
1f

1-Iodo-2-(phenylethynyl)benzene (1.523 g, 5.0 mmol), phenylboronic acid (610 mg, 5.0 mmol), $Pd(PPh_3)_4$ (323 mg, 0.28 mmol), K_2CO_3 (4.159 g, 30.09 mmol), and solvent (160 mL, EtOH : H_2O : PhMe = 1 : 1 : 4.4) were added subsequently into a 250 mL of three-necked flask. The resulting mixture was refluxed and completed after 6 hours as monitored by TLC (eluent: petroleum ether). The mixture was cooled to room temperature and extracted with ethyl acetate (30 mL x 3). The combined organic layer was dried over $MgSO_4$. Filtration, concentration, and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether) to afforded **1f** as

a liquid (1.052 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.59 (m, 3 H), 7.51-7.12 (m, 11 H).

The following compounds were prepared according to Typical Procedure II.

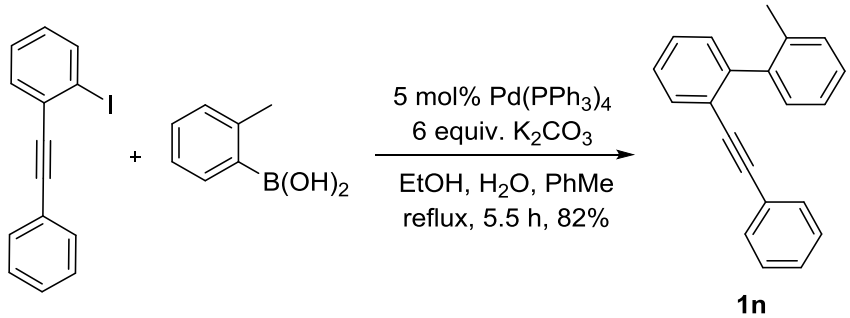
1) 2-Methoxy-2'-(phenylethynyl)-1,1'-biphenyl (1m)



1m

The reaction of 1-iodo-2-(phenylethynyl)benzene (1.204 g, 4.0 mmol), (2-methoxyphenyl)boronic acid (765 mg, 5.0 mmol), $Pd(PPh_3)_4$ (400 mg, 0.35 mmol), K_2CO_3 (4.230 g, 30.6 mmol), and solvent (160 mL, EtOH : H_2O : PhMe = 1 : 1 : 4.4) afforded **1m** as a solid (1.394 g, 98%); mp 59.7-59.9 ^{o}C (ethyl acetate/petroleum ether) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.55 (m, 1 H), 7.41-7.26 (m, 5 H), 7.25-7.16 (m, 5 H), 7.07-6.96 (m, 2 H), 3.76 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 141.5, 132.0, 131.6, 131.5, 130.3, 130.0, 129.1, 128.3, 128.1, 128.0, 127.1, 123.7, 123.3, 120.3, 111.0, 91.8, 89.6, 55.7; IR (neat) 1595, 1580, 1500, 1488, 1459, 1438, 1427 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{16}O$ 284.1201, found 284.1202.

2) 2-Methyl-2'-(phenylethynyl)-1,1'-biphenyl (1n)

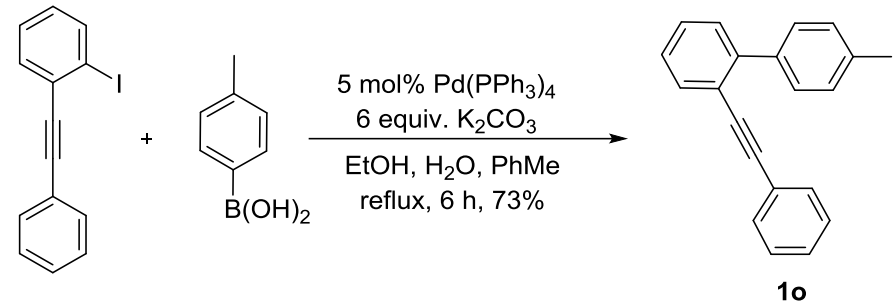


1n

The reaction of 1-iodo-2-(phenylethynyl)benzene (1.528 g, 5.0 mmol), *o*-tolylboronic acid (680 mg, 5.0 mmol), $Pd(PPh_3)_4$ (292 mg, 0.25 mmol), K_2CO_3 (4.147 g, 30.0 mmol), and solvent (160 mL, EtOH : H_2O : PhMe = 1 : 1 : 4.4) afforded **1n** as a liquid (1.101 g, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.2 Hz, 1 H), 7.32-7.10 (m,

12 H), 2.21 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 140.7, 136.3, 131.7, 131.4, 129.9, 129.7, 129.5, 128.2, 128.1, 128.0, 127.6, 127.0, 125.3, 123.4, 122.8, 92.4, 88.9, 20.0; IR (neat) 1598, 1491, 1470, 1443 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{16}$ 268.1252, found 268.1257.

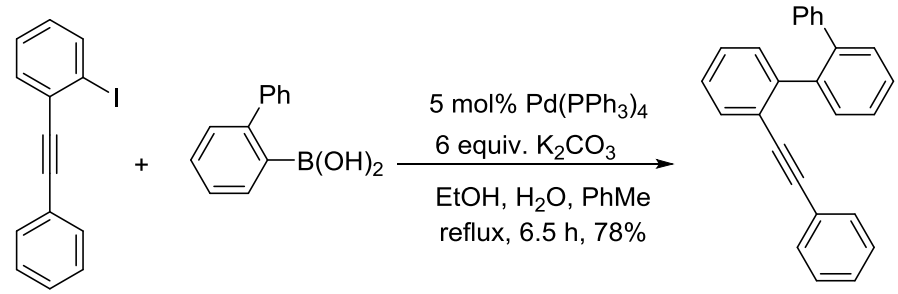
3) 4'-Methyl-2-(phenylethynyl)-1,1'-biphenyl (1o)[6]



1o

The reaction of 1-iodo-2-(phenylethynyl)benzene (2.078 g, 6.8 mmol), *p*-tolylboronic acid (954 mg, 7.0 mmol), $Pd(PPh_3)_4$ (409 mg, 0.35 mmol), K_2CO_3 (5.890 g, 42.6 mmol), and solvent (210 mL, EtOH : H_2O : PhMe = 1 : 1 : 4) afforded **1o** as a liquid (1.324 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.51 (m, 3 H), 7.49-7.16 (m, 10 H), 2.41 (s, 3 H).

4) 2-(Phenylethynyl)-2'-phenyl-1,1'-biphenyl (1p)

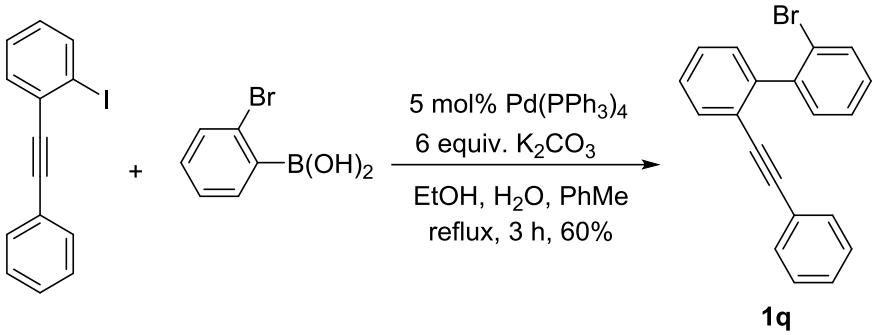


1p

The reaction of 1-iodo-2-(phenylethynyl)benzene (2.105 g, 6.9 mmol), (2-phenylphenyl)boronic acid (1.395 g, 7.0 mmol), $Pd(PPh_3)_4$ (405 mg, 0.35 mmol), K_2CO_3 (5.810 g, 42.0 mmol), and solvent (210 mL, EtOH : H_2O : PhMe = 1 : 1 : 4) afforded **1p** as a solid (1.788 g, 78%); mp 77.7-78.0 ^{o}C (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.37 (m, 5 H), 7.30-7.02 (m, 13 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 141.4, 139.4, 131.7, 131.3, 131.1, 130.6, 129.9, 129.6, 128.1, 127.9, 127.7, 127.6, 127.5, 126.7, 126.6, 126.3, 123.5, 123.0, 92.5, 89.2; IR

(neat) 1653, 1635, 1601, 1567, 1491, 1482, 1464, 1449, 1439, 1424 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{18}$ 330.1409, found 330.1408.

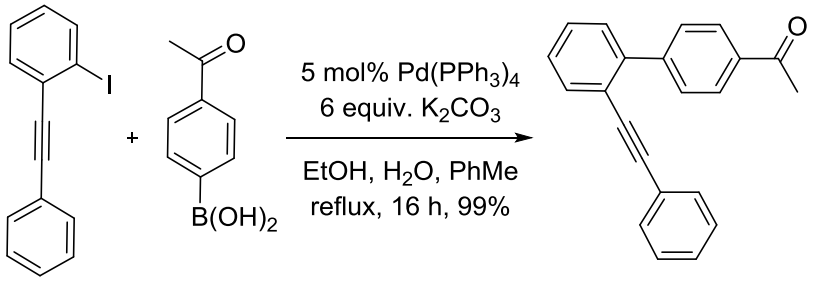
5) 2-Bromo-2'-(phenylethynyl)-1,1'-biphenyl (1q)[7]



1q

The reaction of 1-iodo-2-(phenylethynyl)benzene (1.524 g, 5.0 mmol), (2-bromophenyl)boronic acid (1.004 g, 5.0 mmol), $Pd(PPh_3)_4$ (301 mg, 0.26 mmol), K_2CO_3 (4.204 g, 30.4 mmol), and solvent (160 mL, EtOH : H_2O : PhMe = 1 : 1 : 4.4) afforded **1q** as a solid (985 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 1 H), 7.66-7.60 (m, 1 H), 7.44-7.12 (m, 11 H).

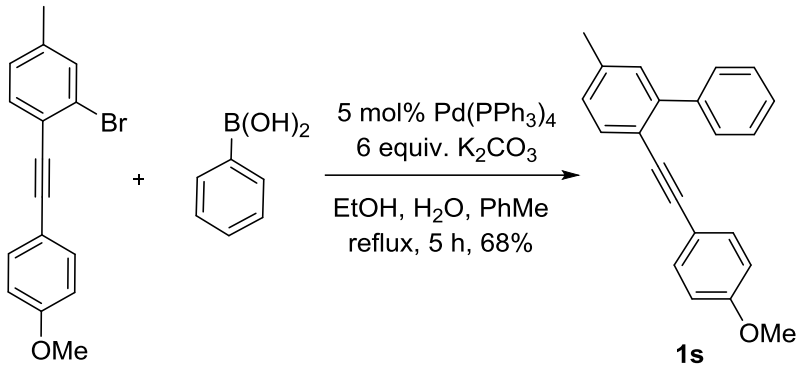
6) 4'-Acetyl-2-(phenylethynyl)-1,1'-biphenyl (1r)



1r

The reaction of 1-iodo-2-(phenylethynyl)benzene (1.532 g, 5.0 mmol), (4-acetylphenyl)boronic acid (823 mg, 5.0 mmol), $Pd(PPh_3)_4$ (294 mg, 0.25 mmol), K_2CO_3 (4.209 g, 30.5 mmol), and solvent (160 mL, EtOH : H_2O : PhMe = 1 : 1 : 4.4) afforded **1r** as a liquid (1.467 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2 H), 7.77 (d, J = 8.4 Hz, 2 H), 7.67 (d, J = 7.2 Hz, 1 H), 7.49-7.20 (m, 8 H), 2.65 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 145.4, 142.5, 136.0, 133.1, 131.3, 129.6, 129.3, 128.6, 128.3, 128.0, 127.8, 123.1, 121.6, 92.6, 88.6, 26.7; IR (neat) 1684, 1604, 1571, 1508, 1490, 1470, 1440, 1425, 1403 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{16}ONa$ 319.1093, found 319.1097.

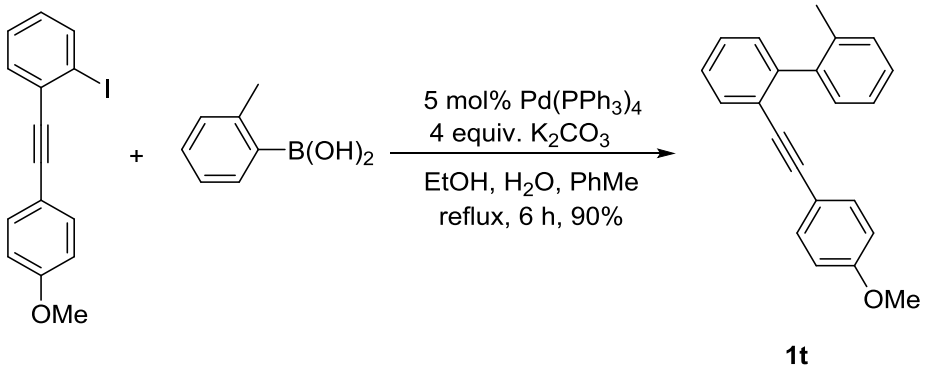
7) 2-((4-Methoxyphenyl)ethynyl)-5-methyl-1,1'-biphenyl (1s)



1s

The reaction of 2-bromo-1-((4-methoxyphenyl)ethynyl)-4-methylbenzene (3.001 g, 10.0 mmol), phenylboronic acid (2.442 g, 20.0 mmol), $Pd(PPh_3)_4$ (579 mg, 0.50 mmol), K_2CO_3 (8.391 g, 60.7 mmol), and solvent (120 mL, EtOH : H_2O : PhMe = 1 : 1 : 4) afforded **1s** as a liquid (2.011 g, 68%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.4 Hz, 2 H), 7.51 (d, J = 8.0 Hz, 1 H), 7.49-7.30 (m, 3 H), 7.29-7.15 (m, 3 H), 7.11 (d, J = 8.0 Hz, 1 H), 6.79 (d, J = 8.8 Hz, 2 H), 3.75 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 143.5, 140.7, 138.2, 132.7, 132.5, 130.2, 129.4, 127.84, 127.77, 127.3, 118.9, 115.8, 113.9, 91.5, 88.2, 55.2, 21.4; IR (neat) 1605, 1567, 1515, 1481, 1462, 1444, 1411 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{18}O$ 298.1358, found 298.1354.

8) 2-((4-Methoxyphenyl)ethynyl)-2'-methyl-1,1'-biphenyl (1t)

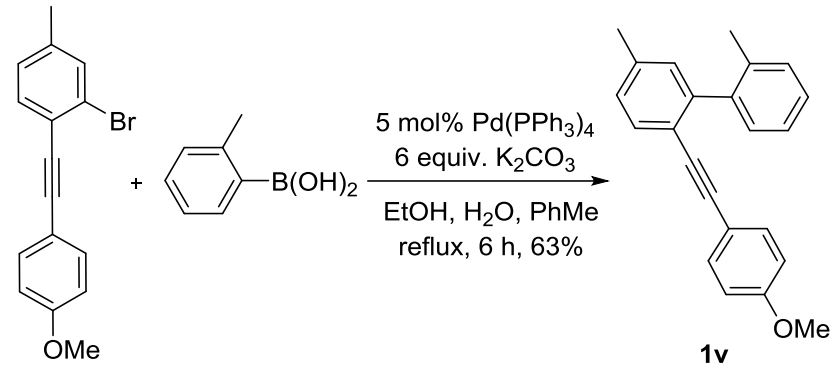


1t

The reaction of 1-iodo-2-((4-methoxyphenyl)ethynyl)benzene (1.000 g, 3.0 mmol), *o*-tolylboronic acid (411 mg, 3.0 mmol), $Pd(PPh_3)_4$ (175 mg, 0.15 mmol), K_2CO_3 (1.670 g, 12.0 mmol), and solvent (30 mL, EtOH : H_2O : PhMe = 1 : 1 : 4) afforded **1t** as a solid (801 mg, 90%); mp 60.3 ^{o}C (ethyl acetate/petroleum ether). ^{1}H NMR δ 7.58

(d, *J* = 7.2 Hz, 1 H), 7.37-7.24 (m, 7 H), 7.06 (d, *J* = 7.6 Hz, 2 H), 6.75 (d, *J* = 7.6 Hz, 2 H), 3.76 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 144.6, 141.1. 136.5, 132.9, 131.5, 130.0, 129.8, 129.6, 127.8, 127.6, 127.1, 125.4, 123.4, 115.7, 114.0, 92.5, 87.8, 55.4, 20.1; IR (neat) 1602, 1591, 1568, 1510, 1463, 1440 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{19}O$ 299.1430, found 299.1429.

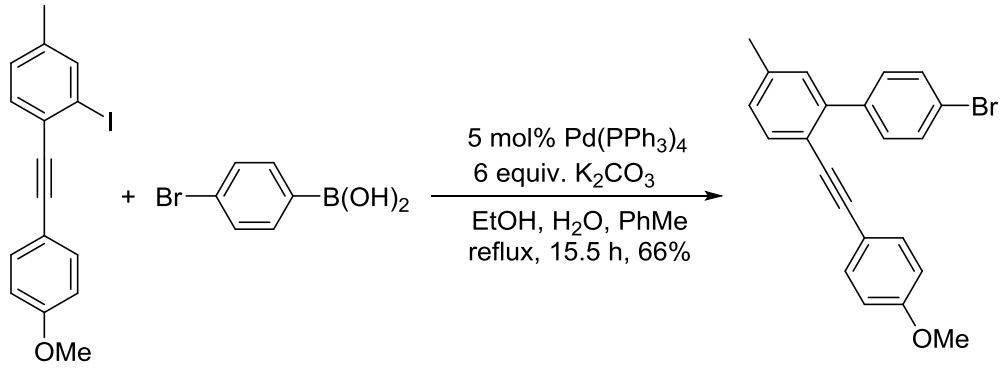
9) 2-((4-Methoxyphenyl)ethynyl)-2',5-dimethyl-1,1'-biphenyl (1v)



1v

The reaction of 2-bromo-1-((4-methoxyphenyl)ethynyl)-4-methylbenzene (3.000 g, 10.0 mmol), *o*-tolylboronic acid (2.700 g, 19.9 mmol), $Pd(PPh_3)_4$ (582 mg, 0.50 mmol), K_2CO_3 (8.292 g, 60.0 mmol), and solvent (120 mL, EtOH : H_2O : PhMe = 1 : 1 : 4) afforded **1v** as a liquid (1.714 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 1 H), 7.32-7.19 (m, 4 H), 7.17-7.00 (m, 4 H), 6.74 (d, *J* = 8.8 Hz, 2 H), 3.75 (s, 3 H), 2.39 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 144.4, 141.0, 137.8, 136.3, 132.7, 131.2, 130.2, 129.8, 129.6, 127.8, 127.3, 125.2, 120.2, 115.7, 113.8, 91.5, 87.7, 55.2, 21.5, 20.0; IR (neat) 1605, 1567, 1514, 1454, 1440 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{20}O$ 312.1514, found 312.1517.

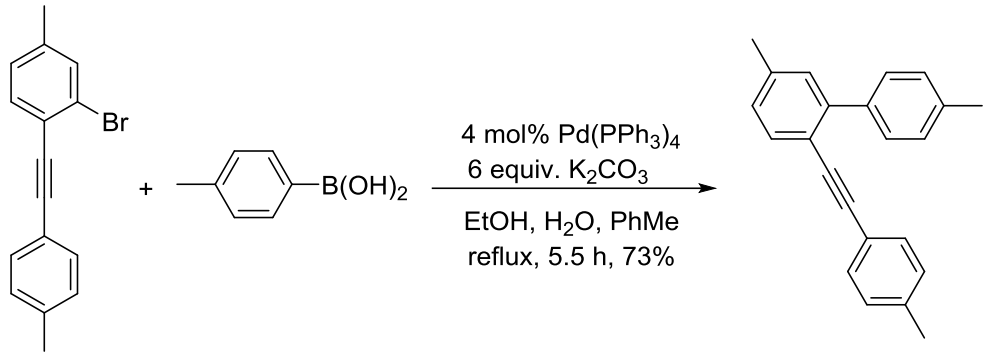
10) 4'-Bromo-2-((4-methoxyphenyl)ethynyl)-5-methyl-1,1'-biphenyl (1w)



1w

The reaction of 2-iodo-1-((4-methoxyphenyl)ethynyl)-4-methylbenzene (3.000 g, 10.0 mmol), (4-bromophenyl)boronic acid (2.400 g, 12.0 mmol), $Pd(PPh_3)_4$ (579 mg, 0.50 mmol), K_2CO_3 (8.293 g, 60.0 mmol), and solvent (120 mL, EtOH : H_2O : PhMe = 1 : 1 : 4) afforded **1w** as a liquid (2.477 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.42 (m, 5 H), 7.31-7.10 (m, 4 H), 6.82 (dd, J = 6.8, 2.0 Hz, 2 H), 3.78 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 142.0, 139.7, 138.4, 132.7, 131.0, 130.9, 130.0, 128.2, 121.5, 118.8, 115.5, 114.0, 91.9, 87.7, 55.2, 21.4; IR (neat) 1602, 1563, 1510, 1496, 1482, 1459, 1437, 1411 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{17}BrO$ 376.0463, found 376.0459.

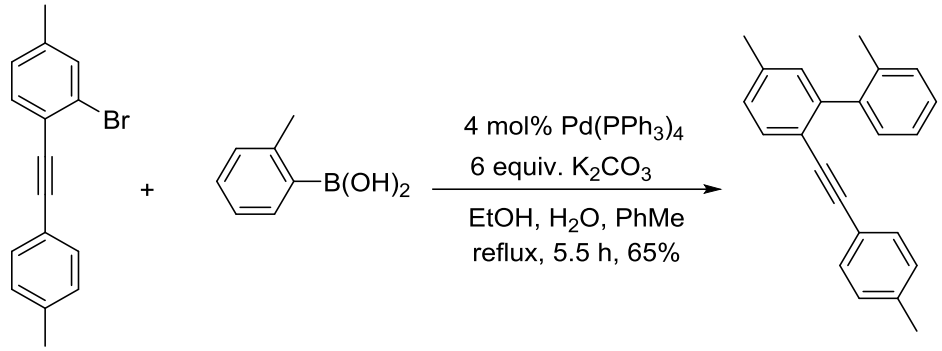
11) 4',5-Dimethyl-2-(*p*-tolylethynyl)-1,1'-biphenyl (1x)



1x

The reaction of 2-bromo-4-methyl-1-(*p*-tolylethynyl)benzene (4.277 g, 15.0 mmol), *p*-tolylboronic acid (2.050 g, 15.1 mmol), $Pd(PPh_3)_4$ (690 mg, 0.60 mmol), K_2CO_3 (12.500 g, 90.4 mmol), and solvent (230 mL, EtOH : H_2O : PhMe = 1 : 1 : 4) afforded **1x** as a solid (3.267 g, 73%); mp 67.9-68.1 ^{o}C (dichloromethane/petroleum ether). ^{1}H NMR δ 7.57 (d, J = 8.0 Hz, 2 H), 7.51 (d, J = 8.0 Hz, 1 H), 7.31-7.20 (m, 5 H), 7.13-7.05 (m, 3 H), 2.41 (s, 3 H), 2.39 (s, 3 H), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.5, 138.1, 137.9, 137.1, 132.9, 131.3, 130.4, 129.3, 129.1, 128.7, 127.8, 120.8, 118.8, 91.7, 89.2, 21.65, 21.62, 21.4; IR (neat) 1604, 1510, 1491, 1449 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{20}$ 296.1565, found 296.1563.

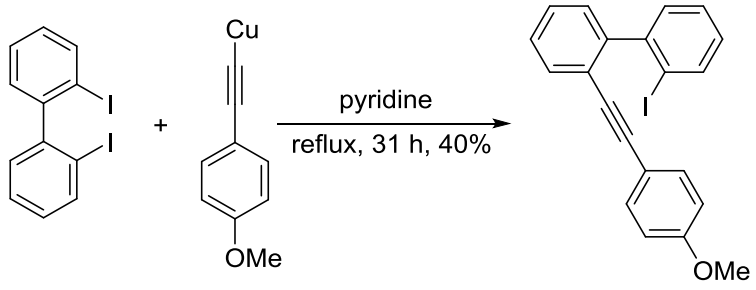
12) 2',5-Dimethyl-2-(*p*-tolylethynyl)-1,1'-biphenyl (1y)



1y

The reaction of 2-bromo-4-methyl-1-(*p*-tolylethynyl)benzene (4.200 g, 14.7 mmol), *o*-tolylboronic acid (2.040 g, 15.0 mmol), $Pd(PPh_3)_4$ (700 mg, 0.61 mmol), K_2CO_3 (12.322 g, 89.2 mmol), and solvent (230 mL, EtOH : H_2O : PhMe = 1 : 1 : 4) afforded **1y** as a solid (2.922 g, 65%); mp 67.8-68.6 ^oC (dichloromethane/petroleum ether). ^1H NMR δ 7.48 (d, J = 8.0 Hz, 1 H), 7.31-7.20 (m, 4 H), 7.14 (d, J = 8.4 Hz, 1 H), 7.09 (s, 1 H), 7.02 (s, 4 H), 2.39 (s,3 H), 2.29 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 141.1, 138.1, 138.0, 136.5, 131.6, 131.3, 130.4, 129.9, 129.7, 129.0, 127.9, 127.5, 125.3, 120.6, 120.2, 91.9, 88.6, 21.65, 21.59, 20.2; IR (neat) 1653, 1635, 1601, 1513, 1476, 1446 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{20}$ 296.1565, found 296.1568.

Synthesis of 2-iodo-2'-((4-methoxyphenyl)ethynyl)-1,1'-biphenyl (1u)



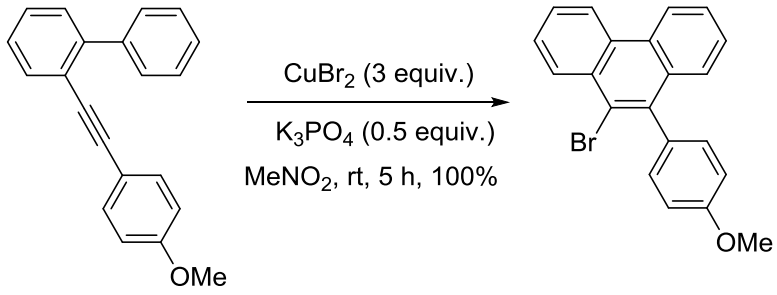
1u

To a 250 mL three necked flask was added 2,2'-diiodo-1,1'-biphenyl (4.150 g, 10.2 mmol), copper(I) (4-methoxyphenyl)ethyn-1-ide (2.000 g, 10.0 mmol), and pyridine (100 mL). After degassing 30 min with argon, the mixture was refluxed for 31 h under argon atmosphere. The solvent was removed under reduced pressure. Purification by silica gel chromatography (eluent: petroleum ether : ethyl acetate = 80:1) afforded **1u** as a solid (1.200 g, 40%); mp 99.6 ^oC (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 1 H), 7.61-7.55 (m, 1 H), 7.43-7.30 (m, 4 H),

7.27-7.21 (m, 1 H), 7.13-7.00 (m, 3 H), 6.74 (d, J = 8.8 Hz, 2 H), 3.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 146.5, 145.8, 138.7, 132.7, 131.3, 130.3, 129.3, 128.9, 127.7, 127.61, 127.56, 123.0, 115.3, 113.8, 99.5, 93.1, 87.1, 55.2; IR (neat) 1952, 1924, 1583, 1558, 1491, 1458, 1443, 1427 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{16}IO$ 411.0246, found 411.0241.

Typical Procedure III for reactions under Condition A.

Synthesis of 9-bromo-10-(4-methoxyphenyl)phenanthrene (2a)

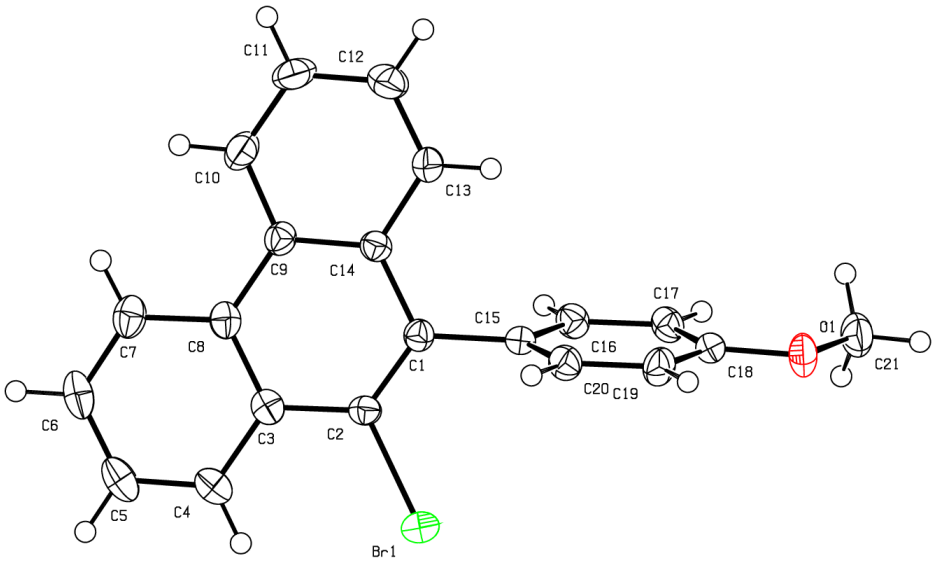


1a **2a**

1a (57 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) were added subsequently to a 25 mL of dry glass reaction tube which was equipped with a magnetic stirrer. The mixture was stirred at rt. The reaction was completed after 5 h as monitored by TLC (eluent: petroleum ether : ethyl acetate = 80:1). The resulting reaction mixture was filtered. Then, the solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether : ethyl acetate = 100:1) to afford **2a** as a solid (72 mg, 100%); mp 155.6-156.8 ^{o}C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72-8.66 (m, 2 H), 8.54-8.48 (m, 1 H), 7.71-7.57 (m, 3 H), 7.49-7.40 (m, 2 H), 7.27-7.20 (m, 2 H), 7.09-7.04 (m, 2 H), 3.90 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 139.5, 133.4, 133.1, 131.3, 131.0, 130.6, 129.8, 129.1, 128.1, 127.8, 127.5, 127.1, 126.9, 124.3, 122.75, 122.73, 113.9, 55.4; IR (neat) 1613, 1525, 1510, 1485, 1461, 1439, 1415 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{15}BrO$ 362.0306, found 362.0301.

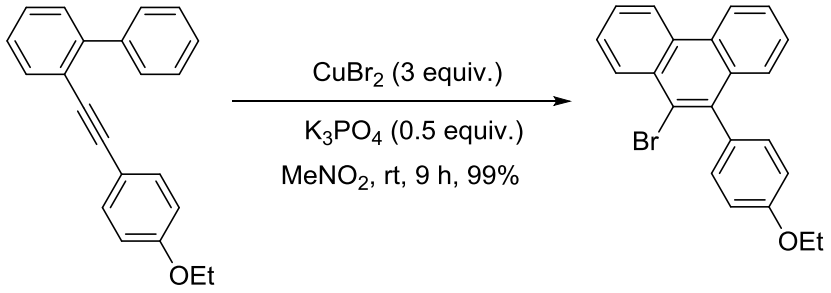
Crystal data for **2a**: $C_{21}H_{15}BrO$, MW = 363.24, Triclinic, space group P -1, mo_50201d_0m, final R indices [I>2sigma(I)], R1 = 0.0340, wR2 = 0.0695, a = 9.2828(11) Å, b = 9.4782(12) Å, c = 10.3493(12) Å, α = 113.833(2) ^{o}, β = 108.559(2)

°, γ = 91.384(2) °, V = 777.26(16) Å^3, T = 296(2) K, Z = 2, reflections collected / unique: 5582 / 3665 [R(int) = 0.0576], parameters 209. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. CCDC: 1438272.



The following compounds were prepared according to Typical Procedure III.

1) 9-Bromo-10-(4-ethoxyphenyl)phenanthrene (2b)

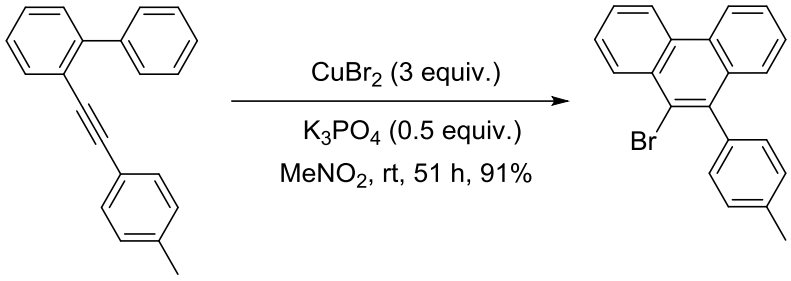


1b **2b**

The reaction of **1b** (60 mg, 0.20 mmol), $CuBr_2$ (135 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2b** as a solid (76 mg, 99%); mp 133.4-133.7 °C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74-8.67 (m, 2 H), 8.57-8.50 (m, 1 H), 7.73-7.61 (m, 3 H), 7.49-7.42 (m, 2 H), 7.26-7.21 (m, 2 H), 7.09-7.02 (m, 2 H), 4.14 (q, J = 7.2 Hz, 2 H), 1.48 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 139.6, 133.3, 133.1, 131.3, 131.1, 130.7,

129.8, 129.1, 128.2, 127.8, 127.5, 127.1, 126.9, 124.3, 122.8, 114.4, 63.6, 15.1; IR (neat) 1607, 1568, 1524, 1507, 1481, 1447, 1418 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{17}BrO$ 376.0463, found 376.0469.

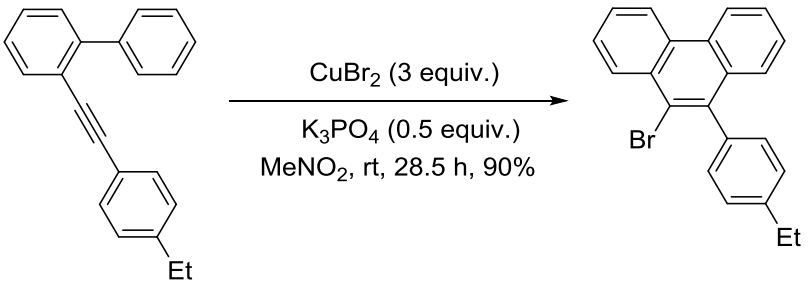
2) 9-Bromo-10-(4-methylphenyl)phenanthrene (2c)



1c **2c**

The reaction of **1c** (54 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (20 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2c** as a solid (63 mg, 91%); mp 151.7-152.6 ºC (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72-8.65 (m, 2 H), 8.55-8.48 (m, 1 H), 7.72-7.65 (m, 2 H), 7.64-7.57 (m, 1 H), 7.45-7.40 (m, 2 H), 7.34 (d, J = 7.6 Hz, 2 H), 7.25-7.18 (m, 2 H), 2.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 138.2, 137.5, 132.9, 131.1, 130.7, 130.0, 129.8, 129.3, 129.1, 128.1, 127.8, 127.5, 127.1, 126.9, 123.8, 122.8, 21.6; IR (neat) 1566, 1506, 1481, 1444, 1419, 1401, 1377 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{15}Br$ 346.0357, found 346.0360.

3) 9-Bromo-10-(4-ethylphenyl)phenanthrene (2d)

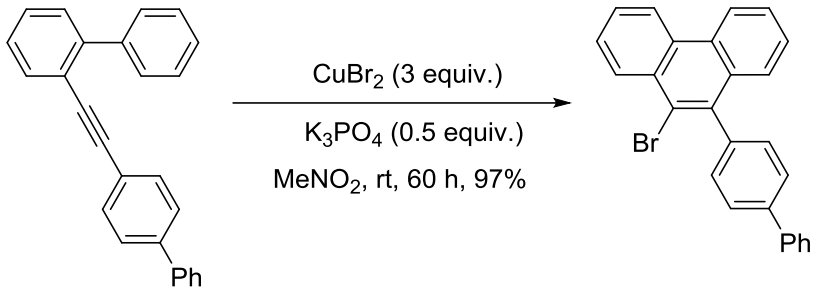


1d **2d**

The reaction of **1d** (56 mg, 0.20 mmol), $CuBr_2$ (133 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2d** as a solid (65 mg, 90%); mp 134.2-134.6 ºC (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76-8.68 (m, 2 H), 8.56-8.49 (m, 1 H), 7.74-7.58 (m, 3 H), 7.47-7.35 (m, 4 H), 7.25

(d, J = 8.0 Hz, 2 H), 2.80 (q, J = 7.6 Hz, 2 H), 1.36 (t, J = 7.6, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 139.9, 138.4, 133.0, 131.1, 130.7, 130.0, 129.8, 129.1, 128.2, 128.0, 127.8, 127.5, 127.1, 126.9, 123.8, 122.8, 28.9, 15.5; IR (neat) 1566, 1559, 1505, 1483, 1458, 1444, 1419 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{17}Br$ 360.0514, found 360.0518.

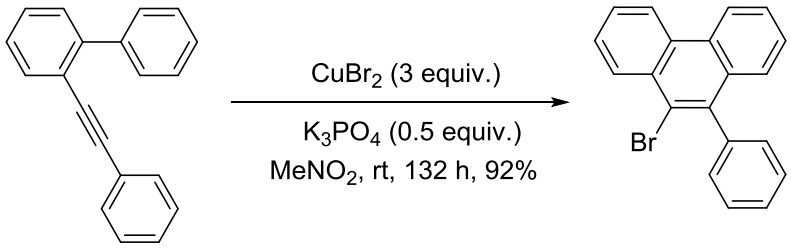
4) 9-Bromo-10-(4-phenylphenyl)phenanthrene (2e)



1e **2e**

The reaction of **1e** (66 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2e** as a solid (79 mg, 97%); mp 209.5-210.3 ^{o}C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75-8.67 (m, 2 H), 8.57-8.50 (m, 1 H), 7.81-7.62 (m, 7 H), 7.51-7.35 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.6, 140.1, 139.5, 132.7, 131.1, 130.6, 129.8, 129.1, 129.0, 128.1, 127.9, 127.60, 127.57, 127.3, 127.2, 127.0, 123.77, 122.81, 122.78; IR (neat) 1600, 1580, 1564, 1483, 1444, 1417, 1399 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{17}Br$ 408.0514, found 408.0512.

5) 9-Bromo-10-phenylphenanthrene (2f)[8]

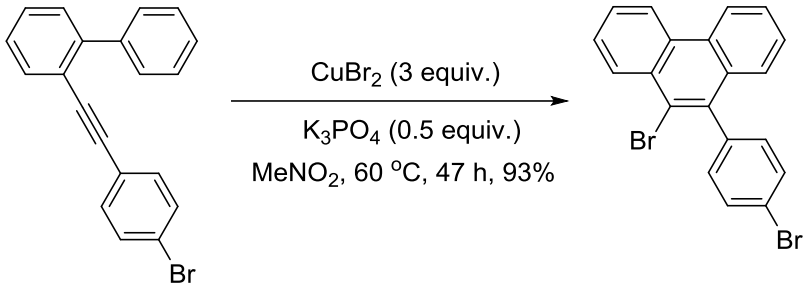


1f **2f**

The reaction of **1f** (51 mg, 0.20 mmol), $CuBr_2$ (133 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2f** as a solid (61 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75-8.66 (m, 2 H), 8.55-8.49 (m, 1 H), 7.74-7.30 (m,

10 H).

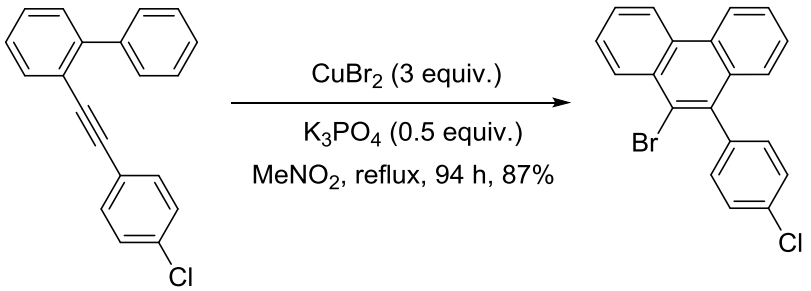
6) 9-Bromo-10-(4-bromophenyl)phenanthrene (2g)



1g **2g**

The reaction of **1g** (67 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2g** as a solid (77 mg, 93%); mp 207.3-207.9 °C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78-8.70 (m, 2 H), 8.55-8.49 (m, 1 H), 7.80-7.63 (m, 5 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 7.39 (d, *J* = 8.2 Hz, 1 H), 7.23 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.8, 138.4, 132.2, 131.8, 131.7, 131.0, 130.3, 129.7, 129.0, 127.8, 127.7, 127.6, 127.2, 127.0, 123.6, 122.8, 122.7, 121.9; IR (neat) 1595, 1567, 1558, 1485, 1443, 1415 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{12}Br_2$ 409.9306, found 409.9307.

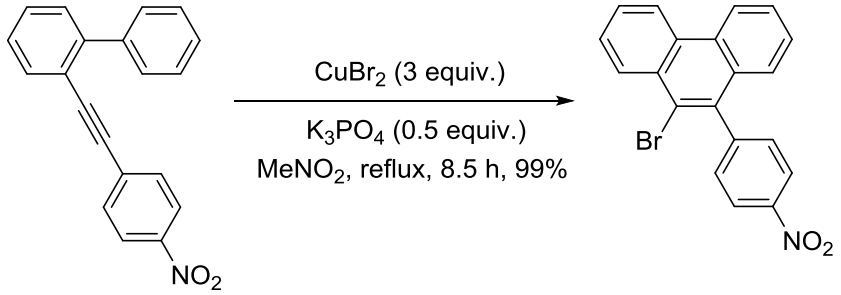
7) 9-Bromo-10-(4-chlorophenyl)phenanthrene (2h)



1h **2h**

The reaction of **1h** (58 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2h** as a solid (64 mg, 87%); mp 207.1-207.2 °C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.76-8.70 (m, 2 H), 8.55-8.48 (m, 1 H), 7.77-7.62 (m, 3 H), 7.55-7.22 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.5, 138.6, 133.9, 132.5, 131.6, 131.2, 130.5, 129.9, 129.1, 128.9, 128.0, 127.80, 127.77, 127.3, 127.2, 123.9, 122.9, 122.8; IR (neat) 1558, 1481, 1442, 1418 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{12}BrCl$ 365.9811, found 365.9819.

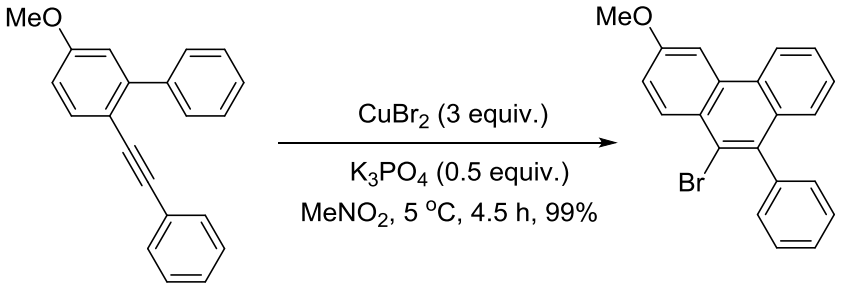
8) 9-Bromo-10-(4-nitrophenyl)phenanthrene (2i)



1i **2i**

The reaction of **1i** (60 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2i** as a solid (75 mg, 99%); mp 192.6-193.0 ºC (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 7.6 Hz, 2 H), 8.55-8.48 (m, 1 H), 8.45-8.39 (m, 2 H), 7.82-7.65 (m, 3 H), 7.57-7.43 (m, 3 H), 7.25 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 147.7, 137.5, 131.8, 131.5, 131.3, 130.2, 129.9, 129.1, 128.2, 127.6, 127.5, 127.2, 124.7, 124.0, 123.4, 123.1, 122.9; IR (neat) 1597, 1515, 1485, 1445 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{12}BrNO_2$ 377.0051, found 377.0058.

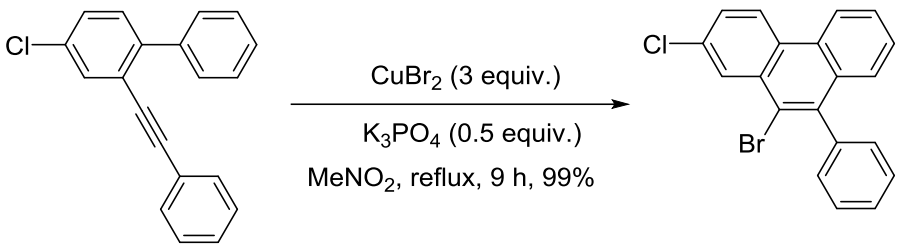
9) 10-Bromo-3-methoxy-9-phenylphenanthrene (2j)



1j **2j**

The reaction of **1j** (57 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2j** as a solid (72 mg, 99%); mp 157.3-157.9 ºC (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 2 H), 7.51-7.20 (m, 8 H), 7.11-6.91 (m, 2 H), 3.88 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 142.7, 140.7, 140.6, 131.9, 131.1, 129.1, 128.9, 128.8, 128.4, 128.1, 127.8, 119.9, 118.8, 115.5, 113.4, 55.6; IR (neat) 1599, 1562, 1490, 1477, 1457, 1443 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{16}BrO$ 363.0379, found 363.0373.

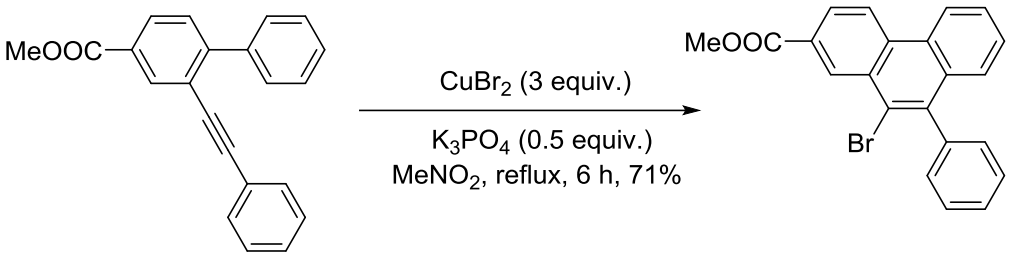
10) 10-Bromo-2-chloro-9-phenylphenanthrene (2k)



1k **2k**

The reaction of **1k** (58 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2k** as a solid (73 mg, 99%); mp 121.4-121.7 ºC (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 8.8 Hz, 2 H), 8.52 (d, J = 2.0 Hz, 1 H), 7.69-7.28 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 140.8, 134.0, 132.6, 131.8, 130.0, 129.43, 129.40, 128.6, 128.4, 128.2, 128.0, 127.5, 127.4, 124.5, 122.7, 122.2; IR (neat) 1603, 1576, 1494, 1478, 1445 1421 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{12}BrCl$ 365.9811, found 365.9812.

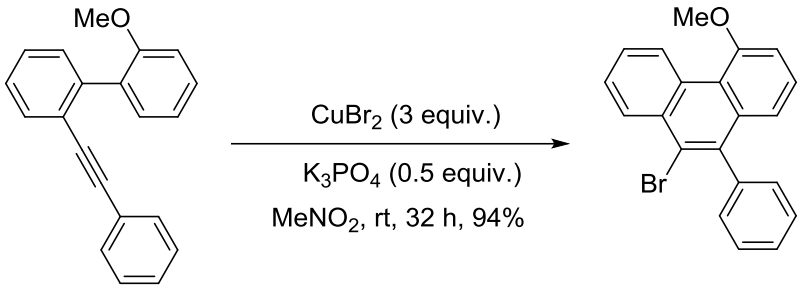
11) 10-Bromo-2-(methoxycarbonyl)-9-phenylphenanthrene (2l)



1l **2l**

The reaction of **1l** (62 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2l** as a solid (55 mg, 71%); mp 198.2-200.3 ºC (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1 H), 8.77-8.68 (m, 2 H), 8.30 (dd, J = 8.8, 1.6 Hz, 1 H), 7.71-7.30 (m, 8 H), 4.02 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 167.0, 140.8, 134.1, 133.6, 131.4, 130.3, 130.0, 129.23, 129.20, 128.7, 128.3, 128.2, 128.0, 127.5, 127.3, 123.8, 123.4, 123.2, 52.5; IR (neat) 1708, 1560, 1497, 1429 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{15}BrO_2$ 390.0255, found 390.0246.

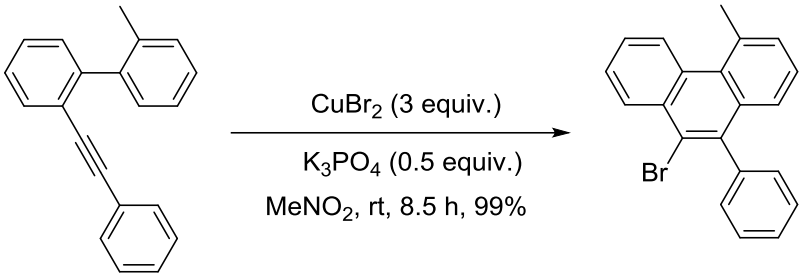
12) 9-Bromo-4-methoxy-10-phenylphenanthrene (2m)



1m **2m**

The reaction of **1m** (57 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2m** as a solid (68 mg, 94%); mp 163.5-164.6 ºC (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80-9.72 (m, 1 H), 8.62-8.55 (m, 1 H), 7.74-7.65 (m, 2 H), 7.55-7.46 (m, 3 H), 7.41-7.28 (m, 3 H), 7.17 (dd, J = 8.0, 0.8 Hz, 1 H), 7.05 (dd, J = 8.4, 1.2 Hz, 1 H), 4.14 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 142.1, 139.7, 135.0, 131.2, 130.8, 130.1, 128.7, 128.6, 128.5, 127.7, 127.3, 127.2, 126.8, 125.0, 121.1, 109.1, 56.1; IR (neat) 1603, 1566, 1523, 1491, 1483, 1448, 1430 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{15}BrO$ 362.0306, found 362.0310.

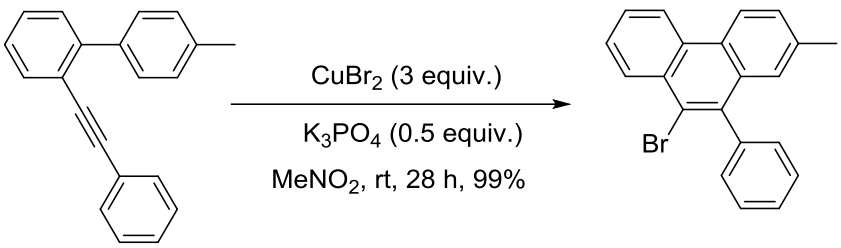
13) 9-Bromo-4-methyl-10-phenylphenanthrene (2n)



1n **2n**

The reaction of **1n** (54 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2n** as a liquid (69 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88-8.81 (m, 1 H), 8.63-8.56 (m, 1 H), 7.75-7.63 (m, 2 H), 7.59-7.44 (m, 4 H), 7.37-7.26 (m, 4 H), 3.16 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 135.2, 132.3, 131.7, 131.5, 130.15, 130.13, 128.8, 128.6, 127.74, 127.71, 127.2, 126.7, 126.23, 126.18, 123.8, 27.5; IR (neat) 1586, 1570, 1493, 1483, 1446 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{15}Br$ 346.0357, found 346.0356.

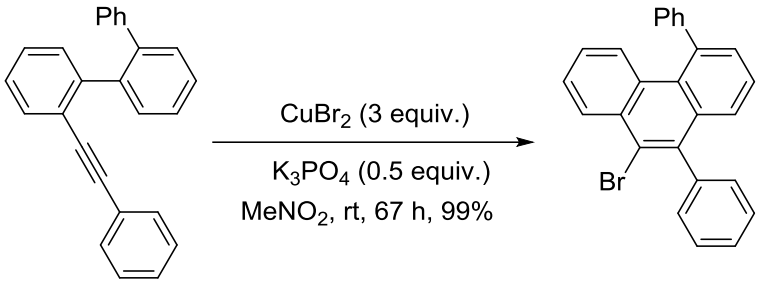
14) 9-Bromo-2-methyl-10-phenylphenanthrene (2o)



1o **2o**

The reaction of **1o** (54 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2o** as a solid (70 mg, 99%); mp 90.9-91.5 ºC (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69-8.62 (m, 1 H), 8.57 (d, J = 8.4 Hz, 1 H), 8.52-8.46 (m, 1 H), 7.72-7.27 (m, 8 H), 7.16 (s, 1 H), 2.37 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 137.1, 132.8, 131.1, 130.2, 129.0, 128.7, 128.6, 128.5, 127.8, 127.7, 127.53, 127.49, 127.4, 126.7, 123.8, 122.7, 122.6, 21.8; IR (neat) 1615, 1578, 1564, 1495, 1477, 1442, 1426 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{15}Br$ 346.0357, found 346.0360.

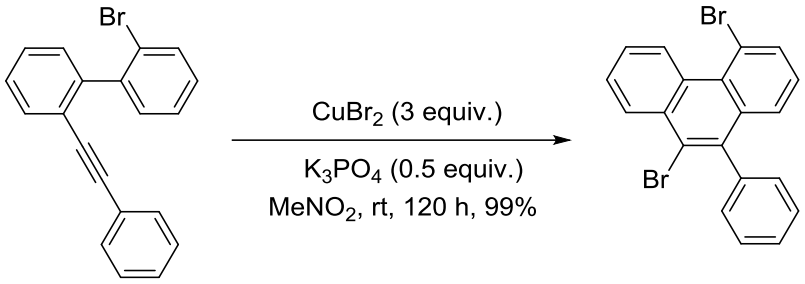
15) 9-Bromo-4-phenyl-10-phenylphenanthrene (2p)



1p **2p**

The reaction of **1p** (66 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2p** as a solid (81 mg, 99%); mp 192.3-192.7 ºC (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, J = 8.4, 1.2 Hz, 1 H), 7.81 (dd, J = 8.8, 0.8 Hz, 1 H), 7.59-7.32 (m, 14 H), 7.16-7.08 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 141.6, 140.4, 139.8, 134.2, 131.5, 131.3, 131.1, 130.2, 129.3, 129.1, 128.9, 128.6, 128.5, 128.4, 127.8, 127.7, 127.3, 126.1, 125.5, 124.3; IR (neat) 1600, 1581, 1564, 1490, 1475, 1442 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{17}Br$ 408.0514, found 408.0509.

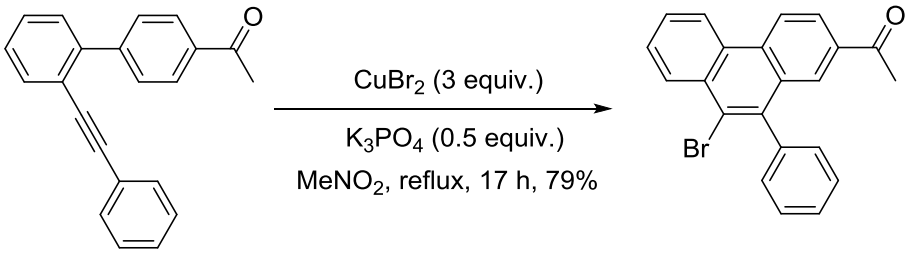
16) 4,9-Dibromo-10-phenylphenanthrene (2q)



1q **2q**

The reaction of **1q** (67 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2q** as a liquid (82 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92-9.84 (m, 1 H), 8.60-8.52 (m, 1 H), 7.97 (dd, J = 7.6, 1.2 Hz, 1 H), 7.79-7.66 (m, 2 H), 7.59-7.46 (m, 3 H), 7.43-7.16 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 139.5, 135.5, 134.9, 131.5, 130.4, 130.1, 128.7, 128.6, 128.4, 128.0, 127.2, 126.9, 126.0, 125.1, 119.4; IR (neat) 1603, 1585, 1553, 1494, 1476, 1445, 1425, 1378 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{12}Br_2$ 409.9306, found 409.9309.

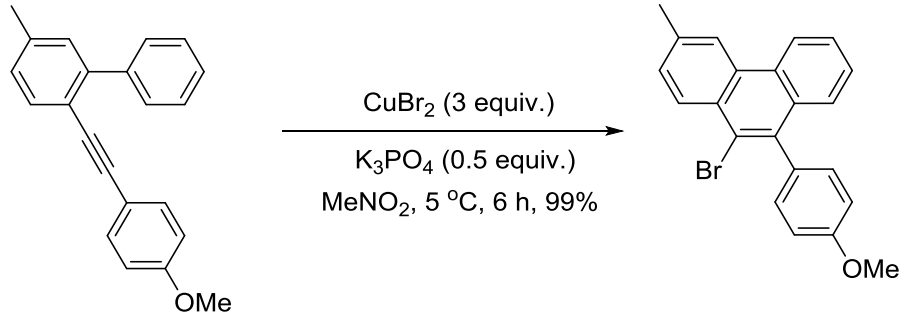
17) 4-Acetyl-9-bromo-10-phenylphenanthrene (2r)



1r **2r**

The reaction of **1r** (59 mg, 0.20 mmol), $CuBr_2$ (133 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2r** as a solid (59 mg, 79%); mp 146.3-146.8 ^{o}C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83-8.71 (m, 2 H), 8.60-8.53 (m, 1 H), 8.21 (dd, J = 8.4, 1.8 Hz, 1 H), 8.09-8.03 (m, 1 H), 7.83-7.73 (m, 2 H), 7.62-7.50 (m, 3 H), 7.39-7.31 (m, 2 H), 4.31 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 140.1, 133.4, 132.3, 132.2, 131.8, 130.3, 130.15, 130.07, 129.4, 128.8, 128.5, 128.4, 128.2, 125.8, 125.0, 123.7, 123.6. 30.8; IR (neat) 1680, 1601, 1568, 1524, 1491, 1473, 1440 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{15}BrO$ 374.0306, found 374.0301.

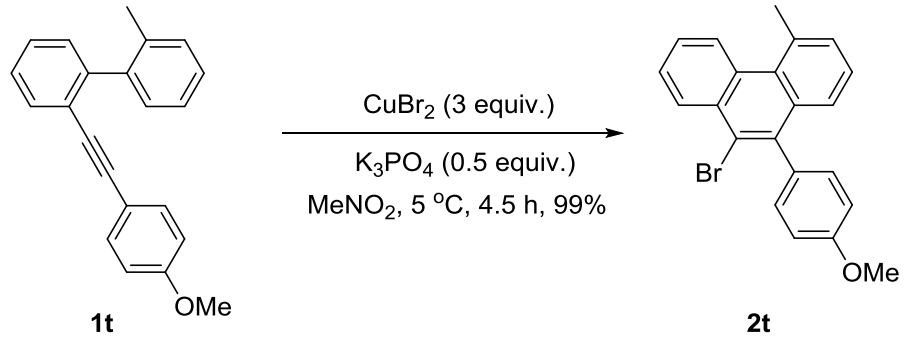
18) 10-Bromo-9-(4-methoxyphenyl)-3-methylphenanthrene (2s)



1s **2s**

The reaction of **1s** (60 mg, 0.20 mmol), $CuBr_2$ (133 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2s** as a solid (75 mg, 99%); mp 139.2-140.3 °C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 8.4 Hz, 1 H), 8.50 (s, 1 H), 8.39 (d, J = 8.4 Hz, 1 H), 7.65-7.40 (m, 4 H), 7.28-7.20 (m, 2 H), 7.11-7.02 (m, 2 H), 3.91 (s, 3 H), 2.64 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 138.5, 137.4, 133.6, 133.2, 131.4, 131.1, 129.5, 129.0, 128.7, 128.1, 127.0, 126.7, 124.2, 122.7, 122.5, 113.9, 55.4, 22.0; IR (neat) 1608, 1520, 1506, 1492, 1456, 1439, 1425 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{17}BrO$ 376.0463, found 376.0458.

19) 9-Bromo-10-(4-methoxyphenyl)-4-methylphenanthrene (2t)

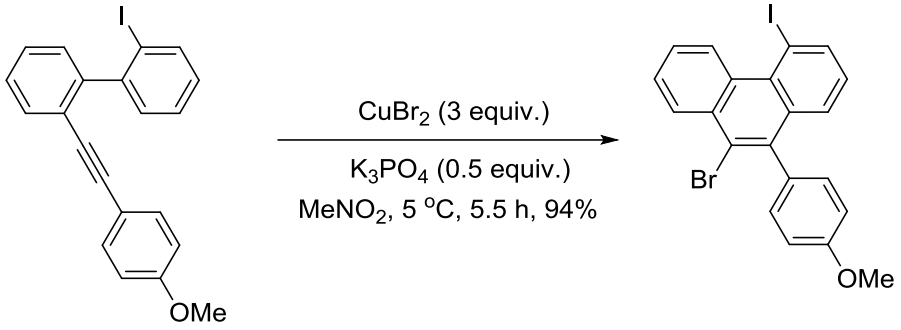


1t **2t**

The reaction of **1t** (60 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2t** as a solid (75 mg, 99%); mp 166.1-166.8 °C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85-8.77 (m, 1 H), 8.62-8.53 (m, 1 H), 7.72-7.61 (m, 2 H), 7.52-7.44 (m, 1 H), 7.39-7.26 (m, 2 H), 7.27-7.17 (m, 2 H), 7.10-7.00 (m, 2 H), 3.90 (s, 3 H), 3.12 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 140.0, 135.2, 134.6, 134.3, 132.2, 131.6, 131.5, 131.3, 130.1, 128.9, 127.7, 127.1, 126.7, 126.1, 124.4, 113.9, 55.4, 27.4; IR (neat)

1607, 1558, 1505, 1478, 1458, 1449, 1436 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{17}BrO$ 376.0463, found 376.0467.

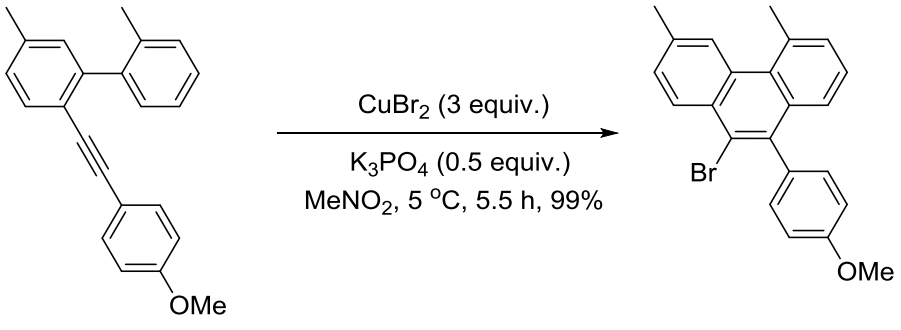
20) 9-Bromo-4-iodo-10-(4-methoxyphenyl)phenanthrene (2u)



1u **2u**

The reaction of **1u** (82 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2u** as a solid (92 mg, 94%); mp 161.3-161.4 ºC (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79-9.70 (m, 1 H), 8.50 (dd, J = 8.4, 1.6 Hz, 1 H), 8.32 (dd, J = 7.6, 1.2 Hz, 1 H), 7.74-7.66 (m, 2 H), 7.43 (dd, J = 8.0, 1.2 Hz, 1 H), 7.28-7.15 (m, 2 H), 7.13-6.97 (m, 3 H), 3.91 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 142.6, 139.1, 135.0, 133.2, 131.5, 131.3, 131.1, 130.8, 128.7, 128.6, 128.4, 127.4, 127.0, 125.3, 125.1, 114.1, 89.7, 55.4; IR (neat) 1610, 1577, 1553, 1515, 1503, 1475 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{14}BrIO$ 487.9273, found 487.9274.

21) 10-Bromo-9-(4-methoxyphenyl)-3,5-dimethylphenanthrene (2v)

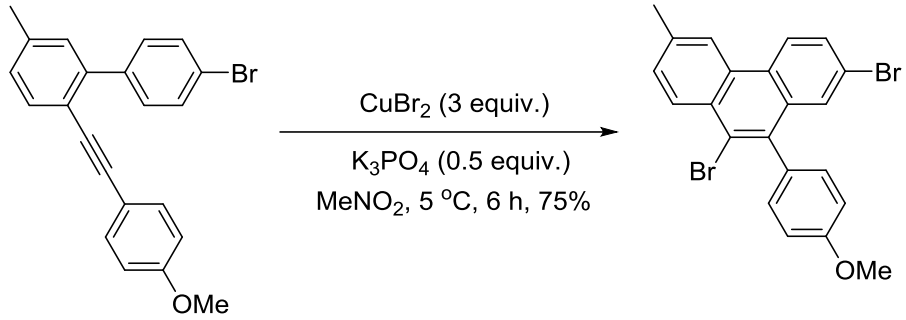


1v **2v**

The reaction of **1v** (62 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (22 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2v** as a solid (78 mg, 99%); mp 148.6-148.9 ºC (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1 H), 8.46 (d, J = 8.4 Hz, 1 H), 7.56-7.42 (m, 2 H), 7.37-7.18 (m, 4 H),

7.09-7.02 (m, 2 H), 3.91 (s, 3 H), 3.14 (s, 3 H), 2.64 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 139.0, 135.8, 135.1, 134.7, 134.3, 132.3, 131.40, 131.35, 129.9, 129.5, 128.7, 128.6, 127.7, 126.6, 126.0, 124.3, 113.9, 55.4, 27.5, 22.2; IR (neat) 1607, 1519, 1507, 1488, 1439, 1461, 1439 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{19}BrO$ 390.0619, found 390.0623.

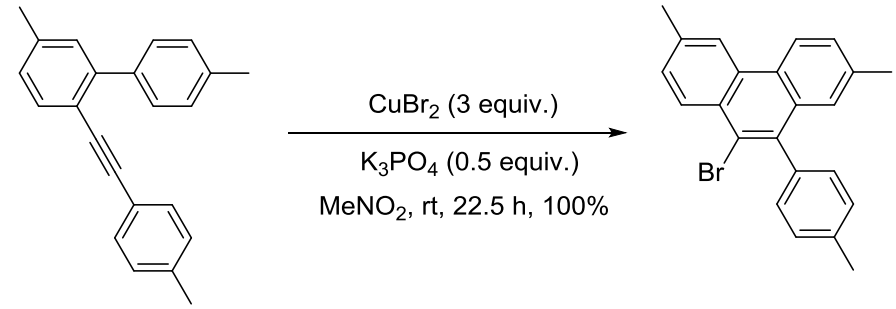
22) 2,9-Dibromo-10-(4-methoxyphenyl)-6-methylphenanthrene (2w)



1w **2w**

The reaction of **1w** (75 mg, 0.20 mmol), $CuBr_2$ (133 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2w** as a solid (68 mg, 75%); mp 168.8-169.1 °C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.8 Hz, 1 H), 8.43-8.32 (m, 2 H), 7.69-7.62 (m, 1 H), 7.58-7.48 (m, 2 H), 7.27-7.17 (m, 2 H), 7.06 (d, J = 8.4 Hz, 2 H), 3.92 (s, 3 H), 2.63 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 137.8, 137.5, 134.5, 132.7, 131.3, 130.5, 130.2, 129.9, 129.8, 129.2, 128.6, 128.2, 125.6, 124.5, 122.4, 121.3, 114.1, 55.4, 22.0; IR (neat) 1611, 1590, 1515, 1507, 1483, 1455 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{16}Br_2O$ 453.9568, found 453.9566.

23) 9-Bromo-2,6-dimethyl-10-(*p*-tolyl)phenanthrene (2x)

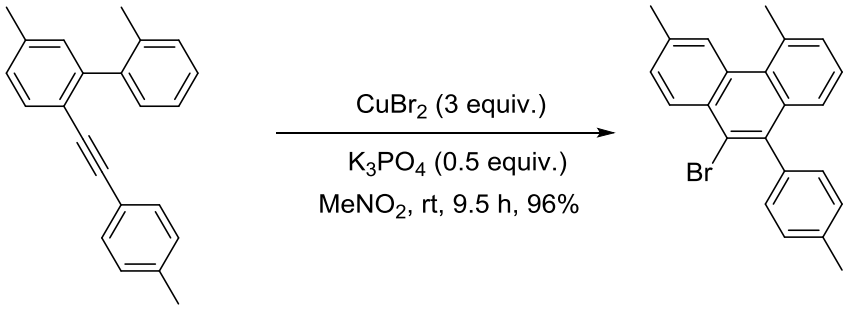


1x **2x**

The reaction of **1x** (59 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded 2**x** as a solid (75 mg,

100%); mp 149.9-150.0 °C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 8.8 Hz, 1 H), 8.43 (s, 1 H), 8.35 (d, J = 8.4 Hz, 1 H), 7.49-7.37 (m, 2 H), 7.33 (d, J = 8.0 Hz, 2 H), 7.23-7.16 (m, 3 H), 2.61 (s, 3 H), 2.48 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.3, 137.2, 136.8, 133.1, 131.1, 130.1, 129.2, 129.0, 128.9, 128.5, 128.3, 127.5, 123.8, 122.7, 122.3, 22.0, 21.8, 21.6; IR (neat) 1616, 1583, 1567, 1510, 1488, 1455 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{19}Br$ 374.0670, found 374.0665.

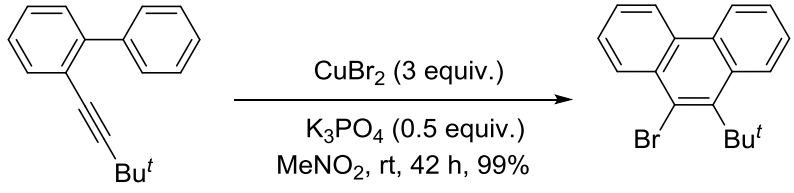
24) 10-Bromo-3,5-dimethyl-9-(*p*-tolyl)phenanthrene (2y)



1y **2y**

The reaction of **1y** (59 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **2y** as a solid (72 mg, 96%); mp 162.6-163.6 °C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1 H), 8.45 (d, J = 8.4 Hz, 1 H), 7.52-7.41 (m, 2 H), 7.36-7.24 (m, 4 H), 7.23-7.16 (m, 2 H), 3.12 (s, 3 H), 2.62 (s, 3 H), 2.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 139.0, 137.3, 135.8, 135.1, 134.5, 132.3, 131.4, 130.1, 129.9, 129.5, 129.2, 128.7, 128.6, 127.7, 126.6, 126.0, 123.9, 27.5, 22.2, 21.6; IR (neat) 1616, 1592, 1558, 1525, 1507, 1488, 1443 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{19}Br$ 374.0670, found 374.0663.

25) 9-Bromo-10-(*tert*-butyl)phenanthrene (5a)

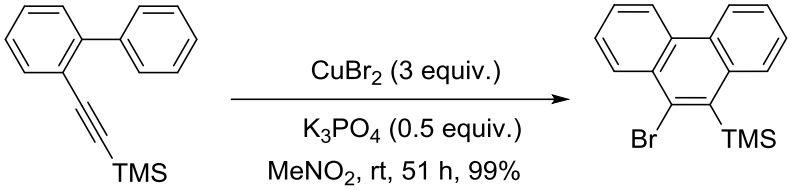


4a **5a**

The reaction of **4a** (47 mg, 0.20 mmol), $CuBr_2$ (134 mg, 0.60 mmol), K_3PO_4 (21 mg,

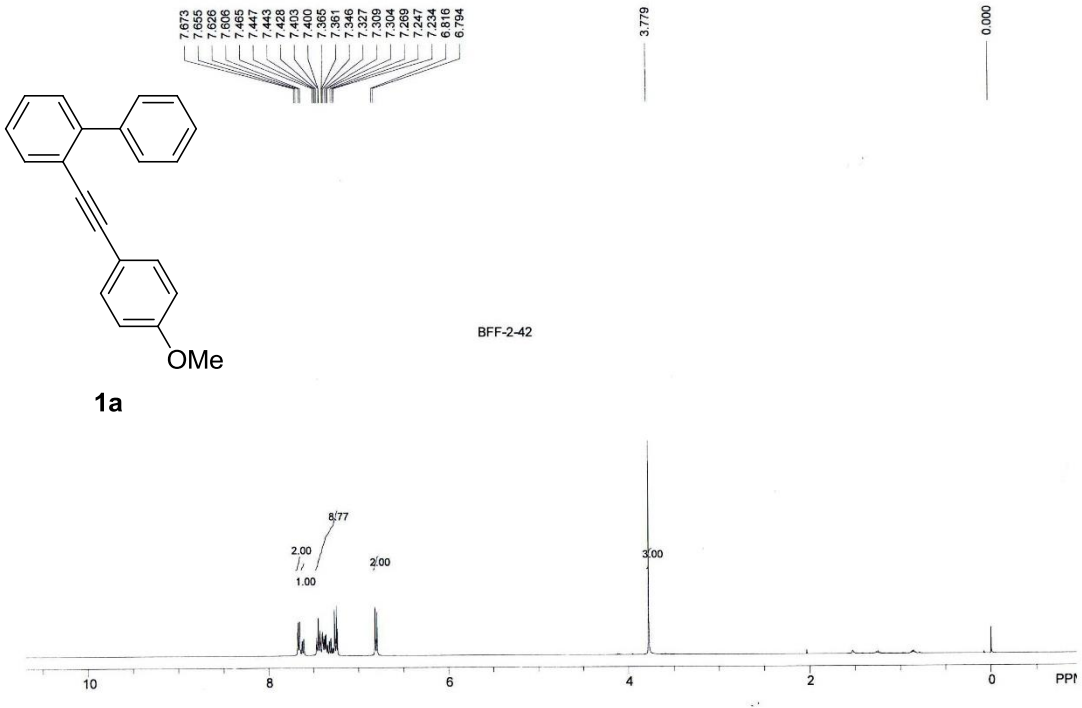
0.10 mmol), and anhydrous nitromethane (3 mL) afforded **5a** as a solid (62 mg, 99%); mp 68.3-69.3 °C (dichloromethane/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.54 (m, 2 H), 7.45-7.30 (m, 6 H), 0.83 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.6, 140.3, 140.2, 130.5, 130.2, 129.29, 129.28, 128.4, 127.6, 127.0, 122.8, 43.1, 31.0; IR (neat) 1598, 1558, 1500, 1473, 1446, 1427 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{17}Br$ 312.0514, found 312.0517.

26) 9-Bromo-10-trimethylsilylphenanthrene (5b)



4b **5b**

The reaction of **4b** (50 mg, 0.20 mmol), $CuBr_2$ (133 mg, 0.60 mmol), K_3PO_4 (21 mg, 0.10 mmol), and anhydrous nitromethane (3 mL) afforded **5b** as a liquid (65 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.48 (m, 2 H), 7.47-7.32 (m, 6 H), -0.18 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.8, 142.1, 135.4, 135.3, 132.9, 132.8, 132.1, 131.5, 130.6, 129.8, 129.4, -3.9; IR (neat) 1585, 1561, 1469, 1445, 1428, 1403 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{17}BrSi$ 328.0283, found 328.0290.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7.428
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7.400
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7.346
7.327
7.309
7.304
7.269
7.247
7.234
6.816
6.794
3.779
0.000
OMe
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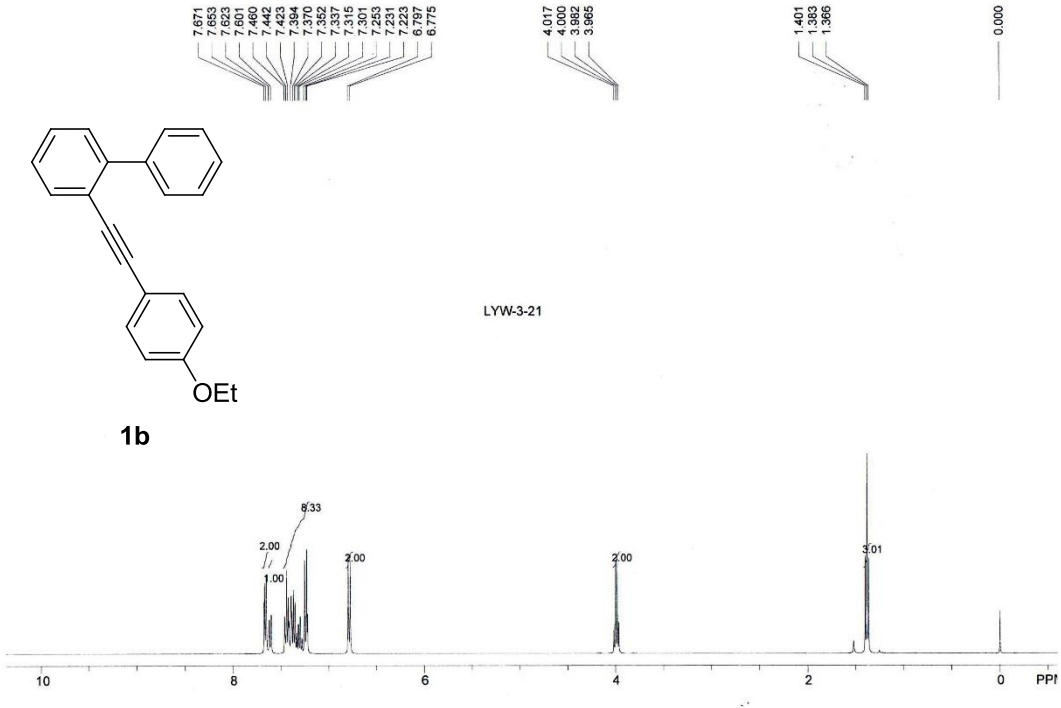
1.00
2.00
3.00
10
8
6
4
2
0
PPM

1a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7.253
7.231
7.223
6.797
6.775
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4.000
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3.965
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1.383
1.366
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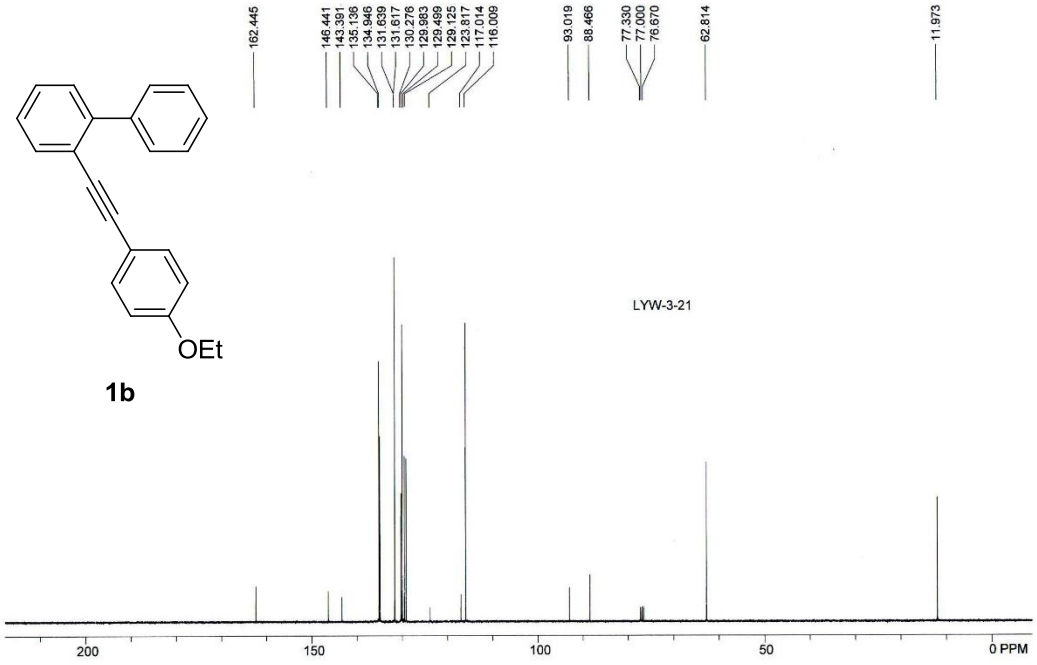
2.00
2.00
3.01
10
8
6
4
2
0
PPM

1b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130.276
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116.009
93.019
88.466
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50
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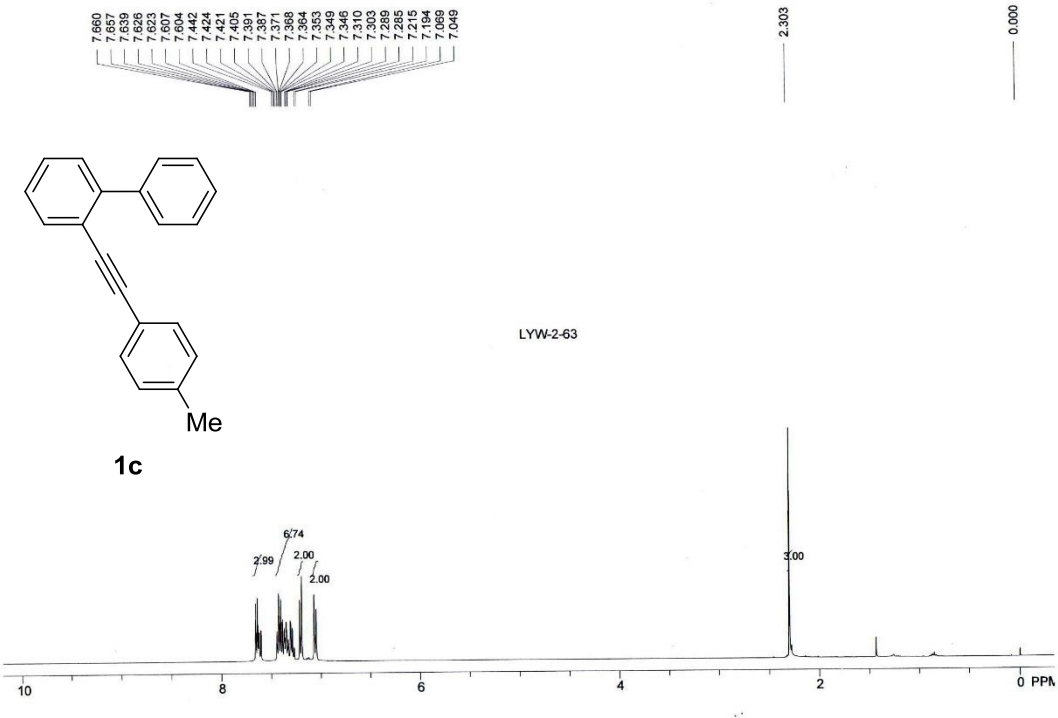
1b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7.371
7.368
7.364
7.353
7.349
7.346
7.310
7.303
7.289
7.285
7.215
7.194
7.069
7.049
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0.000
Me
LYW-2-63
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2.00
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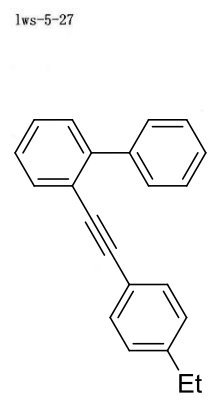
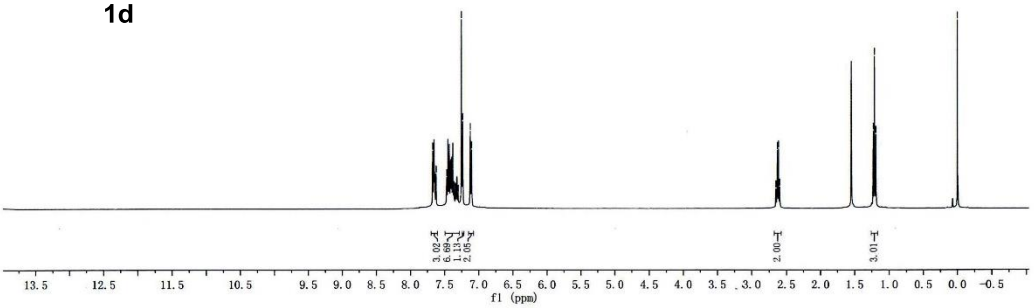
3.00
10
8
6
4
2
0 PPM

1c

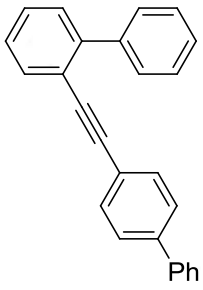
lws-5-27



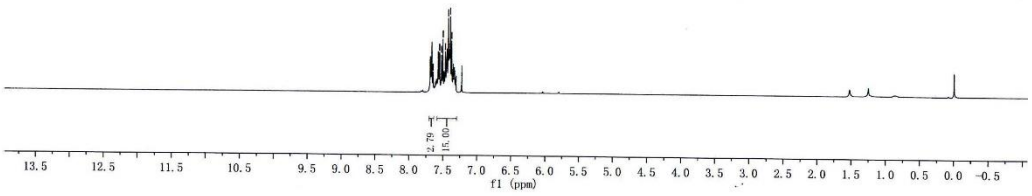
1d



lws-5-26



1e



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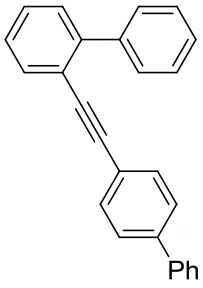

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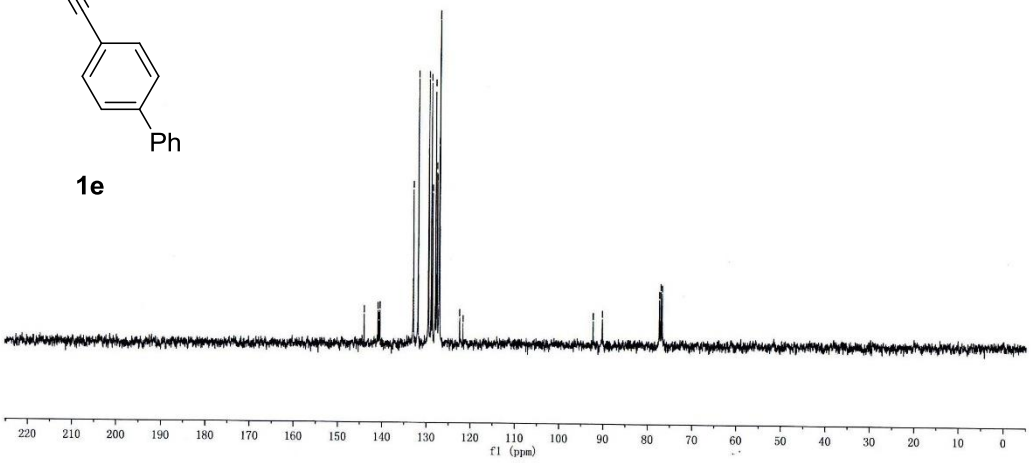
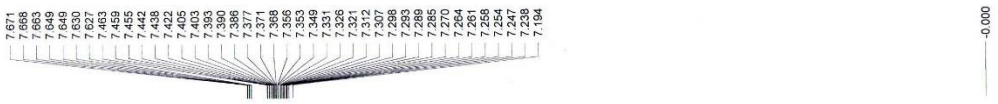
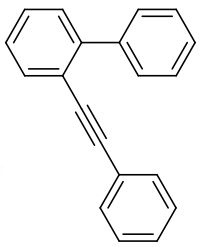
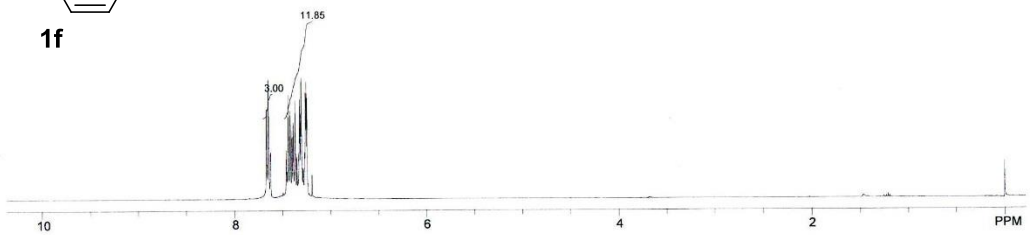


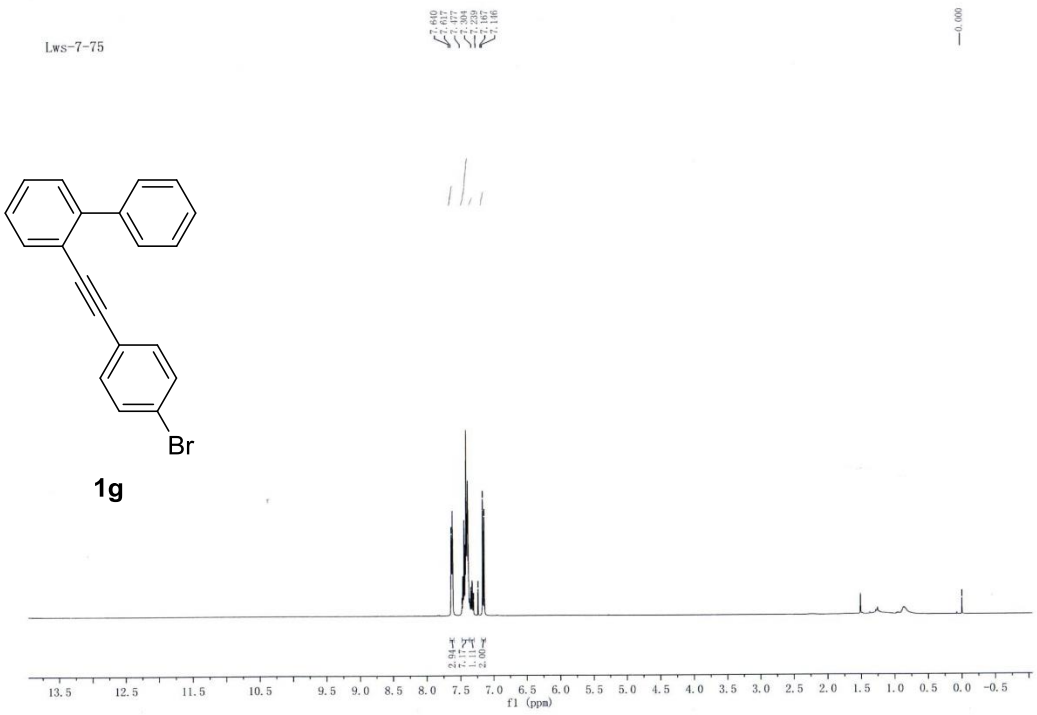




1f

JRW-4-56




Lws-7-75
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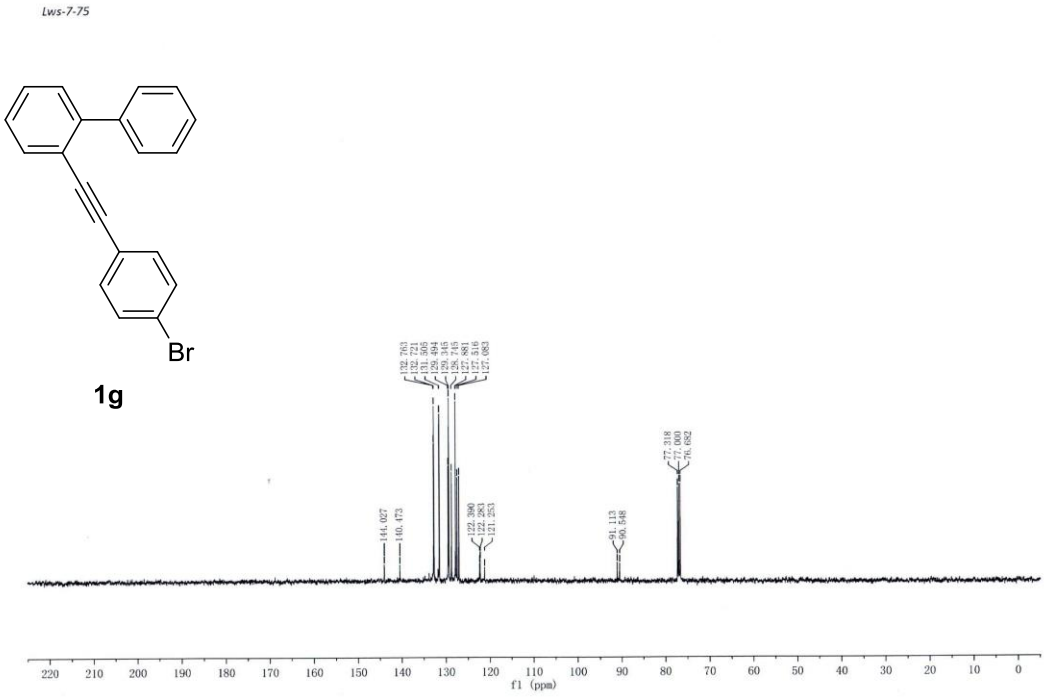
1g
f1 (ppm)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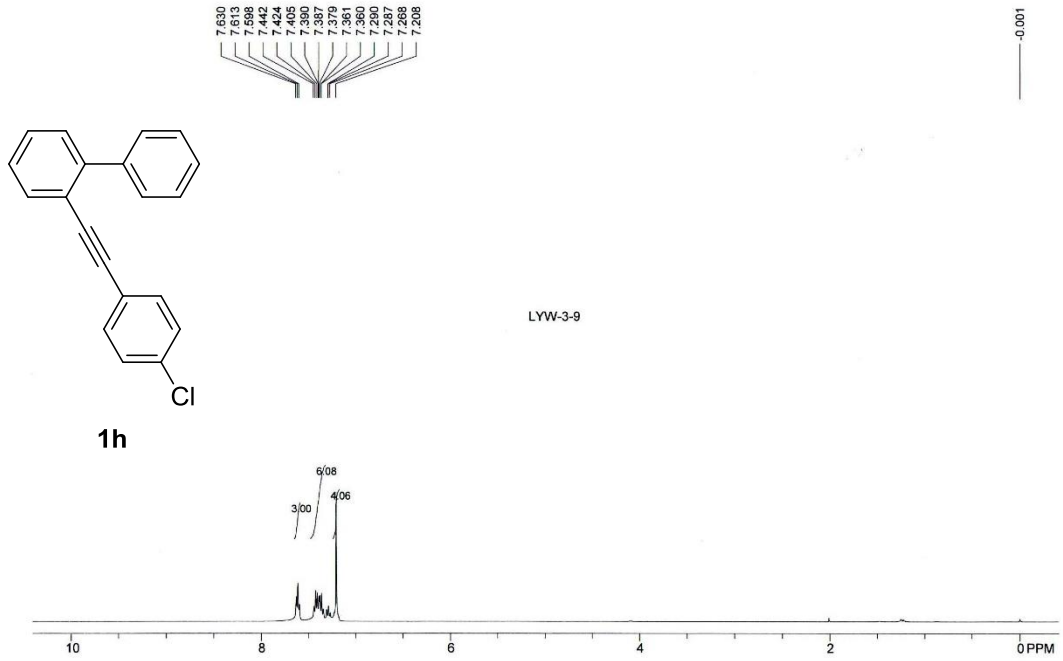
Br
1g
f1 (ppm)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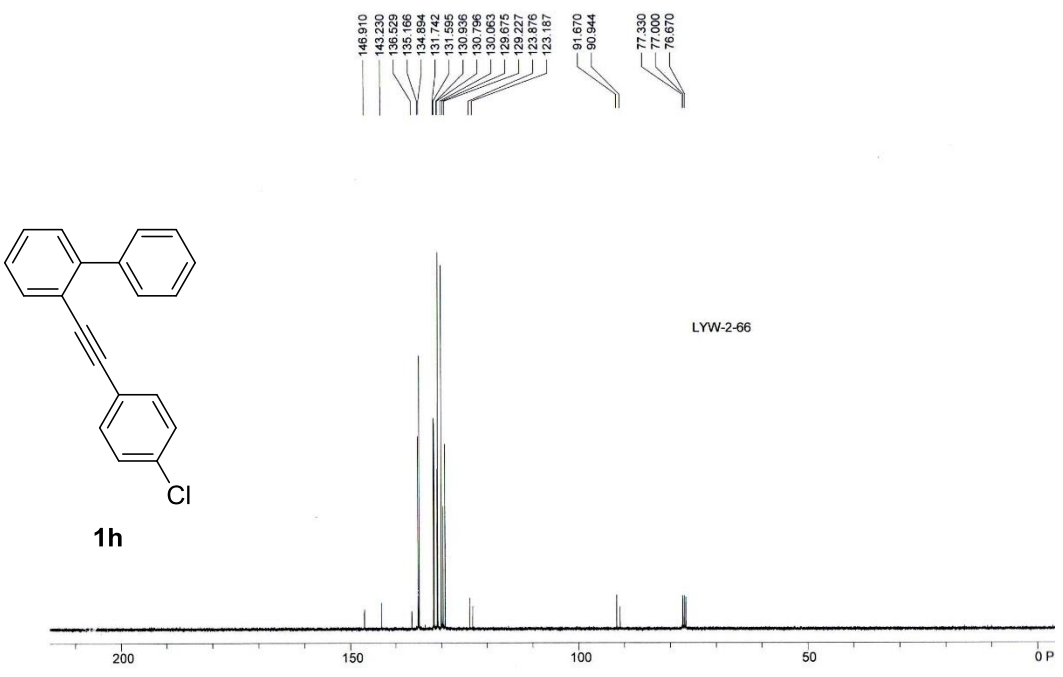
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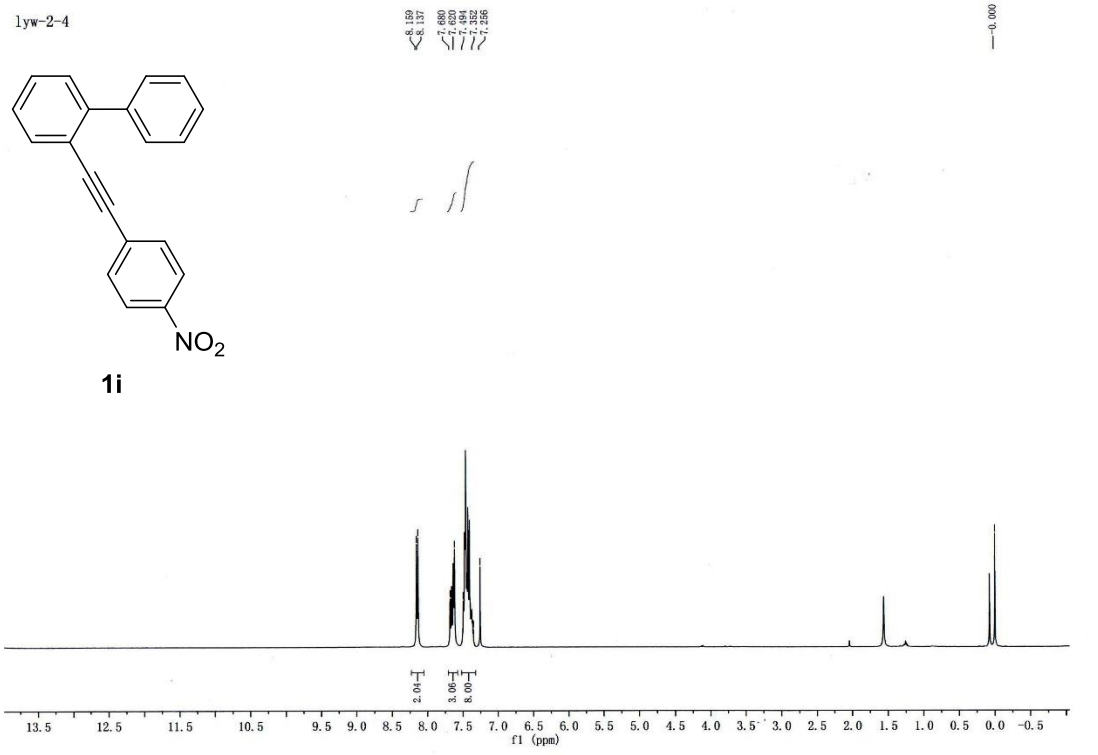
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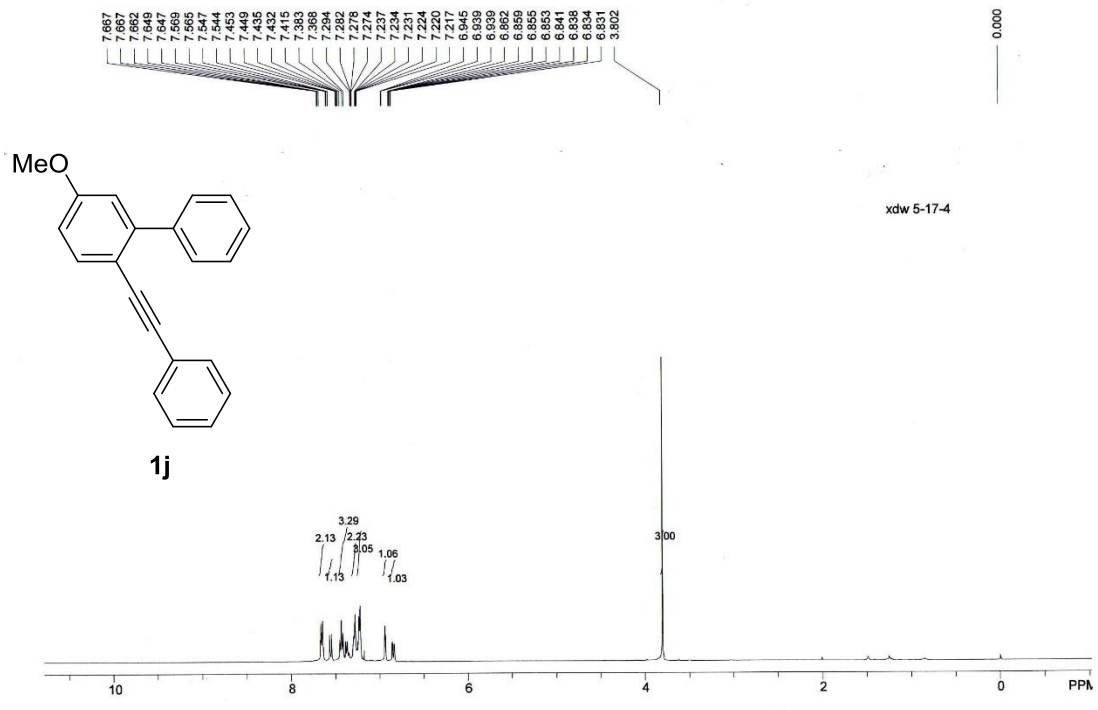
f1 (ppm)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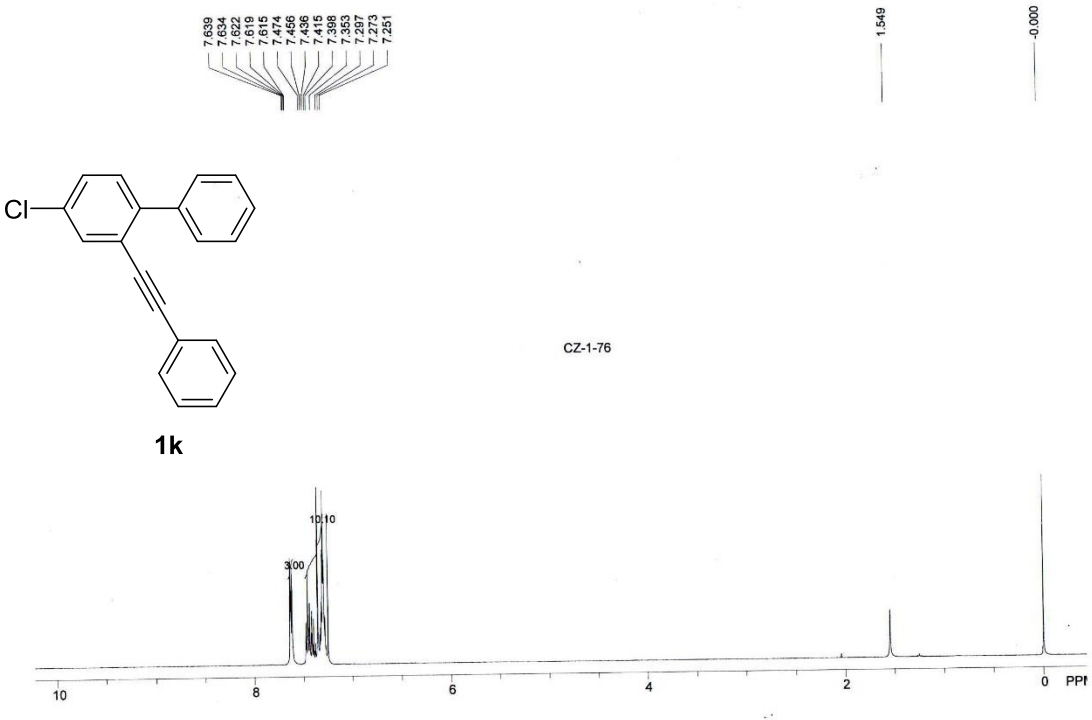
PPM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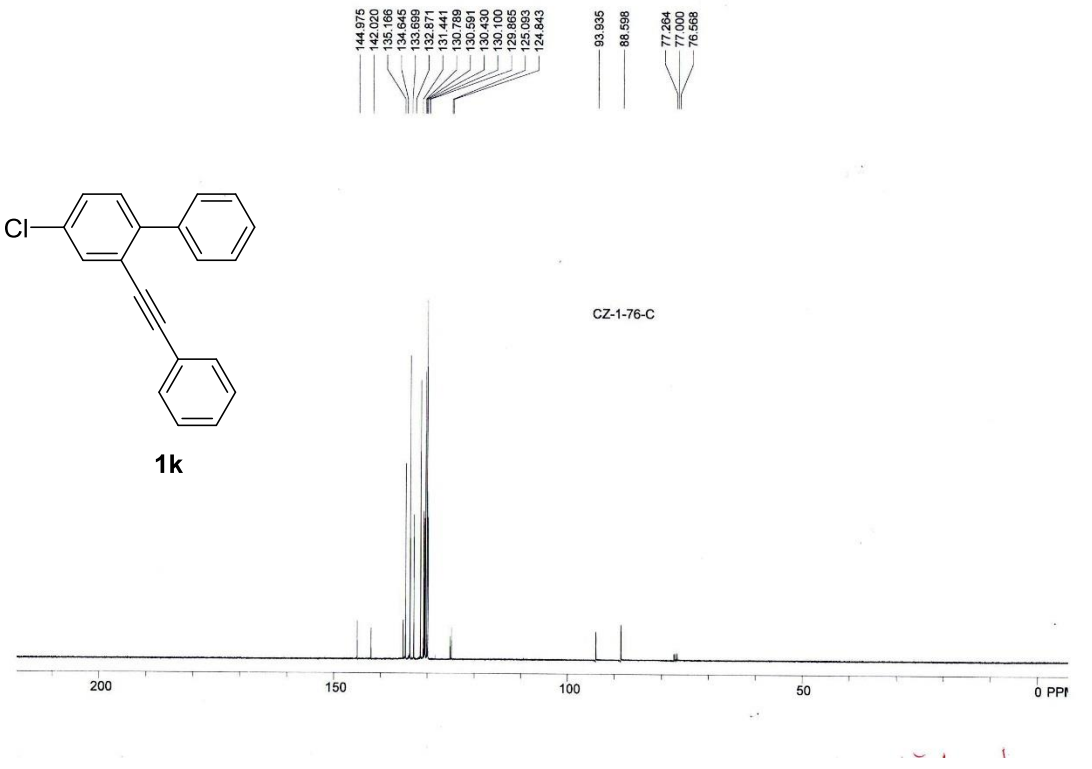
0 PPM

1k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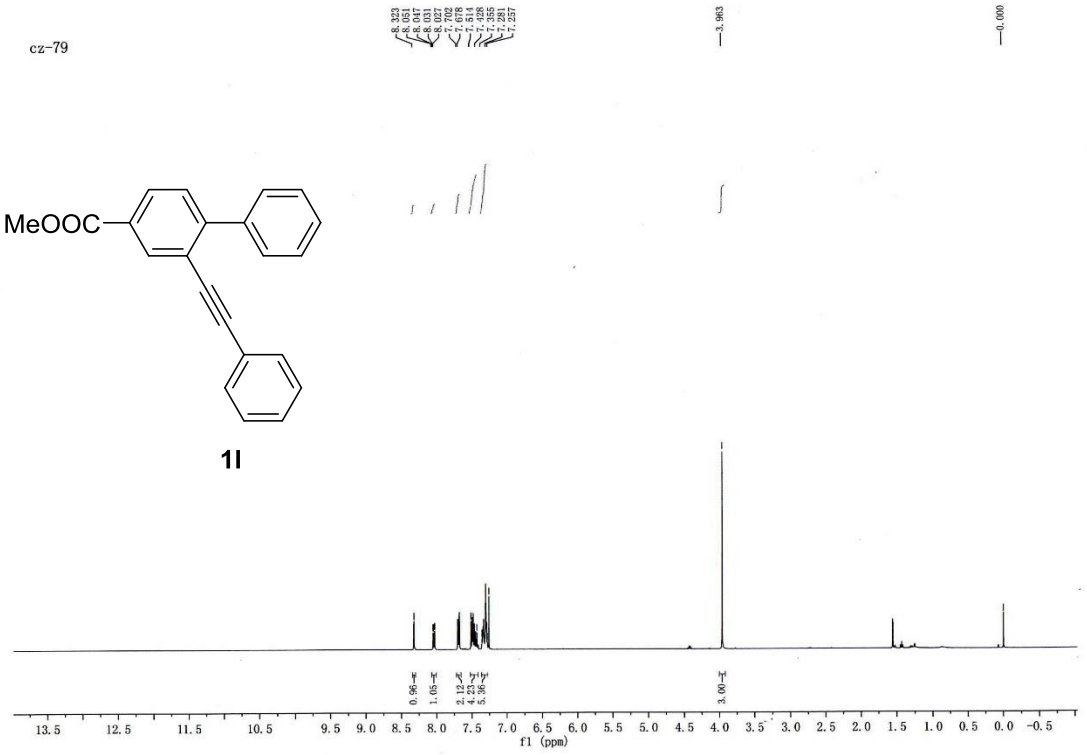
1k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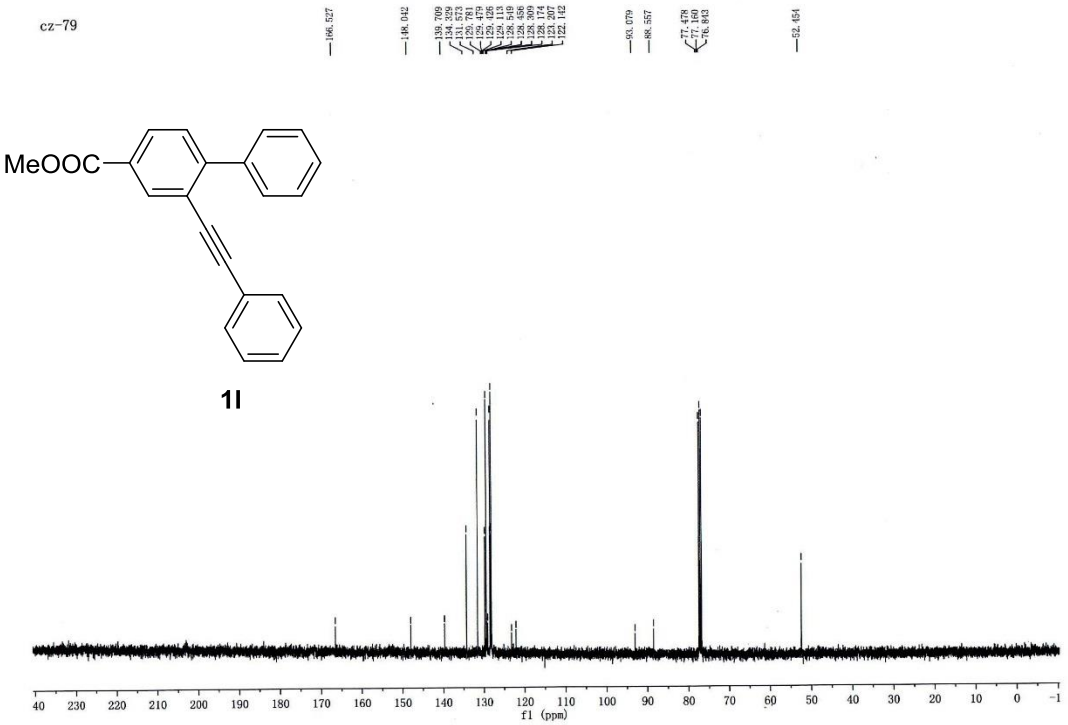
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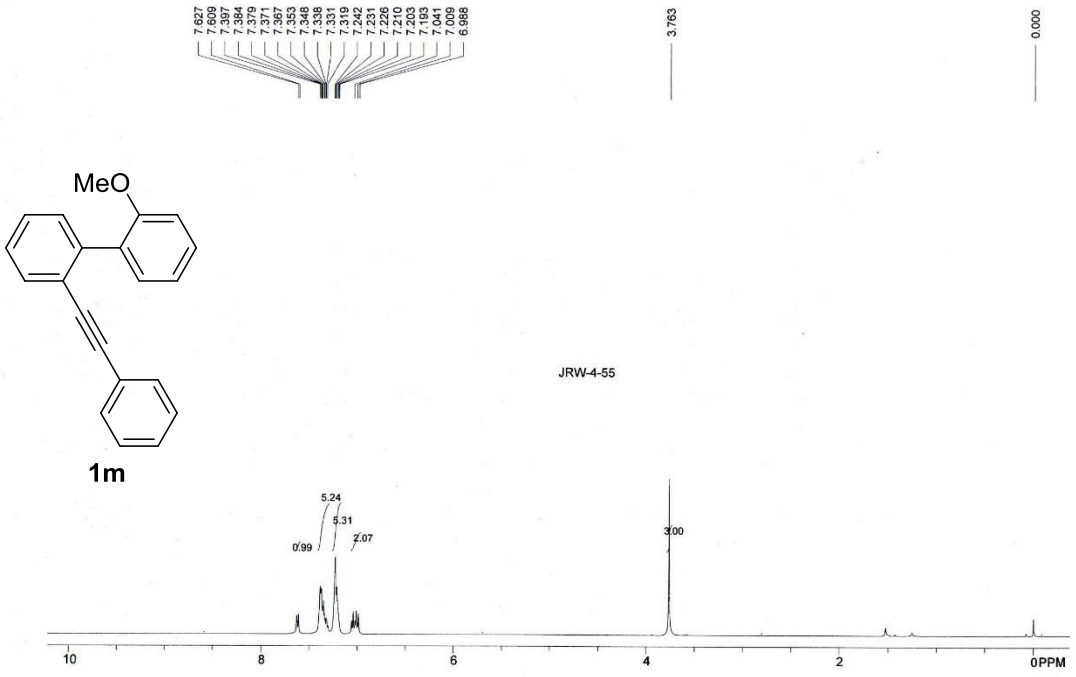
1l
f1 (ppm)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6.988
3.763
0.000
MeO
1m
JRW-4-55
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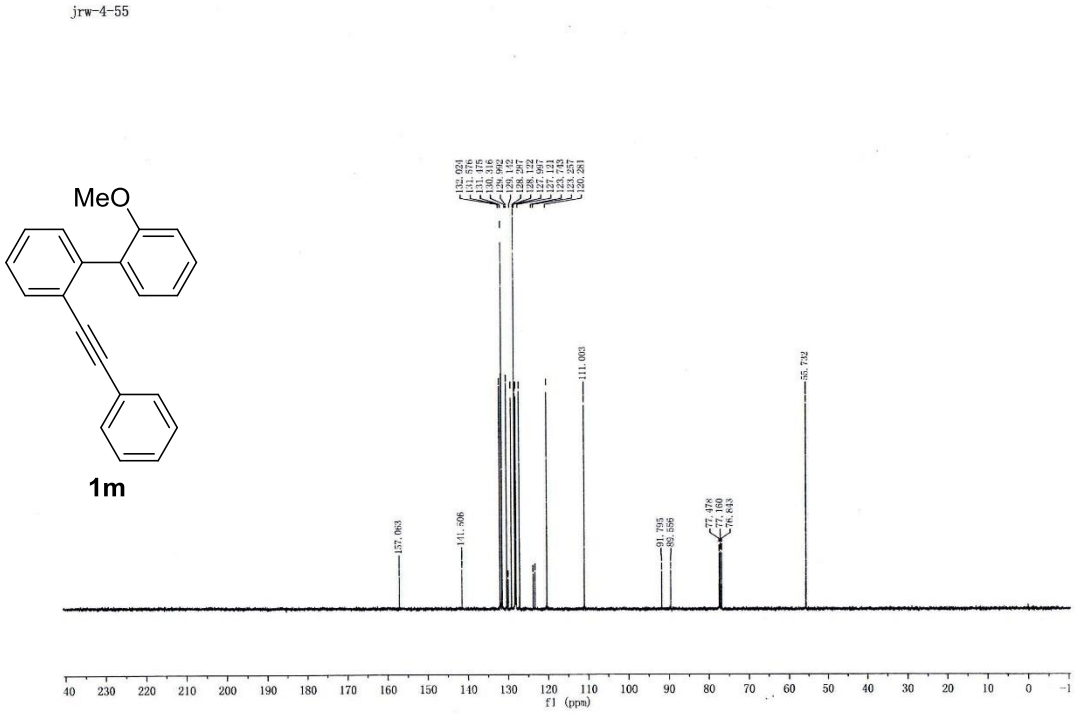
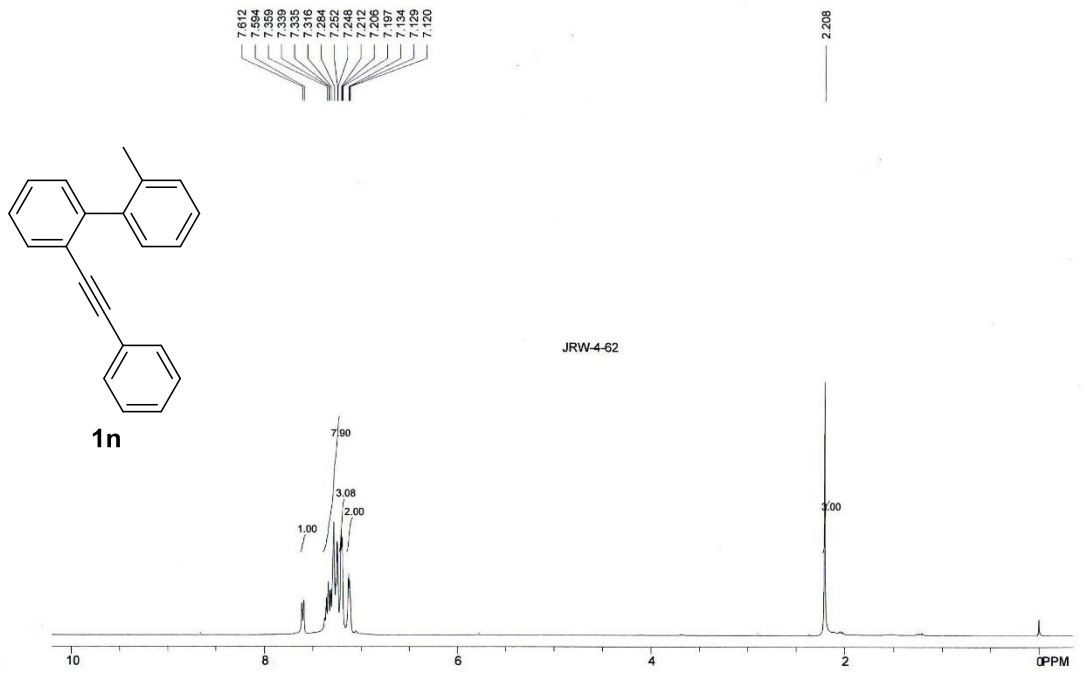
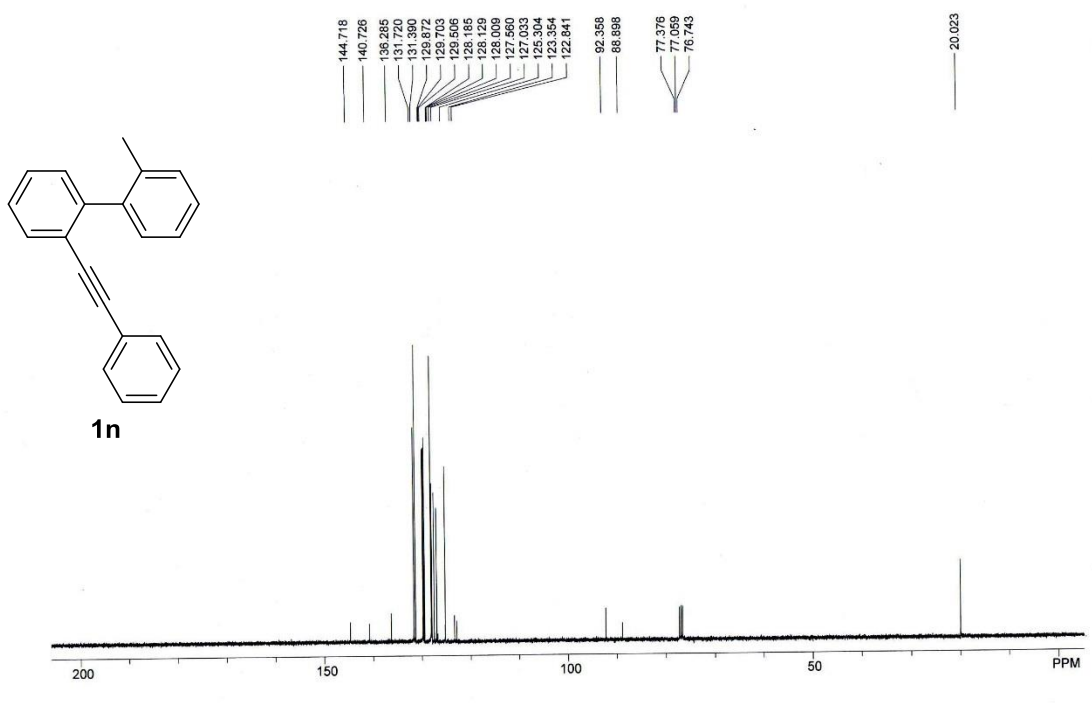
5.31
2.07
0.99
3.00
10
8
6
4
2
0PPM

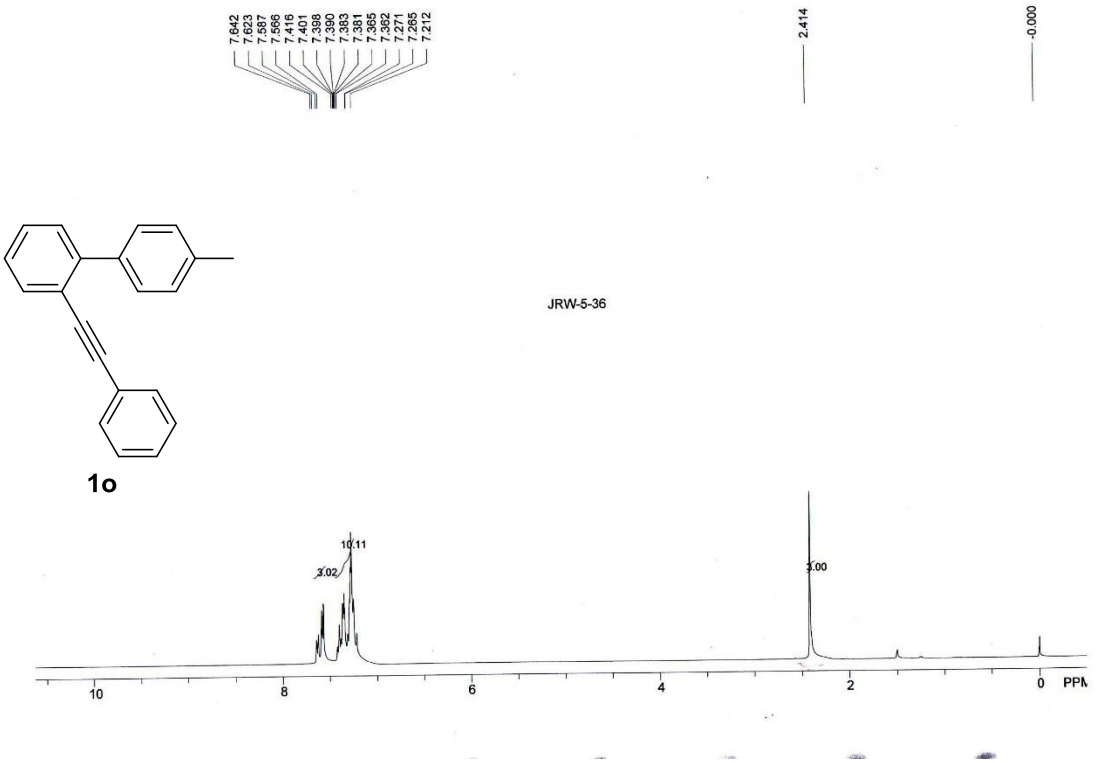

jrw-4-55
MeO
1m
157.063
141.506
111.005
91.795
89.899
77.478
77.160
76.843
55.732
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

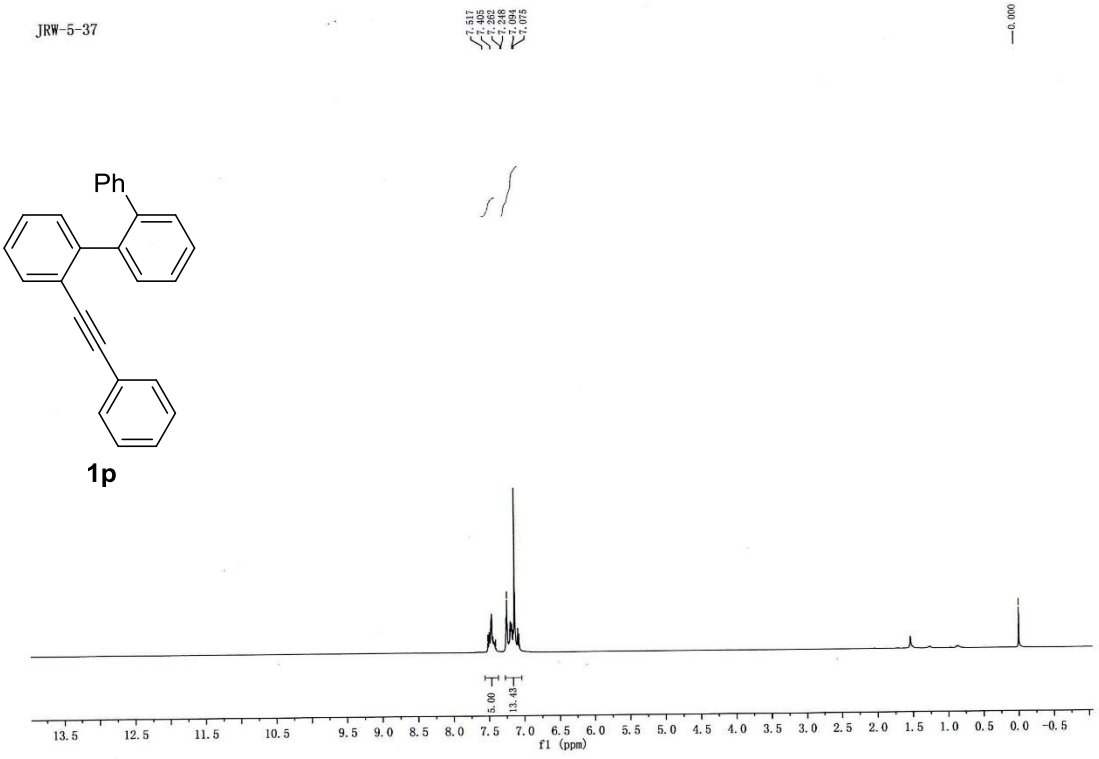

7.612
7.594
7.369
7.339
7.335
7.316
7.264
7.253
7.248
7.212
7.206
7.197
7.134
7.129
7.120
2.208
JRW-4-62
7.90
3.08
2.00
1.00
3.00
10
8
6
4
2
0
PPM

1n

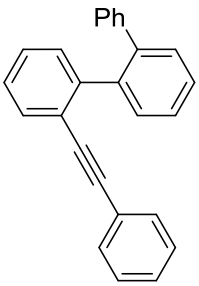

144.718
140.726
136.285
131.720
131.390
129.872
129.703
129.506
128.185
128.129
128.009
127.560
127.033
125.304
123.354
122.841
92.358
88.898
77.376
77.059
76.743
20.023
200
150
100
50
PPM

1n

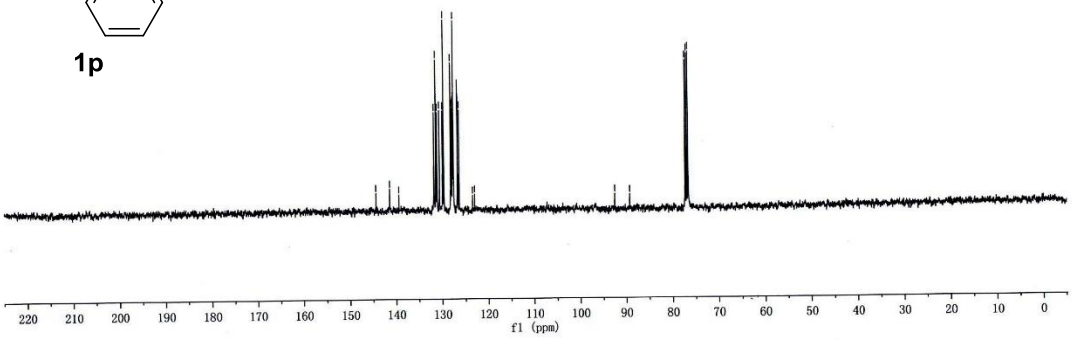

7.642
7.623
7.587
7.566
7.416
7.401
7.398
7.390
7.383
7.381
7.365
7.362
7.271
7.265
7.212
2.414
-0.000
JRW-5-36
1o
10.11
3.02
3.00
10
8
6
4
2
0
PPM

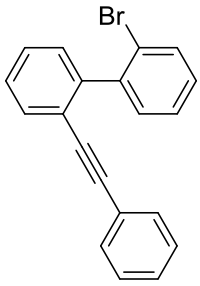

JRW-5-37
7.617
7.405
7.262
7.248
7.094
7.075
-0.000
Ph
1p
5.00
13.43
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

JRW-5-37



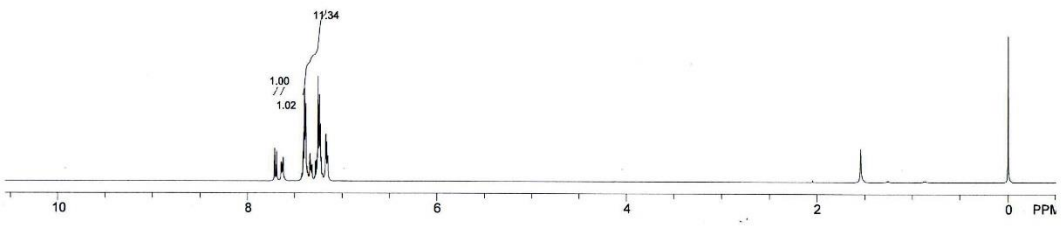
1p

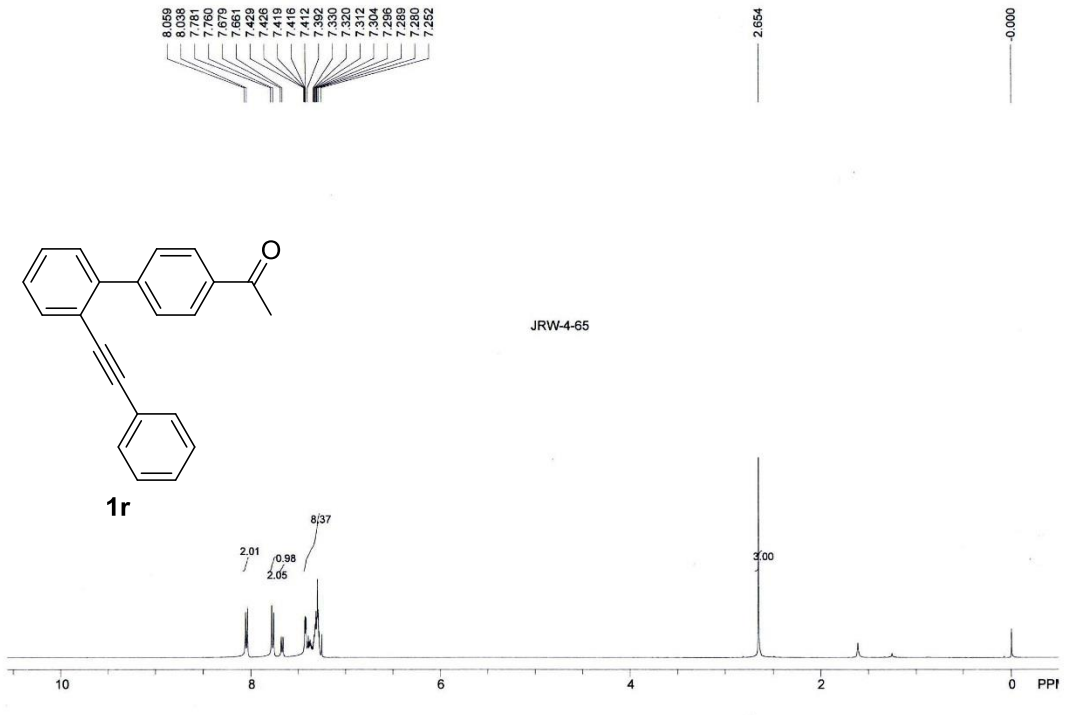


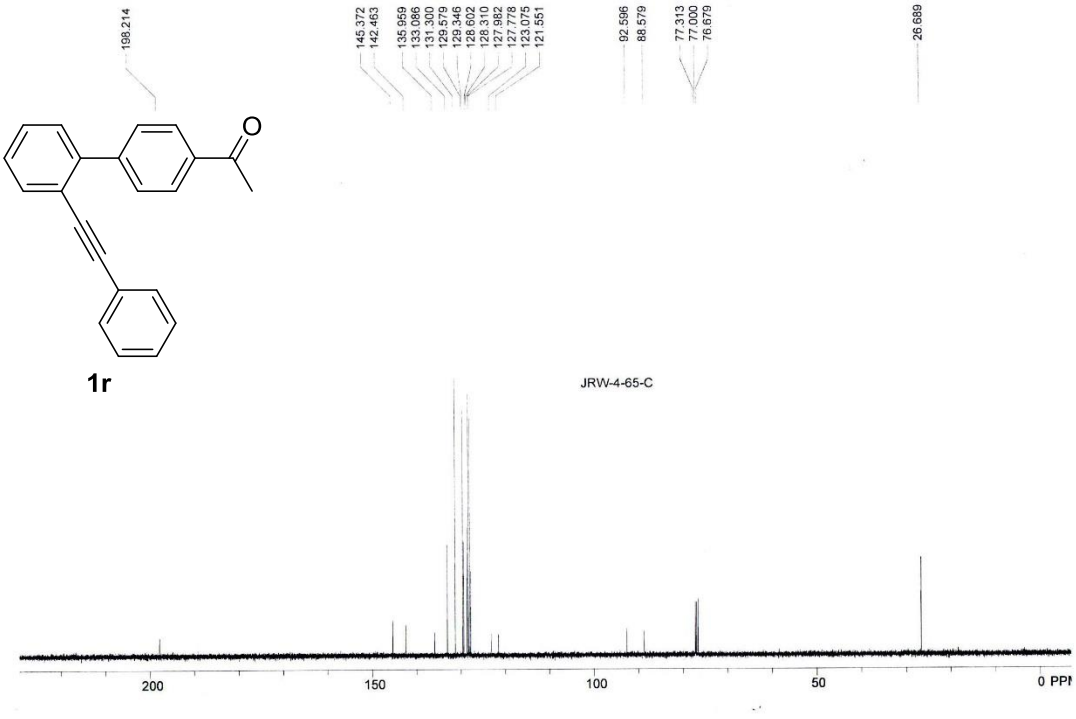


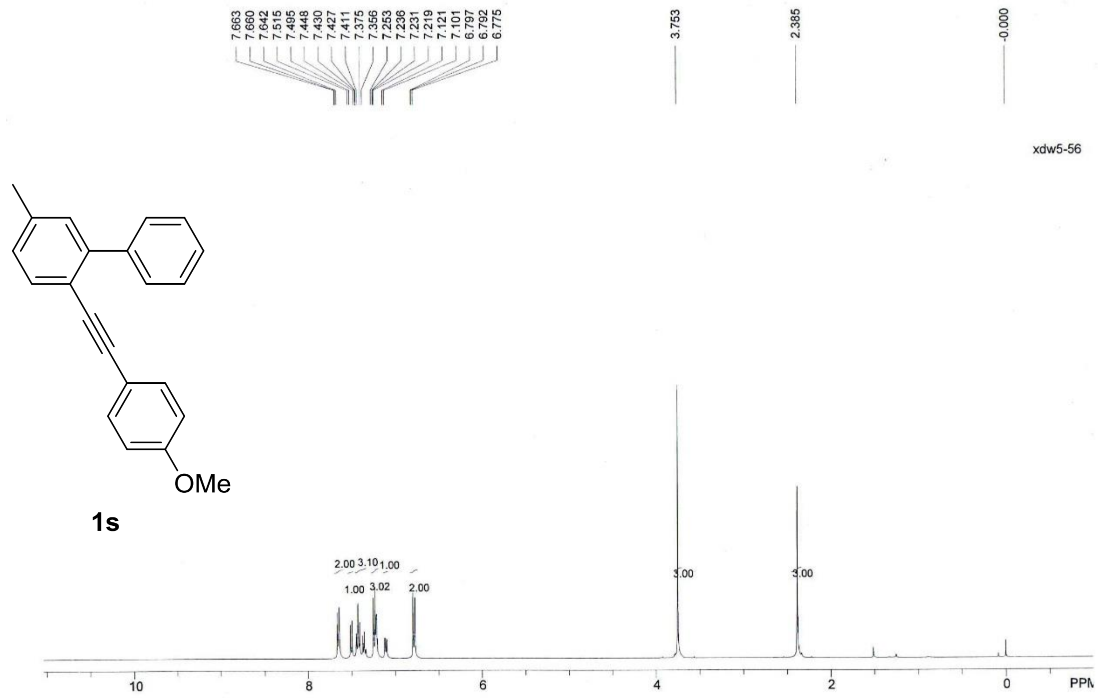
1q

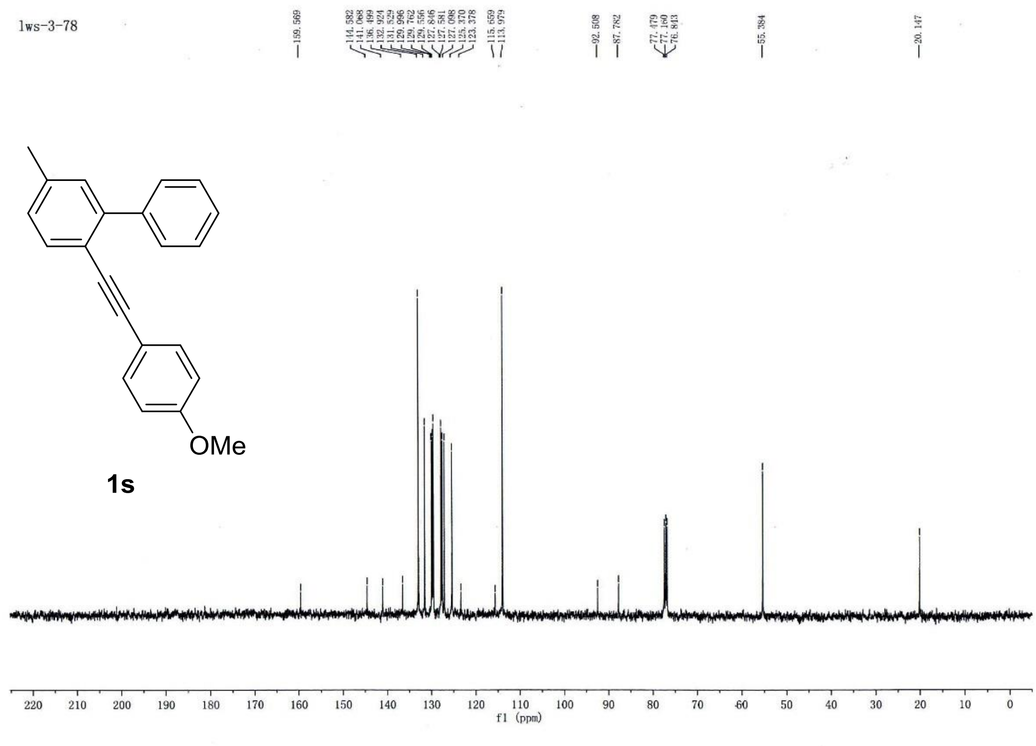
JRW-4-61

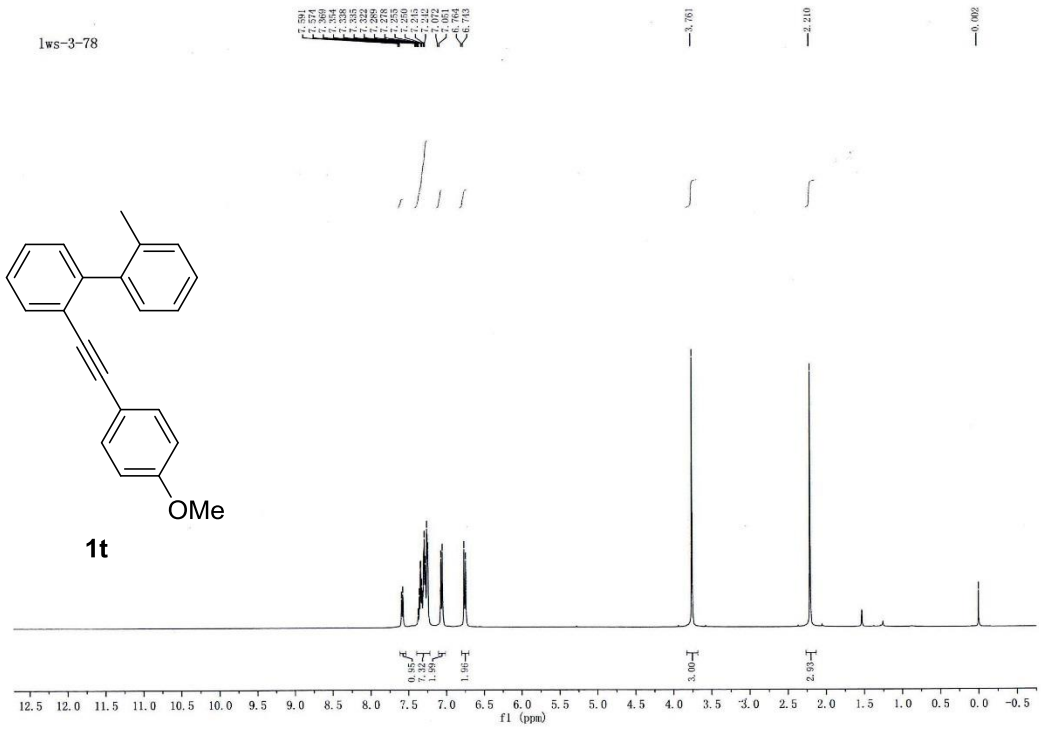


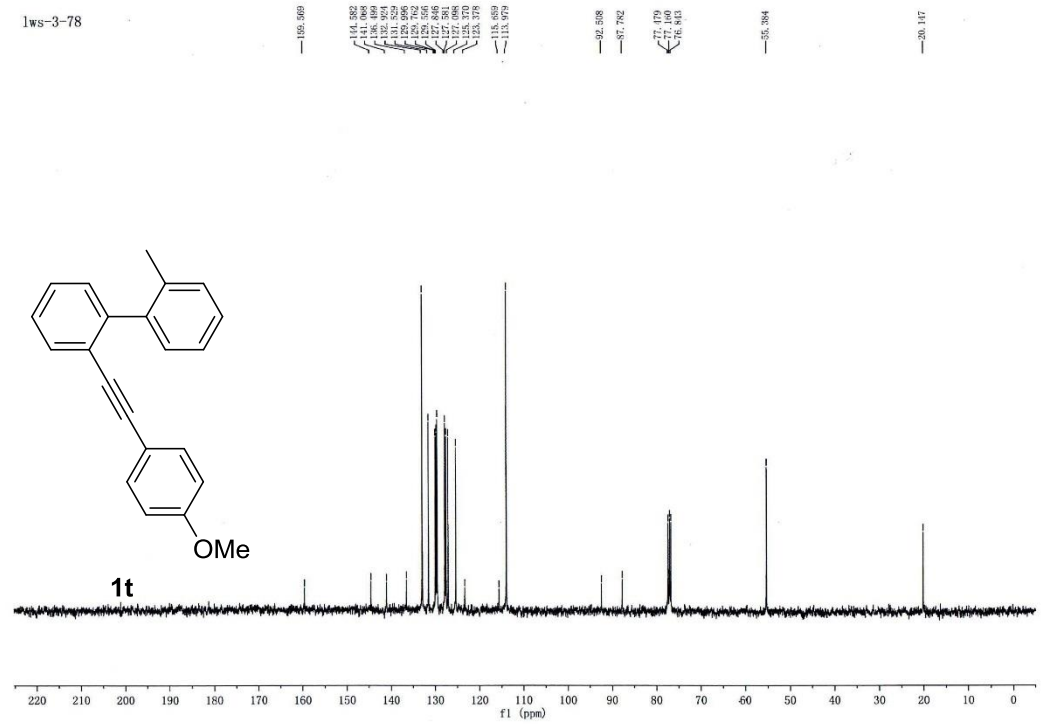

8.059
8.038
7.781
7.760
7.679
7.661
7.429
7.426
7.419
7.416
7.412
7.392
7.330
7.320
7.312
7.304
7.296
7.289
7.280
7.252
2.654
0.000
O
1r
JRW-4-65
8.37
2.01
0.98
2.05
3.00
10
8
6
4
2
0
PPI

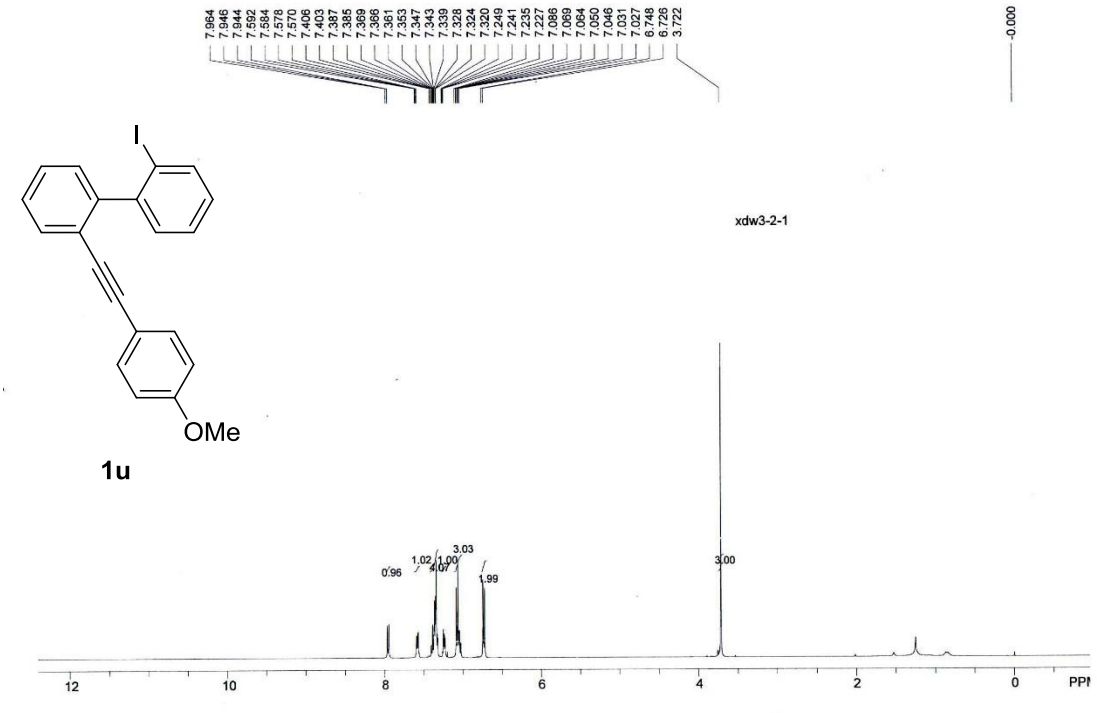

198.214
145.372
142.463
135.959
133.086
131.300
129.579
129.346
128.602
128.310
127.982
127.778
123.075
121.551
92.596
88.579
77.313
77.000
76.679
26.689
O
1r
JRW-4-65-C
200
150
100
50
0
PPI

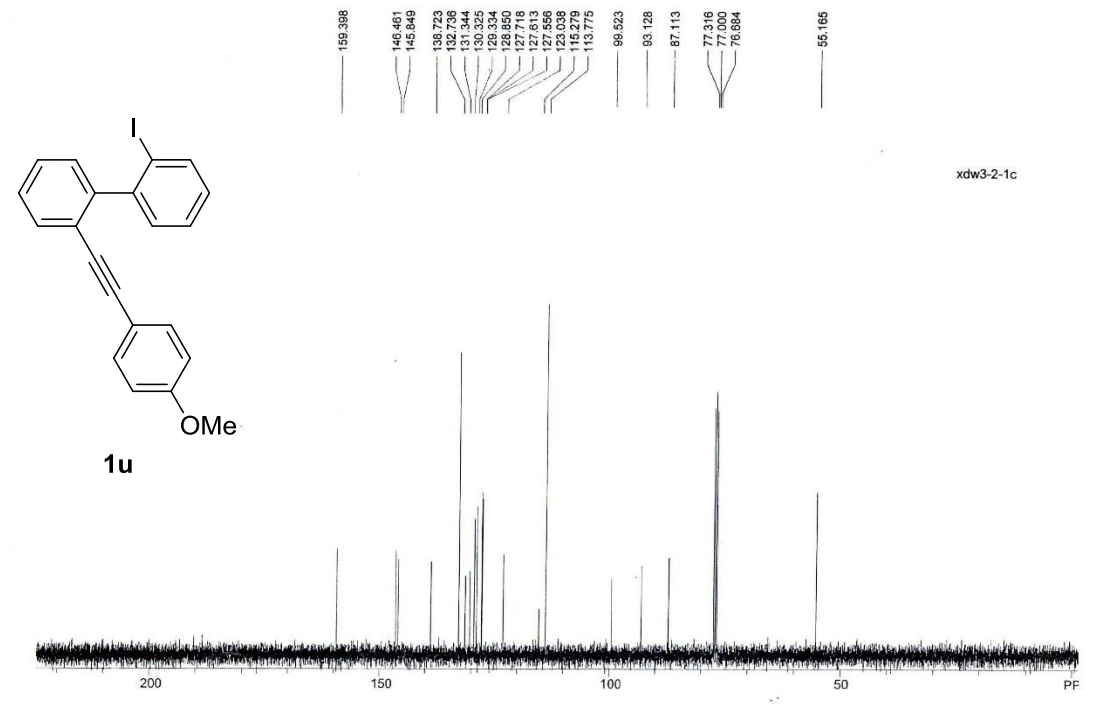

7.663
7.660
7.642
7.515
7.495
7.448
7.430
7.427
7.411
7.375
7.356
7.253
7.236
7.231
7.219
7.121
7.101
6.797
6.792
6.775
3.753
2.385
-0.000
xdw5-56
OMe
1s
2.00 3.10 1.00
1.00 3.02 2.00
3.00
3.00
10
8
6
4
2
0
PPM

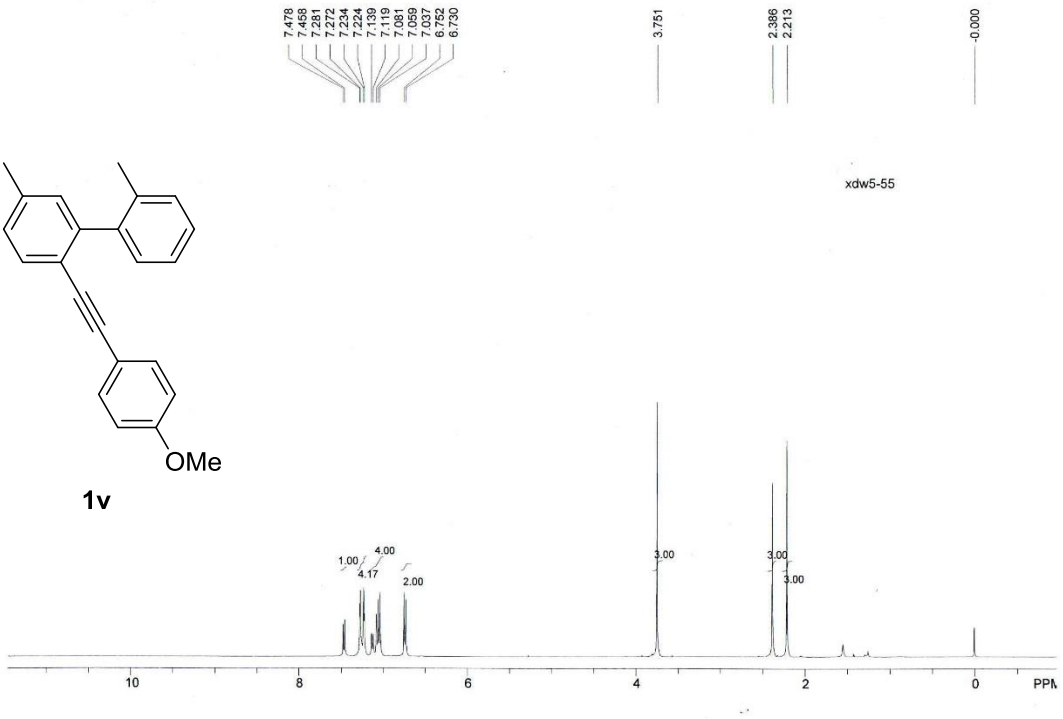

lws-3-78
159.569
144.582
141.068
136.499
132.924
131.529
129.996
129.762
129.556
127.846
127.581
127.098
125.370
123.378
115.659
113.979
92.508
87.782
77.479
77.160
76.843
55.384
20.147
OMe
1s
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

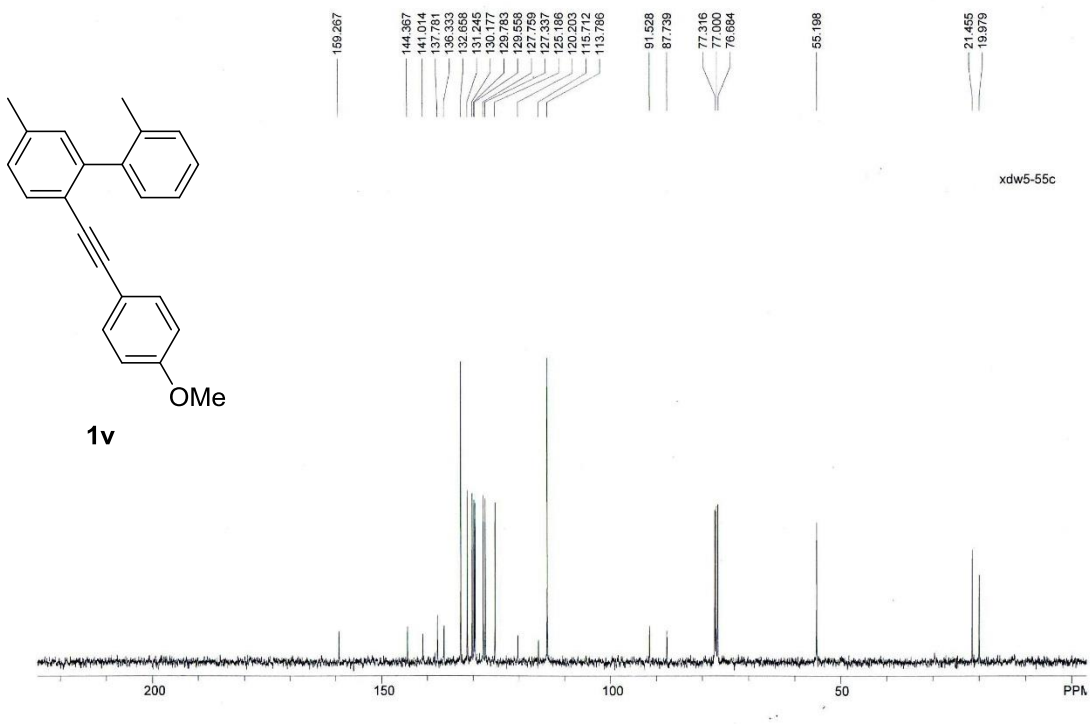

lws-3-78
OMe
1t
f1 (ppm)

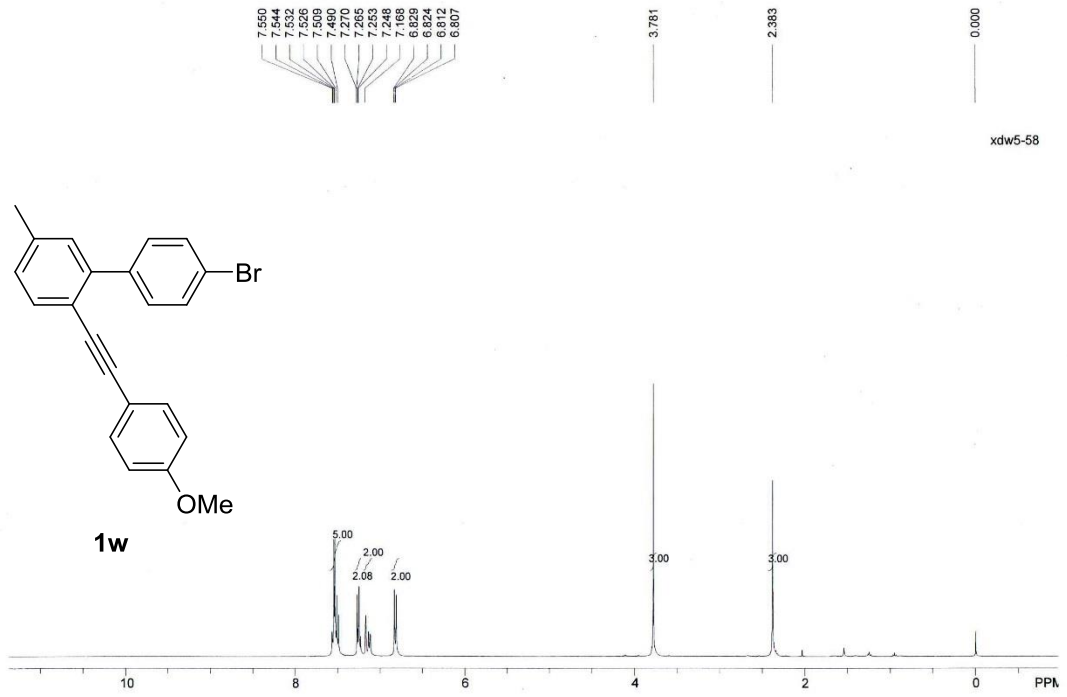

lws-3-78
OMe
1t
f1 (ppm)

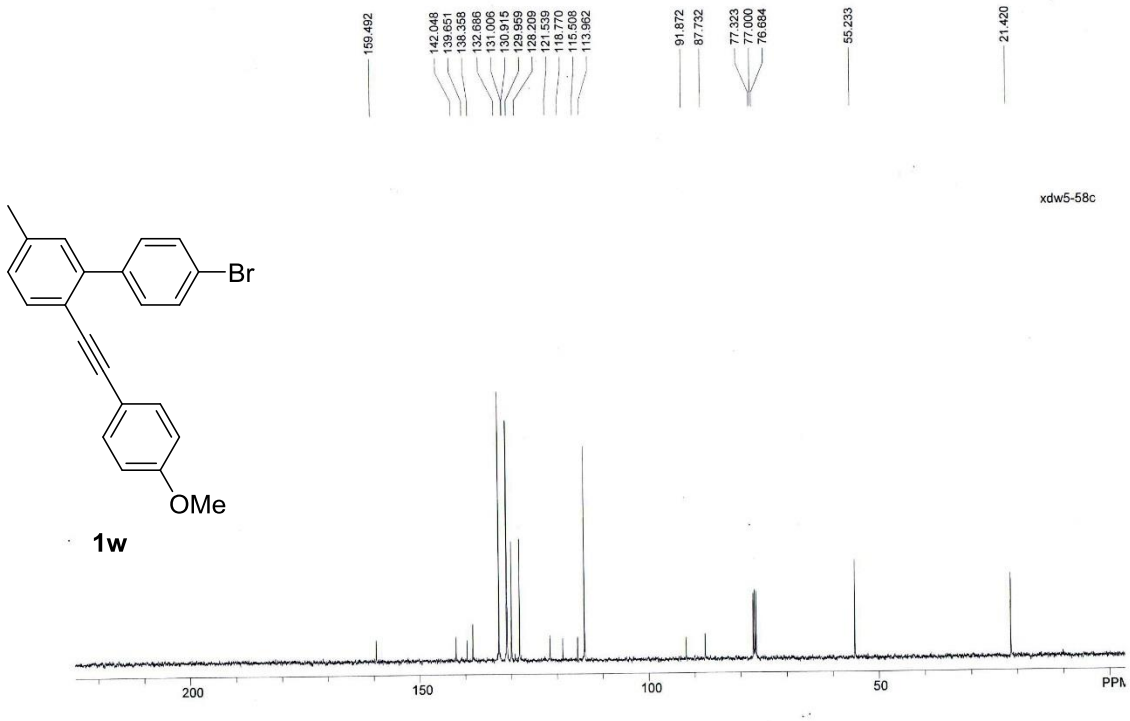

7.964
7.946
7.944
7.592
7.584
7.578
7.570
7.406
7.403
7.387
7.385
7.369
7.366
7.361
7.353
7.347
7.343
7.339
7.328
7.324
7.320
7.249
7.241
7.235
7.227
7.086
7.069
7.064
7.050
7.046
7.031
7.027
6.748
6.726
3.722
-0.000
I
OMe
1u
xdw3-2-1
0.96
1.02
1.00
4.07
3.03
1.99
3.00
12
10
8
6
4
2
0
PPM

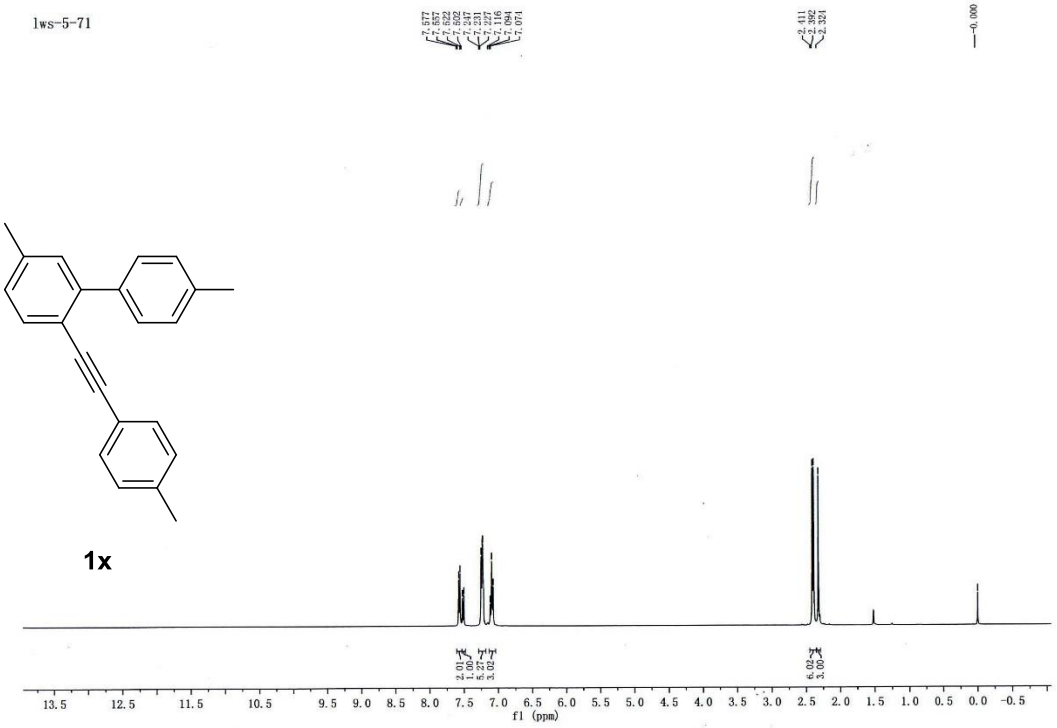

159.398
146.461
145.849
138.723
132.736
131.344
130.325
129.334
128.850
127.718
127.613
127.556
123.038
115.279
113.775
99.523
93.128
87.113
77.316
77.000
76.884
55.165
I
OMe
1u
xdw3-2-1c
200
150
100
50
PPM

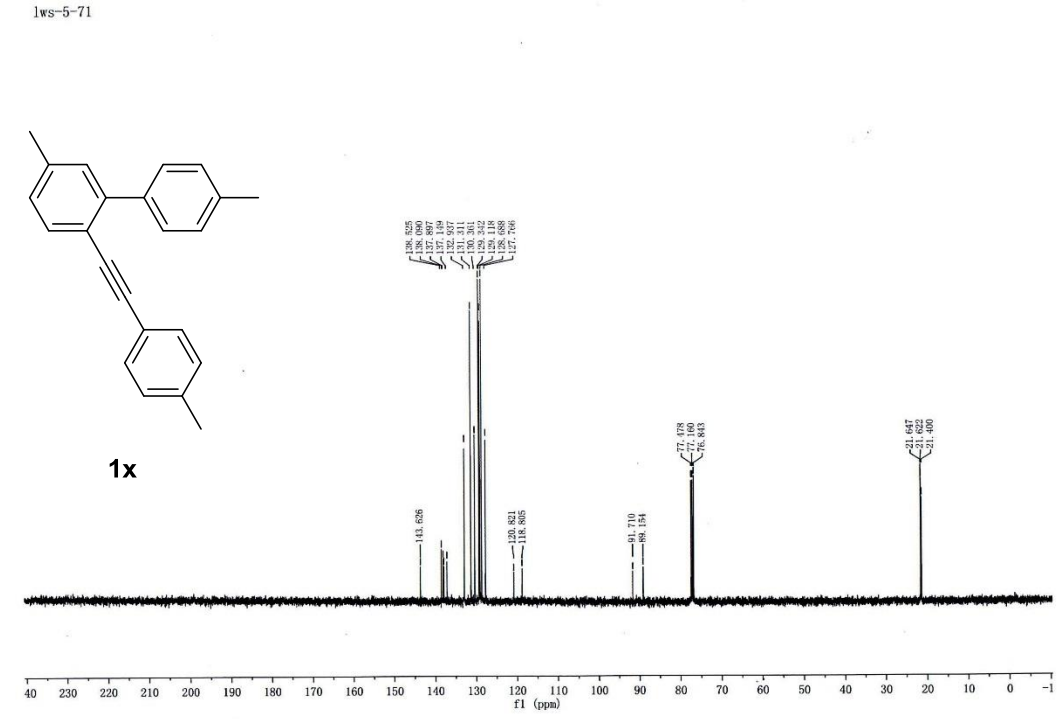

7.478
7.458
7.281
7.272
7.234
7.224
7.139
7.119
7.081
7.059
7.037
6.752
6.730
3.751
2.386
2.213
0.000
xdw5-55
OMe
1v
1.00
4.00
4.17
2.00
3.00
3.00
3.00
10
8
6
4
2
0
PPM

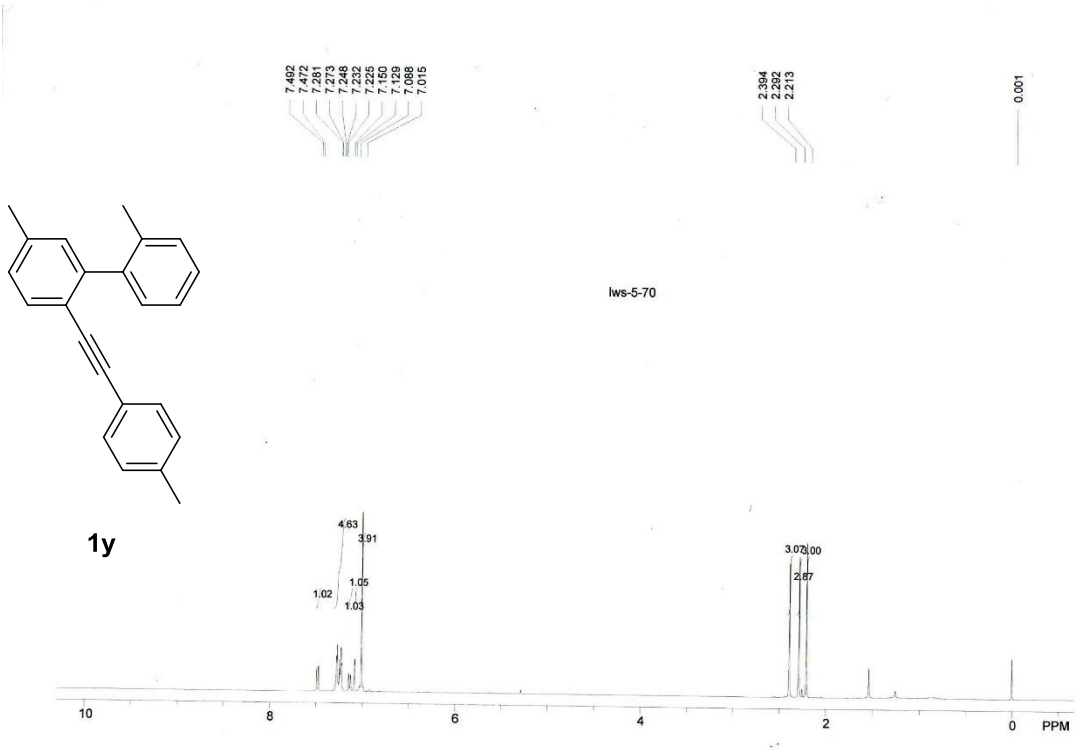

159.267
144.367
141.014
137.781
136.333
132.658
131.245
130.177
129.783
129.558
127.759
127.337
125.186
120.203
115.712
113.786
91.528
87.739
77.316
77.000
76.684
55.198
21.455
19.979
xdw5-55c
OMe
1v
200
150
100
50
PPM

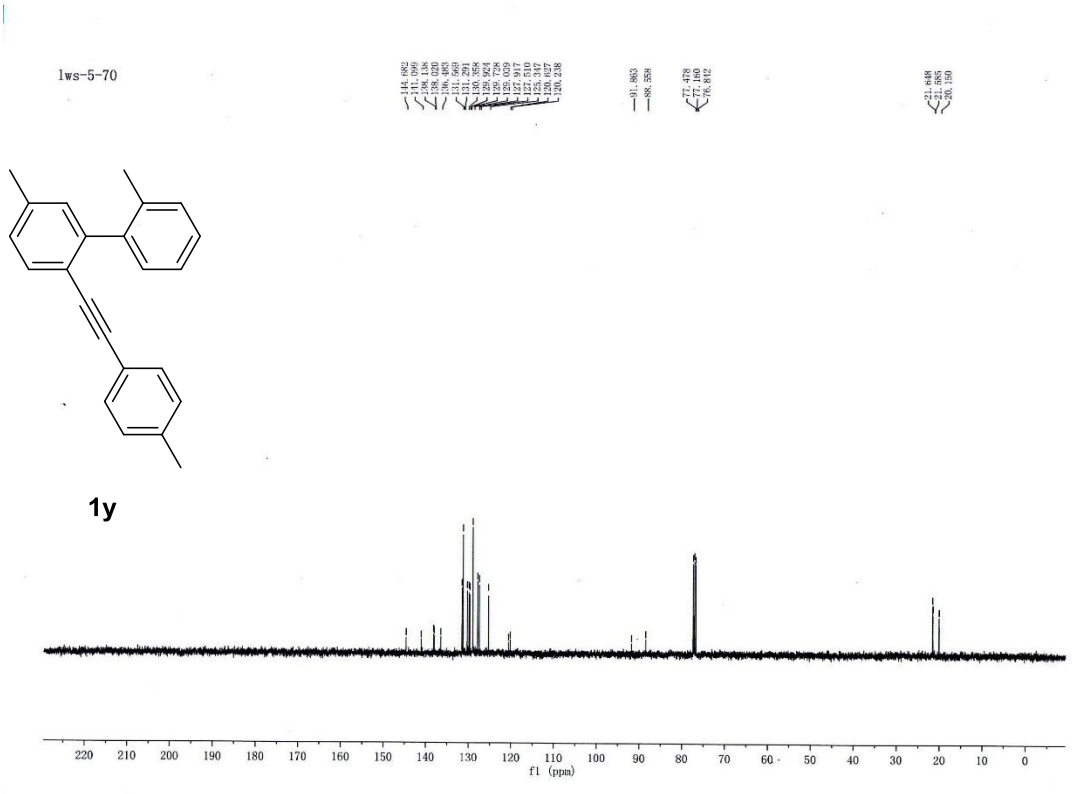

7.550
7.544
7.532
7.526
7.509
7.490
7.270
7.265
7.253
7.248
7.168
6.829
6.824
6.812
6.807
3.781
2.383
0.000
xdw5-58
Br
OMe
1w
5.00
2.00
2.08
2.00
3.00
3.00
10
8
6
4
2
0
PPM

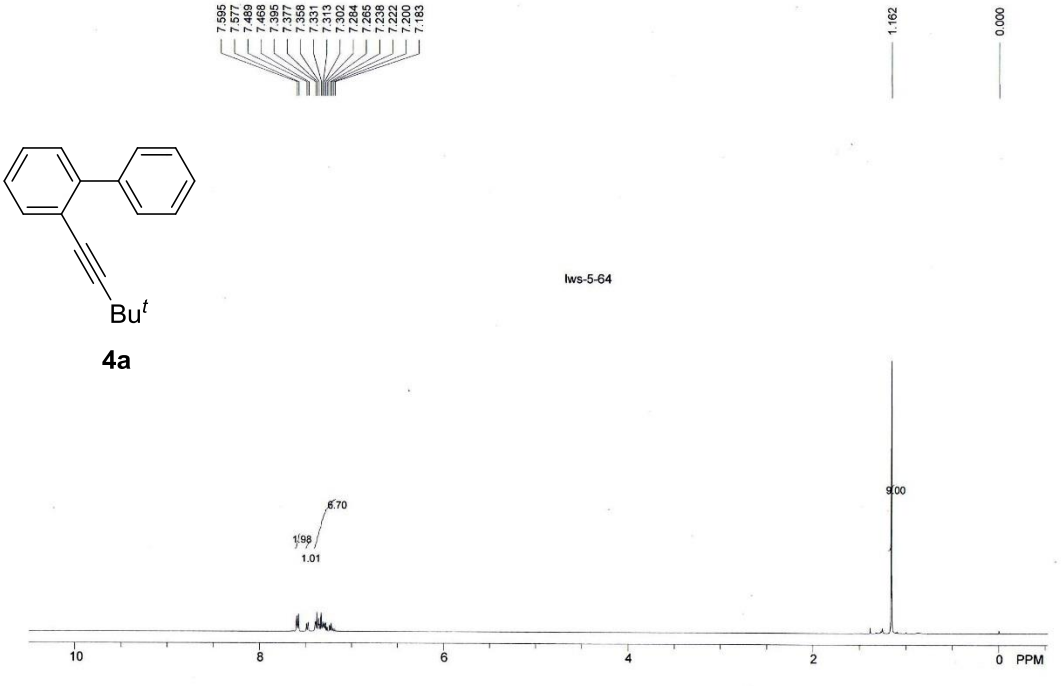

159.492
142.048
139.651
138.358
132.686
131.006
130.915
129.959
128.209
121.539
118.770
115.508
113.962
91.872
87.732
77.323
77.000
76.684
55.233
21.420
xdw5-58c
Br
OMe
1w
200
150
100
50
PPM


lws-5-71
1x
f1 (ppm)

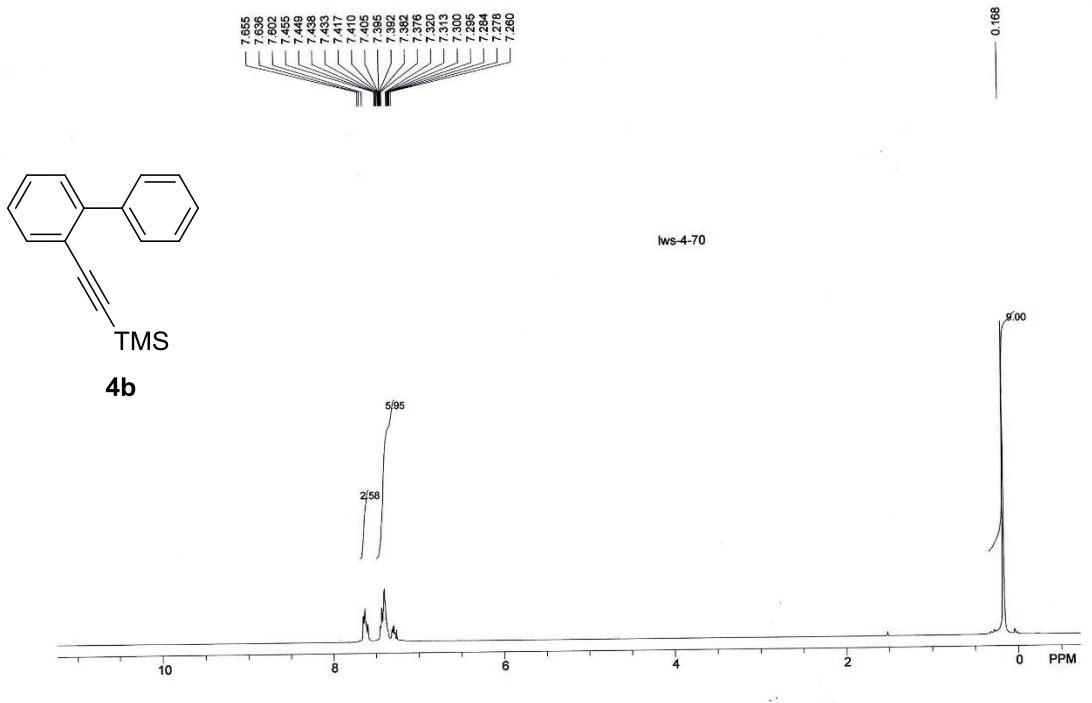

lws-5-71
1x
f1 (ppm)


7.492
7.472
7.281
7.273
7.248
7.232
7.225
7.150
7.129
7.088
7.015
2.394
2.292
2.213
0.001
lws-5-70
1y
4.63
3.91
1.02
1.05
1.03
3.07
3.00
2.87
10
8
6
4
2
0
PPM

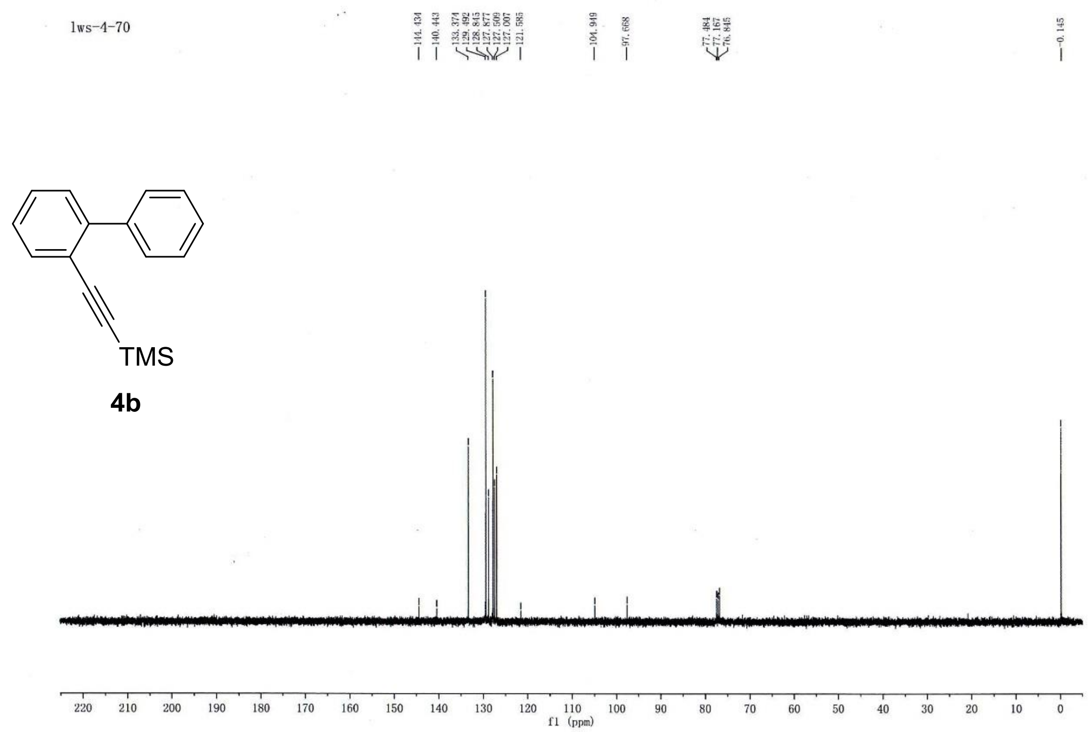

lws-5-70
144.682
141.096
138.136
138.070
136.483
131.569
131.291
130.956
129.924
129.728
129.039
127.947
127.510
125.347
120.677
120.238
91.863
88.358
77.478
77.160
76.812
21.648
21.555
20.159
1y
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.595
7.577
7.489
7.468
7.395
7.377
7.358
7.331
7.313
7.302
7.284
7.265
7.238
7.222
7.200
7.183
1.162
0.000
Bu^t
lws-5-64
9.00
5.70
1.98
1.01
10
8
6
4
2
0 PPM

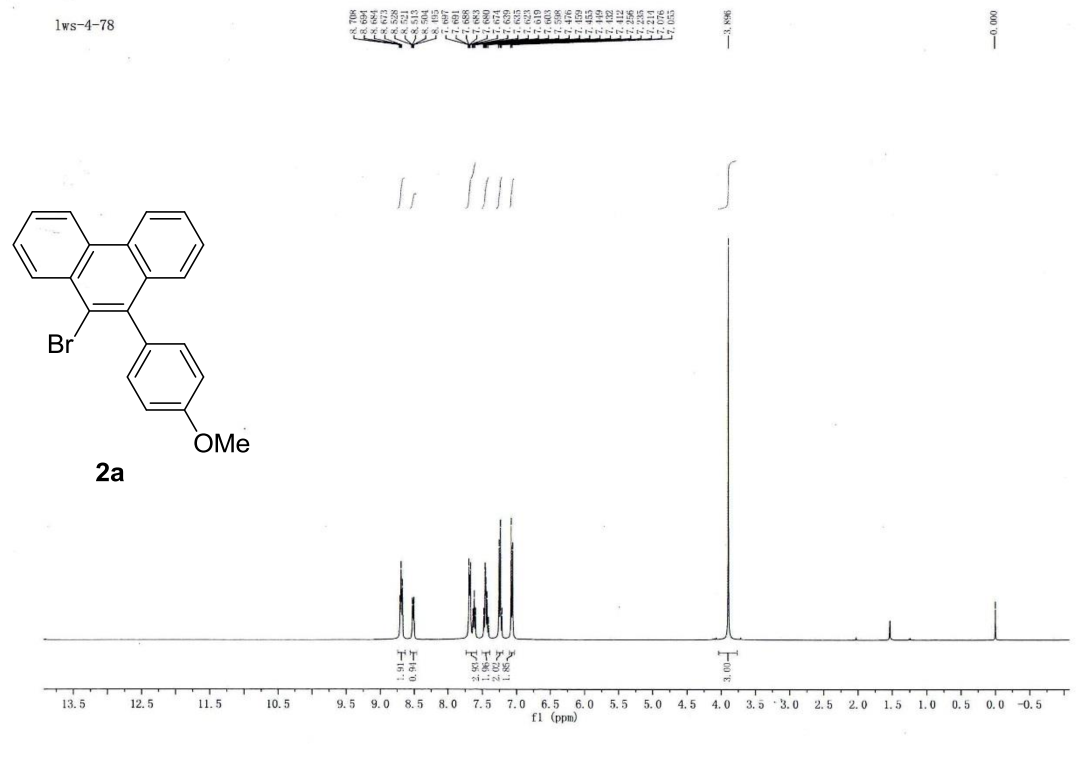
4a


7.655
7.636
7.602
7.455
7.449
7.438
7.433
7.417
7.410
7.405
7.395
7.392
7.382
7.376
7.320
7.313
7.300
7.295
7.284
7.278
7.260
0.168
TMS
lws-4-70
9.00
5.95
2.58
10
8
6
4
2
0 PPM

4b

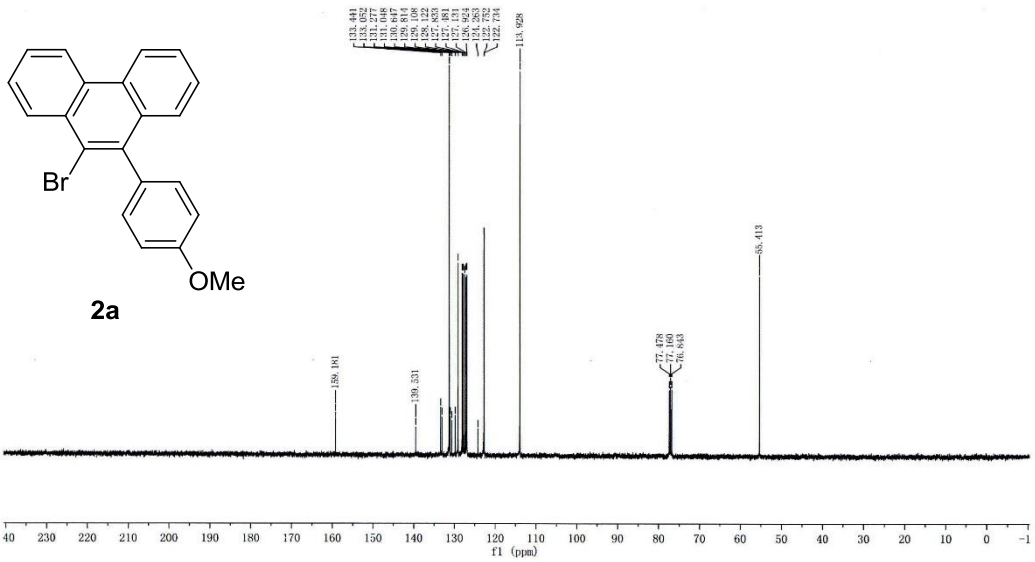

lws-4-70
144.434
140.443
133.374
129.492
128.843
127.877
127.509
127.067
121.585
104.949
97.668
77.484
77.167
76.845
-0.145
TMS
f1 (ppm)

4b

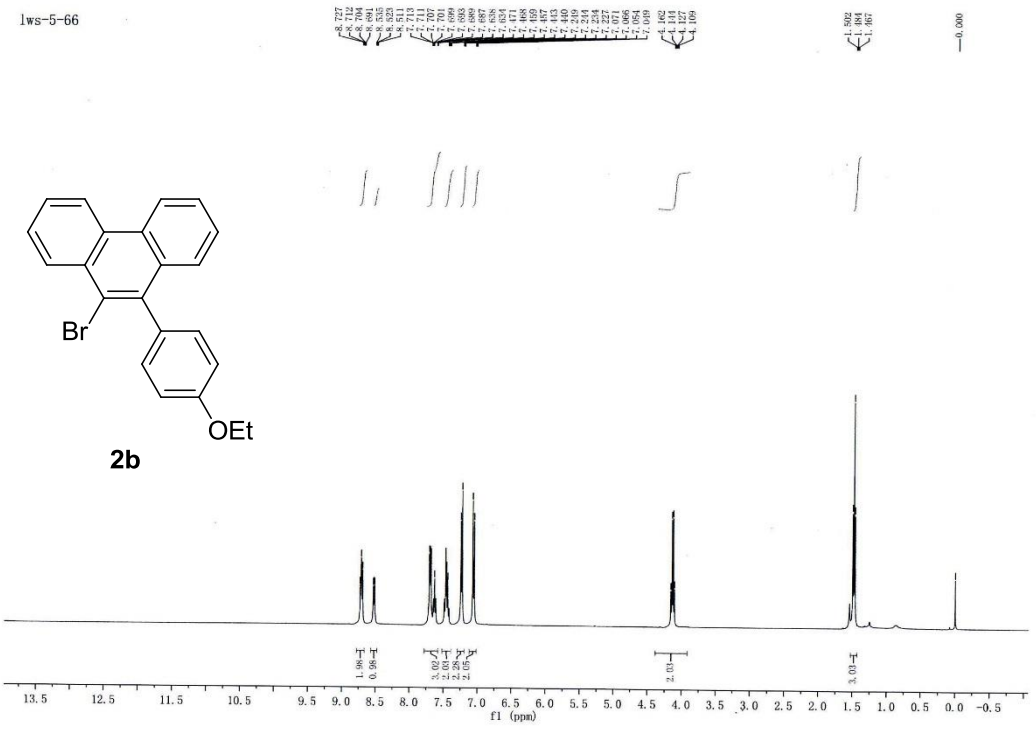

lws-4-78
3.896
0.000
Br
OMe
1.91
0.94
2.93
1.96
2.02
1.85
3.00
f1 (ppm)

2a

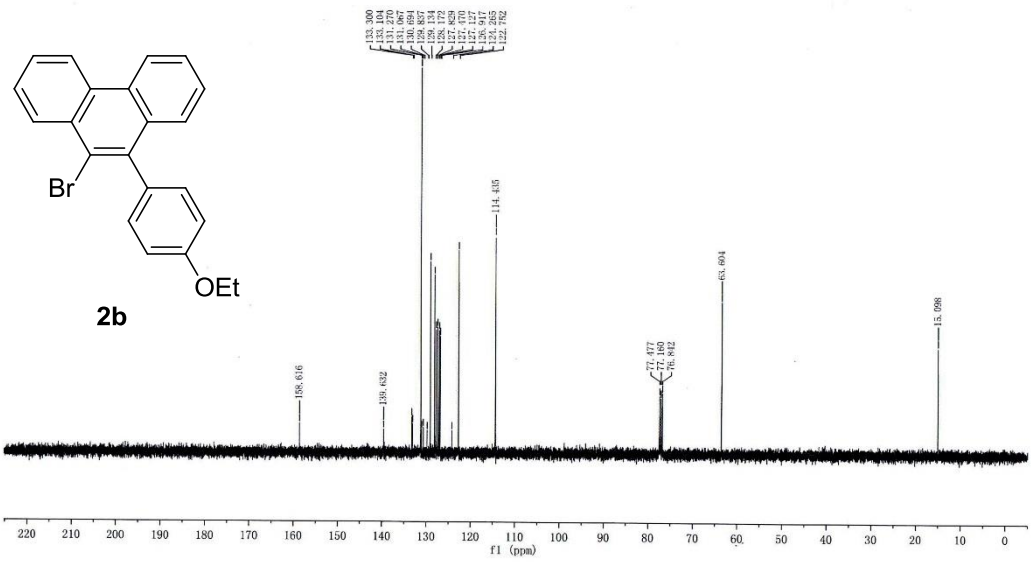
lws-4-78



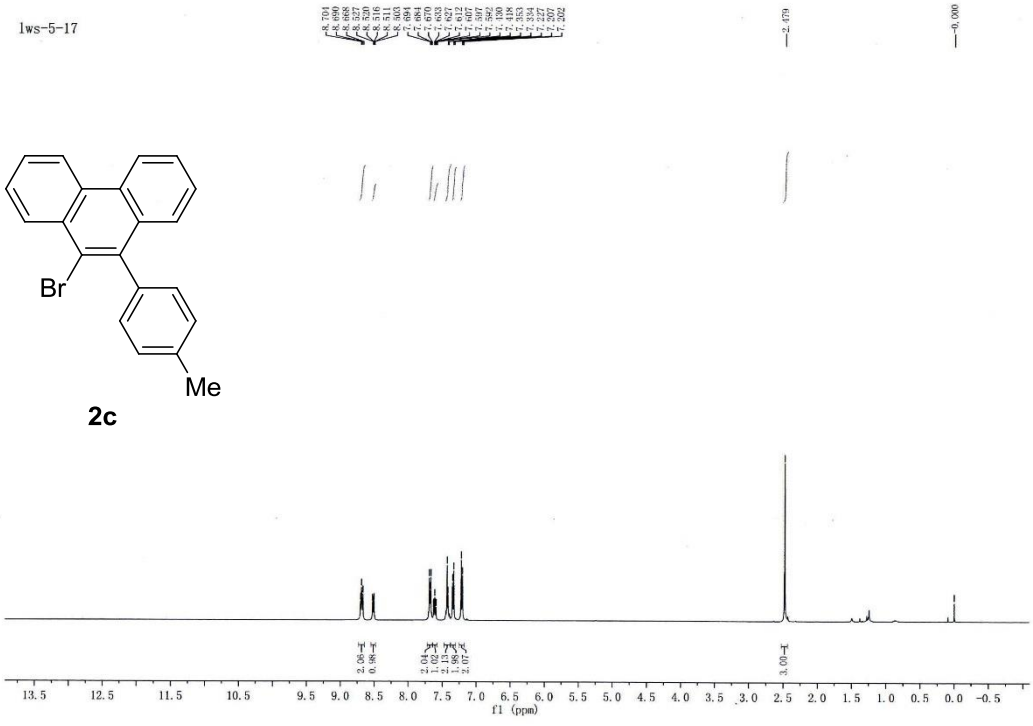
lws-5-66



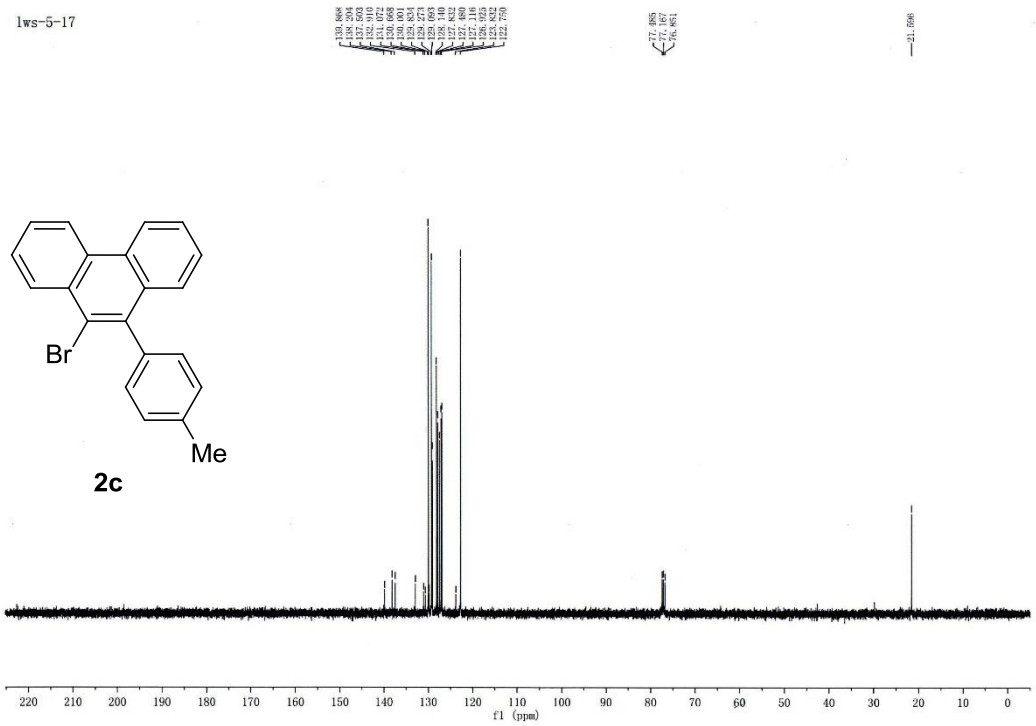
lws-5-66



lws-5-17

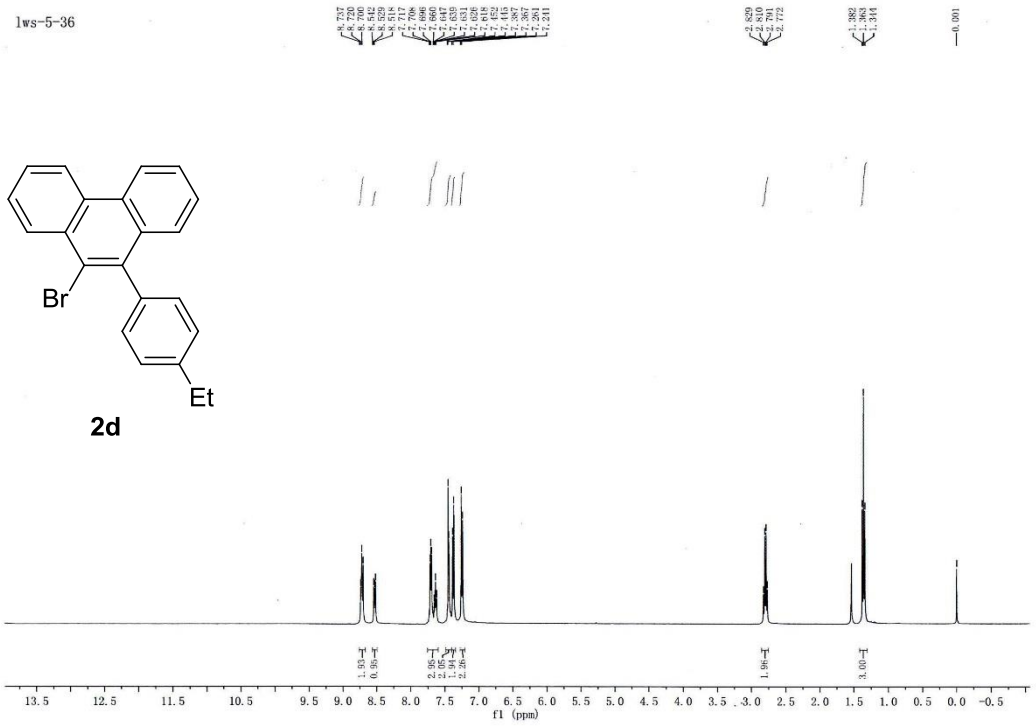


lws-5-17



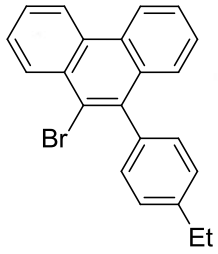
2c

lws-5-36

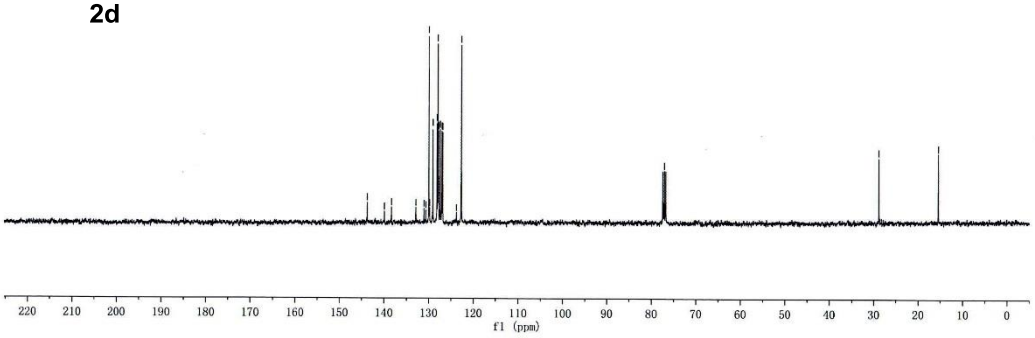


2d

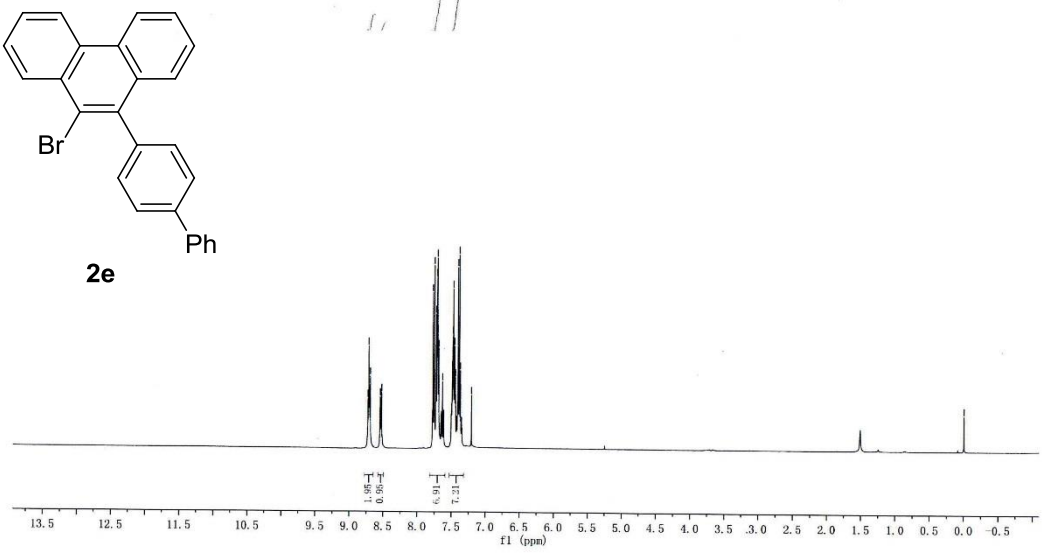
lws-5-36



2d

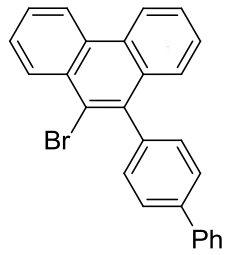


lws-5-37

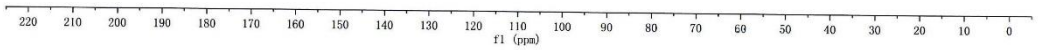


2e

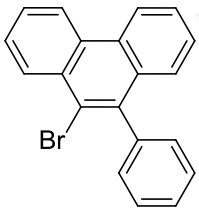
lws-5-37



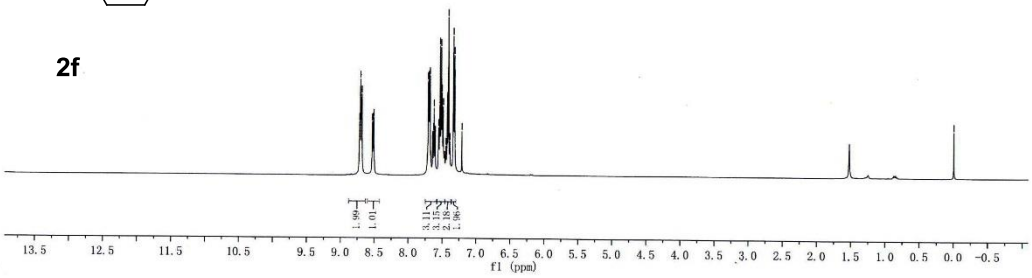
2e

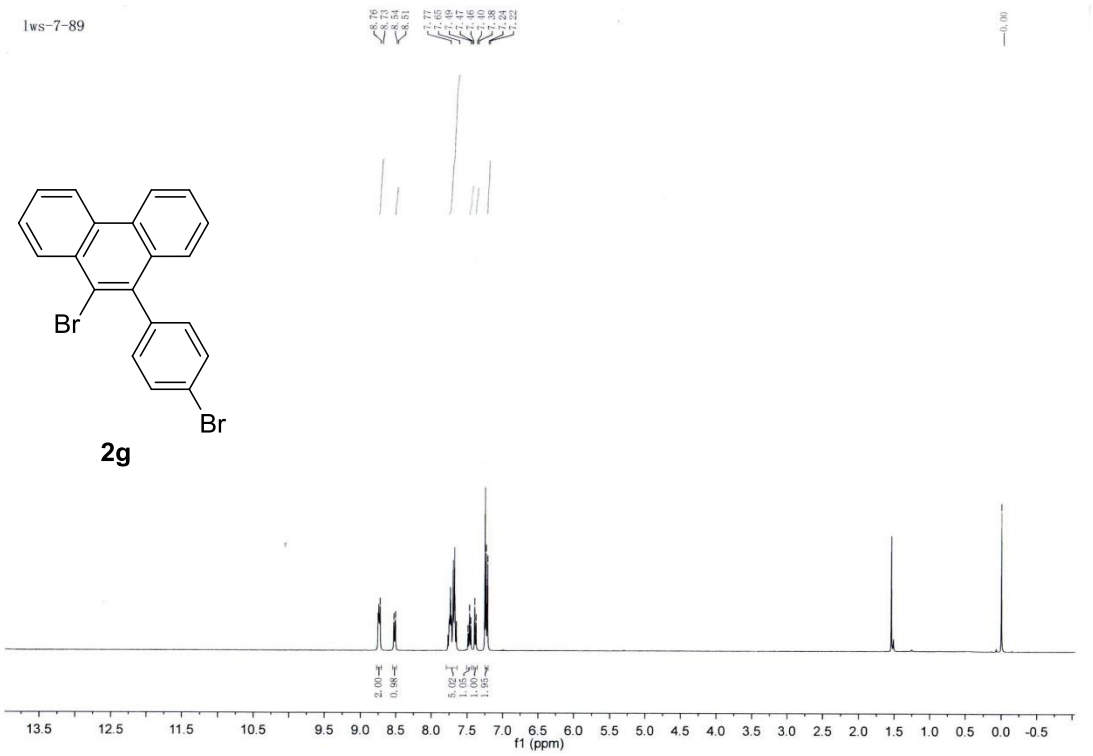


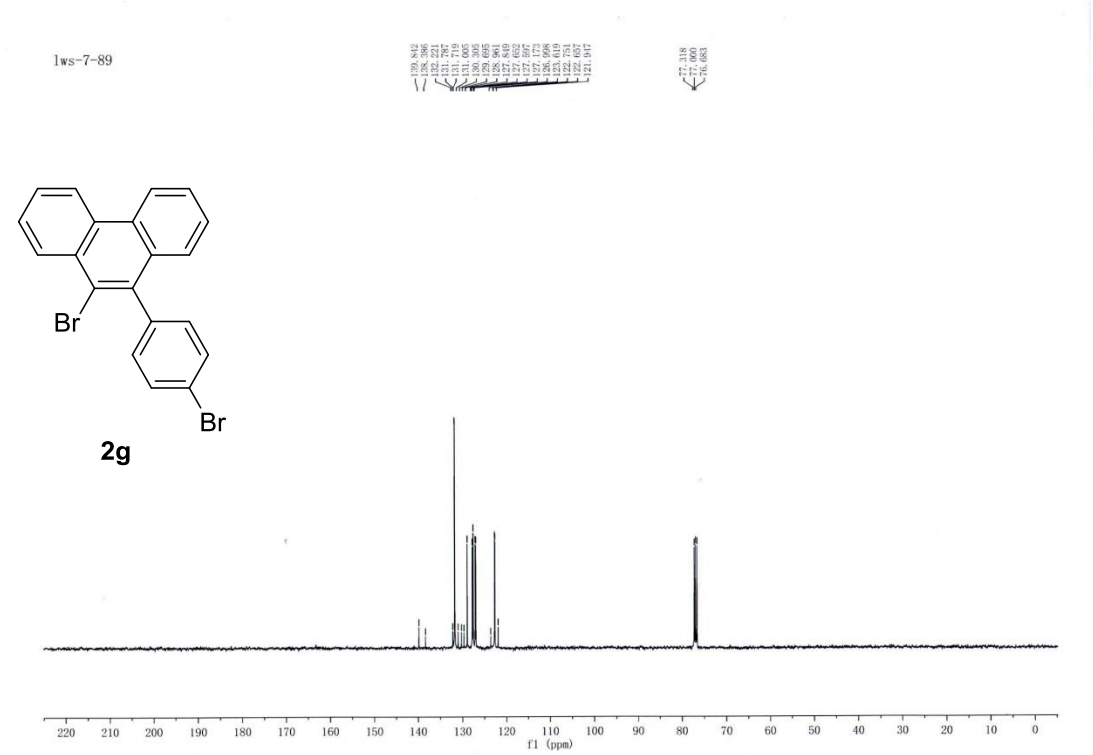
lws-5-7

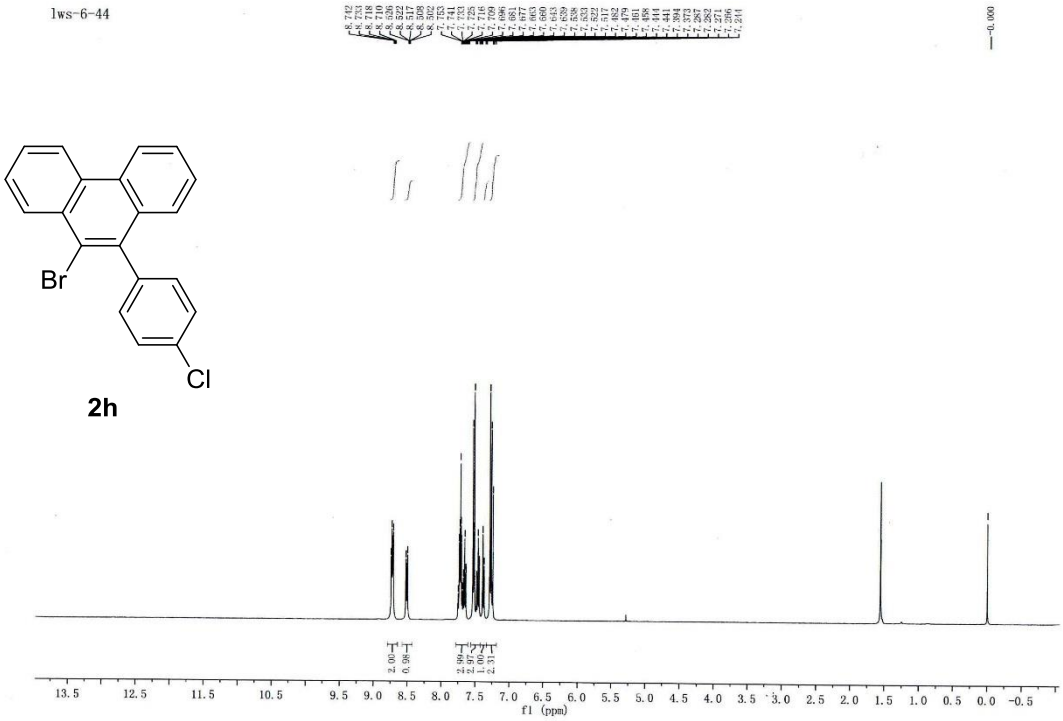


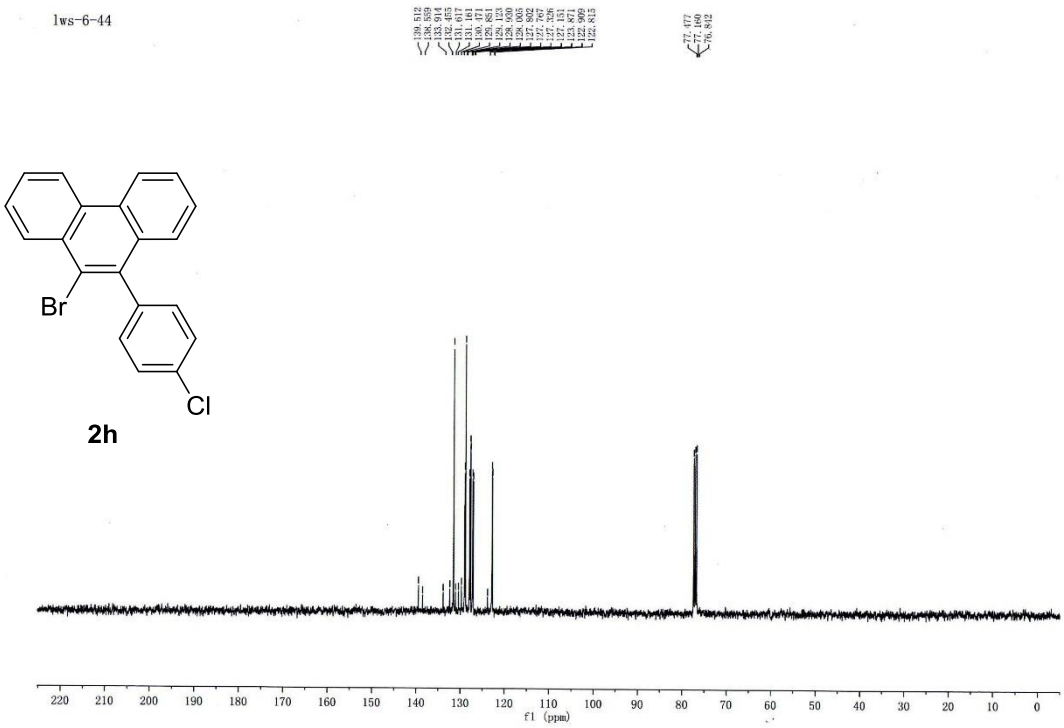
2f



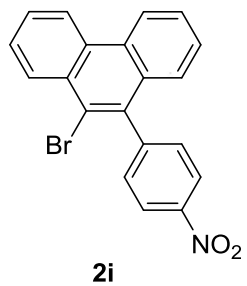

lws-7-89
Br
Br
2g
f1 (ppm)


lws-7-89
Br
Br
2g
f1 (ppm)

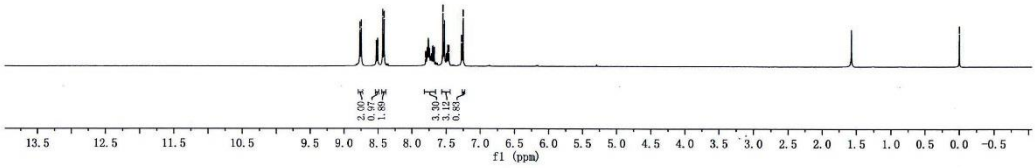

lws-6-44
Br
Cl
2h
f1 (ppm)


lws-6-44
Br
Cl
2h
f1 (ppm)

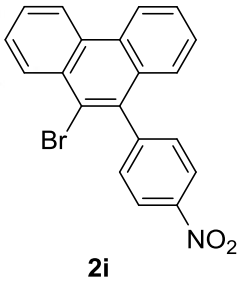
lws-6-54



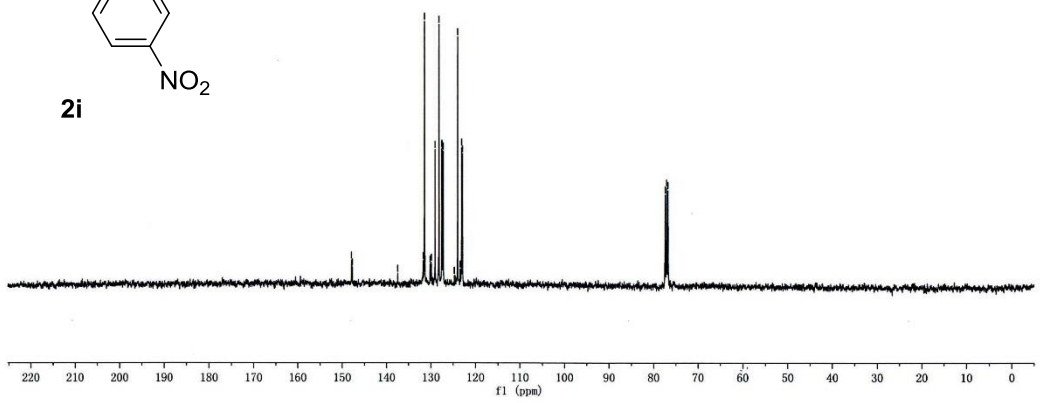
2i

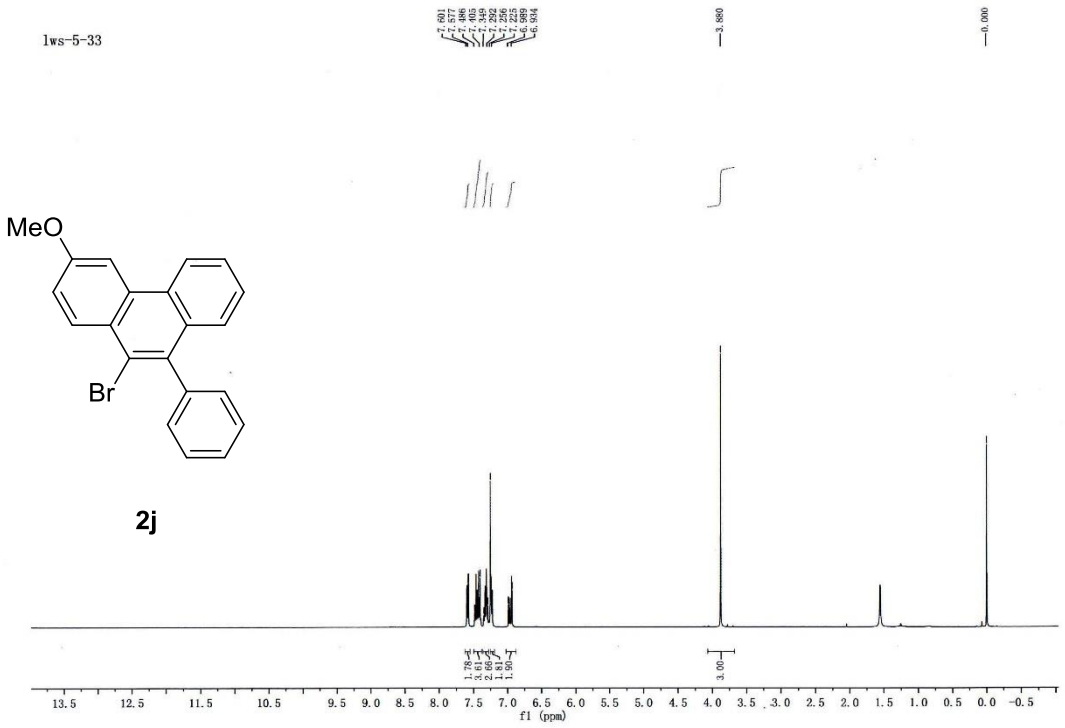


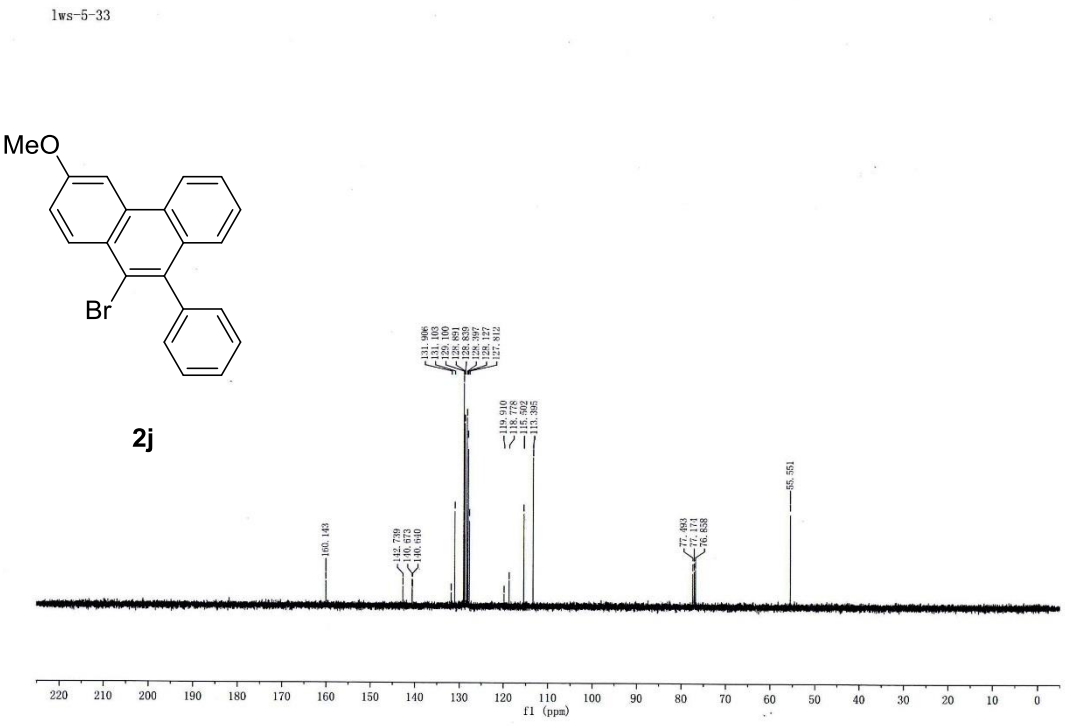
lws-6-54

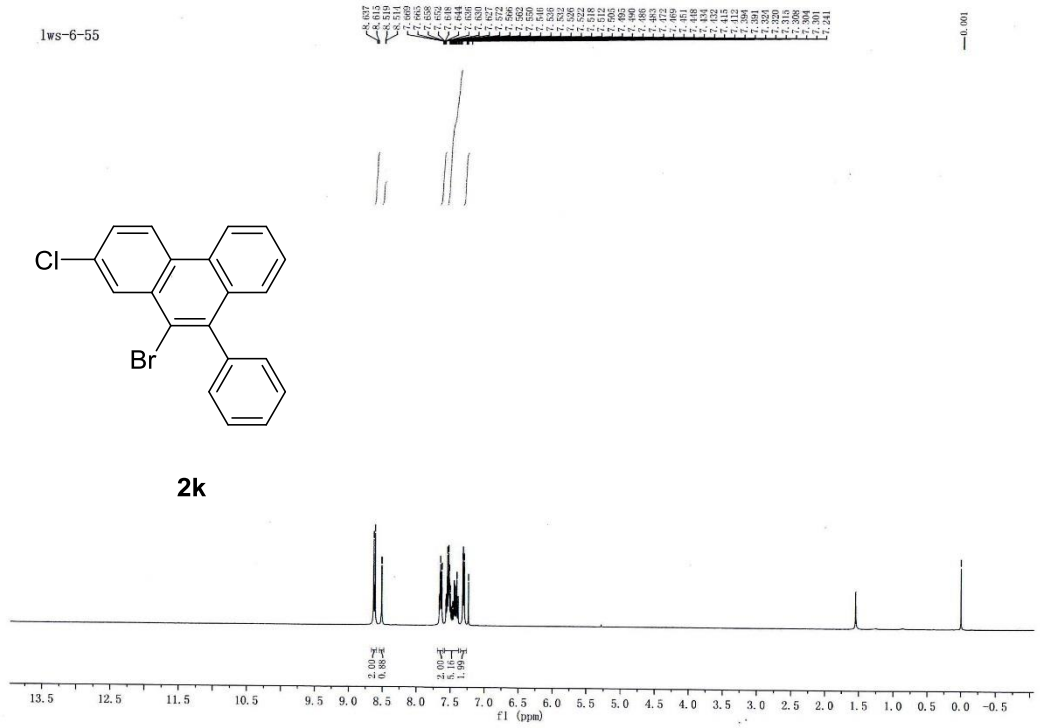


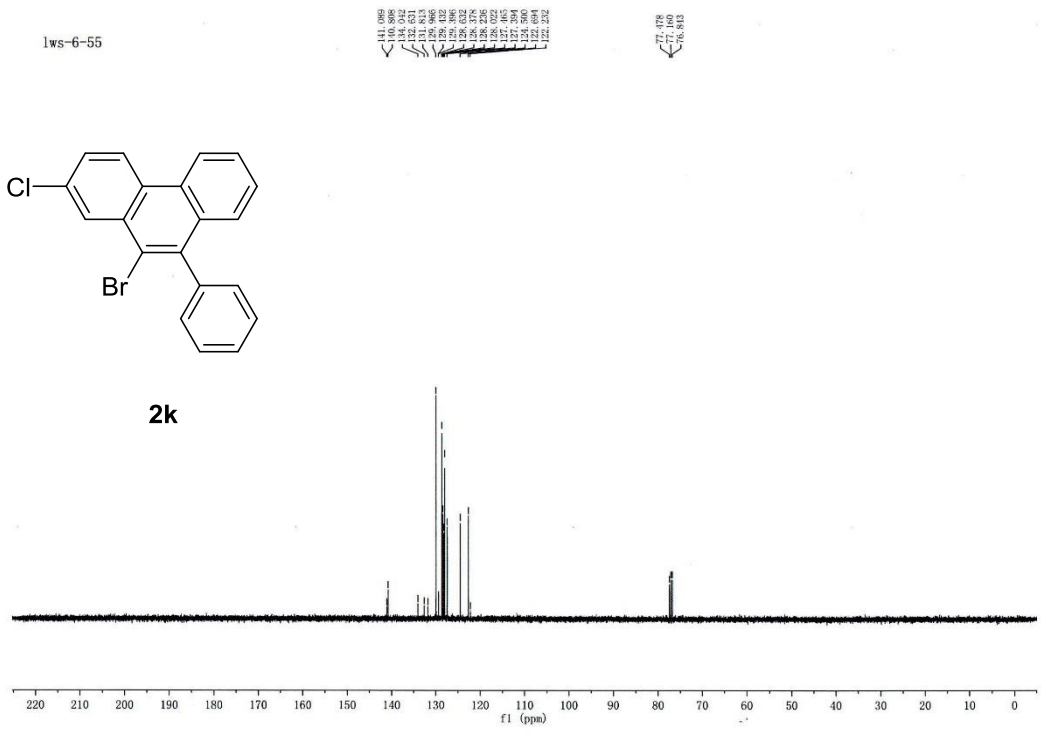
2i

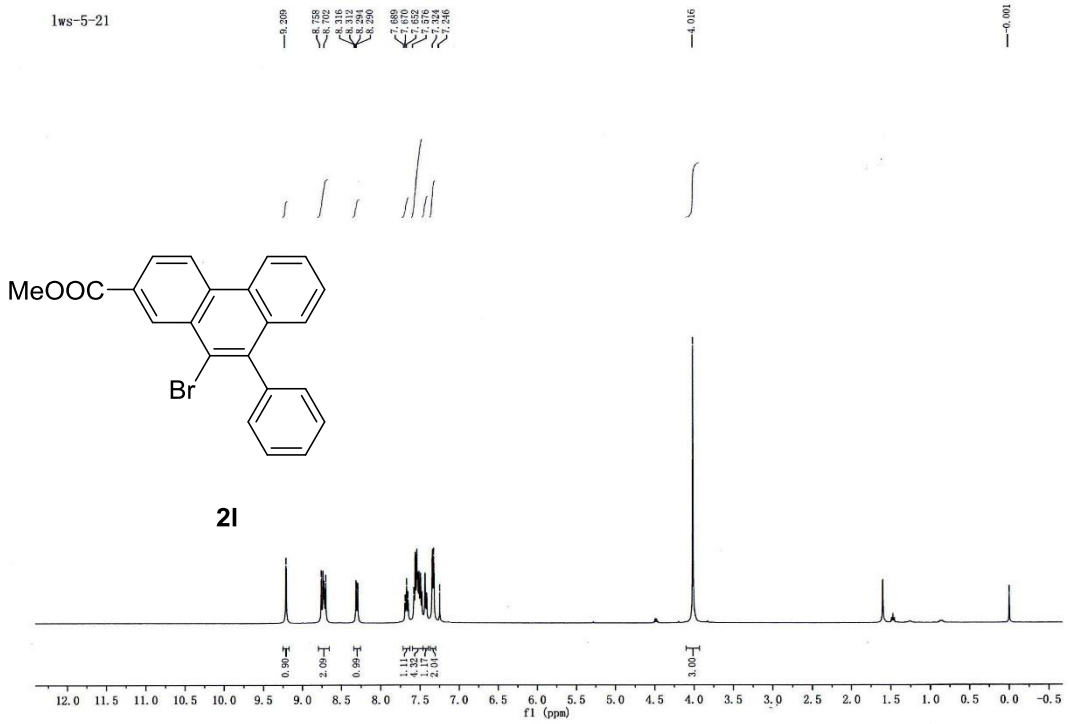


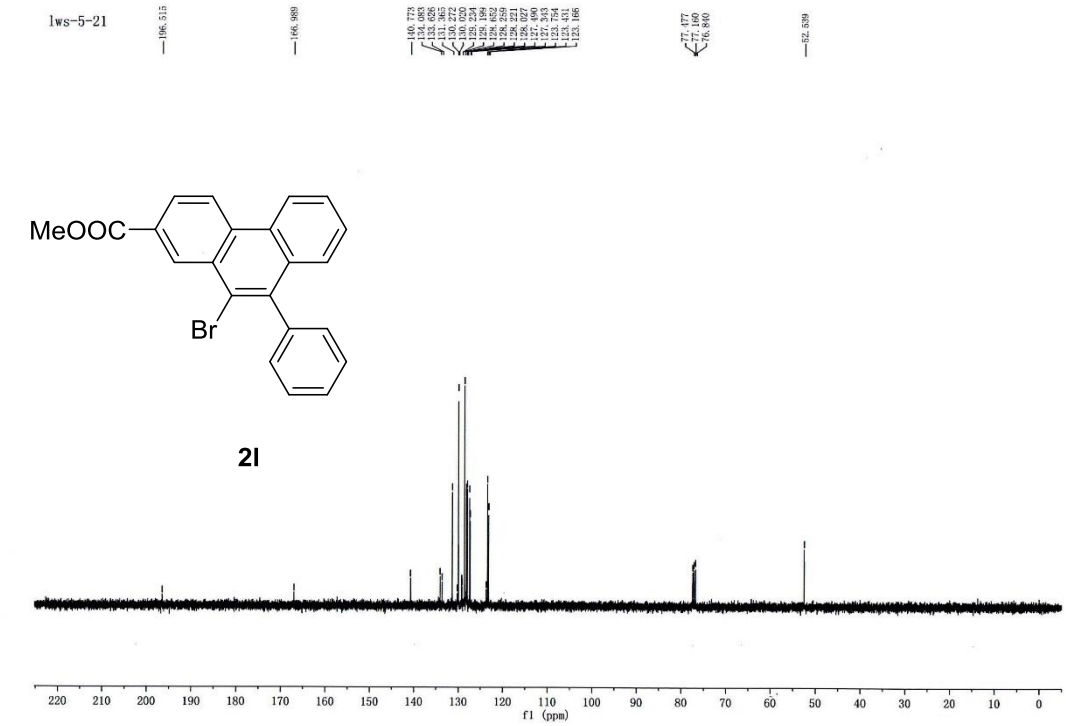

lws-5-33
MeO
Br
2j
f1 (ppm)

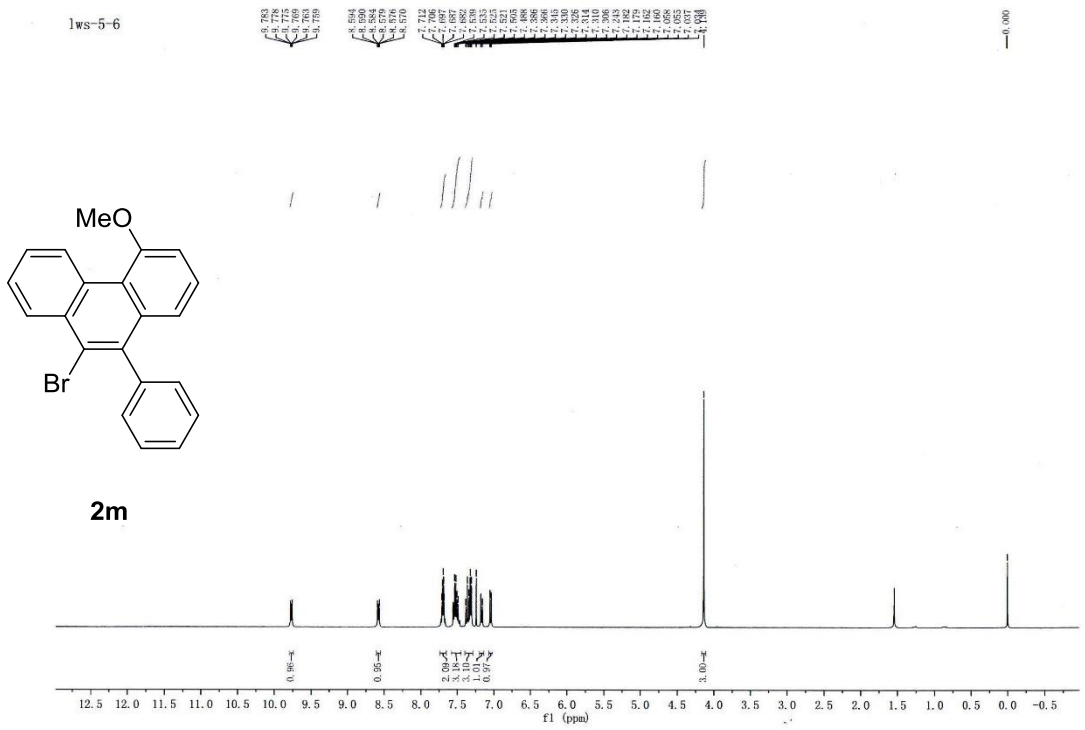

lws-5-33
MeO
Br
2j
f1 (ppm)

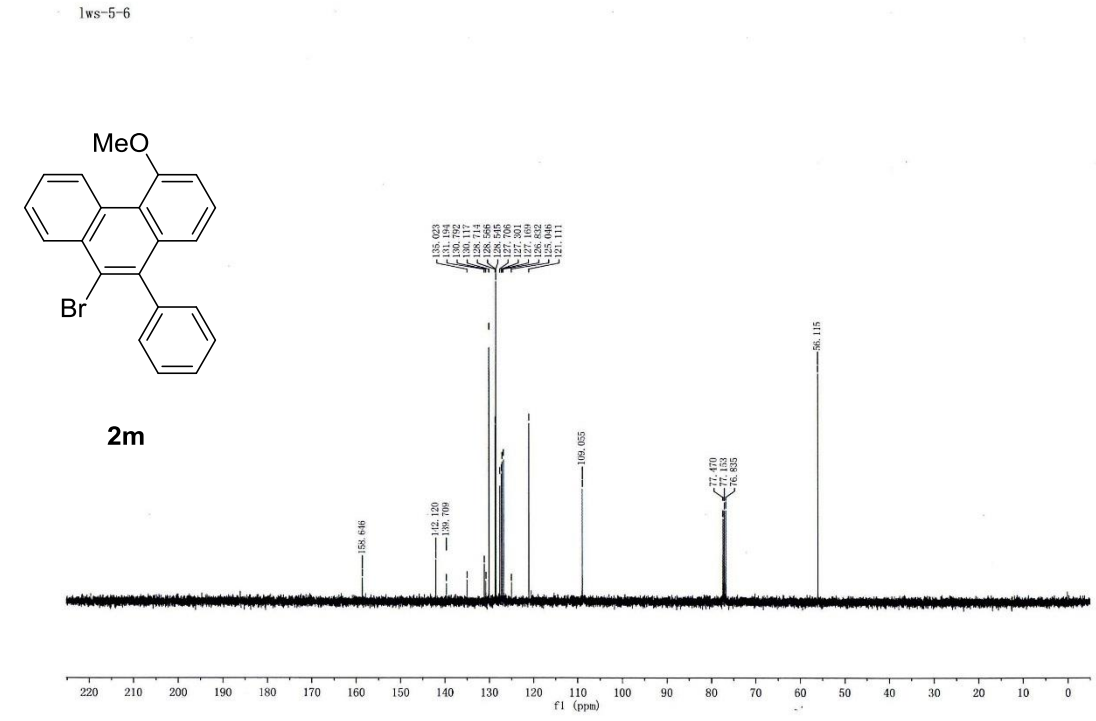

lws-6-55
Cl
Br
2k
f1 (ppm)

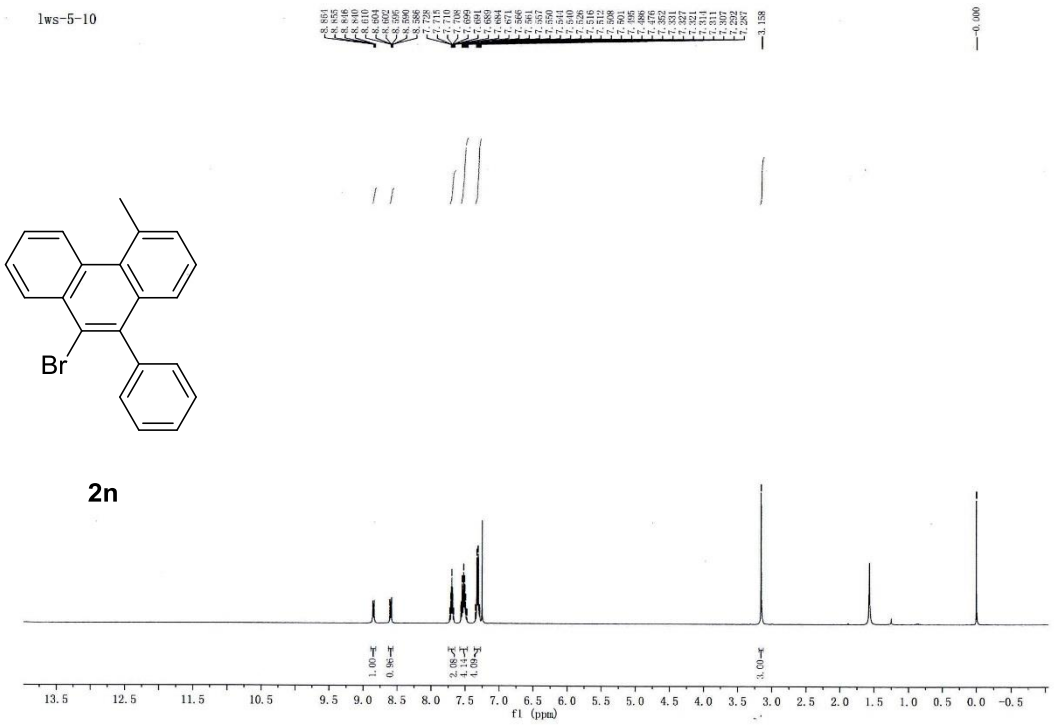

lws-6-55
Cl
Br
2k
f1 (ppm)

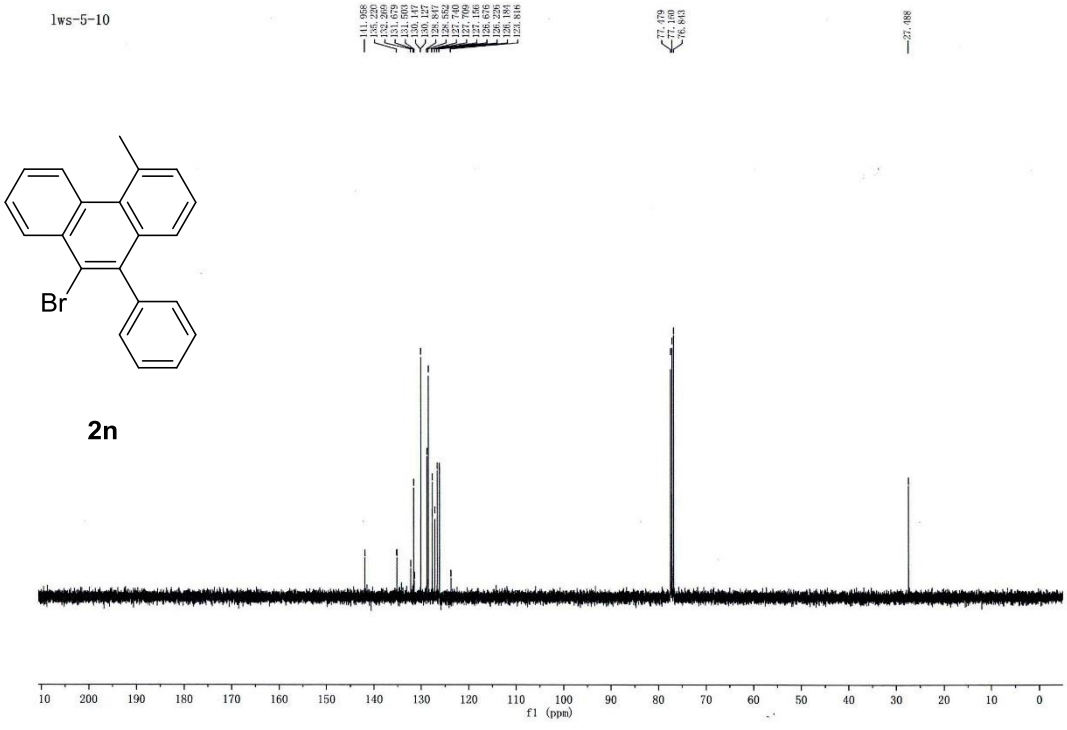

lws-5-21
MeOOC
Br
2l
f1 (ppm)

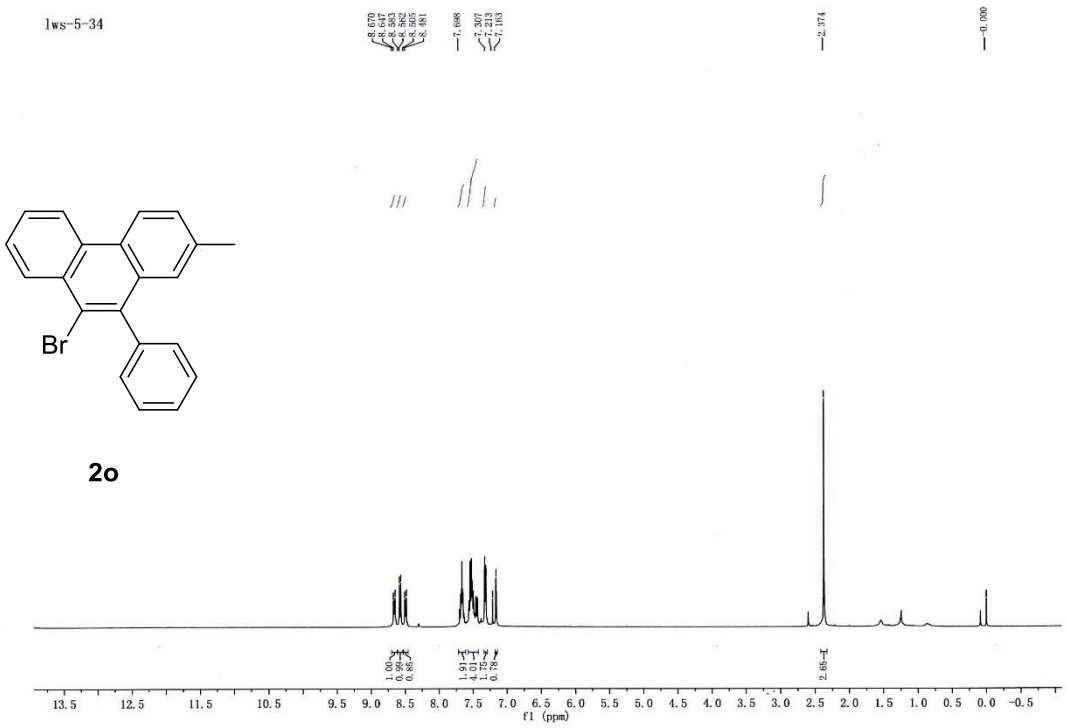

lws-5-21
MeOOC
Br
2l
f1 (ppm)


lws-5-6
MeO
Br
2m
f1 (ppm)

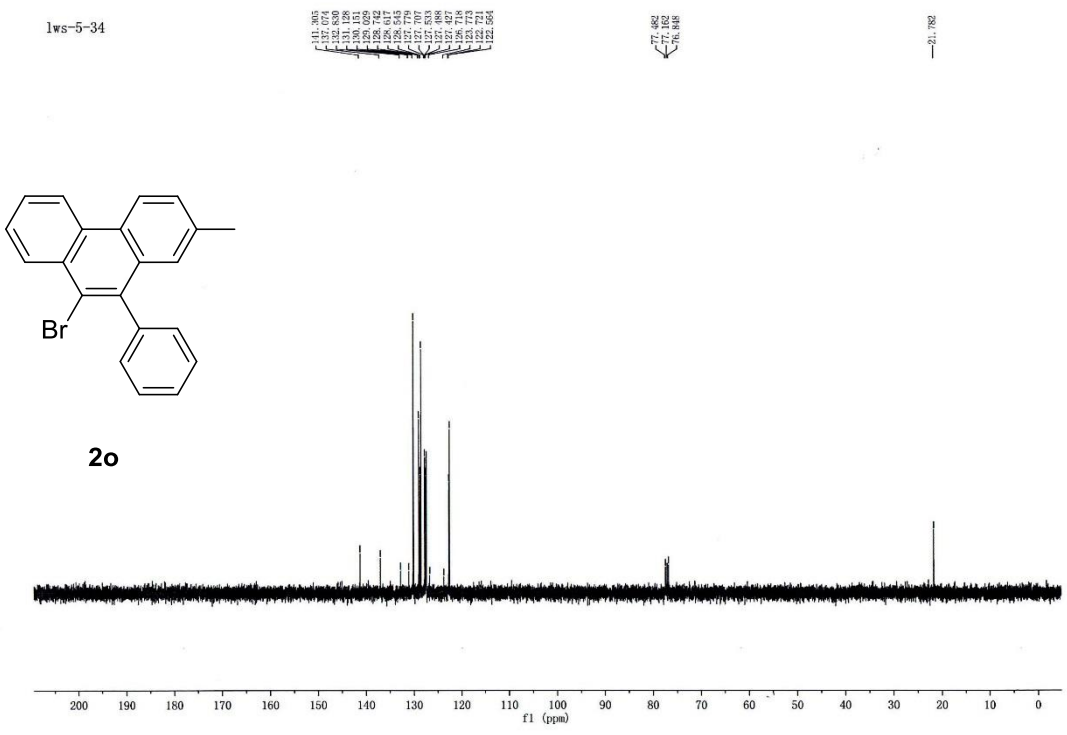

lws-5-6
MeO
Br
2m
f1 (ppm)


lws-5-10
Br
2n
1.00
0.96
2.08
4.14
1.09
3.00
f1 (ppm)

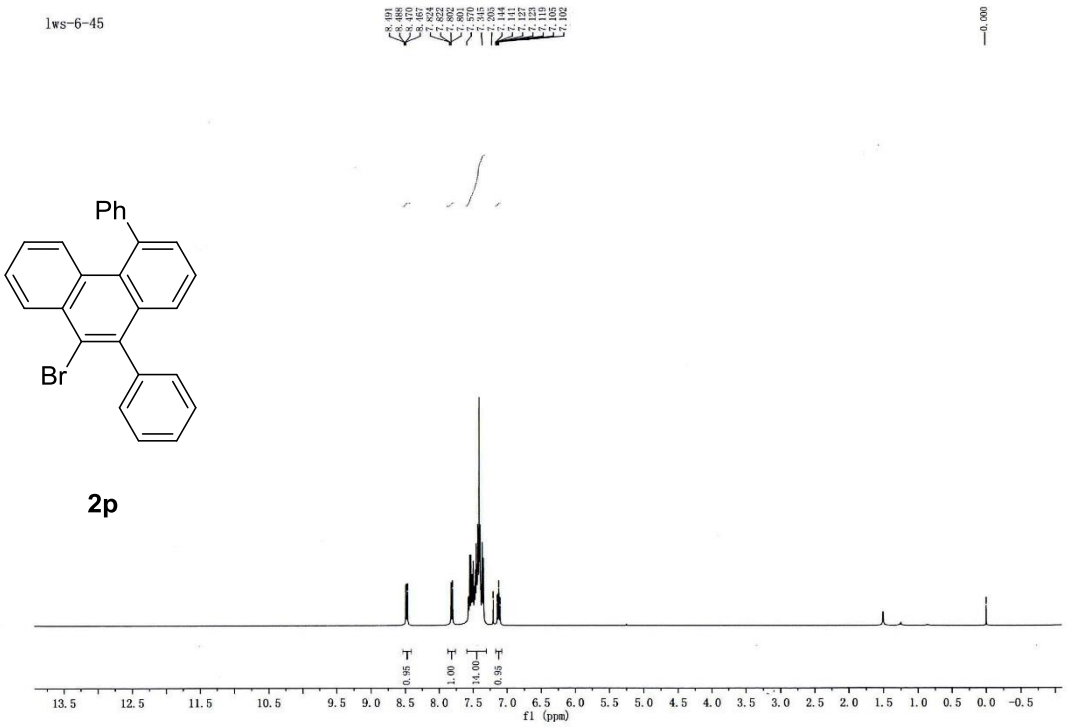

lws-5-10
Br
2n
f1 (ppm)

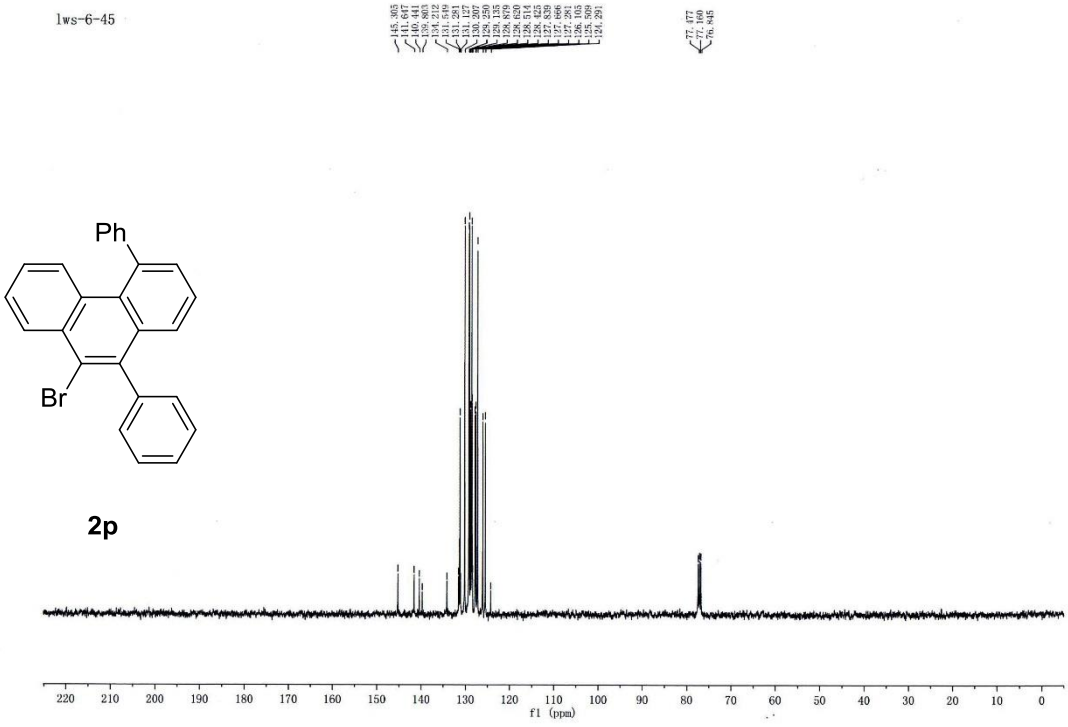

lws-5-34
8.670
8.647
8.583
8.562
8.505
8.481
7.648
7.307
7.213
7.103
2.374
-0.000
Br
1.00
0.99
0.85
1.91
4.01
1.15
0.78
2.65
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

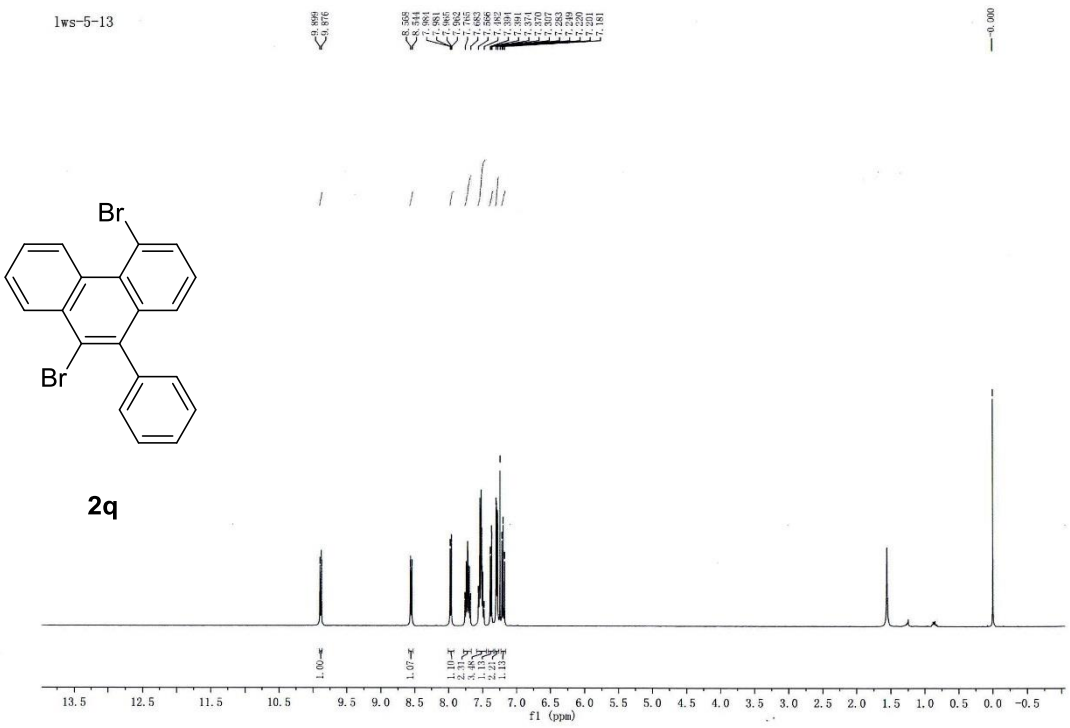
2o

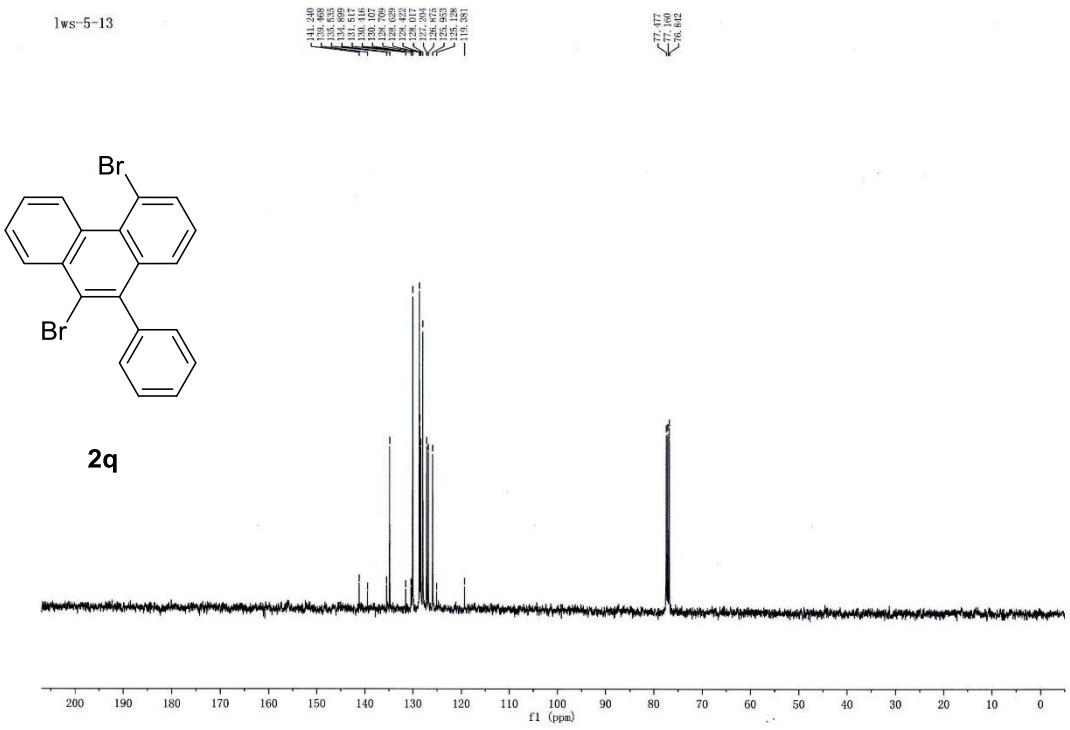

lws-5-34
141.305
137.074
132.830
131.106
130.151
129.029
128.742
128.617
128.545
127.779
127.707
127.553
127.488
127.427
127.274
125.774
122.721
122.564
77.482
77.162
76.848
21.782
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

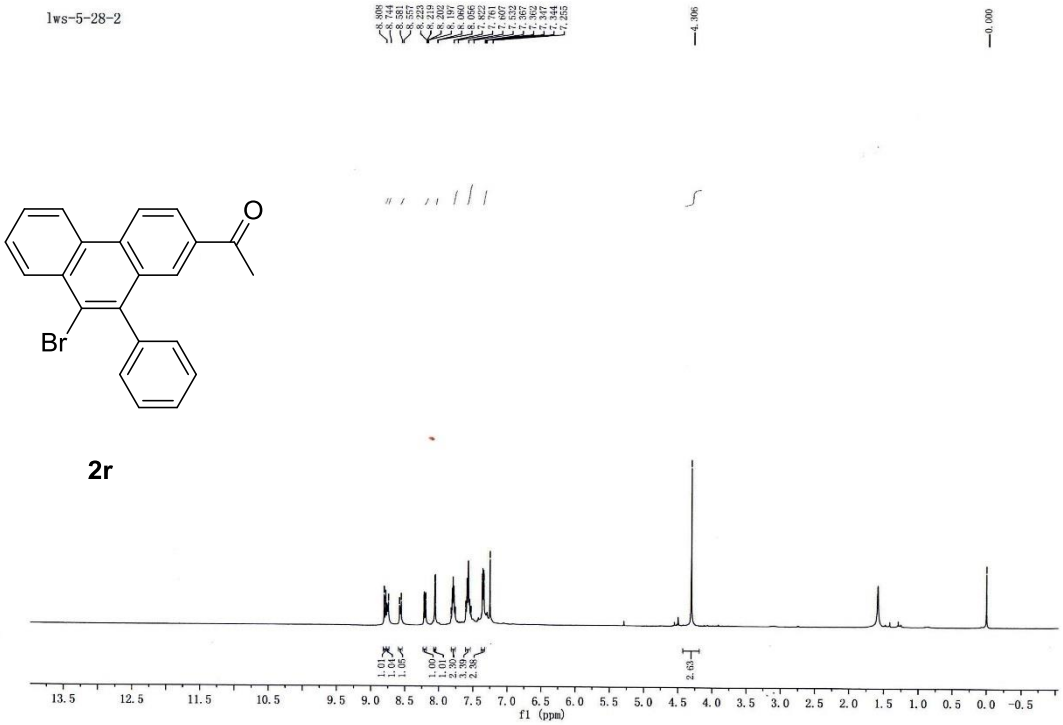
2o

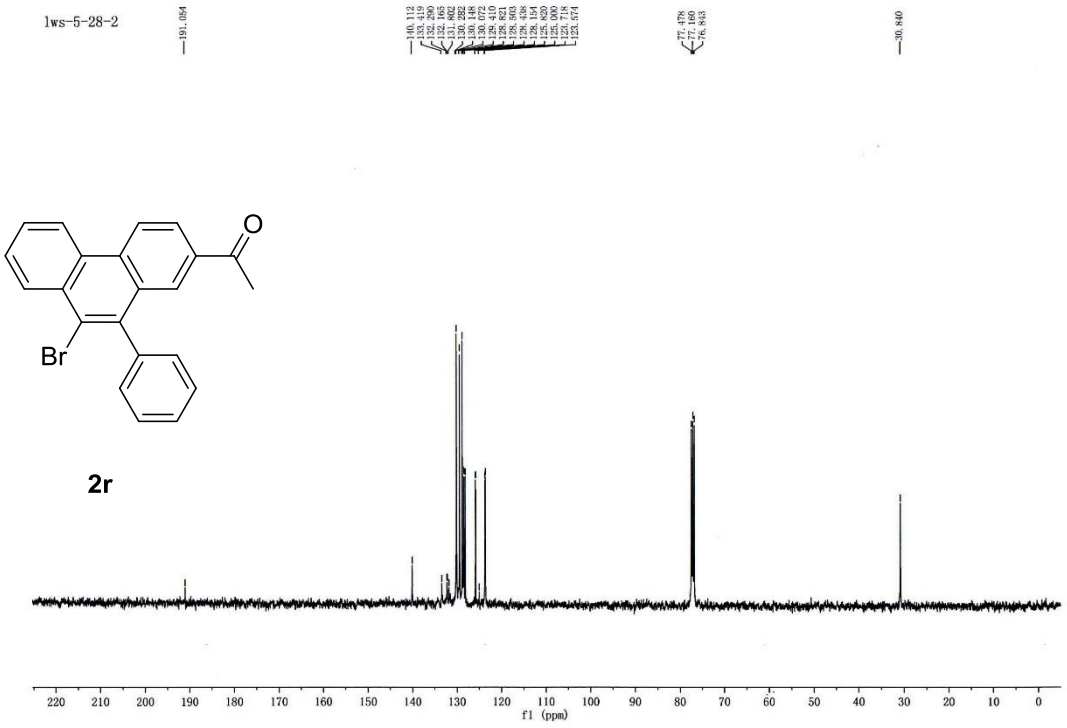

lws-6-45
Ph
Br
2p
0.95
1.00
14.00
0.95
f1 (ppm)

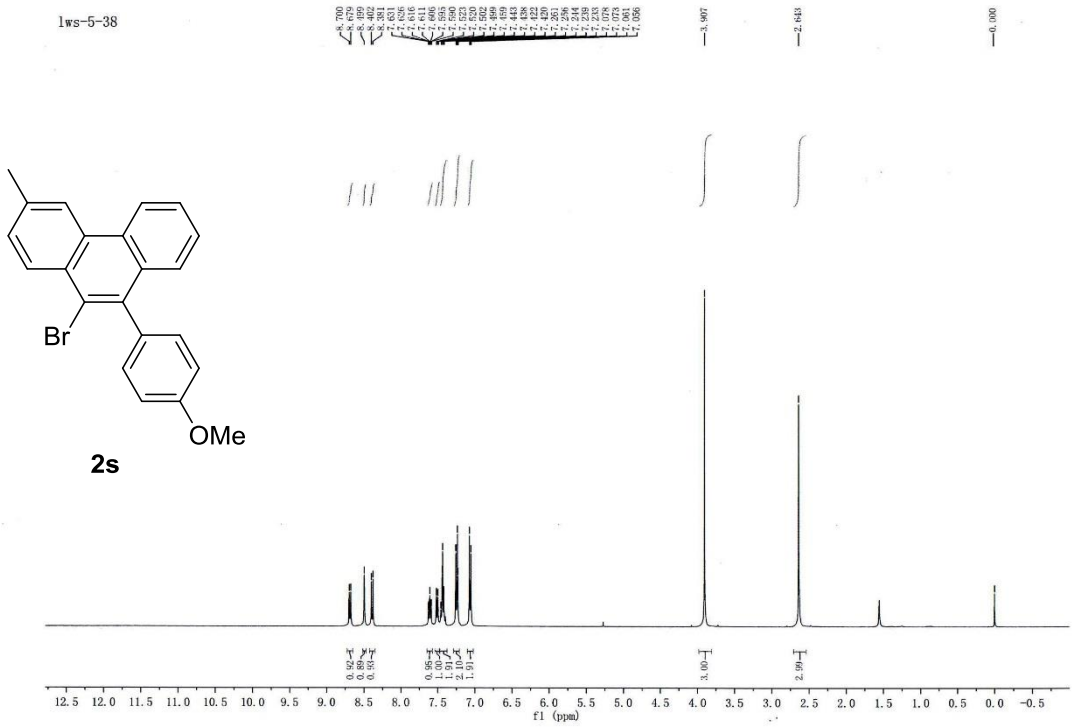

lws-6-45
Ph
Br
2p
f1 (ppm)

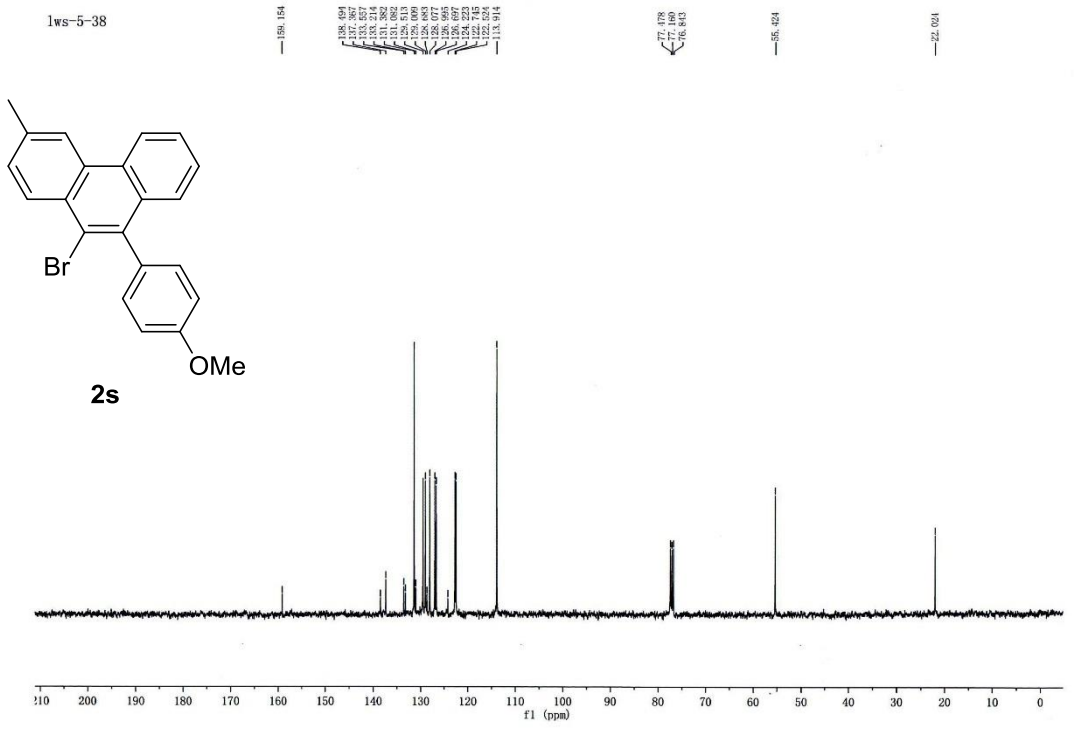

lws-5-13
Br
Br
2q
f1 (ppm)


lws-5-13
Br
Br
2q
f1 (ppm)

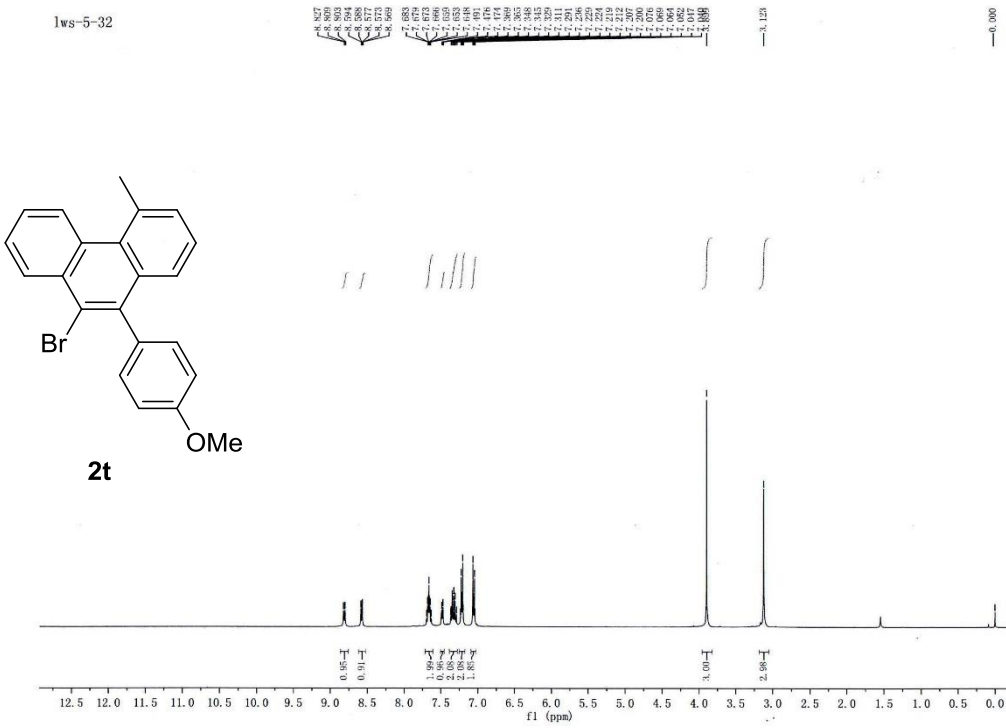

lws-5-28-2
8.898
8.644
8.581
8.557
8.223
8.219
8.202
8.197
8.060
8.055
7.852
7.761
7.697
7.692
7.367
7.302
7.347
7.344
7.255
4.906
0.000
O
Br
2r
1.01
1.04
1.00
2.30
3.39
2.38
2.63
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


lws-5-28-2
191.054
140.112
133.419
132.490
131.802
130.382
130.072
129.410
128.821
128.660
128.438
128.154
125.620
125.000
123.718
123.574
77.478
77.160
76.843
30.840
O
Br
2r
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)

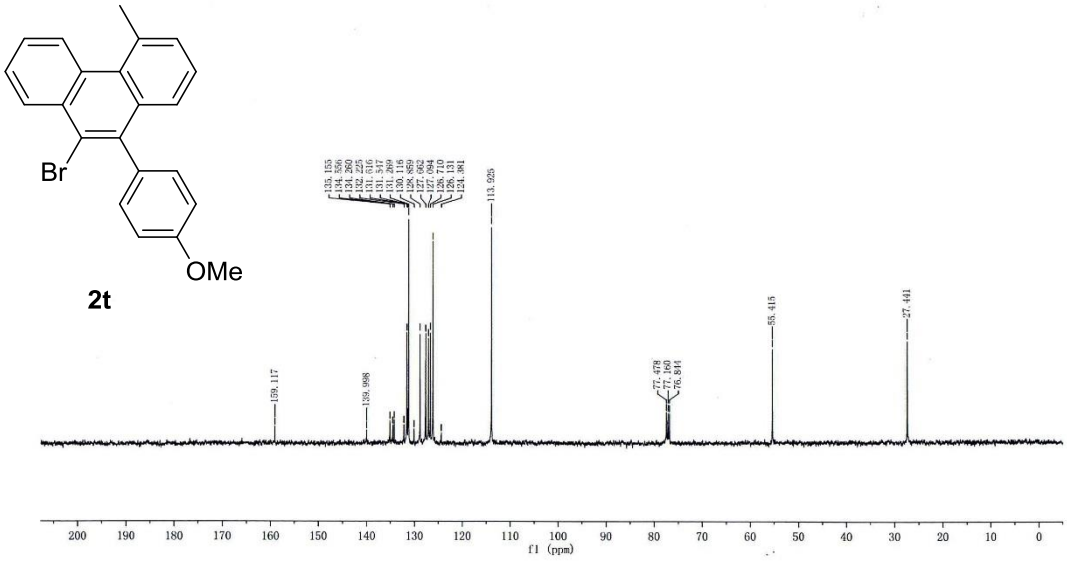

lws-5-38
Br
OMe
2s
f1 (ppm)

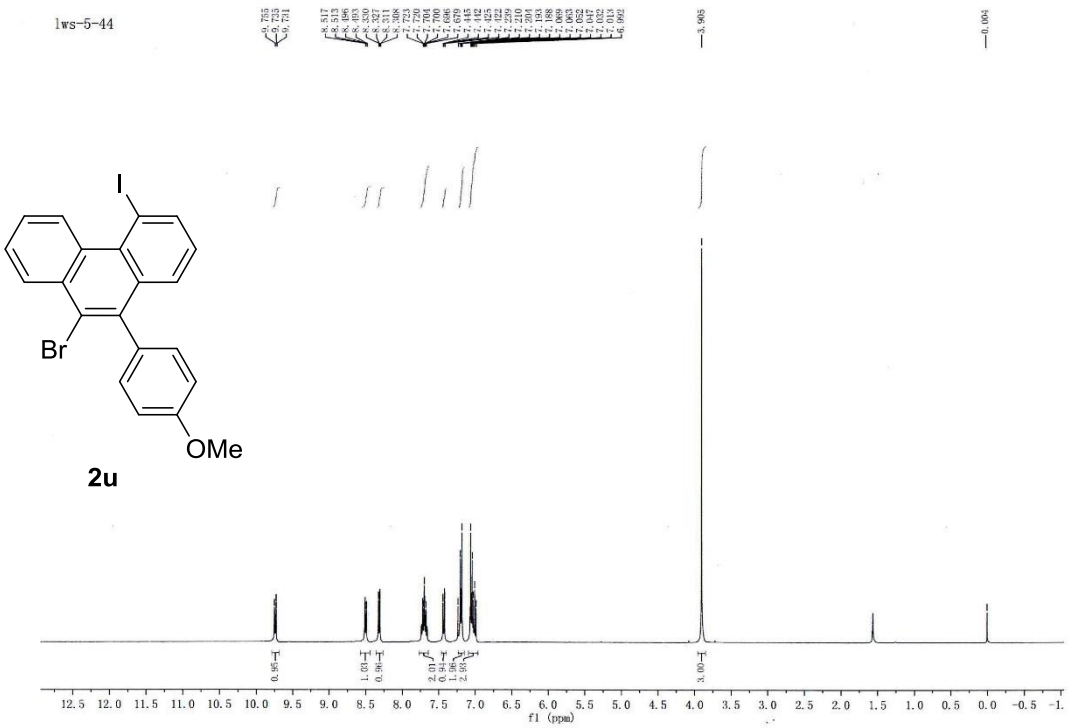

lws-5-38
Br
OMe
2s
f1 (ppm)

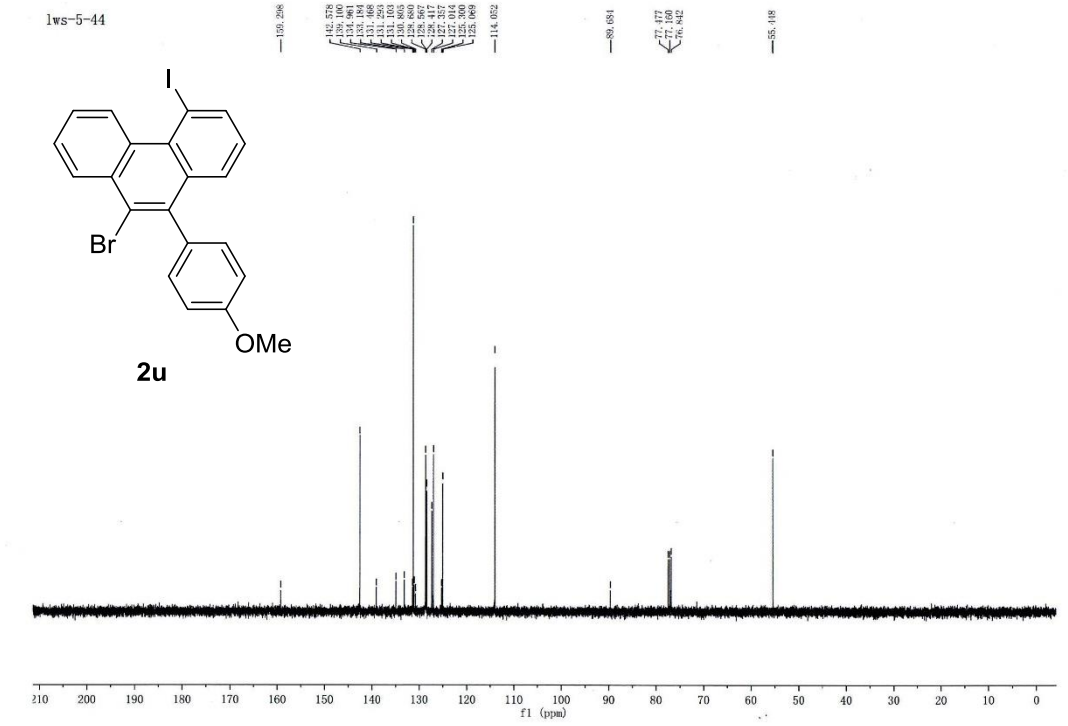
lws-5-32

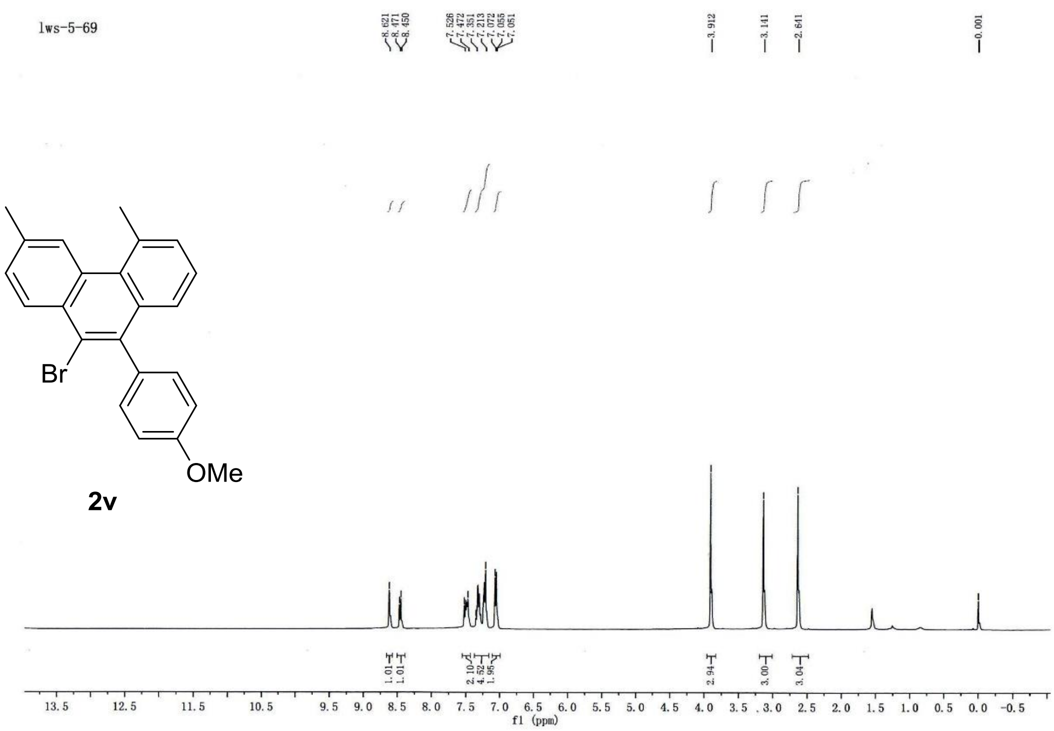


lws-5-32

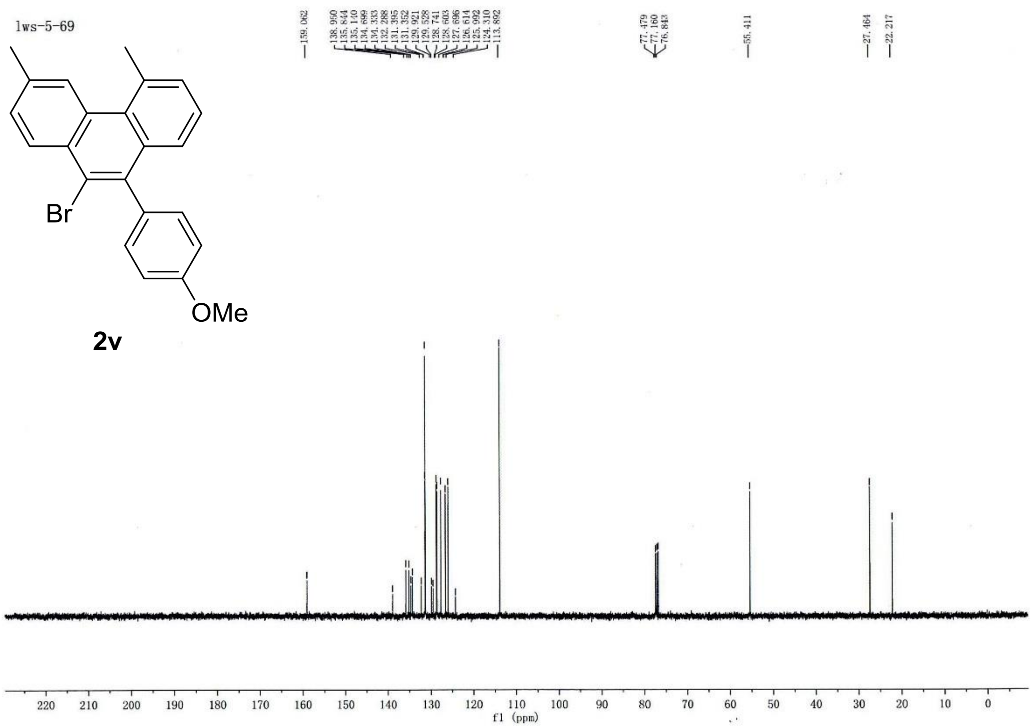



lws-5-44
I
Br
OMe
2u
f1 (ppm)

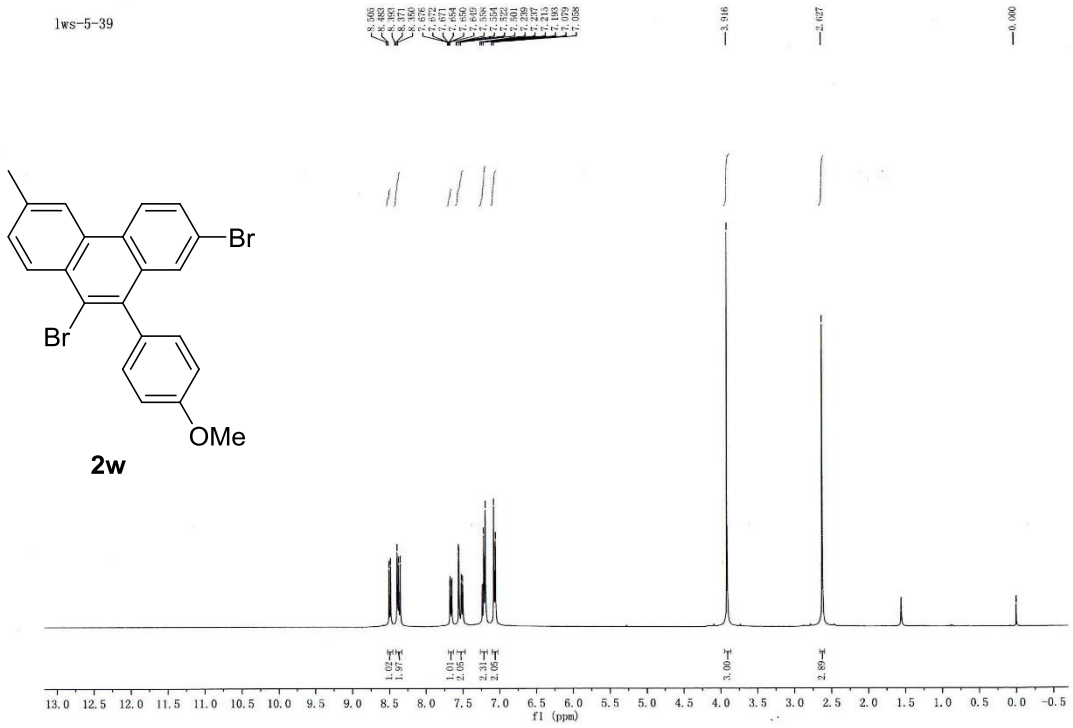

lws-5-44
I
Br
OMe
2u
f1 (ppm)

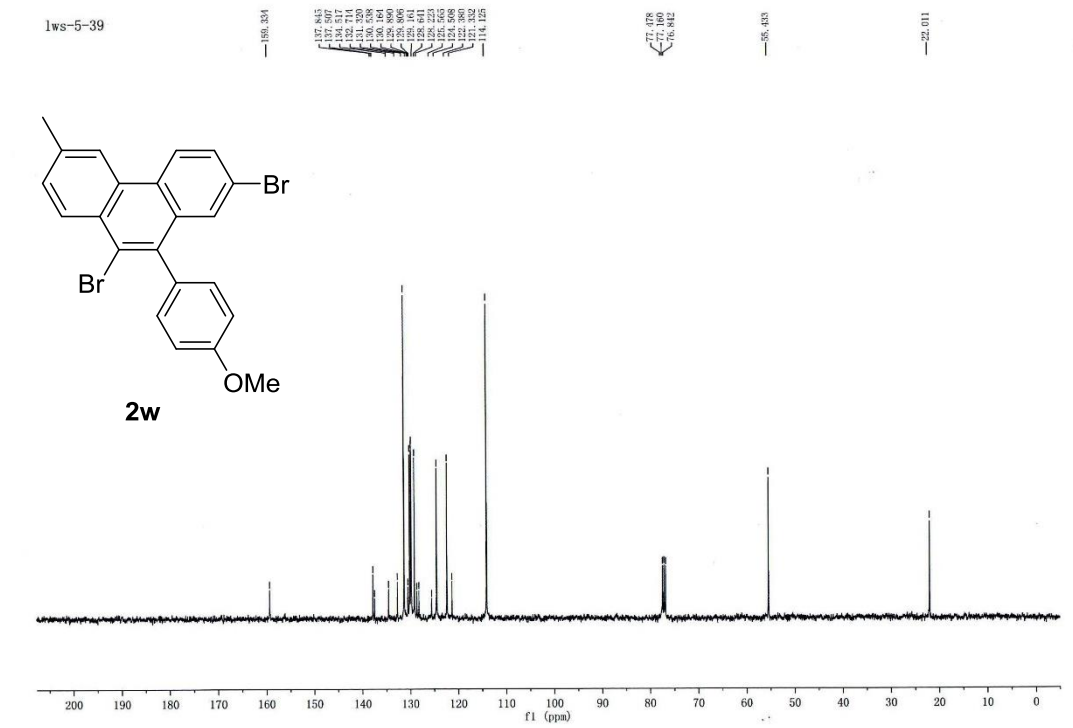

lws-5-69
8.621
8.471
8.450
7.526
7.472
7.351
7.213
7.072
7.055
7.051
3.912
3.141
2.641
0.001
Br
OMe
1.01
1.01
2.10
4.52
1.95
2.94
3.00
3.04
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

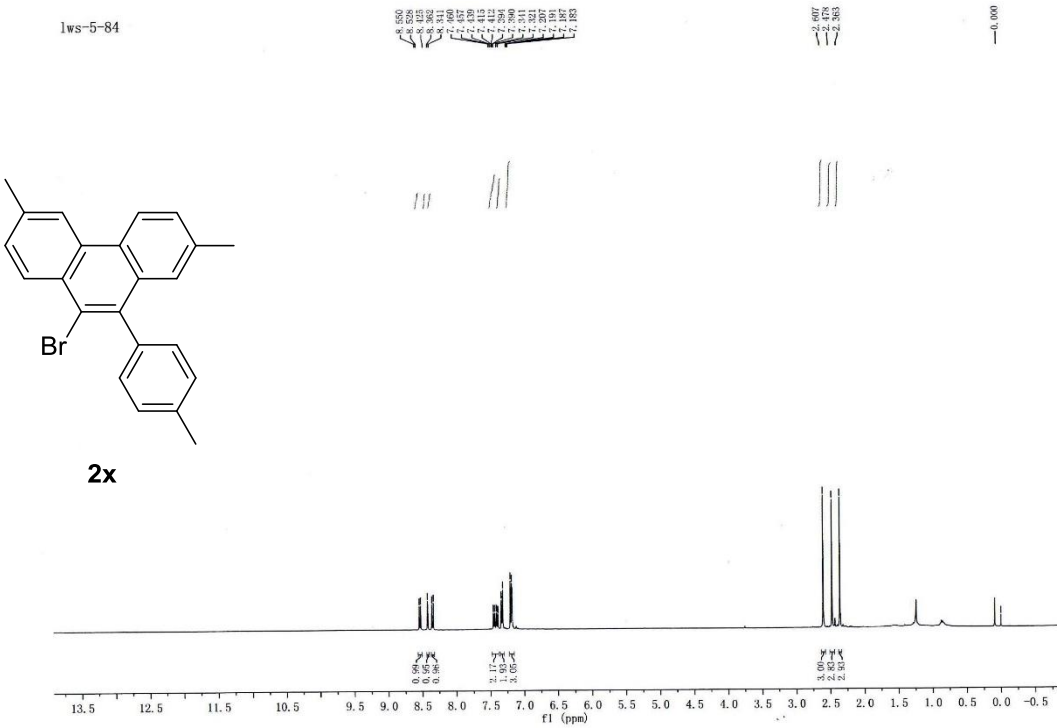
2v

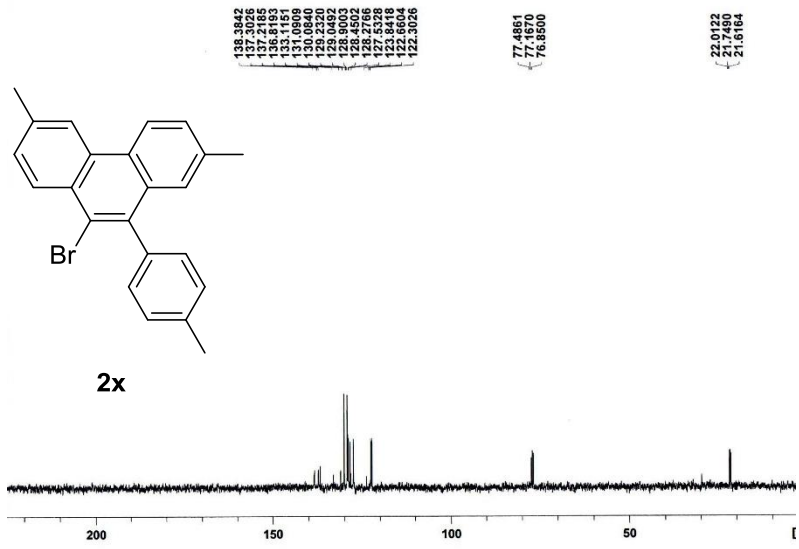

lws-5-69
159.062
138.950
135.844
135.110
134.699
134.333
132.288
131.395
131.352
129.921
129.528
128.741
128.603
127.896
126.614
125.992
124.310
113.892
77.479
77.160
76.843
55.411
27.464
22.217
Br
OMe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

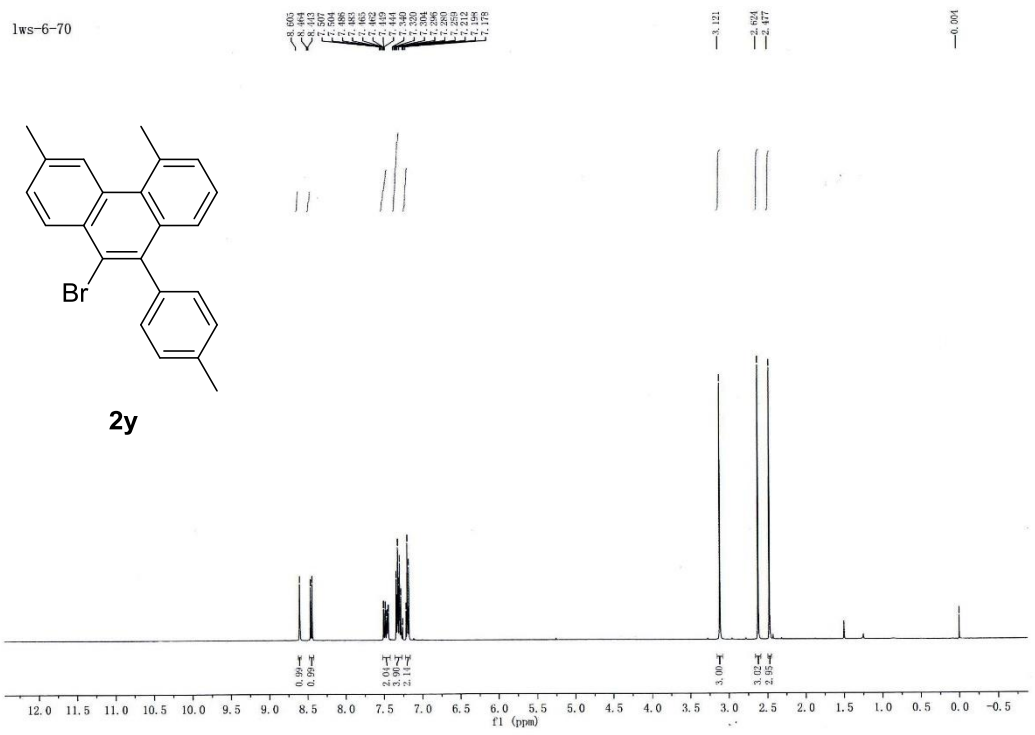
2v

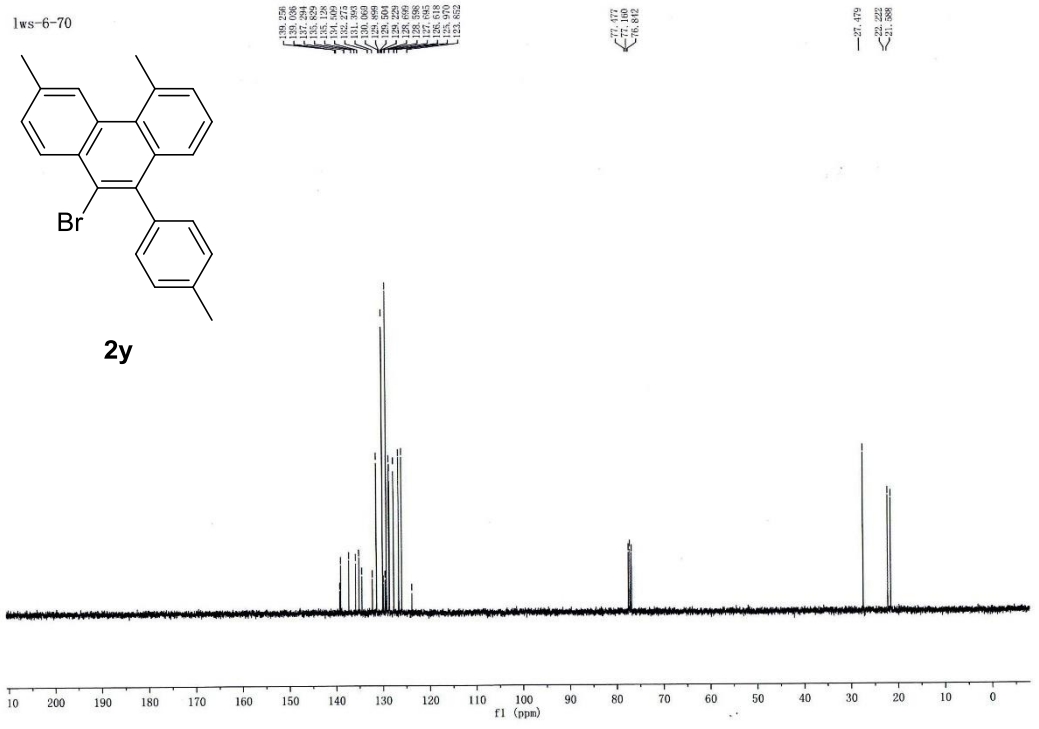

lws-5-39
Br
Br
OMe
2w
f1 (ppm)


lws-5-39
Br
Br
OMe
2w
f1 (ppm)


lws-5-84
Br
2x
fl (ppm)

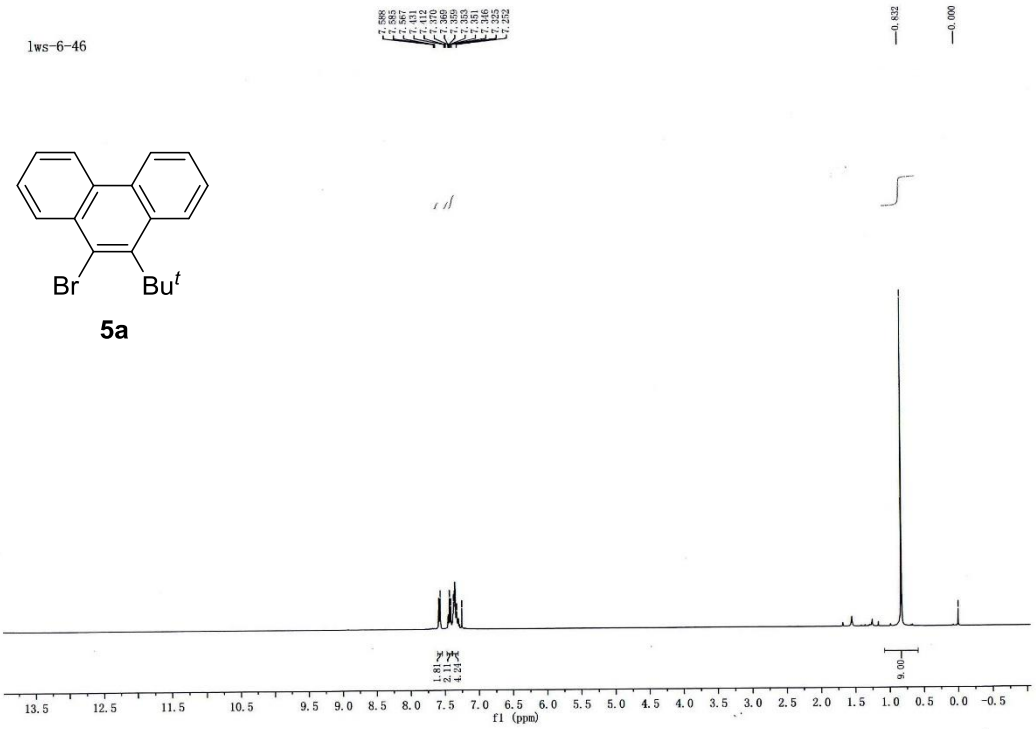

Br
2x


lws-6-70
Br
2y
f1 (ppm)

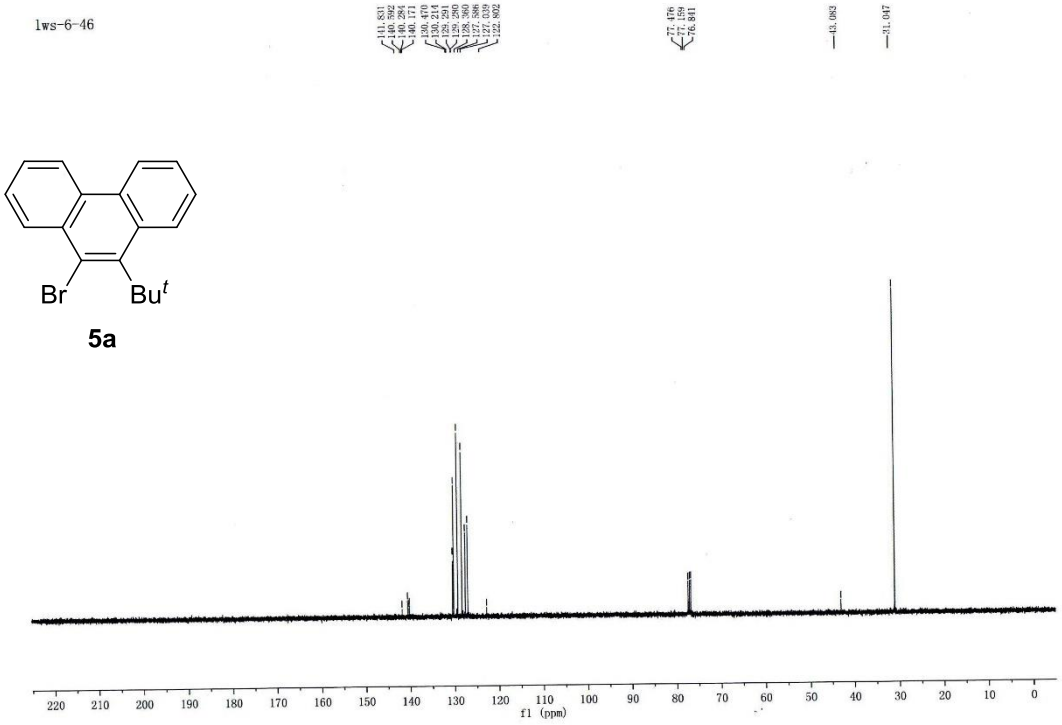

lws-6-70
Br
2y
f1 (ppm)

lws-6-46

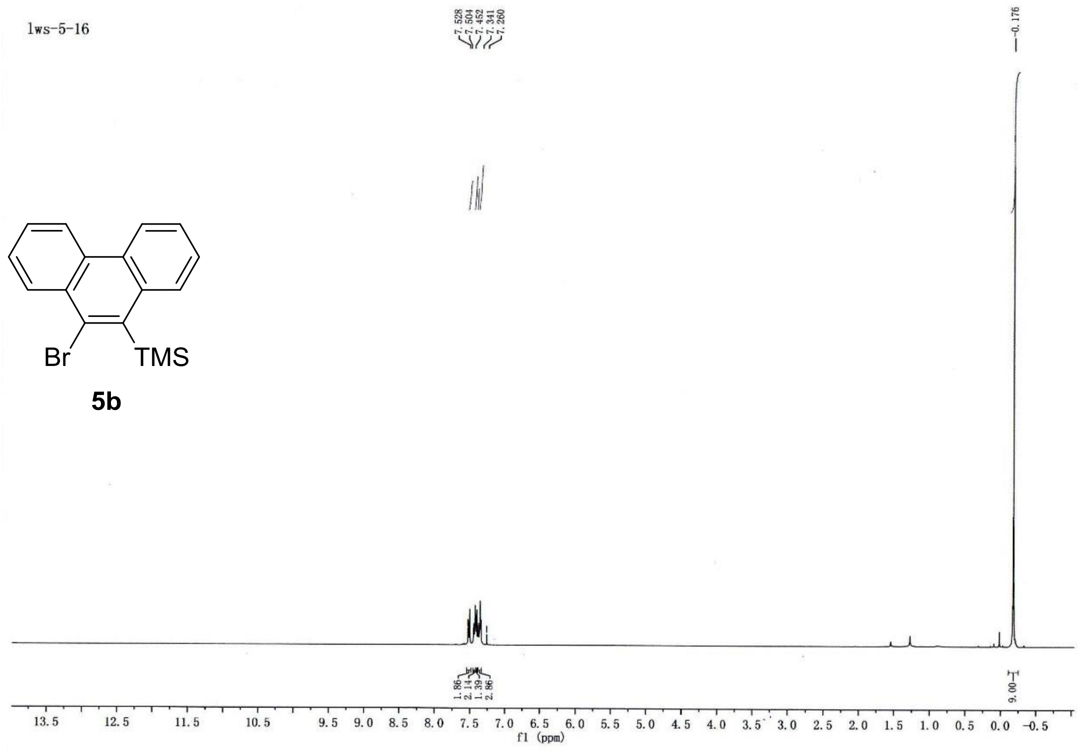
5a

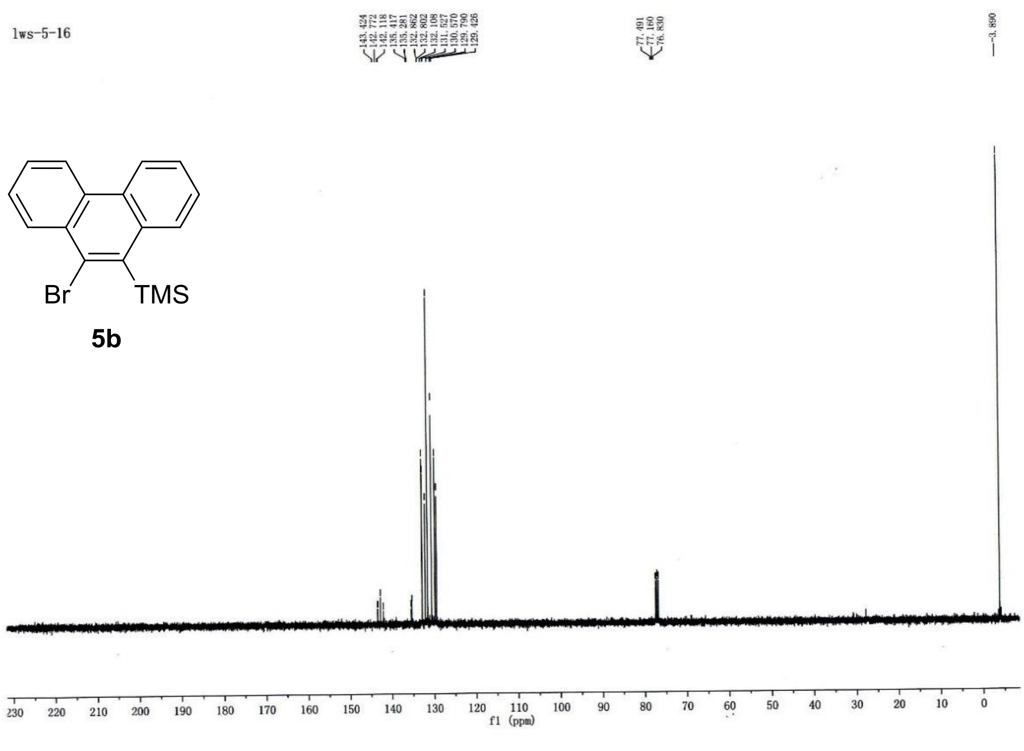


lws-6-46



5a


lws-5-16
7.528
7.504
7.452
7.341
7.260
-0.176
Br
TMS
5b
1.86
2.14
1.39
2.86
9.00
13.5 12.5 11.5 10.5 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)


lws-5-16
143.424
142.772
142.118
135.417
135.291
132.862
132.802
132.108
131.527
130.570
129.790
129.426
77.491
77.160
76.830
3.890
Br
TMS
5b
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)

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