Supporting Information

Tandem Rh-Catalyzed [4+2] Vinylic C−H *O*-Annulation of Exocyclic Enones with Alkynes and 1,5-H Shift

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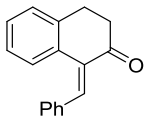
I. General Remarks

All commercial available reagents were used without further purification unless otherwise noted. DCE was dried through manual solvent purification system from Innovative Technology. DME were dried by refluxing over sodium and freshly distilled prior to use. $[Cp^*RhCl_2]_2$,[1] exocyclic enones **1**,[2] alkynes **2**,[3] and pyrylium tetrafluoroborate (**4**)[4] were prepared based on previous reports.

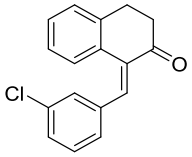
NMR spectra were measured on a Bruker AV II-400 MHz. The ^1H NMR (400 MHz) chemical shifts were recorded relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ 7.26 ppm, $(CD_3)_2CO$: δ 2.05 ppm, $(CD_3)_2SO$: δ 2.50 ppm, CD_3CN: δ 1.94 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ 77.16 ppm, $(CD_3)_2SO$: δ 39.52 ppm, CD_3CN: δ 1.32 ppm). High resolution mass spectra (HRMS) were collected on Waters-Q-TOF-Premier and Shimadzu LCMS-IT-TOF (ESI). X-Ray single-crystal diffraction data were obtained on an Agilent Technologies Gemini single crystal diffractometer. Melting points were measured with SGW®X-4/4A/4B and are uncorrected.

II. Preparation of Exocyclic Enones[2]

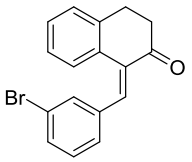
To a mixture of a 3,4-dihydronaphthalen-2(1*H*)-one (2 mmol), an aryl aldehyde derivative (2 mmol) and 4Å molecular sieves (1.0 g) in toluene (4 mL) was added piperidine (24 μL) and AcOH (24 μL). The solution was stirred at room temperature for 24 h. Then the mixture was filtered through a celite pad and washed with EtOAc. The filtrate was then concentrated under vacuum and the residue was purified by flash chromatography on silica gel column (PE/EA = 20/1 ~ 5/1, v/v) to provide the desired enones.



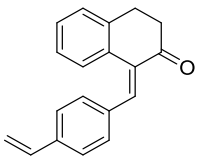
(*E*)-1-Benzylidene-3,4-dihydronaphthalen-2(1*H*)-one (1b)[2]: 355 mg, 76% yield, an off-white solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.63 (t, J = 6.0 Hz, 2H), 3.04 (t, J = 6.0 Hz, 2H), 7.00 (t, J = 7.6 Hz, 1H), 7.18-7.26 (m, 5H), 7.34 (d, J = 7.6 Hz, 1H), 7.40 (s, 2H), 7.68 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 37,1, 126.2, 128.0, 128.3, 128.6, 129.1, 129.2, 129.7, 132.7, 134.0, 135.3, 135.4, 138.6, 202.0 ppm.



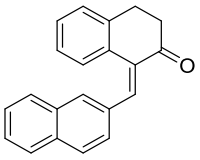
(*E*)-1-(3-Chlorobenzylidene)-3,4-dihydronaphthalen-2(1*H*)-one (1l): 422 mg, 79% yield, a light-yellow solid. M.p.: 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.64 (t, *J* = 6.4 Hz, 2H), 3.05 (t, *J* = 6.4 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.05-7.29 (m, 5H), 7.38 (s, 1H), 7.58 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 37.0, 126.4, 127.7, 128.2, 128.7, 129.0, 129.2, 129.4, 129.8, 132.1, 133.5, 134.5, 135.1, 137.4, 138.7, 201.6 ppm. HRMS (ESI^+): calcd for $C_{17}H_{13}ClNaO$ $[M+Na]^+$ 291.0547 found 291.0550.



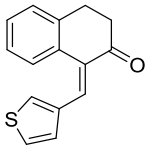
(*E*)-1-(3-Bromobenzylidene)-3,4-dihydronaphthalen-2(1*H*)-one (1j): 530 mg, 85% yield, a light-yellow solid. M.p.: 89-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (t, *J* = 6.4 Hz, 2H), 3.05 (t, *J* = 6.4 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.21-7.32 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 7.57 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 37.0, 122.6, 126.4, 128.1, 128.2, 128.7, 129.2, 130.1, 131.9, 132.0, 132.3, 133.3, 135.1, 137.6, 138.7, 201.6 ppm. HRMS (ESI^+): calcd for $C_{17}H_{13}BrNaO$ $[M+Na]^+$ 335.0042 found 335.0047.



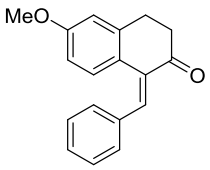
(*E*)-1-(4-Vinylbenzylidene)-3,4-dihydronaphthalen-2(1*H*)-one (1m): 431 mg, 83% yield, an off-white solid. M.p.: 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (t, *J* = 6.4 Hz, 2H), 3.04 (t, *J* = 6.4 Hz, 2H), 5.28 (d, *J* = 10.8 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 6.68 (dd, *J* = 17.6 Hz, 10.8 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 7.20-7.31 (m, 3H), 7.39-7.41 (m, 3H), 7.65 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 37.1, 115.0, 126.29, 126.34, 128.0, 128.3, 129.2, 130.1, 132.8, 133.8, 134.8, 135.0, 136.4, 138.4, 138.6, 201.9 ppm. HRMS (ESI^+): calcd for $C_{19}H_{17}O$ $[M+H]^+$ 261.1274 found 261.1275.



(*E*)-1-(Naphthalen-2-ylmethylene)-3,4-dihydronaphthalen-2(1*H*)-one (1n): 299 mg, 78% yield, a thick oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (t, *J* = 6.8 Hz, 2H), 3.09 (t, *J* = 6.8 Hz, 2H), 6.99 (td, *J* = 7.6 Hz, 1.2Hz, 1H), 7.25 (td, *J* = 7.6 Hz, 1.2Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.43-7.49 (m, 3H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.75-7.79 (m, 2H), 7.86 (s, 1H), 7.95 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.0, 37.2, 126.27, 126.34, 126.5, 127.0, 127.8, 127.83, 128.0, 128.4, 128.5, 129.3, 130.6, 132.8, 133.0, 133.5, 133.6, 134.0, 135.4, 138.6, 201.9 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{17}O$ $[M+H]^+$ 285.1274 found 285.1271.



(E)-1-(Thiophen-3-ylmethylene)-3,4-dihydronaphthalen-2(1*H*)-one (1q): 311 mg, 65% yield, an off-white solid. M.p.: 76-78°C. ^{1}H NMR (400 MHz, $CDCl_3$):δ = 2.60 (t, *J* = 6.0 Hz, 2H), 3.00 (t, *J* = 6.0 Hz, 2H), 7.11-7.19 m, 3H), 7.22-7.29 (m, 2H), 7.53-7.55 (m, 2H), 7.63 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 37.1, 125.7, 126.2, 127.6, 127.9, 128.4, 129.0, 129.1, 129.7, 132.7, 133.0, 136.7, 138.6, 202.2 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{13}OS$ $[M+H]^+$ 241.0682 found 241.0682.

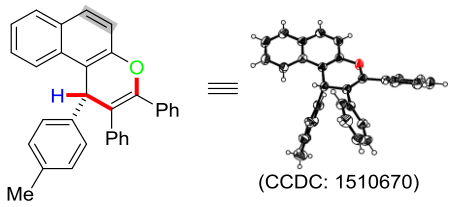


(*E*)-1-Benzylidene-6-methoxy-3,4-dihydronaphthalen-2(1*H*)-one (1r): 420 mg, 80% yield, a light-yellow solid. M.p.: 80-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.62 (t, *J* = 6.4 Hz, 2H), 3.01 (t, *J* = 6.4 Hz, 2H), 3.82 (s, 3H), 6.57 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.80 (d, *J* = 2.8 Hz, 1H), 7.25-7.28 (m, 4H), 7.41-7.43 (m, 2H), 7.60 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.2, 37.2, 55.4, 112.2, 113.0, 125.1, 128.5, 128.8, 129.6, 130.6, 133.4, 133.5, 135.7, 140.2, 159.6, 202.0 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{17}O_2$ $[M+H]^+$ 265.1223 found 265.1225.

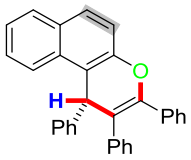
III. Rh-Catalyzed Annulation of Exocyclic Enones with Alkynes

General procedure: A Schlenk tube containing an exocyclic enones **1** (0.2 mmol), an alkyne **2** (0.24 mmol), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (16.6 mg, 10 mol %), $Cu(OAc)_2\cdot H_2O$ (79.2 mg, 0.4 mmol), Cu_2O (14.1 mg, 0.1 mmol) and DCM (1 mL) was sealed with a teflon-coated screw cap and the mixture was stirred at 100 ºC for 24-48 h. After cooled down to room temperature, the mixture was filtered

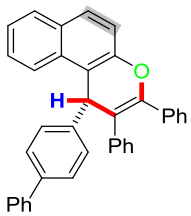
through a celite pad and washed with DCM. The filtrate was then concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/DCM=15:1~10:1) to provide the final product. (For 1 mmol scale synthesis, 234 mg **1b**, 213 mg **2a**, [Cp*Rh(CH_3CN)$_3$](SbF_6)$_2$ (10 mol %), Cu(OAc)$_2$·H_2O (2.0 eq.), Cu_2O (0.5 eq.) and DCM (5 mL) were used instead.)



2,3-Diphenyl-1-(*p*-tolyl)-1*H*-benzo[*f*]chromene (3a): 24 h, 63.6 mg, 75% yield, a white solid. M.p.: 85-87 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 5.36 (s, 1H), 7.01-7.03 (m, 4H), 7.16-7.25 (m, 8H), 7.34-7.45 (m, 5H), 7.76-7.81 (m, 2H), 7.96 (d, J = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 44.9, 116.5, 117.2, 117.9, 123.1, 124.2, 126.7, 126.9, 127.9, 128.2, 128.4, 128.57, 128.64, 129.34, 129.36, 130.2, 131.17, 131.25, 135.0, 136.2, 139.9, 142.2, 146.0, 149.2 ppm. HRMS (ESI$^+$): calcd for $C_{32}H_{25}O$ $[M+H]^+$ 425.1900, found 425.1902.

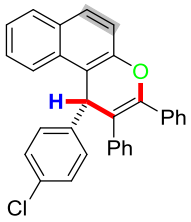


1,2,3-Triphenyl-1*H*-benzo[*f*]chromene (3b): 24 h, 59.9 mg, 73% yield (For a 1 mmol scale, 275 mg, 67% yield, 48 h), a white solid. M.p.: 118-120 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.39 (s, 1H), 6.98 (m, 2H), 7.13-7.21 (m, 9H), 7.32-7.45 (m, 7H), 7.78-7.82 (m, 2H), 7.94 (d, J = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.5, 116.4, 116.9, 118.0, 123.1, 124.3, 126.7, 126.8, 126.9, 127.9, 128.2, 128.3, 128.58, 128.62, 128.66, 128.72, 129.3, 130.2, 131.2, 131.3, 134.9, 139.8, 145.2, 146.0, 149.2 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{22}NaO$ $[M+Na]^+$ 433.1563, found 433.1571.

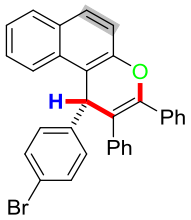


1-([1,1'-Biphenyl]-4-yl)-2,3-diphenyl-1*H*-benzo[*f*]chromene (3c): 24 h, 66.1 mg, 68% yield, a white solid. M.p.: 112-123 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.43 (s, 1H), 7.03-7.06 (m, 2H), 7.18-7.24 (m, 6H), 7.30 (t, J = 7.6 Hz, 1H), 7.37-7.49 (m, 11H), 7.53 (d, J = 7.2 Hz, 2H), 7.80-7.84 (m, 2H), 8.00 (d, J = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.1, 116.2, 116.9, 118.0,

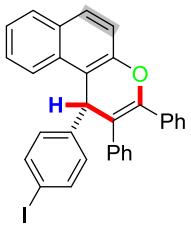
123.1, 124.3, 126.8, 126.97, 127.04, 127.2, 127.3, 127.9, 128.3, 128.4, 128.7, 128.75, 128.8, 128.9, 129.4, 130.2, 131.18, 131.24, 134.9, 139.4, 139.8, 140.9, 144.2, 146.2, 149.2 ppm. HRMS (ESI^+): calcd for $C_{37}H_{27}O$ $[M+H]^+$ 487.2056, found 487.2060.



1-(4-Chlorophenyl)-2,3-diphenyl-1*H*-benzo*[f]*chromene (3d): 24 h, 62.1 mg, 70% yield, a white solid. M.p.: 124-126 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.38 (s, 1H), 6.97-6.98 (m, 2H), 7.15-7.20 (m, 10H), 7.35-7.44 (m, 5H), 7.78-7.85 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.0, 116.0, 116.2, 118.0, 122.9, 124.4, 126.9, 127.1, 127.9, 128.3, 128.5, 128.8, 129.0, 129.3, 129.8, 130.2, 131.1, 131.2, 132.4, 134.7, 139.5, 143.7, 146.1, 149.3 ppm. HRMS (ESI^+): calcd for $C_{31}H_2ClNaO$ $[M+Na]^+$ 467.1173, found 467.1176.

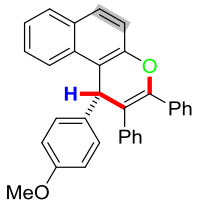


1-(4-Bromophenyl)-2,3-diphenyl-1*H*-benzo*[f]*chromene (3e): 24 h, 63.4 mg, 65% yield, a white solid. M.p.: 82-84 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.35 (s, 1H), 6.97-6.98 (m, 2H), 7.15-7.21 (m, 8H), 7.30-7.44 (m, 7H), 7.78-7.84 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.0, 115.9, 116.1, 118.0, 120.6,122.9, 124.4, 126.9, 127.1, 127.9, 128.4, 128.5, 128.9, 129.0, 129.3, 130.15, 130.19, 131.1, 131.2, 134.7, 139.4, 144.2, 146.2, 149.3 ppm. HRMS (ESI^+): calcd for $C_{31}H_{22}BrO$ $[M+H]^+$ 489.0849, found 489.0855.

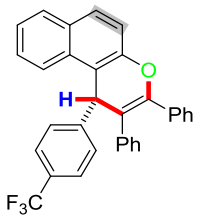


1-(4-Iodophenyl)-2,3-diphenyl-1*H*-benzo*[f]*chromene (3f): 24h, 67.2 mg, 60% yield, a white solid. M.p.: 135-137 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.39 (s, 1H), 6.96-6.97 (m, 2H), 7.04 (d, J = 7.6 Hz, 2H), 7.19-7.21 (m, 6H), 7.34-7.43 (m, 5H), 7.51 (d, J = 7.2 Hz, 2H), 7.78-7.84 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.1, 115.9, 116.1, 117.9, 122.9, 124.4, 126.9, 127.1, 127.9,

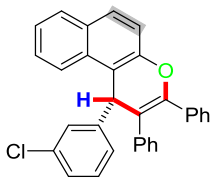
128.4, 128.5, 128.8, 129.0, 129.3, 130.1, 130.5, 131.1, 131.2, 134.7, 137.7, 139.4, 144.9, 146.2, 149.2 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{22}IO$ $[M+H]^+$ 537.0710, found 537.0713.



1-(4-Methoxyphenyl)-2,3-diphenyl-1*H*-benzo*[f]*chromene (3g): 24 h, 58.1 mg, 66% yield, a white solid. M.p.:70-72 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.72 (s, 3H), 5.33 (s, 1H), 6.74 (d, J = 8.0 Hz, 2H), 6.98-6.99 (m, 2H), 7.17-7.26 (m, 8H), 7.35-7.44 (m, 5H), 7.76-7.81 (m, 2H), 7.93 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.5,55.3, 114.0, 116.6, 117.1, 118.0, 123.1, 124.2, 126.7, 126.9, 127.8, 128.2, 128.3, 128.6, 129.3, 129.5, 130.2, 131.16, 131.24, 135.0, 137.5, 139.9, 145.8, 149.1, 158.2 ppm. HRMS (ESI$^+$): calcd for $C_{32}H_{24}NaO_2$ $[M+Na]^+$ 463.1669, found 463.1677.

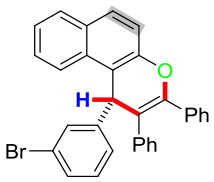


2,3-Diphenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-benzo*[f]*chromene (3h): 36 h. 59.3 mg, 62% yield, a white solid. M.p.: 139-141 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.50 (s, 1H), 6.96-6.98 (m, 2H), 7.19-7.26 (m, 6H), 7.36-7.47 (m, 9H), 7.81-7.86 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.4, 115.7, 115.8, 118.0, 122.8, 124.3 (q, J_{CF} = 276.7 Hz), 124.5, 125.62 (q, J_{CF} = 3.8 Hz), 127.0, 127.2, 127.9, 128.4, 128.5, 128.7, 128.8, 128.9 (q, J_{CF} = 31.0 Hz), 129.2, 129.3, 130.1, 131.0, 131.2, 139.3, 146.4, 149.0, 149.3 ppm. HRMS (ESI$^+$): calcd for $C_{32}H_{21}F_3NaO$ $[M+Na]^+$ 501.1437, found 501.1443.

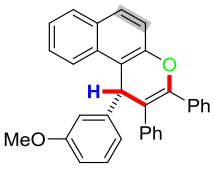


1-(3-Chlorophenyl)-2,3-diphenyl-1*H*-benzo*[f]*chromene (3i): 24 h, 56.8 mg, 64% yield, a white solid. M.p.: 132-134 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.40 (s, 1H), 6.97-6.99 (m, 2H), 7.11-7.22 (m, 9H), 7.27 (s, 1H), 7.37-7.46 (m, 5H), 7.80-7.87 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.3, 115.8, 115.9, 118.0, 122.9, 124.4, 126.7, 126.9, 127.0, 127.1, 127.9, 128.4, 128.47, 128.54, 128.8, 129.1, 129.3, 129.7, 130.1, 131.1, 131.2, 134.5, 134.6, 139.4, 146.2, 147.1, 149.3 ppm.

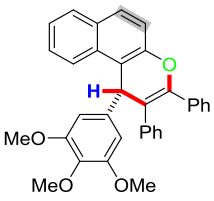
HRMS (ESI$^+$): calcd for $C_{31}H_{22}ClO$ $[M+H]^+$ 445.1354, found 445,1360.



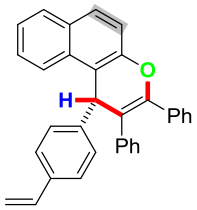
1-(3-Bromophenyl)-2,3-diphenyl-1*H*-benzo*[f]*chromene (3j): 24 h, 54.6 mg, 56% yield, a white solid. M.p.: 62-64 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.37 (s, 1H), 6.97 (bs, 2H), 7.06 (t, J = 7.2 Hz, 1H), 7.20-7.26 (m, 8H), 7.36-7.45 (m, 6H), 7.80-7.86 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.3, 115.8, 118.0, 122.8, 122.9, 124.4, 127.0, 127.1, 127.2, 127.9, 128.4, 128.5, 128.8, 129.1, 129.3, 129.9, 130.07, 130.14, 131.1, 131.2, 131.4, 134.6, 139.4, 146.2, 147.4, 149.3 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{22}BrO$ $[M+H]^+$ 489.0849, found 489.0858.



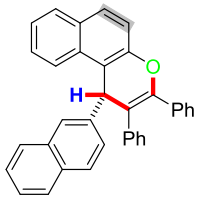
1-(3-Methoxyphenyl)-2,3-diphenyl-1*H*-benzo*[f]*chromene (3k): 24 h, 59.8 mg, 68% yield, a white solid. M.p.: 53-55 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 3H), 5.38 (s, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.87 (s, 1H), 6.93 (d, J = 7.6 Hz, 1H), 7.00-7.01 (m, 2H), 7.11-7.22 (m, 7H), 7.37-7.45 (m, 5H), 7.78-7.82 (m, 2H), 7.96 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.4, 55.2, 111.8, 114.5, 116.2, 116.7, 118.0, 121.1, 123.1, 124.3, 126.8, 126.9, 127.8, 128.2, 128.3, 128.6, 128.7, 129.3, 129.4, 130.2, 131.2, 131.3, 134.9, 139.8, 146.1, 146.7, 149.2, 159.8 ppm. HRMS (ESI$^+$): calcd for $C_{32}H_{24}O_2$ $[M+Na]^+$ 463.1669, found 463.1679.



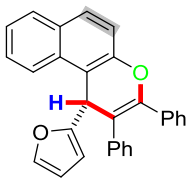
2,3-Diphenyl-1-(3,4,5-trimethoxyphenyl)-1*H*-benzo*[f]*chromene (3l): 48 h. 57 mg, 57% yield, a white solid. M.p.: 158-160 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 6H), 3.76 (s, 3H), 5.32 (s, 1H), 6.48 (s, 2H), 7.00-7.01 (m, 6H), 7.37-7.47 (m, 6H), 7.79-7.84 (m, 2H), 7.95 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.6, 56.2, 60.9, 105.7, 110.2, 116.3, 116.5, 118.0, 123.2, 124.3, 126.7, 127.0, 127.9, 128.29, 128.33, 128.7, 128.8, 129.3, 130.3, 131.2, 131.4, 134.9, 136.8, 139.7, 140.6, 146.0, 149.4, 153.2 ppm. HRMS (ESI$^+$): calcd for $C_{34}H_{29}O_4$ $[M+H]^+$ 501.2060, found 501.2069.



2,3-Diphenyl-1-(4-vinylphenyl)-1*H*-benzo[*f*]chromene (3m): 24 h, 54.9 mg, 63% yield, a white solid. M.p.: 80-82 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.16 (d, J = 10.8 Hz, 1H), 5.39 (s, 1H), 5.65 (d, J = 17.6 Hz, 1H), 6.62 (dd, J = 17.6 Hz, 10.8 Hz, 1H), 6.99-7.00 (m, 2H), 7.16-7.30 (m, 10H), 7.34-7.45 (m, 5H), 7.77-7.82 (m, 2H), 7.93 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.2, 113.5, 116.2, 116.7, 118.0, 123.0, 124.3, 126.6, 126.8, 127.0, 127.9, 128.3, 128.68, 128.71, 128.8, 129.3, 130.2, 131.19, 131.25, 134.9, 136.0, 136.6, 139.8, 144.9, 146.1, 149.2 ppm. HRMS (ESI$^+$): calcd for $C_{33}H_{25}O$ $[M+H]^+$ 437.1900, found 437.1902.

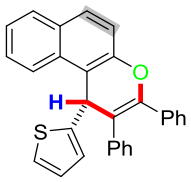


1-(Naphthalen-2-yl)-2,3-diphenyl-1*H*-benzo[*f*]chromene (3n): 36 h. 59.8 mg, 65% yield, a white solid. M.p.: 74-76 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.56 (s, 1H), 6.97-6.98 (m, 2H), 7.13-7.22 (m, 6H), 7.32-7.49 (m, 8H), 7.69-7.75 (m, 4H), 7.79-7.81 (m, 2H), 8.01 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.6, 116.2, 116.7, 118.0, 123.1, 124.3, 125.7, 126.0, 126.8, 126.9, 127.0, 127.7, 127.9, 128.1, 128.3, 128.4, 128.6, 128.7, 128.9, 129.4, 130.2, 131.2, 131.3, 132.5, 133.4, 134.9, 139.8, 142.5, 146.2, 149.3 ppm. HRMS (ESI$^+$): calcd for $C_{35}H_{24}NaO$ $[M+Na]^+$ 483.1719, found 483.1722.

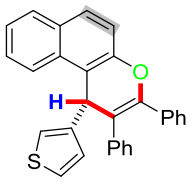


1-(Furan-2-yl)-2,3-diphenyl-1*H*-benzo[*f*]chromene (3o): 24 h, 47.2 mg, 59% yield, a white solid. M.p.: 140-142 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.55 (s, 1H), 6.16 (brs, 1H), 6.23 (brs, 1H), 7.12-7.26 (m, 9H), 7.38-7.42 (m, 4H), 7.50 (t, J = 8.0 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.4, 106.8, 110.6, 112.7, 114.9, 117.9, 122.9, 124.4, 126.8, 127.0, 128.0, 128.4, 128.5, 128.6, 128.8, 129.6, 129.9, 131.1, 131.3, 134.8, 139.6, 141.7, 147.9, 149.4, 156.8 ppm. HRMS (ESI$^+$): calcd for $C_{29}H_{21}O_2$

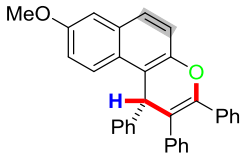
$[M+H]^+$ 401.1536, found 401.1529.



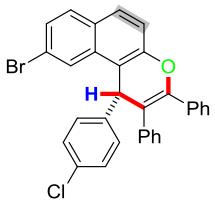
2,3-Diphenyl-1-(thiophen-2-yl)-1*H*-benzo*[f]*chromene (3p): 24 h, 54.1 mg, 65% yield, a white solid. M.p.: 130-132 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.77 (s, 1H), 6.85 (t, J = 3.6 Hz, 1H), 6.97 (d, J = 3.2 Hz, 1H), 7.11 (d, J = 4.4 Hz, 1H), 7.15-7.27 (m, 8H), 7.40-7.55 (m, 4H), 7.80 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.7, 115.4, 117.0, 118.0, 122.8, 124.4, 124.5, 124.7, 126.7, 126.9, 127.1, 128.0, 128.4, 128.5, 128.8, 129.5, 130.1, 130.9, 131.2, 134.7, 139.4, 147.2, 149.0, 149.3 ppm. HRMS (ESI$^+$): calcd for $C_{29}H_{21}OS$ $[M+H]^+$ 417.1308, found 417.1313.



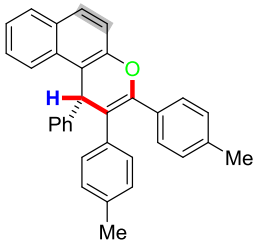
2,3-Diphenyl-1-(thiophen-3-yl) -1*H*-benzo*[f]*chromene (3q): 24 h, 51.6 mg, 62% yield, a white solid. M.p.: 150-152 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.56 (s, 1H), 7.00 (d, J = 4.0 Hz, 1H), 7.08-7.26 (m, 10H), 7.38-7.49 (m, 5H), 7.79 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.3, 115.6, 116.9, 117.9, 121.4, 122.8, 124.3, 125.9, 126.8, 127.0, 127.8, 127.9, 128.35, 128.38, 128.6, 128.7, 129.4, 130.0, 131.1, 134.8, 139.8, 145.4, 146.7, 149.2 ppm. HRMS (ESI$^+$): calcd for $C_{29}H_{20}NaOS$ $[M+Na]^+$ 439.1127, found 439.1137.



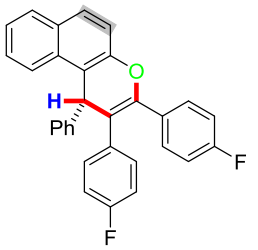
8-Methoxy-1,2,3-triphenyl-1*H*-benzo*[f]*chromene (3r): 24 h, 67.8 mg, 77% yield, a white solid. M.p.: 75-77 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.72 (s, 3H), 5.35 (s, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.99-7.01 (m, 2H), 7.16-7.26 (m, 8H), 7.34-7.45 (m, 5H), 7.78 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.6, 55.3, 114.0, 116.6, 117.1, 118.0, 123.1, 124.2, 126.7, 126.9, 127.8, 128.2, 128.3, 128.6, 128.7, 129.3, 129.5, 130.2, 131.19, 131.25, 135.0, 137.5, 139.9, 145.8, 149.2, 158.3 ppm. HRMS (ESI$^+$): calcd for $C_{32}H_{25}O_2$ $[M+H]^+$ 441.1849, found 441.1853.



9-Bromo-1-(4-chlorophenyl)-2,3-diphenyl-1*H*-benzo*[f]*chromene (3s): 36 h. 65.8 mg, 63% yield, a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.30 (s, 1H), 6.98-6.99 (m, 2H), 7.17 -7.27 (m, 8H), 7.34-7.47 (m, 6H), 7.66 (d, J = 9.6 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 8.11 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.4, 116.3, 116.4, 118.4, 121.3, 125.6, 126.9, 127.1, 127.6, 127.9, 128.35, 128.38, 128.5, 128.6, 128.8, 129.3, 129.6, 130.1, 130.2, 132.6, 134.6, 139.5, 144.7, 146.0, 149.8 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{21}BrClO$ $[M+H]^+$ 523.0459, found 523.0466.

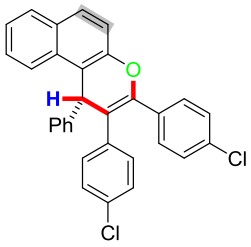


1-Phenyl-2,3-di-*p*-tolyl-1*H*-benzo*[f]*chromene (3t): 24 h, 60 mg, 69% yield, a white solid. M.p.: 136-138 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (brs, 6H), 5.34 (s, 1H), 6.87 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 2H), 7.26-7.29 (m, 2H), 7.33-7.37 (m, 3H), 7.40-7.44 (m, 2H), 7.76-7.81 (m, 2H), 7.95 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.36, 21.43, 45.5, 115.7, 117.1, 118.0, 123.1, 124.2, 126.6, 126.7, 128.57, 128.58, 128.59, 128.63, 129.0, 129.2, 129.9, 131.1, 131.3, 132.2, 136.4, 137.0, 138.0, 145.4, 145.9, 149.2 ppm. HRMS (ESI$^+$): calcd for $C_{33}H_{27}O$ $[M+H]^+$ 439.2056, found 439.2068.

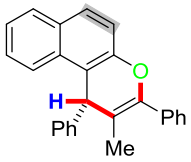


2,3-Bis(4-fluorophenyl)-1-phenyl-1*H*-benzo*[f]*chromene (3u): 36 h. 55.3 mg, 62% yield, a white solid. M.p.: 145-147 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.32 (s, 1H), 6.84-6.92 (m, 6H), 7.13 (t, J = 7.2 Hz, 1H), 7.19-7.24 (m, 2H), 7.26-7.45 (m, 7H), 7.78-7.82 (m, 2H), 7.90 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.6, 115.0 (d, J_{CF} = 21.4 Hz), 115.43, 115.44 (d, J_{CF} = 21.2 Hz), 116.5, 117.8, 123.1, 124.4, 126.8, 128.5, 128.69, 128.72, 128.9, 130.8 (d, J_{CF} = 3.4 Hz), 131.1 (d, J_{CF} = 8.1 Hz), 131.22, 131.24, 131.7 (d, J_{CF} = 7.8 Hz), 135.47, 135.51, 144.9, 145.2, 149.0, 161.9

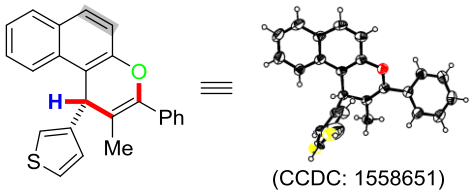
(d, J_{CF} = 244.9 Hz), 162.5 (d, J_{CF} = 247.3 Hz) ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{20}F_2NaO$ $[M+Na]^+$ 469.1374, found 469.1383.



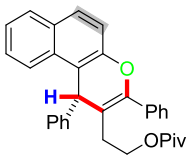
2,3-Bis(4-chlorophenyl)-1-phenyl-1*H*-benzo[*f*]chromene (3v): 36 h. 56.5 mg, 59% yield, a white solid. M.p.: 170-172 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.31 (s, 1H), 6.86-6.88 (m, 2H), 7.11-7.28 (m, 11H), 7.34-7.44 (m, 3H), 7.78-7.81 (m, 2H), 7.89 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.4, 115.8, 116.4, 117.8, 123.1, 124.5, 126.92, 126.93, 128.3, 128.5, 128.7, 128.8, 129.0, 130.6, 131.17, 131.24, 131.4, 133.0, 134.3, 137.9, 144.7, 145.2, 148.9 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{20}Cl_2NaO$ $[M+Na]^+$ 501.0783, found 501.0786.



2-Methyl-1,3-diphenyl-1*H*-benzo[*f*]chromene (3w): 24 h, 48.7 mg, 70% yield, a white solid. M.p.: 156-158 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.84 (s, 3H), 5.00 (s, 1H), 7.15 (t, J = 7.2 Hz, 1H), 7.26-7.43 (m, 10H), 7.52 (d, J = 7.2 Hz, 2H), 7.73-7.79 (m, 2H), 7.85 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.7, 45.4, 109.9, 115.3, 118.0, 123.2, 124.0, 126.6, 128.2, 128.4, 128.5, 128.6, 128.7, 129.3, 131.0, 131.6, 135.2, 143.6, 145.2, 149.4 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{21}O$ $[M+H]^+$ 349.1587, found 349. 1591.



2-Methyl-3-phenyl-1-(thiophen-3-yl)-1*H*-benzo[*f*]chromene (3x): 36 h. 42.5 mg, 60% yield, a white solid. M.p.: 135-137 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91 (s, 3H), 5.17 (s, 1H), 6.98-7.00 (m, 1H), 7.15-7.17 (m, 2H), 7.31 (d, J = 8.8 Hz, 1H), 7.34-7.47 (m, 5H), 7.54 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8, 40.2, 109.3, 115.1, 118.0, 121.1, 122.9, 124.0, 125.8, 126.6, 127.8, 128.2, 128.4, 128.6, 129.2, 130.9, 131.5, 135.1, 144.0, 145.4, 149.2 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{19}SO$ $[M+H]^+$ 355.1151, found 355.1556.

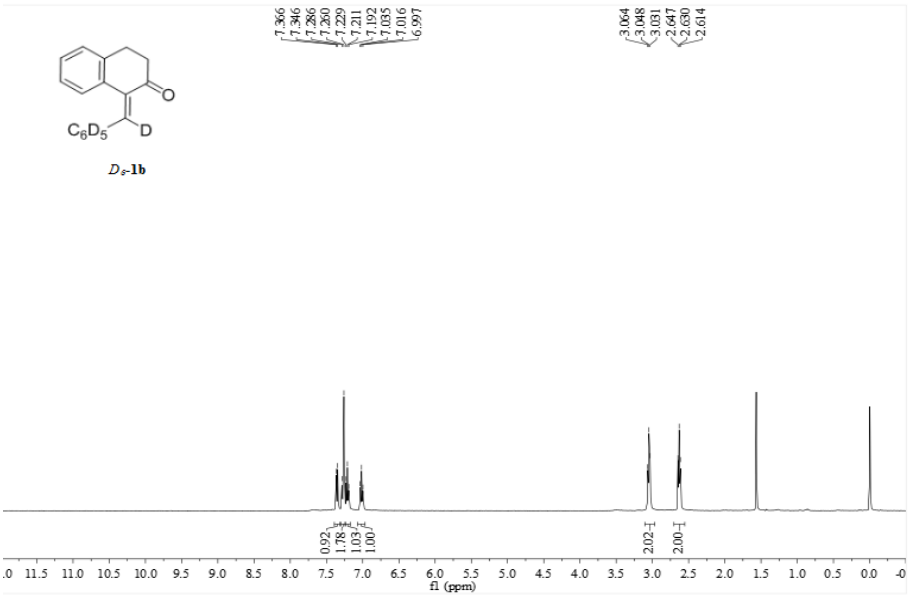


2-(1,3-Diphenyl-1*H*-benzo[*f*]chromen-2-yl)ethyl pivalate (3y): 36 h. 54.6 mg, 59% yield, a clear viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (s, 9H), 2.34-2.41 (m, 1H), 2.58-2.65 (m, 1H), 4.15-4.25 (m, 2H), 5.25 (s, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.26-7.46 (m, 10H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.3, 29.2, 38.8, 41.9, 62.6, 110.3, 115.6, 117.8, 123.2, 124.2, 126.7, 126.8, 128.5, 128.6, 128.8, 128.9, 129.3, 131.1, 131.4, 134.8, 145.2, 146.7, 149.1, 178.7 ppm. HRMS (ESI$^+$): calcd for $C_{32}H_{31}O_3$ $[M+H]^+$ 463.2268, found 463.2275.

IV. Mechanism Study

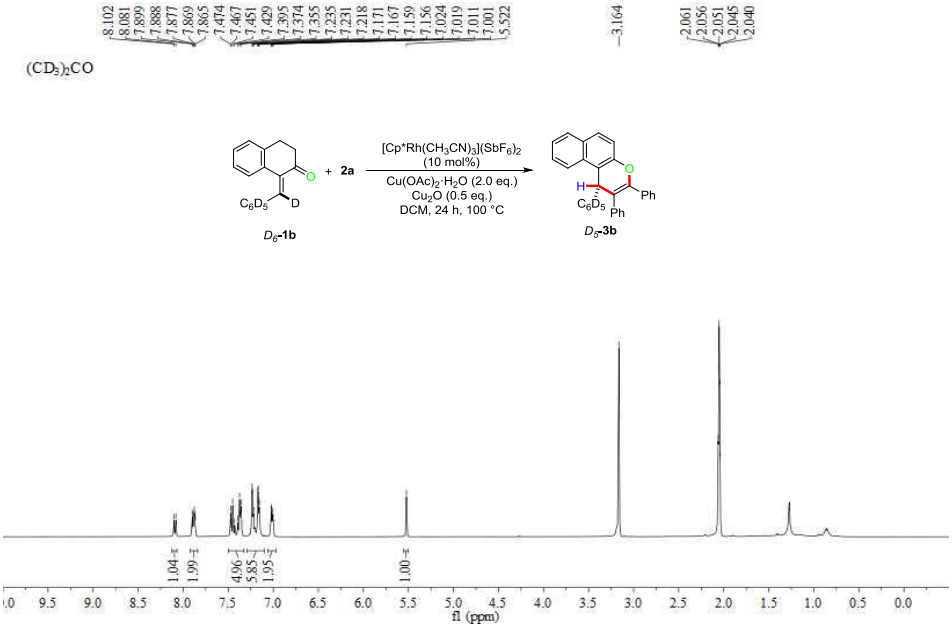
1. Experiment to verify the vinylic C−H bond cleavage

Preparation of *D*$_6$-1b: Following the general procedure by using *D*$_6$-benzaldehyde instead of benzaldehyde. ***D*$_6$-1b** was obtained as an off-white solid in 70% yield, (>99% D). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (t, *J* = 6.8 Hz, 2H), 3.05 (t, *J* = 6.8 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.26-7.29 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 1H) ppm.



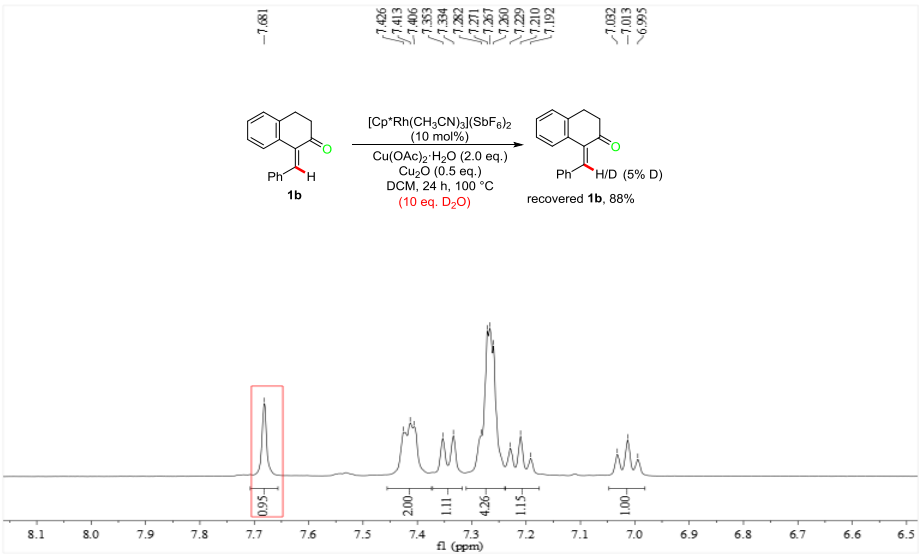
The reaction of *D*$_6$-1b with 2a: A suspension of $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (16.6 mg, 10 mol %), *D*$_6$-**1b** (48.0 mg, 0.2 mmol), **2a** (42.7 mg, 0.24 mmol), $Cu(OAc)_2{\cdot}H_2O$ (79.2 mg, 0.4 mmol) and Cu_2O (14.1 mg, 0.1 mmol) in DCM (1 mL) was sealed with a teflon-coated screw cap and the reaction was stirred at 100 ºC for 24 h. At the end of the reaction, the mixture was filtered through a celite pad and washed with DCM. The filtrate was concentrated under reduced pressure and the

residue was purified by flash chromatography on silica gel column (PE/DCM = 10:1, v/v) to provide 45 mg of D_m-**3b** as a white solid. The ^{1}H-NMR analysis of the product D_m-**3b** showed no benzylic deuterium, indicating that this reaction underwent a vinylic C(sp^2)–H bond cleavage process.



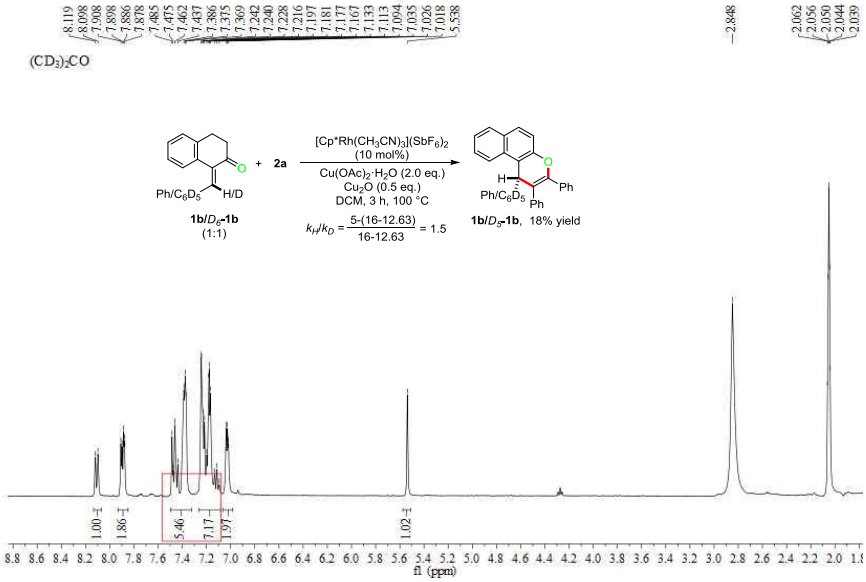
2. H/D exchange experiment

H/D exchange in the reaction of **1b** with D_2O (10 equiv.) without **2a**: A solution of $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (16.6 mg, 10 mol %), **1b** (46.8 mg, 0.2 mmol), $Cu(OAc)_2{\cdot}H_2O$ (79.2 mg, 0.4 mmol), Cu_2O (14.1 mg, 0.1 mmol) and D_2O (2 mmol, 40 μL) in DCM was sealed with a teflon-coated screw cap and the reaction was stirred at 100 ºC for 24 h. At the end of the reaction, the mixture was filtered through a celite pad and washed with DCM. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/EA) to provide recovered **1b** (41.4 mg, 88%) as an off-white solid. The D-incorporation in recovered **1b** was estimated by ^{1}H NMR spectroscopy and 5% of vinylic-H was deuterated, which indicated that the vinylic C–H bond cleavage is irreversible.



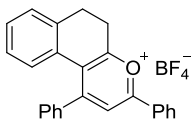
3. KIE using D_6-1b and 1b as substrates

A suspension of [Cp*Rh(CH_3CN)$_3$](SbF_6)$_2$ (16.6 mg, 10 mol %), **1b** (23.4 mg, 0.1 mmol), D_6-**1b** (24.0 mg, 0.1 mmol), **2a** (42.7 mg, 0.24 mmol), Cu(OAc)$_2$·H_2O (79.2 mg, 0.4 mmol) and Cu_2O (14.1 mg, 0.1 mmol) in DCM (1 mL) was sealed with a teflon-coated screw cap and the reaction was stirred at 100 ºC for 3 h. At the end of the reaction, the mixture was filtered through a celite pad and washed with DCM. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/DCM = 10:1, v/v) to provide a mixture of **3b** and D_5-**3b** in 18% yield as a white solid. The ratio of **3b** and D_5-**3b** was determined by ^{1}H NMR spectroscopy to give intermolecular kinetic isotopic effect (*KIE*) k_H/k_D = 1.5. This result revealed that the vinylic C–H activation is not involved in the rate-determining step.



4. Control experiments to verify the reaction intermediate

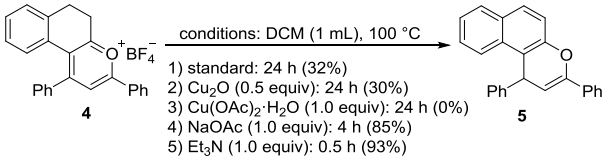
Synthesis of pyrylium tetrafluoroborate 4: According to a reported procedure[4], chalcone (416 mg, 2 mmol) was heated to its melting point on a steam-bath. *β*-Tetralone (2.34 g, 16 mmol) was added followed by the addition of BF_3·Et_2O (2 mL) with stirring. The mixture was heated to 100 ºC and stirred continued for 12 h. After cooled down to room temperature, an excess amount of Et_2O was added to give the orange pyrylium tetrafluoroborate **4** (369 mg, 55%. *Note: **4** slowly decomposes when stored under ambient conditions.*).



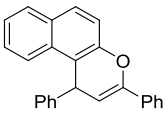
1,3-Diphenyl-5,6-dihydrobenzo[*f*]chromen-4-ium tetrafluoroborate (4): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30 (t, J = 7.2 Hz, 2H), 3.45 (t, J = 7.2 Hz, 2H), 6.85 (d, J = 8.0 Hz, 1H), 6.92 (t, J =

7.2 Hz, 1H), 7.24-7.31 (m, 2H), 7.45-7.63 (m, 8H), 8.08 (s, 1H), 8.17 (d, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.8, 29.7, 121.1, 126.8, 127.3, 128.3, 128.6, 128.8, 128.87, 128.9, 129.0, 129.8, 130.0, 130.6, 132.5, 135.1, 135.7, 137.2, 164.8, 169.2, 180.0 ppm. ^{19}F NMR(376 MHz, $CDCl_3$): δ = -153.1 ppm. HRMS (ESI^+): calcd for $C_{25}H_{19}O$ $[M\text{-}BF_4]^+$ 335.1430, found 335.1423.

Conversion of pyrylium tetrafluoroborate 4 into 1,3-diphenyl-1*H*-benzo[*f*]chromene 5:



A Schlenk tube containing pyrylium tetrafluoroborate **4** (0.2 mmol), 1) standard conditions: $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (16.6 mg, 10 mol %), $Cu(OAc)_2{\cdot}H_2O$ (79.2 mg, 0.4 mmol) and Cu_2O (14.1 mg, 0.1 mmol), or a base [2) Cu_2O (14.1 mg, 0.1 mmol); 3) $Cu(OAc)_2{\cdot}H_2O$ (39.6 mg, 0.2 mmol); 4) NaOAc (8.2 mg, 0.2 mmol); and 5) Et_3N (28 μL, 0.2 mmol), respectively], and DCM (1 mL) was sealed with a teflon-coated screw cap and the reaction was stirred at 100 ºC for the indicated time (standard conditions, Cu_2O or $Cu(OAc)_2{\cdot}H_2O$: 24 h; NaOAc: 4 h; and Et_3N: 0.5 h, respectively). After cooled down to room temperature, the mixture was diluted with DCM, filtered through a celite pad and washed with DCM. The filtrate was then concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/DCM = 10/1, v/v) to afford **5** as a white solid in the indicated yield (standard conditions: 32%； Cu_2O: 30%; $Cu(OAc)_2{\cdot}H_2O$: 0%; NaOAc: 85%; and Et_3N: 93 %, respectively).

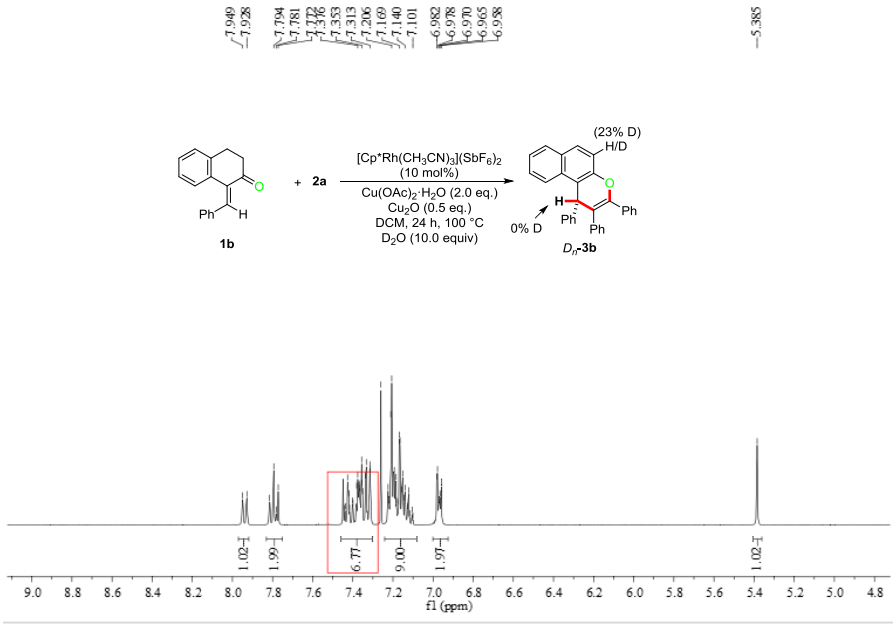


1,3-Diphenyl-1*H*-benzo[*f*]chromene (5):[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.37 (d, J = 5.6 Hz, 1H), 5.81 (t, J = 5.2 Hz, 2H), 7.15 (t, J = 6.4Hz, 1H), 7.24-7.43 (m, 10H), 7.73-7.75 (m, 3H), 7.80 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.3, 102.3, 114.4, 118.2, 123.8, 124.2, 124.8, 126.5, 126.7, 127.8, 129.1, 131.2, 131.9, 134.1, 146.5, 146.8, 149.7 ppm.

5. The reaction of 1b with 2a in the presence of D_2O:

A suspension of $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (16.6 mg, 10 mol %), **1b** (47.2 mg, 0.2 mmol), **2a** (42.7 mg, 0.24 mmol), $Cu(OAc)_2{\cdot}H_2O$ (79.2 mg, 0.4 mmol), Cu_2O (14.1 mg, 0.1 mmol) and D_2O (2 mmol, 40 μL) in DCM (1 mL) was sealed with a teflon-coated screw cap and the reaction was stirred at 100 ºC for 24 h. At the end of the reaction, the mixture was filtered through a celite pad and washed with DCM. The filtrate was concentrated under reduced pressure and the residue was purified by flash

chromatography on silica gel column (PE/DCM = 10:1, v/v) to provide 25 mg of ***D**$_n$*-**3b** as a white solid. The ^{1}H NMR analysis of the product *D$_n$*-**3b** showed no benzylic deuterium, indicating that the formation of the benzylic C–H bond might not involve a protonation process.

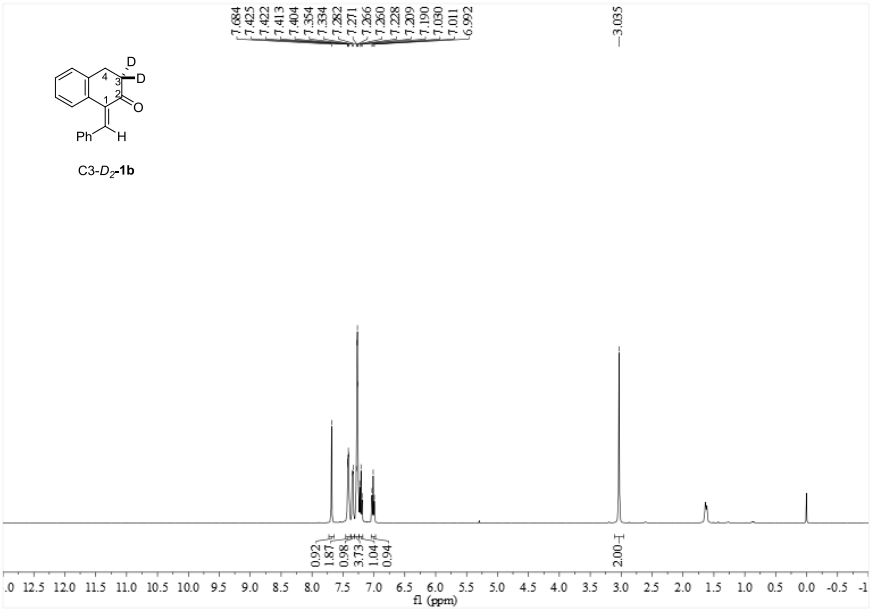


6. The benzylic H scrambling reaction of 3b with D_2O

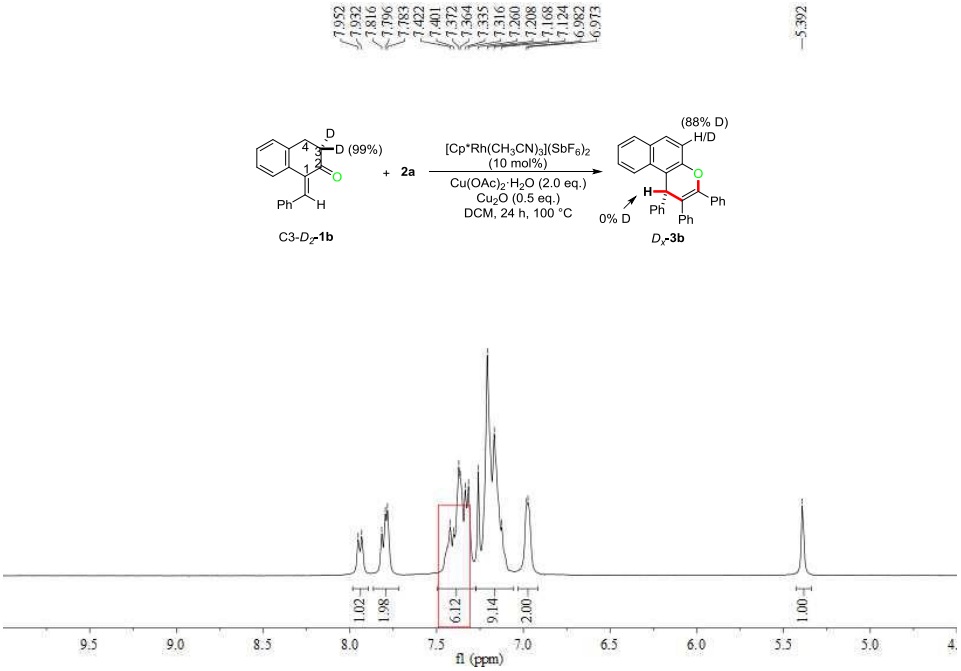
A suspension of $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (16.6 mg, 10 mol %), **3b** (82.0 mg, 0.2 mmol) $Cu(OAc)_2{\cdot}H_2O$ (79.2 mg, 0.4 mmol), Cu_2O (14.1 mg, 0.1 mmol) and D_2O (2 mmol, 40 μL) in DCM (1 mL) was sealed with a teflon-coated screw cap and the reaction was stirred at 100 ºC for 24 h. At the end of the reaction, the mixture was filtered through a celite pad and washed with DCM. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/DCM = 5:1, v/v) to provide 80 mg of recovered **3b** as a white solid. The ^{1}H NMR analysis of recovered **3b** showed no benzylic deuterium, indicating that the benzylic H in **3b** could not undergo H/D exchange with D_2O.

7. The reaction of C3-*D$_2$*-1b with 2a

Synthesis of C3-*D$_2$*-1b:[6] To a solution of 10 mol % of pyrrolidine (7.1 mg, 0.1 mmol) in 1.5 mL of D_2O with 1.5 mL anhydrous dioxane as cosolvent was added **1b** (234 mg, 1 mmol). The reaction mixture was stirred at 60 ºC for 12 h. After cooled down to room temperature, water (10 mL) was added and the mixture was extracted with EA (2 × 10 mL). The organic layer was washed with water (5 mL) and brine (5 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure to afford C3-*D$_2$*-**1b** in 90% yield (>99% D). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.02 (d, J = 6.4 Hz, 2H), 7.01 (t, J = 7.6 Hz, 1H), 7.19-7.28 (m, 5H), 7.34 (d, J = 8.0 Hz, 1H), 7.40-7.43 (m, 2H), 7.68 (s, 1H) ppm.

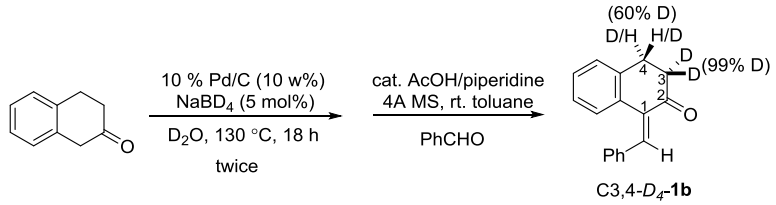


The reaction of C3-D_2-1b with 2a under the optimal conditions： A suspension of $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (16.6 mg, 10 mol %), C3-D_2-**1b** (47.2 mg, 0.2 mmol), **2a** (42.7 mg, 0.24 mmol), $Cu(OAc)_2 \cdot H_2O$ (79.2 mg, 0.4 mmol) and Cu_2O (14.1 mg, 0.1 mmol) in DCM (1 mL) was sealed with a teflon-coated screw cap and the reaction was stirred at 100 ºC for 24 h. At the end of the reaction, the mixture was filtered through a celite pad and washed with DCM. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/DCM = 10:1, v/v) to provide 40 mg of ***D**$_x$*-**3b** as a white solid. The ^{1}H NMR analysis of the product *D*$_x$-**3b** showed no benzylic deuterium, indicating that the benzylic H did not come from that of C3-position.

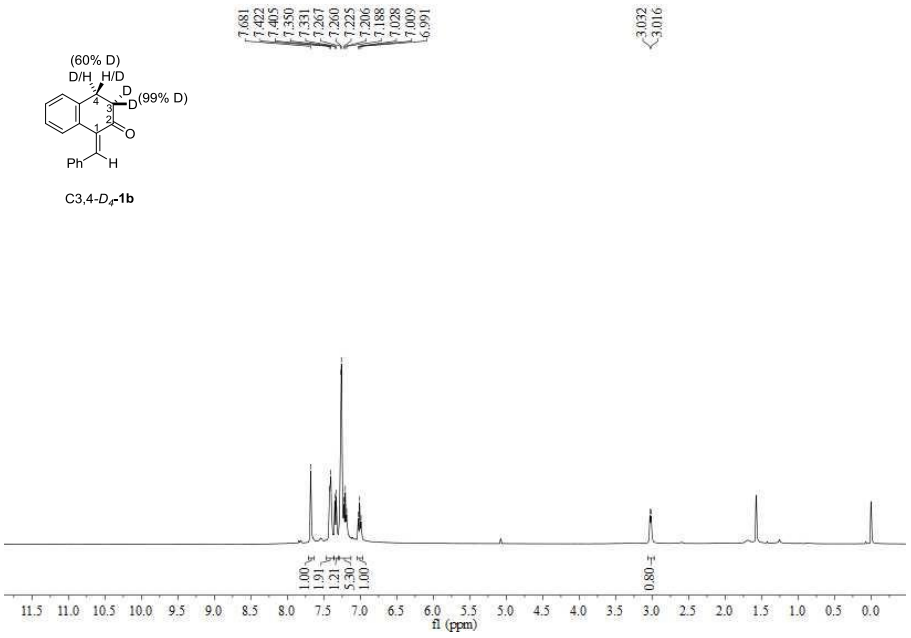


8. The reaction of C3,4-D_4-1b with 2a

Synthesis of C3,4-D_4-1b:

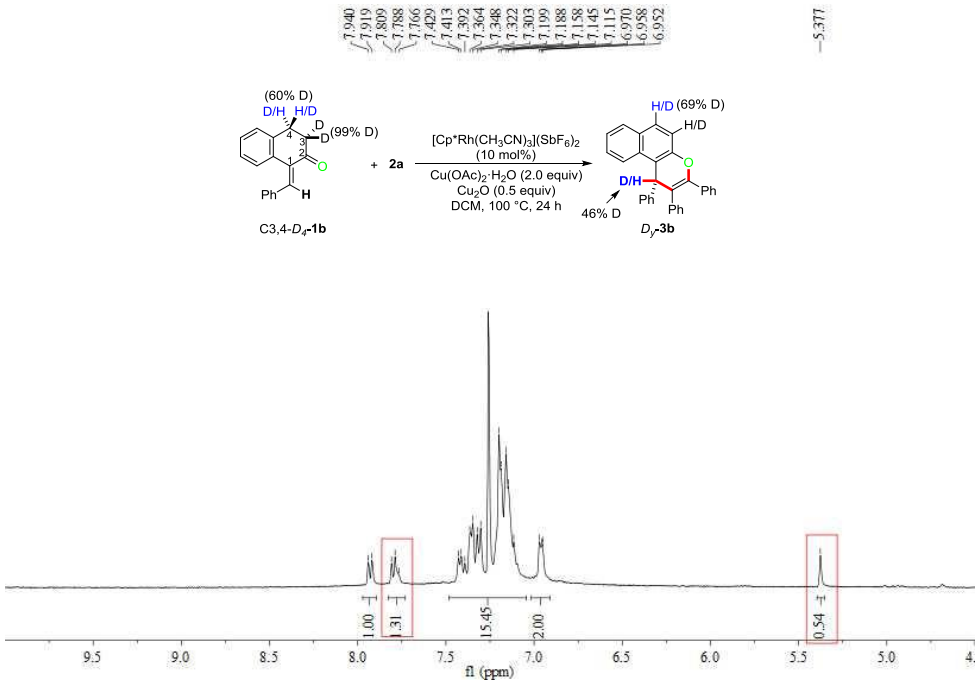


A suspension of 10 % Pd/C (29.2 mg, 10 wt% of the ketone), $NaBD_4$ (4.2 mg, 5 mol %), 3,4-dihydronaphthalen-2(1*H*)-one (292 mg, 2 mmol) in D_2O (3 mL) was sealed with a teflon-coated screw cap and the reaction was stirred at 130 ºC for 18 h in N_2. After cooled down to room temperature, water (10 mL) was added and the mixture was extracted with EA (2 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$, and filtered and the filtrate was concentrated under reduced pressure to afford 155 mg of D_n-3,4-dihydronaphthalen-2(1*H*)-one which was used for the next step without further purification (Note: The above H/D exchange experiment of 3,4-dihydronaphthalen-2(1*H*)-one with D_2O was conducted for twice.).[7] Following the general procedure by using D_n-3,4-dihydronaphthalen-2(1*H*)-one with benzaldehyde to provide C3,4-D_4-**1b** as an off-white solid in 72% yield, (C4-position, 60% D; C3-position, >99% D). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.02 (d, *J* = 6.4 Hz, 0.8H), 7.01 (t, *J* = 7.2 Hz, 1H), 7.19-7.27 (m, 5H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.41-7.42 (m, 2H), 7.68 (s, 1H) ppm.



The reaction of C3,4-D_4-1b with 2a under the optimal conditions： A suspension of $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (16.6 mg, 10 mol %), C3,4-D_4-**1b** (48 mg, 0.2 mmol), **2a** (42.7 mg, 0.24 mmol), $Cu(OAc)_2 \cdot H_2O$ (79.2 mg, 0.4 mmol) and Cu_2O (14.1 mg, 0.1 mmol) in DCM (1 mL) was

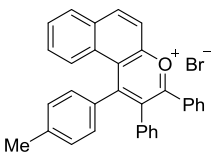
sealed with a teflon-coated screw cap and the reaction was stirred at 100 ºC for 24 h. At the end of the reaction, the mixture was filtered through a celite pad and washed with DCM. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel column (PE/DCM = 10:1, v/v) to provide 36 mg of ***D***$_y$**-3b** as a white solid. The ^{1}H NMR analysis of the product D_y-**3b** showed 46% benzylic deuterium, indicating that it was the C4-H in **1b** transferred to the benzylic position in **3b**.



V. Conversion of 3 into Cationic *O*-Containing PHAs

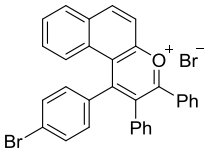
1. Oxidation of 3 into pyrylium salt 6 by Br_2[8]

A suspension of **3** (0.2 mmol) in AcOH (2 mL) stirred at 100 ºC was added a solution of Br_2 (0.24 mmol) in AcOH (1 mL) dropwise. The mixture was stirred continuously at the same temperature for 1h. At the end of the reaction, the excess Br_2 was blown off by N_2 and a large amount of Et_2O was added into the resulted mixture. An orange solid precipitated out, which was collected and dried under reduced pressure to provide **6**.



2,3-Diphenyl-1-(*p*-tolyl)benzo[*f*]chromen-4-ium bromide (6a): 97% yield, an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 7.13-7.28 (m, 9H), 7.36-7.45 (m, 4H), 7.52 (t, J = 7.6 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.75 (d, J = 7.6 Hz, 2H), 8.09 (d, J = 7.6 Hz, 1H), 8.25 (d, J = 9.2 Hz,

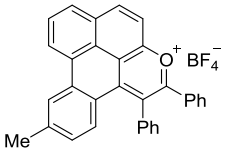
1H), 8.64 (d, J = 9.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 21.7, 118.1, 123.8, 128.0, 128.3, 128.8, 128.9, 129.09, 129.12, 129.8, 130.1, 130.3, 130.4, 131.0, 131.4, 131.7, 131.9, 133.2, 133.5, 133.8, 134.8, 140.7, 144.6, 161.0, 169.0, 169.3 ppm. HRMS (ESI$^+$): calcd for $C_{32}H_{23}O$ [M-Br]$^+$ 423.1743, found 423.1745.



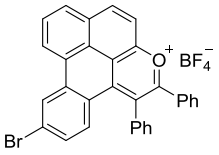
1-(4-Bromophenyl)-2,3-diphenylbenzo[f]chromen-4-ium bromide (6e): 95% yield, an orange solid. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.14-7.19 (m, 4H), 7.30 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.43-7.50 (m, 3H), 7.53-7.58 (m, 1H), 7.62-7.66 (m, 3H), 7.71-7.73 (m, 2H), 7.85(t, J = 8.0 Hz, 1H), 8.29 (d, J = 7.2 Hz, 1H), 8.35 (d, J = 10.6 Hz, 1H), 8.86 (d, J = 9.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 118.5, 124.0, 125.1, 128.4, 129.0, 129.7, 130.0, 130.1, 130.4, 131.0, 131.2, 131.3, 131.9, 132.2, 132.3, 132.8, 133.6, 134.0, 135.0, 135.8, 136.6, 145.8, 161.8, 168.0, 170.1 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{20}BrO$ [M-Br]$^+$ 487.0692, found 487.0691.

2. Photooxidation of 6 into 7[8]

A stirring solution of pyrylium salt **6** (0.05 mmol) and 50 w% HBF_4 (0.05 mmol) in AcOH (50 mL) was irradiated at 254 nm wavelength in air for 24 hours at room temperature and an orange solid precipitated out gradully. At the end of the reaction, the solid was collected and dried under reduced pressure to provide the π-extended pyrylium salt **7**.



10-Methyl-1,2-diphenylphenanthro[9,10,1-*def*]chromen-3-ium tetrafluoroborate (7a): 24.9 mg, 98% yield, an orange solid. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ = 2.66 (s, 3H), 7.37 (d, J = 8.8 Hz, 1H), 7.47-7.61 (m, 10H), 7.71 (d, J = 8.8 Hz, 1H), 8.60 (t, J = 8.0 Hz, 1H), 8.80 (d, J = 9.2 Hz, 1H), 9.04 (d, J = 7.6 Hz, 1H), 9.25 (s, 1H), 9.41 (d, J = 9.2 Hz, 1H), 9.77 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ = 21.9, 116.5, 118.9, 119.2, 123.9, 125.4, 128.0, 128.4, 128.6, 128.9, 129.1, 129.6, 129.8, 130.1, 130.4, 130.6, 130.7, 131.4, 131.8, 133.9, 135.6, 136.8, 143.8, 147.1, 148.4, 159.8, 165.9 ppm. ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ = -148.2 ppm. HRMS (ESI$^+$): calcd for $C_{32}H_{21}O$ [M-BF_4]$^+$ 421.1587, found 421.1565.



10-Bromo-1,2-diphenylphenanthro[9,10,1-*def*]chromen-3-ium tetrafluoroborate (7e): 27.7 mg, 97% yield, an orange solid. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.44-7.67 (m, 11H), 7.73 (d, J = 9.2 Hz, 1H), 8.47 (t, J = 8.0 Hz, 1H), 8.57 (d, J = 9.2 Hz, 1H), 8.89 (d, J = 7.6 Hz, 1H), 8.24 (d, J = 9.2 Hz, 1H), 9.27 (s, 1H), 9.43 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 119.7, 120.7, 126.2, 129.0, 129.1, 129.5, 129.7, 130.1, 130.4, 131.0, 131.3, 131.5, 131.55, 131.63, 131.7, 132.1, 132.6, 132.8, 133.6, 135.5, 136.2, 139.4, 145.4, 150.0, 161.3, 167.8 ppm. ^{19}F NMR (376 MHz, CD_3CN): δ = -152.7 ppm. HRMS (ESI^+): calcd for $C_{31}H_{18}BrO$ $[M\text{-}BF_4]^+$ 485.0536, found 485.0539.

VI. References

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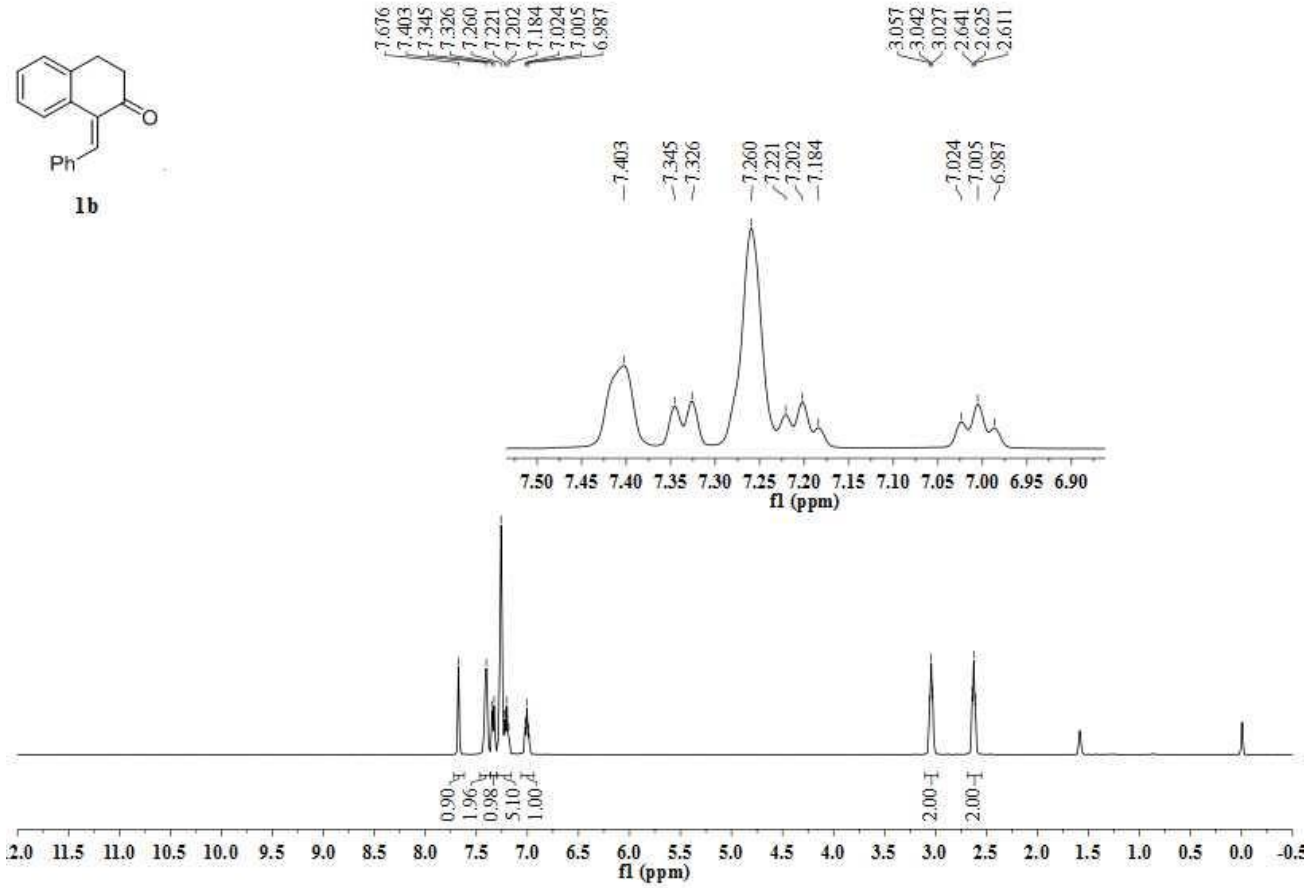
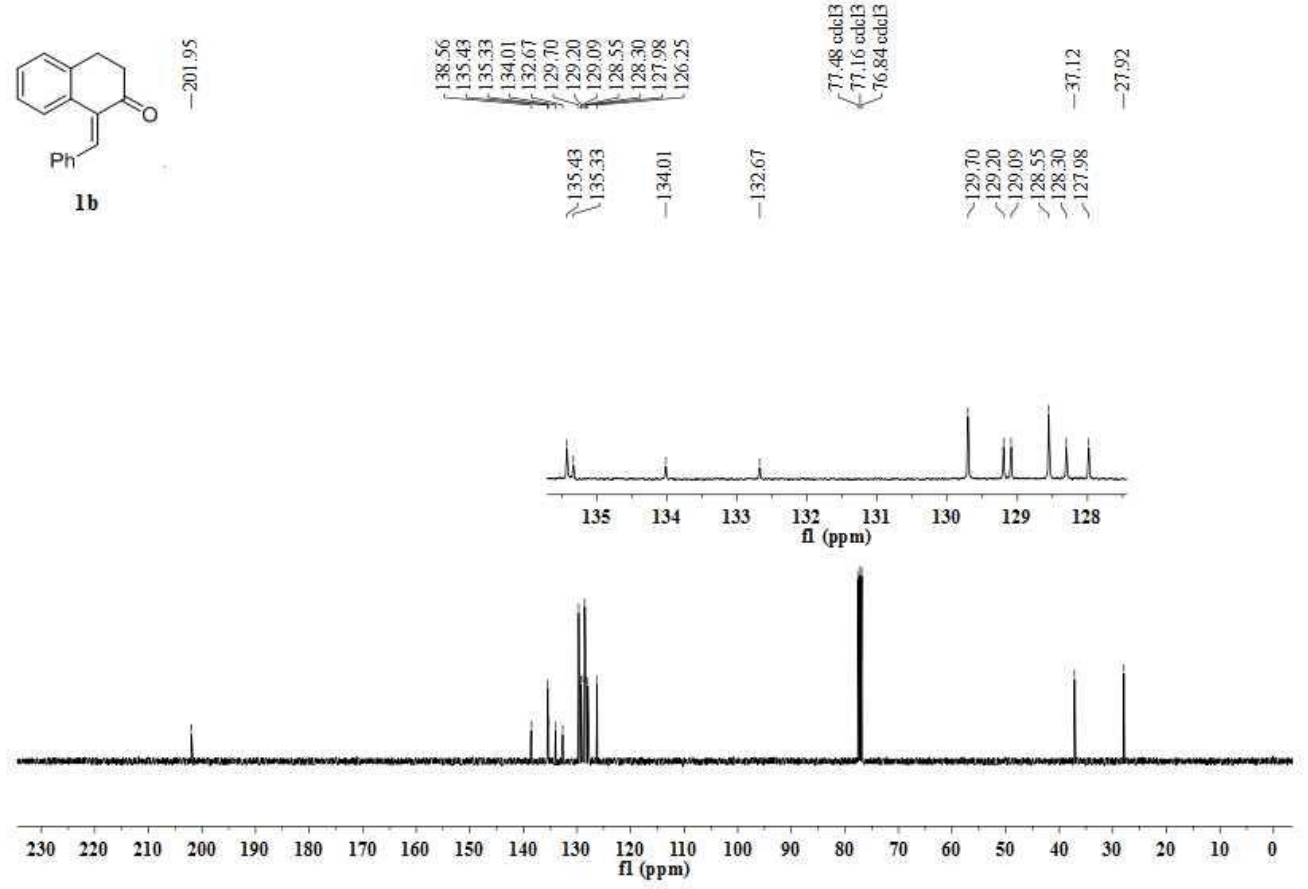
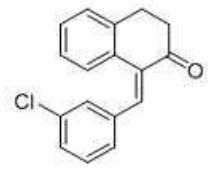
VII. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra






Cl
O

1i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7.379
7.292
7.273
7.260
7.253
7.232
7.207
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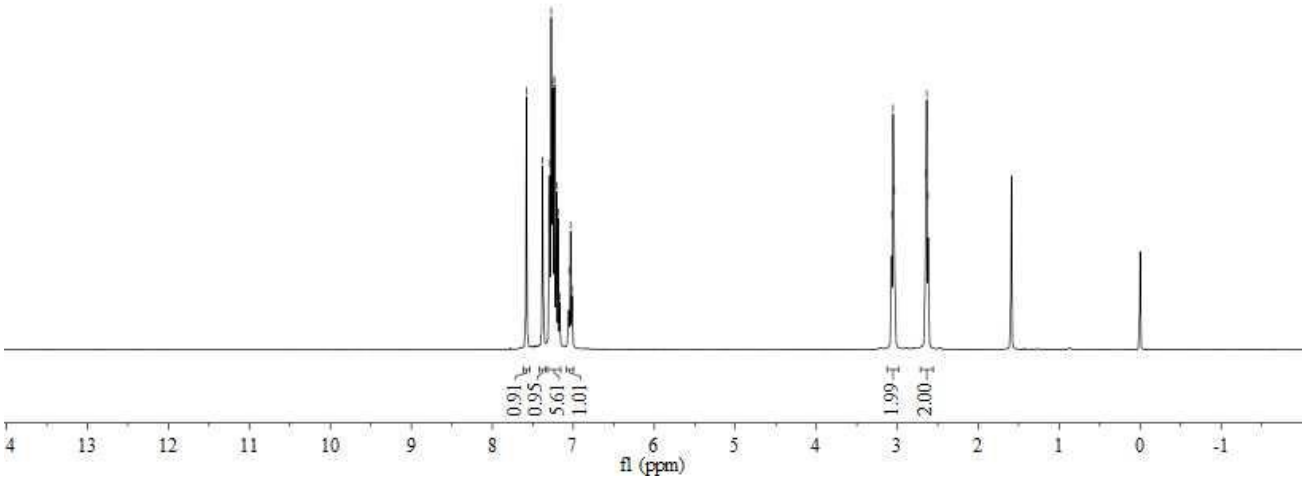
3.067
3.051
3.035
2.652
2.636
2.620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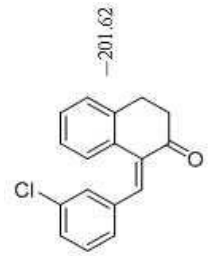
0.95
5.61
1.01
1.99
2.00
f1 (ppm)


Cl
O

1i

201.62
138.69
137.35
135.07
134.50
133.47
132.08
129.84
129.39
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128.72
128.16
127.73
126.40
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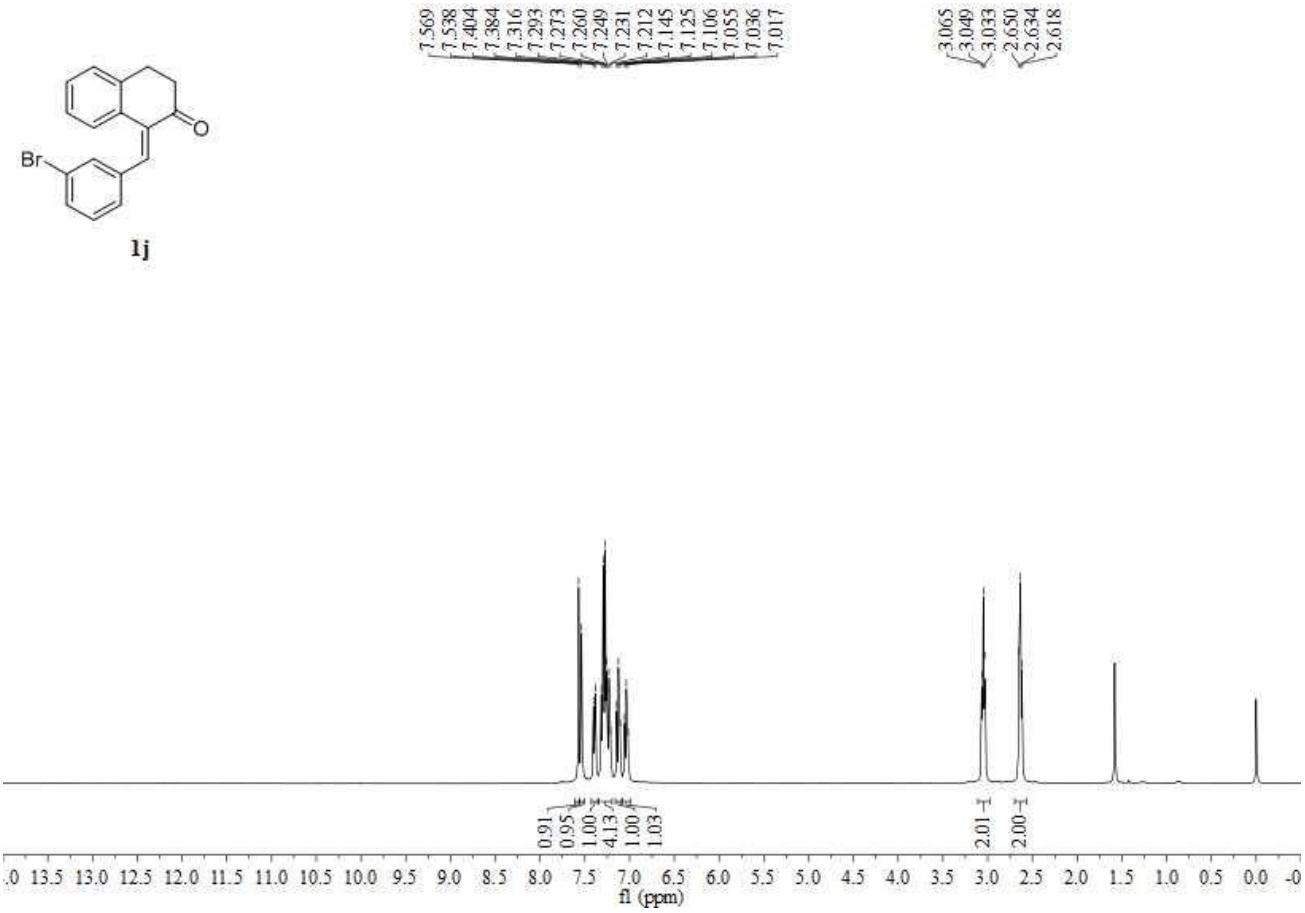
77.16
76.84
37.01
27.87
f1 (ppm)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7.260
7.249
7.231
7.212
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7.125
7.106
7.055
7.036
7.017
3.065
3.049
3.033
2.650
2.634
2.618
Br
O
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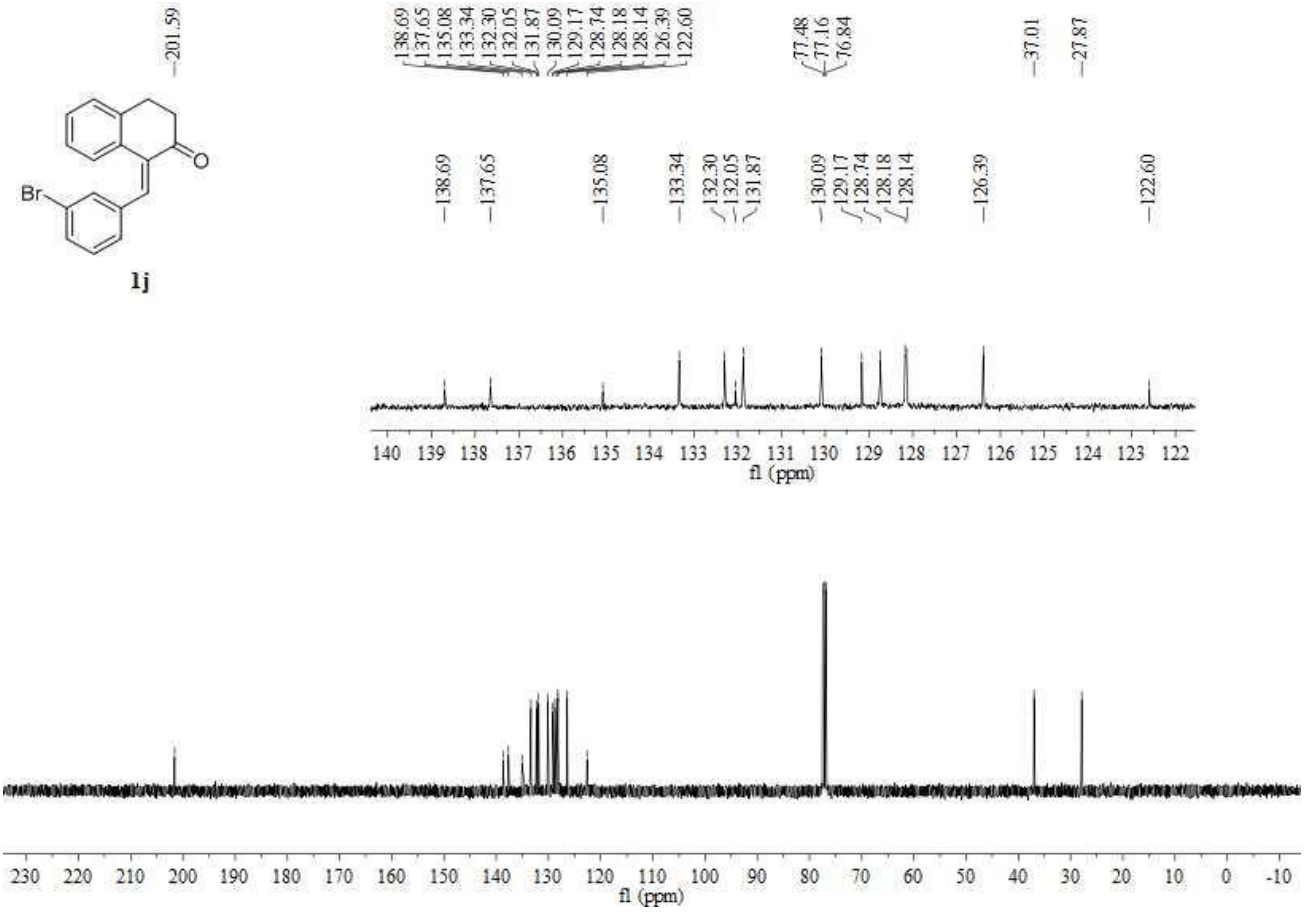
0.95
1.00
4.13
1.00
1.03
2.01
2.00
fl (ppm)

1j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132.30
132.05
131.87
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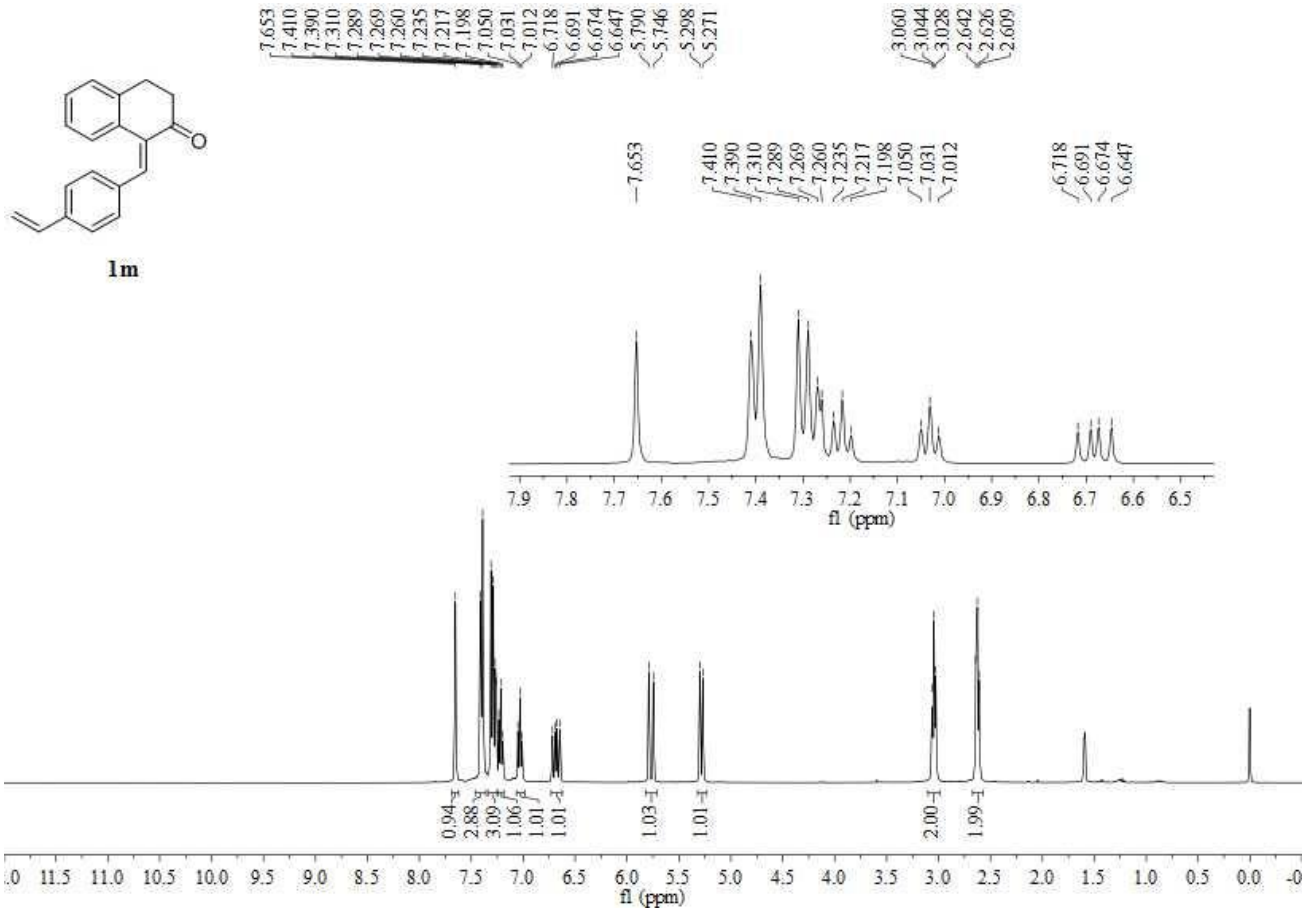
128.14
126.39
122.60
77.48
77.16
76.84
37.01
27.87
Br
O
fl (ppm)

1j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7.235
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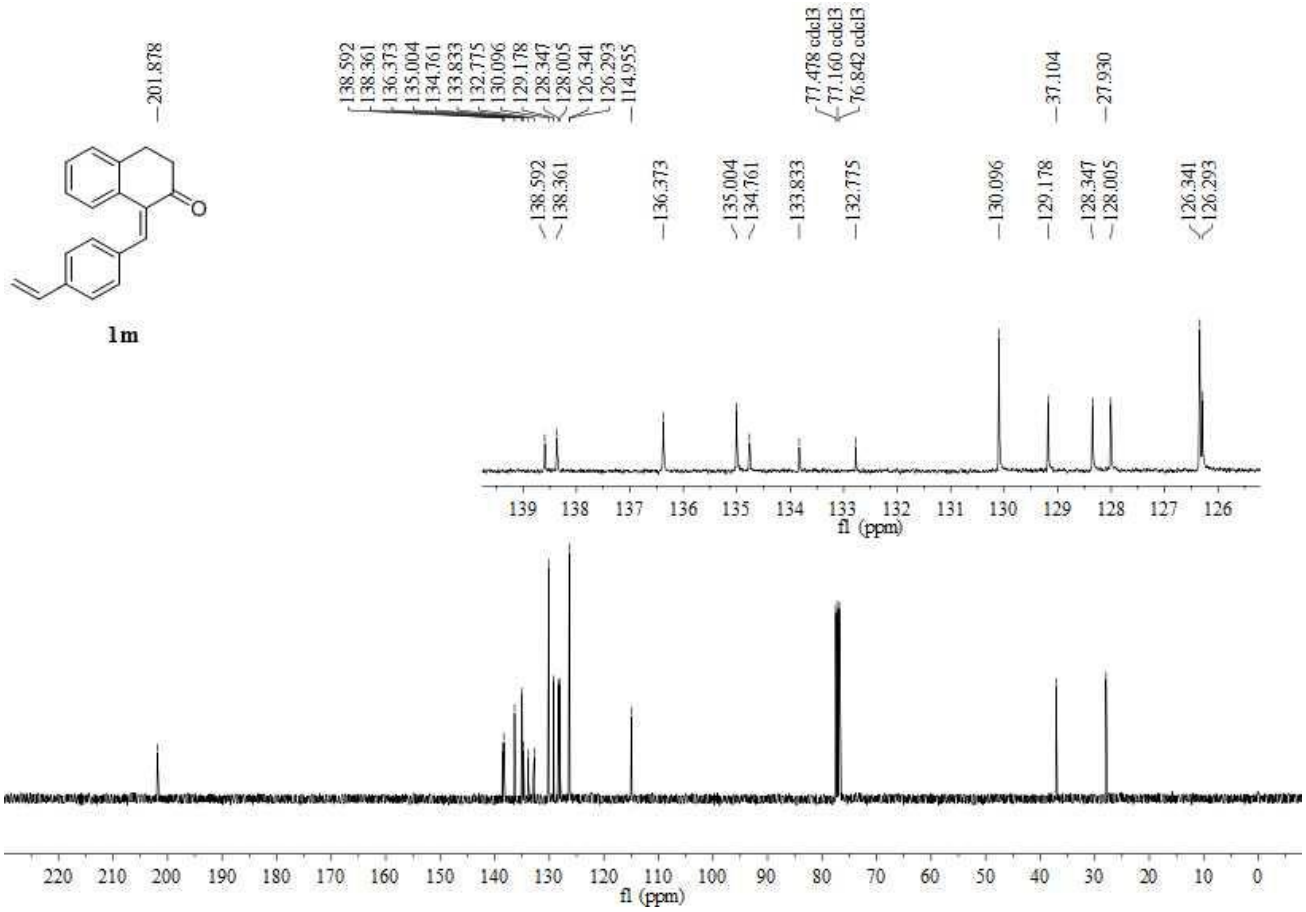
7.012
6.718
6.691
6.674
6.647
5.790
5.746
5.298
5.271
3.060
3.044
3.028
2.642
2.626
2.609
1m
0.94
2.88
3.09
1.06
1.01
1.01
1.03
1.01
2.00
1.99
fl (ppm)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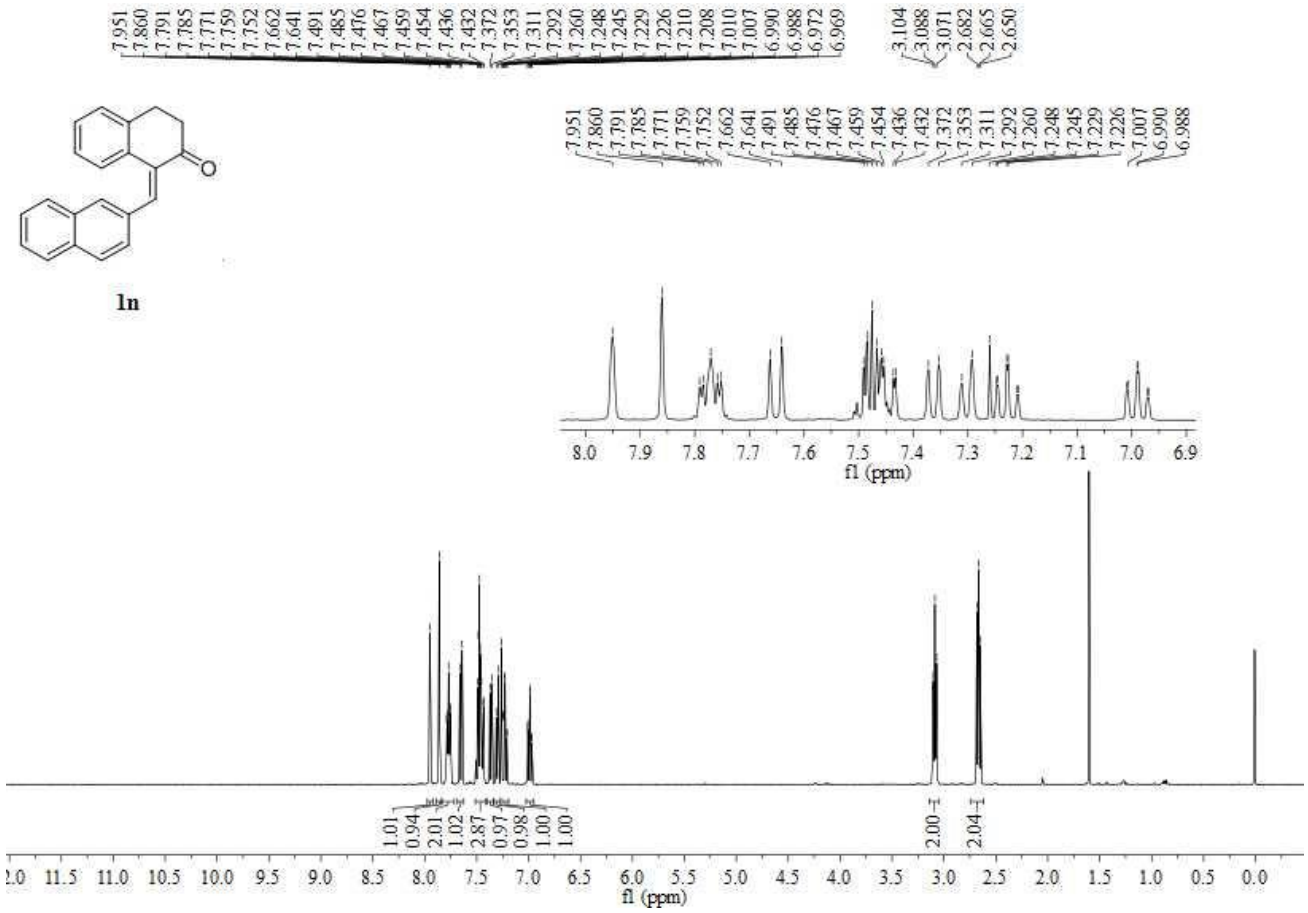
37.104
27.930
1m
fl (ppm)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7.467
7.459
7.454
7.436
7.432
7.372
7.353
7.311
7.292
7.260
7.248
7.245
7.229
7.226
7.210
7.208
7.010
7.007
6.990
6.988
6.972
6.969
3.104
3.088
3.071
2.682
2.665
2.650
O
1n
fl (ppm)
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2.01
1.02
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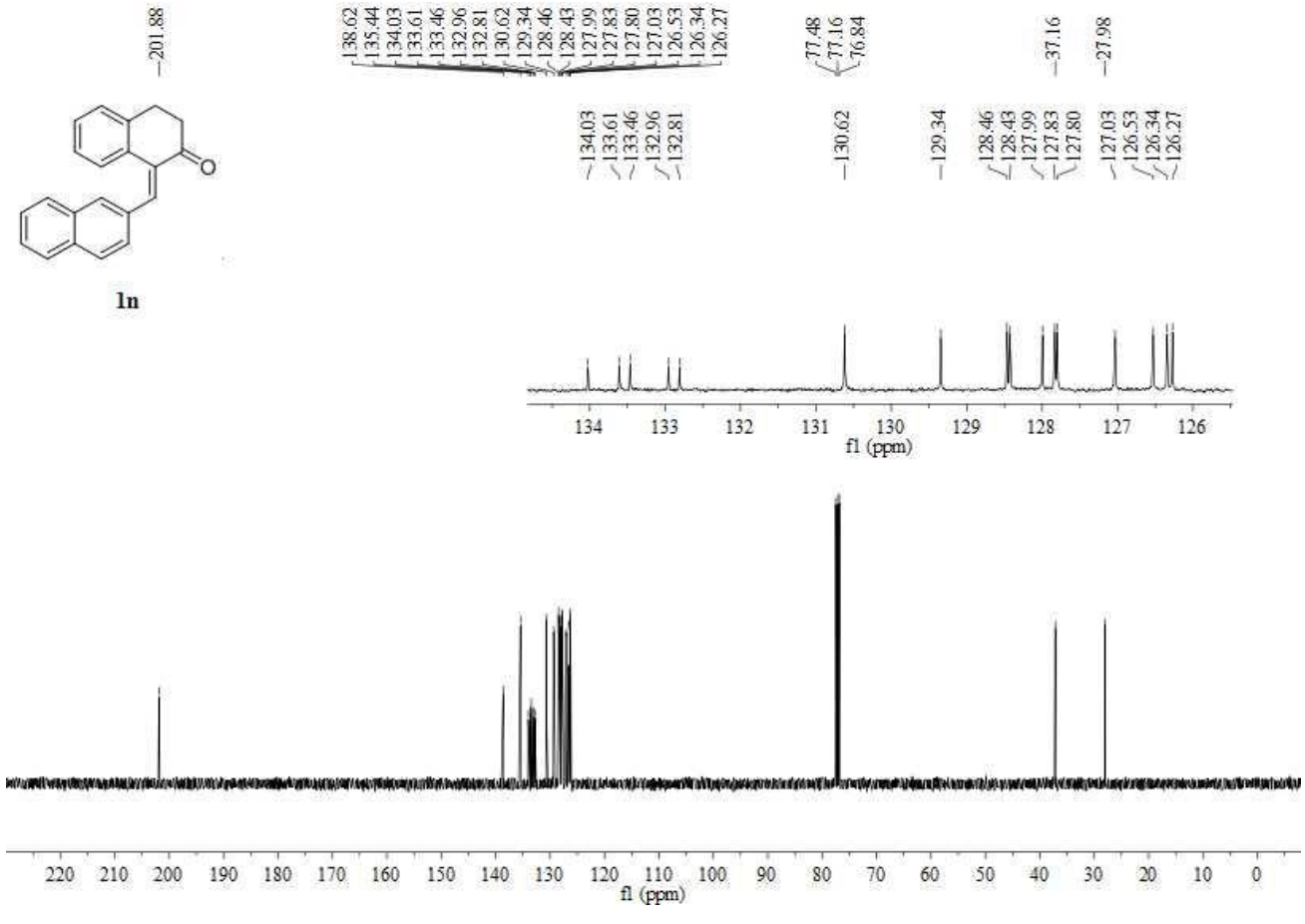
1.00
1.00
2.00
2.04
fl (ppm)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133.46
132.96
132.81
130.62
129.34
128.46
128.43
127.99
127.83
127.80
127.03
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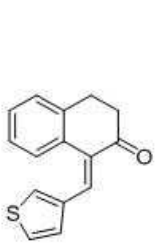
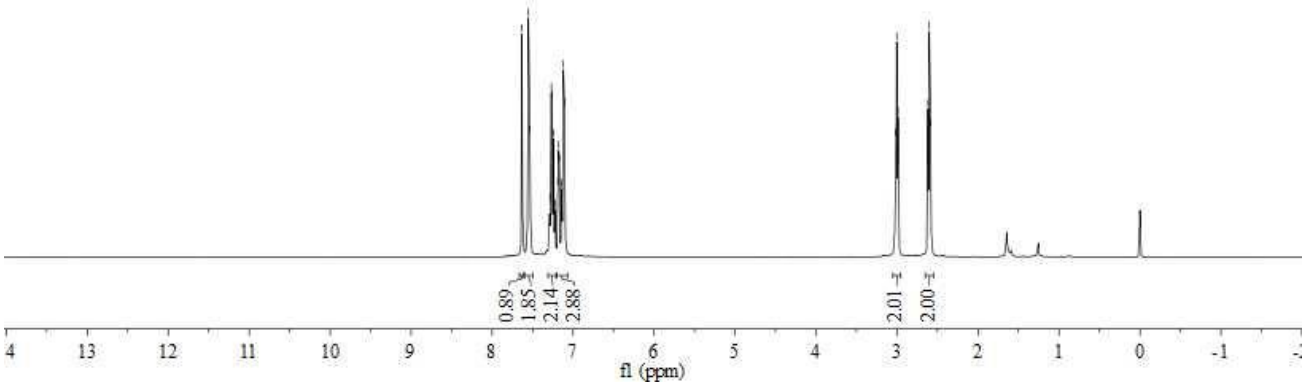
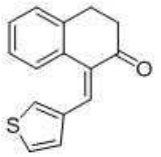
126.34
126.27
77.48
77.16
76.84
37.16
27.98
O
1n
fl (ppm)
fl (ppm)



1q





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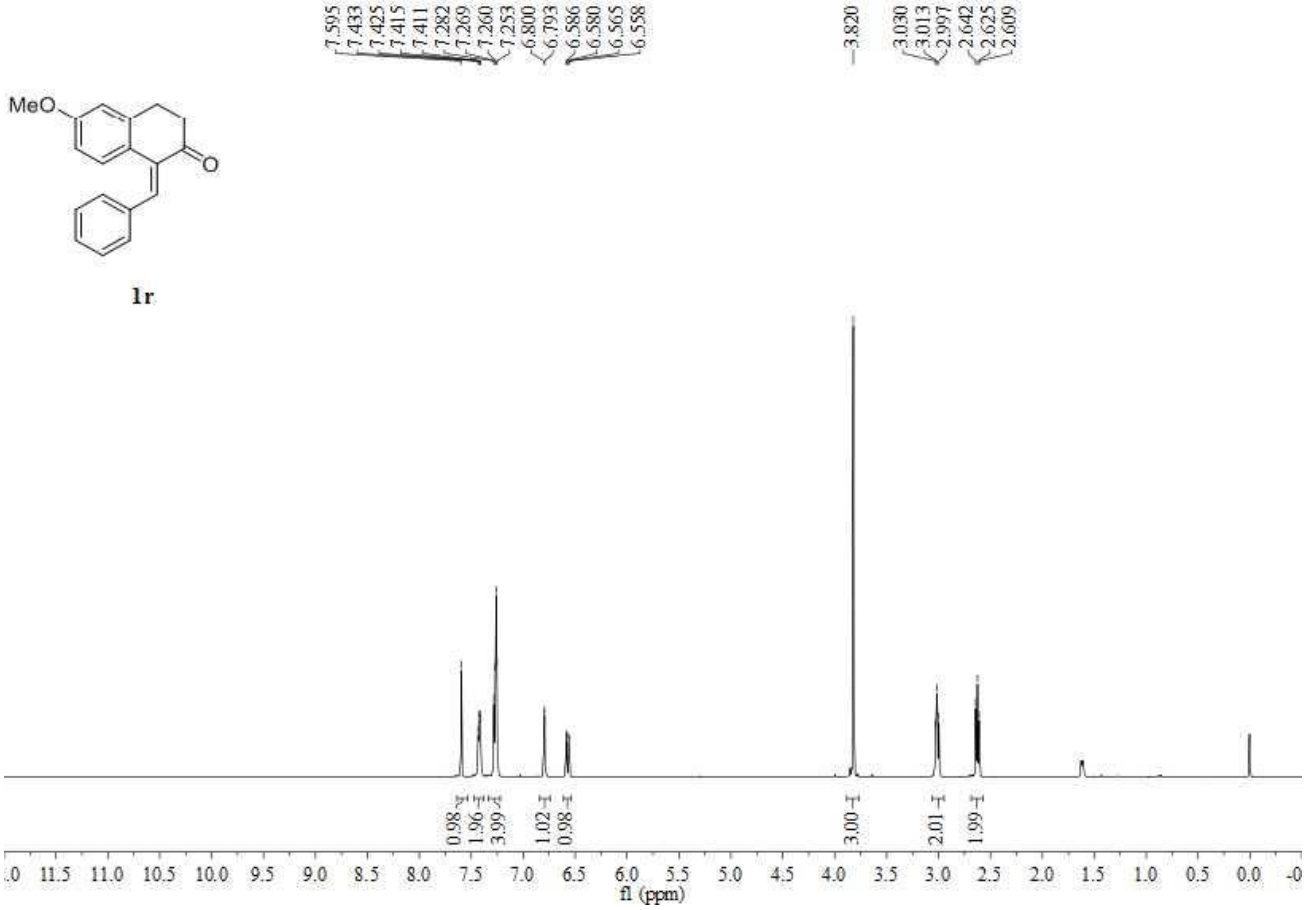
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7.260
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6.800
6.793
6.586
6.580
6.565
6.558
3.820
3.030
3.013
2.997
2.642
2.625
2.609
MeO
O
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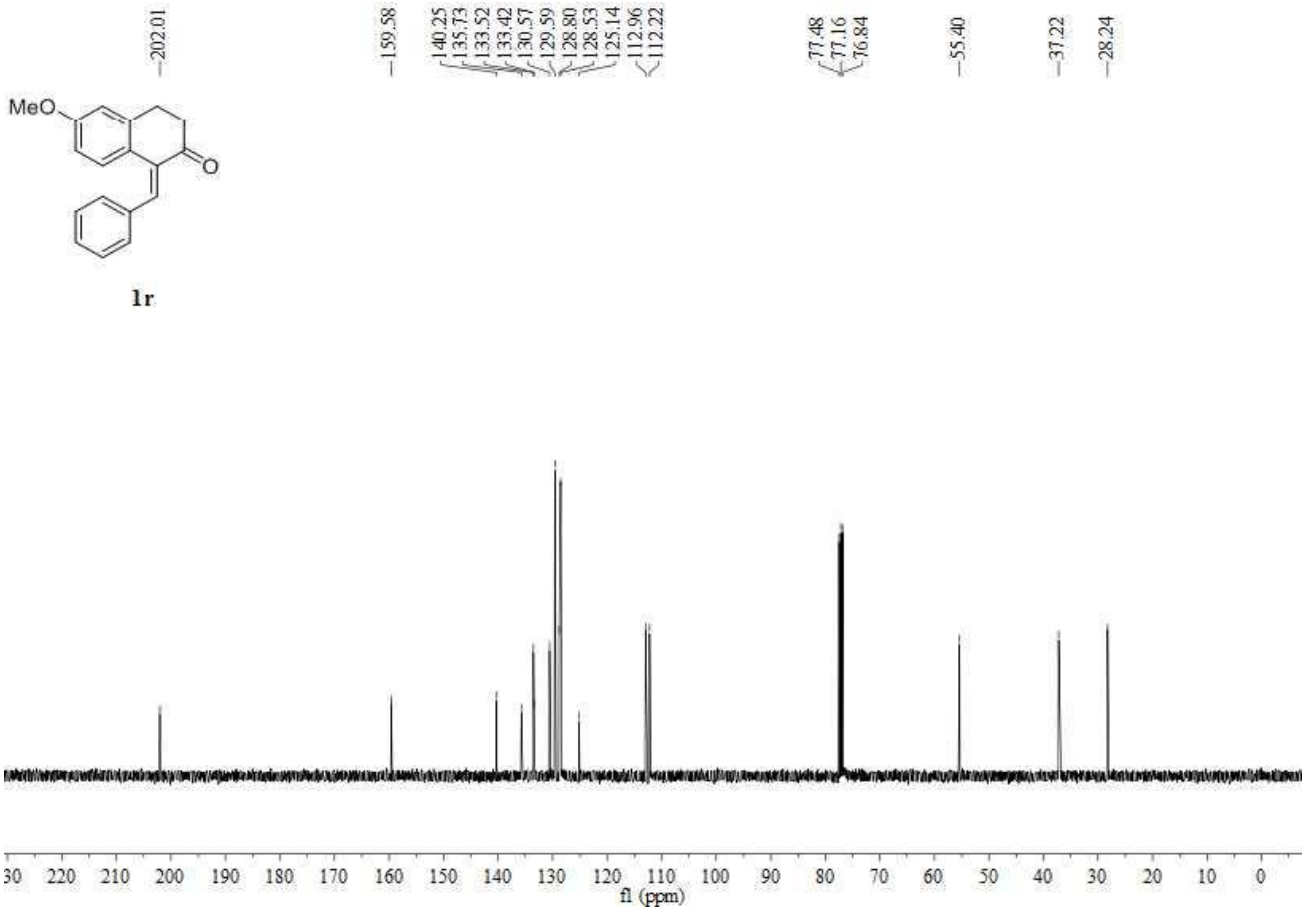
1.96
3.99
1.02
0.98
3.00
2.01
1.99
f1 (ppm)

1r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128.53
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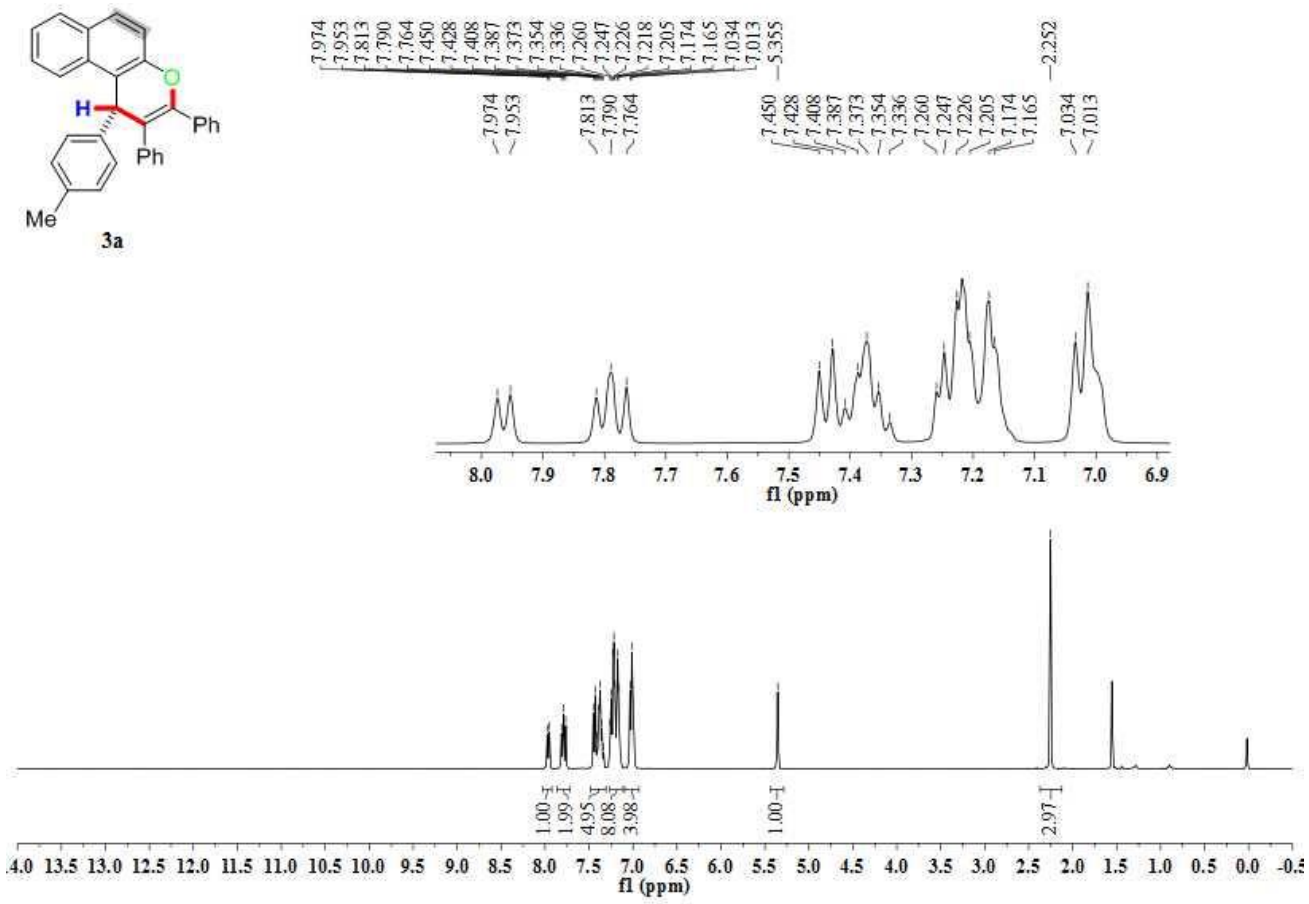
77.48
77.16
76.84
55.40
37.22
28.24
MeO
O
f1 (ppm)

1r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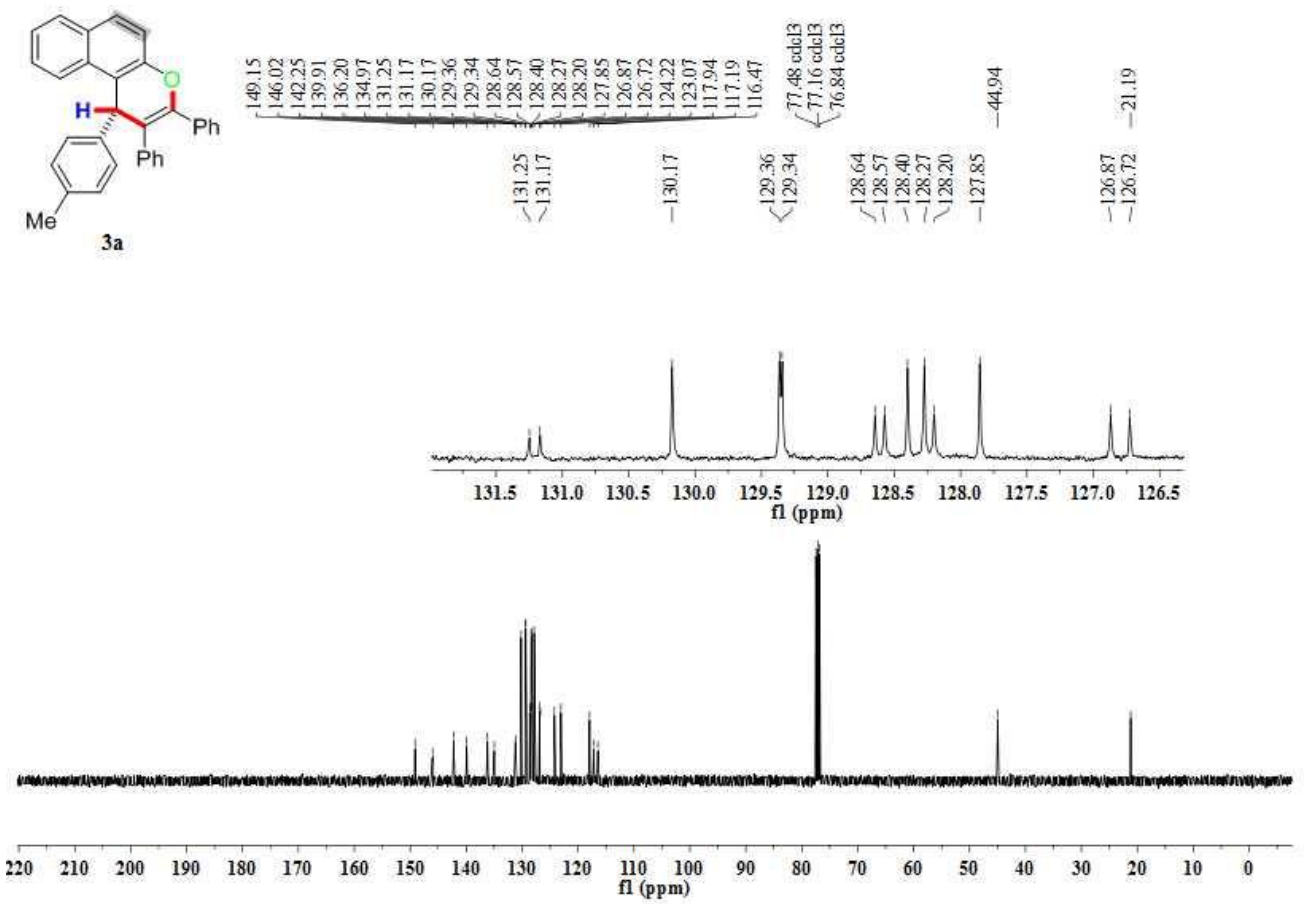
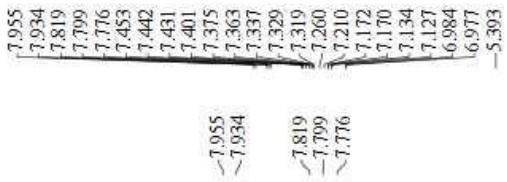
Ph
Me
3a
fl (ppm)


Ph
Ph
Me
3a
fl (ppm)


H
Ph
Ph
Ph
O

3b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7.776
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7.431
7.401
7.375
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7.260
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7.172
7.170
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7.127
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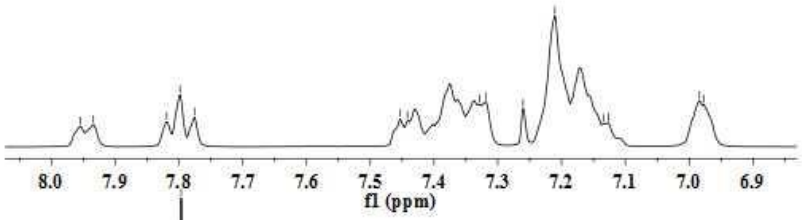
6.977
5.393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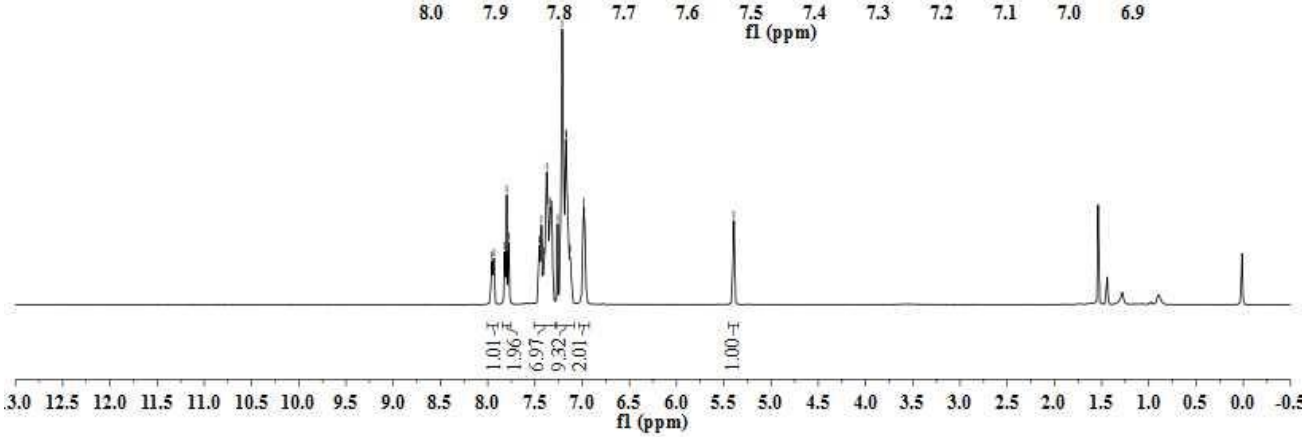
7.2
7.1
7.0
6.9
f1 (ppm)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2.01
1.00
f1 (ppm)


H
Ph
Ph
Ph
O

3b


149.25
146.01
145.18
139.80
134.92
131.30
131.18
130.19
129.33
128.72
128.66
128.62
128.58
128.32
128.23
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126.92
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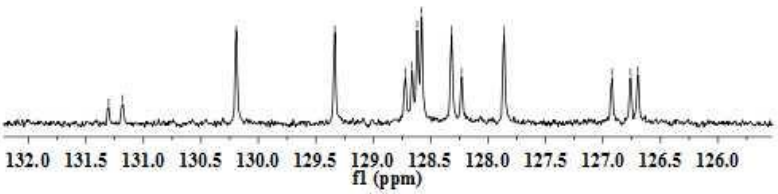
45.51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130.0
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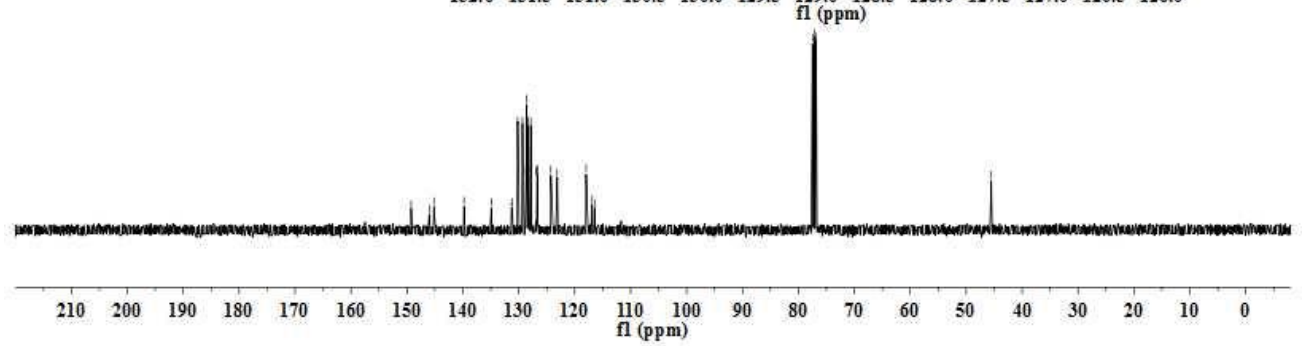
128.5
128.0
127.5
127.0
126.5
126.0
f1 (ppm)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200
190
180
170
160
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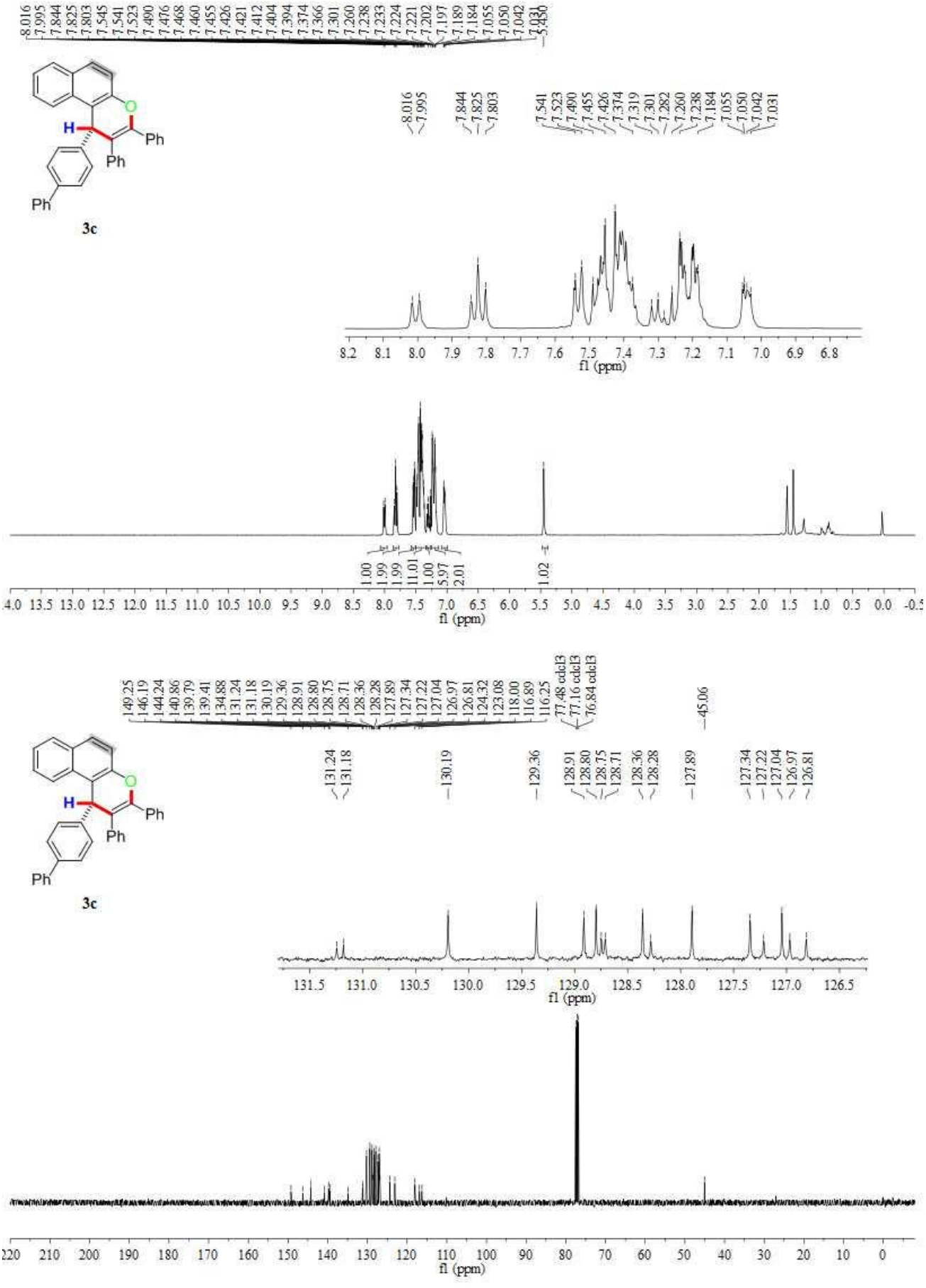
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.460
7.455
7.426
7.421
7.412
7.404
7.394
7.374
7.366
7.301
7.260
7.238
7.233
7.224
7.221
7.202
7.197
7.189
7.184
7.055
7.050
7.042
7.031
5.450
O
H
Ph
Ph
Ph
3c
f1 (ppm)
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1.99
1.99
11.01
1.00
5.97
2.01
1.02
149.25
146.19
144.24
140.86
139.79
139.41
134.88
131.24
131.18
130.19
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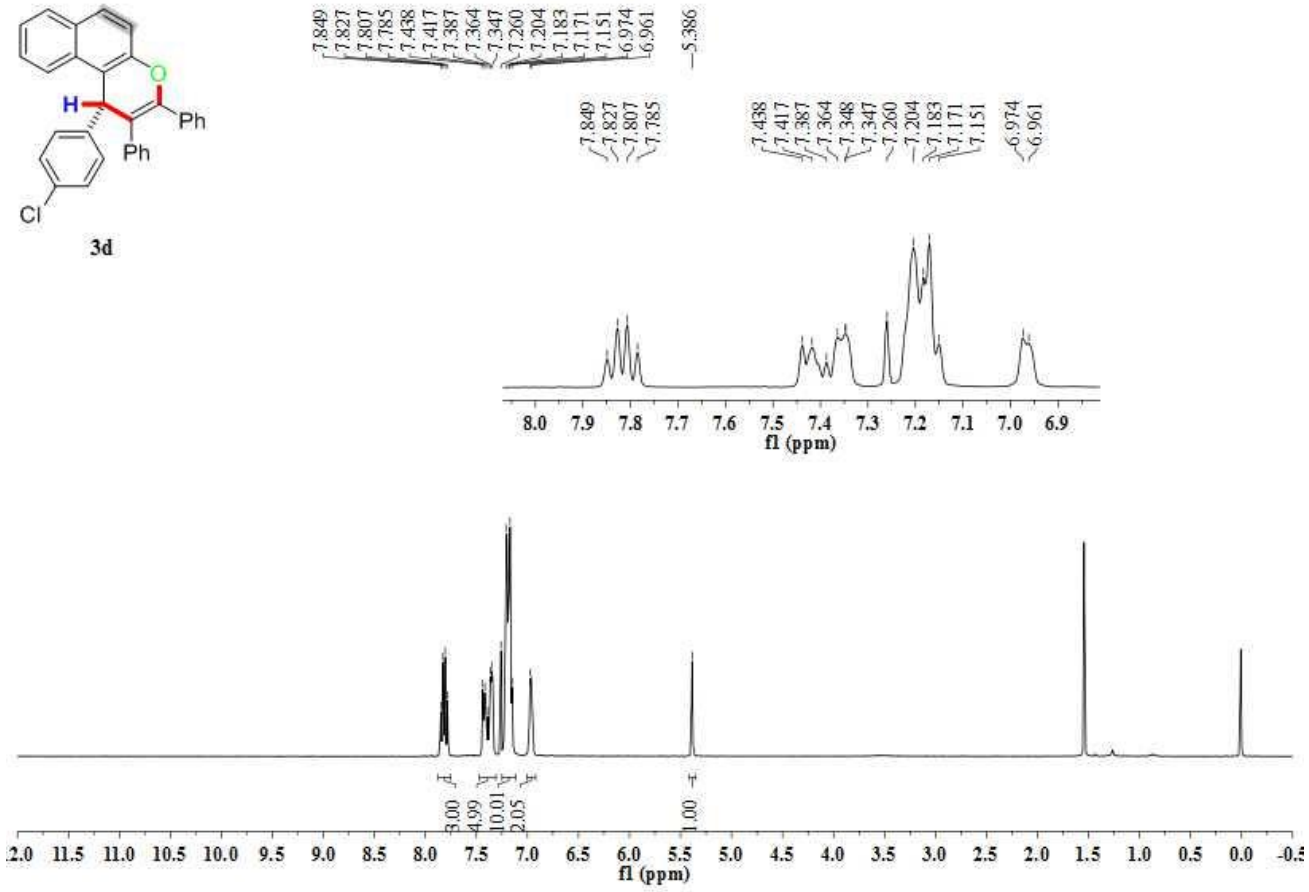
76.84 cdcl3
45.06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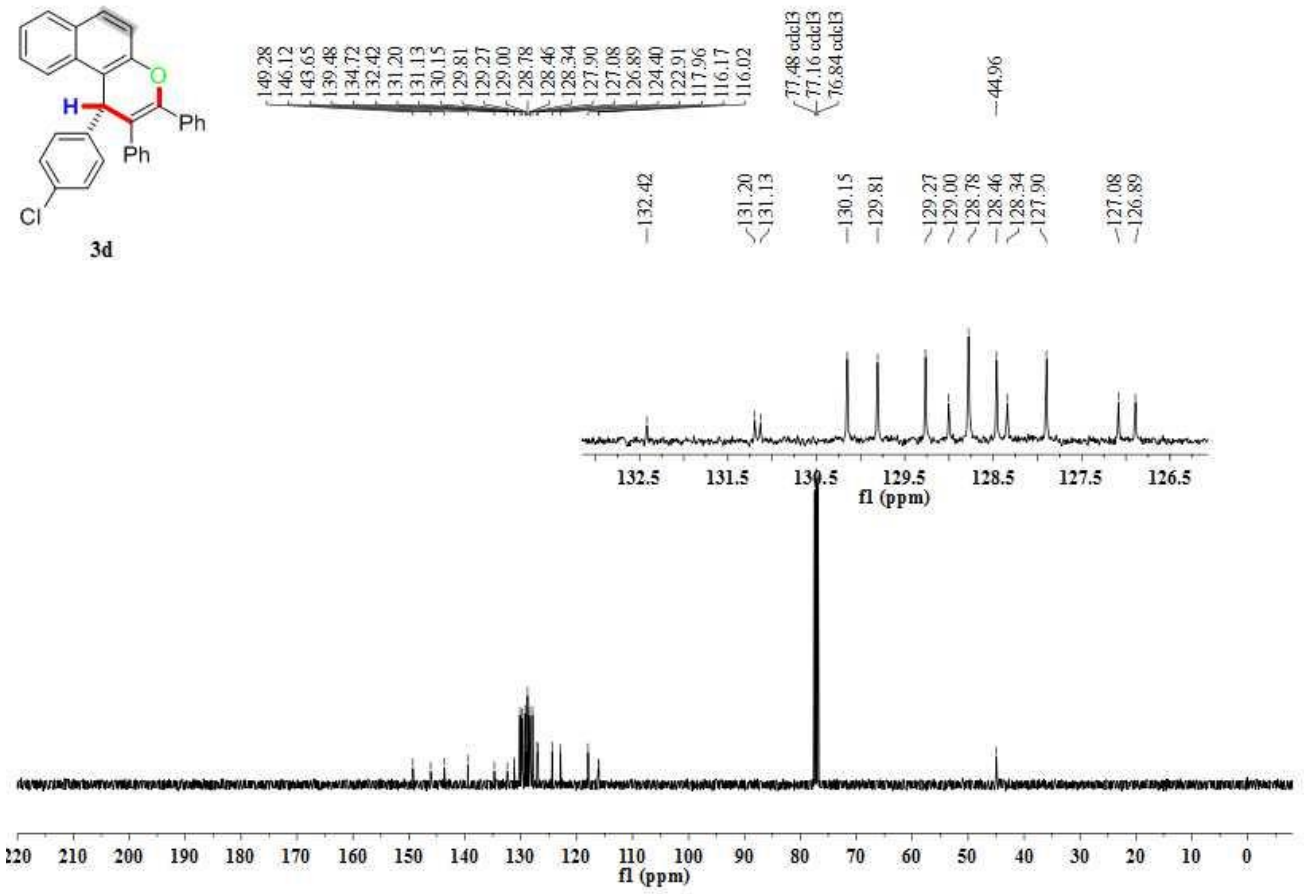
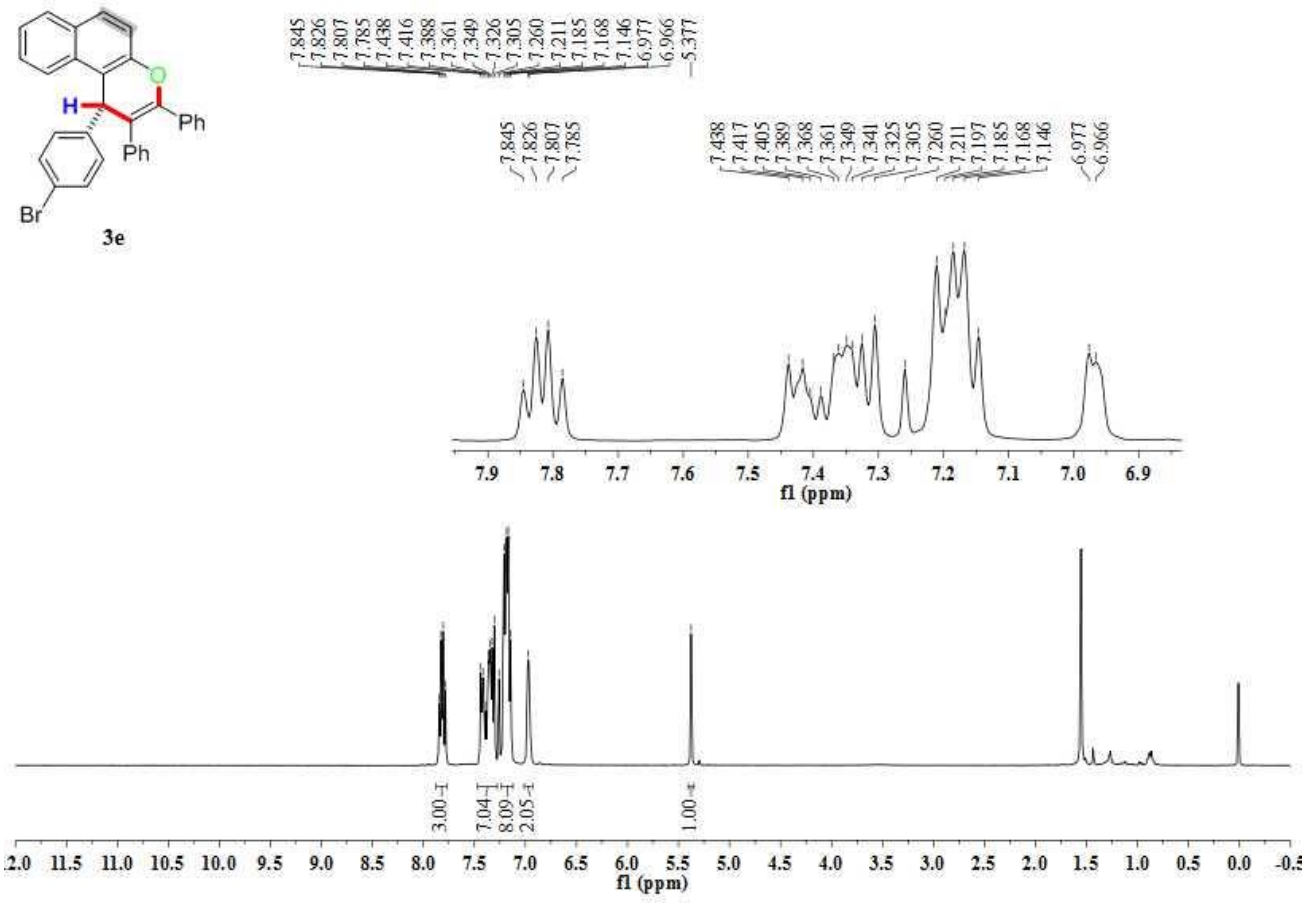
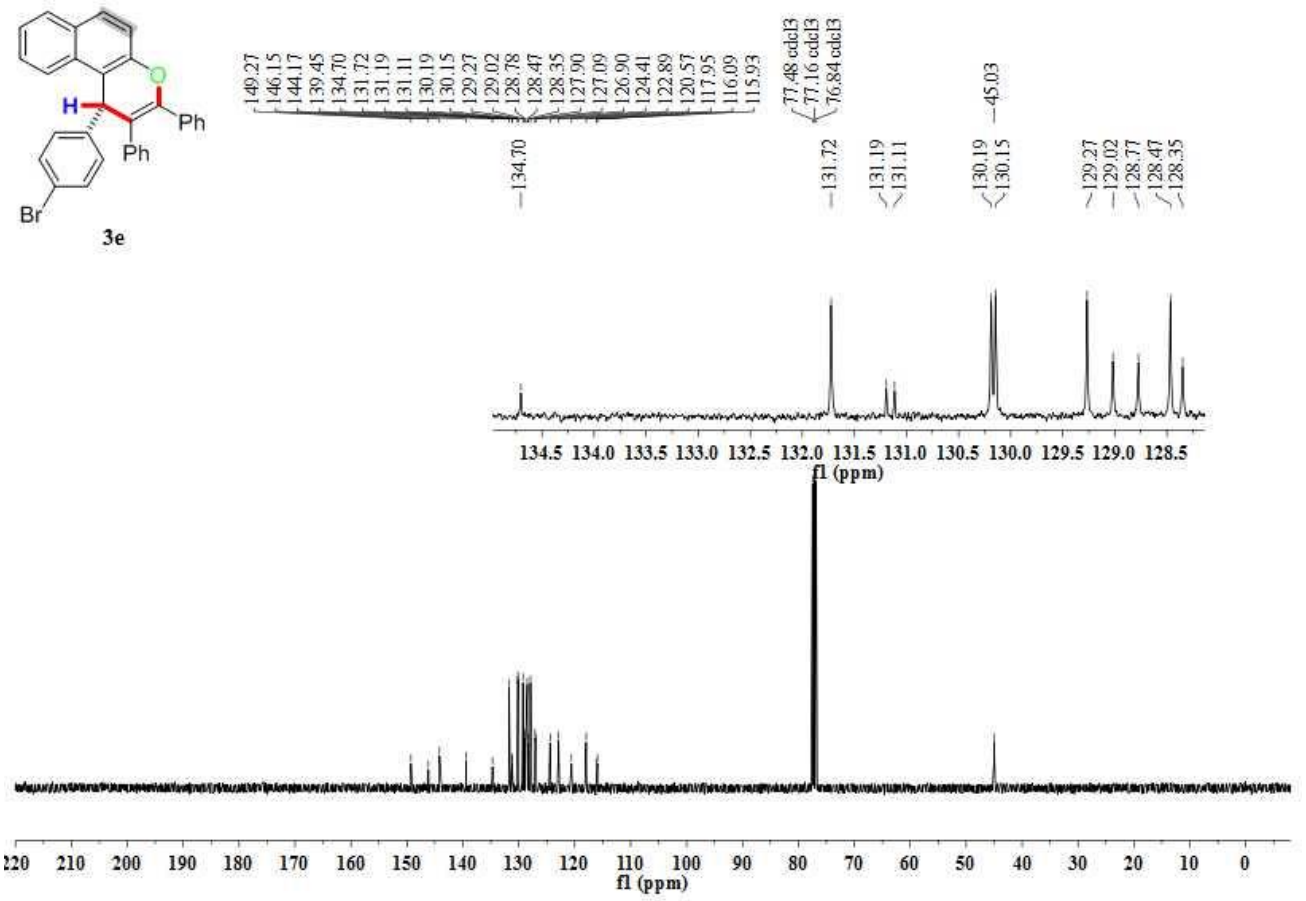
7.183
7.171
7.151
6.974
6.961
5.386
3.00
4.99
10.01
2.05
1.00
f1 (ppm)


3d
149.28
146.12
143.65
139.48
134.72
132.42
131.20
131.13
130.15
129.81
129.27
129.00
128.78
128.46
128.34
127.90
127.08
126.89
124.40
122.91
117.96
116.17
116.02
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
44.96
f1 (ppm)


3e
7.845
7.826
7.807
7.785
7.438
7.416
7.388
7.361
7.349
7.326
7.305
7.260
7.211
7.185
7.168
7.146
6.977
6.966
5.377
3.00
7.04
8.09
2.05
1.00
fl (ppm)


3e
149.27
146.15
144.17
139.45
134.70
131.72
131.19
131.11
130.19
130.15
129.27
129.02
128.78
128.47
128.35
127.90
127.09
126.90
124.41
122.89
120.57
117.95
116.09
115.93
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
45.03
fl (ppm)


O
H
Ph
Ph
I

3f

7.845
7.825
7.805
7.783
7.523
7.505
7.432
7.410
7.388
7.352
7.340
7.260
7.210
7.185
7.049
7.030
6.975
6.967
5.352
2.97
1.93
5.00
6.27
2.03
2.08
1.00
f1 (ppm)

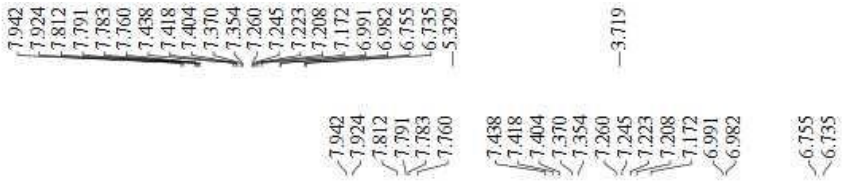

O
H
Ph
Ph
I

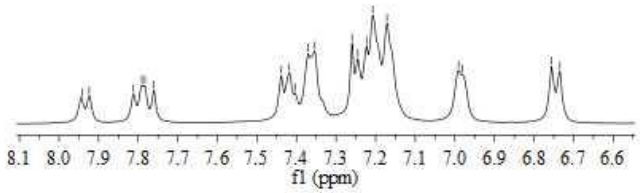
3f

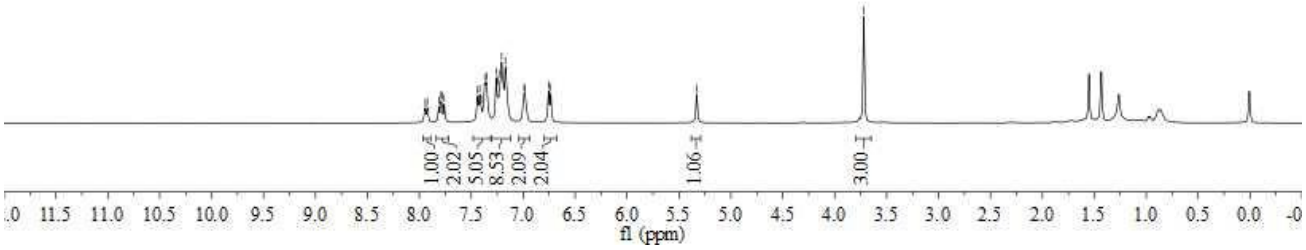
149.24
146.19
144.86
139.45
137.69
134.68
131.17
131.09
130.49
130.13
129.27
129.00
128.77
128.46
128.36
127.90
127.09
126.91
124.41
122.86
117.94
116.09
115.86
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
45.08
f1 (ppm)


H
O
Ph
Ph
MeO

3g

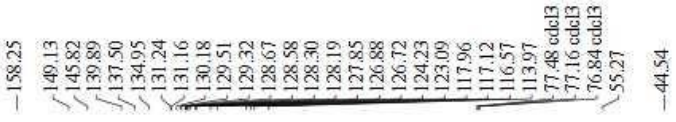

7.942
7.924
7.812
7.791
7.783
7.760
7.438
7.418
7.404
7.370
7.354
7.260
7.245
7.223
7.208
7.172
6.991
6.982
6.755
6.735
5.329
3.719


8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)


1.00
2.02
5.05
8.53
2.09
2.04
1.06
3.00
f1 (ppm)


H
O
Ph
Ph
MeO

3g


158.25
149.13
145.82
139.89
137.50
134.95
131.24
131.16
130.18
129.51
129.32
128.67
128.58
128.30
128.19
127.85
126.88
126.72
124.23
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116.57
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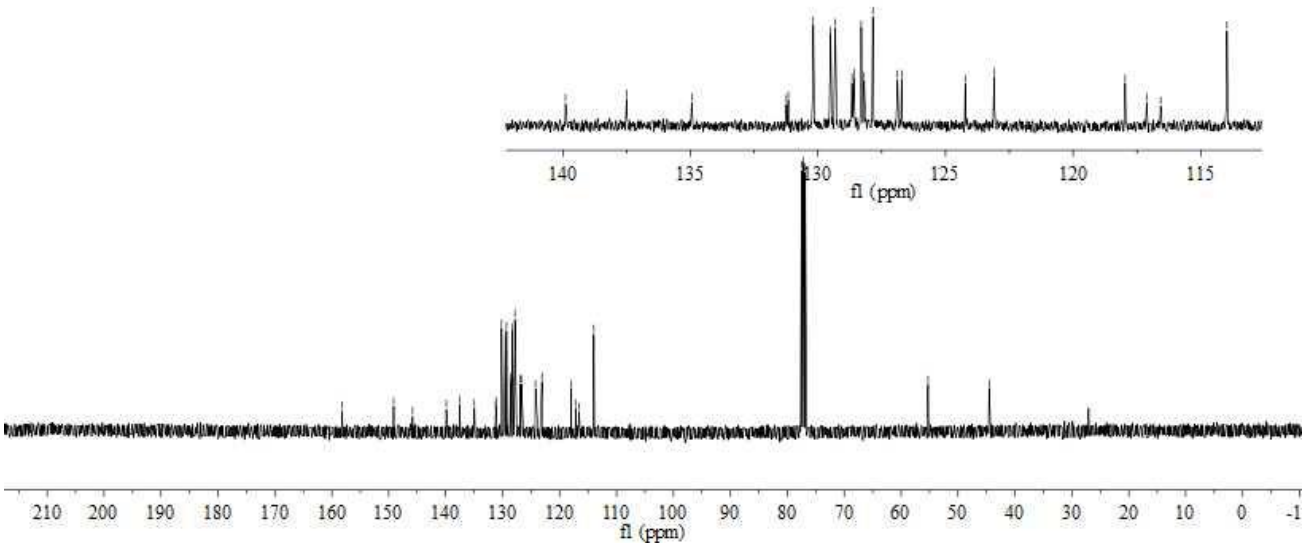
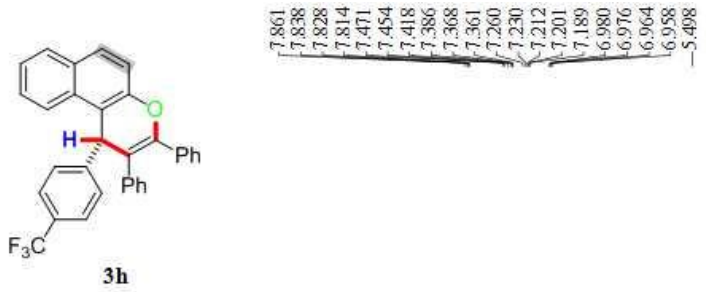
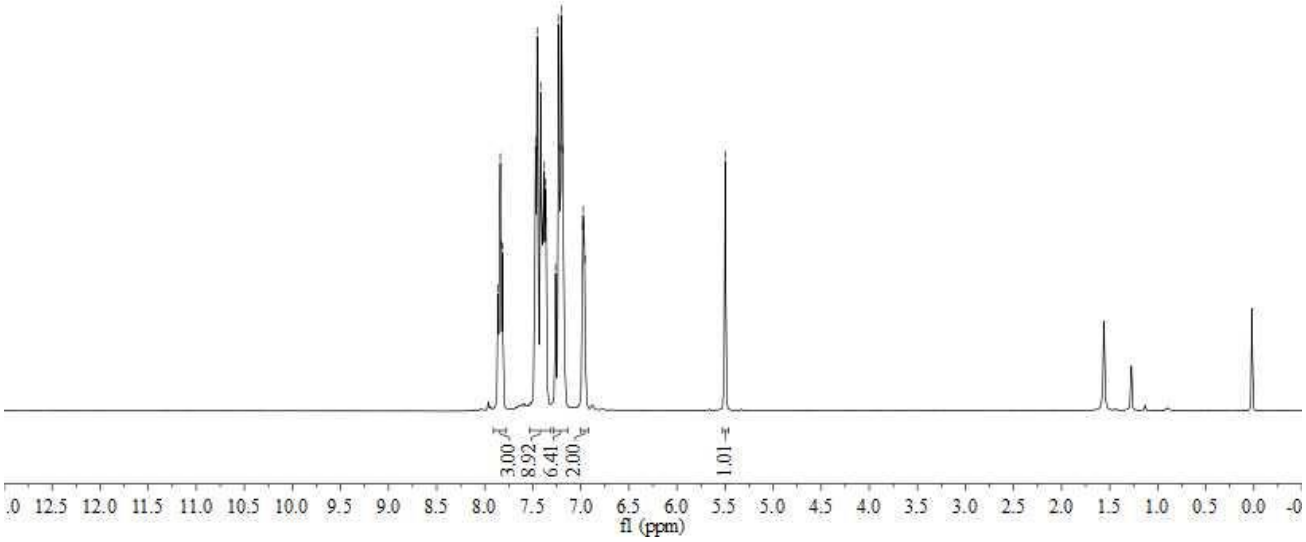
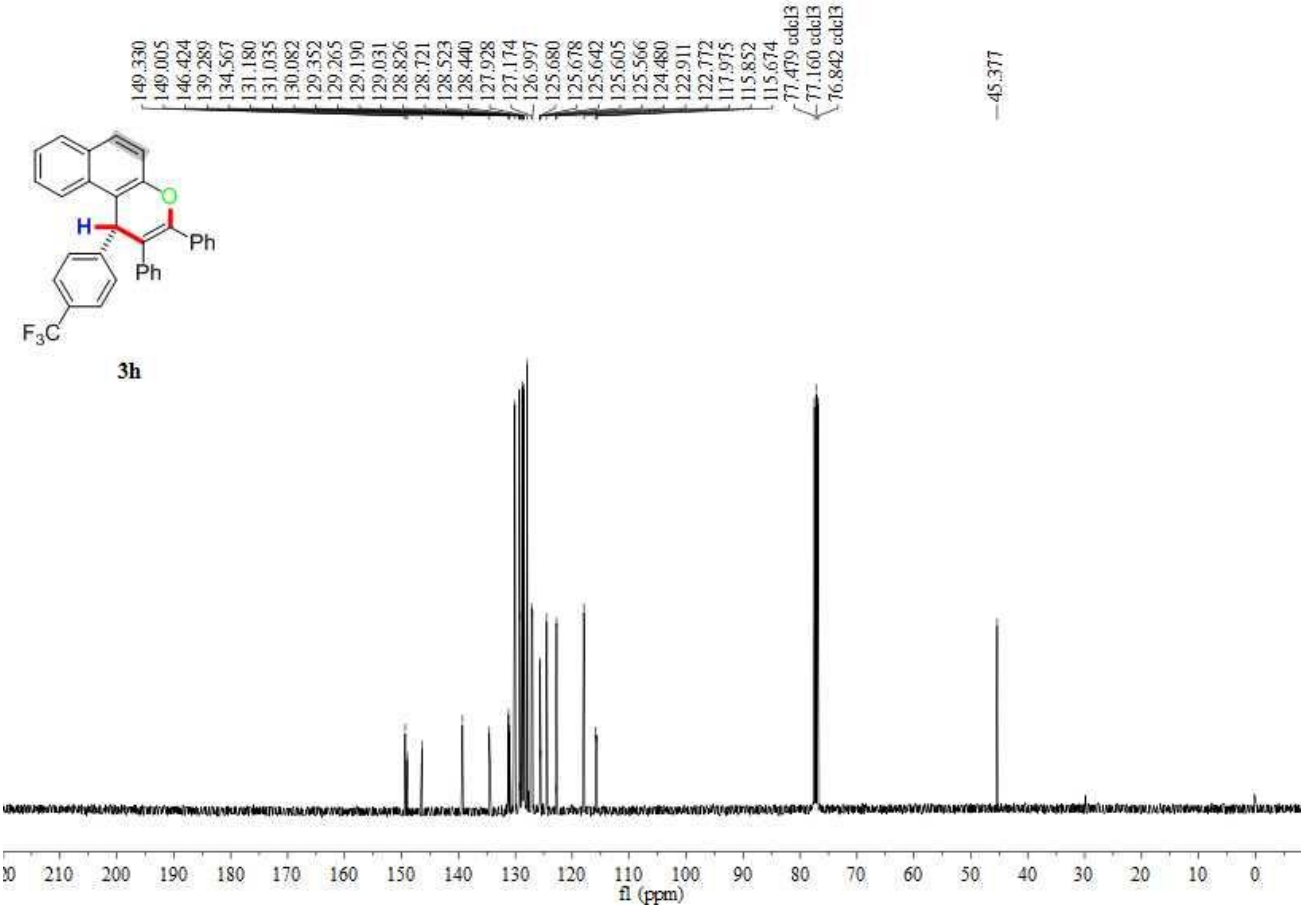
77.16 cdcl3
76.84 cdcl3
55.27
44.54


140
135
130
125
120
115
f1 (ppm)
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)

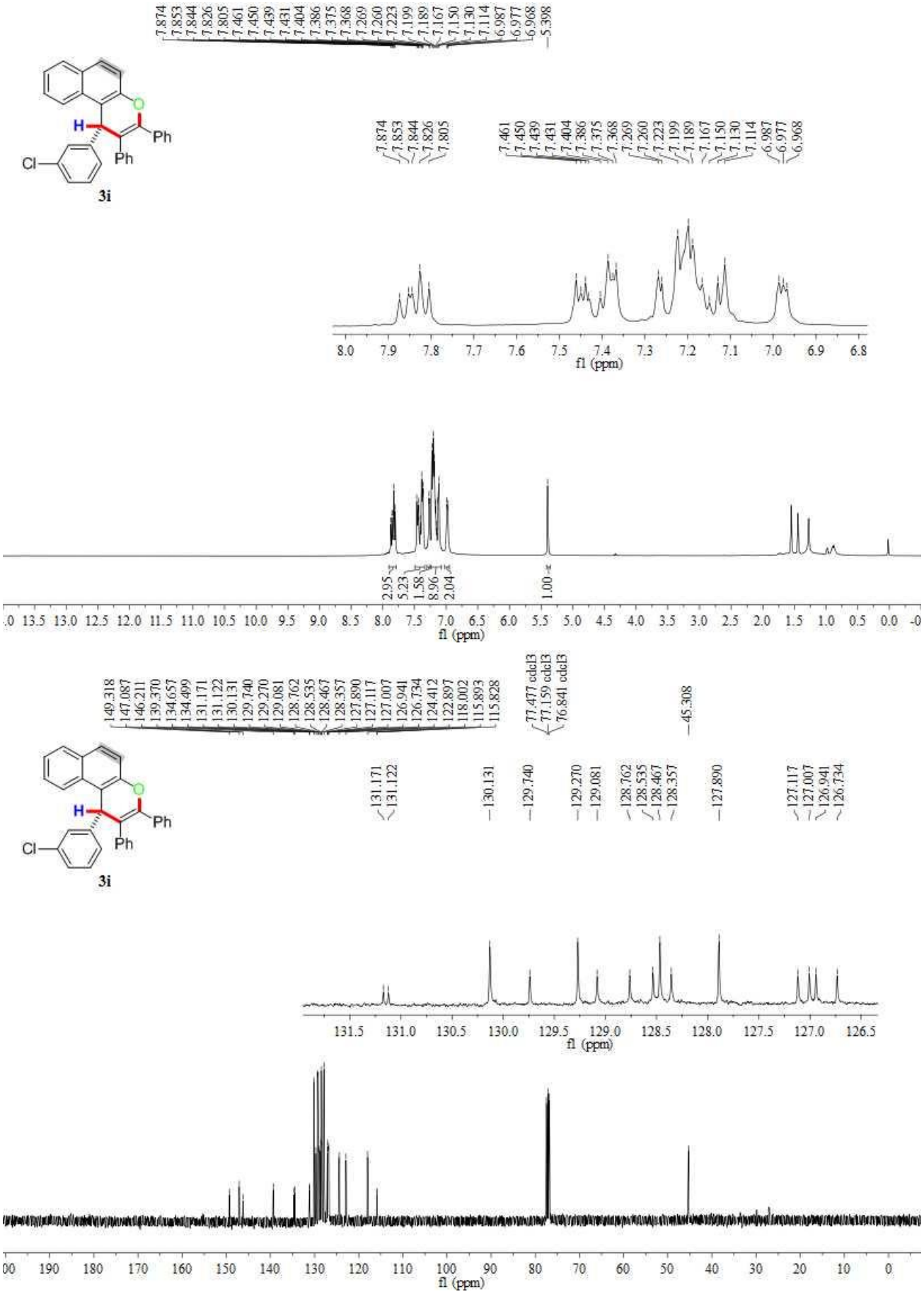

7.861
7.838
7.828
7.814
7.471
7.454
7.418
7.386
7.368
7.361
7.260
7.230
7.212
7.201
7.189
6.980
6.976
6.964
6.958
5.498
O
H
Ph
Ph
F3C

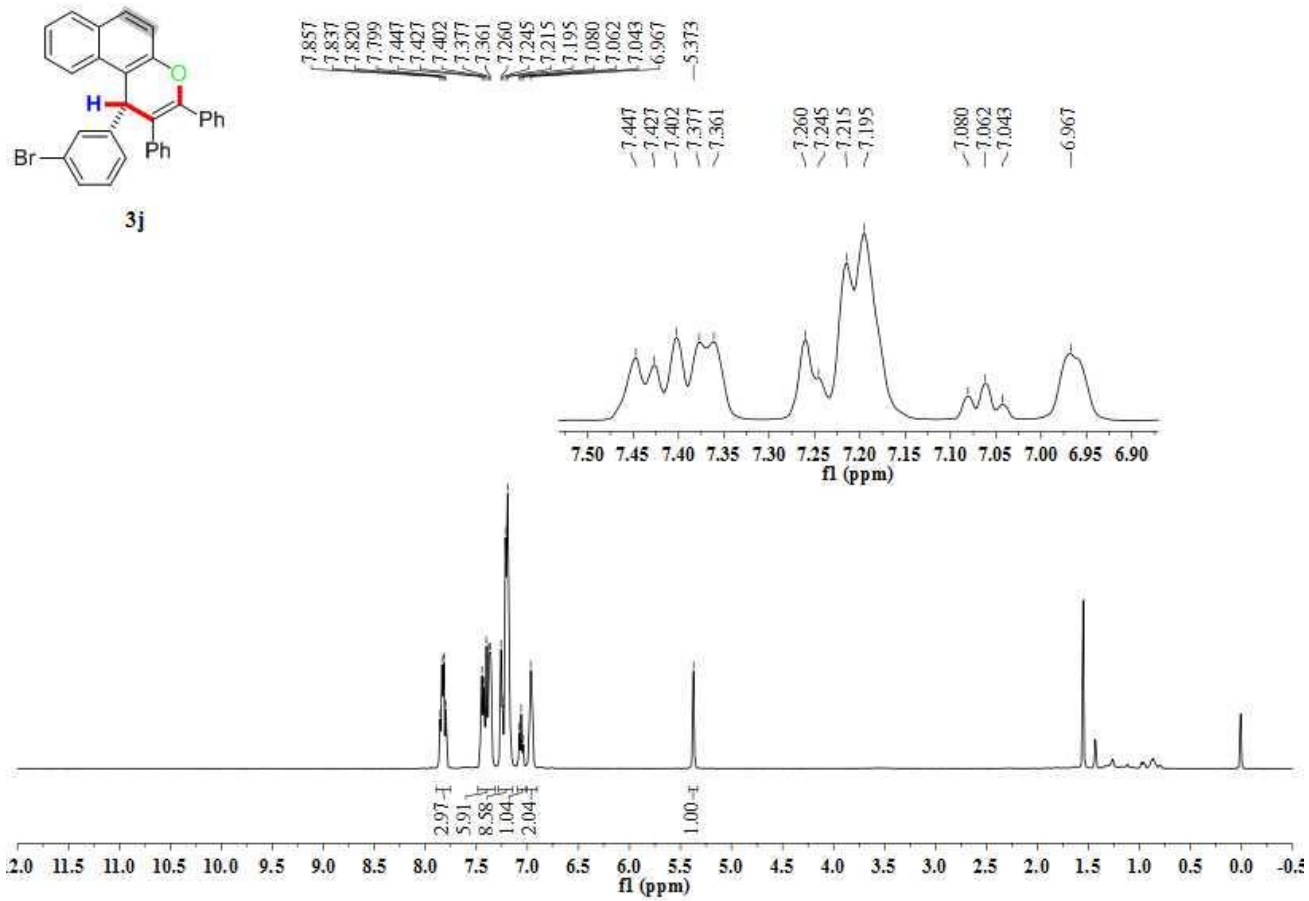
3h

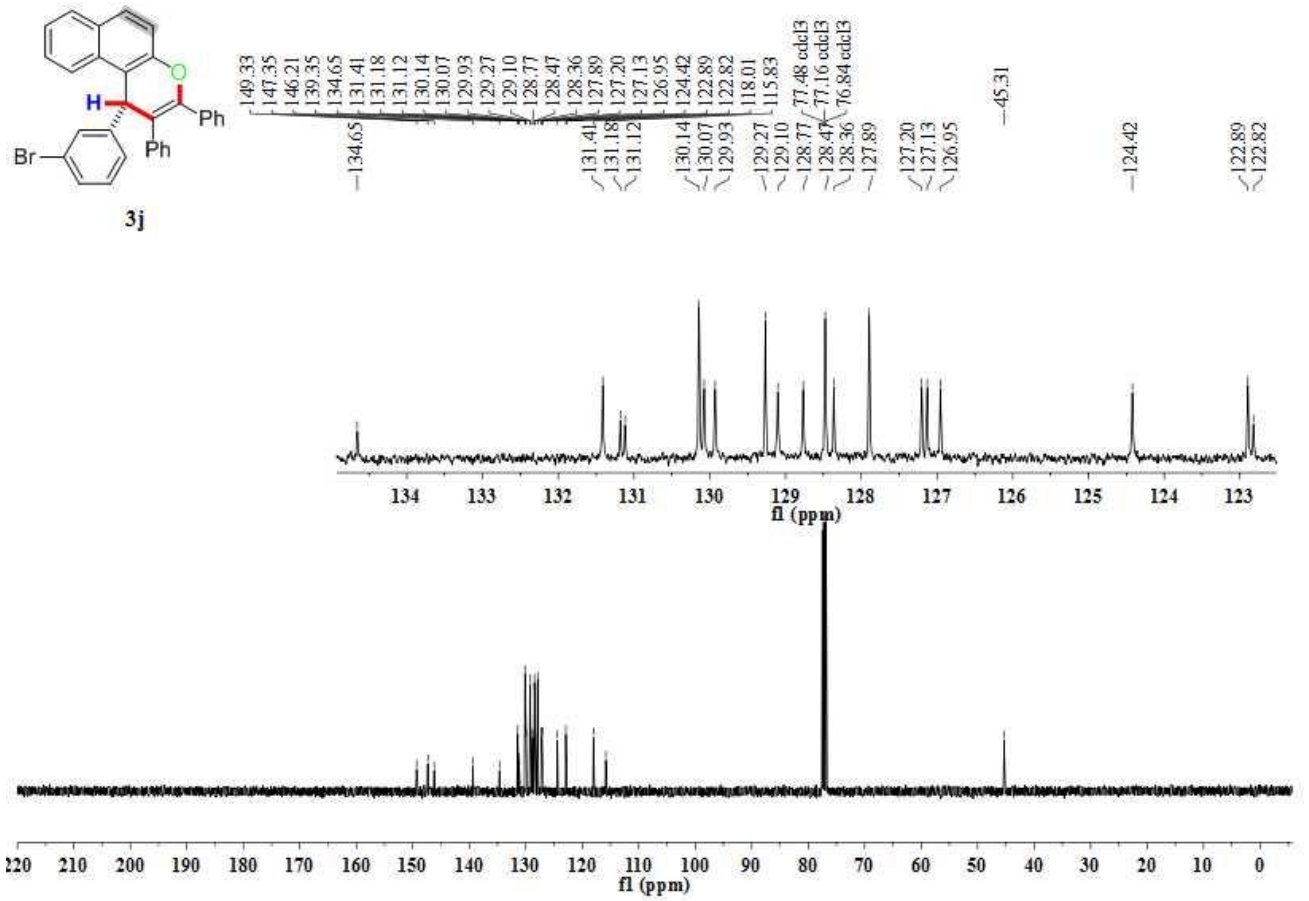

3.00
8.92
6.41
2.00
1.01
fl (ppm)

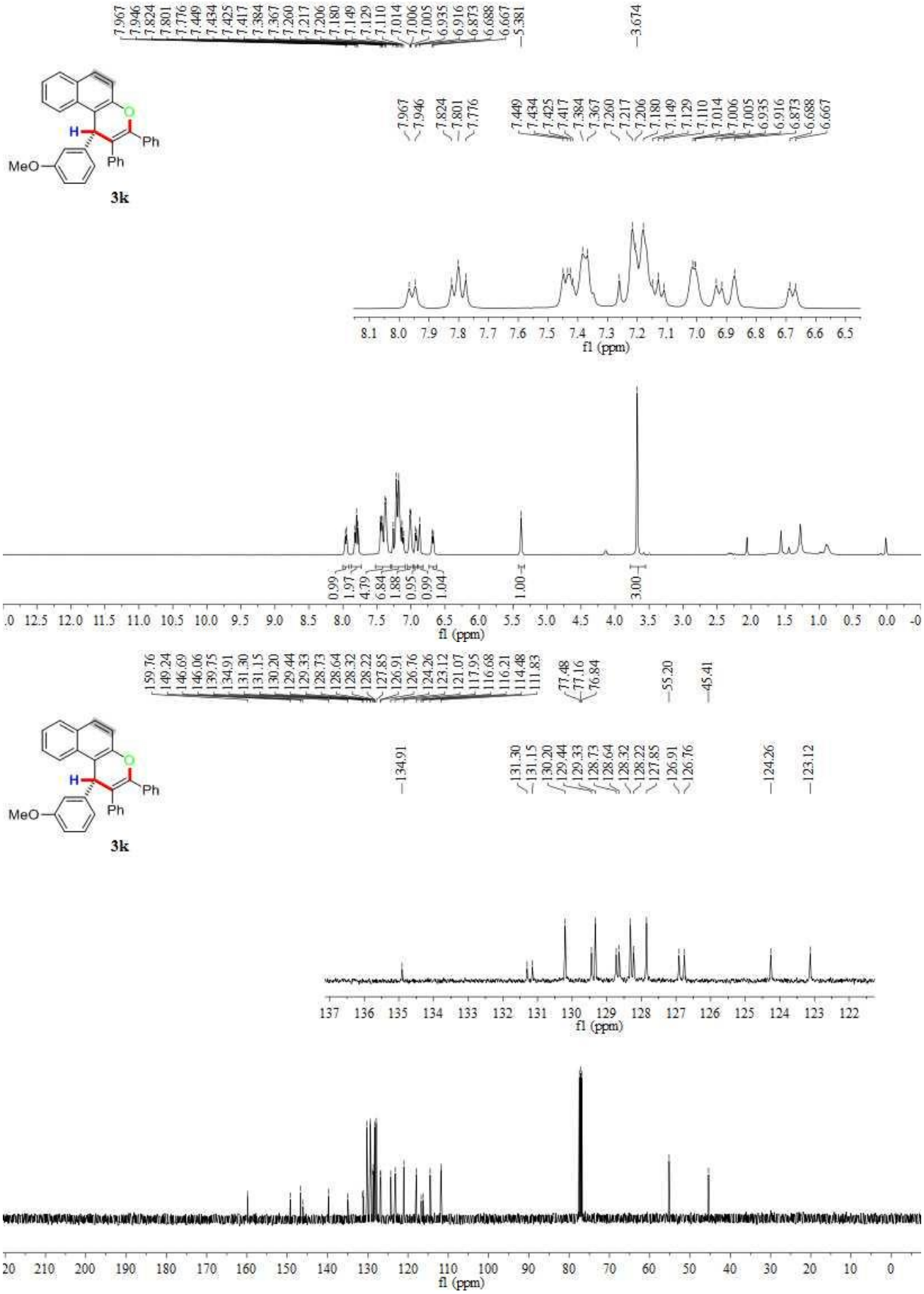

149.330
149.005
146.424
139.289
134.567
131.180
131.035
130.082
129.352
129.265
129.190
129.031
128.826
128.721
128.523
128.440
127.928
127.174
126.997
125.680
125.678
125.642
125.605
125.566
124.480
122.911
122.772
117.975
115.852
115.674
77.479 cdcl3
77.160 cdcl3
76.842 cdcl3
45.377
O
H
Ph
Ph
F3C
fl (ppm)

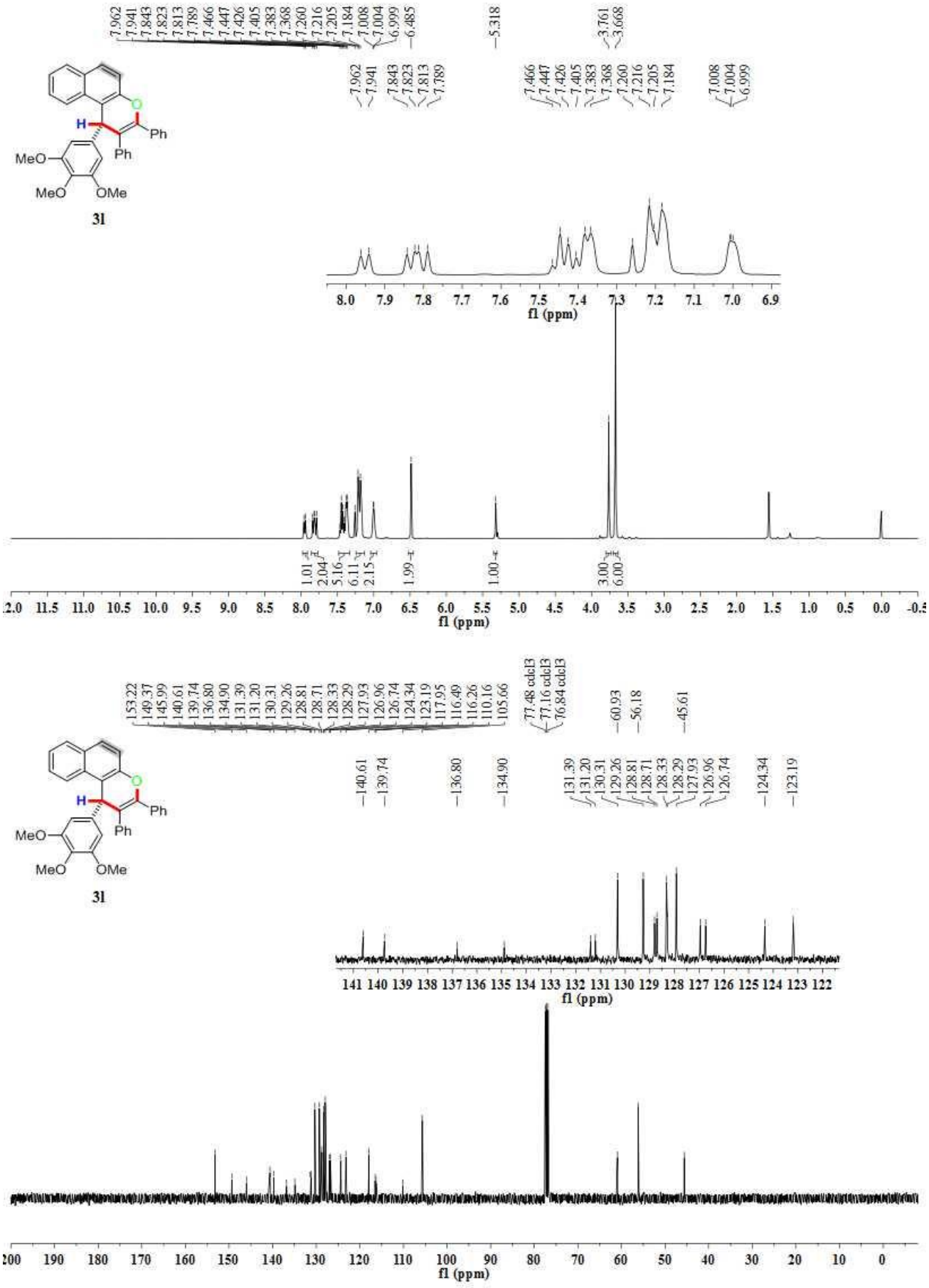
3h

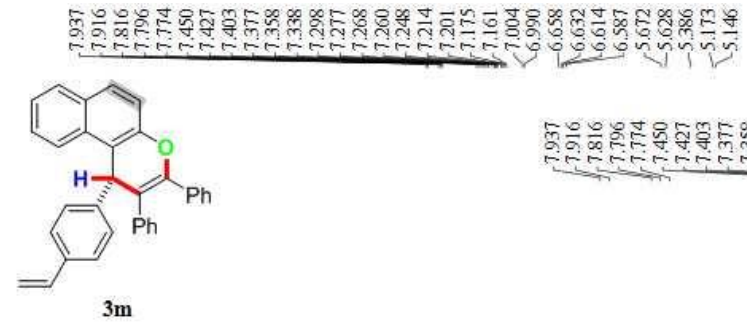

7.874
7.853
7.844
7.826
7.805
7.461
7.450
7.439
7.431
7.404
7.386
7.375
7.368
7.269
7.260
7.223
7.199
7.189
7.167
7.150
7.130
7.114
6.987
6.977
6.968
5.398
H
Ph
Ph
Cl
3i
fl (ppm)
2.95
5.23
1.58
8.96
2.04
1.00
149.318
147.087
146.211
139.370
134.657
134.499
131.171
131.122
130.131
129.740
129.270
129.081
128.762
128.535
128.467
128.357
127.890
127.117
127.007
126.941
126.734
124.412
122.897
118.002
115.893
115.828
77.477 cdcl3
77.159 cdcl3
76.841 cdcl3
45.308


3j
7.857
7.837
7.820
7.799
7.447
7.427
7.402
7.377
7.361
7.260
7.245
7.215
7.195
7.080
7.062
7.043
6.967
5.373
f1 (ppm)
2.97
5.91
8.58
1.04
2.04
1.00


3j
149.33
147.35
146.21
139.35
134.65
131.41
131.18
131.12
130.14
130.07
129.93
129.27
129.10
128.77
128.47
128.36
127.89
127.20
127.13
126.95
124.42
122.89
122.82
118.01
115.83
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
45.31
f1 (ppm)

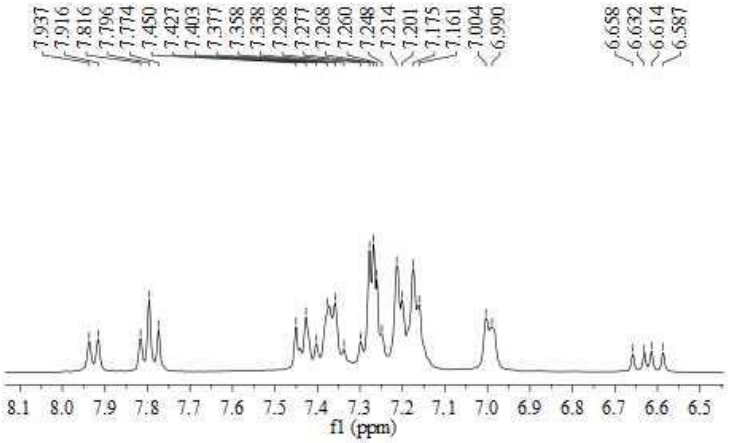

7.967
7.946
7.824
7.801
7.776
7.449
7.434
7.425
7.417
7.384
7.367
7.260
7.217
7.206
7.180
7.149
7.129
7.110
7.014
7.006
7.005
6.935
6.916
6.873
6.688
6.667
5.381
3.674
MeO
Ph
Ph
H
O
3k
fl (ppm)
0.99
1.97
4.79
6.84
1.88
0.95
0.99
1.04
1.00
3.00
159.76
149.24
146.69
146.06
139.75
134.91
131.30
131.15
130.20
129.44
129.33
128.73
128.64
128.32
128.22
127.85
126.91
126.76
124.26
123.12
121.07
117.95
116.68
116.21
114.48
111.83
77.48
77.16
76.84
55.20
45.41

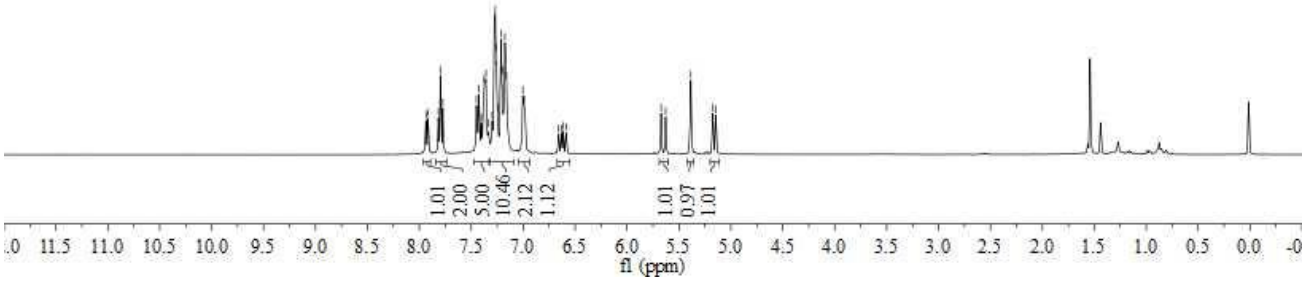

7.962
7.941
7.843
7.823
7.813
7.789
7.466
7.447
7.426
7.405
7.383
7.368
7.260
7.216
7.205
7.184
7.008
7.004
6.999
6.485
5.318
3.761
3.668
Ph
Ph
MeO
MeO
OMe
H
O
31
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.01
2.04
5.16
6.11
2.15
1.99
1.00
3.00
6.00
f1 (ppm)
153.22
149.37
145.99
140.61
139.74
136.80
134.90
131.39
131.20
130.31
129.26
128.81
128.71
128.33
128.29
127.93
126.96
126.74
124.34
123.19
117.95
116.49
116.26
110.16
105.66
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
60.93
56.18
45.61
141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122
f1 (ppm)
f1 (ppm)

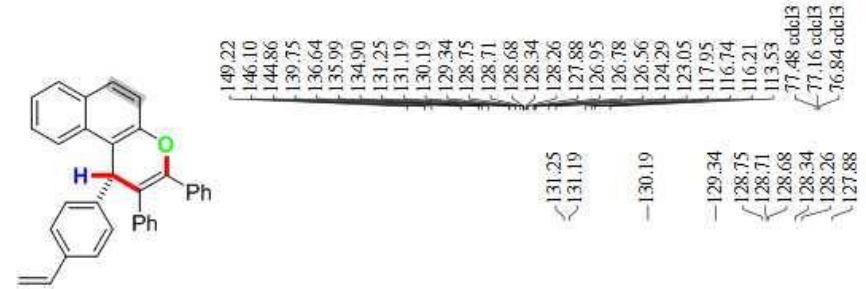

7.937
7.916
7.816
7.796
7.774
7.450
7.427
7.403
7.377
7.358
7.338
7.298
7.277
7.268
7.260
7.248
7.214
7.201
7.175
7.161
7.004
6.990
6.658
6.632
6.614
6.587
5.672
5.628
5.386
5.173
5.146

O
H
Ph
Ph

3m

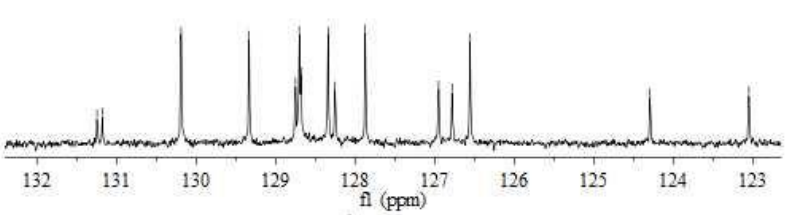

7.937
7.916
7.816
7.796
7.774
7.450
7.427
7.403
7.377
7.358
7.338
7.298
7.277
7.268
7.260
7.248
7.214
7.201
7.175
7.161
7.004
6.990
6.658
6.632
6.614
6.587
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
f1 (ppm)

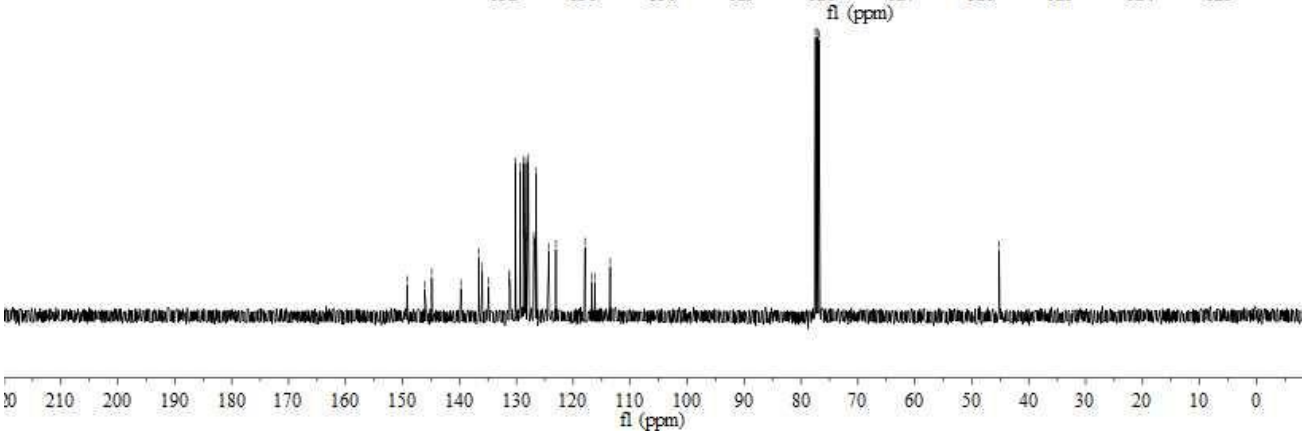

1.01
2.00
5.00
10.46
2.12
1.12
1.01
0.97
1.01
f1 (ppm)

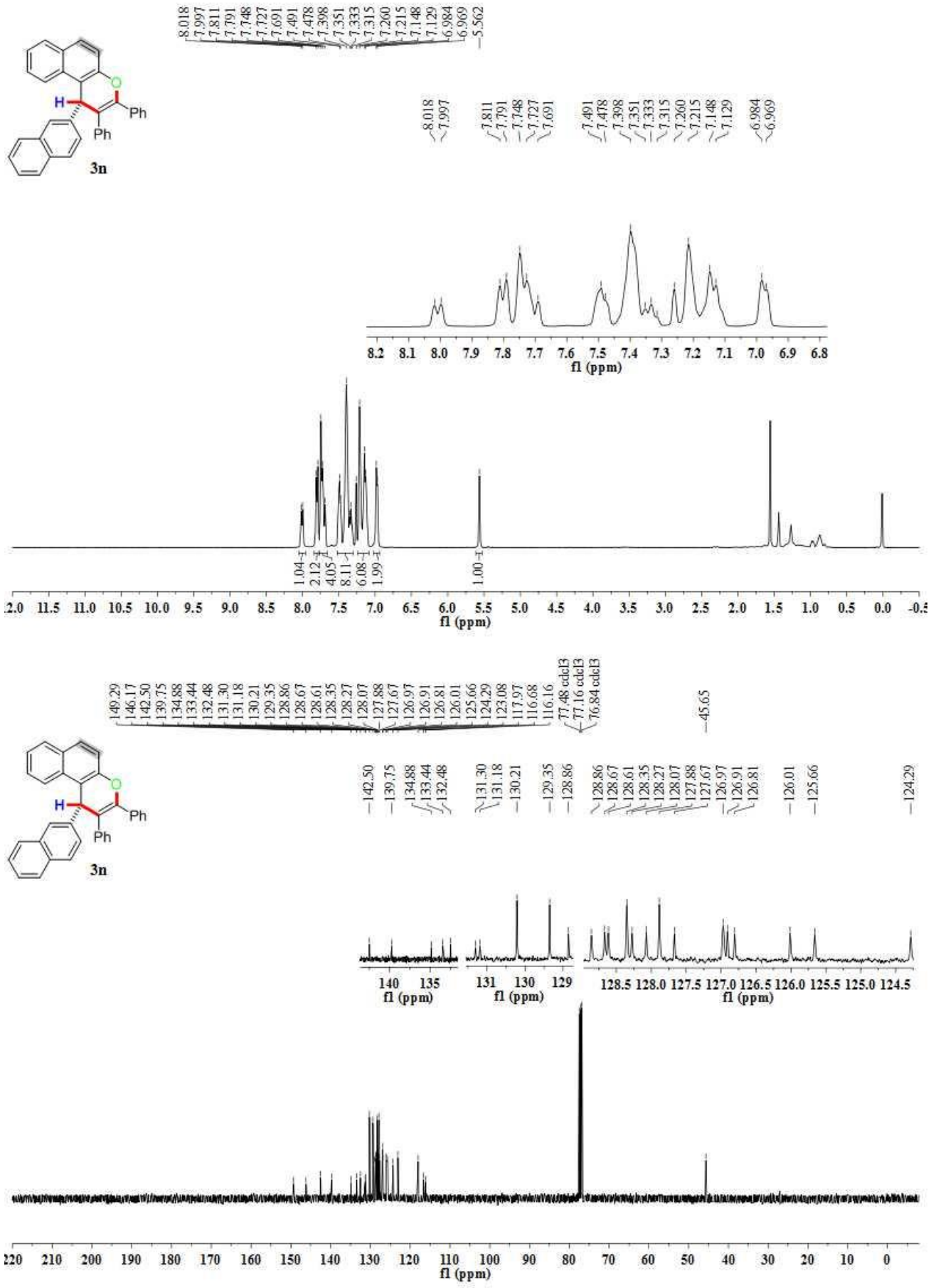

149.22
146.10
144.86
139.75
136.64
135.99
134.90
131.25
131.19
130.19
129.34
128.75
128.71
128.68
128.34
128.26
127.88
126.95
126.78
126.56
124.29
123.05
117.95
116.74
116.21
113.53
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
45.19

O
H
Ph
Ph

3m

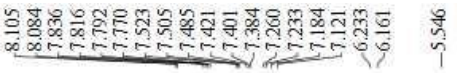

132 131 130 129 128 127 126 125 124 123
f1 (ppm)


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


3n
fl (ppm)
3n
fl (ppm)


H
O
Ph
O
Ph

3o


8.105
8.084
7.836
7.816
7.792
7.770
7.523
7.505
7.485
7.421
7.401
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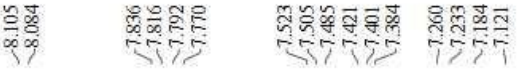
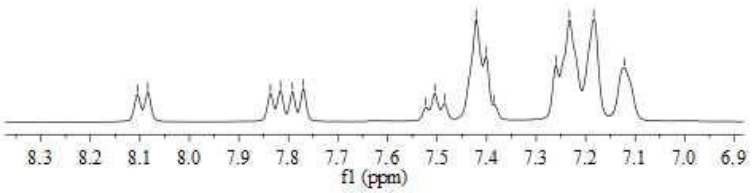
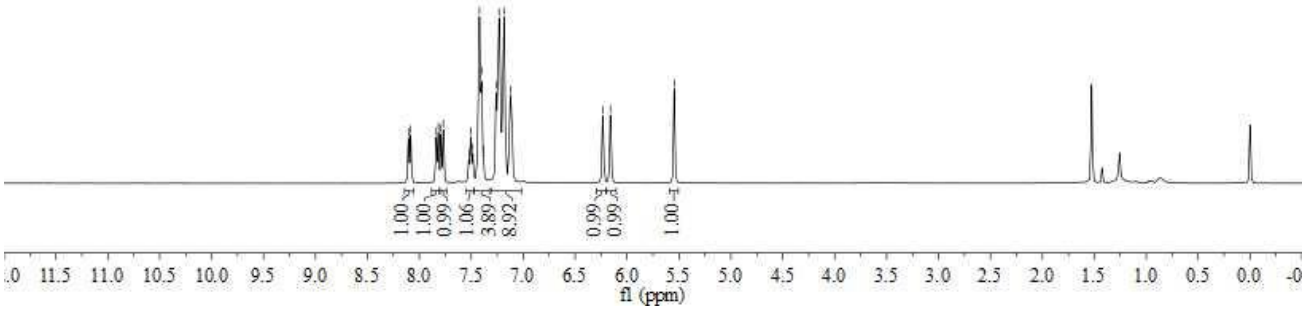
7.233
7.184
7.121
6.233
6.161
5.546

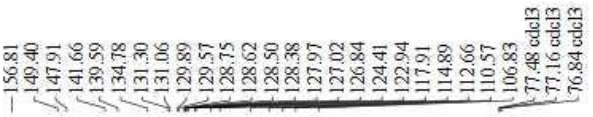

8.105
8.084
7.836
7.816
7.792
7.770
7.523
7.505
7.485
7.421
7.401
7.384
7.260
7.233
7.184
7.121


8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)

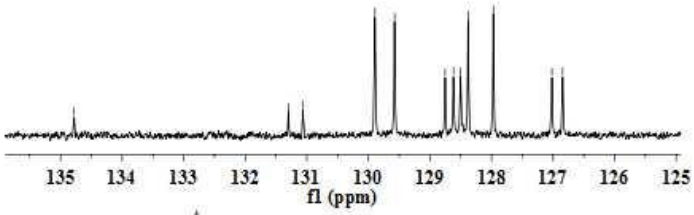

1.00
1.00
0.99
1.06
3.89
8.92
0.99
0.99
1.00
f1 (ppm)

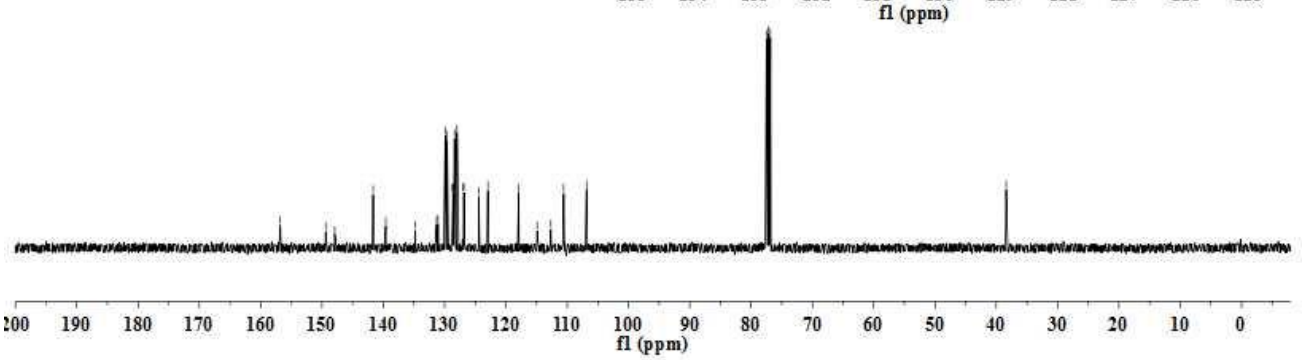

H
O
Ph
O
Ph

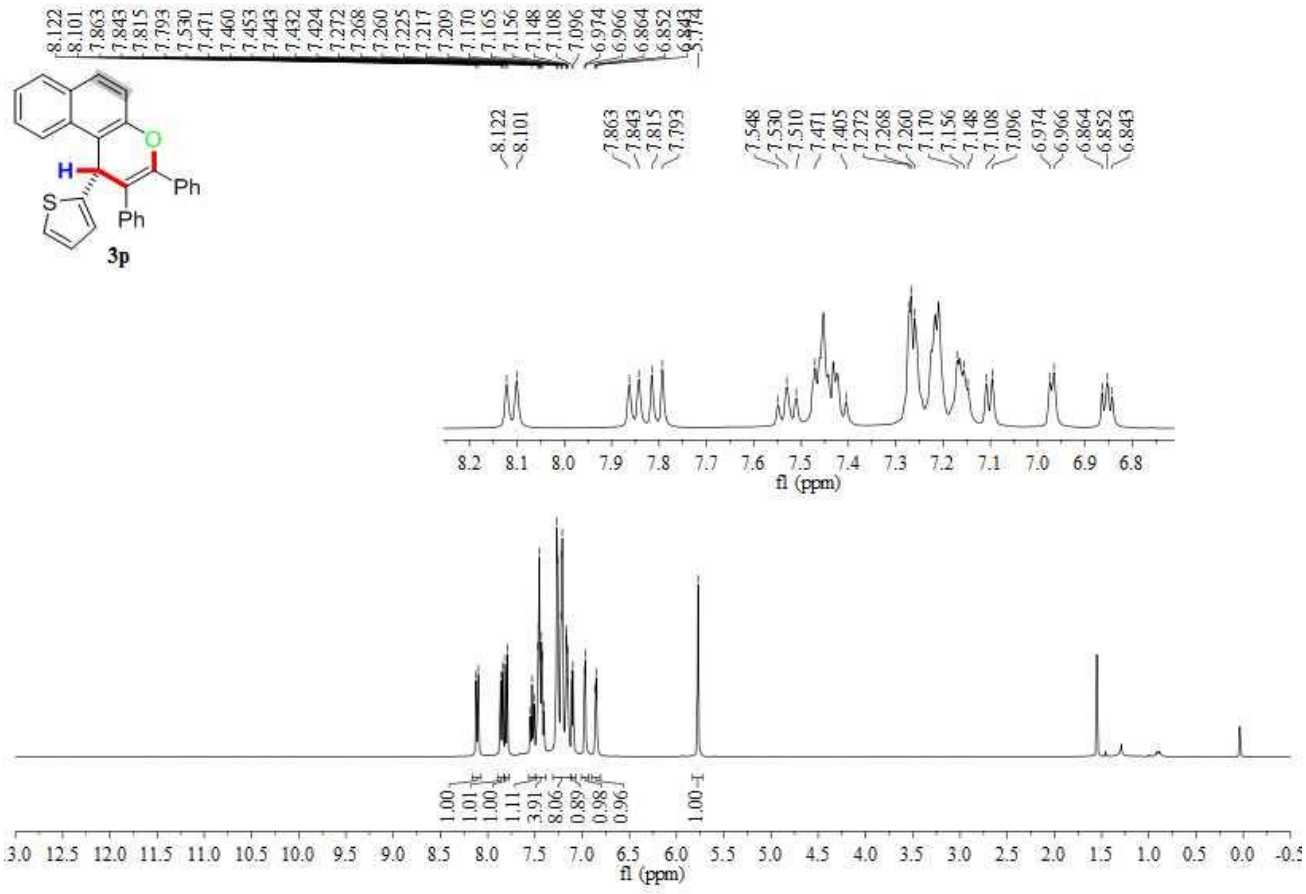
3o

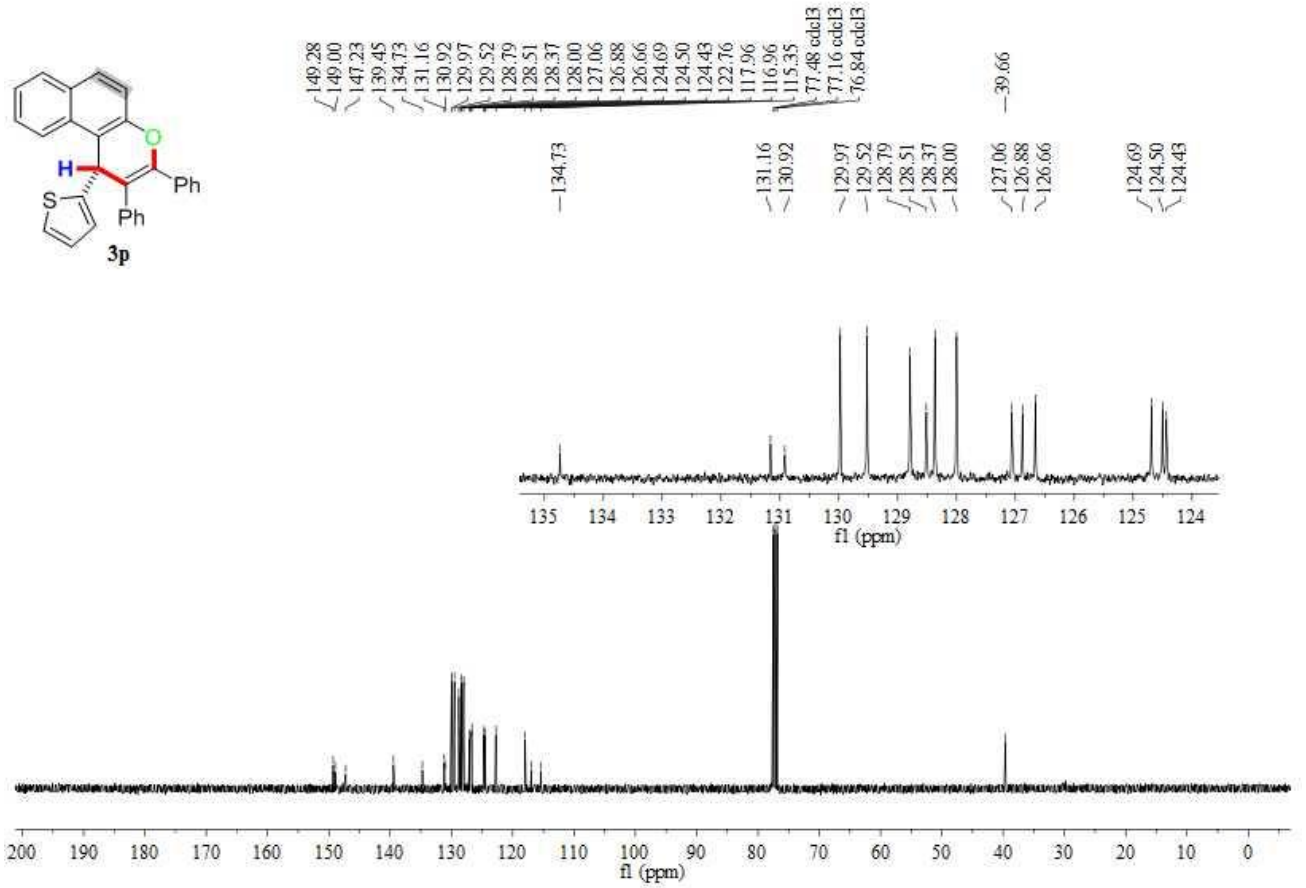

156.81
149.40
147.91
141.66
139.59
134.78
131.30
131.06
129.89
129.57
128.75
128.62
128.50
128.38
127.97
127.02
126.84
124.41
122.94
117.91
114.89
112.66
110.57
106.83
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
38.38

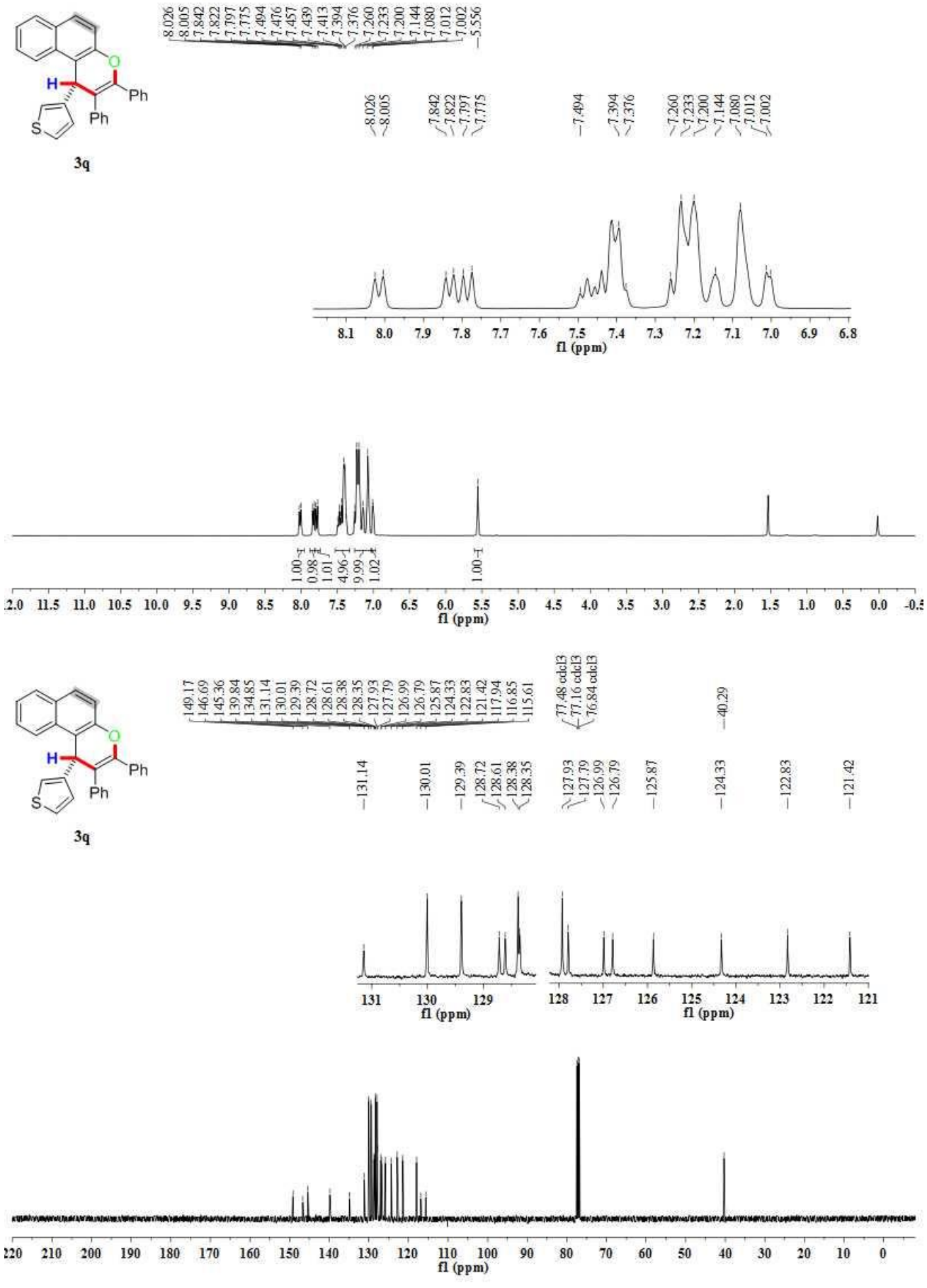

134.78
131.30
131.06
129.89
129.57
128.75
128.62
128.50
128.38
127.97
127.02
126.84

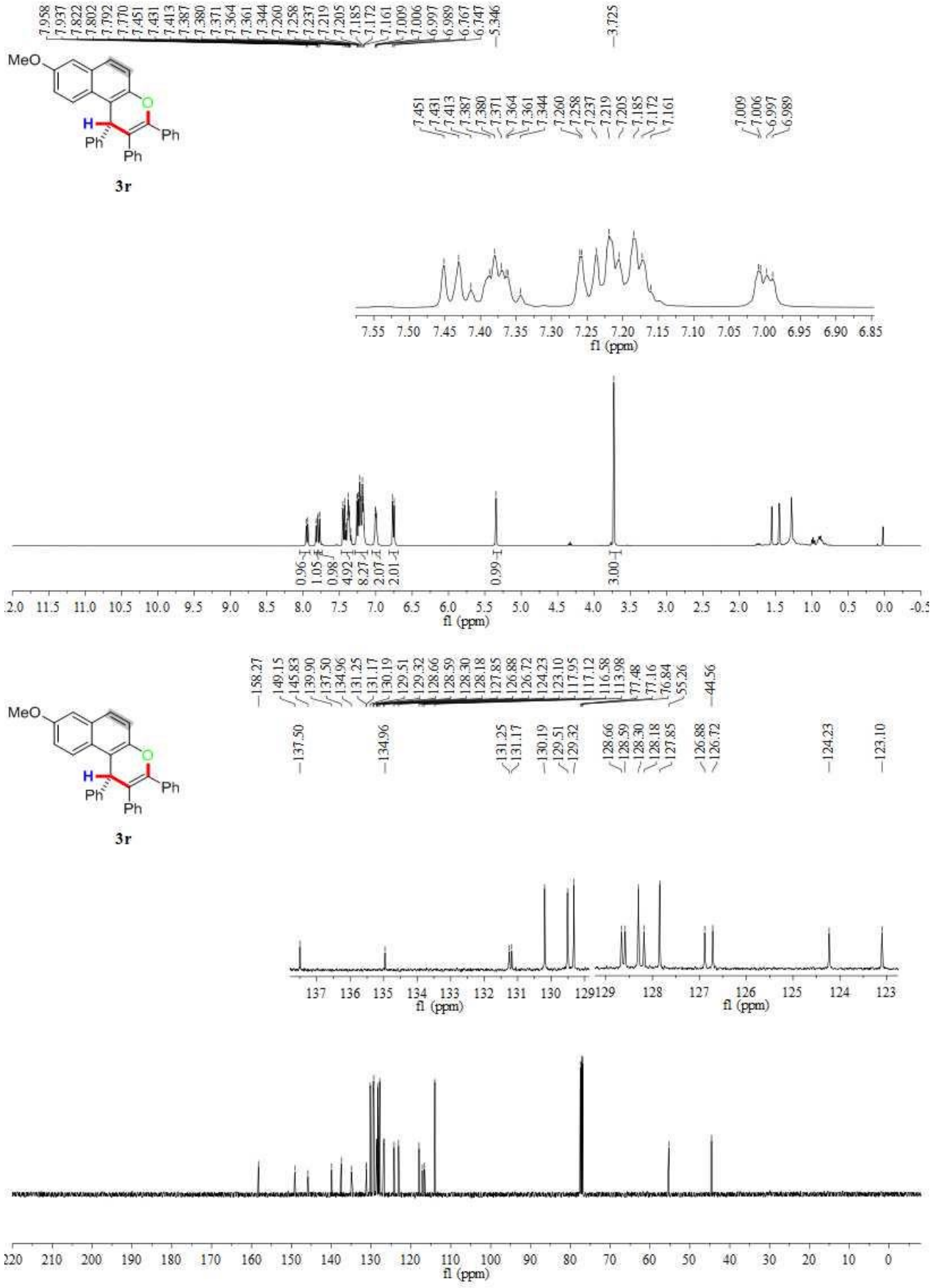

135 134 133 132 131 130 129 128 127 126 125
f1 (ppm)


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


8.122
8.101
7.863
7.843
7.815
7.793
7.530
7.471
7.460
7.453
7.443
7.432
7.424
7.272
7.268
7.260
7.225
7.217
7.209
7.170
7.165
7.156
7.148
7.108
7.096
6.974
6.966
6.864
6.852
6.843
3.744
O
H
S
Ph
Ph
3p
7.548
7.530
7.510
7.471
7.405
7.272
7.268
7.260
7.170
7.156
7.148
7.108
7.096
6.974
6.966
6.864
6.852
6.843
f1 (ppm)
1.00
1.01
1.00
1.11
3.91
8.06
0.89
0.98
0.96
1.00
f1 (ppm)


149.28
149.00
147.23
139.45
134.73
131.16
130.92
129.97
129.52
128.79
128.51
128.37
128.00
127.06
126.88
126.66
124.69
124.50
124.43
122.76
117.96
116.96
115.35
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
39.66
O
H
S
Ph
Ph
3p
134.73
131.16
130.92
129.97
129.52
128.79
128.51
128.37
128.00
127.06
126.88
126.66
124.69
124.50
124.43
f1 (ppm)
f1 (ppm)

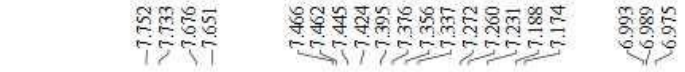

3q
8.026
8.005
7.842
7.822
7.797
7.775
7.494
7.476
7.457
7.439
7.413
7.394
7.376
7.260
7.233
7.200
7.144
7.080
7.012
7.002
5.556
fl (ppm)
1.00
0.98
1.01
4.96
9.99
1.02
1.00
3q
149.17
146.69
145.36
139.84
134.85
131.14
130.01
129.39
128.72
128.61
128.38
128.35
127.93
127.79
126.99
126.79
125.87
124.33
122.83
121.42
117.94
116.85
115.61
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
40.29
fl (ppm)


7.958
7.937
7.822
7.802
7.792
7.770
7.451
7.431
7.413
7.387
7.380
7.371
7.364
7.361
7.344
7.260
7.258
7.237
7.219
7.205
7.185
7.172
7.161
7.009
7.006
6.997
6.989
6.767
6.747
5.346
3.725
MeO
O
H
Ph
Ph
Ph
3r
7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85
f1 (ppm)
0.96
1.05
0.98
4.92
8.27
2.07
2.01
0.99
3.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
158.27
149.15
145.83
139.90
137.50
134.96
131.25
131.17
130.19
129.51
129.32
128.66
128.59
128.30
128.18
127.85
126.88
126.72
124.23
123.10
117.95
117.12
116.58
113.98
77.48
77.16
76.84
55.26
44.56
137 136 135 134 133 132 131 130 129
f1 (ppm)
129 128 127 126 125 124 123
f1 (ppm)
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)


Br
O
H
Ph
Ph
Cl

3s


8.114
7.752
7.733
7.676
7.651
7.466
7.462
7.445
7.424
7.395
7.376
7.356
7.337
7.272
7.260
7.231
7.188
7.174
6.993
6.975
5.304


7.752
7.733
7.676
7.651
7.466
7.462
7.445
7.424
7.395
7.376
7.356
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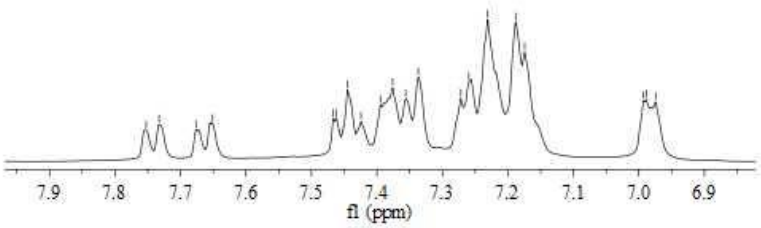
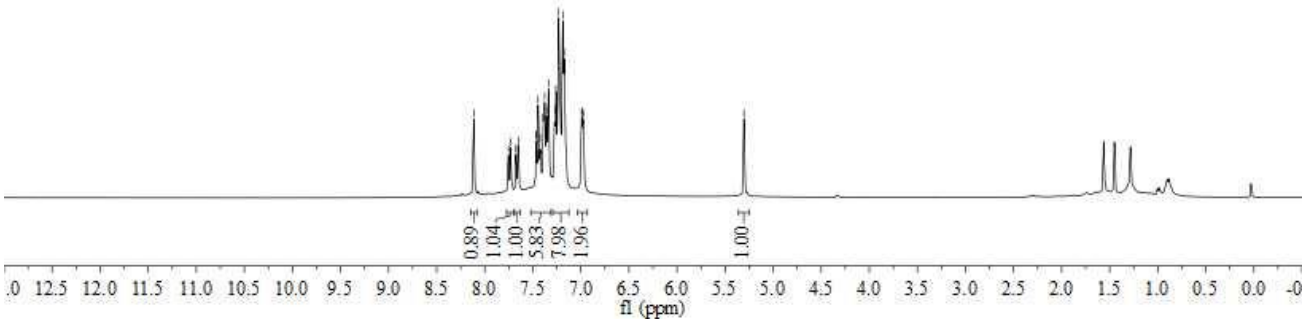
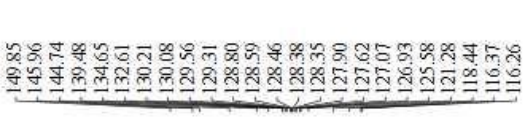
7.272
7.260
7.231
7.188
7.174
6.993
6.989
6.975

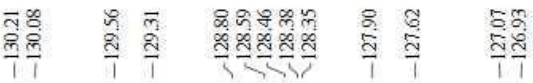

7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)

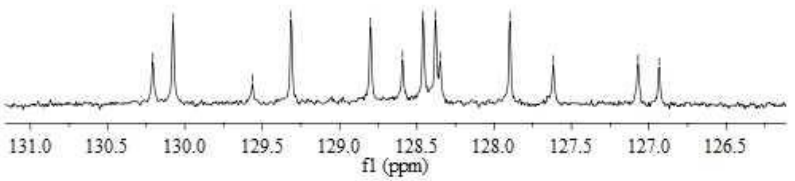

0.89
1.04
1.00
5.83
7.98
1.96
1.00
f1 (ppm)

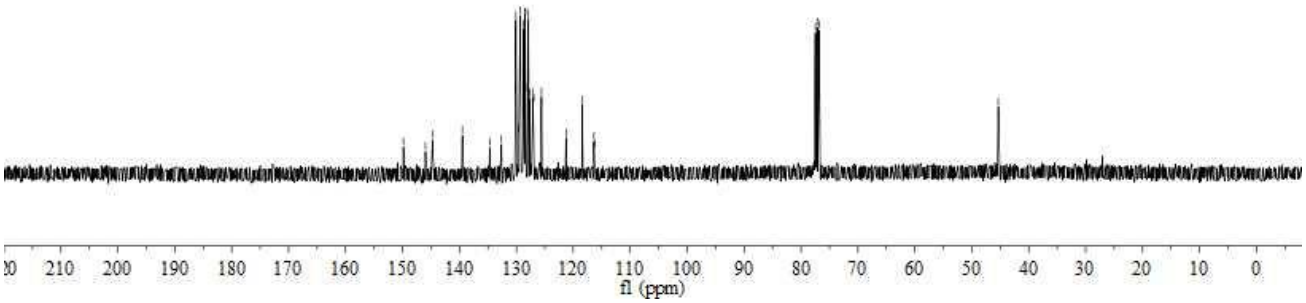
Br
O
H
Ph
Ph
Cl

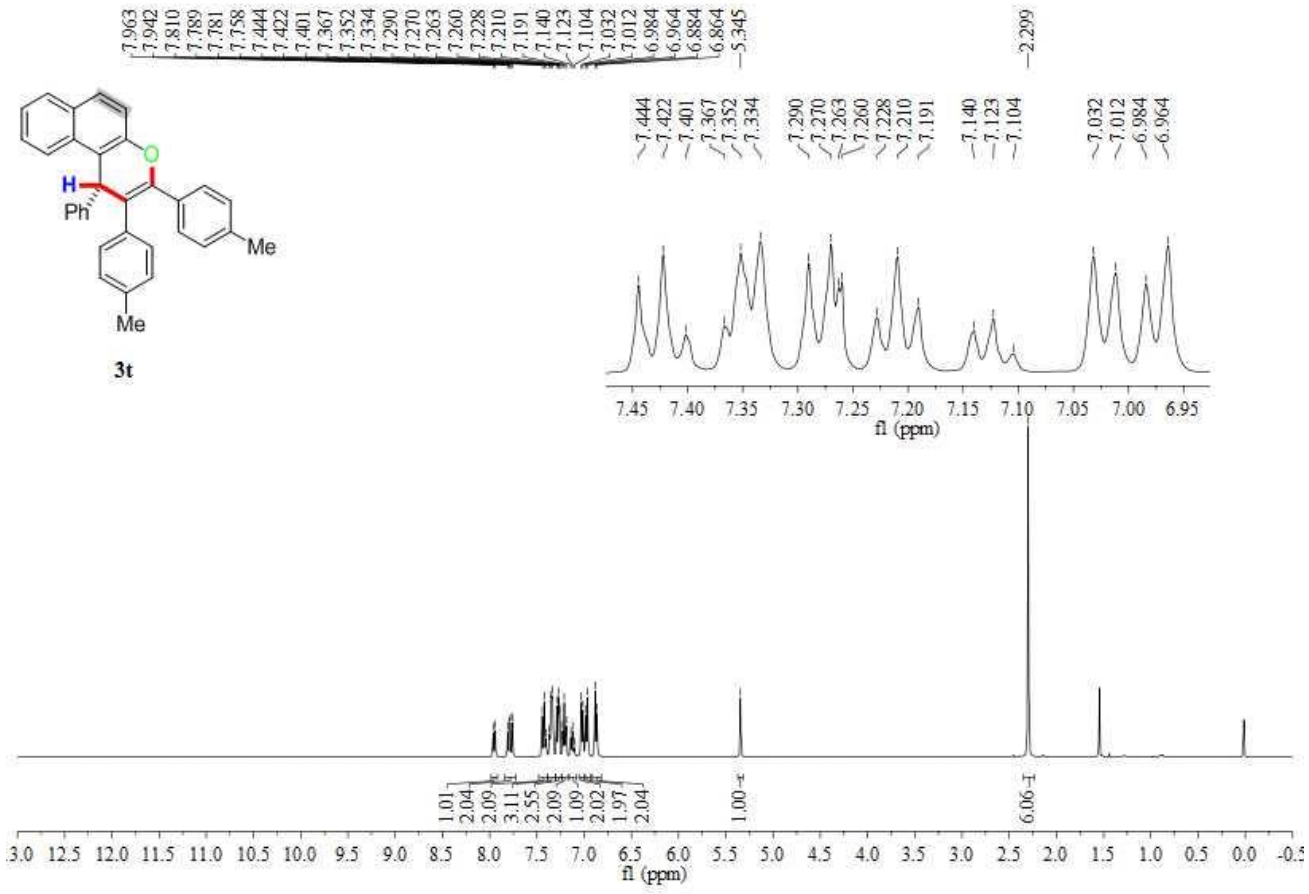
3s

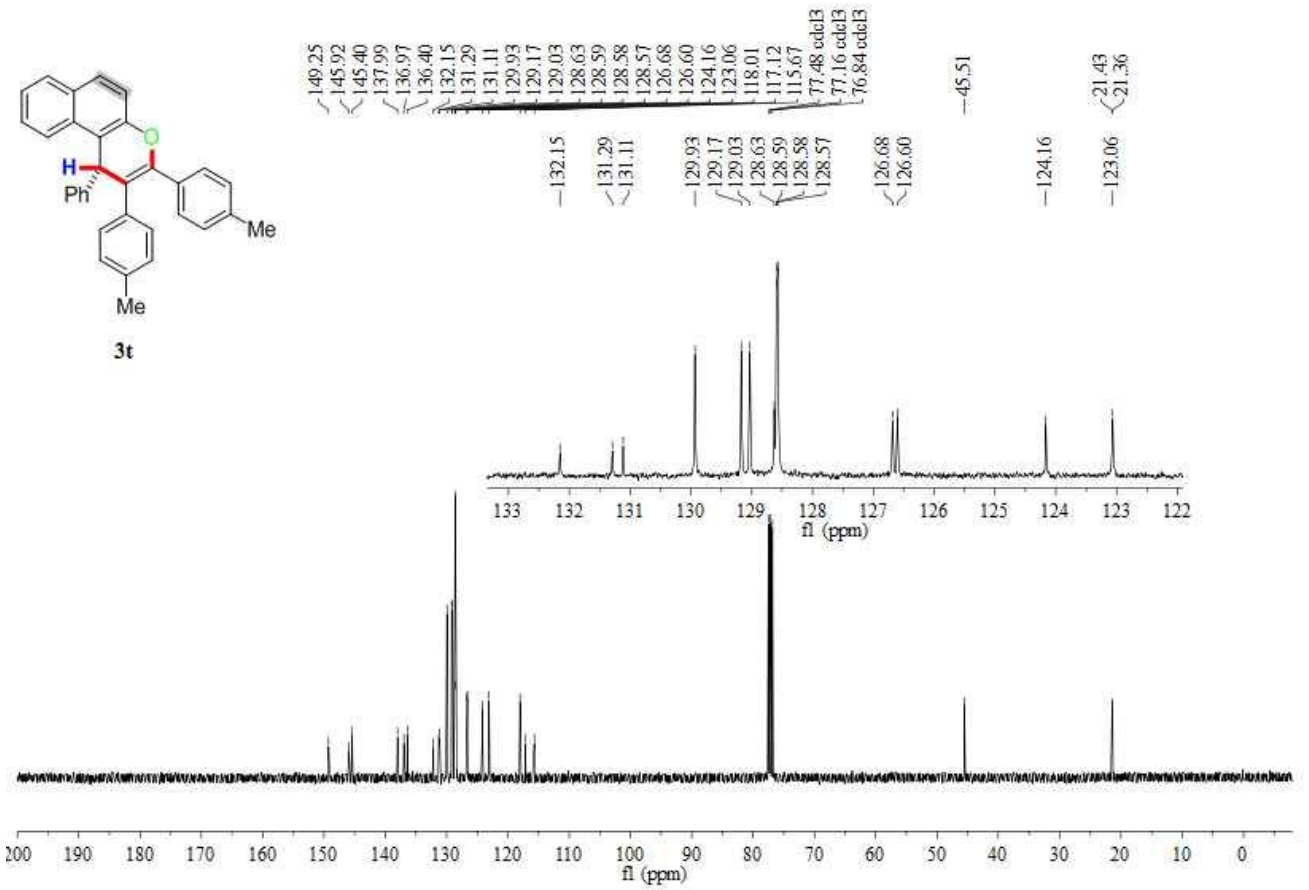

149.85
145.96
144.74
139.48
134.65
132.61
130.21
130.08
129.56
129.31
128.80
128.59
128.46
128.38
128.35
127.90
127.62
127.07
126.93
125.58
121.28
118.44
116.37
116.26
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
45.35

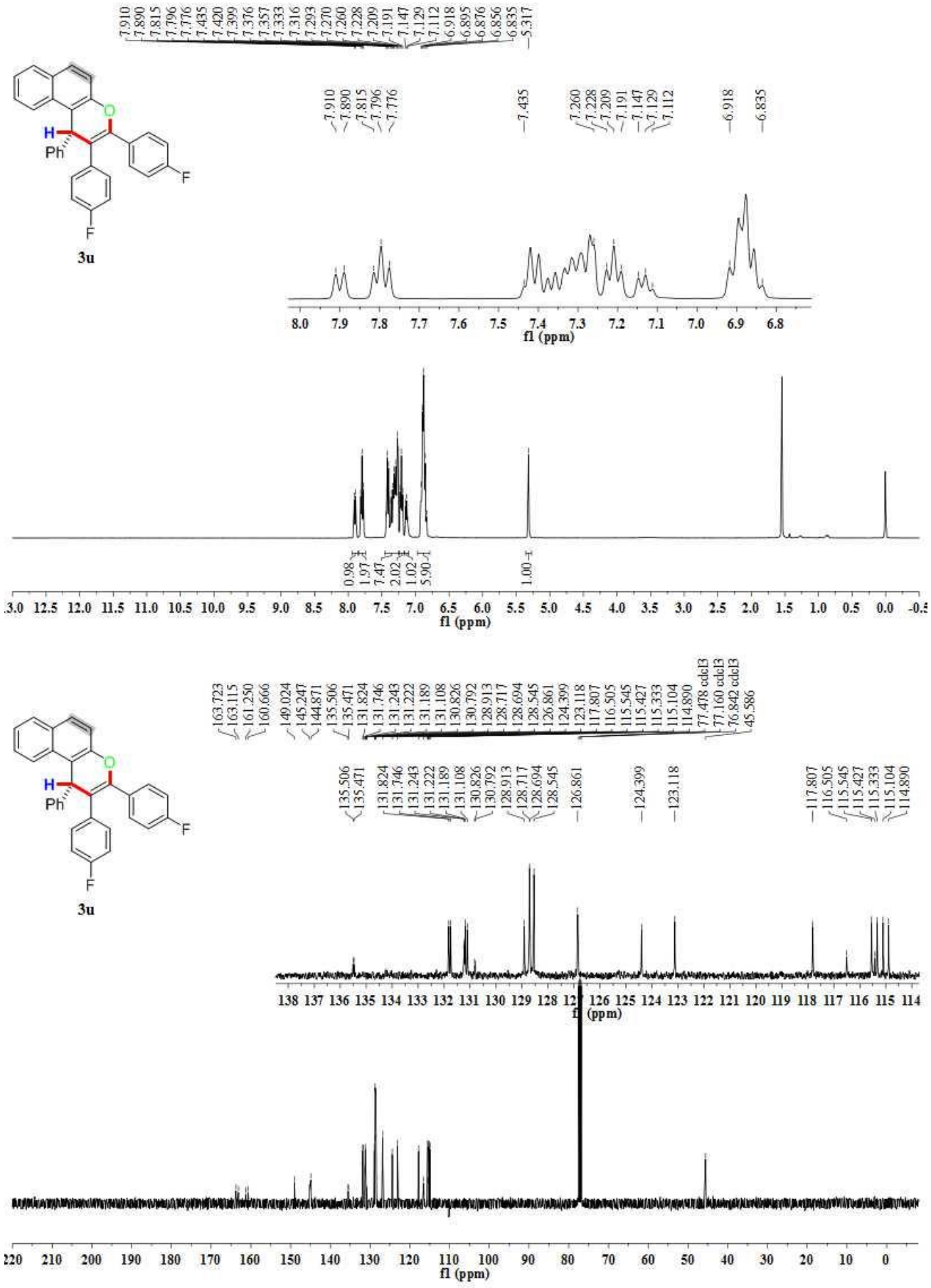

130.21
130.08
129.56
129.31
128.80
128.59
128.46
128.38
128.35
127.90
127.62
127.07
126.93

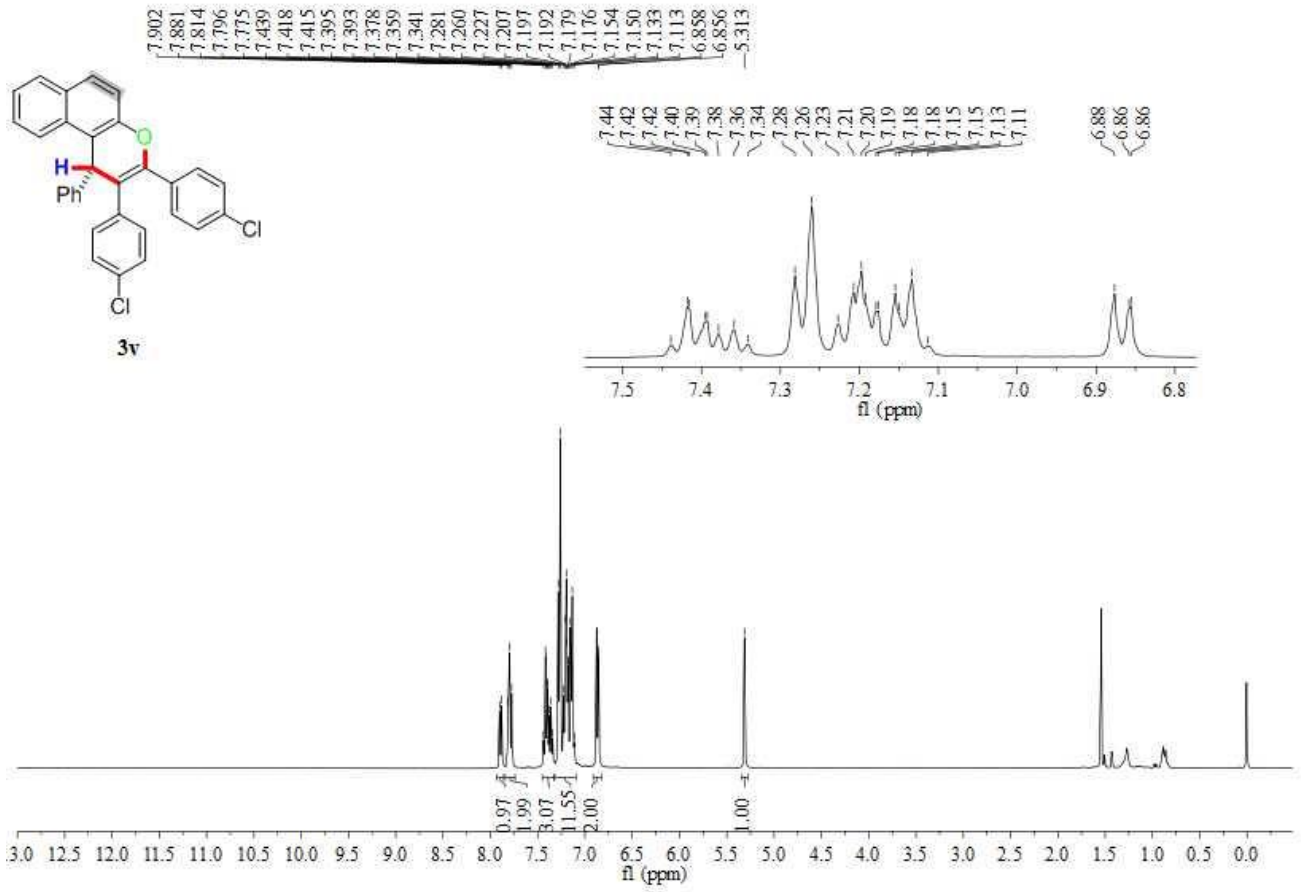

131.0
130.5
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
f1 (ppm)

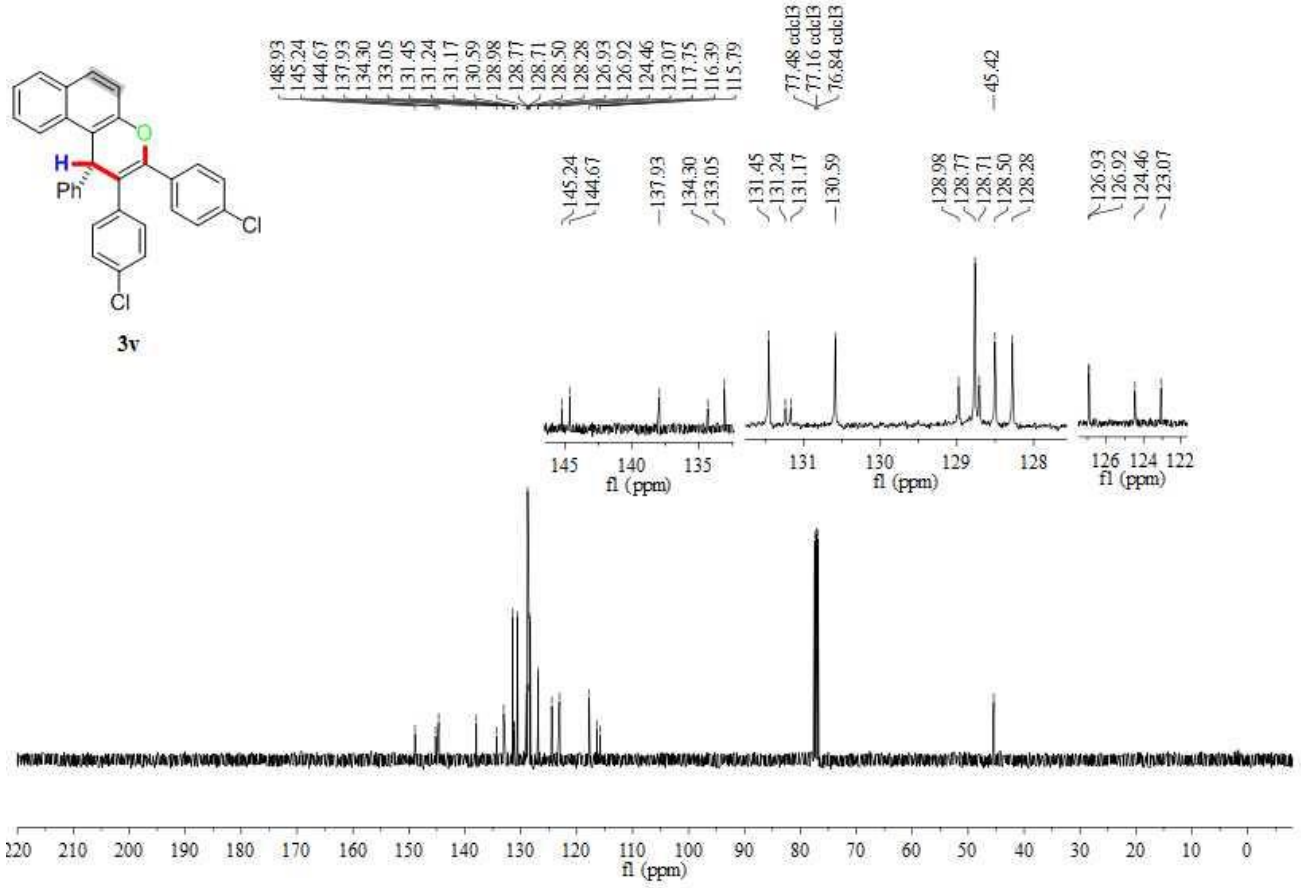

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.963
7.942
7.810
7.789
7.781
7.758
7.444
7.422
7.401
7.367
7.352
7.334
7.290
7.270
7.263
7.260
7.228
7.210
7.191
7.140
7.123
7.104
7.032
7.012
6.984
6.964
6.884
6.864
5.345
2.299
Ph
Me
Me
3t
fl (ppm)
1.01
2.04
2.09
3.11
2.55
2.09
1.09
2.02
1.97
2.04
1.00
6.06
fl (ppm)


149.25
145.92
145.40
137.99
136.97
136.40
132.15
131.29
131.11
129.93
129.17
129.03
128.63
128.59
128.58
128.57
126.68
126.60
124.16
123.06
118.01
117.12
115.67
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
45.51
21.43
21.36
Ph
Me
Me
3t
fl (ppm)
fl (ppm)


3u
fl (ppm)
3u
fl (ppm)
fl (ppm)


7.902
7.881
7.814
7.796
7.775
7.439
7.418
7.415
7.395
7.393
7.378
7.359
7.341
7.281
7.260
7.227
7.207
7.197
7.192
7.179
7.176
7.154
7.150
7.133
7.113
6.858
6.856
5.313
7.44
7.42
7.42
7.40
7.39
7.38
7.36
7.34
7.28
7.26
7.23
7.21
7.20
7.19
7.18
7.18
7.15
7.15
7.13
7.11
6.88
6.86
6.86
H
Ph
O
Cl
Cl
3v
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
0.97
1.99
3.07
11.55
2.00
1.00
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


148.93
145.24
144.67
137.93
134.30
133.05
131.45
131.24
131.17
130.59
128.98
128.77
128.71
128.50
128.28
126.93
126.92
124.46
123.07
117.75
116.39
115.79
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
45.42
H
Ph
O
Cl
Cl
3v
145
140
135
f1 (ppm)
131
130
129
128
f1 (ppm)
126 124 122
f1 (ppm)
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)


H
Ph
Ph
Me

3w

7.863
7.842
7.786
7.765
7.758
7.731
7.533
7.515
7.431
7.414
7.394
7.375
7.346
7.326
7.280
7.260
7.172
7.154
7.136
4.996
1.845
f1 (ppm)
1.00
1.99
1.97
10.13
1.00
1.00
3.00


H
Ph
Ph
Me

3w

149.37
145.23
143.57
135.20
131.58
130.99
129.32
128.69
128.62
128.53
128.43
128.42
128.19
126.64
123.98
123.24
117.95
115.26
109.90
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
45.39
17.65
f1 (ppm)


H
O
Ph
Me
S

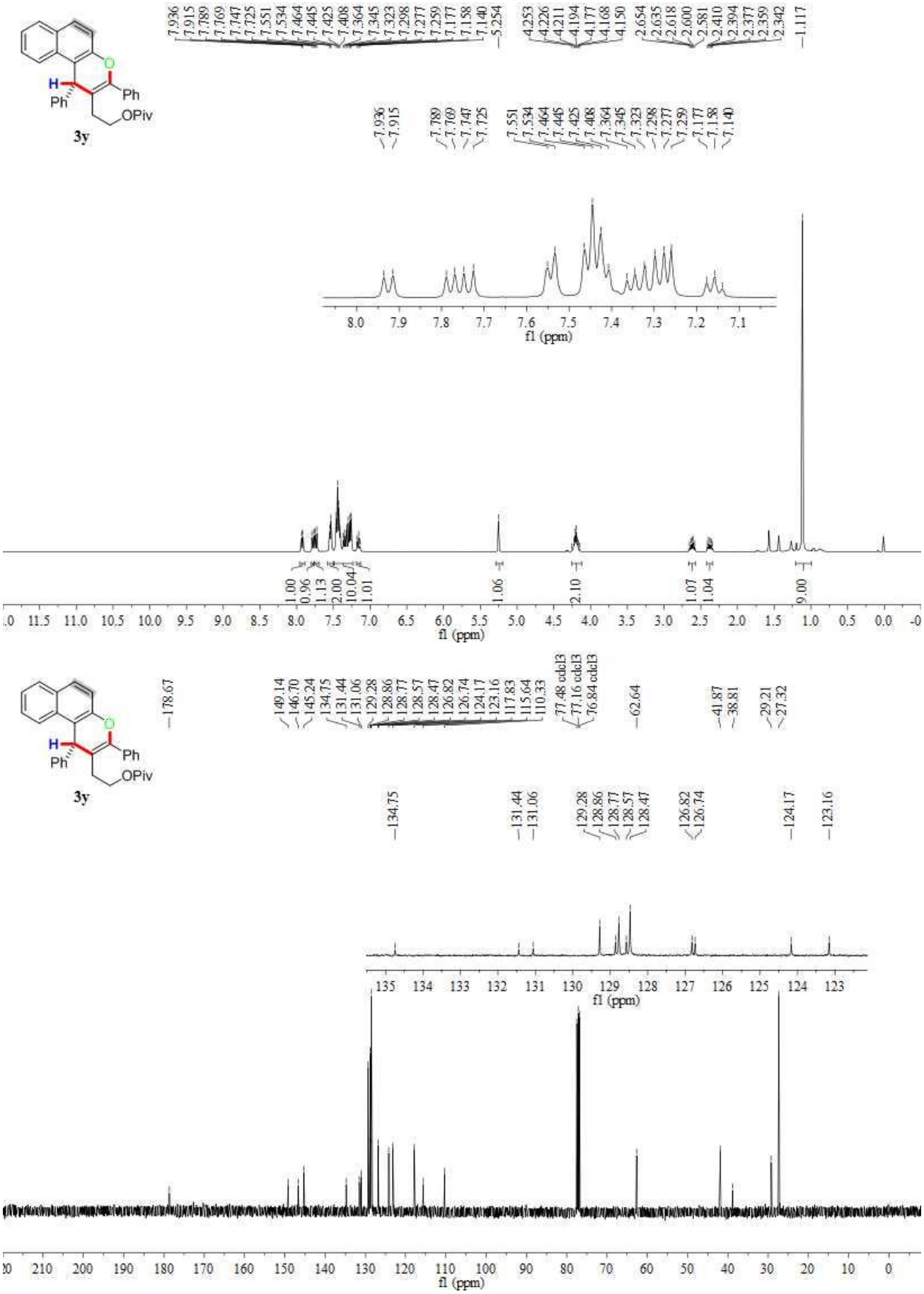
3x

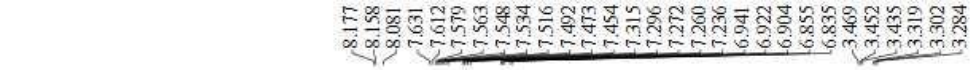
7.937
7.916
7.806
7.786
7.750
7.728
7.550
7.532
7.468
7.448
7.430
7.417
7.411
7.391
7.382
7.373
7.362
7.345
7.325
7.303
7.260
7.168
7.156
7.149
6.998
6.986
6.983
5.171
1.909
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.00
1.02
1.01
1.90
4.98
1.02
1.87
0.98
1.00
3.00
f1 (ppm)

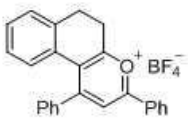

H
O
Ph
Me
S

3x

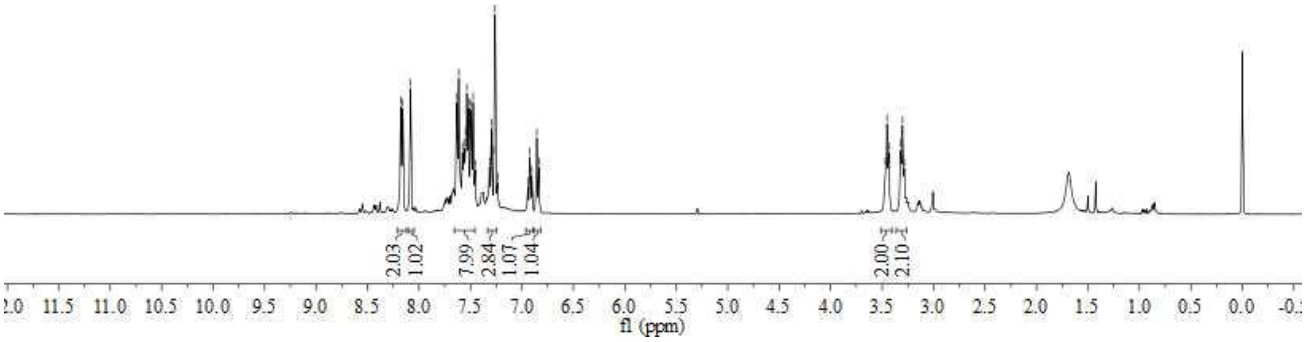
149.17
145.43
144.03
135.13
131.49
130.90
129.25
128.62
128.57
128.45
128.20
127.81
126.65
125.76
124.04
122.92
121.13
117.98
115.12
109.30
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
40.16
17.83
132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

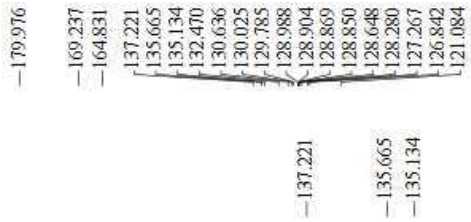

3y
fl (ppm)
3y
fl (ppm)
fl (ppm)

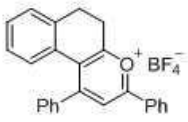

8.177
8.158
8.081
7.631
7.612
7.579
7.563
7.548
7.534
7.516
7.492
7.473
7.454
7.315
7.296
7.272
7.260
7.236
6.941
6.922
6.904
6.855
6.835
3.469
3.452
3.435
3.319
3.302
3.284


BF4
Ph
Ph

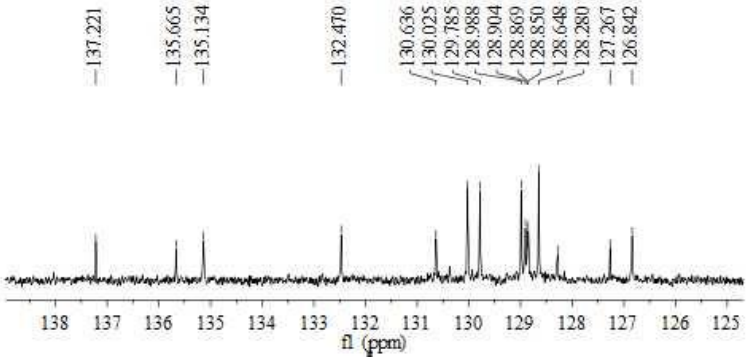
4

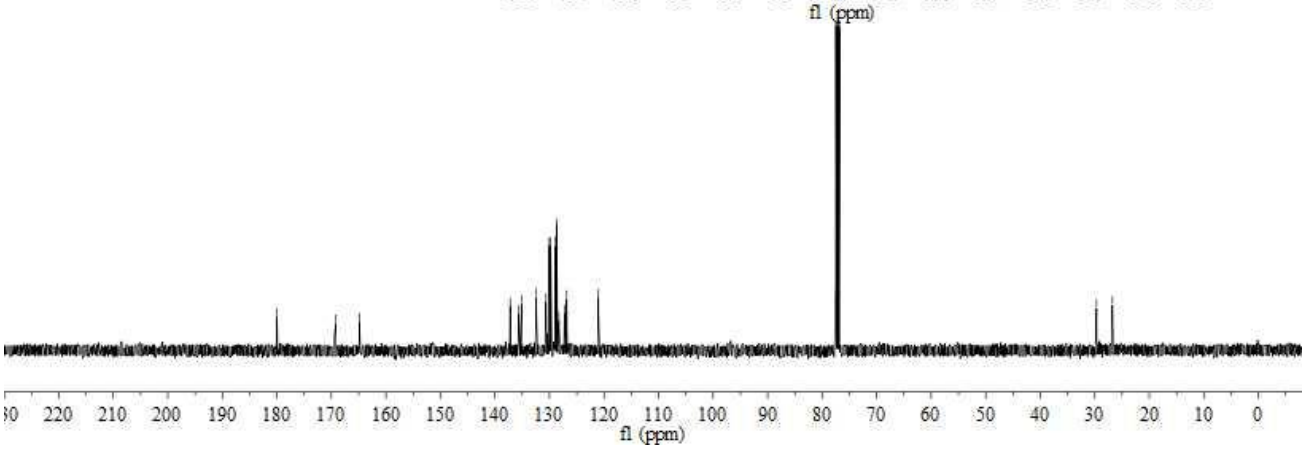

2.03
1.02
7.99
2.84
1.07
1.04
2.00
2.10
f1 (ppm)

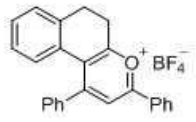

179.976
169.237
164.831
137.221
135.665
135.134
132.470
130.636
130.025
129.785
128.988
128.904
128.869
128.850
128.648
128.280
127.267
126.842
121.084
77.477
77.160
76.842
29.672
26.769


BF4
Ph
Ph

4

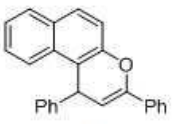

137.221
135.665
135.134
132.470
130.636
130.025
129.785
128.988
128.904
128.869
128.850
128.648
128.280
127.267
126.842
f1 (ppm)


f1 (ppm)

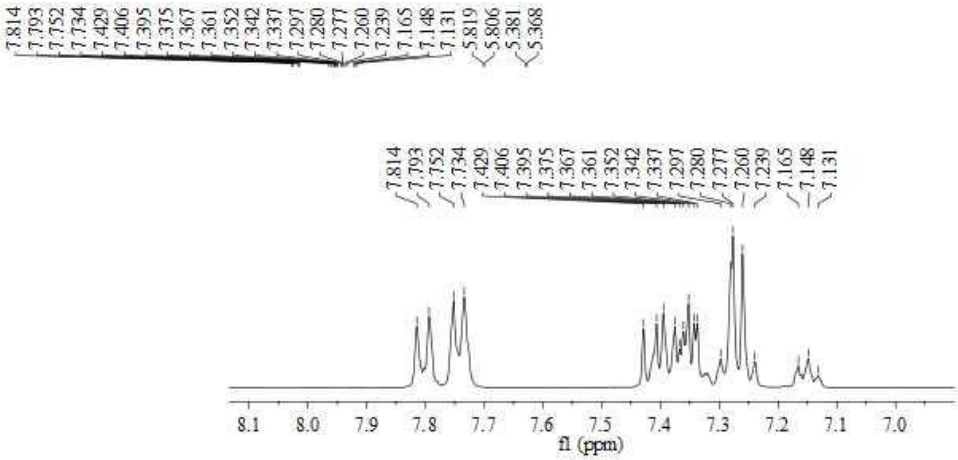

Ph
Ph
BF4

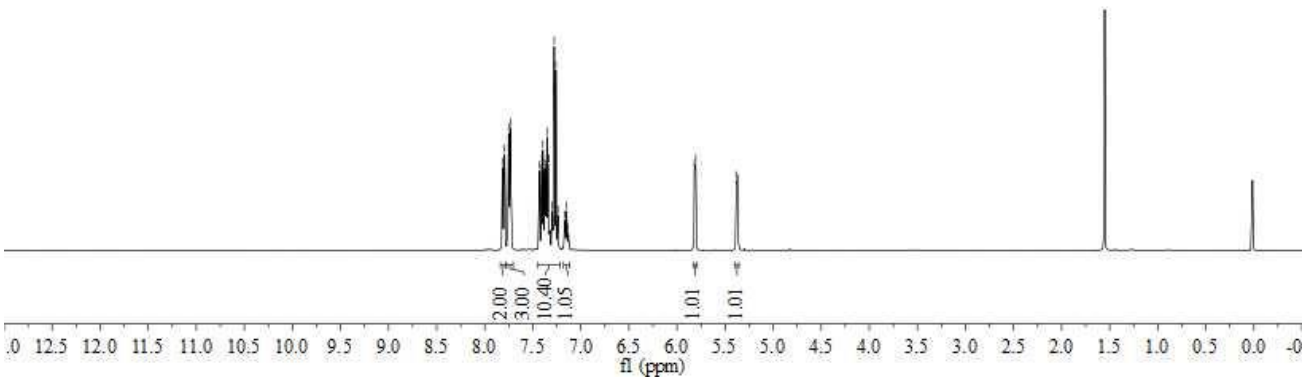
4

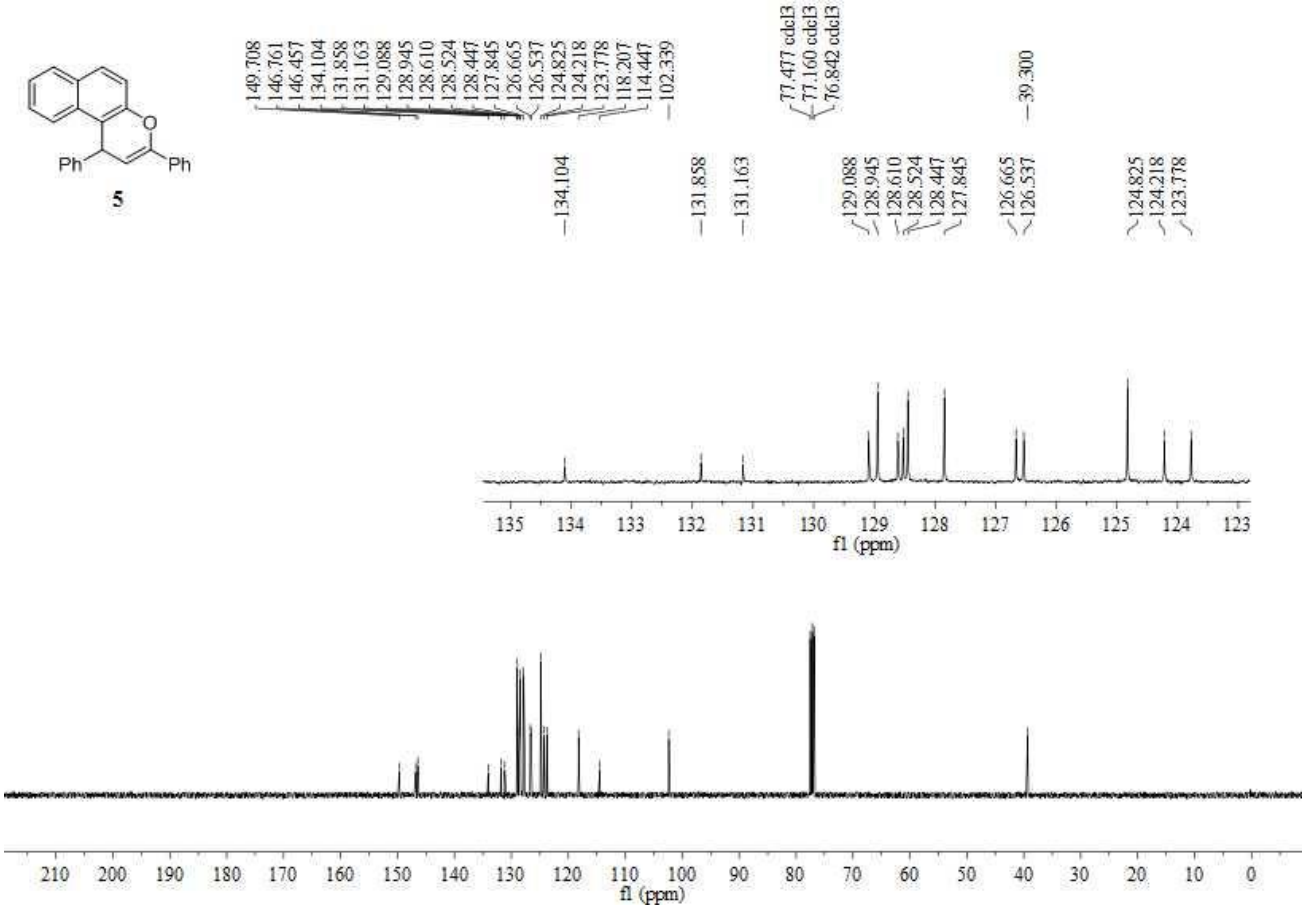
-153.08
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

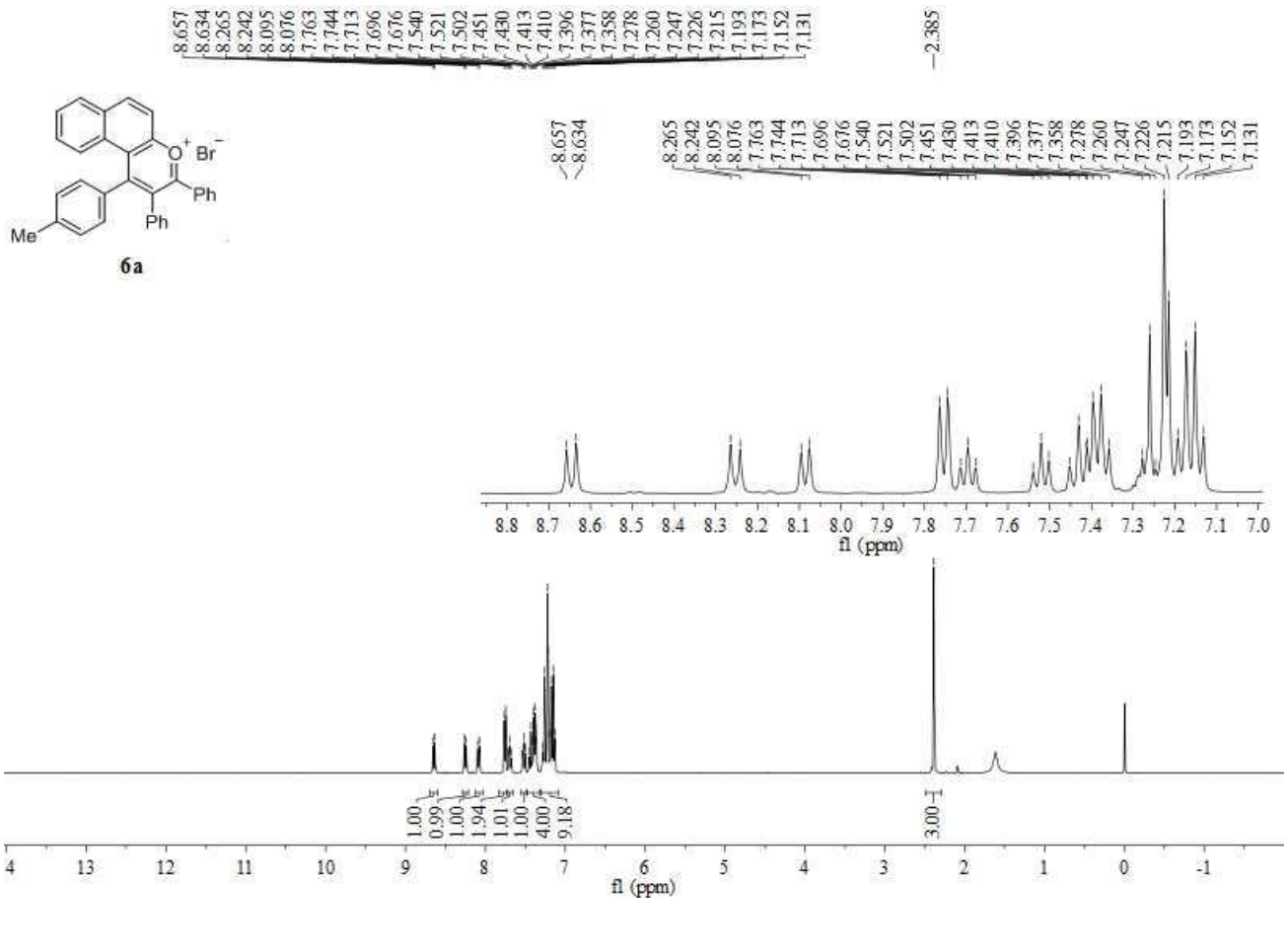

Ph
Ph
O

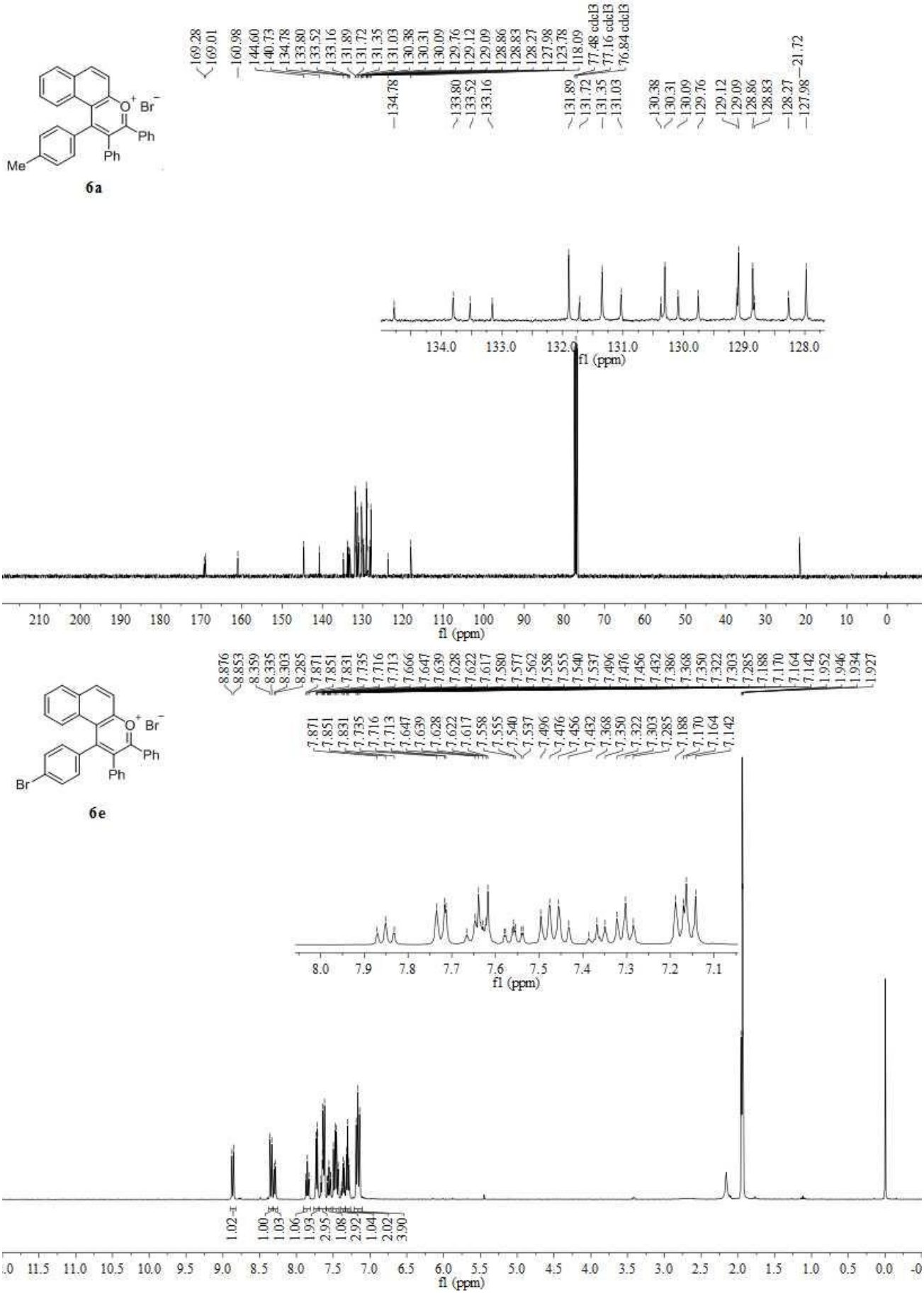
5

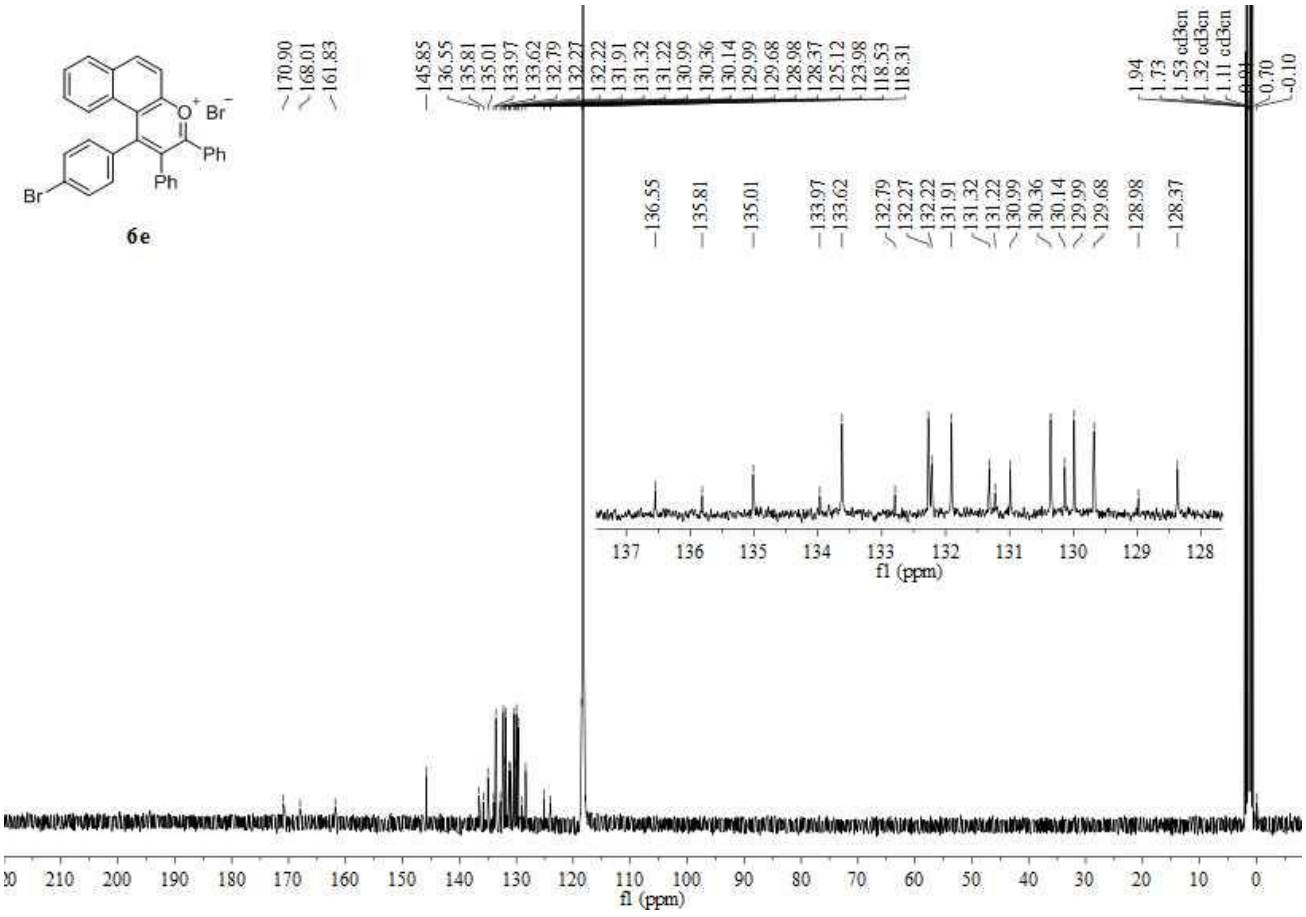

7.814
7.793
7.752
7.734
7.429
7.406
7.395
7.375
7.367
7.361
7.352
7.342
7.337
7.297
7.280
7.277
7.260
7.239
7.165
7.148
7.131
5.819
5.806
5.381
5.368
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)

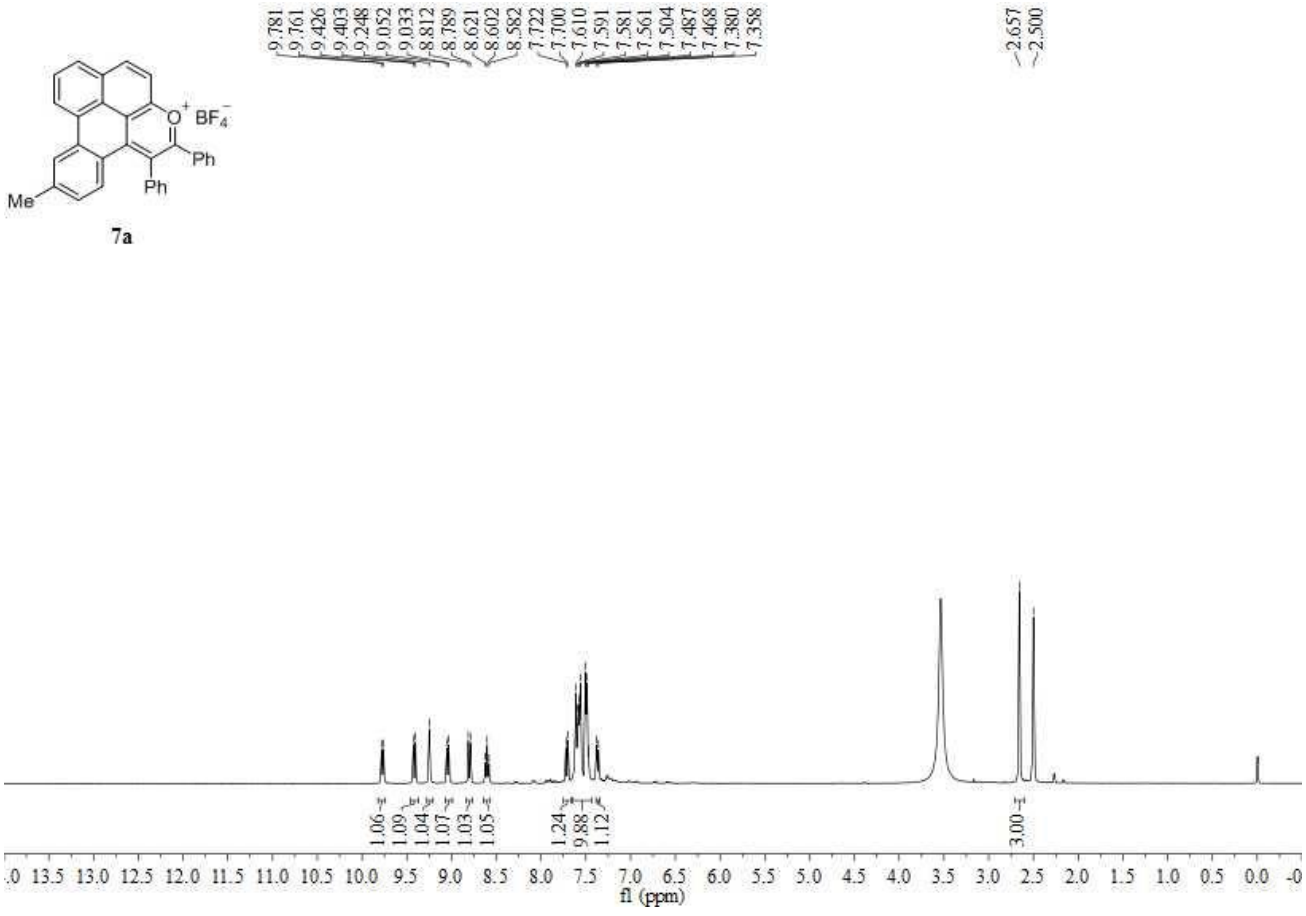

2.00
3.00
10.40
1.05
1.01
1.01
f1 (ppm)

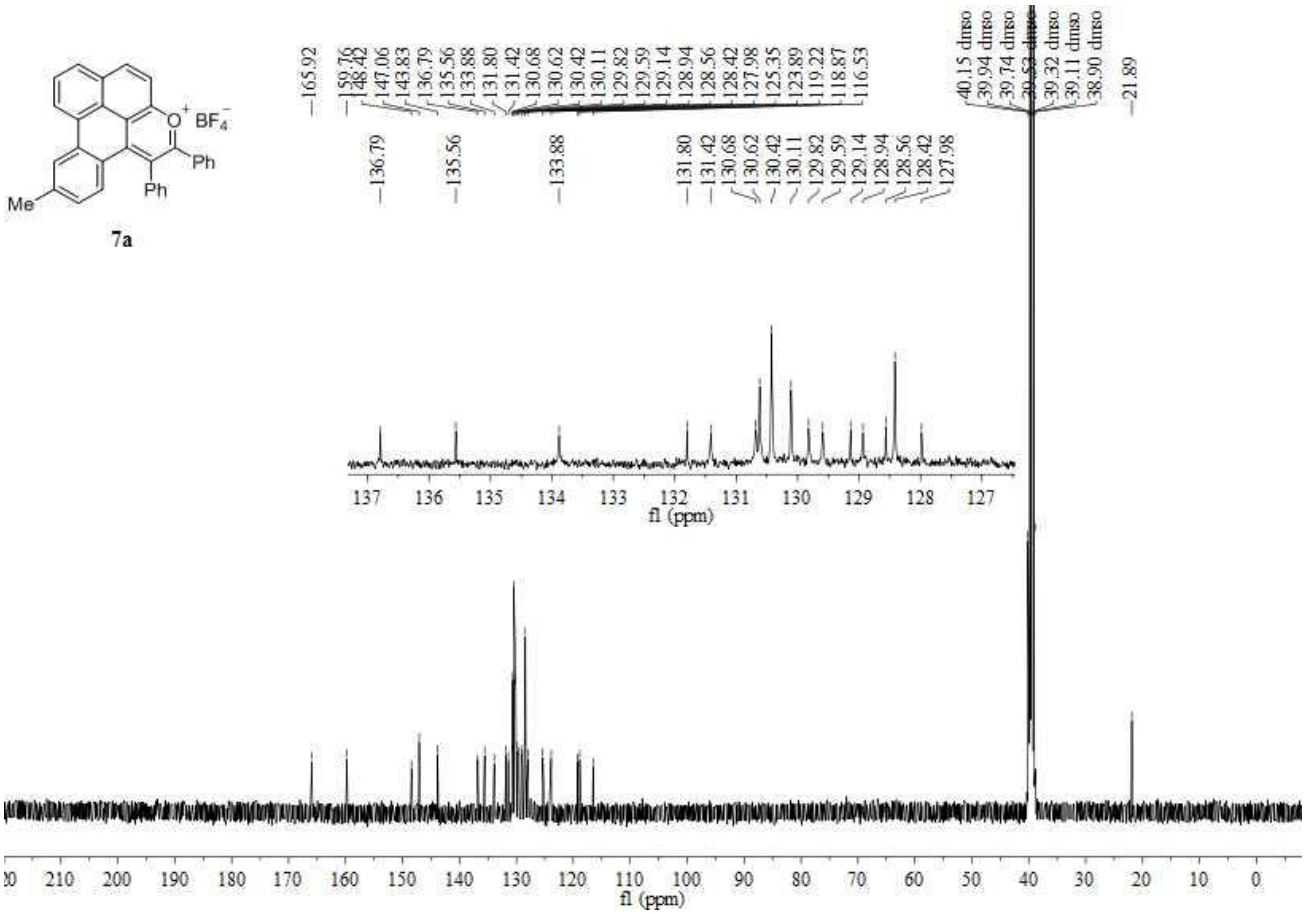

5
149.708
146.761
146.457
134.104
131.858
131.163
129.088
128.945
128.610
128.524
128.447
127.845
126.665
126.537
124.825
124.218
123.778
118.207
114.447
102.339
77.477 cdcl3
77.160 cdcl3
76.842 cdcl3
39.300
fl (ppm)

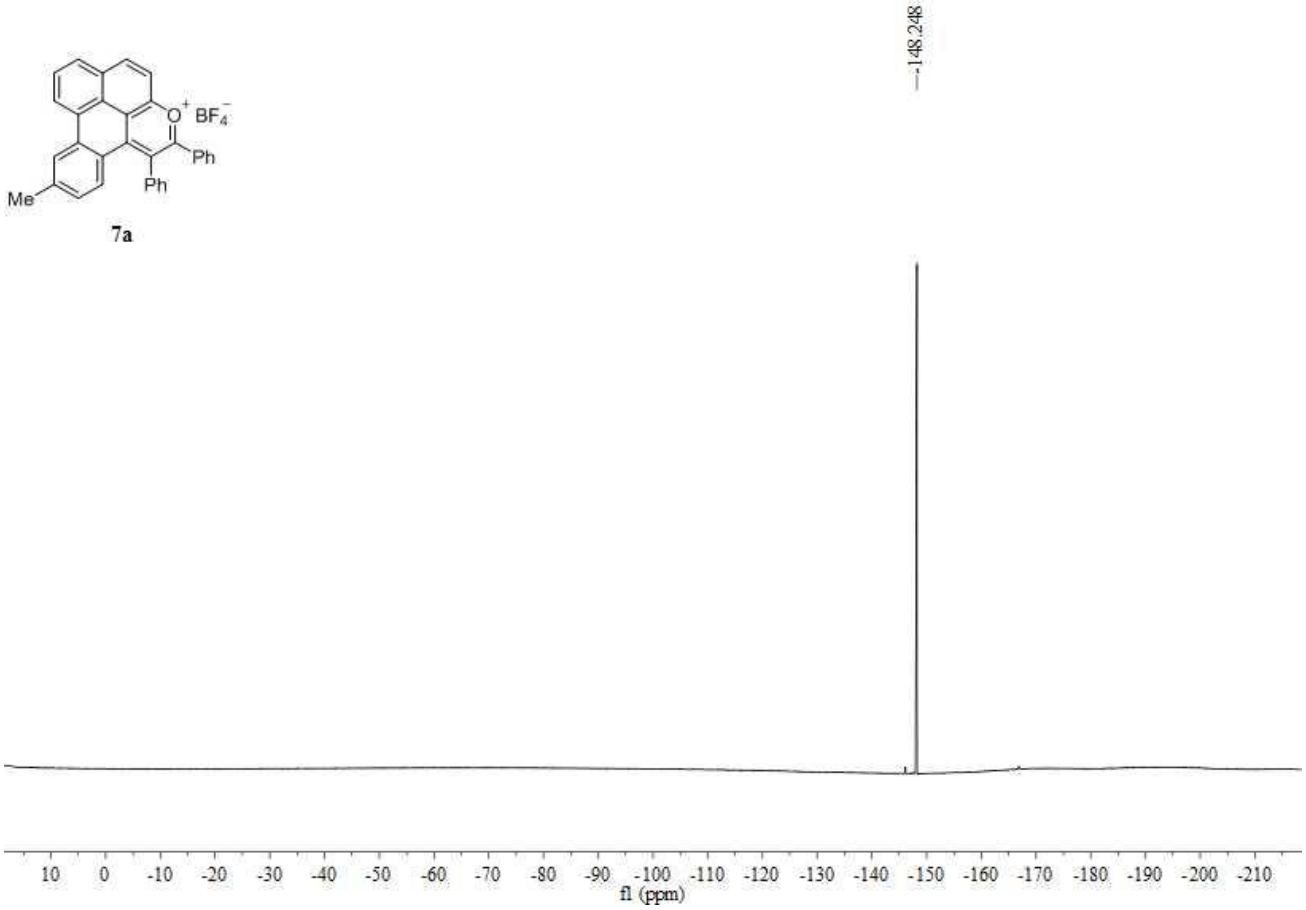

6a
8.657
8.634
8.265
8.242
8.095
8.076
7.763
7.744
7.713
7.696
7.676
7.540
7.521
7.502
7.451
7.430
7.413
7.410
7.396
7.377
7.358
7.278
7.260
7.247
7.226
7.215
7.193
7.173
7.152
7.131
2.385
1.00
0.99
1.00
1.94
1.01
1.00
4.00
9.18
3.00
fl (ppm)

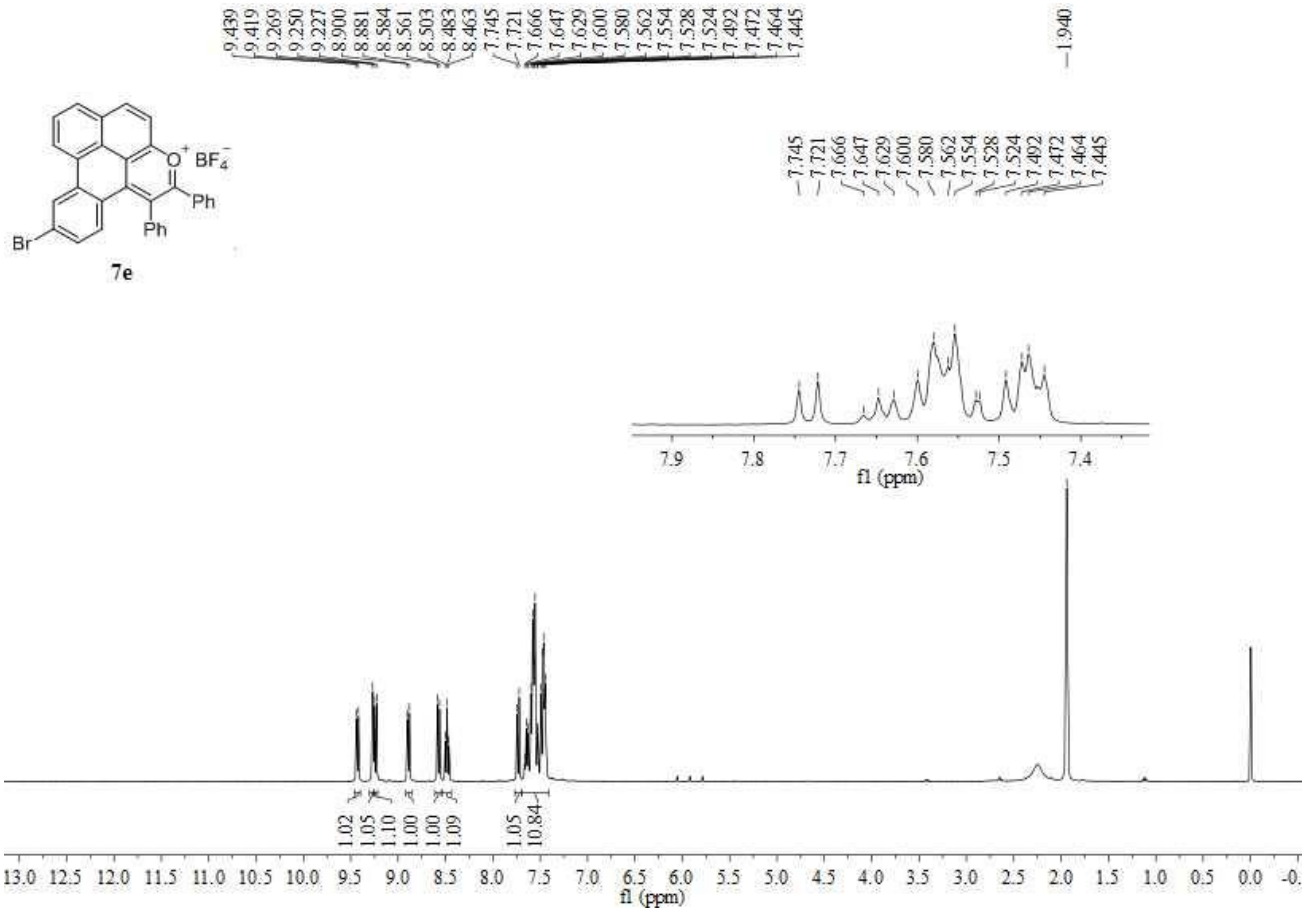

Me
Ph
Ph
Br
6a
6e
fl (ppm)

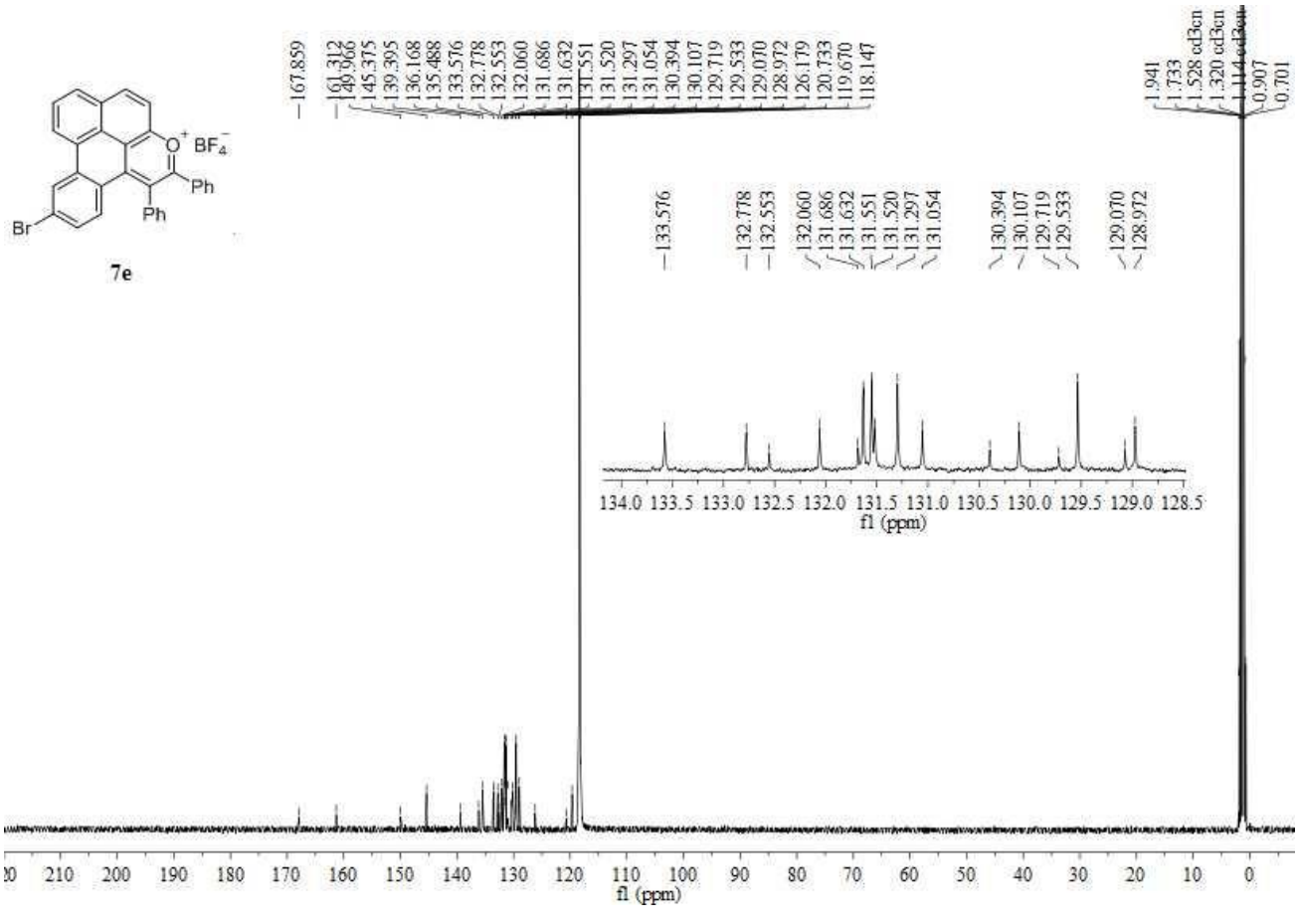

Br
Ph
Ph
Br
6e
170.90
168.01
161.83
145.85
136.55
135.81
135.01
133.97
133.62
132.79
132.27
132.22
131.91
131.32
131.22
130.99
130.36
130.14
129.99
129.68
128.98
128.37
125.12
123.98
118.53
118.31
1.94
1.73
1.53 cd3cn
1.32 cd3cn
1.11 cd3cn
0.70
-0.10
f1 (ppm)

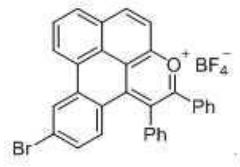

BF4
Ph
Ph
Me
7a
9.781
9.761
9.426
9.403
9.248
9.052
9.033
8.812
8.789
8.621
8.602
8.582
7.722
7.700
7.610
7.591
7.581
7.561
7.504
7.487
7.468
7.380
7.358
2.657
2.500
1.06
1.09
1.04
1.07
1.03
1.05
1.24
9.88
1.12
3.00
f1 (ppm)


7a
165.92
159.76
148.42
147.06
143.83
136.79
135.56
133.88
131.80
131.42
130.68
130.62
130.42
130.11
129.82
129.59
129.14
128.94
128.56
128.42
127.98
125.35
123.89
119.22
118.87
116.53
40.15 dmso
39.94 dmso
39.74 dmso
39.32 dmso
39.11 dmso
38.90 dmso
21.89
fl (ppm)


7a
148.248
fl (ppm)


9.439
9.419
9.269
9.250
9.227
8.900
8.881
8.584
8.561
8.503
8.483
8.463
7.745
7.721
7.666
7.647
7.629
7.600
7.580
7.562
7.554
7.528
7.524
7.492
7.472
7.464
7.445
1.940
BF4
Ph
Ph
Br
7e
fl (ppm)
1.02
1.05
1.10
1.00
1.00
1.09
1.05
10.84


167.859
161.312
149.966
145.375
139.395
136.168
135.488
133.576
132.778
132.553
132.060
131.686
131.632
131.551
131.520
131.297
131.054
130.394
130.107
129.719
129.533
129.070
128.972
126.179
120.733
119.670
118.147
1.941
1.733
1.528 cd3cn
1.320 cd3cn
0.907
0.701
BF4
Ph
Ph
Br
7e
fl (ppm)


O+
BF4−
Ph
Ph
Br

7e

-152.69
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)