

## Supporting Information

### *gem-Digold Acetylide Complexes for Catalytic Intermolecular [4+2] Cycloaddition: Having Two Gold Centers Is Better for Asymmetric Catalysis*

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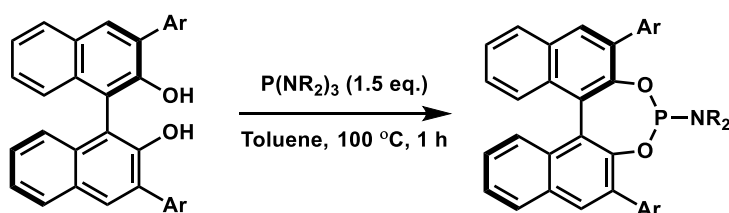
## General Information:

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were measured on Bruker AV300M (300 MHz) spectrometers. Chemical shifts of  $^1\text{H}$  NMR were expressed in parts per million relative to the singlet ( $\delta = 7.26$ ) for  $\text{CDCl}_3$ . Chemical shifts of  $^{13}\text{C}$  NMR were expressed in parts per million relative to the central line of the triplet ( $\delta = 77.0$ ) for  $\text{CDCl}_3$ . Chemical shifts of  $^{31}\text{P}$  NMR were expressed in parts per million downfield from 85%  $\text{H}_3\text{PO}_4$  as an external standard ( $\delta = 0.00$ ) in  $\text{CDCl}_3$ . Chemical shifts of  $^{19}\text{F}$  NMR were expressed in parts per million downfield from BTF as an external standard ( $\delta = -63.24$ ) in  $\text{CDCl}_3$ . Analytical thin layer chromatography (TLC) was performed on glass plates pre-coated with silica-gel (Merck Kieselgel 60 F<sub>254</sub>, layer thickness 0.25 mm). Visualization was accomplished by UV light (254 nm), anisaldehyde,  $\text{KMnO}_4$ , phosphomolybdic acid. Column chromatography was performed on KANTO Silica Gel 60N (spherical, neutral). IR spectra were measured on a JASCO FT/IR-4200 spectrometer. High performance liquid chromatography (HPLC) was conducted on JASCO PU-980, LG-980-02, DG-980-50, MD-2010, and CO-966 instrument equipped with model UV-975 spectrometers as an ultra violet light. Peak areas were calculated by JASCO chrom NAV (Windows 7) as an automatic integrator. DAICEL CHIRALPAK AD-3, DAICEL CHIRALPAK AD-H, DAICEL CHIRALPAK AS-H, DAICEL CHIRALCEL OD-3, and DAICEL CHIRALCEL OJ-3 were used as chiral columns. Mass spectra were measured on a JEOL JMS-T100CS (Accu-TOF) spectrometer. Optical rotations were measured on a JASCO P-1020. All experiments were carried out under argon atmosphere unless otherwise noted.

## Synthetic Procedure of Chiral Phosphoramidites

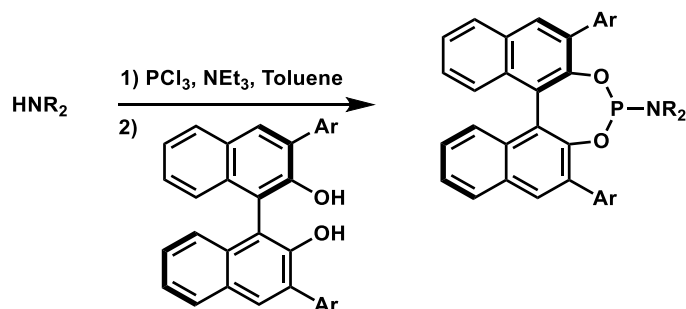
Phosphoramidites (**(R)**-L<sub>1</sub>,<sup>[S1]</sup> (**(R)**-L<sub>2</sub>,<sup>[S1]</sup> (**(R)**-L<sub>3</sub>,<sup>[S2]</sup> (**(R)**-L<sub>5</sub>,<sup>[S1]</sup> and (**(R, R, R)**-L<sub>7</sub>,<sup>[S3]</sup> were synthesized employing the procedure reported. All other phosphoramidites (**(R)**-L<sub>4</sub>, (**(R)**-L<sub>6</sub>, (**(R)**-L<sub>8</sub> ~ (**(R, R)**-L<sub>10</sub> were synthesized as follows.

## General Procedure for Preparation of Phosphoramidite (GP-1)



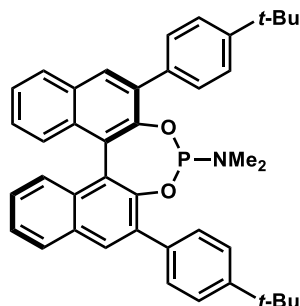
To a solution of corresponding diol (0.1 mmol) in dry toluene (1 mL) was added  $\text{P}(\text{NR}_2)_3$  (0.15 mmol) at room temperature in Ar atmosphere. The reaction mixture was warmed to  $100\text{ }^\circ\text{C}$ , and stirred for 1 h. After the reaction was completed, the residue was filtered by celite and the volatiles evaporated. The residue was purified by silica-gel column chromatography (hexane only ~ hexane/EtOAc = 100/1) to give the corresponding phosphoramidite.

## General Procedure for Preparation of Phosphoramidite (GP-2)



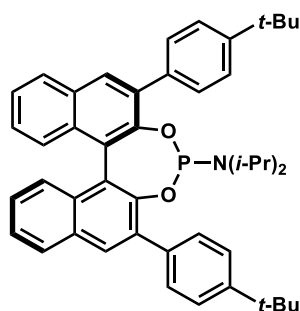
To a solution of distilled  $\text{PCl}_3$  (10  $\mu\text{L}$ , 0.11 mmol) in dry toluene (1 mL) was added  $\text{NEt}_3$  (68  $\mu\text{L}$ , 0.49 mmol) at room temperature in Ar atmosphere. After the reaction mixture was stirred for 40 min at the same temperature, corresponding amine (0.11 mmol) was added. After stirring additional 2 h, the mixture was cooled to 0  $^\circ\text{C}$  and corresponding diol (0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.3 mL) was added. The resulting mixture was warmed to room temperature and stirred for 12 h. Then, the reaction mixture was filtered by celite and the volatiles evaporated. The residue was purified by silica-gel column chromatography (hexane only  $\sim$  hexane/EtOAc = 100/1) to give the corresponding phosphoramidite.

### (*R*)-L4



**GP-1**; Pale yellow solid (91% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.39 (s, 18H, alkyl), 1.94 (s, 3H, Me), 1.97 (s, 3H, Me), 7.24-7.30 (m, 2H, arom.), 7.39-7.52 (m, 8H, arom.), 7.67 (d,  $J$  = 8.3 Hz, 2H, arom.), 7.74 (d,  $J$  = 8.1 Hz, 2H, arom.), 7.95 (dd,  $J$  = 3.3, 8.0 Hz, 2H, arom.), 8.03 (d,  $J$  = 10.7 Hz, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 147.5 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 31.7, 31.8, 34.5, 34.8, 34.9, 124.80, 124.83, 125.1, 125.2, 125.3, 125.4, 126.1, 126.2, 127.1, 127.3, 128.6, 128.7, 129.87, 129.91, 130.1, 131.1, 131.3, 131.5, 132.6, 132.7, 134.4, 135.11, 135.14, 135.5, 147.7, 147.9, 150.4, 150.7 (As the coupling patterns could not be determined, all peaks were shown.); HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{42}\text{H}_{42}\text{NaNO}_2\text{P}$  [ $\text{M}+\text{Na}$ ] $^+$  646.2851, found 646.2839; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1396, 1589, 1727, 2802, 2871, 2898, 2928, 2959, 3050.

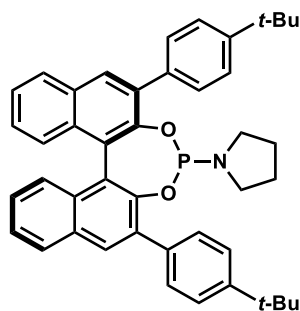
**(R)-L6**



**GP-2**; Pale yellow solid (75% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.59 (s, 3H, Me), 0.61 (s, 3H, Me), 0.83 (s, 3H, Me), 0.86 (s, 3H, Me), 1.39 (s, 9H, *t*-Bu), 1.40 (s, 9H, *t*-Bu), 3.08-3.21 (m, 2H, CH), 7.30-7.38 (m, 2H, arom.), 7.44-7.52 (m, 6H, arom.), 7.70 (d,  $J$  = 8.4 Hz, 2H, arom.), 7.86 (d,  $J$  = 8.4 Hz, 2H, arom.), 7.99 (d,  $J$  = 8.1 Hz, 2H, arom.), 8.11 (d,  $J$  = 7.8 Hz, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 148.0 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 23.6, 23.7, 24.5, 24.6, 31.7, 34.5, 44.9, 45.1, 123.50, 123.53, 124.8, 125.0, 125.2, 125.4, 125.5, 125.9, 126.0, 127.4, 127.5, 128.6, 128.7, 129.7, 130.0, 130.2, 130.3, 130.6, 130.8, 131.6, 132.77, 132.84, 134.4, 135.2, 135.4, 135.45, 135.48, 148.5, 148.7, 148.8, 150.5, 150.6 (As the coupling patterns could not be determined, all peaks were shown.); HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{44}\text{H}_{45}\text{NO}_2\text{P}$   $[\text{M}+\text{H}]^+$  680.3657, found 680.3673; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1211, 1268, 1397, 1590, 1732, 1794, 2852, 2933, 2961, 3052.

Optical Rotation:  $[\alpha]_{\text{D}}^{26}$  -499.6 ( $c$  0.22,  $\text{CHCl}_3$ ).

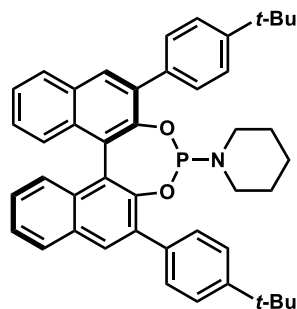
**(R)-L8**



**GP-1**; Pale yellow solid (47% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.34-1.40 (m, 4H, alkyl), 1.44 (s, 18H, alkyl), 2.51 (bs, 4H, alkyl), 7.28-7.33 (m, 2H, arom.), 7.44-7.59 (m, 8H, arom.), 7.74 (d,  $J$  = 8.4 Hz, 2H, arom.), 7.79 (d,  $J$  = 8.4 Hz, 2H, arom.), 7.99 (d,  $J$  = 9.0 Hz, 2H, arom.), 8.07 (d,  $J$  = 7.2 Hz, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 149.9 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 25.7, 25.8, 31.70, 31.74, 34.9, 44.8, 45.1, 125.16, 125.24, 125.4, 126.06, 126.12, 127.2, 127.3, 128.6, 128.7, 129.2, 129.7, 129.89, 129.93, 130.2, 130.4, 131.0, 131.2, 131.4, 132.7, 132.8, 134.5, 135.1, 135.6, 135.7, 148.0, 148.7, 150.4, 150.5 (As the coupling patterns could not be determined, all peaks were shown.); HRMS (APCI-TOF)  $m/z$  calculated for  $\text{C}_{44}\text{H}_{45}\text{NO}_2\text{P}$   $[\text{M}+\text{H}]^+$  650.3188, found 650.3156; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1183, 1272, 1396, 1592, 1726, 2868, 2903, 2929, 2965, 3053.

Optical Rotation:  $[\alpha]_{\text{D}}^{26}$  -223.1 ( $c$  0.12,  $\text{CHCl}_3$ ).

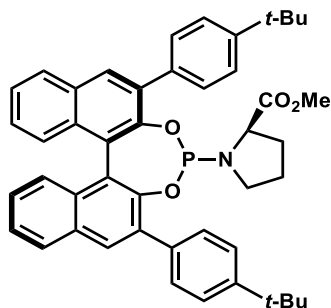
**(R)-L9**



**GP-2**; Pale yellow solid (47% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.07 (bs, 4H, alkyl), 1.28-1.33 (m, 2H, alkyl), 1.37 (s, 18H, alkyl), 2.30-2.46 (m, 4H, alkyl), 7.24-7.30 (m, 2H, arom.), 7.39-7.48 (m, 8H, arom.), 7.50 (d,  $J$  = 6.6 Hz, 2H, arom.), 7.75 (d,  $J$  = 8.3 Hz, 2H, arom.), 7.95 (d,  $J$  = 8.6 Hz, 2H, arom.), 8.05 (s, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 142.5 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 25.2, 27.0, 27.1, 31.7, 31.8, 34.9, 44.1, 44.3, 124.6, 125.0, 125.1, 125.3, 125.5, 125.6, 126.1, 126.2, 127.2, 127.4, 128.67, 128.71, 129.9, 129.99, 130.02, 130.3, 130.6, 131.2, 131.6, 132.59, 132.61, 132.77, 132.79, 134.5, 135.05, 135.08, 135.4, 135.7, 147.8, 148.1, 150.5, 150.6 (As the coupling patterns could not be determined, all peaks were shown.); HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{45}\text{H}_{47}\text{NO}_2\text{P} [\text{M}+\text{H}]^+$  664.3362, found 664.3344; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1268, 1396, 1592, 1729, 2868, 2905, 2932, 2958, 3051.

Optical Rotation:  $[\alpha]_{\text{D}}^{26}$  -223.1 ( $c$  0.12,  $\text{CHCl}_3$ ).

**(R,R)-L10**

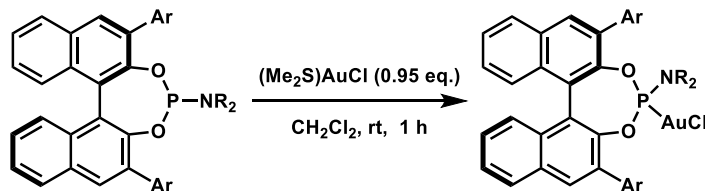


**GP-2**; Colorless solid (49% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.386 (s, 9H, *t*-Bu), 1.394 (s, 9H, *t*-Bu), 1.50-1.60 (m, 3H, alkyl), 1.64-1.77 (m, 1H, alkyl), 2.14-2.23 (m, 1H, alkyl), 2.96-3.04 (m, 1H, alkyl), 3.21 (s, 3H, OMe), 3.31-3.36 (m, 1H, alkyl), 7.23-7.30 (m, 2H, arom.), 7.36-7.38 (m, 2H, arom.), 7.41-7.51 (m, 6H, arom.), 7.64 (d,  $J$  = 8.2 Hz, 2H, arom.), 7.77 (d,  $J$  = 8.4 Hz, 2H, arom.), 7.95 (t,  $J$  = 8.4 Hz, 2H, arom.), 8.05 (d,  $J$  = 19.2 Hz, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 148.6 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.3 (d,  $J$  = 7.5 Hz), 31.1, 31.4 (d,  $J$  = 4.5 Hz), 45.6 (d,  $J$  = 30.0 Hz), 51.4, 58.5, 124.3, 124.9, 125.0, 125.1, 125.2, 125.3, 125.9, 126.9, 127.0, 128.3, 128.4, 129.1, 129.2, 129.6, 129.7, 129.9, 130.6, 131.1, 131.2, 132.38, 132.44, 133.6, 134.5, 134.6, 134.7, 134.9, 135.1, 147.2, 147.57, 147.62, 150.2, 150.4, 174.5 (d,  $J$  = 1.5 Hz); HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{46}\text{H}_{47}\text{NO}_4\text{P} [\text{M}+\text{H}]^+$  708.3243, found 708.3230; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1417, 1593,

1727, 2872, 2910, 2930, 2959, 3055.

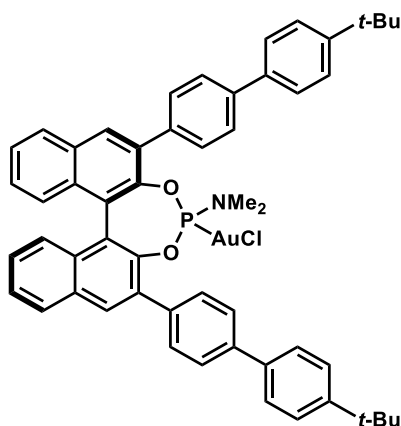
Optical Rotation:  $[\alpha]_D^{26}$  -290.8 ( $c$  0.13,  $\text{CHCl}_3$ ).

### General Procedure for Preparation of Au(I) Complexes



To a mixture of  $(\text{Me}_2\text{S})\text{AuCl}$  (28.0 mg, 0.095 mmol) and phosphoramidite (0.10 mmol) was added  $\text{CH}_2\text{Cl}_2$  (1 mL) under Ar atmosphere at room temperature, and the reaction mixture was stirred for 1 h at that temperature. After evaporation under reduced pressure, the resultant residue was washed with hexane (1 mL) three times and dried *in vacuo*. The residue was purified by silica-gel column chromatography (hexane/EtOAc = 100/0 ~ hexane/EtOAc = 5/1) to give the corresponding phosphoramidite-Au(I) complex.

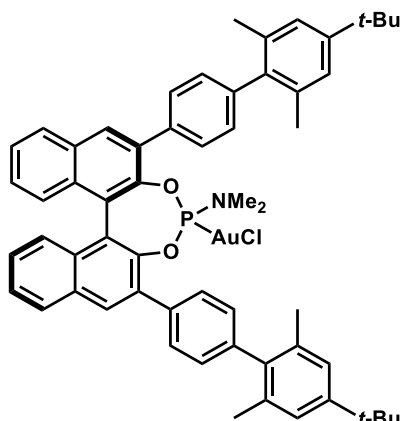
### (*R*)-L<sub>1</sub>-AuCl



Colorless solid (99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.36 (s, 9H, *t*-Bu), 1.38 (s, 9H, *t*-Bu), 2.11 (s, 3H, Me), 2.15 (s, 3H, Me), 7.35-7.40 (m, 2H, arom.), 7.44-7.50 (m, 4H, arom.), 7.53-7.60 (m, 4H, arom.), 7.65 (dd,  $J$  = 1.5, 8.4 Hz, 4H, arom.), 7.73 (s, 4H, arom.), 7.78 (s, 4H, arom.), 8.04 (d,  $J$  = 8.1 Hz, 2H, arom.), 8.16 (d,  $J$  = 2.7 Hz, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 125.4 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 29.7, 31.4, 34.6 (d,  $J$  = 4.5 Hz), 35.9 (d,  $J$  = 11.3 Hz), 123.90, 123.93, 124.1, 124.2, 125.7, 125.9, 126.3, 126.4, 126.6, 126.8, 126.9, 126.99, 127.04, 127.2, 128.9, 128.7, 128.9, 130.2, 130.7, 130.8, 131.6, 131.71, 131.73, 131.89, 131.91, 131.97, 132.00, 132.03, 132.1, 132.96, 132.99, 134.27, 134.31, 135.2, 137.1, 137.7, 140.59, 140.63, 144.4, 144.5, 145.0, 145.1, 150.4, 150.9 (As the coupling patterns could not be determined, all peaks were shown.); HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{54}\text{H}_{50}\text{AuClINNaO}_2\text{P}$   $[\text{M}+\text{Na}]^+$  1030.2831, found 1030.2819; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1400, 1498, 1730, 2817, 2869, 2906, 2928, 2954, 3034, 3055; Elemental analysis calcd. (%) for  $\text{C}_{54}\text{H}_{50}\text{AuClINO}_2\text{P}$ : C 64.26, H 4.95, N 1.39; found C 63.95, H 4.48, N 1.38.

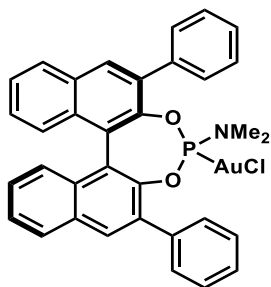
Optical Rotation:  $[\alpha]_D^{26}$  -135.1 ( $c$  1.05,  $\text{CHCl}_3$ ).

### (R)-L<sub>2</sub>-AuCl



Colorless solid (99% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 1.36 (s, 9H, *t*-Bu), 1.38 (s, 9H, *t*-Bu), 2.07 (s, 6H, Me), 2.14 (s, 6H, Me), 2.24 (s, 3H, Me), 2.28 (s, 3H, Me), 7.15 (d, *J* = 6.9 Hz, 4H, arom.), 7.32 (d, *J* = 5.1, 8.1 Hz, 4H, arom.), 7.39-7.48 (m, 3H, arom.), 7.55-7.60 (m, 3H, arom.), 7.76 (dd, *J* = 8.4, 10.5 Hz, 4H, arom.), 8.03-8.07 (m, 2H, arom.), 8.22 (d, *J* = 11.4 Hz, 2H, arom.); <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>) δ = 125.4 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ = 21.5, 21.8, 30.0, 31.8, 34.66, 34.70, 36.2, 36.4, 124.2, 124.3, 124.6, 124.8, 126.6, 126.7, 127.1, 127.2, 127.3, 127.4, 129.0, 129.1, 130.0, 130.2, 131.0, 131.4, 131.8, 132.1, 132.22, 132.24, 132.31, 132.34, 132.46, 132.48, 133.60, 133.63, 134.7, 134.8, 134.9, 135.2, 135.6, 136.0, 138.5, 139.0, 141.5, 141.7, 144.7, 144.8, 145.4, 145.6, 150.1, 150.4 (As the coupling patterns could not be determined, all peaks were shown.); HRMS (APCI-TOF) *m/z* calculated for C<sub>58</sub>H<sub>59</sub>AuClINO<sub>2</sub>P [M+H]<sup>+</sup> 1064.3637, found 1064.3625; FT-IR (KBr pellet, cm<sup>-1</sup>) 1484, 1606, 1722, 2737, 2820, 2856, 2926, 2961, 3026, 3052; Elemental analysis calcd. (%) for C<sub>45</sub>H<sub>46</sub>AuClINO<sub>2</sub>P: C 65.44, H 5.49, N 1.32; found C 66.16, H 5.42, N 1.31. Optical Rotation: [α]<sub>D</sub><sup>26</sup> -127.3 (*c* 0.99, CHCl<sub>3</sub>).

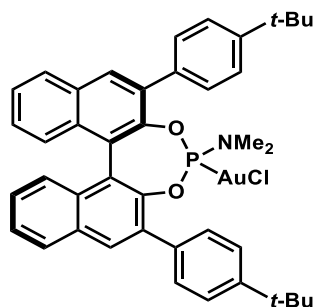
### (R)-L<sub>3</sub> AuCl



Light yellow solid (90% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 2.09 (s, 3H, Me), 2.13 (s, 3H, Me), 7.34-7.58 (m, 12H, arom.), 7.66-7.72 (m, 4H, arom.), 8.02 (d, *J* = 8.4 Hz, 2H, arom.), 8.11 (d, *J* = 4.5 Hz, 2H, arom.); <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>) δ = 125.2 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ = 36.1, 36.3, 124.15, 124.19, 124.4, 124.5, 126.6, 126.7, 127.1, 127.2, 127.3, 128.47, 128.51, 128.96, 128.99, 129.1, 130.2, 130.8, 131.1, 132.0, 132.21, 132.24, 132.29, 132.31, 133.6, 133.7, 134.8, 134.9, 136.8, 136.9, 144.6, 144.7, 145.2, 145.3 (As the coupling patterns could not be determined, all peaks

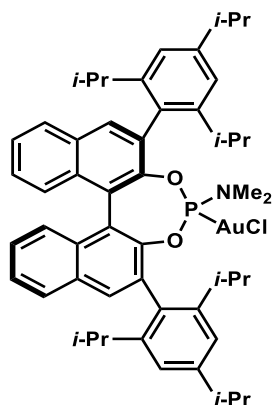
were shown.); HRMS (APCI-TOF)  $m/z$  calculated for  $C_{34}H_{27}AuClNO_2P$   $[M+H]^+$  744.1134, found 744.1161; FT-IR (KBr pellet,  $cm^{-1}$ ) 1491, 1603, 1726, 2819, 2856, 2924, 3032, 3057; Elemental analysis calcd. (%) for  $C_{34}H_{26}AuClNO_2P$ : C 54.84, H 3.49, N 1.88; found C 53.07, H 3.67, N 1.78. Optical Rotation:  $[\alpha]_D^{26}$  -201.5 ( $c$  1.75,  $CHCl_3$ ).

### (R)-L4-AuCl



Yellow solid (99% yield):  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  = 1.39 (s, 9H, *t*-Bu), 1.40 (s, 9H, *t*-Bu), 2.09 (s, 3H, Me), 2.13 (s, 3H, Me), 7.31-7.44 (m, 3H, arom.), 7.51-7.56 (m, 7H, arom.), 7.61-7.67 (m, 4H, arom.), 8.00 (d,  $J$  = 8.1 Hz, 2H, arom.), 8.11 (s, 2H, arom.);  $^{31}P\{^1H\}$  NMR (121 MHz,  $CDCl_3$ )  $\delta$  = 125.3 (s);  $^{13}C\{^1H\}$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  = 31.6, 31.7, 35.0, 35.9, 36.1, 124.17, 124.20, 124.37, 124.40, 125.86, 125.92, 126.46, 126.53, 126.9, 127.0, 127.2, 127.3, 128.90, 128.94, 129.9, 130.3, 130.8, 131.2, 131.9, 132.0, 132.2, 132.3, 133.5, 133.85, 133.90, 134.7, 144.7, 144.8, 145.3, 145.5, 151.4, 151.7 (As the coupling patterns could not be determined, all peaks were shown.); HRMS (APCI-TOF)  $m/z$  calculated for  $C_{42}H_{43}AuClNO_2P$   $[M+H]^+$  856.2385, found 856.2353; FT-IR (KBr pellet,  $cm^{-1}$ ) 1410, 1602, 1723, 2814, 2871, 2905, 2957, 3028, 3054, 3129; Elemental analysis calcd. (%) for  $C_{45}H_{46}AuClNO_2P$ : C 58.92, H 4.94, N 1.64; found C 59.31, H 5.06, N 1.58. Optical Rotation:  $[\alpha]_D^{26}$  -213.1 ( $c$  0.50,  $CHCl_3$ ).

### (R)-L5-AuCl

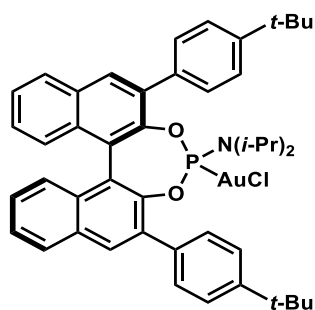


Colorless solid (99% yield):  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  = 0.87-0.92 (m, 6H,  $CH_3$ ), 1.07-1.09 (m, 3H,  $CH_3$ ), 1.26-1.28 (m, 9H,  $CH_3$ ), 1.29-1.35 (m, 12H,  $CH_3$ ), 1.42-1.45 (m, 6H,  $CH_3$ ), 2.35 (s, 3H, Me), 2.39 (s, 3H, Me), 2.61-2.76 (m, 2H, CH), 2.83-3.02 (m, 3H, CH), 3.04-3.13 (m, 1H, CH), 7.03-7.11 (m, 4H, arom.), 7.18 (d,  $J$  = 13.4 Hz, 2H, arom.), 7.29 (d,  $J$  = 8.3 Hz, 2H, arom.), 7.51 (t,  $J$  = 6.8

Hz, 2H, arom.), 7.91-7.97 (m, 4H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 125.0 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 23.3, 23.8, 24.1, 24.29, 24.33, 24.5, 24.6, 25.2, 25.8, 26.5, 27.0, 28.0, 30.8, 31.2, 31.5, 31.7, 34.48, 34.54, 36.9, 37.1, 120.7, 131.5, 122.0, 122.4, 122.9 (d,  $J$  = 3.0 Hz), 126.1, 126.3, 126.77, 126.81, 127.2, 127.4, 128.5, 128.6, 130.4, 131.0, 131.1 (d,  $J$  = 2.3 Hz), 131.5, 132.0, 132.1, 132.8 (q,  $J$  = 3.0 Hz), 133.2, 133.5, 145.9, 146.0, 146.4, 146.7, 146.9, 147.3, 147.7, 148.8, 149.0, 149.4; HRMS (APCI-TOF)  $m/z$  calculated for  $\text{C}_{52}\text{H}_{62}\text{AuClINO}_2\text{P}$   $[\text{M}+\text{Na}]^+$  1018.3767, found 1018.3726; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1406, 1458, 1606, 1733, 2817, 2866, 2923, 2959, 3052, 3066; Elemental analysis calcd. (%) for  $\text{C}_{52}\text{H}_{62}\text{AuClINO}_2\text{P}$ : C 62.62, H 6.22, N 1.40; found C 62.67, H 6.71, N 1.35.

Optical Rotation:  $[\alpha]_{\text{D}}^{21}$  -0.67 ( $c$  0.50,  $\text{CHCl}_3$ ).

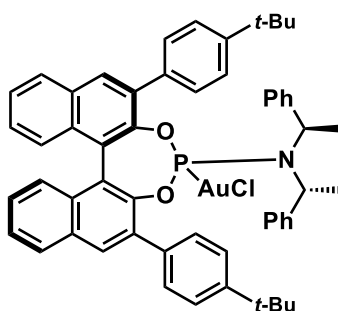
### (*R*)- $\text{L}_6$ -AuCl



Pale yellow solid (92% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.76 (s, 3H, Me), 0.79 (s, 3H, Me), 0.81 (s, 3H, Me), 0.83 (s, 3H, Me), 1.34 (s, 9H, *t*-Bu), 1.36 (s, 9H, *t*-Bu), 3.19-3.33 (m, 2H, alkyl), 7.29-7.36 (m, 3H, arom.), 7.45-7.54 (m, 7H, arom.), 7.60-7.71 (m, 8H, arom.), 7.65 (d,  $J$  = 8.1 Hz, 2H, arom.), 7.69 (d,  $J$  = 8.1 Hz, 2H, arom.), 7.99 (t,  $J$  = 7.2 Hz, 2H, arom.), 8.12 (d,  $J$  = 10.2 Hz, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 122.8 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 23.3, 23.4, 23.8, 23.9, 31.6, 31.7, 34.97, 35.00, 48.0, 48.1, 122.87, 122.91, 124.47, 124.53, 125.6, 125.7, 126.1, 126.4, 126.7, 126.8, 127.3, 127.7, 128.7, 129.1, 130.3, 130.9, 131.1, 131.4, 131.5, 132.4, 133.57, 133.59, 133.7, 134.0, 135.0, 135.1, 145.6, 145.7, 146.6, 146.9, 151.4, 151.6 (As the coupling patterns could not be determined, all peaks were shown.); HRMS (APCI-TOF)  $m/z$  calculated for  $\text{C}_{46}\text{H}_{51}\text{AuClINO}_2\text{P}$   $[\text{M}+\text{H}]^+$  912.3011, found 912.2972; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1193, 1363, 1402, 1463, 1729, 2867, 2905, 2962, 3031, 3053; Elemental analysis calcd. (%) for  $\text{C}_{46}\text{H}_{50}\text{AuClINO}_2\text{P}$ : C 60.59, H 5.49, N 1.54; found C 61.68, H 5.97, N 1.35.

Optical Rotation:  $[\alpha]_{\text{D}}^{26}$  -283.2 ( $c$  0.41,  $\text{CHCl}_3$ ).

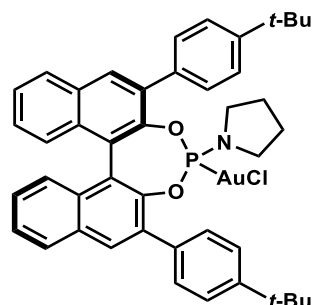
### **(R,R,R)-L7-AuCl**



Pale yellow solid (99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.09-1.14 (s, 36H, alkyl), 1.40-1.49 (m, 6H, CH), 2.08 (s, 3H, Me), 2.12 (s, 3H, Me), 7.34-7.46 (m, 2H, arom.), 7.53-7.57 (m, 4H, arom.), 7.60-7.71 (m, 8H, arom.), 8.00-8.04 (m, 2H, arom.), 8.15 (d,  $J$  = 4.2 Hz, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 125.3 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 19.3, 29.9, 31.65, 31.72, 34.9, 35.0, 55.1, 55.3, 122.78, 122.82, 124.58, 124.64, 125.6, 126.0, 126.2, 126.4, 126.8, 126.9, 127.1, 127.6, 127.7, 128.1, 128.4, 128.5, 129.0, 130.4, 130.7, 131.1, 131.2, 131.8, 132.2, 132.3, 132.38, 132.40, 132.56, 132.58, 133.3, 133.87, 133.90, 134.3, 134.65, 134.70, 140.75, 140.81, 144.9, 145.0, 146.8, 147.0, 151.0, 151.7 (As the coupling patterns could not be determined, all peaks were shown.); HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{56}\text{H}_{54}\text{AuClINaO}_2\text{P}$   $[\text{M}+\text{Na}]^+$  1058.3144, found 1058.3128; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1201, 1393, 1725, 1803, 2868, 2904, 2962, 3030; Elemental analysis calcd. (%) for  $\text{C}_{56}\text{H}_{54}\text{AuClINO}_2\text{P}$ : C 64.91, H 5.22, N 1.35; found C 63.99, H 5.32, N 1.29.

Optical Rotation:  $[\alpha]_{\text{D}}^{26}$  -250.8 ( $c$  0.33,  $\text{CHCl}_3$ ).

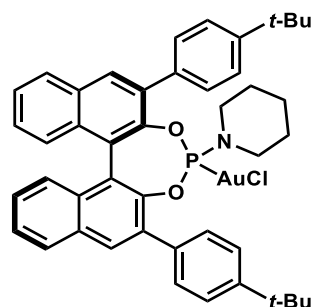
### **(R)-L8-AuCl**



Pale yellow solid (74% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.35-1.44 (m, 22H, alkyl), 2.46 (bs, 2H, alkyl), 2.67 (bs, 2H, alkyl), 7.34-7.44 (m, 3H, arom.), 7.49-7.54 (m, 7H, arom.), 7.64 (t,  $J$  = 8.6 Hz, 2H, arom.), 8.00 (d,  $J$  = 8.2 Hz, 2H, arom.), 8.10 (d,  $J$  = 3.6 Hz, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 121.5 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 25.9, 26.0, 31.6, 31.7, 35.0, 47.1, 47.2, 124.1, 124.5, 125.8, 125.9, 126.4, 126.5, 126.9, 127.0, 127.3, 127.4, 128.9, 129.0, 129.2, 130.0, 130.3, 130.7, 131.3, 131.9, 132.0, 132.17, 132.24, 132.3, 133.5, 134.0, 134.1, 134.6, 145.0, 145.1, 146.0, 146.1, 151.4, 151.6 (As the coupling patterns could not be determined, all peaks were shown.); HRMS (APCI-TOF)  $m/z$  calculated for  $\text{C}_{44}\text{H}_{45}\text{AuClINO}_2\text{P}$   $[\text{M}+\text{H}]^+$  882.2542, found 882.2536; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1193, 1269, 1462, 1730, 1795, 2873, 2902, 2927, 2958; Elemental analysis calcd. (%) for  $\text{C}_{44}\text{H}_{44}\text{AuClINO}_4\text{P}$ : C 59.86, H 4.99, N 1.59; found C 58.39, H 5.10, N 1.38.

Optical Rotation:  $[\alpha]_D^{26}$  -217.4 (*c* 0.5, CHCl<sub>3</sub>).

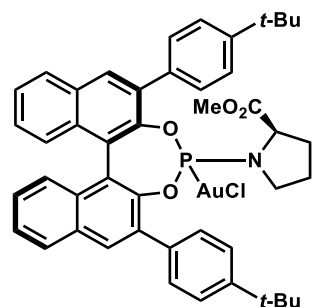
### (*R*)-L<sub>9</sub>-AuCl



Pale yellow solid (94% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.84-0.89 (m, 4H, alkyl), 1.10 (bs, 4H, alkyl), 1.37 (s, 9H, *t*-Bu), 1.38 (s, 9H, *t*-Bu), 2.28-2.39 (m, 2H, alkyl), 2.71-2.83 (m, 2H, alkyl), 7.31-7.44 (m, 3H, arom.), 7.50-7.56 (m, 7H, arom.), 7.61-7.66 (m, 8H, arom.), 8.00 (dd, *J* = 3.6, 8.1 Hz, 2H, arom.), 8.11 (d, *J* = 6.9 Hz, 2H, arom.); <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>)  $\delta$  = 121.3 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 24.4, 26.3 (d, *J* = 4.5 Hz), 30.0, 31.7 (d, *J* = 4.5 Hz), 35.0, 46.0 (d, *J* = 9.0 Hz), 123.9, 124.4, 125.7, 125.8, 126.3, 126.5, 126.9, 127.3, 127.4, 128.9, 129.1, 129.2, 130.0, 130.6, 130.8, 131.3, 131.5, 131.9, 132.1, 132.2, 132.4, 133.66, 133.69, 133.8, 134.1, 134.7, 134.8, 144.8, 144.9, 145.6, 145.8, 151.5 (As the coupling patterns could not be determined, all peaks were shown.); HRMS (APCI-TOF) *m/z* calculated for C<sub>45</sub>H<sub>47</sub>AuClNO<sub>2</sub>P [M+H]<sup>+</sup> 896.2698, found 896.2679; FT-IR (KBr pellet, cm<sup>-1</sup>) 1204, 1409, 1731, 2862, 2904, 2937, 2955, 3029, 3054; Elemental analysis calcd. (%) for C<sub>45</sub>H<sub>46</sub>AuClNO<sub>2</sub>P: C 60.25, H 5.13, N 1.56; found C 60.39, H 5.26, N 1.40.

Optical Rotation:  $[\alpha]_D^{26}$  -331.8 (*c* 0.33, CHCl<sub>3</sub>).

### (*R,R*)-L<sub>10</sub>-AuCl



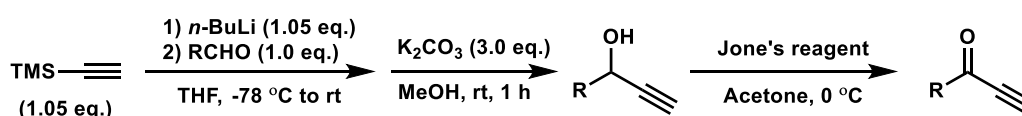
Colorless solid (99% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.38 (s, 9H, *t*-Bu), 1.40 (s, 9H, *t*-Bu), 1.52-1.65 (m, 2H, alkyl), 1.69-1.77 (m, 2H, alkyl), 2.03-2.12 (m, 1H, alkyl), 3.19-3.25 (m, 1H, alkyl), 3.34-3.39 (m, 1H, alkyl), 3.42 (s, 3H, OMe), 7.33-7.39 (m, 3H, arom.), 7.45-7.59 (m, 9H, arom.), 7.68 (d, *J* = 8.4 Hz, 2H, arom.), 8.00 (t, *J* = 7.2 Hz, 2H, arom.), 8.11 (d, *J* = 17.4 Hz, 2H, arom.); <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>)  $\delta$  = 122.9 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 23.8 (d, *J* = 12.0 Hz), 31.7 (d, *J* = 8.3 Hz), 35.0 (d, *J* = 2.3 Hz), 47.6 (d, *J* = 21.0 Hz), 52.5, 60.2 (d, *J* = 2.3 Hz), 124.10, 124.13, 124.45, 125.00, 125.8, 125.9, 126.6, 127.0, 127.1, 127.3, 127.5, 128.9, 129.0, 130.0, 130.4,

130.9, 132.0, 132.17, 132.19, 132.4, 132.97, 133.0, 133.67, 133.72, 134.4, 134.5, 144.7, 144.8, 145.3, 145.5, 151.4, 151.8, 172.7 (d,  $J = 1.5$  Hz); HRMS (ESI-TOF)  $m/z$  calculated for  $C_{46}H_{46}AuClINaO_4P$   $[M+Na]^+$  962.2416, found 962.2385; FT-IR (KBr pellet,  $cm^{-1}$ ) 1393, 1601, 1745, 2870, 2905, 2955, 3029, 3054; Elemental analysis calcd. (%) for  $C_{46}H_{46}AuClINO_4P$ : C 58.77, H 4.90, N 1.49; found C 59.01, H 4.84, N 1.43.

Optical Rotation:  $[\alpha]_D^{26} -344.3$  ( $c$  0.22,  $CHCl_3$ ).

### Synthetic Procedure of Ynones

The compound **1a** ~ **1f**, **1h** ~ **1m**, **1o**, **1p**, **1r** ~ **1w** were synthesized as shown below. The spectral data were in accordance with the literature. All other alkynes (**1g**, **1n**, **2q**) were synthesized.

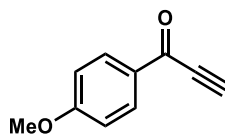


To a solution of trimethylsilylacetylene (3.0 mL, 21 mmol) in dry THF (50 mL) under Ar atmosphere was added *n*-butyllithium (8.1 mL, 21 mmol, 2.6 M solution in hexane, 1 M = 1 mol  $dm^{-3}$ ) at  $-78$  °C and the mixture was stirred for 15 min. Corresponding aldehyde (20 mmol) was added to the solution, and the reaction mixture was warmed up to room temperature. After stirring at that temperature (monitored by TLC), the reaction was quenched with saturated aq.  $NH_4Cl$ . The organic layer was separated and aqueous layer was extracted with  $Et_2O$  three times. The combined organic layers were washed with brine and dried over  $MgSO_4$ , and the solvent was removed under reduced pressure.

After concentration, the crude mixture was dissolved by MeOH (30 mL) under air at room temperature. Then potassium carbonate (8.3 g, 60 mmol) was added, and the reaction mixture was stirred for 1 h at that temperature (monitored by TLC). Then, the mixture was filtrated over celite. The residue was washed with diethyl ether (10 mL). The collected filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica-gel (hexane: EtOAc = 10:1 ~ 3:1), affording the corresponding ynol product.

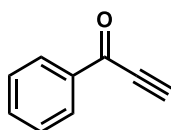
To the solution of crude alcohol in acetone at 0 °C, Jones' reagent (10.8 mL, 0.54 M solution in water, 1 M = 1 mol  $dm^{-3}$ ) was added slowly and the reaction mixture was stirred at that temperature (monitored by TLC). Reaction mixture was warmed to room temperature and quenched with *i*-PrOH (10 mL). The reaction mixture was diluted with  $CHCl_3$  (20 mL) and water (20 mL). Organic layer was separated and the aqueous layer was extracted with  $CHCl_3$  (20 mL  $\times$  2). The combined organic layers were washed with brine (20 mL  $\times$  1), dried over  $MgSO_4$  and concentrated under reduced pressure. The crude product was purified by column chromatography on silica-gel (hexane: EtOAc = 10:1) to yield the corresponding compounds.

### 1-(4-Methoxyphenyl)prop-2-yn-1-one (1a) <sup>[S4]</sup>



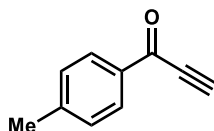
Colorless solid (2 steps, 61% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 3.43 (s, 1H, CH), 3.79 (s, 3H, OMe), 6.86 (d,  $J$  = 8.9 Hz, 2H, arom.), 8.03 (d,  $J$  = 8.9 Hz, 1H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 55.6, 80.4, 114.0, 129.5, 132.1, 164.8, 175.9.

### 1-Phenylprop-2-yn-1-one (1b) <sup>[S4]</sup>



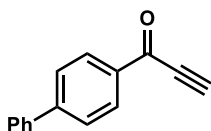
Colorless solid (2 steps, 72% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 3.61 (s, 1H, CH), 7.35 (t,  $J$  = 7.8 Hz, 2H, arom.), 7.50 (t,  $J$  = 7.4 Hz, 1H, arom.), 8.04-8.02 (m, 2H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 80.3, 81.7, 128.7, 129.6, 134.6, 136.0, 177.4.

### 1-(4-Methylphenyl)prop-2-yn-1-one (1c) <sup>[S4]</sup>



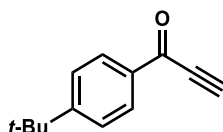
Yellow solid (2 steps, 49% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.46 (s, 6H, Me), 3.41 (s, 1H, CH), 7.31 (d,  $J$  = 7.7 Hz, 2H, arom.), 8.08 (d,  $J$  = 7.6 Hz, 2H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 21.9, 129.4, 129.9, 133.9, 146.7, 177.1.

### 1-(4-Phenylphenyl)prop-2-yn-1-one (1d) <sup>[S4]</sup>



Colorless solid (2 steps, 80% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 3.48 (s, 1H, CH), 7.40-7.51 (m, 3H, arom.), 7.63 (d,  $J$  = 7.6 Hz, 2H, arom.), 7.71 (d,  $J$  = 8.4 Hz, 2H, arom.), 8.23 (d,  $J$  = 8.3 Hz, 2H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 80.4, 81.0, 127.4 (d,  $J$  = 3.0 Hz), 128.6, 129.1, 130.3, 135.0, 139.6, 147.2, 177.0.

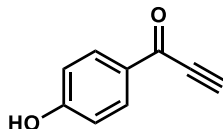
### 1-(4-*tert*-Butylphenyl)prop-2-yn-1-one (1e) <sup>[S4]</sup>



Yellow solid (2 steps, 53% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.35 (s, 9H, *t*-Bu), 3.46 (s, 1H,

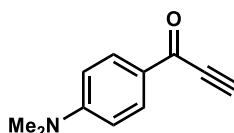
CH), 7.51 (d,  $J = 8.4$  Hz, 2H, arom.), 8.10 (d,  $J = 8.4$  Hz, 2H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 31.0, 35.3, 80.5, 80.5, 125.7, 129.7, 133.8, 158.6, 177.0$ .

#### 1-(4-Hydroxyphenyl)prop-2-yn-1-one (1f)



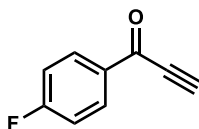
Brown solid (2 steps, 77% yield):  $^1\text{H}$  NMR (300 MHz,  $(\text{CD}_3)_2\text{CO}$ )  $\delta = 4.27$  (s, 1H, CH), 7.03 (d,  $J = 8.8$  Hz, 2H, arom.), 8.09 (d,  $J = 8.8$  Hz, 2H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $(\text{CD}_3)_2\text{CO}$ )  $\delta = 80.3, 81.0, 115.6, 128.9, 132.0, 163.4, 175.2$ ; HRMS (APCI-TOF)  $m/z$  calculated for  $\text{C}_9\text{H}_7\text{O}_2$   $[\text{M}+\text{H}]^+$  147.0446, found 147.0457; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1255, 1596, 2831, 3245, 3888, 3965.

#### 1-(4-Dimethylaminophenyl)prop-2-yn-1-one (1g) <sup>[S5]</sup>



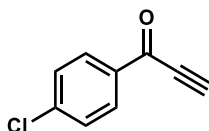
Orange solid (2 steps, 53% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta = 3.09$  (s, 6H, NMe), 3.29 (s, 1H, CH), 6.65 (d,  $J = 6.5$  Hz, 2H, arom.), 8.04 (d,  $J = 9.2$  Hz, 2H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 40.1, 110.6, 124.8, 132.2, 154.4, 175.2$ .

#### 1-(4-Fluorophenyl)prop-2-yn-1-one (1h) <sup>[S6]</sup>



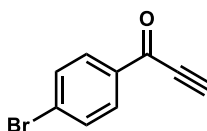
Colorless solid (2 steps, 74% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta = 3.54$  (s, 1H, CH), 7.05 (t,  $J = 8.6$  Hz, 2H, arom.), 8.06 (dd,  $J = 5.4, 8.9$  Hz, 2H, arom.);  $^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta = -102.3$  (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 80.0, 81.7, 116.0$  (d,  $J = 22.5$  Hz), 132.5 (d,  $J = 9.8$  Hz), 132.7 (d,  $J = 3.0$  Hz), 166.7 (d,  $J = 255.8$  Hz), 175.8.

#### 1-(4-Chlorophenyl)prop-2-yn-1-one (1i) <sup>[S4]</sup>



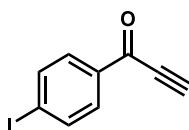
Pink solid (2 steps, 79% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta = 3.50$  (s, 1H, CH), 7.42 (d,  $J = 8.6$  Hz, 2H, arom.), 8.04 (d,  $J = 8.6$  Hz, 2H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 80.1, 81.8, 129.3, 131.2, 134.7, 141.4, 176.3$ .

### 1-(4-Bromophenyl)prop-2-yn-1-one (1j) <sup>[S4]</sup>



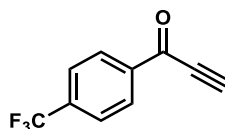
Pale yellow solid (2 steps, 93% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 3.50 (s, 1H, CH), 7.60 (d, *J* = 8.0 Hz, 2H, arom.), 7.97 (d, *J* = 8.1 Hz, 2H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ = 80.1, 81.8, 130.4, 131.3, 132.3, 135.1, 176.5.

### 1-(4-Iodophenyl)prop-2-yn-1-one (1k) <sup>[S8]</sup>



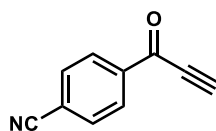
Red solid (2 steps, 85% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 3.48 (s, 1H, CH), 7.80-7.87 (m, 4H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ = 80.1, 81.7, 103.6, 131.1, 135.7, 138.3, 176.9.

### 1-(4-Trifluoromethylphenyl)prop-2-yn-1-one (1l) <sup>[S7]</sup>



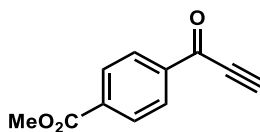
Colorless solid (2 steps, 89% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 3.59 (s, 1H, CH), 7.70 (d, *J* = 8.3 Hz, 2H, arom.), 8.20 (d, *J* = 8.2 Hz, 2H, arom.); <sup>19</sup>F{<sup>1</sup>H} NMR (282 MHz, CDCl<sub>3</sub>) δ = -63.4 (s, 3F); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ = 79.7, 82.2, 123.4 (q, *J* = 271.1 Hz), 125.7 (q, *J* = 3.8 Hz), 129.9, 135.4 (q, *J* = 32.6 Hz), 138.5, 176.1.

### 1-(4-Cyanophenyl)prop-2-yn-1-one (1m) <sup>[S8]</sup>



Colorless solid (2 steps, 99% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 3.64 (s, 1H, CH), 7.77 (d, *J* = 8.3 Hz, 2H, arom.), 8.19 (d, *J* = 8.3 Hz, 2H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ = 79.7, 83.2, 117.6, 117.8, 130.0, 132.7, 138.8, 175.9.

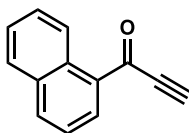
### Methyl 4-propioloylbenzoate (1n)



Pale yellow solid (2 steps, 72% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 3.69 (s, 1H, CH), 3.92 (s, 3H, Me), 8.09 (d, *J* = 8.6 Hz, 2H, arom.), 8.16 (d, *J* = 8.6 Hz, 2H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)

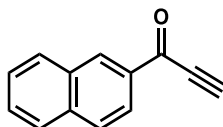
$\delta = 52.8, 80.2, 82.3, 129.7, 130.0, 135.2, 139.2, 166.1, 176.8$ ; HRMS (APCI-TOF)  $m/z$  calculated for  $C_{11}H_9O_3 [M+H]^+$  189.0552, found 189.0556; FT-IR (KBr pellet,  $cm^{-1}$ ) 1276, 1451, 1726, 2853, 2956, 3068, 3223, 3427.

**1-(1-Naphthyl)prop-2-yn-1-one (1o)** <sup>[S4]</sup>



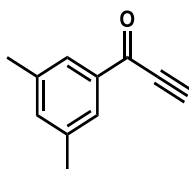
Colorless solid (2 steps, 74% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 3.52$  (s, 1H, CH), 7.45-7.55 (m, 2H, arom.), 7.65 (t,  $J = 7.5$  Hz, 1H, arom.), 7.83 (d,  $J = 7.8$  Hz, 1H, arom.), 8.00 (d,  $J = 8.1$  Hz, 1H, arom.), 8.56 (d,  $J = 7.2$  Hz, 1H, arom.), 9.24 (d,  $J = 8.7$  Hz, 1H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 80.0, 81.7, 124.5, 125.8, 126.9, 128.7, 129.3, 130.6, 131.7, 133.8, 135.7, 135.8, 178.9$ .

**1-(2-Naphthyl)prop-2-yn-1-one (1p)** <sup>[S4]</sup>



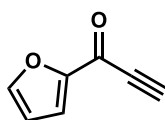
Light brown solid (2 steps, 92% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 3.51$  (s, 1H, CH), 7.56-7.67 (m, 2H, arom.), 7.88-7.92 (m, 2H, arom.), 8.01 (d,  $J = 8.0$  Hz, 1H, arom.), 8.14 (dd,  $J = 7.0, 1.7$  Hz, 1H, arom.), 8.75 (s, 1H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 80.8, 81.0, 123.9, 127.4, 128.3, 129.0, 129.6, 132.7, 133.7, 134.1, 136.6, 177.7$ .

**1-(3,5-Dimethylphenyl)prop-2-yn-1-one (1q)** <sup>[S9]</sup>

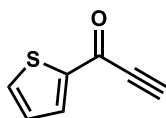


Yellow solid (2 steps, 24% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 2.31$  (s, 6H, Me), 3.50 (s, 1H, CH), 7.16 (s, 1H, arom.), 7.69 (s, 2H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 21.1, 80.5, 80.8, 127.4, 136.3, 138.4, 177.7$ .

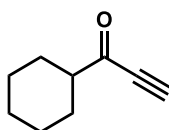
**1-(2-Furyl)prop-2-yn-1-one (1r)** <sup>[S10]</sup>



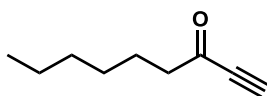
Yellow solid (2 steps, 21% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 3.35$  (s, 1H, CH), 7.09 (dd,  $J = 1.6, 3.6$  Hz, 1H, arom.), 7.35 (d,  $J = 3.8$  Hz, 1H, arom.), 7.64 (d,  $J = 0.7$  Hz, 1H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 79.6, 79.7, 112.9, 122.3, 148.6, 152.7, 163.8$ .

**1-(2-Thiophenyl)prop-2-yn-1-one (1s)** <sup>[S11]</sup>

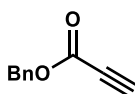
Yellow solid (2 steps, 29% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 3.45 (s, 1H, CH), 7.09 (t,  $J$  = 4.5 Hz, 1H, arom.), 7.68 (d,  $J$  = 4.9 Hz, 1H, arom.), 7.88 (d,  $J$  = 3.8 Hz, 1H, arom.); <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 79.9, 80.0, 128.7, 136.2, 136.4, 144.1, 169.2.

**1-Cyclohexylprop-2-yn-1-one (1t)** <sup>[S12]</sup>

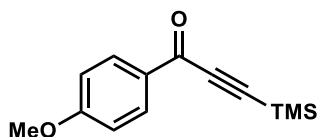
Colorless solid (2 steps, 61% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.13-1.40 (m, 5H, alkyl), 1.55-1.59 (m, 1H, alkyl), 1.68-1.72 (m, 2H, alkyl), 1.88-1.92 (m, 2H, alkyl), 2.29-2.39 (m, 1H, alkyl), 3.24 (s, 1H, CH); <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 25.2, 25.6, 27.8, 52.0, 79.3, 80.7.

**Non-1-yn-3-one (1u)** <sup>[S13]</sup>

Pale yellow liquid (2 steps, 61% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.81-0.86 (m, 2H, alkyl), 1.25-1.30 (m, 6H, alkyl), 1.57-1.65 (m, 2H, alkyl), 2.53 (t,  $J$  = 7.4 Hz, 2H, alkyl), 3.23 (s, 1H, CH); <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 13.9, 22.4, 23.7, 28.5, 31.4, 45.4, 78.4, 81.4, 187.4.

**Benzyl propiolate (1v)** <sup>[S14]</sup>

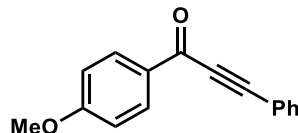
Colorless liquid (88% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.92 (s, 1H, CH), 5.25 (s, 2H, CH<sub>2</sub>), 7.41 (s, 5H, arom.); <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 67.9, 74.6, 75.1, 128.6, 128.70, 128.74, 134.6, 152.6.

**1-(4-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-one (1w)** <sup>[S15]</sup>

Colorless liquid (2 steps, 81% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.29 (s, 9H, TMS), 3.85 (s, 3H,

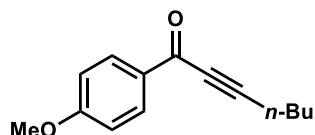
OMe), 6.93 (d, 2H,  $J = 8.9$  Hz, arom.), 8.09 (d, 2H,  $J = 8.8$  Hz, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = -0.7, 56.6, 99.5, 101.0, 129.9, 132.0, 164.5, 176.3$ .

#### 1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one (1x) <sup>[S16]</sup>



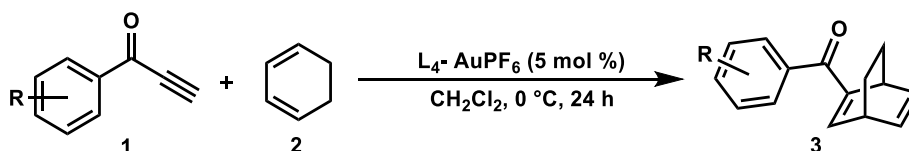
Colorless solid (2 steps, 90% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta = 3.90$  (s, 3H, OMe), 6.99 (d,  $J = 8.9$  Hz, 2H, arom.), 7.26-7.50 (m, 3H, arom.), 7.66-7.69 (m, 2H, arom.), 8.19 (d,  $J = 8.9$  Hz, 2H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 55.7, 87.1, 92.4, 114.0, 120.5, 128.8, 130.5, 130.7, 132.1, 133.1, 164.6, 176.8$ .

#### 1-(4-Methoxyphenyl)hept-2-yn-1-one (1y) <sup>[S17]</sup>



Colorless solid (2 steps, 85% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta = 0.95$  (t,  $J = 7.3$  Hz, 3H, alkyl), 1.42-1.62 (m, 2H, alkyl), 1.63-1.73 (m, 2H, alkyl), 2.47 (t,  $J = 7.1$  Hz, 2H, alkyl), 3.86 (s, 3H, OMe), 6.93 (d,  $J = 8.9$  Hz, 2H, arom.), 8.09 (d,  $J = 8.9$  Hz, 1H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 13.6, 19.0, 22.2, 30.0, 55.6, 79.7, 96.0, 113.8, 130.5, 132.0, 164.4, 177.1$ .

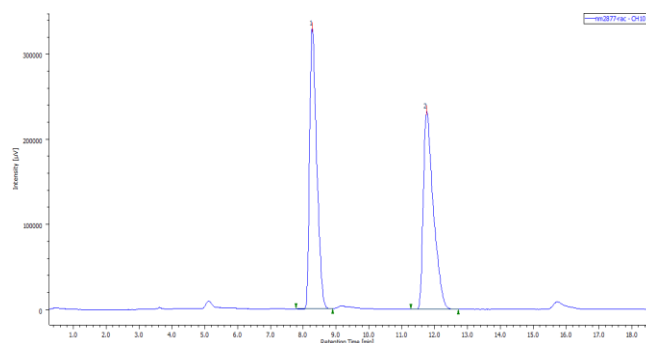
#### Large Scale Experiment of Asymmetric Intermolecular [4+2] Cycloaddition (1 mmol scale)



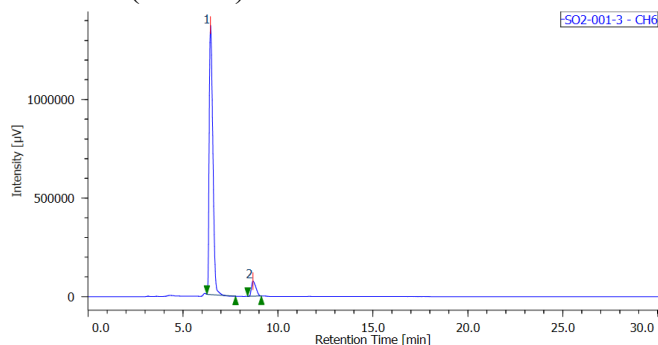
A solution of 1-phenylprop-2-yn-1-one (**1b**, R = H) (130 mg, 1.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (5.0 mL) and cyclohexadiene (190  $\mu\text{L}$ , 2.0 mmol) was added to a solution of (*R*)- $\text{L}_4\text{-AuPF}_6$  (5.0 mol %) in  $\text{CH}_2\text{Cl}_2$  (5.0 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 24 h. The reaction mixture was directly loaded onto a silica-gel short column (hexane/AcOEt = 3/1) to remove the catalyst. The filtrate was concentrated under reduced pressure. Purification by silica-gel column chromatography (hexane/AcOEt = 10/1 as eluent) gave the [4+2] cycloadduct (148.3 mg, 71% isolated yield, 87% *ee*).

HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 98/2, flow rate 1.0 mL/min, 20 °C, detection UV 245 nm light);  $t_{\text{R}}$  of major-isomer 6.4 min,  $t_{\text{R}}$  of minor-isomer 8.7 min.

Racemic:



Chiral (87% ee):

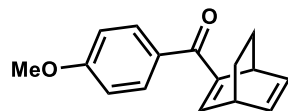


$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
8.267	4920543	49.904	6.440	18328893	93.677
11.747	4939487	50.096	8.680	1237180	6.323

### General Procedure of Asymmetric Intermolecular [4+2] Cycloaddition (0.1 mmol scale)

A solution of alkyne (0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL) and diene (0.2 mmol) was added to a solution of (*R*)-L-AuPF<sub>6</sub> (5 mol %) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 24 h. The reaction mixture was directly loaded onto a silica-gel short column (hexane/AcOEt = 3/1) to remove the catalyst, and then the solution was concentrated under reduced pressure. The residue was purified by silica-gel chromatography (hexane/AcOEt = 10/1) to give the [4+2] cycloadduct.

### (1*S*,4*R*)-2-(4-Methoxybenzoyl)bicyclo[2.2.2]octa-2,5-diene (3a)

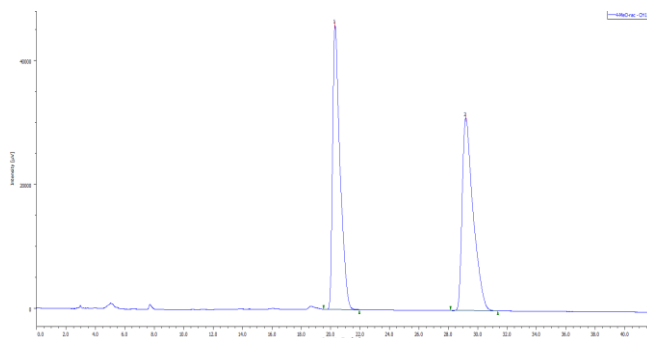


Yellow liquid (25.2 mg, 95% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.39 (s, 4H, alkyl), 3.77-3.80 (m, 1H, alkyl), 3.85 (s, 3H, OMe), 4.36 (d,  $J$  = 5.4 Hz, 1H, alkyl), 6.36 (dd,  $J$  = 6.0, 6.0 Hz, 1H, vinyl), 6.46 (dd,  $J$  = 6.0, 6.0 Hz, 1H, vinyl), 6.88-6.91 (m, 3H, vinyl + arom.), 7.67 (d,  $J$  = 8.3 Hz, 2H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 24.7, 24.8, 37.1, 38.2, 55.4, 113.3, 130.8, 131.5, 133.2, 135.1, 146.5, 147.7, 162.6, 192.3; HRMS (ESI-TOF)  $m/z$  calculated for C<sub>16</sub>H<sub>16</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 263.1048, found 263.1036; FT-IR (neat, cm<sup>-1</sup>) 1033, 1174, 1255, 1354, 1600, 1637, 1730, 2870, 2957, 3054.

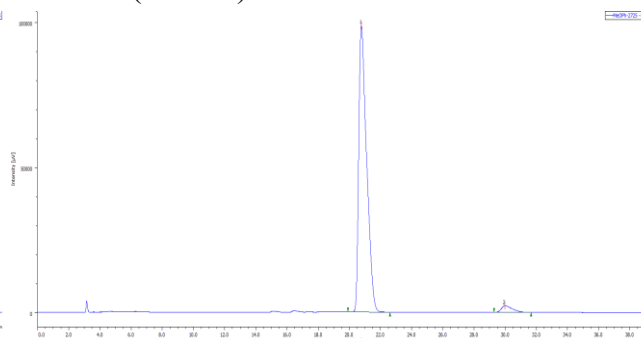
Optical Rotation:  $[\alpha]_D^{26}$  +39.9 ( $c$  2.52, CHCl<sub>3</sub>) for an enantiomerically enriched sample of 94% ee.

HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 98/2, flow rate 1.0 mL/min, 20 °C, detection UV 250 nm light);  $t_R$  of major-isomer 20.7 min,  $t_R$  of minor-isomer 30.0 min.

Racemic:

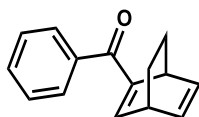


Chiral (94% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
20.292	1602366	49.948	20.767	3474057	96.866
29.175	1605685	50.052	29.967	112408	3.134

**(1*S*,4*R*)-2-Benzoylbicyclo[2.2.2]octa-2,5-diene (3b)** <sup>[S18]</sup>

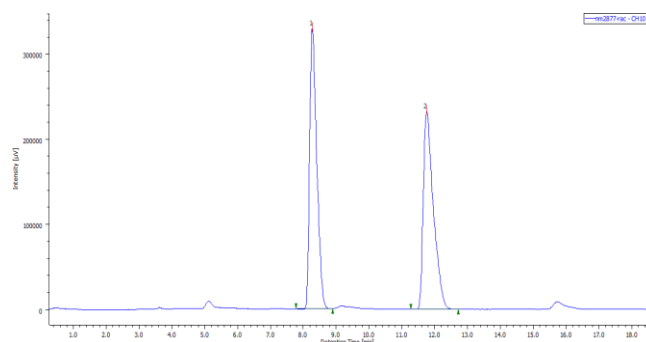


Yellow liquid (24.8 mg, 97% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.39 (s, 4H, alkyl), 3.79 (brs, 1H, alkyl), 4.41 (brs, 1H, alkyl), 6.35 (dd,  $J$  = 6.2, 6.2 Hz, 1H, vinyl), 6.46 (dd,  $J$  = 6.3, 6.3 Hz, 1H, vinyl), 6.95 (d,  $J$  = 5.7 Hz, 1H, vinyl), 7.39 (t,  $J$  = 6.9 Hz, 2H, arom.), 7.49 (t,  $J$  = 6.6 Hz, 1H, arom.), 7.62 (d,  $J$  = 7.2 Hz, 2H, arom.); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 24.6, 24.8, 36.6, 38.2, 128.0, 129.2, 131.6, 133.2, 135.1, 138.2, 146.5, 149.5, 193.2; HRMS (ESI-TOF)  $m/z$  calculated for C<sub>15</sub>H<sub>14</sub>NaO [M+Na]<sup>+</sup> 233.0942, found 233.0948; FT-IR (neat, cm<sup>-1</sup>) 695, 717, 1275, 1354, 1641, 1726, 2871, 2939, 2958, 3056.

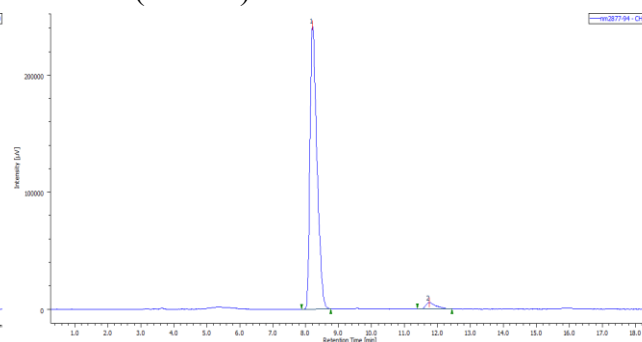
Optical Rotation:  $[\alpha]_D^{25}$  +38.5 ( $c$  2.48, CHCl<sub>3</sub>) for an enantiomerically enriched sample of 94% ee.

HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 98/2, flow rate 1.0 mL/min, 20 °C, detection UV 245 nm light);  $t_R$  of major-isomer 8.20 min,  $t_R$  of minor-isomer 11.7 min.

Racemic:

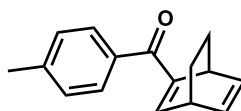


Chiral (94% ee):



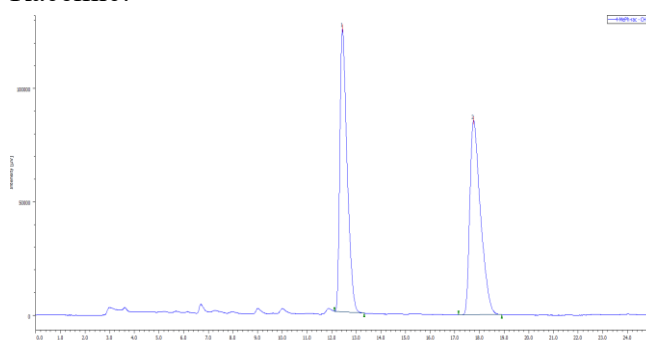
$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
8.267	4920543	49.904	8.200	3576178	96.859
11.747	4939487	50.096	11.733	115960	3.141

**(1S,4R)-2-(4-Methylbenzoyl)bicyclo[2.2.2]octa-2,5-diene (3c)**

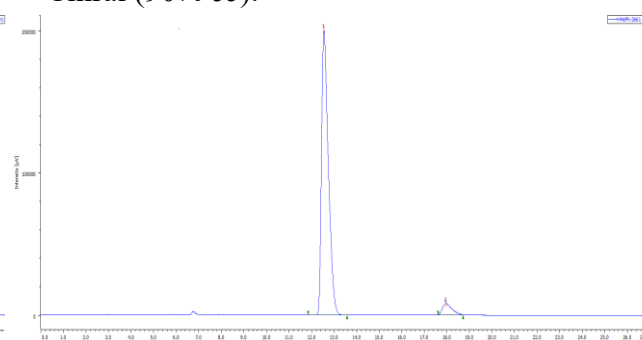


Yellow liquid (22.0 mg, 99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.32 (s, 9H, alkyl), 1.38 (s, 4H, alkyl), 3.78 (brs, 1H, alkyl), 4.40 (brs, 1H, alkyl), 6.35 (dd,  $J$  = 6.2, 6.2 Hz, 1H, vinyl), 6.46 (dd,  $J$  = 6.7, 6.7 Hz, 1H, vinyl), 6.96 (d,  $J$  = 5.5 Hz, 1H, vinyl), 7.40 (d,  $J$  = 8.0 Hz, 2H, arom.), 7.58 (d,  $J$  = 8.1 Hz, 2H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 21.9, 24.9, 25.1, 37.1, 38.5, 129.1, 129.7, 133.5, 135.5, 135.8, 142.6, 146.8, 149.1, 193.4; HRMS (APCI-TOF)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{17}\text{O}$   $[\text{M}+\text{H}]^+$  225.1279, found 225.1278; FT-IR (neat,  $\text{cm}^{-1}$ ) 1276, 1357, 1449, 1605, 1641, 2854, 2870, 2926, 3053. Optical Rotation:  $[\alpha]_D^{25}$  +41.4 ( $c$  2.20,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 90% ee. HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 99/1, flow rate 1.0 mL/min, 20 °C, detection UV 250 nm light);  $t_R$  of major-isomer 12.5 min,  $t_R$  of minor-isomer 18.0 min.

Racemic:

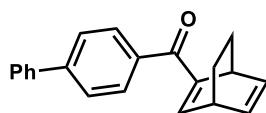


Chiral (90% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
12.433	2554578	49.754	12.542	4226356	94.796
17.750	2579794	50.246	17.950	232006	5.204

**(1*S*,4*R*)-2-(4-Phenylbenzoyl)bicyclo[2.2.2]octa-2,5-diene (3d)**

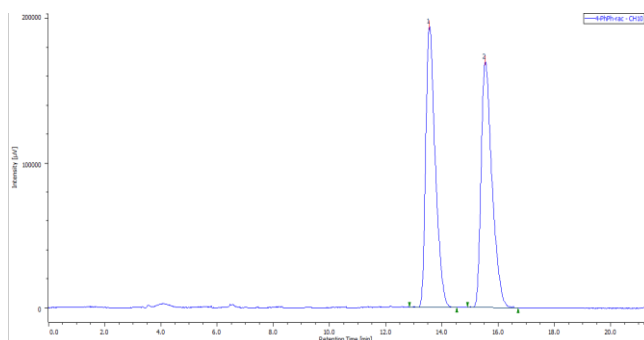


Yellow solid (31.2 mg, 99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.42 (s, 4H, alkyl), 3.82 (brs, 1H, alkyl), 4.44 (brs, 1H, alkyl), 6.38 (dd,  $J$  = 6.0, 6.0 Hz, 1H, vinyl), 6.48 (dd,  $J$  = 5.8, 5.8 Hz, 1H, vinyl), 7.00 (d,  $J$  = 1.1 Hz, 1H, vinyl), 7.38-7.48 (m, 3H, arom.), 7.62 (d,  $J$  = 7.8 Hz, 4H, arom.), 7.73 (d,  $J$  = 7.5 Hz, 2H, arom.);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.6, 24.8, 36.7, 38.2, 126.8, 127.2, 128.0, 128.9, 129.9, 133.2, 135.1, 136.8, 140.2, 144.5, 146.6, 149.3, 192.9; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{21}\text{H}_{18}\text{NaO} [\text{M}+\text{Na}]^+$  309.1255, found 309.1264; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1273, 1634, 1732, 2871, 2954, 3060.

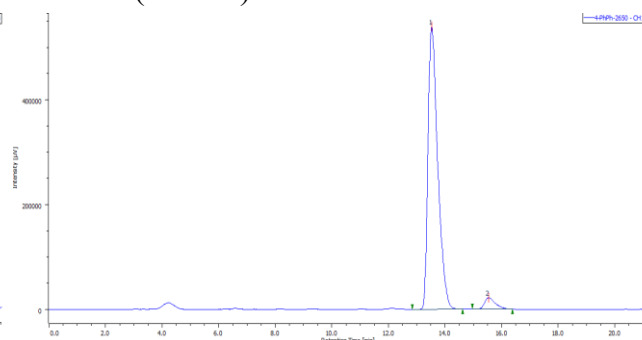
Optical Rotation:  $[\alpha]_{\text{D}}^{25}$  +38.5 ( $c$  3.12,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 91% *ee*.

HPLC analysis (column, CHIRALPAK OD-3, hexane/2-propanol = 98/2, flow rate 1.0 mL/min, 20  $^\circ\text{C}$ , detection UV 280 nm light);  $t_{\text{R}}$  of major-isomer 13.5 min,  $t_{\text{R}}$  of minor-isomer 15.5 min.

Racemic:

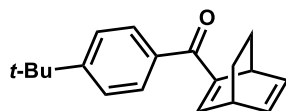


Chiral (91% *ee*):



$t_{\text{R}}$ (min)	Area	Area Percent	$t_{\text{R}}$ (min)	Area	Area Percent
13.547	4556947	49.972	13.520	12841696	95.694
15.533	4562140	50.028	15.533	577838	4.306

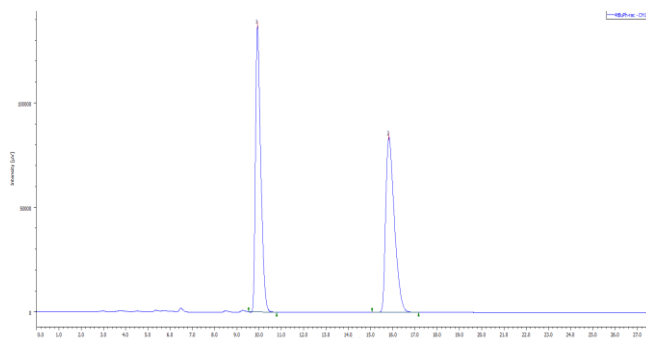
**(1*S*,4*R*)-2-(4-*tert*-Butylbenzoyl)bicyclo[2.2.2]octa-2,5-diene (3e)**



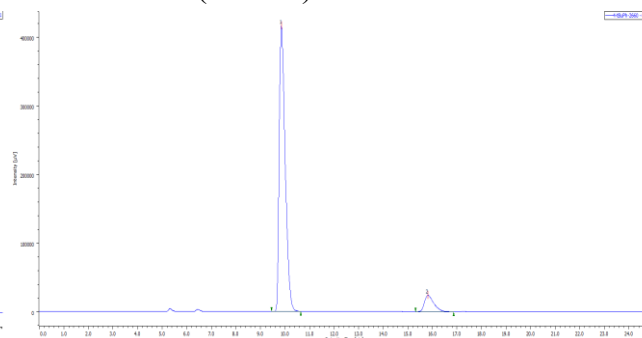
Yellow liquid (27.0 mg, 99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.32 (s, 9H, alkyl), 1.38 (s, 4H, alkyl), 3.78 (brs, 1H, alkyl), 4.40 (brs, 1H, alkyl), 6.35 (dd,  $J$  = 6.2, 6.2 Hz, 1H, vinyl), 6.46 (dd,  $J$  = 6.7, 6.7 Hz, 1H, vinyl), 6.96 (d,  $J$  = 5.5 Hz, 1H, vinyl), 7.40 (d,  $J$  = 8.0 Hz, 2H, arom.), 7.58 (d,  $J$  = 8.1 Hz, 2H, arom.);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.9, 25.1, 31.5, 35.3, 37.0, 38.5, 125.3, 129.5, 133.5, 135.5, 135.7, 146.8, 149.2, 155.6, 193.4; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{19}\text{H}_{22}\text{NaO} [\text{M}+\text{Na}]^+$  289.1568, found 289.1575; FT-IR (neat,  $\text{cm}^{-1}$ ) 1276, 1354, 1638, 1733, 2871, 2907, 2963, 3053.

Optical Rotation:  $[\alpha]_D^{24} +41.9$  (*c* 2.70, CHCl<sub>3</sub>) for an enantiomerically enriched sample of 84% *ee*.  
HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 99/1, flow rate 1.0 mL/min, 20 °C, detection UV 250 nm light); *t<sub>R</sub>* of major-isomer 9.85 min, *t<sub>R</sub>* of minor-isomer 15.8 min.

Racemic:

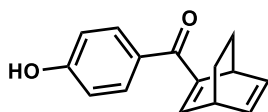


Chiral (84% *ee*):



<i>t<sub>R</sub></i> (min)	Area	Area Percent	<i>t<sub>R</sub></i> (min)	Area	Area Percent
9.917	2257105	49.945	9.850	6996762	91.804
15.825	2262097	50.055	15.808	624688	8.196

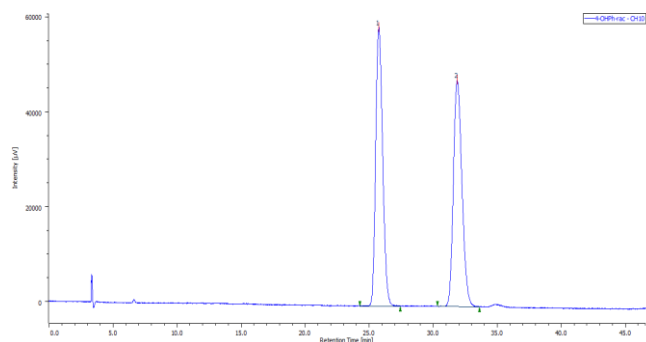
### (1*S*,4*R*)-2-(4-Hydroxybenzoyl)bicyclo[2.2.2]octa-2,5-diene (3f)



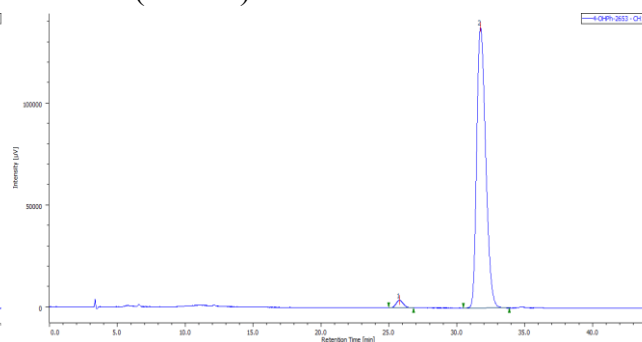
Yellow solid (22.4 mg, 99% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.34-1.43 (m, 4H, alkyl), 3.80 (brs, 1H, alkyl), 4.39 (d, *J* = 5.6 Hz, 1H, alkyl), 6.35 (dd, *J* = 6.1, 6.1 Hz, 1H, vinyl), 6.45 (dd, *J* = 6.2, 6.2 Hz, 1H, vinyl), 6.94 (d, *J* = 6.2 Hz, 1H, vinyl), 7.35 (d, *J* = 8.3 Hz, 2H, arom.), 7.76 (d, *J* = 8.3 Hz, 2H, arom.); <sup>13</sup>C {<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 25.0, 25.1, 37.5, 38.6, 115.5, 130.3, 132.3, 133.5, 135.4, 146.7, 149.4, 160.7, 193.9; HRMS (ESI-TOF) *m/z* calculated for C<sub>15</sub>H<sub>14</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 249.0892, found 249.0897; FT-IR (KBr pellet, cm<sup>-1</sup>) 1295, 1576, 1728, 2606, 2957, 3160.

Optical Rotation:  $[\alpha]_D^{23} +25.7$  (*c* 2.24, CHCl<sub>3</sub>) for an enantiomerically enriched sample of 96% *ee*.  
HPLC analysis (column, CHIRALPAK OJ-3, hexane/2-propanol = 95/5, flow rate 1.0 mL/min, 20 °C, detection UV 245 nm light); *t<sub>R</sub>* of major-isomer 31.7 min, *t<sub>R</sub>* of minor-isomer 25.8 min.

Racemic:

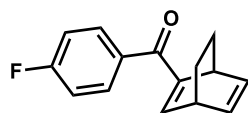


Chiral (96% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
25.733	2218736	50.027	25.773	129245	1.992
31.853	2216353	49.973	31.720	6357384	98.008

### (1*S*,4*R*)-2-(4-Fluorobenzoyl)bicyclo[2.2.2]octa-2,5-diene (3h)

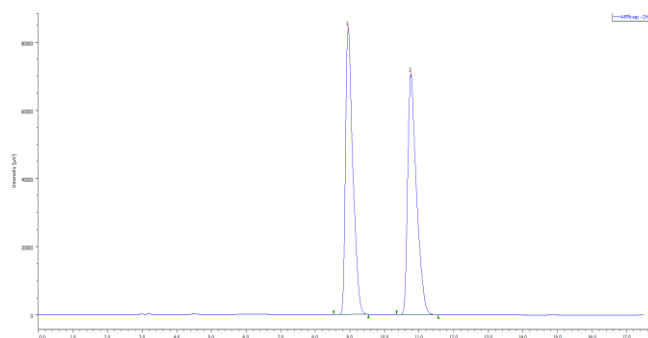


Colorless liquid (23.1 mg, 99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.33-1.42 (m, 4H, alkyl), 3.79 (t,  $J$  = 5.8 Hz, 1H, alkyl), 4.37 (d,  $J$  = 6.0 Hz, 1H, alkyl), 6.32-6.37 (m, 1H, vinyl), 6.42-6.46 (m, 1H, vinyl), 6.91 (dd,  $J$  = 1.8, 6.3 Hz, 1H, vinyl), 7.06 (t,  $J$  = 8.7 Hz, 2H, arom.), 7.66 (dd,  $J$  = 5.5, 8.7 Hz, 2H, arom.);  $^{19}\text{F}$   $\{^1\text{H}\}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  = -107.5 (s);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.9, 25.1, 37.1, 38.5, 115.4 (d,  $J$  = 21.8 Hz), 132.0 (d,  $J$  = 9.0 Hz), 133.5, 134.6 (d,  $J$  = 3.8 Hz), 135.4, 146.7, 149.5, 165.3 (d,  $J$  = 250.5 Hz), 192.1; HRMS (APCI-TOF)  $m/z$  calculated for  $\text{C}_{15}\text{H}_{14}\text{FO}$   $[\text{M}+\text{H}]^+$  229.1029, found 229.1027; FT-IR (neat,  $\text{cm}^{-1}$ ) 1276, 1351, 1504, 1594, 1645, 1728, 2872, 2912, 2942, 2961, 3055.

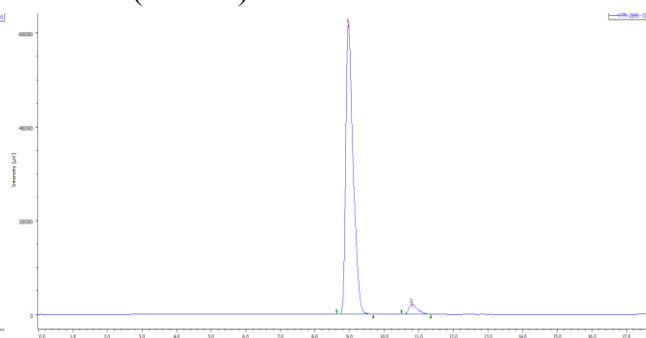
Optical Rotation:  $[\alpha]_{\text{D}}^{26}$  +45.0 ( $c$  2.31,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 92% *ee*.

HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 99/1, flow rate 1.0 mL/min, 20 °C, detection UV 250 nm light);  $t_R$  of major-isomer 9.0 min,  $t_R$  of minor-isomer 10.8 min.

Racemic:

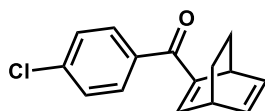


Chiral (92% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
8.942	1234966	49.955	8.958	9180771	96.073
10.758	1237182	50.045	10.792	375310	3.927

**(1*S*,4*R*)-2-(4-Chlorobenzoyl)bicyclo[2.2.2]octa-2,5-diene (3i)**

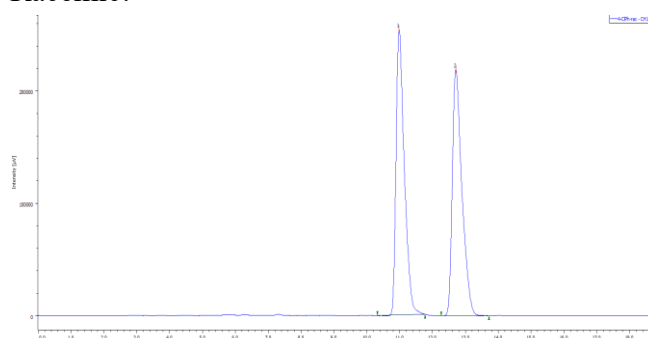


Yellow liquid (24.4 mg, 99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.34-1.43 (m, 4H, alkyl), 3.79 (d,  $J$  = 5.7 Hz, 1H, alkyl), 4.39 (d,  $J$  = 6.0 Hz, 1H, alkyl), 6.33-6.38 (m, 1H, vinyl), 6.43-6.48 (m, 1H, vinyl), 6.93 (dd,  $J$  = 1.8, 6.3 Hz, 1H, vinyl), 7.37 (d,  $J$  = 8.6 Hz, 2H, arom.), 7.58 (d,  $J$  = 8.5 Hz, 1H, arom.);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.6, 24.7, 36.6, 38.2, 126.5, 130.8, 131.4, 133.1, 135.1, 136.9, 146.4, 149.7, 192.0; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{15}\text{H}_{13}\text{ClNaO}$   $[\text{M}+\text{Na}]^+$  267.0553, found 267.0543; FT-IR (neat,  $\text{cm}^{-1}$ ) 1586, 1646, 1728, 2875, 2947, 3055.

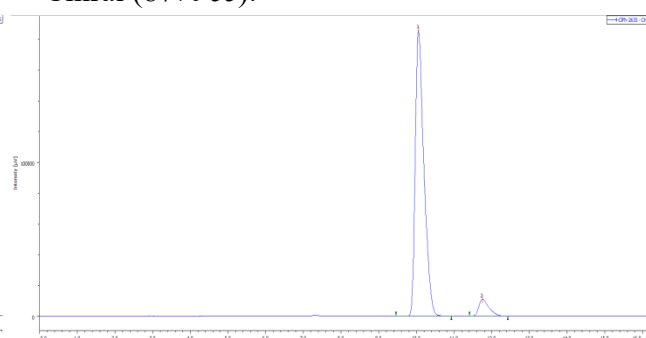
Optical Rotation:  $[\alpha]_D^{27} +40.7$  ( $c$  2.44,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 87% ee.

HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 99/1, flow rate 1.0 mL/min, 20 °C, detection UV 250 nm light);  $t_R$  of major-isomer 10.1 min,  $t_R$  of minor-isomer 11.8 min.

Racemic:

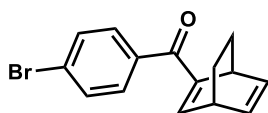


Chiral (87% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
10.975	4436179	50.091	10.050	2951043	93.647
12.700	4420102	49.909	11.750	200188	6.353

**(1*S*,4*R*)-2-(4-Bromobenzoyl)bicyclo[2.2.2]octa-2,5-diene (3j)**

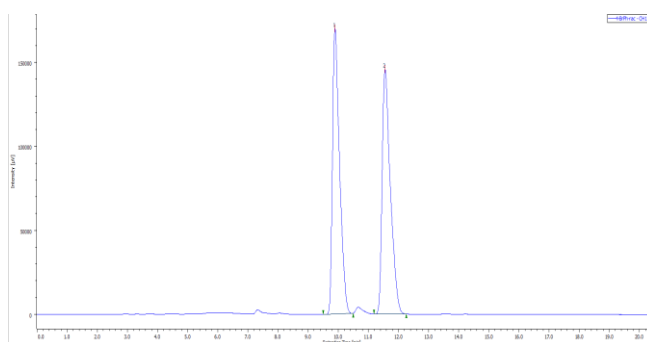


Yellow solid (28.8 mg, 99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.33-1.42 (m, 4H, alkyl), 3.80 (brs, 1H, alkyl), 4.38 (d,  $J$  = 5.3 Hz, 1H, alkyl), 6.35 (dd,  $J$  = 6.9, 6.9 Hz, 1H, vinyl), 6.44 (dd,  $J$  = 6.4, 6.4 Hz, 1H, vinyl), 6.93 (d,  $J$  = 5.9 Hz, 1H, vinyl), 7.36 (d,  $J$  = 8.4 Hz, 2H, arom.), 7.58 (d,  $J$  = 8.2 Hz, 2H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.6, 24.7, 36.6, 38.0, 128.4, 130.6, 133.2, 135.1, 136.4, 138.0, 146.4, 149.6, 191.9; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{15}\text{H}_{13}\text{BrNaO}$   $[\text{M}+\text{Na}]^+$  311.0048, found 311.0050; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1277, 1638, 1728, 2868, 2939, 3051.

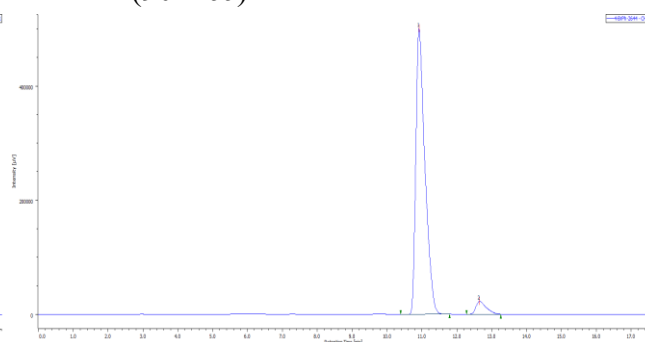
Optical Rotation:  $[\alpha]_{\text{D}}^{25}$  +39.1 ( $c$  1.15,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 90% *ee*.

HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 99/1, flow rate 1.0 mL/min, 20 °C, detection UV nm light);  $t_{\text{R}}$  of major-isomer 10.9 min,  $t_{\text{R}}$  of minor-isomer 12.7 min.

Racemic:

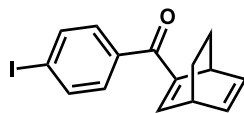


Chiral (90% *ee*):



$t_{\text{R}}$ (min)	Area	Area Percent	$t_{\text{R}}$ (min)	Area	Area Percent
9.892	2748268	49.978	10.917	9078002	95.132
11.550	2750706	50.022	12.650	464521	4.868

**(1*S*,4*R*)-2-(4-Iodobenzoyl)bicyclo[2.2.2]octa-2,5-diene (3k)**



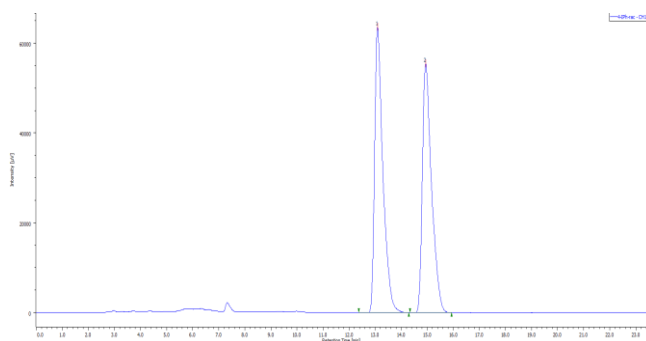
Yellow solid (33.4 mg, 98% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.34-1.43 (m, 4H, alkyl), 3.80 (brs, 1H, alkyl), 4.39 (d,  $J$  = 5.6 Hz, 1H, alkyl), 6.35 (dd,  $J$  = 6.1, 6.1 Hz, 1H, vinyl), 6.45 (dd,  $J$  = 6.2, 6.2 Hz, 1H, vinyl), 6.94 (d,  $J$  = 6.2 Hz, 1H, vinyl), 7.35 (d,  $J$  = 8.3 Hz, 2H, arom.), 7.76 (d,  $J$  = 8.3 Hz, 2H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.5, 24.7, 36.5, 38.2, 99.0, 130.7, 133.1, 135.0, 137.3, 137.4, 146.3, 149.8, 192.3; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{15}\text{H}_{13}\text{INaO}$   $[\text{M}+\text{Na}]^+$  358.9909, found 358.9911; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1273, 1631, 1728, 2875, 2932, 3089.

Optical Rotation:  $[\alpha]_{\text{D}}^{25}$  +34.4 ( $c$  1.08,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 87% *ee*.

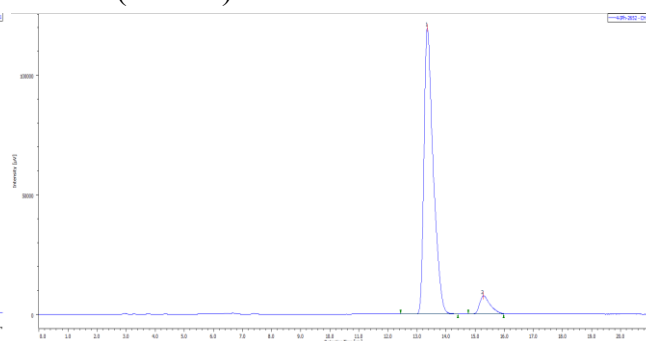
HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 99/1, flow rate 1.0 mL/min, 20 °C,

detection UV 280 nm light);  $t_R$  of major-isomer 13.4 min,  $t_R$  of minor-isomer 15.3 min.

Racemic:

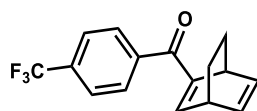


Chiral (87% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
13.083	1394170	50.751	13.350	2622703	93.386
14.933	1352936	49.249	15.275	185764	6.614

**(1*S*,4*R*)-2-(4-Trifluoromethylbenzoyl)bicyclo[2.2.2]octa-2,5-diene (3I)**

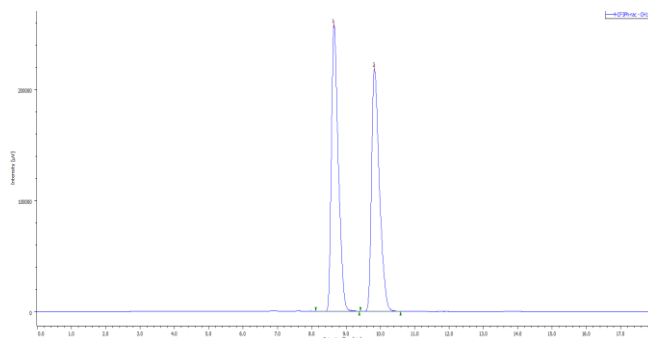


Yellow solid (27.6 mg, 99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.35-1.45 (m, 4H, alkyl), 3.81 (brs, 1H, alkyl), 4.43 (d,  $J$  = 5.0 Hz, 1H, alkyl), 6.35 (dd,  $J$  = 6.4, 6.4 Hz, 1H, vinyl), 6.46 (dd,  $J$  = 6.6, 6.6 Hz, 1H, vinyl), 7.64-7.73 (m, 4H, arom.);  $^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  = -62.9 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.5, 24.7, 36.3, 38.3, 123.7 (q,  $J_{\text{CF}}$  = 270.8 Hz), 125.1 (q,  $J_{\text{CF}}$  = 3.8 Hz), 129.3, 133.1 (q,  $J_{\text{CF}}$  = 32.4 Hz), 133.1, 141.3, 146.4, 150.9, 191.8; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NaO}$   $[\text{M}+\text{Na}]^+$  301.0816, found 301.0819; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1646, 1728, 2635, 2935, 3062.

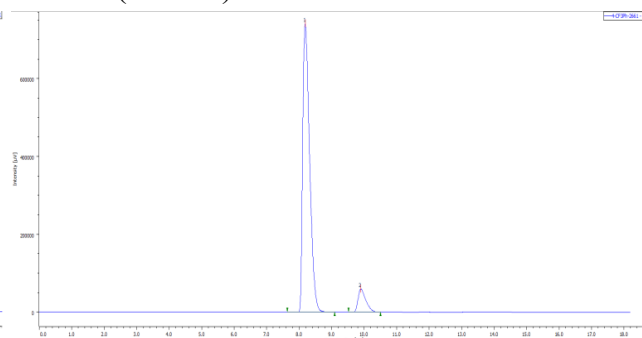
Optical Rotation:  $[\alpha]_{\text{D}}^{25}$  +44.6 ( $c$  2.76,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 84% ee.

HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 99/1, flow rate 1.0 mL/min, 20 °C, detection UV 240 nm light);  $t_R$  of major-isomer 8.18 min,  $t_R$  of minor-isomer 9.89 min.

Racemic:

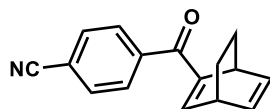


Chiral (84% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
8.642	3603256	50.872	8.183	10866618	91.757
9.825	3479782	49.128	9.892	976237	8.243

**(1*S*,4*R*)-2-(4-Cyanobenzoyl)bicyclo[2.2.2]octa-2,5-diene (3*m*)**

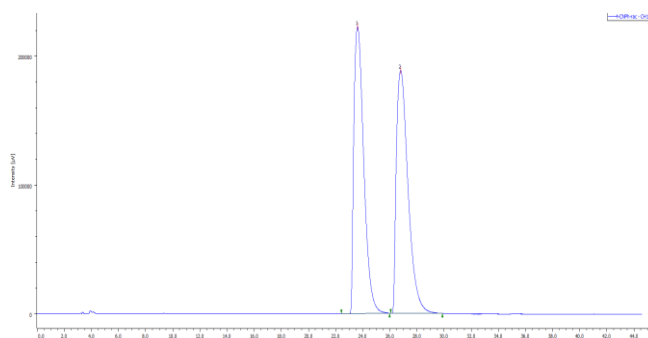


Colorless solid (21.5 mg, 90% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.33-1.43 (m, 4H, alkyl), 3.81 (t,  $J$  = 5.3 Hz, 1H, alkyl), 4.41 (d,  $J$  = 5.8 Hz, 1H, alkyl), 6.32-6.37 (m, 1H, vinyl), 6.42-6.47 (m, 1H, vinyl), 6.95 (dd,  $J$  = 1.8, 6.4 Hz, 1H, vinyl), 7.69 (s, 4H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.8, 25.0, 36.5, 38.6, 115.2, 118.4, 129.8, 132.3, 133.4, 135.3, 142.1, 146.6, 151.5, 191.5; HRMS (APCI-TOF)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{14}\text{NO}$   $[\text{M}+\text{H}]^+$  236.1075, found 236.1081; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1630, 1733, 1820, 2225, 2865, 2962, 3065, 3263.

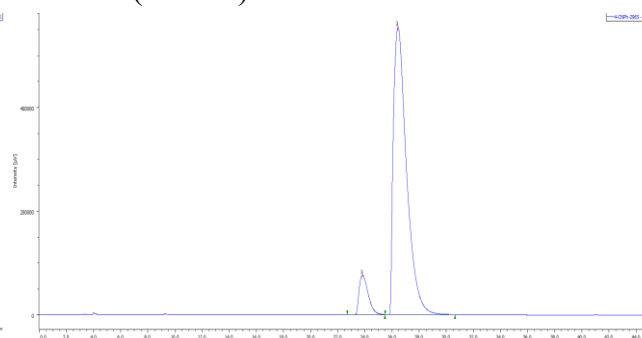
Optical Rotation:  $[\alpha]_D^{25} +41.5$  ( $c$  2.15,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 83% ee.

HPLC analysis (column, CHIRALPAK OJ-3, hexane/2-propanol = 98/2, flow rate 1.0 mL/min, 20 °C, detection UV 250 nm light);  $t_R$  of major-isomer 26.4 min,  $t_R$  of minor-isomer 23.8 min.

Racemic:

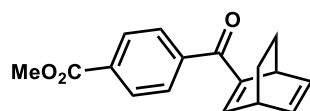


Chiral (83% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
23.608	11248750	49.972	23.808	3520631	8.627
26.783	11261452	50.028	26.433	37289097	91.373

**(1*S*,4*R*)-Methyl 4-(bicyclo[2.2.2]octa-2,5-diene-2-carbonyl)benzoate (3n)**

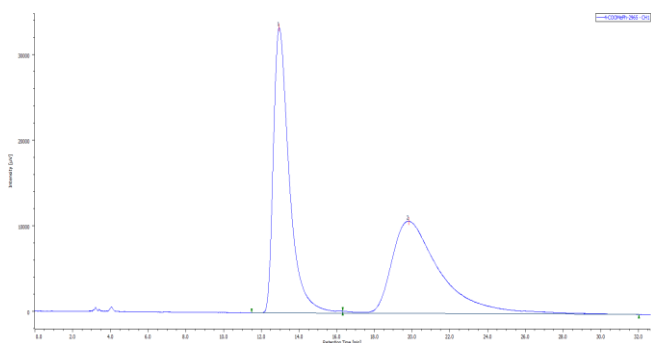


Colorless solid (27.0 mg, 99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.32-1.37 (m, 4H, alkyl), 3.78 (t,  $J$  = 5.2 Hz, 1H, alkyl), 3.90 (s, 3H, OMe), 4.40 (d,  $J$  = 6.0 Hz, 1H, alkyl), 6.30-6.35 (m, 1H, vinyl), 6.40-6.45 (m, 1H, vinyl), 6.93 (dd,  $J$  = 1.8, 6.4 Hz, 1H, vinyl), 7.63 (d,  $J$  = 8.3 Hz, 2H, arom.), 8.03 (d,  $J$  = 8.3 Hz, 2H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.8, 24.9, 36.5, 38.5, 52.6, 129.2, 129.6, 132.8, 133.4, 135.3, 142.2, 146.7, 150.9, 166.6, 192.5; HRMS (APCI-TOF)  $m/z$  calculated for  $\text{C}_{17}\text{H}_{17}\text{O}_3$   $[\text{M}+\text{H}]^+$  269.1178, found 269.1179; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1298, 1448, 1733, 2869, 2955, 3019, 3055, 3264.

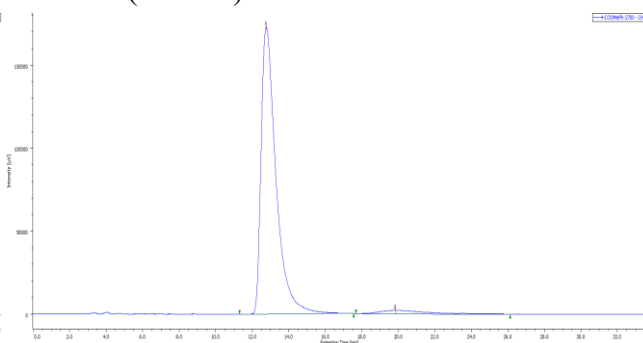
Optical Rotation:  $[\alpha]_{\text{D}}^{25}$  +52.0 ( $c$  2.70,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 94% *ee*.

HPLC analysis (column, CHIRALPAK AS-H, hexane/2-propanol = 98/2, flow rate 1.0 mL/min, 20 °C, detection UV 250 nm light);  $t_{\text{R}}$  of major-isomer 12.8 min,  $t_{\text{R}}$  of minor-isomer 19.8 min.

Racemic:

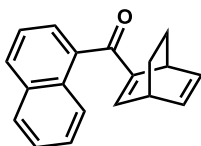


Chiral (94% *ee*):



$t_{\text{R}}$ (min)	Area	Area Percent	$t_{\text{R}}$ (min)	Area	Area Percent
12.950	1942858	50.250	12.758	9775576	96.809
19.792	1923492	49.750	19.842	322224	3.191

**(1*S*,4*R*)-2-(1-Naphthoyl)bicyclo[2.2.2]octa-2,5-diene (3o)**



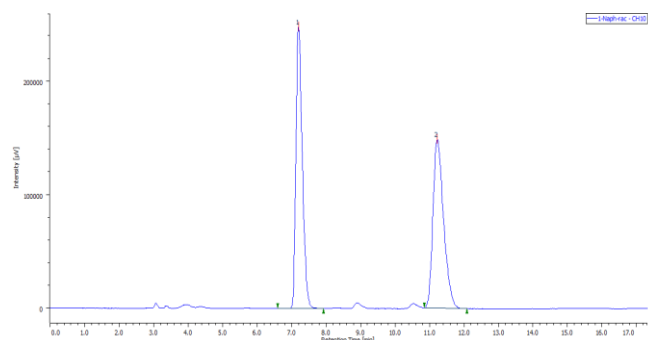
Yellow liquid (25.5 mg, 99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.42-1.44 (m, 4H, alkyl), 3.69-3.73 (m, 1H, alkyl), 4.59-4.61 (m, 1H, alkyl), 6.31-6.36 (m, 1H, vinyl), 6.48-6.53 (m, 1H, vinyl), 6.86 (dd,  $J$  = 1.8, 6.4 Hz, 1H, vinyl), 7.41-7.50 (m, 4H, arom.), 7.85-7.99 (m, 3H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.9, 24.9, 35.7, 38.6, 124.5, 125.8, 126.5, 127.0, 127.2, 128.6, 130.7, 131.1, 133.5, 134.0, 135.4, 137.0, 148.8, 152.1, 194.6; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{19}\text{H}_{16}\text{NaO}$   $[\text{M}+\text{Na}]^+$  283.1099, found 283.1112; FT-IR (neat,  $\text{cm}^{-1}$ ) 1126, 1280, 1643, 1730, 2855, 2871, 2938,

2956, 3054.

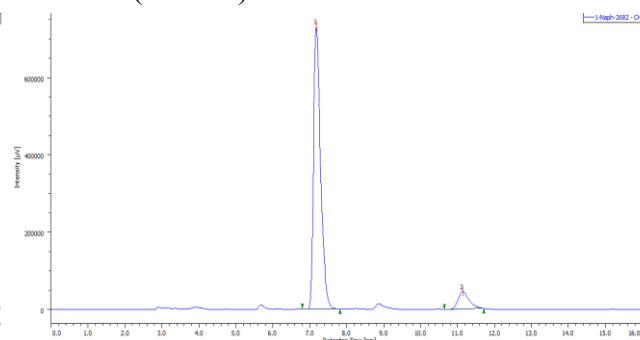
Optical Rotation:  $[\alpha]_D^{25} +17.3$  ( $c$  2.55,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 82%  $ee$ .

HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 97/3, flow rate 1.0 mL/min, 20 °C, detection UV 215 nm light);  $t_R$  of major-isomer 7.17 min,  $t_R$  of minor-isomer 11.1 min.

Racemic:

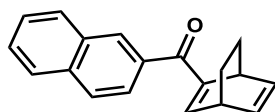


Chiral (82%  $ee$ ):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
7.200	4861383	49.554	7.173	9578445	91.278
11.213	4948974	50.446	11.133	915273	8.722

### (1*S*,4*R*)-2-(2-Naphthoyl)bicyclo[2.2.2]octa-2,5-diene (3p)

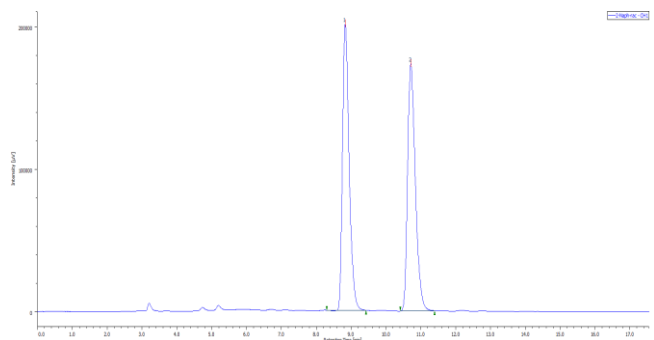


Yellow solid (25.5 mg, 99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.43 (s, 4H, alkyl), 3.83 (brs, 1H, alkyl), 4.47 (brs, 1H, alkyl), 6.40 (dd,  $J$  = 6.0, 6.0 Hz, 1H, vinyl), 6.50 (dd,  $J$  = 6.9, 6.9 Hz, 1H, vinyl), 7.01 (d,  $J$  = 5.4 Hz, 1H, vinyl), 7.54 (quin,  $J$  = 6.9 Hz, 2H, arom.), 7.76 (d,  $J$  = 8.0 Hz, 1H, arom.), 7.85-7.92 (m, 3H, arom.), 8.10 (s, 1H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.7, 24.8, 36.8, 38.3, 125.6, 126.6, 127.8, 127.8, 128.0, 129.2, 130.3, 132.3, 133.3, 135.0, 135.2, 135.4, 146.7, 149.4, 193.2; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{19}\text{H}_{16}\text{NaO}$   $[\text{M}+\text{Na}]^+$  283.1099, found 283.1095; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1459, 1631, 1725, 2868, 2939, 3059.

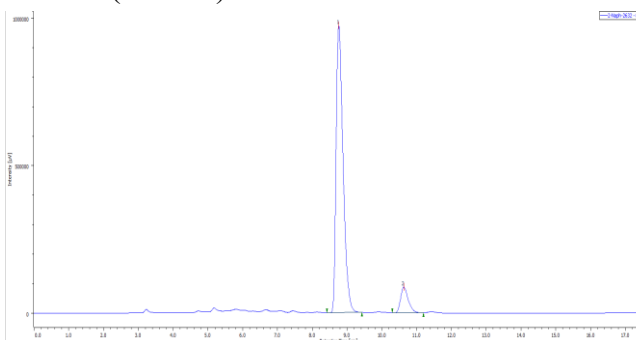
Optical Rotation:  $[\alpha]_D^{24} +29.4$  ( $c$  2.55,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 82%  $ee$ .

HPLC analysis (column, CHIRALPAK OD-3, hexane/2-propanol = 99/1, flow rate 1.0 mL/min, 20 °C, detection UV 245 nm light);  $t_R$  of major-isomer 8.76 min,  $t_R$  of minor-isomer 10.6 min.

Racemic:

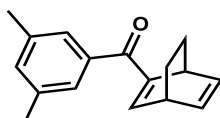


Chiral (82% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
8.825	2644083	49.801	8.758	972168	91.095
10.708	2665239	50.199	10.625	87381	8.905

**(1*S*,4*R*)-2-(3,5-Dimethylbenzoyl)bicyclo[2.2.2]octa-2,5-diene (3q)**

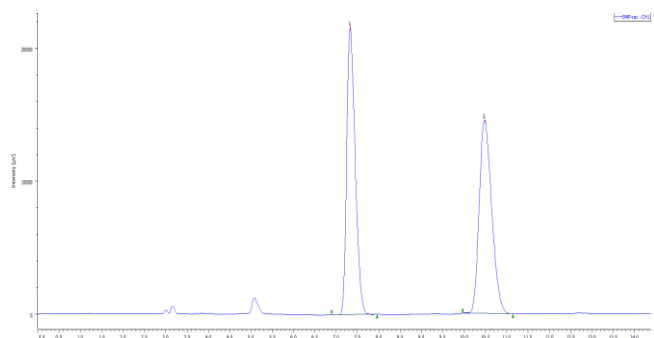


Yellow liquid (23.1 mg, 99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.34-1.42 (m, 4H, alkyl), 2.33 (s, 6H, Me), 3.79 (t,  $J$  = 5.6 Hz, 1H, alkyl), 4.40 (d,  $J$  = 6.0 Hz, 1H, alkyl), 6.33-6.38 (m, 1H, vinyl), 6.43-6.48 (m, 1H, vinyl), 6.94 (dd,  $J$  = 1.8, 6.4 Hz, 1H, vinyl), 7.12 (s, 1H, arom.), 7.22 (s, 2H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 21.5, 24.9, 25.1, 36.8, 28.5, 127.2, 133.50, 133.54, 135.4, 137.9, 138.6, 146.9, 149.6, 193.9; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{17}\text{H}_{18}\text{NaO}$   $[\text{M}+\text{Na}]^+$  261.1255, found 261.1264; FT-IR (neat,  $\text{cm}^{-1}$ ) 1308, 1350, 1452, 1589, 1648, 1733, 2869, 2950, 3055.

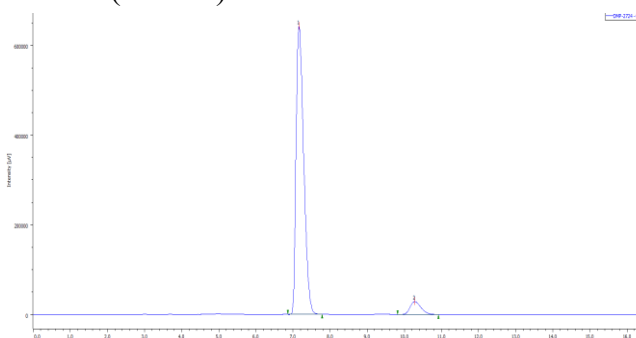
Optical Rotation:  $[\alpha]_D^{26} +52.7$  ( $c$  2.31,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 88% ee.

HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 99/1, flow rate 1.0 mL/min, 20 °C, detection UV 250 nm light);  $t_R$  of major-isomer 7.16 min,  $t_R$  of minor-isomer 10.3 min.

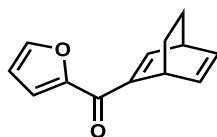
Racemic:



Chiral (88% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
7.325	296847	50.147	7.158	9157572	94.000
10.475	295102	49.853	10.275	584573	6.000

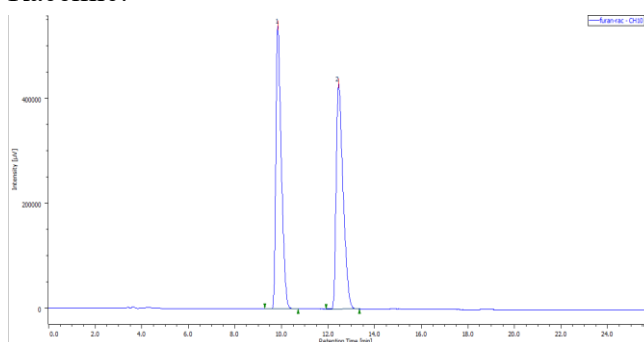
**(1*R*,4*S*)-2-(2-Furoyl)bicyclo[2.2.2]octa-2,5-diene (3r)**

Yellow liquid (17.3mg, 84% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.36-1.41 (m, 4H, alkyl), 3.83 (t,  $J$  = 5.8 Hz, 1H, alkyl), 4.39 (d,  $J$  = 5.9 Hz, 1H, alkyl), 6.30-6.35 (m, 1H, vinyl), 6.39-6.44 (m, 1H, vinyl), 6.48 (dd,  $J$  = 1.6, 3.4 Hz, 1H, vinyl), 7.08 (d,  $J$  = 3.6 Hz, 1H, arom.), 7.46 (dd,  $J$  = 1.8, 6.3 Hz, 1H, vinyl), 7.56 (bs, 1H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.95, 25.01, 36.7, 38.6, 112.1, 118.4, 133.4, 135.4, 146.1, 146.3, 148.0, 153.0, 179.3; HRMS (APCI-TOF)  $m/z$  calculated for  $\text{C}_{13}\text{H}_{13}\text{O}_2$   $[\text{M}+\text{H}]^+$  201.0916, found 201.0912; FT-IR (neat,  $\text{cm}^{-1}$ ) 1174, 1286, 1392, 1465, 1627, 1725, 2870, 2942, 3054, 3134.

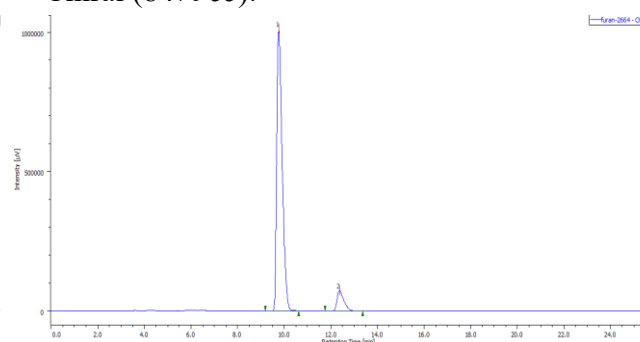
Optical Rotation:  $[\alpha]_{\text{D}}^{25}$  -14.6 ( $c$  1.73,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 84% *ee*.

HPLC analysis (column, CHIRALPAK OJ-3, hexane/2-propanol = 98/2, flow rate 1.0 mL/min, 20 °C, detection UV 215 nm light);  $t_{\text{R}}$  of major-isomer 9.8 min,  $t_{\text{R}}$  of minor-isomer 12.4 min.

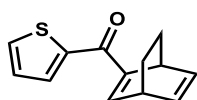
Racemic:



Chiral (84% *ee*):



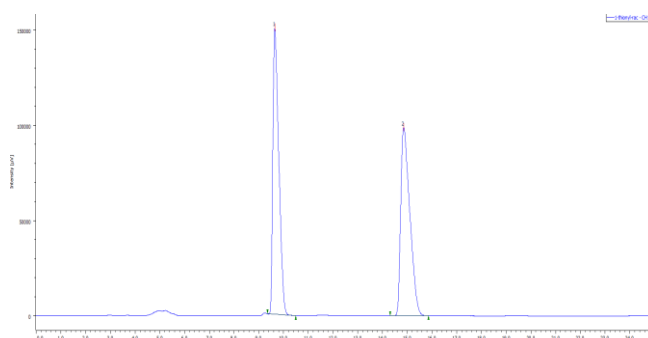
$t_{\text{R}}$ (min)	Area	Area Percent	$t_{\text{R}}$ (min)	Area	Area Percent
9.840	8794375	49.972	9.760	1010696	91.922
12.440	8804100	50.028	12.360	73088	8.078

**(1*S*,4*R*)-2-(2-Thiophenyl)bicyclo[2.2.2]octa-2,5-diene (3s)**

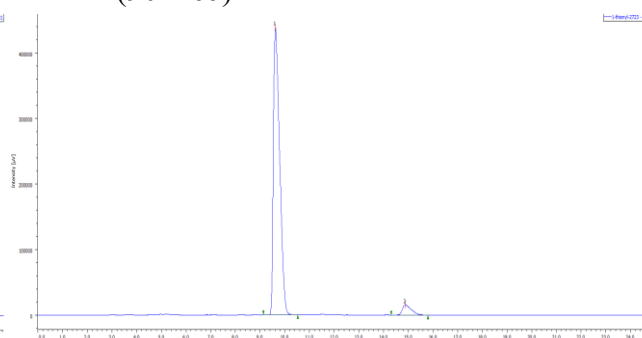
Yellow liquid (21.0 mg, 91% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.33-1.43 (m, 4H, alkyl), 3.82 (t,  $J$  = 5.0 Hz, 1H, alkyl), 4.33 (d,  $J$  = 5.1 Hz, 1H, alkyl), 6.32-6.37 (m, 1H, vinyl), 6.40-6.45 (m, 1H, vinyl), 7.06 (t,  $J$  = 4.0 Hz, 1H, arom.), 7.18 (dd,  $J$  = 1.8, 6.3 Hz, 1H, vinyl), 7.54-7.58 (m, 2H, arom.), 7.46 (dd,  $J$  = 1.8, 6.3 Hz, 1H, vinyl), 7.56 (bs, 1H, arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 25.0, 25.1, 37.5, 28.5, 127.9, 132.9, 133.0, 133.5, 135.3, 146.8, 147.2, 185.0; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{13}\text{H}_{12}\text{NaOS}$   $[\text{M}+\text{Na}]^+$  239.0507, found 239.0516; FT-IR (neat,  $\text{cm}^{-1}$ ) 1281, 1360, 1468, 1615, 1739, 1834, 2085, 2873, 2960, 3057, 3096, 3184.

Optical Rotation:  $[\alpha]_D^{25} +30.2$  (*c* 2.10, CHCl<sub>3</sub>) for an enantiomerically enriched sample of 90% *ee*.  
HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 99/1, flow rate 1.0 mL/min, 20 °C, detection UV 250 nm light); *t<sub>R</sub>* of major-isomer 9.6 min, *t<sub>R</sub>* of minor-isomer 14.9 min.

Racemic:

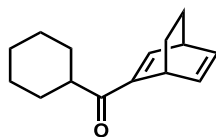


Chiral (90% *ee*):



<i>t<sub>R</sub></i> (min)	Area	Area Percent	<i>t<sub>R</sub></i> (min)	Area	Area Percent
9.642	2493217	49.747	9.617	7699823	95.268
14.850	2518582	50.253	14.875	382460	4.732

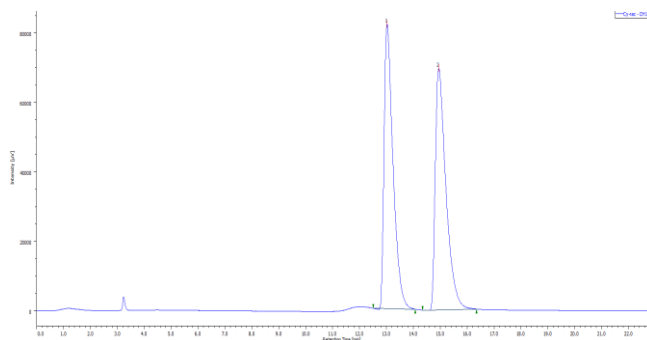
### (1*R*,4*S*)-2-(Cyclohexanecarbonyl)bicyclo[2.2.2]octa-2,5-diene (3t)



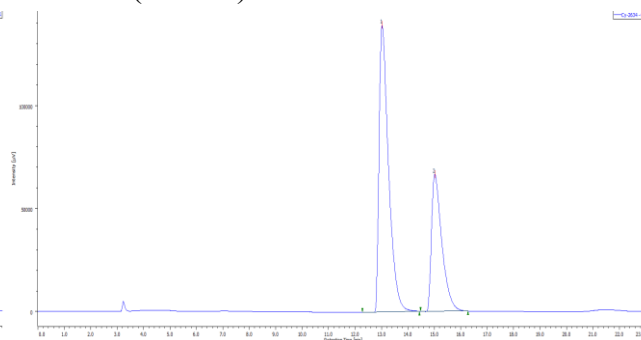
Yellow liquid (21.0 mg, 95% yield): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.22-1.49 (m, 9H, alkyl), 1.69-1.79 (m, 6H, alkyl), 2.87 (t, *J* = 11.1 Hz, 1H, alkyl), 3.78 (brs, 1H, alkyl), 4.34 (brs, 1H, alkyl), 6.30 (dd, *J* = 6.0, 6.0 Hz, 1H, vinyl), 6.37 (dd, *J* = 6.1, 6.1 Hz, 1H, vinyl), 7.26 (d, *J* = 6.3 Hz, 1H, vinyl); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 14.4, 22.9, 24.6, 24.9, 25.2, 29.4, 32.0, 35.0, 37.7, 38.2, 133.4, 135.4, 145.8, 147.8, 197.8; HRMS (ESI-TOF) *m/z* calculated for C<sub>15</sub>H<sub>20</sub>NaO [M+Na]<sup>+</sup> 239.1412, found 239.1403; FT-IR (neat, cm<sup>-1</sup>) 1194, 1255, 1377, 1448, 1585, 1660, 1730, 2853, 2929, 3055.

Optical Rotation:  $[\alpha]_D^{25} -21.3$  (*c* 2.10, CHCl<sub>3</sub>) for an enantiomerically enriched sample of 30% *ee*.  
HPLC analysis (column, CHIRALPAK OD-3, hexane/2-propanol = 100/0, flow rate 1.0 mL/min, 20 °C, detection UV nm light); *t<sub>R</sub>* of major-isomer 13.0 min, *t<sub>R</sub>* of minor-isomer 15.0 min.

Racemic:

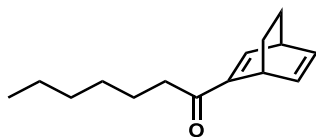


Chiral (30% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
13.017	1890410	49.811	13.017	3433261	65.520
14.933	1904731	50.189	15.017	1806740	34.480

**(1*R*,4*S*)-2-(Heptanoyl)bicyclo[2.2.2]octa-2,5-diene (3u)**

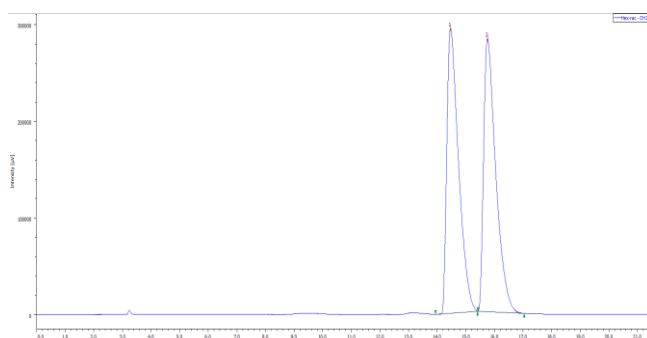


Yellow liquid (20.6 mg, 88% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.84-0.88 (m, 3H, alkyl), 1.19-1.39 (m, 10H, alkyl), 1.52-1.59 (m, 2H, alkyl), 3.73-3.78 (m, 1H, alkyl), 4.32-4.35 (m, 1H, alkyl), 6.26-6.31 (m, 1H, vinyl), 6.33-6.38 (m, 1H, vinyl), 7.22 (dd,  $J$  = 1.8, 6.4 Hz, 1H, vinyl);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 14.4, 22.8, 24.6, 24.9, 25.2, 29.4, 32.0, 35.0, 37.8, 38.2, 133.4, 135.4, 145.7, 147.8, 197.8; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{15}\text{H}_{22}\text{NaO}$   $[\text{M}+\text{Na}]^+$  241.1568, found 241.1578; FT-IR (neat,  $\text{cm}^{-1}$ ) 1276, 1462, 1666, 1731, 2857, 2871, 2929, 2956, 3057.

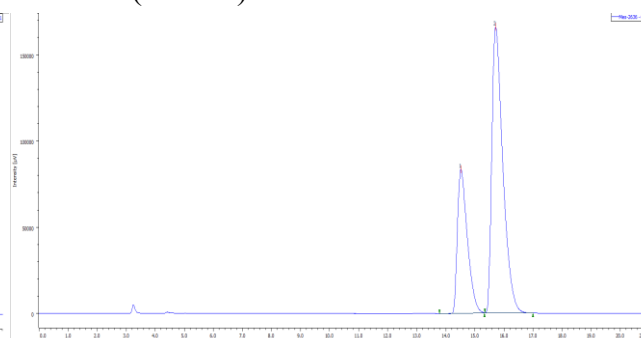
Optical Rotation:  $[\alpha]_D^{25}$  -25.1 ( $c$  2.06,  $\text{CHCl}_3$ ) for an enantiomerically enriched sample of 38% ee.

HPLC analysis (column, CHIRALPAK OD-3, hexane/2-propanol = 100/0, flow rate 1.0 mL/min, 20  $^\circ\text{C}$ , detection UV nm light);  $t_R$  of major-isomer 15.7 min,  $t_R$  of minor-isomer 14.5 min.

Racemic:

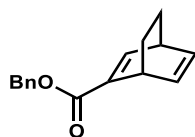


Chiral (38% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
14.458	8327960	49.925	14.508	1960129	30.956
15.750	8353055	50.075	15.708	4371902	69.044

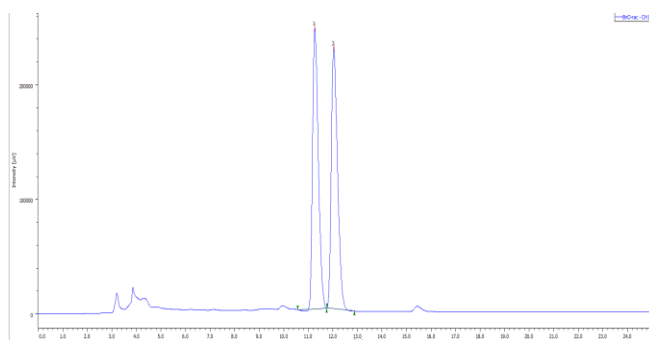
### Benzyl bicyclo[2.2.2]octa-2,5-diene-2-carboxylate (3v)



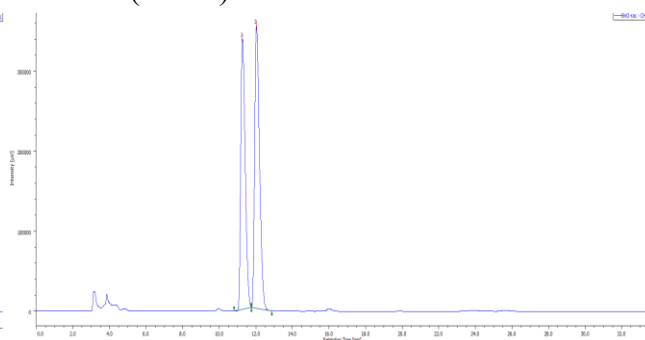
Yellow liquid (18.9 mg, 79% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.25-1.37 (m, 4H, alkyl), 3.73-3.77 (m, 1H, alkyl), 4.22 (d,  $J$  = 5.9 Hz, 1H, alkyl), 5.17 (s, 2H,  $\text{CH}_2$ ), 6.23-6.28 (m, 1H, vinyl), 6.35-6.40 (m, 1H, vinyl), 7.30-7.37 (m, 5H, arom.);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.6, 24.9, 36.8, 38.2, 66.3, 128.4, 128.8, 133.2, 135.1, 136.7, 138.9, 146.6, 165.0; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{16}\text{H}_{16}\text{NaO}_2$   $[\text{M}+\text{Na}]^+$  263.1048, found 263.1061; FT-IR (neat,  $\text{cm}^{-1}$ ) 1076, 1266, 1457, 1709, 2872, 2935, 2957, 3034, 3060.

HPLC analysis (column, CHIRALPAK OD-3, hexane/2-propanol = 99/1, flow rate 1.0 mL/min, 20 °C, detection UV 220 nm light);  $t_R$  of major-isomer 12.0 min,  $t_R$  of minor-isomer 11.3 min.

Racemic:

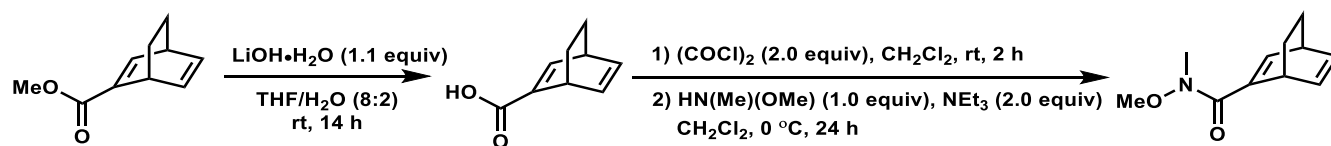


Chiral (7% ee):



$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
11.258	4009978	49.853	11.258	5682904	46.611
12.033	4033608	50.147	12.025	6509410	53.389

### Synthesis of (1*R*,4*S*)-*N*-methoxy-*N*-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamide (4z)



To a solution of (1*R*,4*S*) methyl bicyclo[2.2.2]octa-2,5-diene-2-carboxylate (32.8 mg, 0.2 mmol) in dry THF (0.8 mL) in Ar atmosphere was added lithium hydroxide monohydrate (10 mg, 0.22 mmol) in  $\text{H}_2\text{O}$  (0.2 mL) at 0 °C and the mixture was stirred for 13 h. After, the reaction was quenched with 1M HCl aq. The organic layer was separated and aqueous layer was extracted with EtOAc three times. The combined organic layers were washed with brine and dried over  $\text{MgSO}_4$ , and the solvent was removed under reduced pressure.

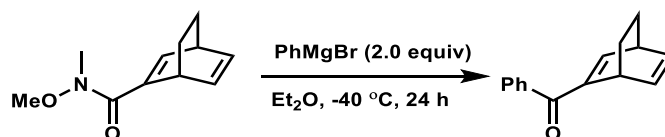
After concentration, the crude mixture was dissolved by  $\text{CH}_2\text{Cl}_2$  (1.0 mL) under Ar atmosphere at room temperature. Oxalyl chloride (34  $\mu\text{L}$ , 0.4 mmol) and one drop of *N,N*-dimethylformamide was added to the reaction, which initiated the evolution of gas. The reaction mixture was stirred for 2 h at room temperature. Then the solvent and unreacted

oxalyl chloride was removed in vacuo. A solution of carboxylic acid chloride in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was cooled at 0 °C and catalytic amount of DMAP and *O,N*-dimethylhydroxylamine hydrochloride (19.5 mg, 0.2 mmol) was added followed by triethylamine (27.9 μL, 0.4 mmol). The solution was stirred for 24 h at 0 °C and MeOH (1 mL) was added to dissolve the precipitate. After evaporation of the mixture, the crude product was purified by column chromatography on silica-gel (hexane: EtOAc = 10:1 to 4:1) to yield the corresponding compounds.

Yellow liquid (21.6 mg, 56% yield from **4z**): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 1.24 - 1.41 (m, 4H, alkyl), 3.22 (s, 3H, Me), 3.54 (s, 3H, OMe), 3.67 – 3.73 (m, 1H, alkyl), 4.06 – 4.08 (m, 1H, alkyl), 6.28 (dd, 1H, *J* = 6.5, 6.5 Hz, vinyl), 6.37 (dd, 1H, *J* = 6.6, 6.6 Hz, vinyl), 6.95 (d, 1H, *J* = 6.0 Hz, vinyl); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ = 24.4, 25.2, 33.3, 37.4, 38.4, 61.2, 133.8, 135.1, 140.9, 141.0, 168.4; HRMS (ESI-TOF) *m/z* calculated for C<sub>11</sub>H<sub>15</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 216.1001, found 216.0993; FT-IR (KBr pellet, cm<sup>-1</sup>) 1414, 1640, 1734, 2815, 2869, 2937, 2959, 3053.

Optical Rotation: [α]<sub>D</sub><sup>22</sup> -30.3 (*c* 2.16 CHCl<sub>3</sub>).

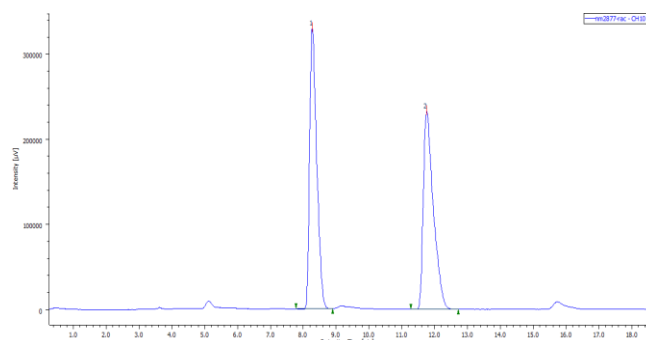
#### Synthesis of (1*R*,4*S*)-2-Benzoylbicyclo[2.2.2]octa-2,5-diene (**3b**)



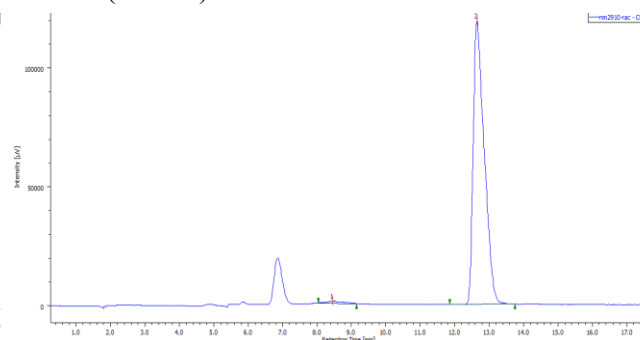
To a solution of (1*R*,4*S*)-*N*-methoxy-*N*-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamide (21.6 mg, 0.11 mmol) in dry diethyl ether (1.0 mL) in Ar atmosphere was added Phenylmagnesium bromide solution (0.22 mmol, 2.0 eq., 1.0 M solution in THF, 1 M = 1 mol dm<sup>-3</sup>) at -40 °C and the mixture was stirred for 24 h. After, the reaction was quenched with saturated NaNH<sub>4</sub> aq. and organic layer was extracted by diethyl ether (20 mL × 3). The combined organic phase was washed with brine (20 mL × 1), dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica-gel (hexane: EtOAc = 20:1) to yield the corresponding compounds. Yellow liquid (6.0 mg, 26% yield); Optical Rotation: [α]<sub>D</sub><sup>25</sup> -38.8 (*c* 0.45, CHCl<sub>3</sub>) for an enantiomerically enriched sample of 98% *ee*.

HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 98/2, flow rate 1.0 mL/min, 20 °C, detection UV 245 nm light); *t*<sub>R</sub> of major-isomer 8.20 min, *t*<sub>R</sub> of minor-isomer 8.45 min.

Racemic:



Chiral (98% ee):

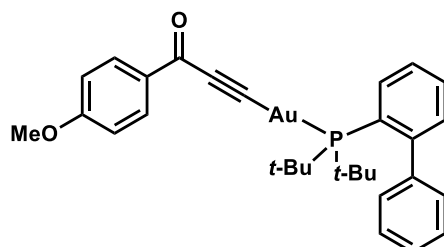


$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
8.267	4920543	49.904	8.453	28281	0.796
11.747	4939487	50.096	12.640	2650950	99.204

### General Procedure for the Gold Acetylide Complex

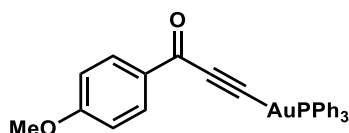
To a solution of cationic gold complex (0.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.1 mL) under Ar atmosphere was added triethylamine (0.033 mL, 0.24 mmol) at room temperature. Then, a solution of ynone (0.2 mmol) was added to the solution, and the reaction mixture was stirred for 2 h (monitored by TLC). The residue was purified by directly loaded silica-gel chromatography (hexane/AcOEt = 4/1 ~ 2/1).

### Acetylide 4b



Colorless solid (76% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.43 (s, 9H, t-Bu), 1.48 (s, 9H, t-Bu), 3.93 (s, 3H, OMe), 7.02 (d,  $J$  = 8.9 Hz, 2H, arom.), 7.24-7.33 (m, 3H, arom.), 7.46-7.57 (m, 5H, arom.), 7.73-7.97 (m, 1H, arom.), 8.21-8.24 (m, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 63.6 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 31.2, 31.3, 37.7, 38.0, 55.8, 100.3 (d,  $J_{\text{CP}}$  = 21.0 Hz), 113.4, 127.1 (d,  $J_{\text{CP}}$  = 19.5 Hz), 127.2 (d,  $J_{\text{CP}}$  = 27.4 Hz), 128.5, 129.3, 129.5, 130.7 (d,  $J_{\text{CP}}$  = 2.3 Hz), 132.0, 132.3, 133.3 (d,  $J_{\text{CP}}$  = 7.2 Hz), 134.5 (d,  $J_{\text{CP}}$  = 1.3 Hz), 127.1 (d,  $J_{\text{CP}}$  = 19.5 Hz), 142.6 (d,  $J_{\text{CP}}$  = 6.0 Hz), 145.8 (d,  $J_{\text{CP}}$  = 127.5 Hz), 150.3 (d,  $J_{\text{CP}}$  = 15.0 Hz), 163.7, 177.3 (d,  $J_{\text{CP}}$  = 2.3 Hz); HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{30}\text{H}_{34}\text{AuNaO}_2\text{P}$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> 677.1860, found 677.1832; FT-IR (KBr pellet,  $\text{cm}^{-1}$ ) 1252, 1456, 1604, 1735, 2103, 2858, 2958, 3052; Elemental analysis calcd. (%) for  $\text{C}_{30}\text{H}_{34}\text{AuO}_2\text{P}$ : C 55.03, H 5.20; found C 55.91, H 5.27.

## Acetylide 4c

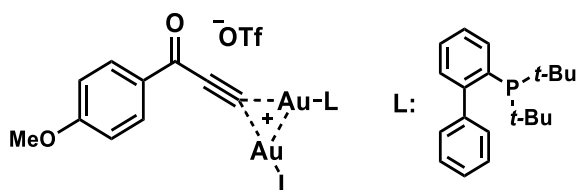


Colorless solid (84% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 3.87 (s, 3H, OMe), 6.93 (d,  $J$  = 8.9 Hz, 2H, arom.), 7.45-7.58 (m, 15H, arom.), 8.28 (d,  $J$  = 8.9 Hz, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ )  $\delta$  = 41.5 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 55.5, 101.0, 113.4, 128.9, 129.2, 129.4, 129.6, 131.3, 131.80, 131.83, 132.0, 132.2, 134.4, 163.7, 176.8; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{28}\text{H}_{22}\text{AuNaO}_2\text{P}$  [ $\text{M}+\text{Na}$ ] $^+$  641.0921, found 641.0920; Elemental analysis calcd. (%) for  $\text{C}_{28}\text{H}_{22}\text{AuO}_2\text{P}$ : C 54.36, H 3.56; found C 54.49, H 3.63.

## Experimental Procedure of *gem*-Gold Intermediate

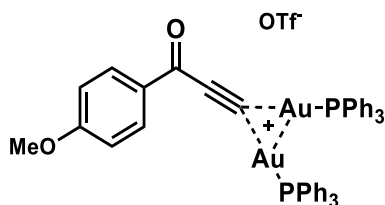
A solution of gold acetylide (0.01 mmol) in  $\text{CD}_2\text{Cl}_2$  (0.55 mL) was added to a solution of gold(I) catalyst (0.01 mmol) in  $\text{CD}_2\text{Cl}_2$  (0.2 mL) at 0 °C for 5 min. Then, cyclohexadiene (0.04 mmol) was added and monitored by NMR analysis.

### *gem*-Gold active species 5b



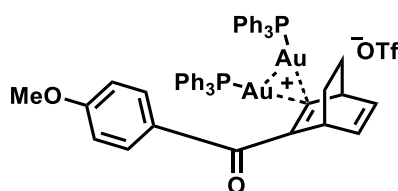
Colorless solid (99% yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 1.49 (s, 18H, *t*-Bu), 1.54 (s, 18H, *t*-Bu), 4.02 (s, 3H, OMe), 7.15-7.32 (m, 14H, arom.), 7.62-7.64 (m, 4H, arom.), 7.93-7.99 (m, 2H, arom.), 8.10 (d,  $J$  = 8.8 Hz, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 62.4 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 31.6, 31.7, 38.8, 39.1, 106.2 (t,  $J_{\text{CP}}$  = 12.8 Hz), 114.8, 125.3, 125.9, 128.4 (d,  $J$  = 7.1 Hz), 128.7, 129.7, 130.2, 132.0, 132.9, 133.9 (d,  $J$  = 7.7 Hz), 134.5 (d,  $J$  = 2.2 Hz), 139.3 (t,  $J_{\text{CP}}$  = 64.3 Hz), 143.4 (d,  $J$  = 6.7 Hz), 149.9 (d,  $J$  = 13.6 Hz), 166.0, 174.0; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{50}\text{H}_{61}\text{Au}_2\text{O}_2\text{P}_2$  [ $\text{M}-\text{OTf}$ ] $^+$  1149.3478, found 1149.3474.

### *gem*-Gold active species 5c



quant. (NMR yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 3.93 (s, 3H, OMe), 7.05 (d,  $J$  = 8.0 Hz, 2H, arom.), 7.45-7.60 (m, 30H, arom.), 8.20 (d,  $J$  = 7.6 Hz, 2H, arom.);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 35.2 (s, 10% of impurity was obtained);  $^{13}\text{C}\{^1\text{H}\}$  NMR was not measured because of instability; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{46}\text{H}_{37}\text{Au}_2\text{O}_2\text{P}_2$  [ $\text{M}-\text{OTf}$ ] $^+$  1077.1600, found 1077.1592.

### *gem*-Gold intermediate **6c**



88% (NMR yield):  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 1.64 – 1.87 (m, 4H, arom.), 3.68 (s, 3H, OMe), 4.37 (bs, 1H, vinyl), 4.55 (bs, 1H, vinyl), 6.66 (d, 2H,  $J$  = 8.6 Hz, arom.), 7.28 – 7.53 (m, 24H, arom.), 7.56 – 7.70 (m, 6H, arom.), 7.80 (d, 2H,  $J$  = 8.8 Hz);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 36.3 (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR was not measured because of instability; HRMS (ESI-TOF)  $m/z$  calculated for  $\text{C}_{52}\text{H}_{45}\text{Au}_2\text{O}_2\text{P}_2$  [M-OTf] $^+$  1157.2276, found 1157.2211.

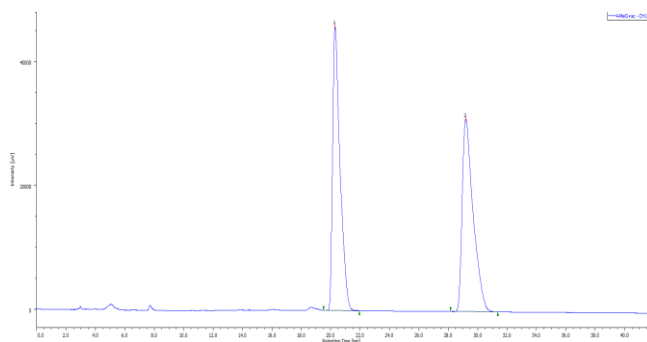
### Observation of non-linear effects

(*S*)- $\text{L}_8\text{-AuCl}$  was synthesized in the same as (*R*)- $\text{L}_8\text{-AuCl}$ .

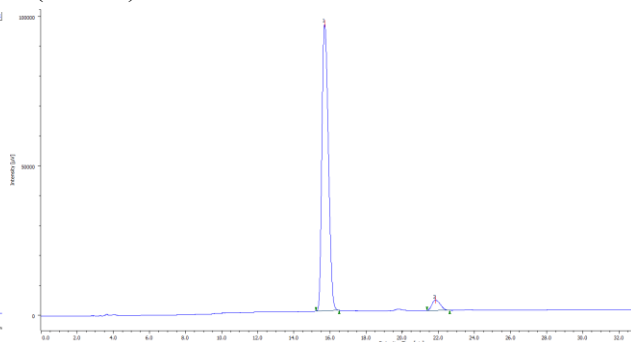
A solution of 1-(4-methoxyphenyl)prop-2-yn-1-one (**1a**) (0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL) and cyclohexadiene (**2**) (0.2 mmol) was added to a solution of (*R*)- $\text{L}_8\text{-AuPF}_6$  (3.75 mol%) and (*S*)- $\text{L}_8\text{-AuPF}_6$  (1.25 mol%) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL) at 0 °C. The reaction was stirred at the same temperature for 32 h. The reaction mixture was directly loaded onto a silica-gel short column (hexane/AcOEt = 3/1) to remove the catalyst, and then the solution was concentrated under reduced pressure. Purification by silica-gel chromatography (hexane/AcOEt = 10/1) gave the compound **3a** (28% yield, 91% *ee*).

HPLC analysis (column, CHIRALPAK AD-3, hexane/2-propanol = 98/2, flow rate 1.0 mL/min, 20 °C, detection UV 250 nm light);  $t_R$  of major-isomer 15.7 min,  $t_R$  of minor-isomer 21.8 min.

Racemic:



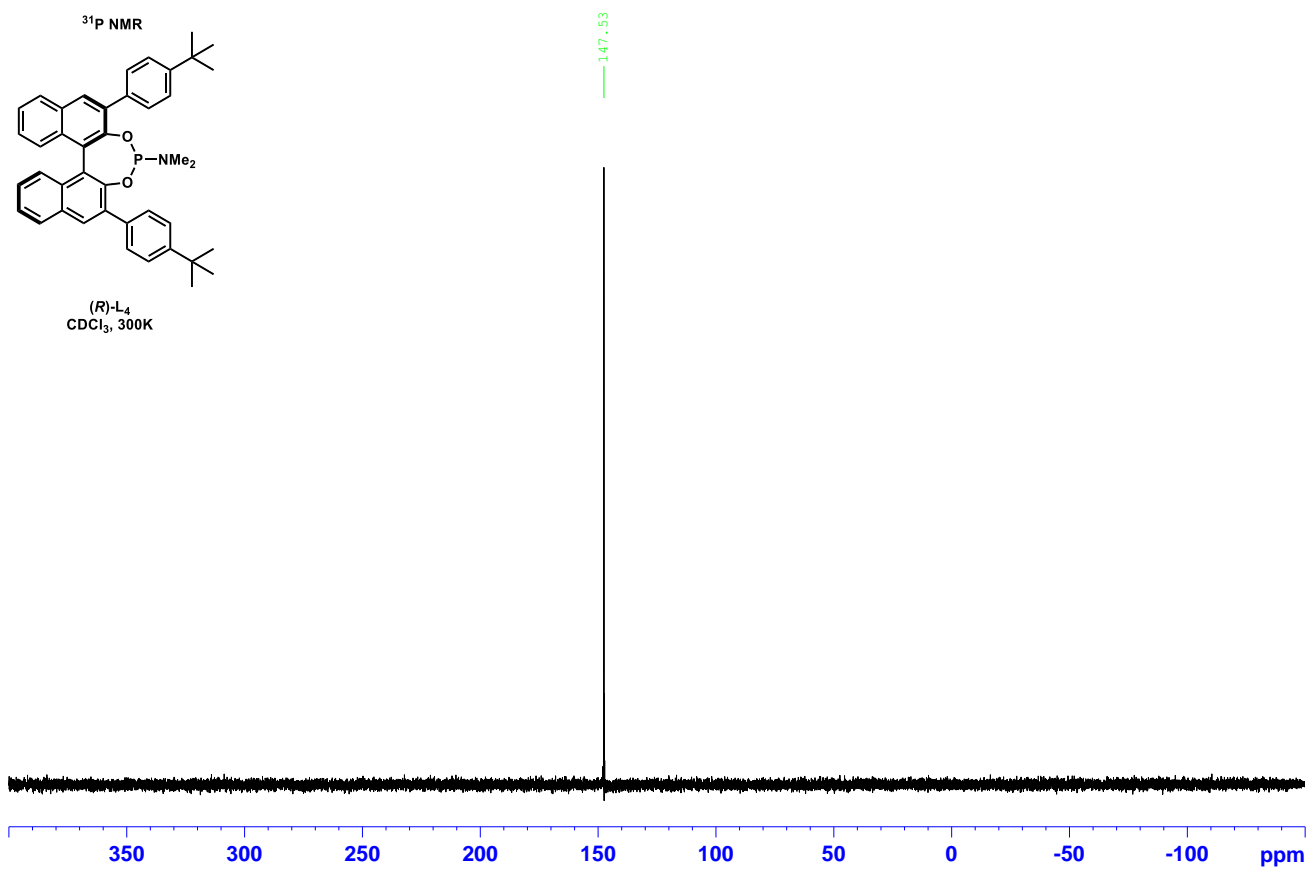
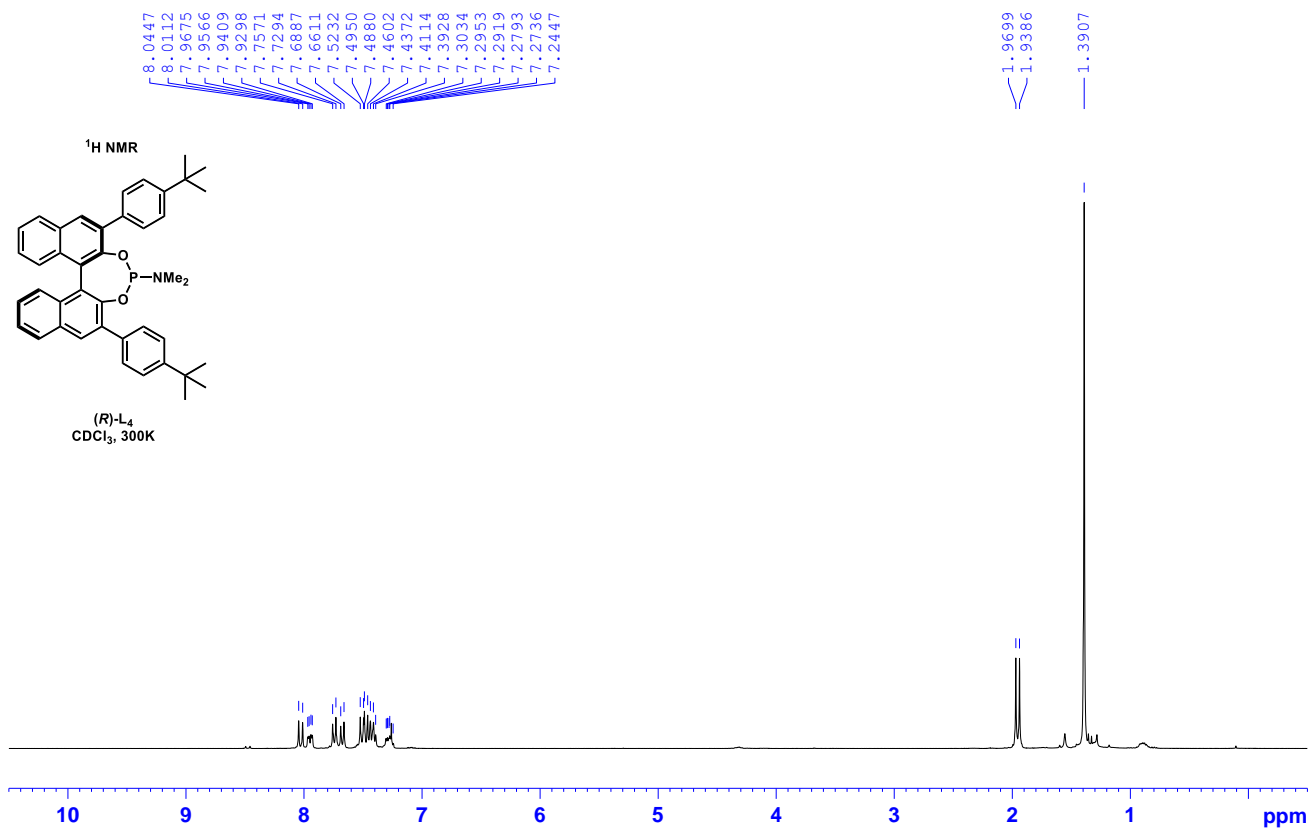
Chiral (91% *ee*):

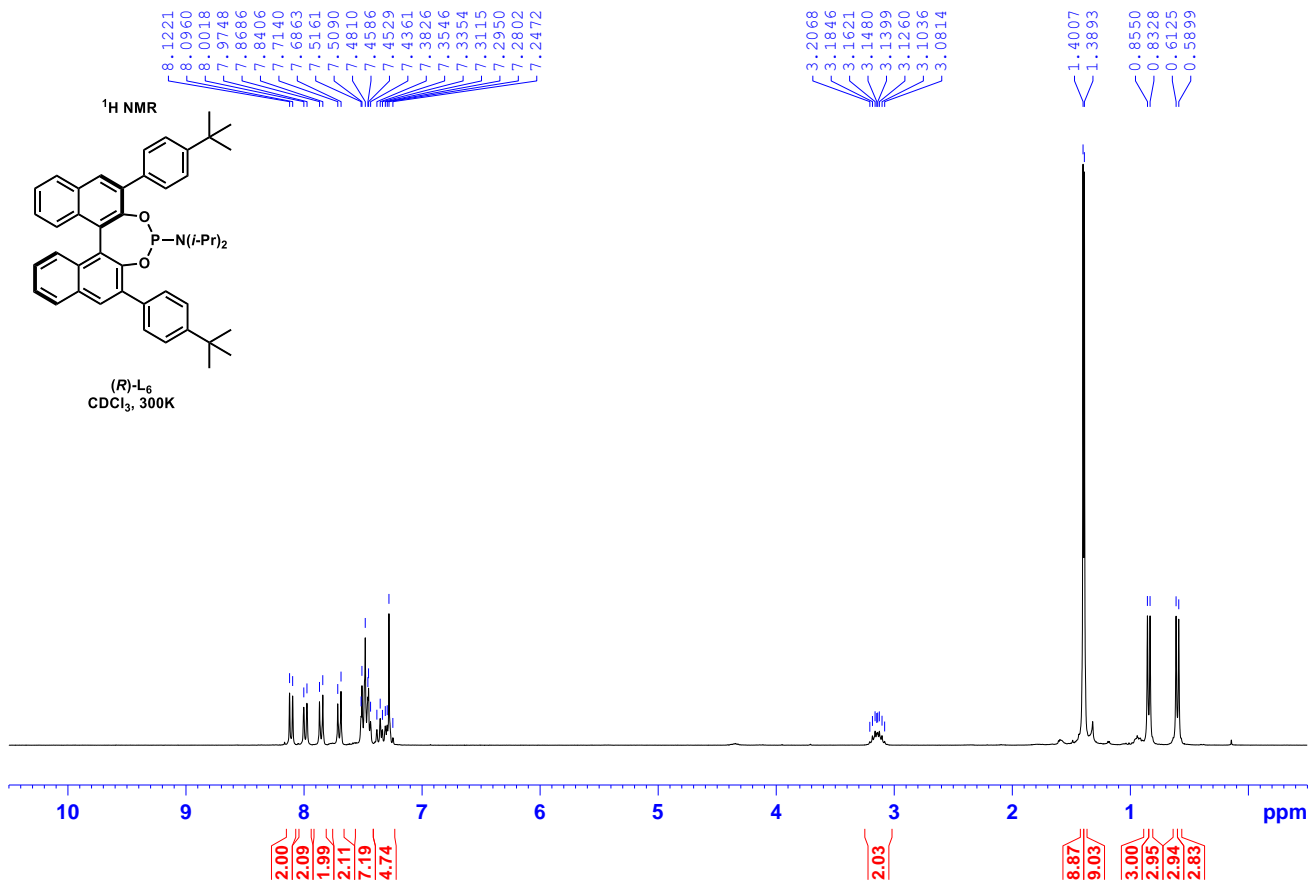
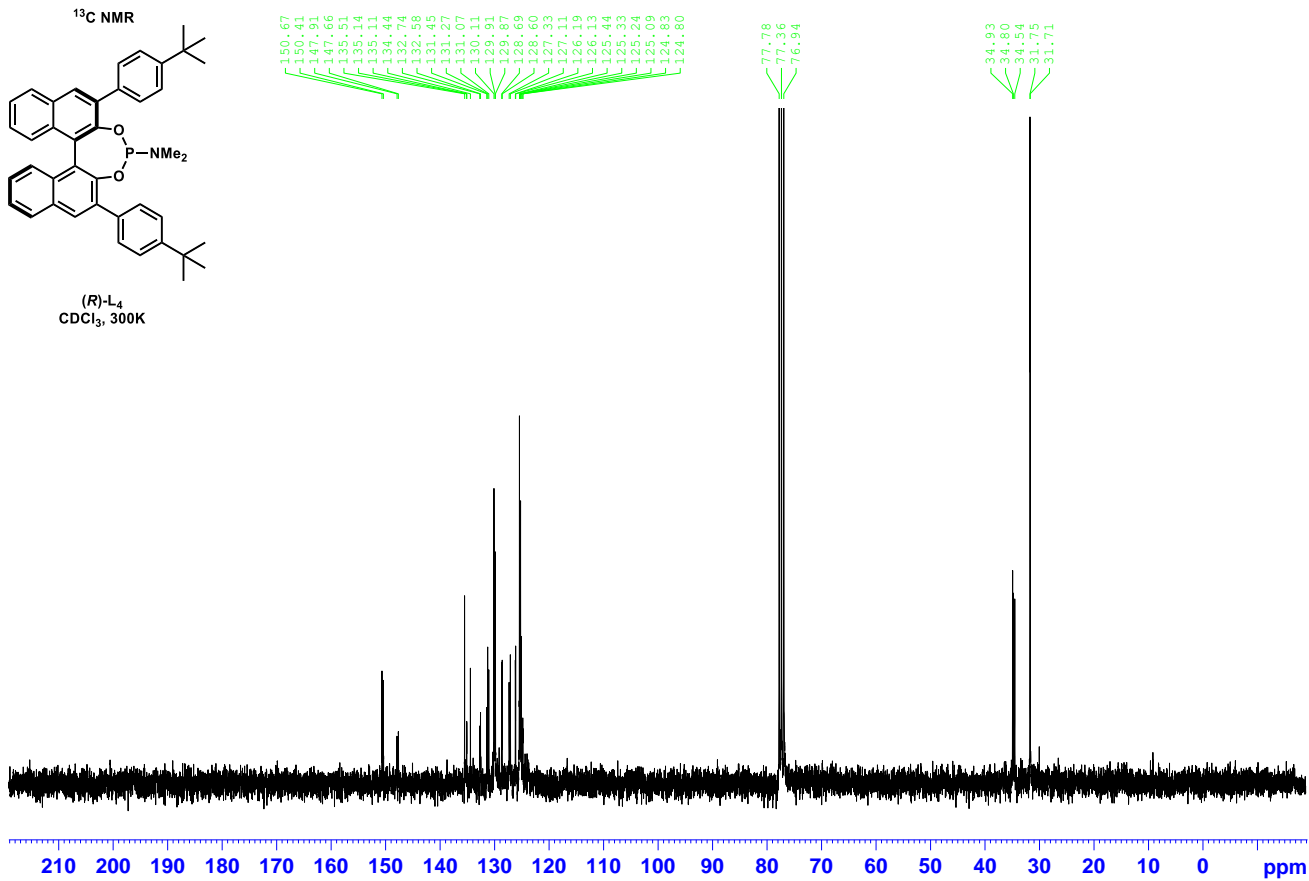


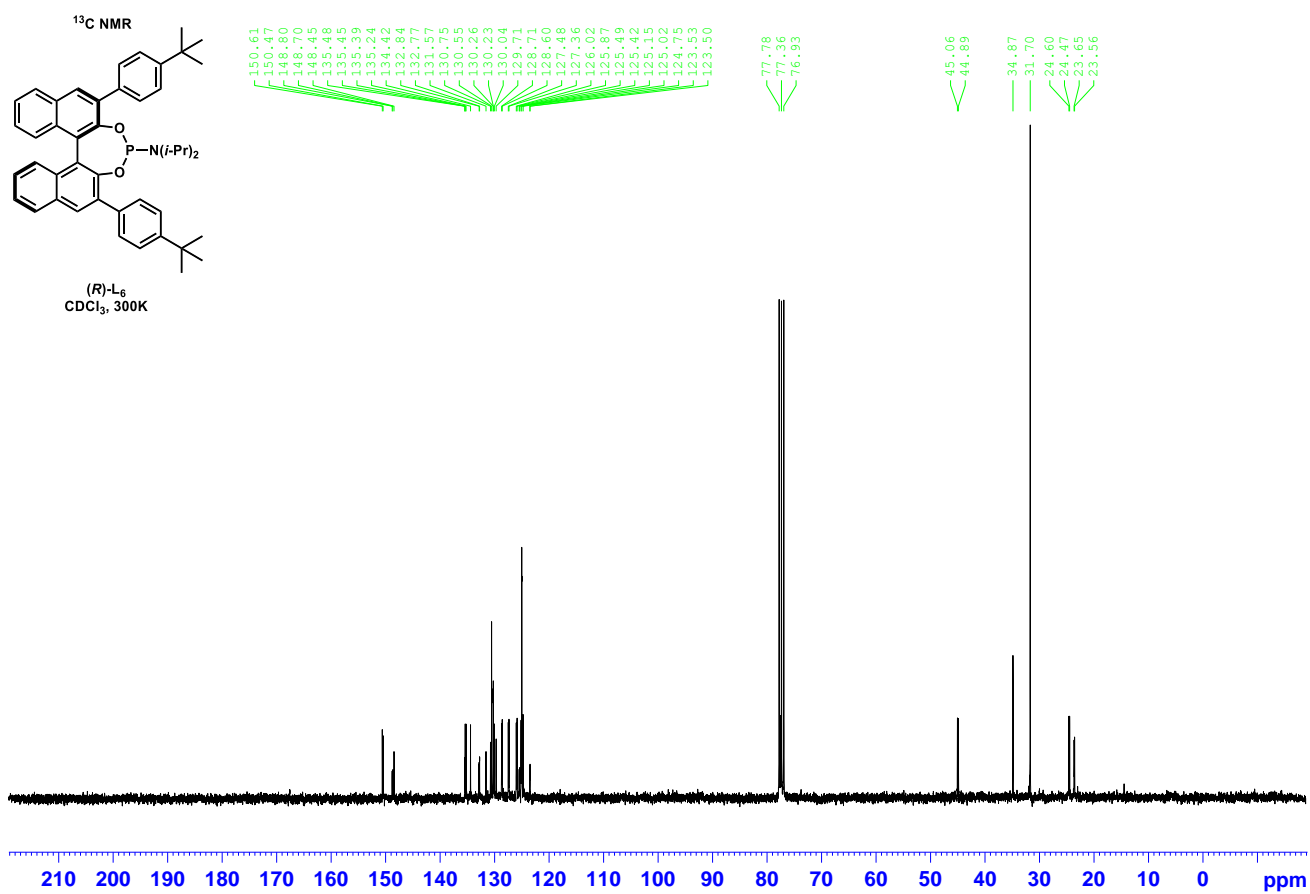
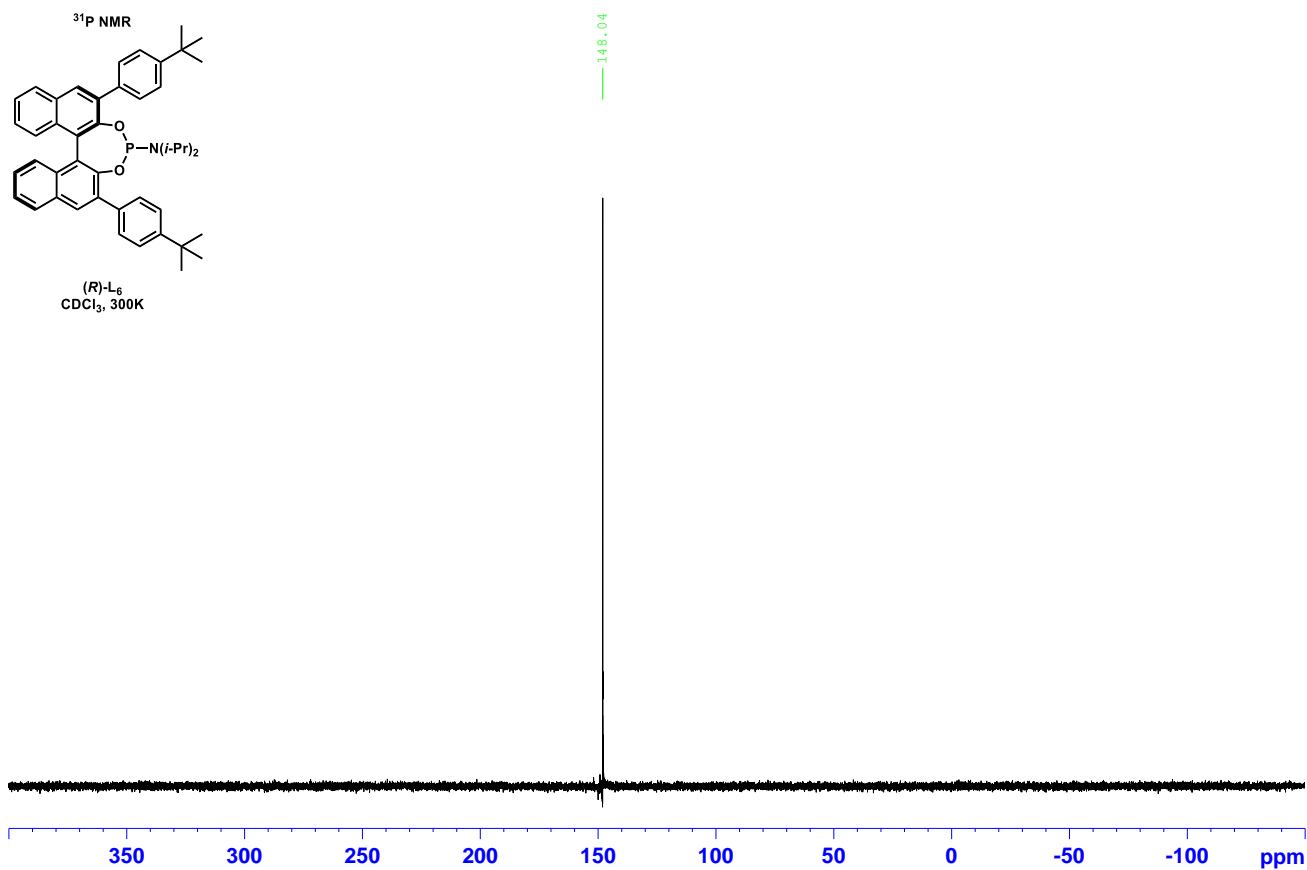
$t_R$ (min)	Area	Area Percent	$t_R$ (min)	Area	Area Percent
20.292	1602366	49.948	15.692	2368106	95.542
29.175	1605685	50.052	21.842	3407	4.458

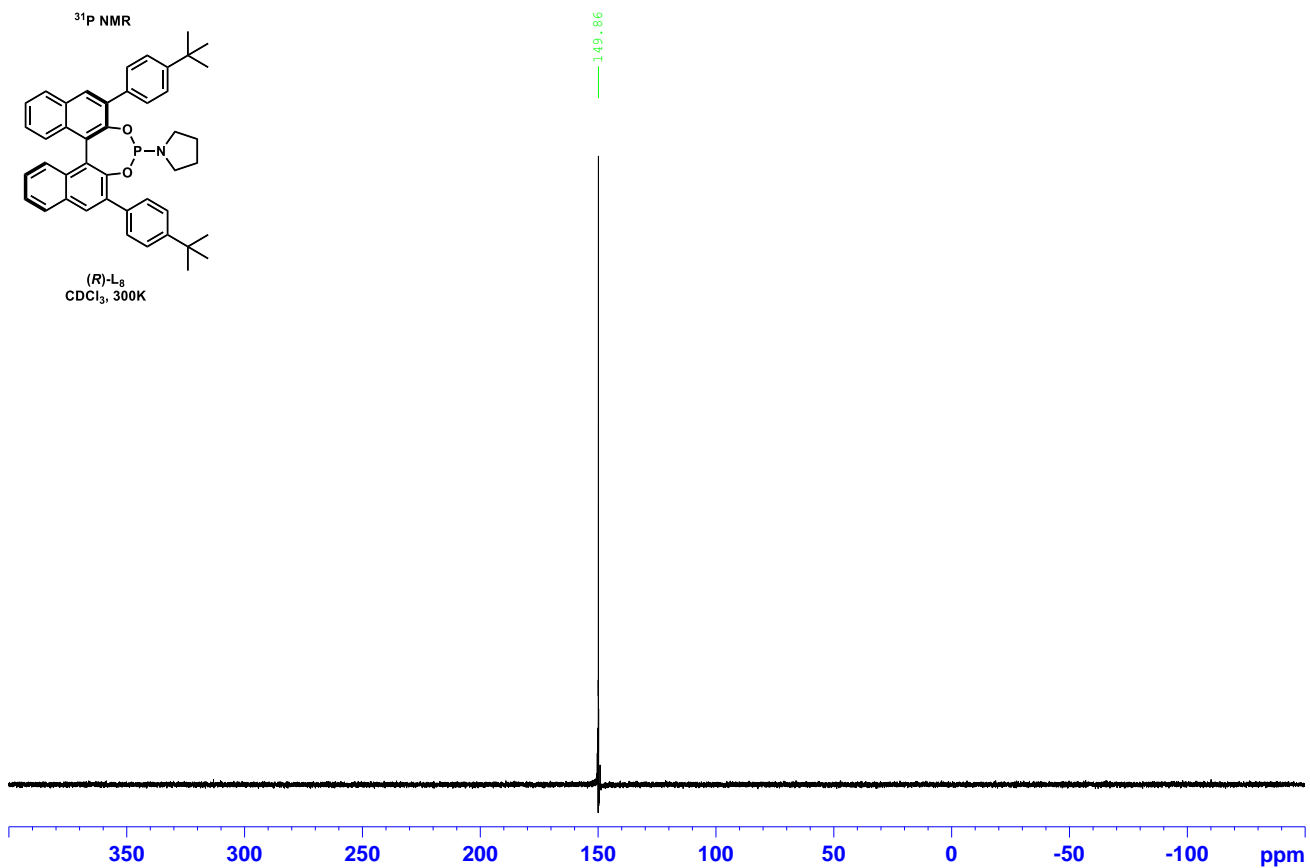
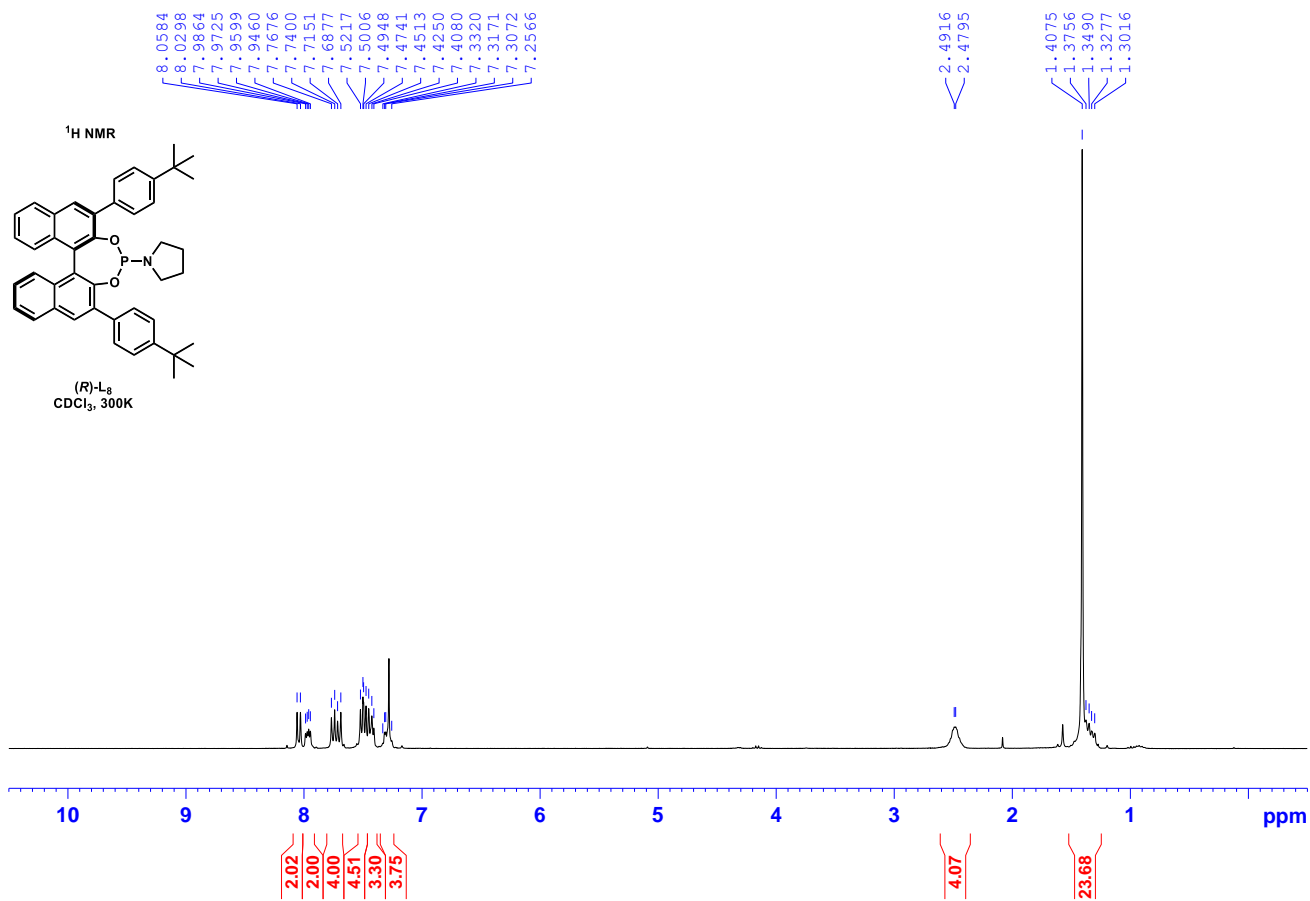
### References for Experimental Section 3

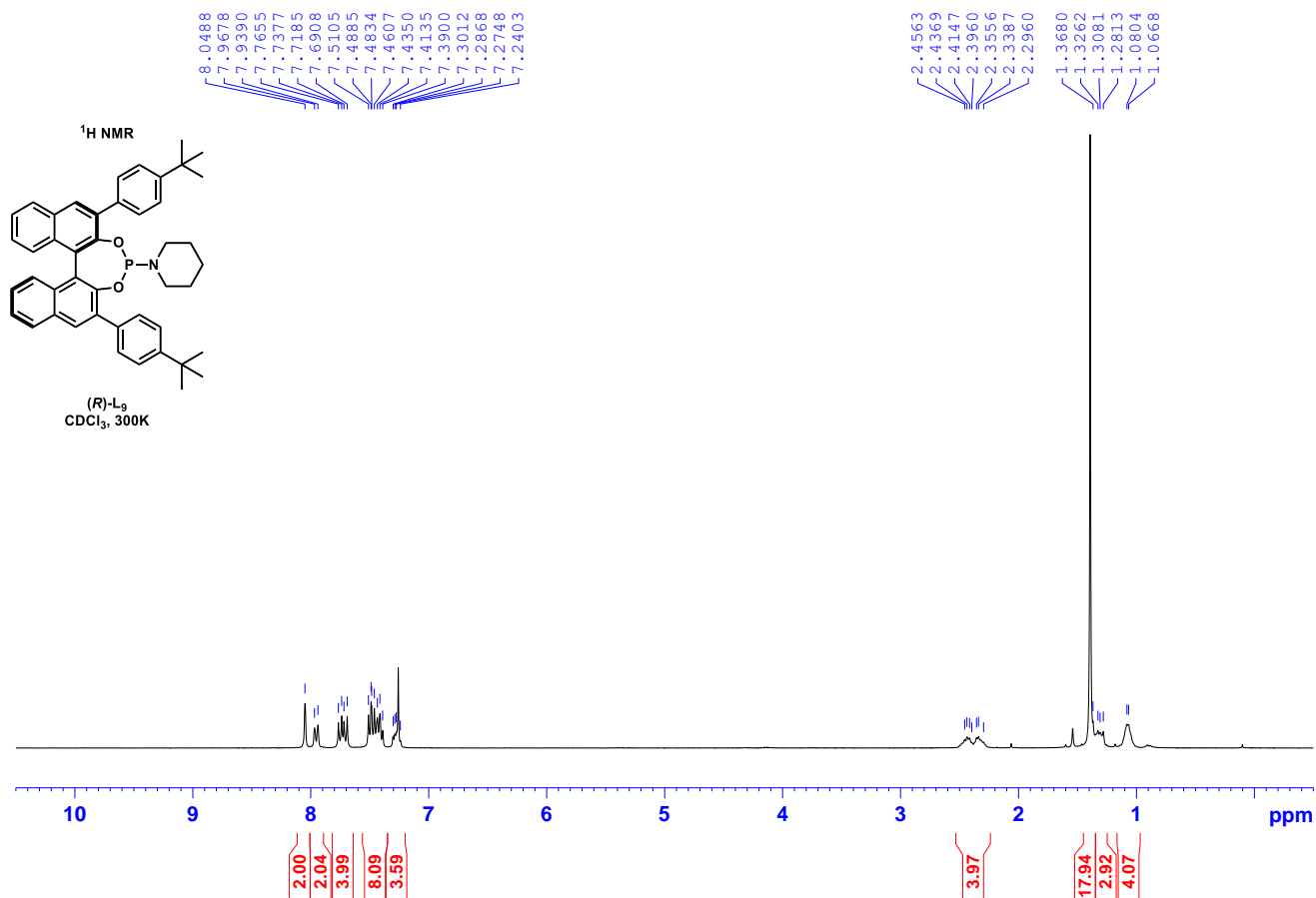
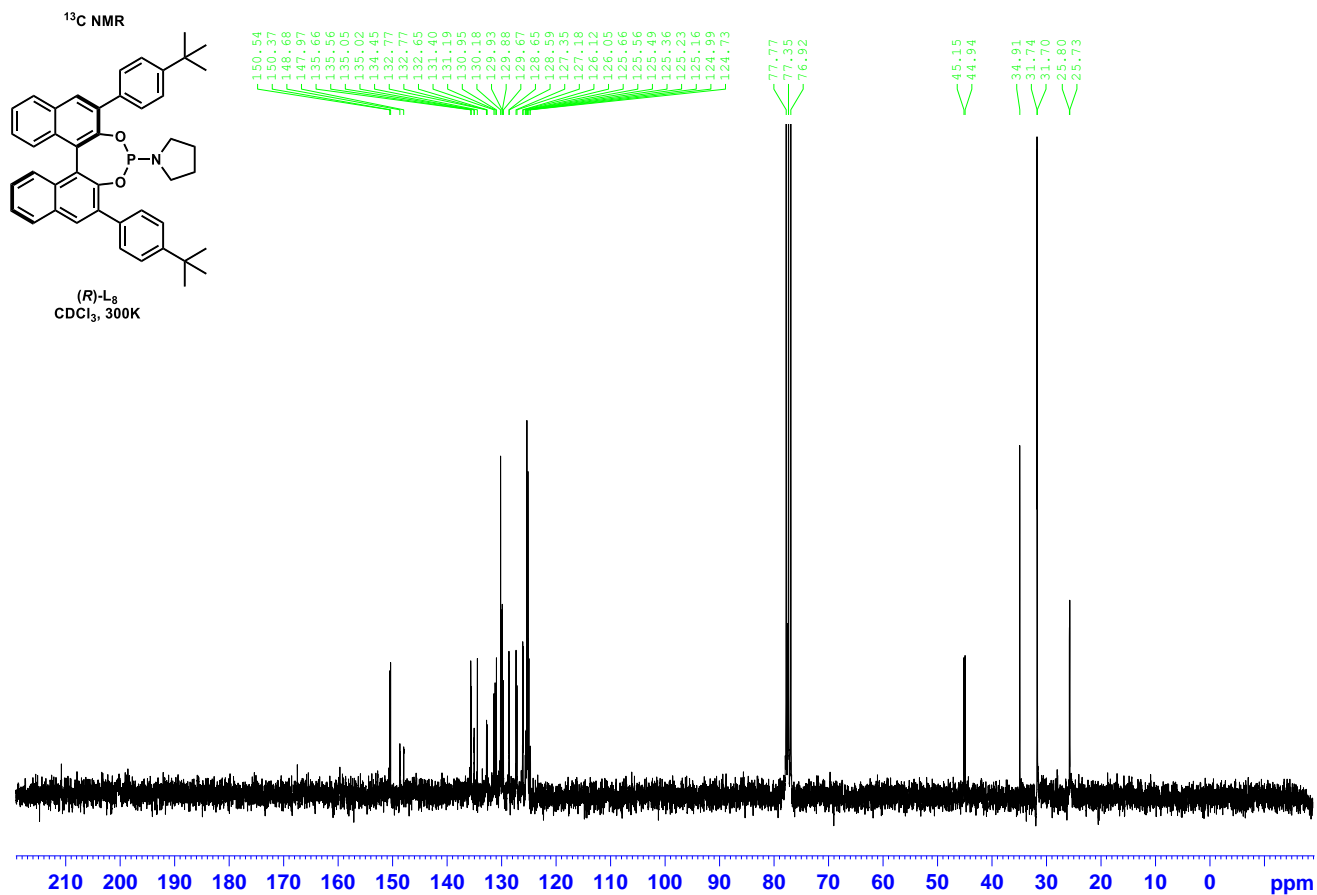
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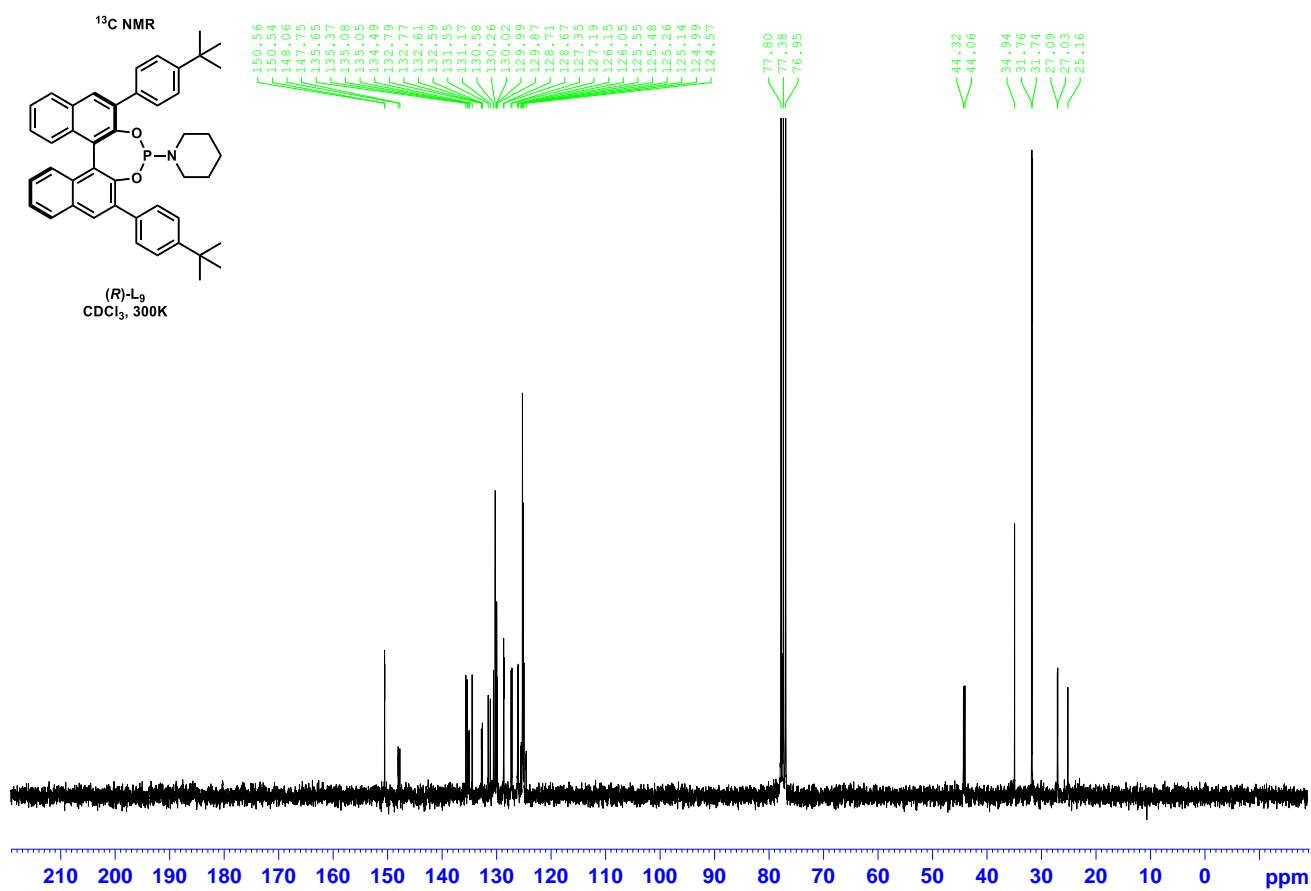
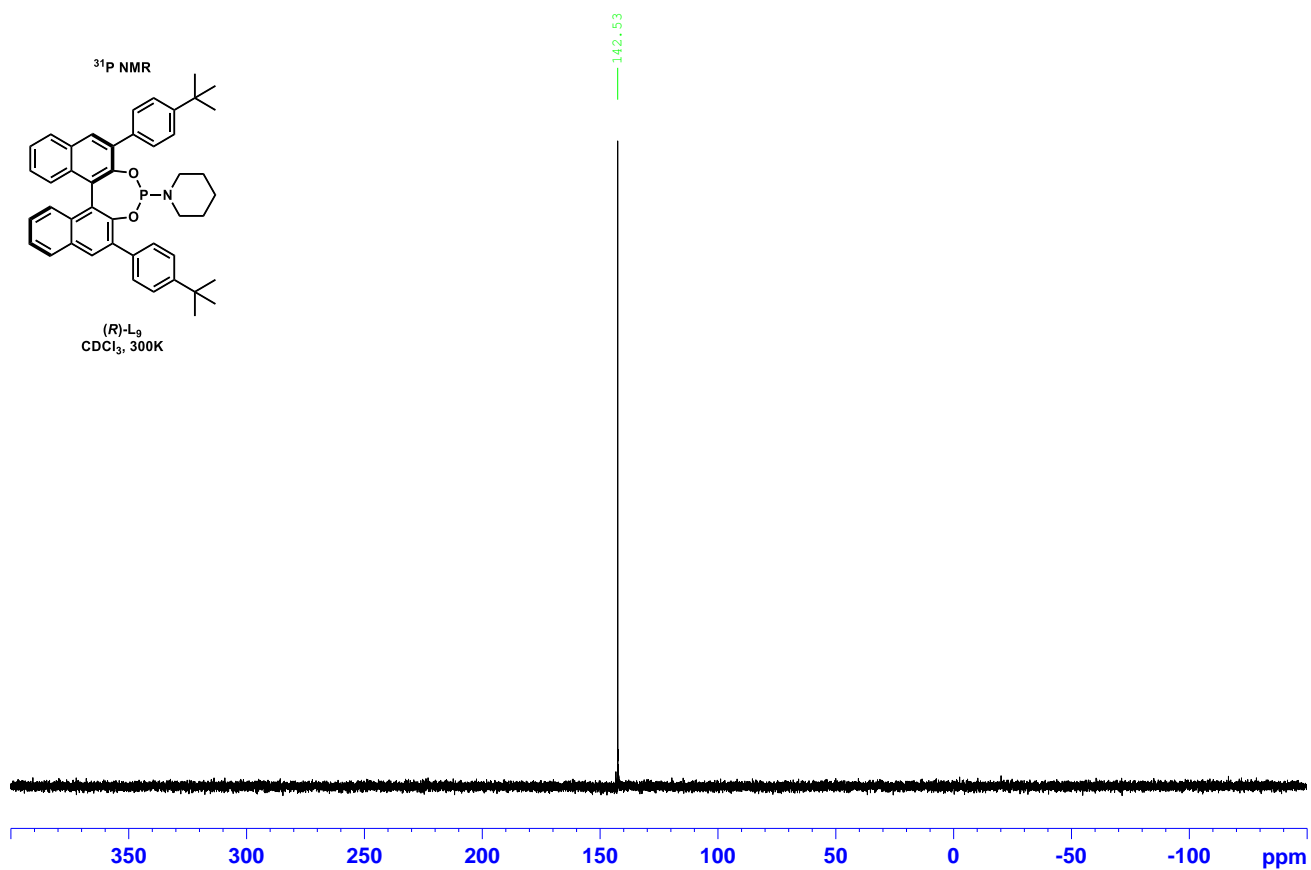


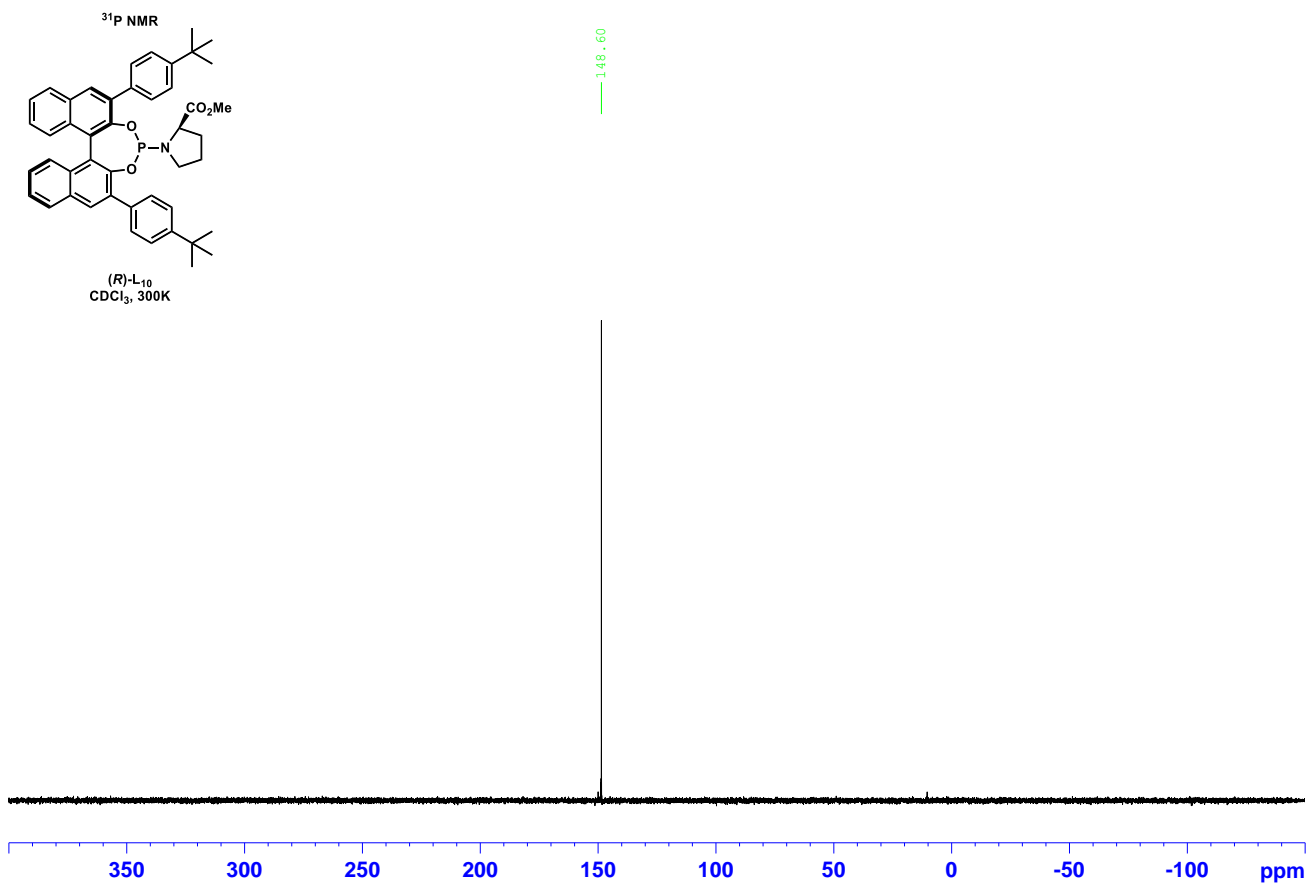
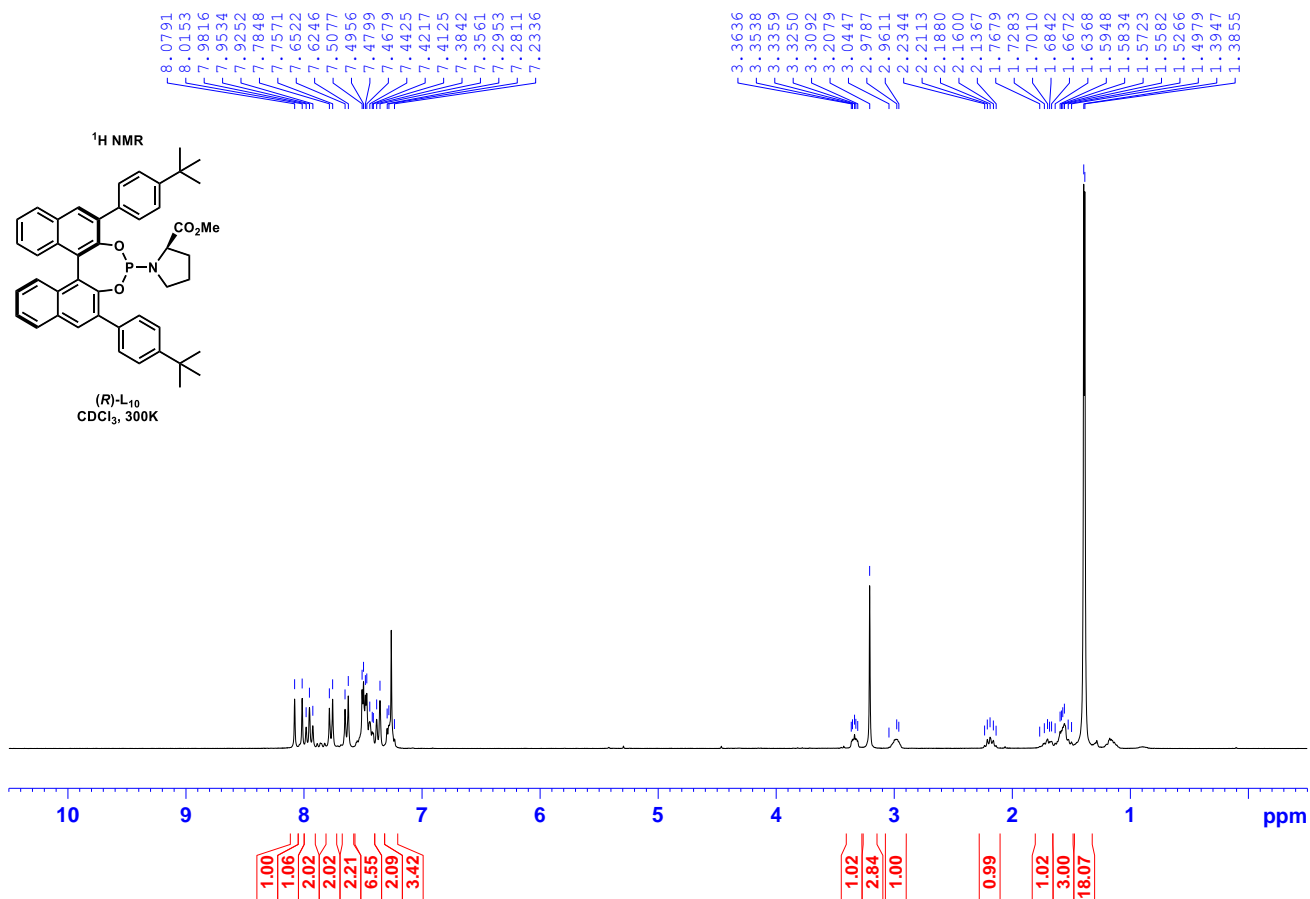




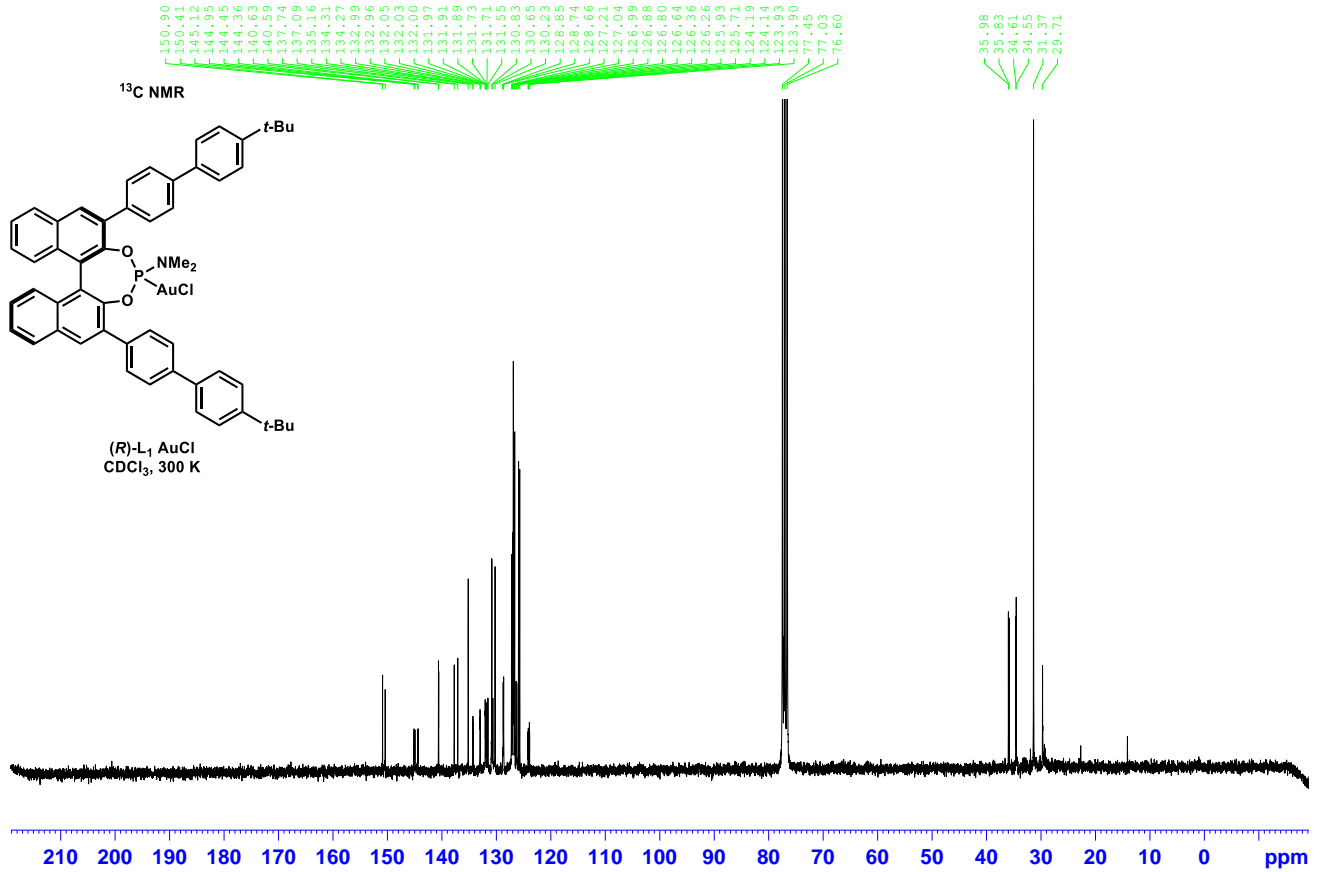
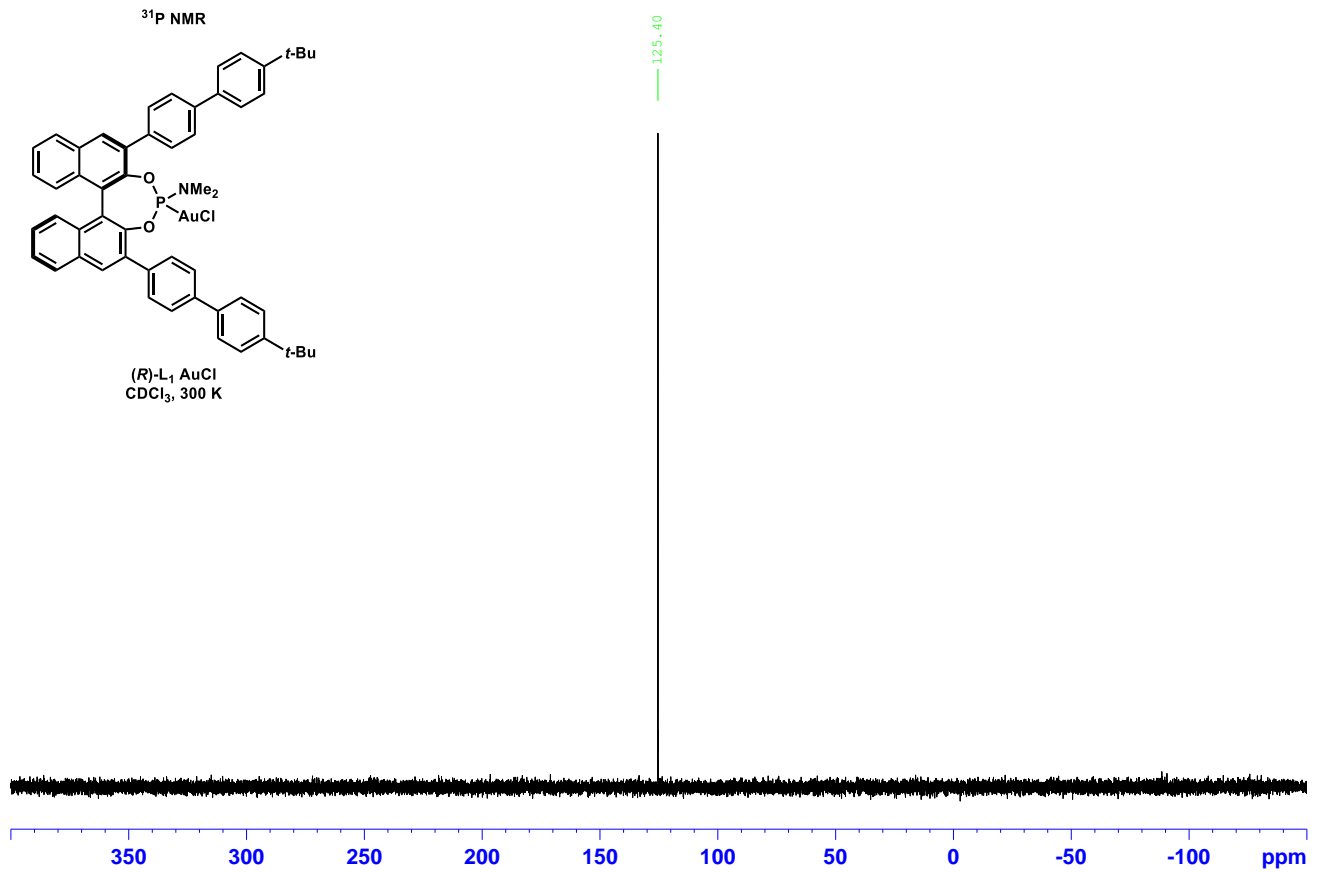


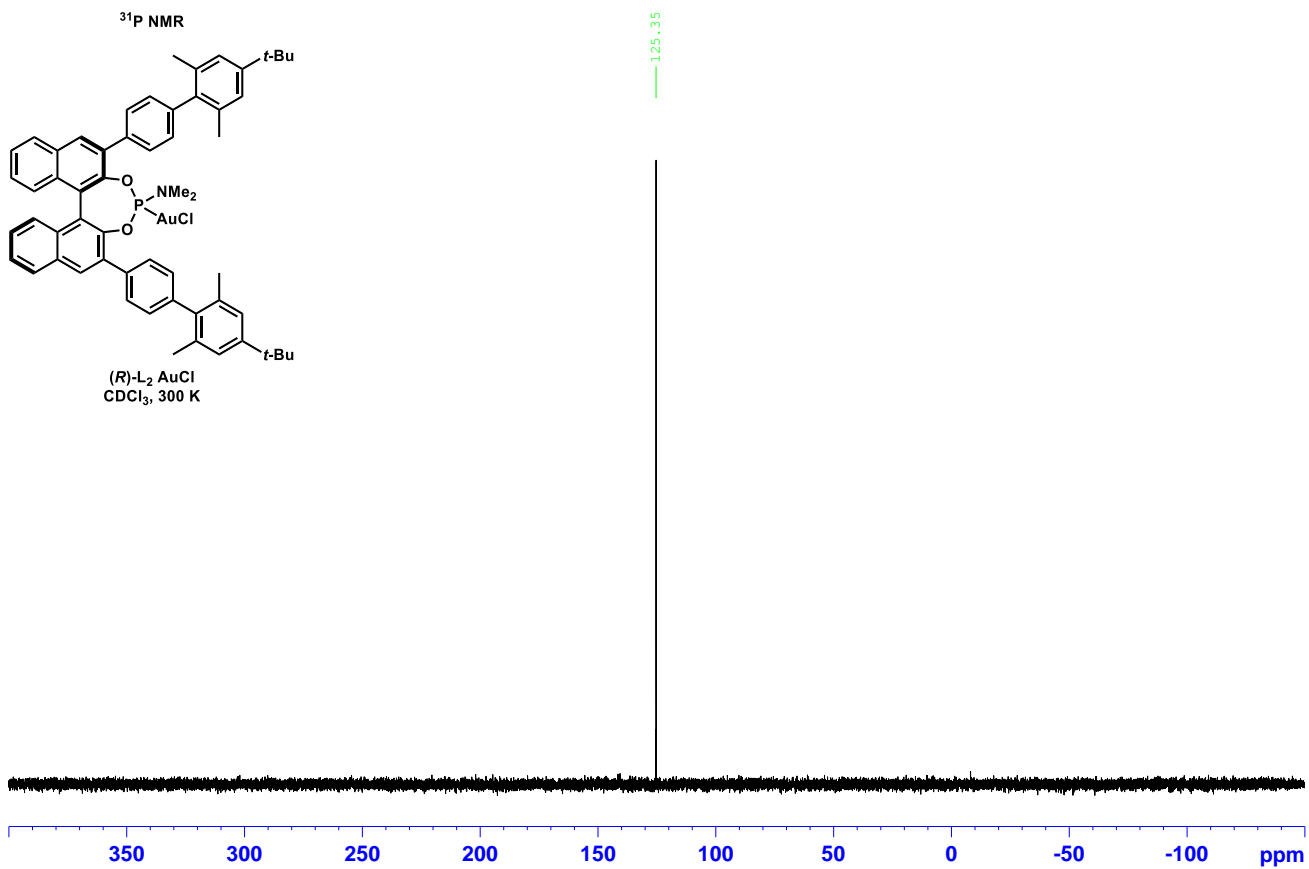
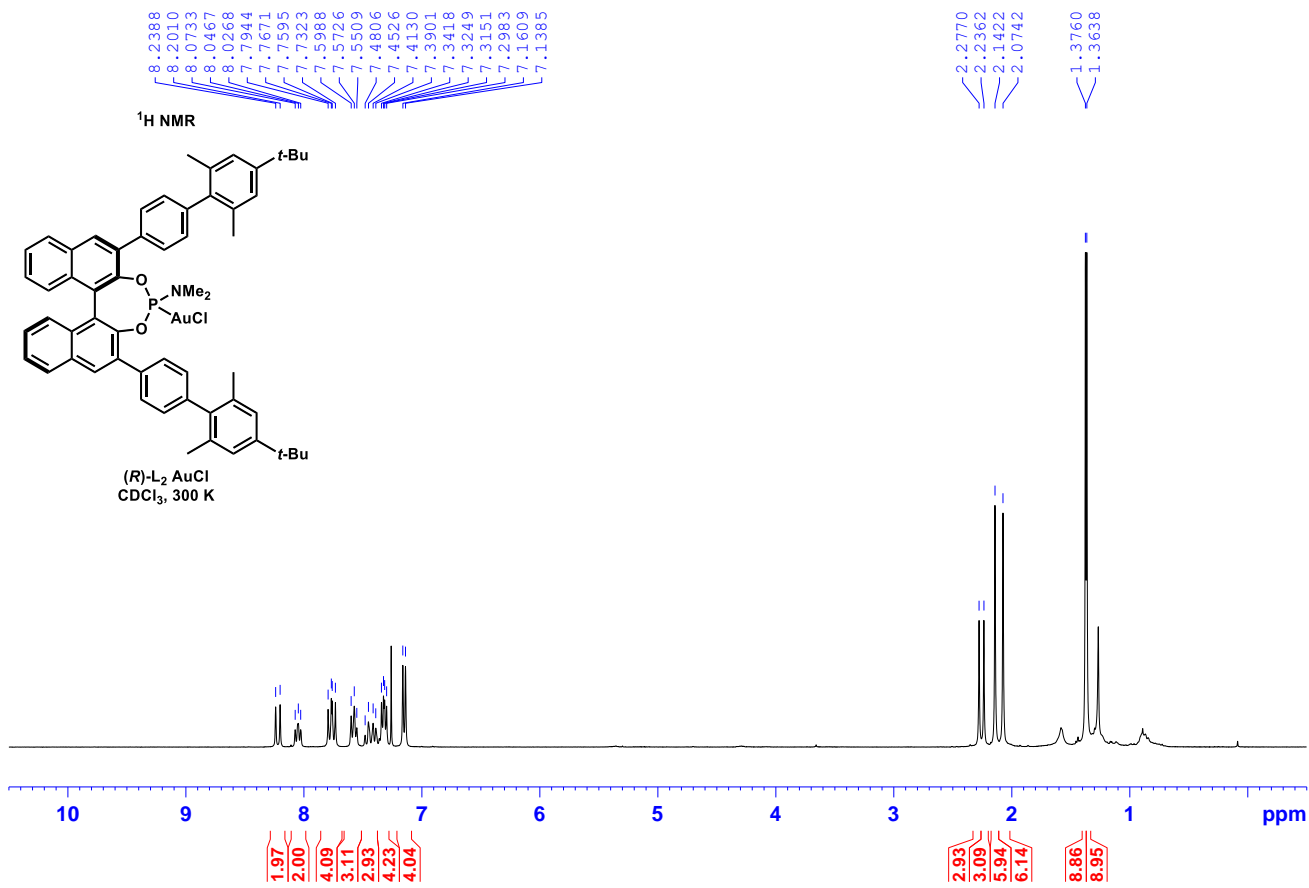


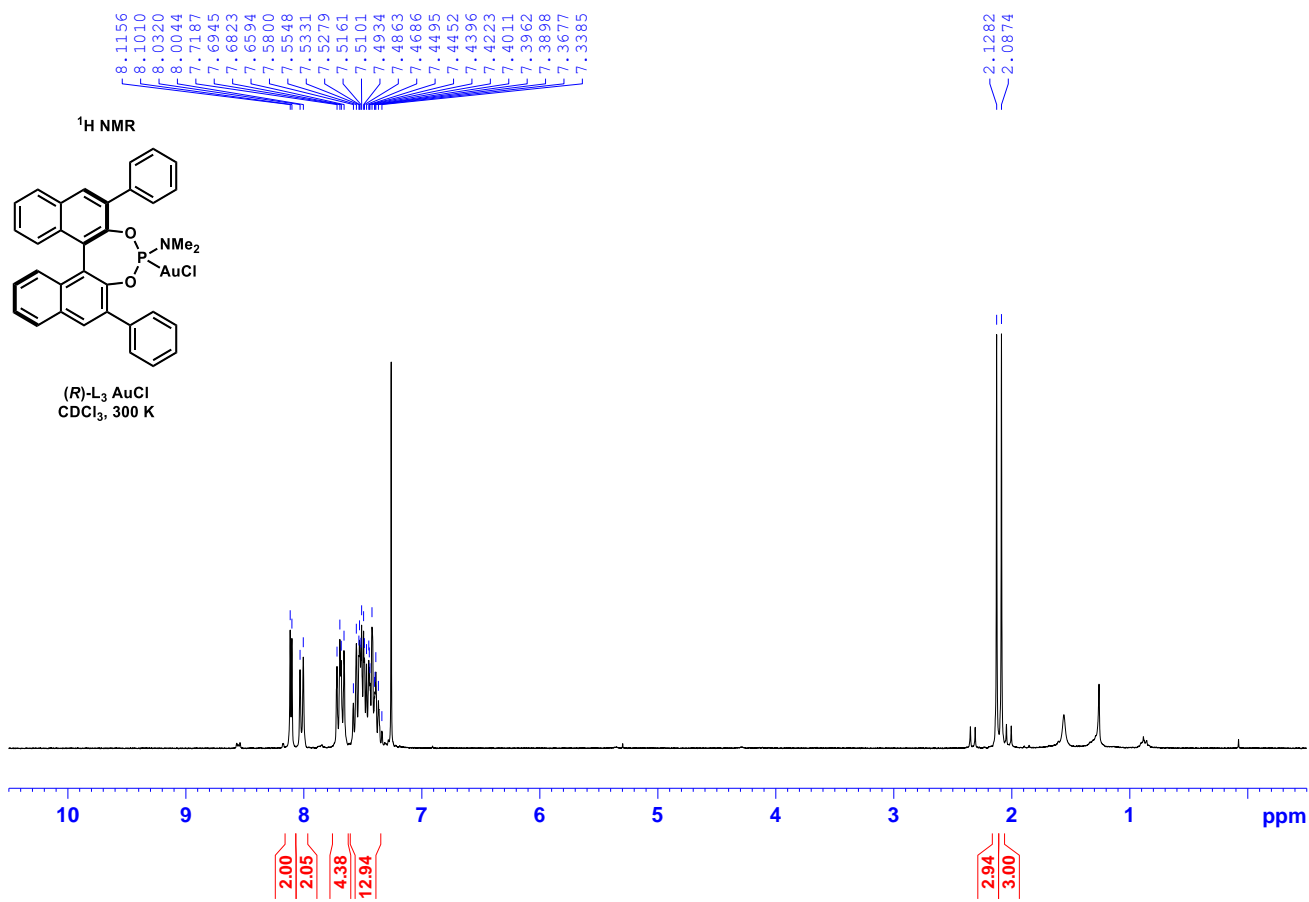
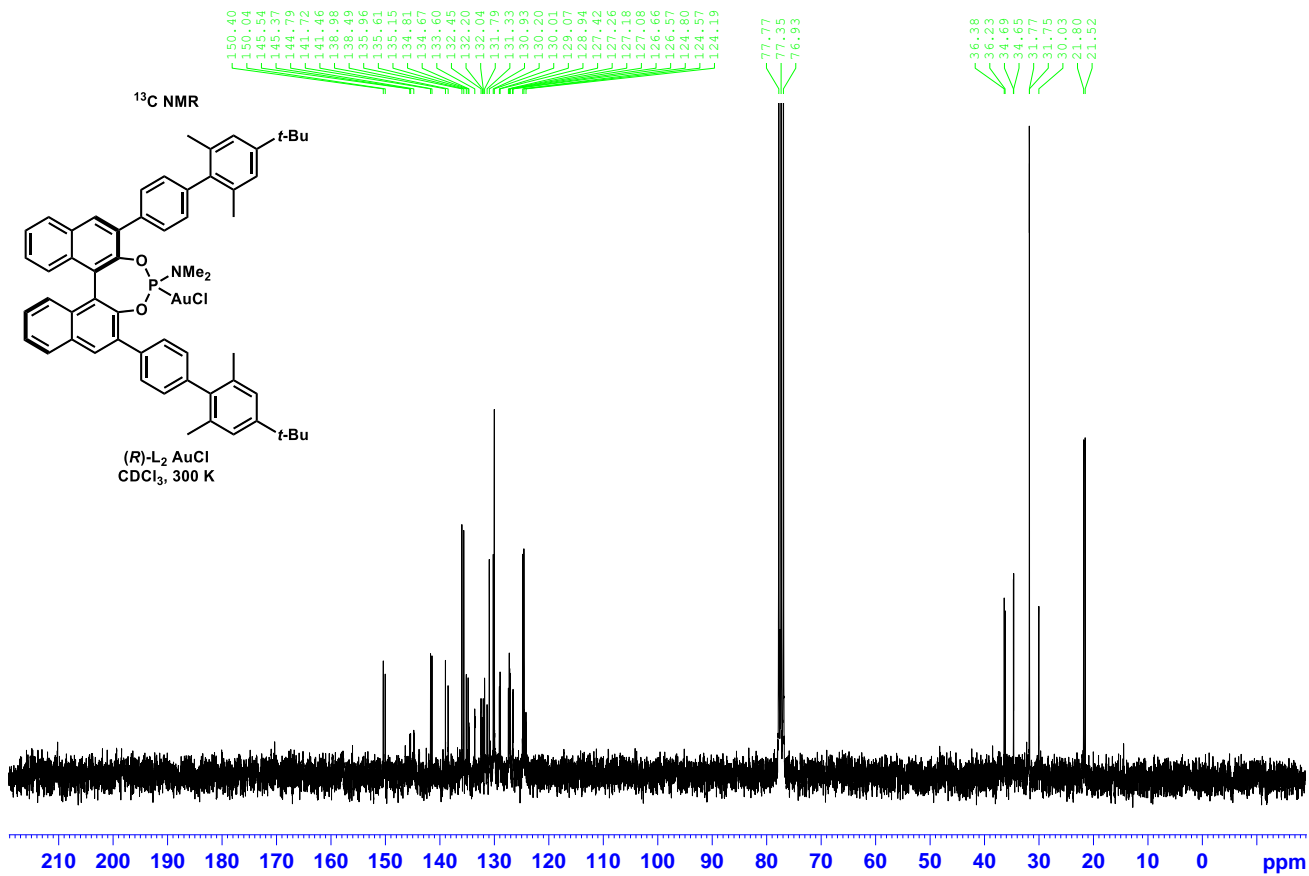


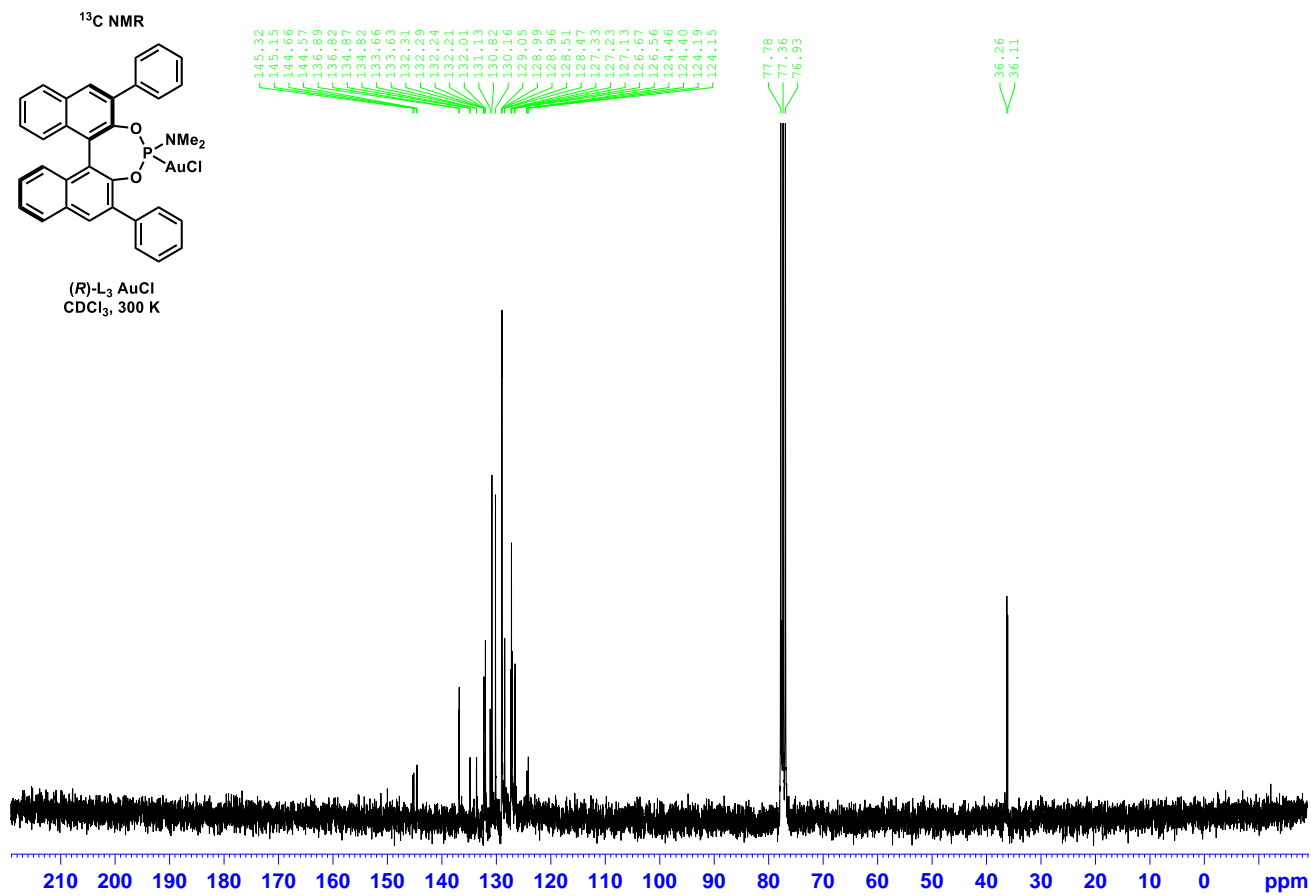
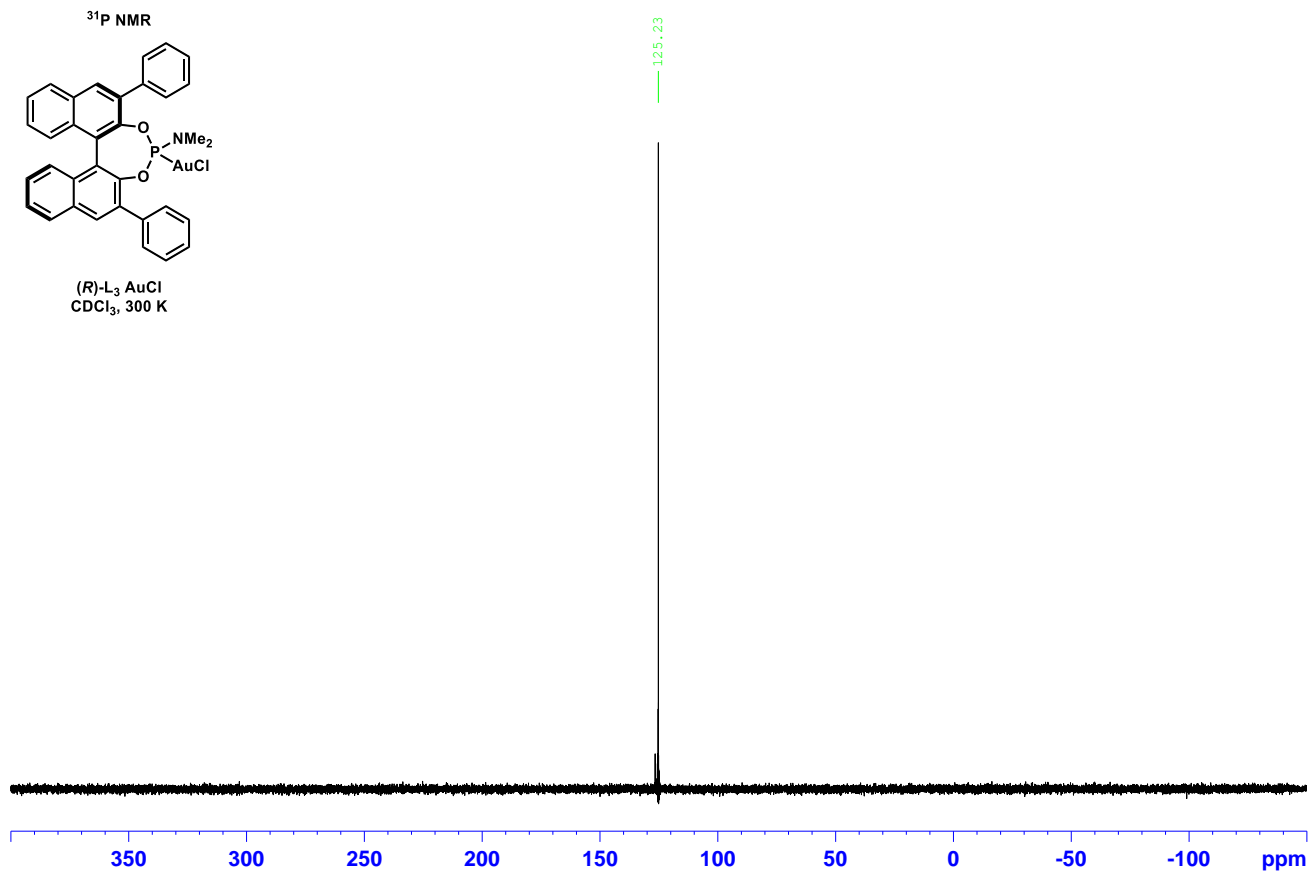


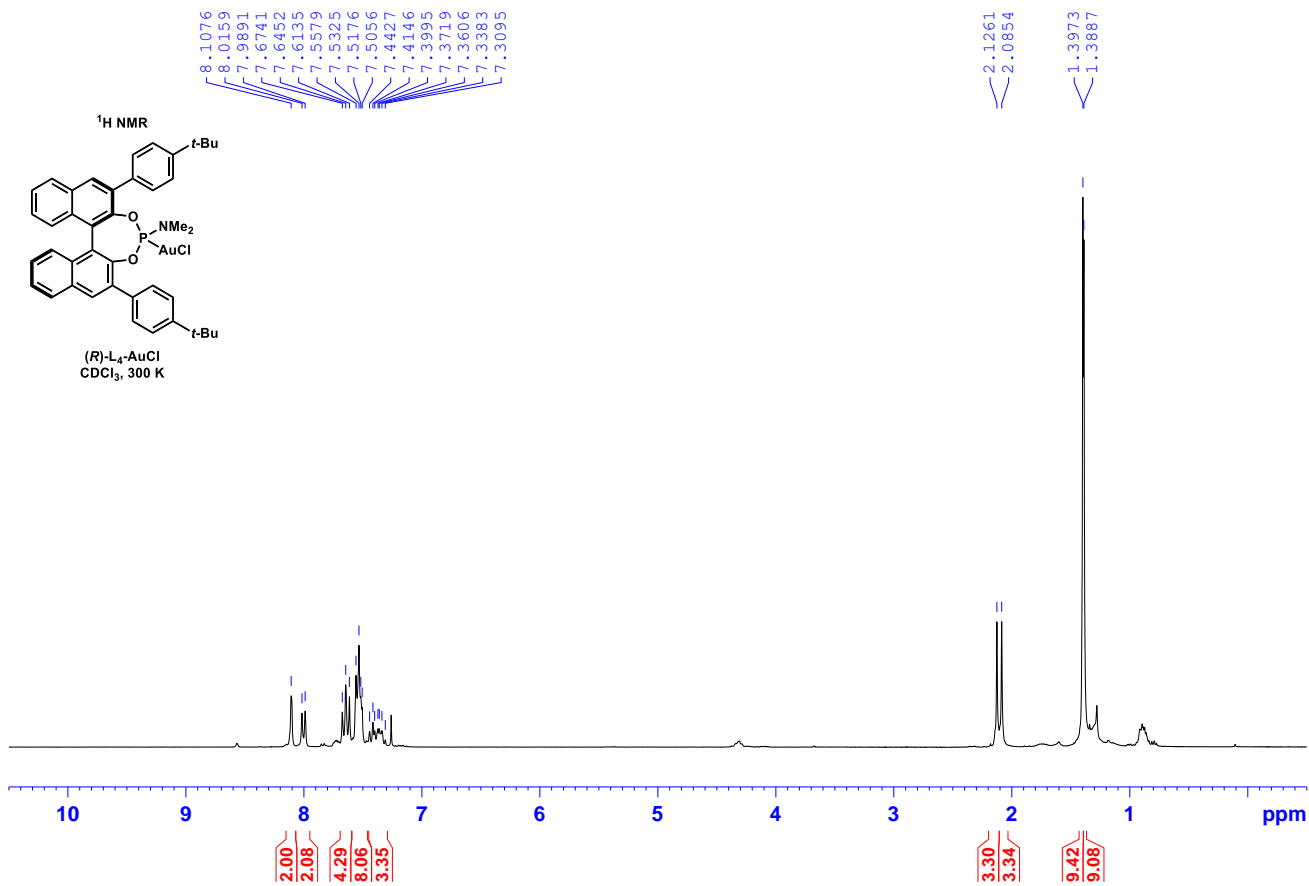


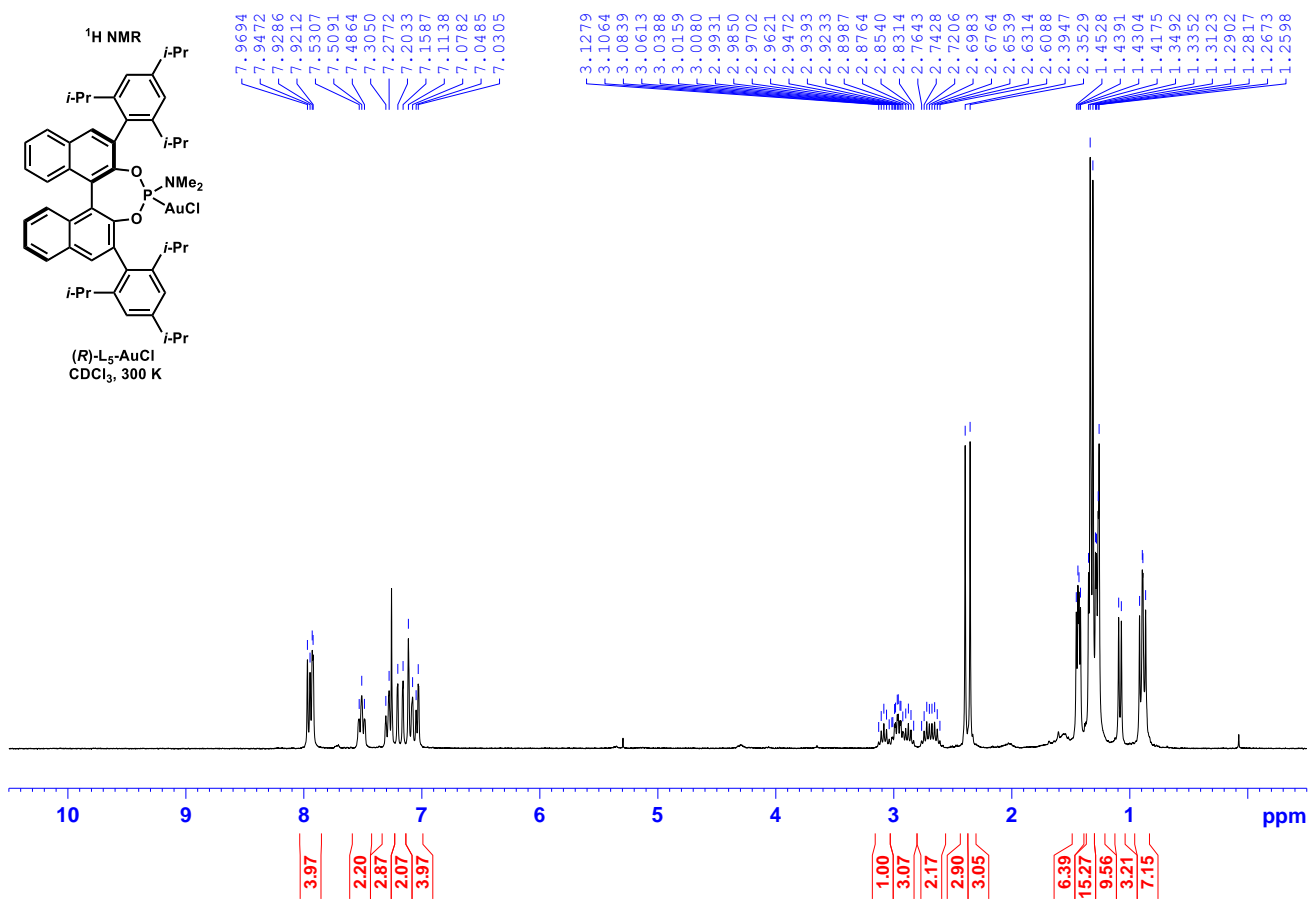
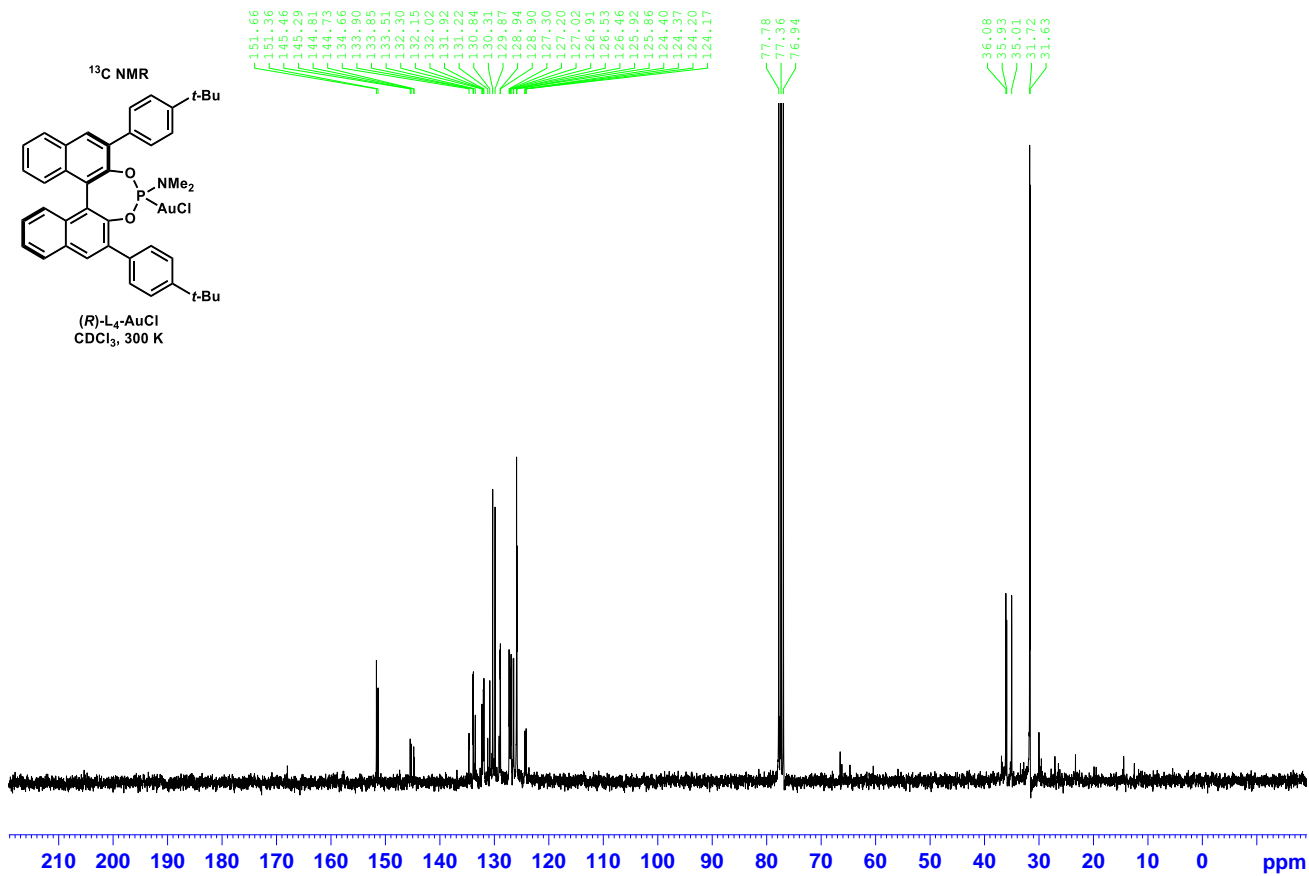




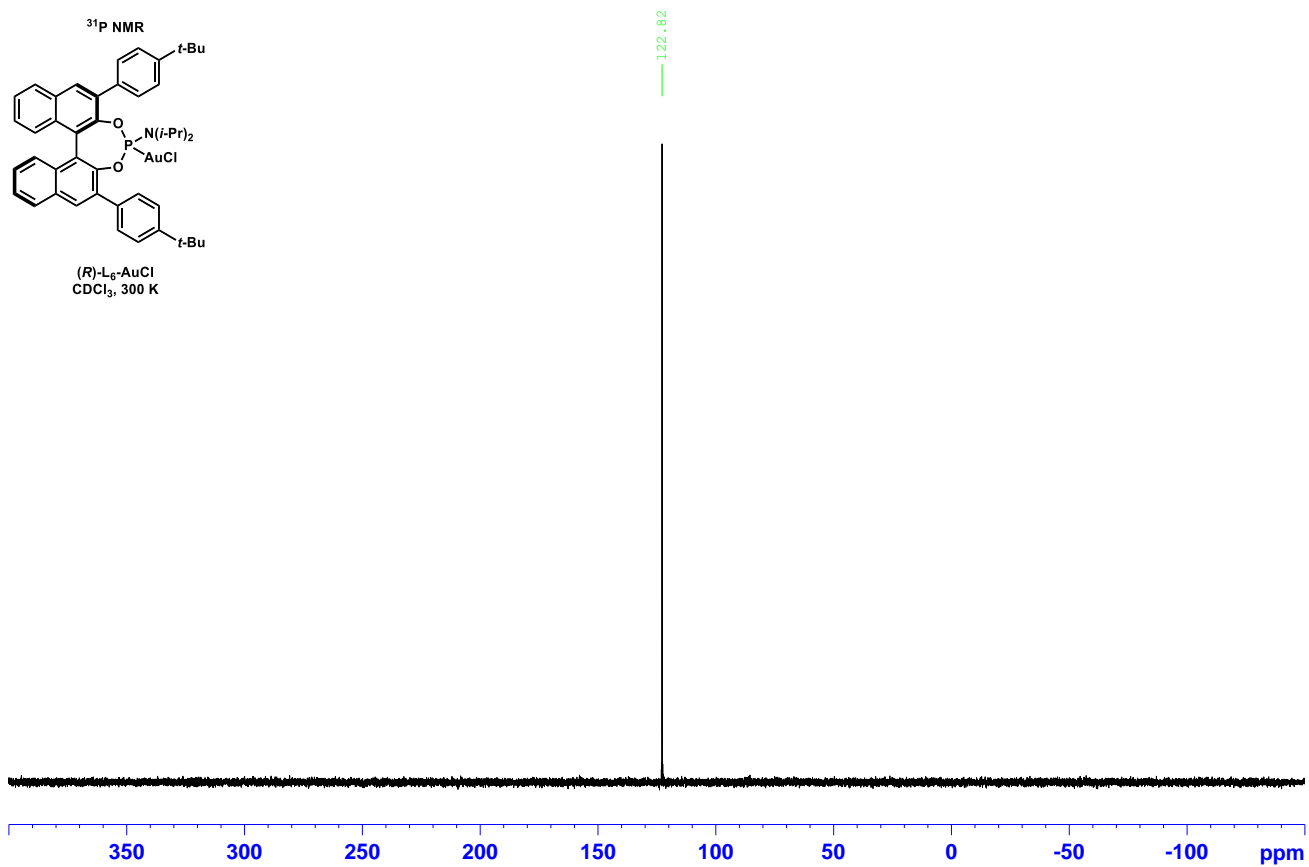
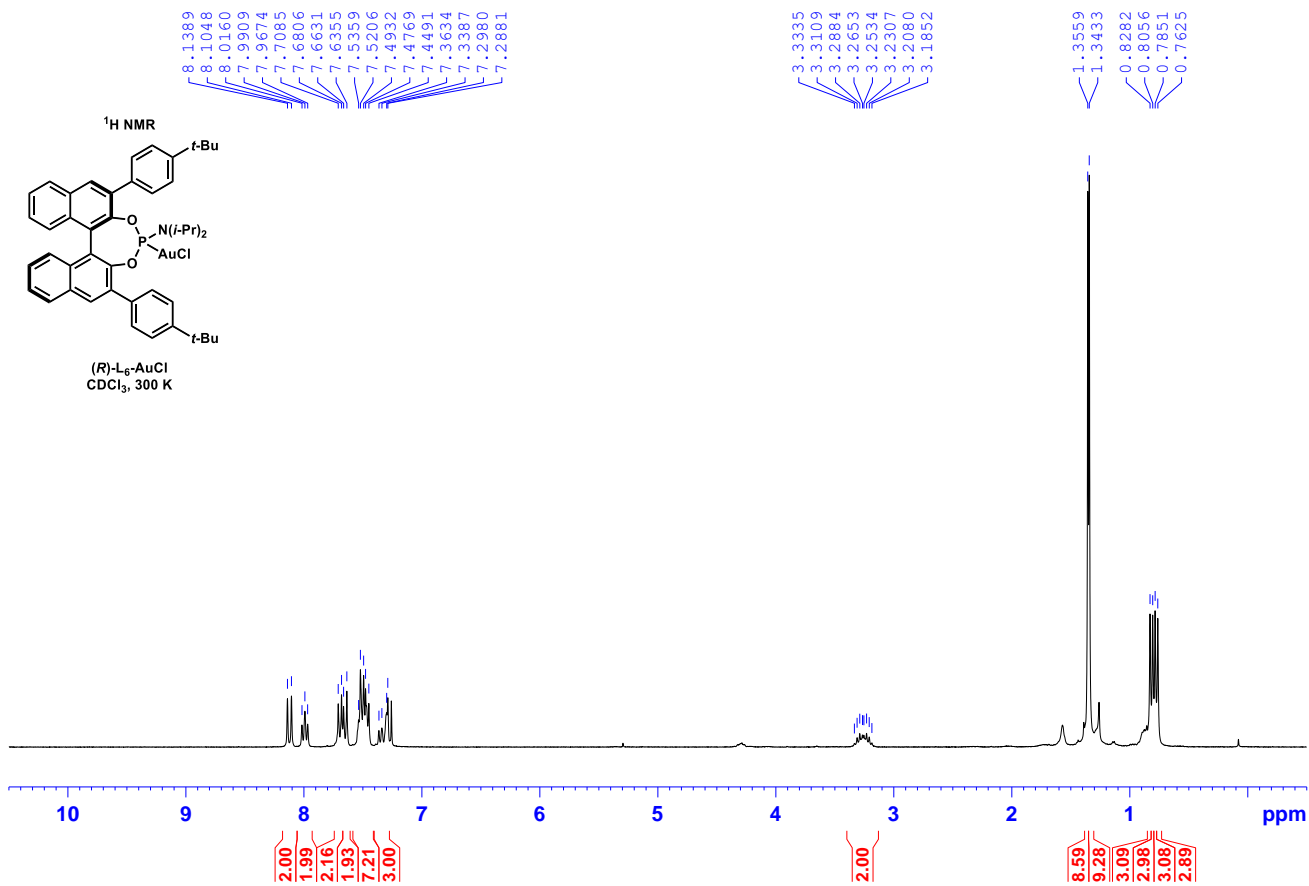


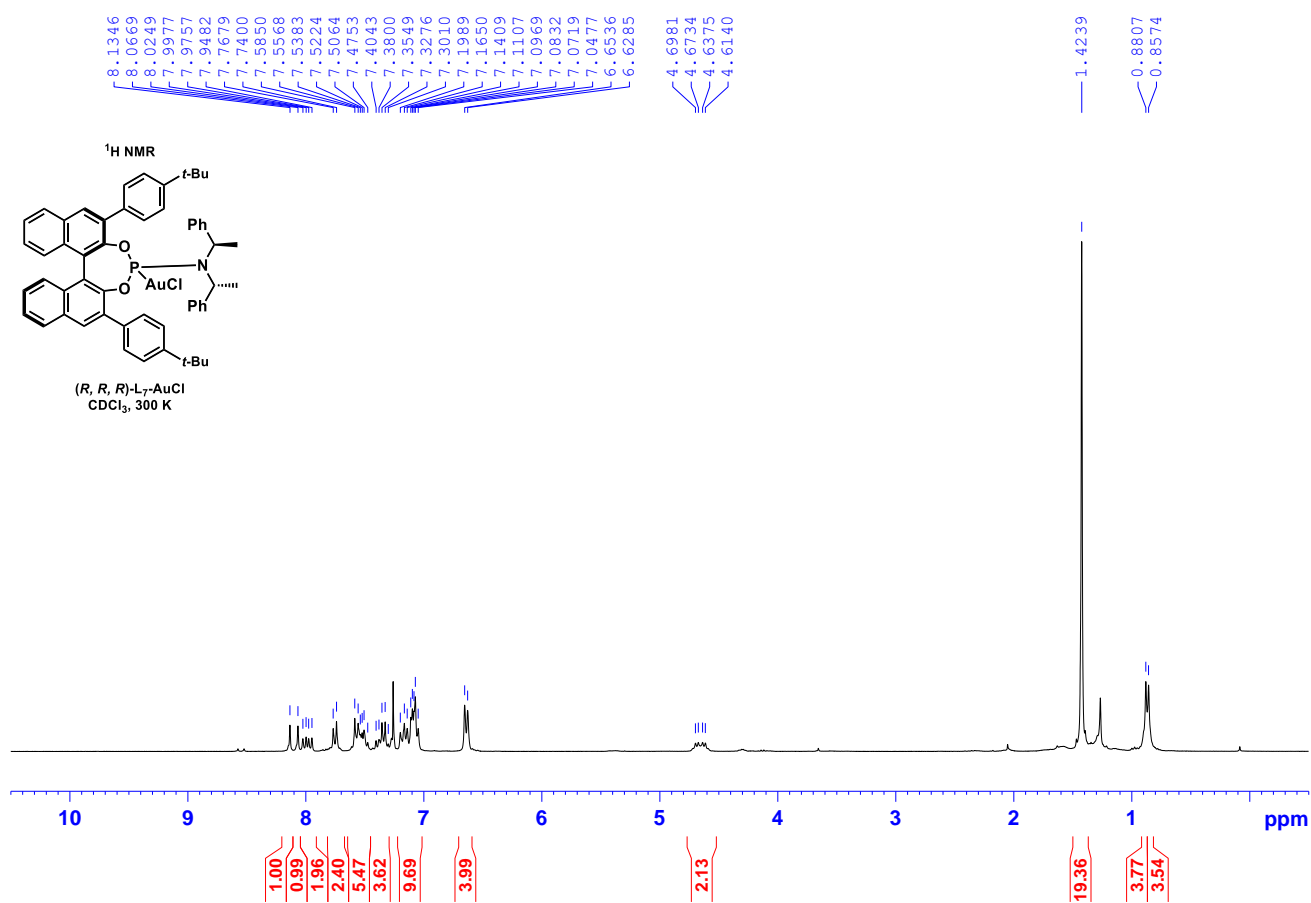
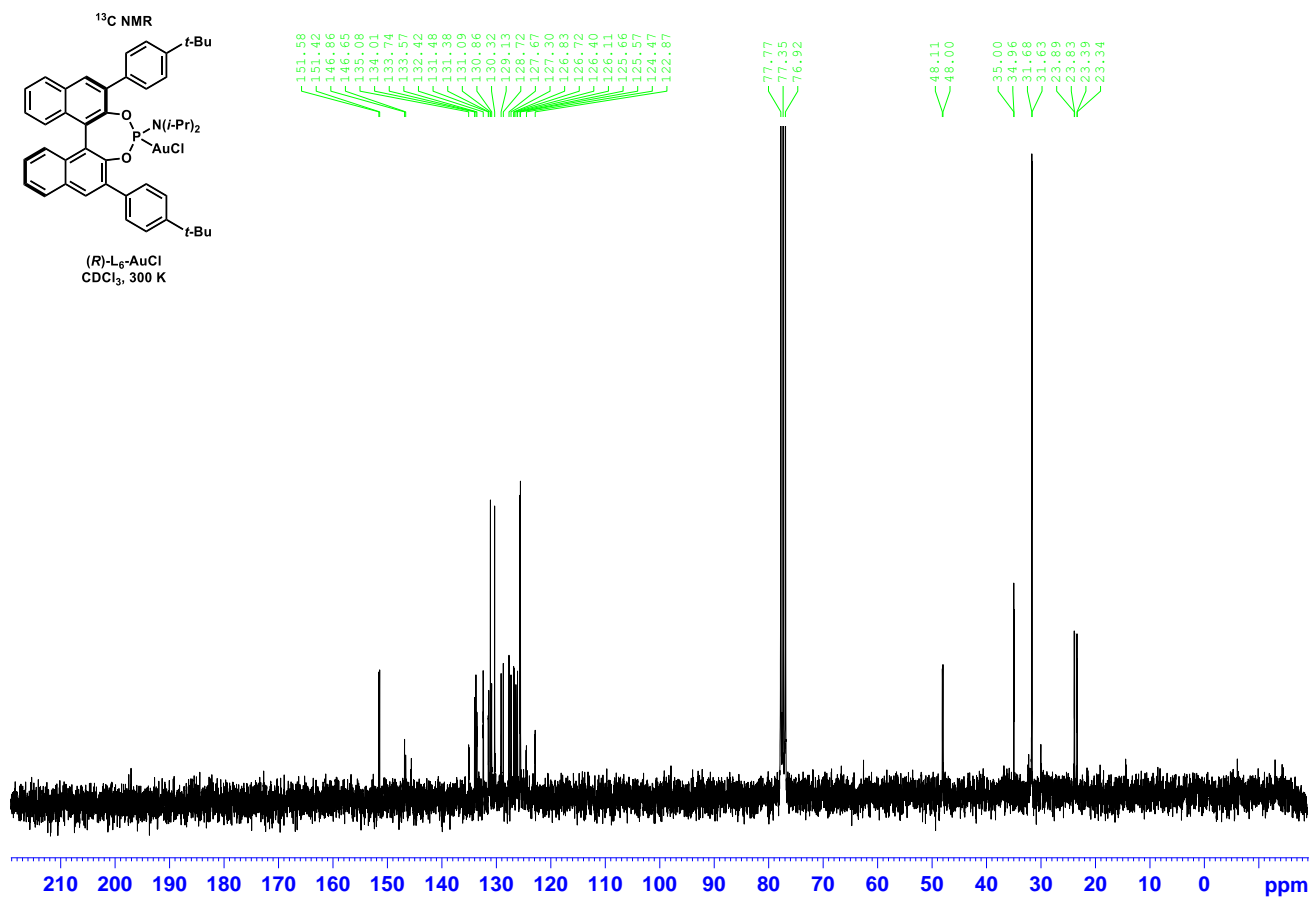


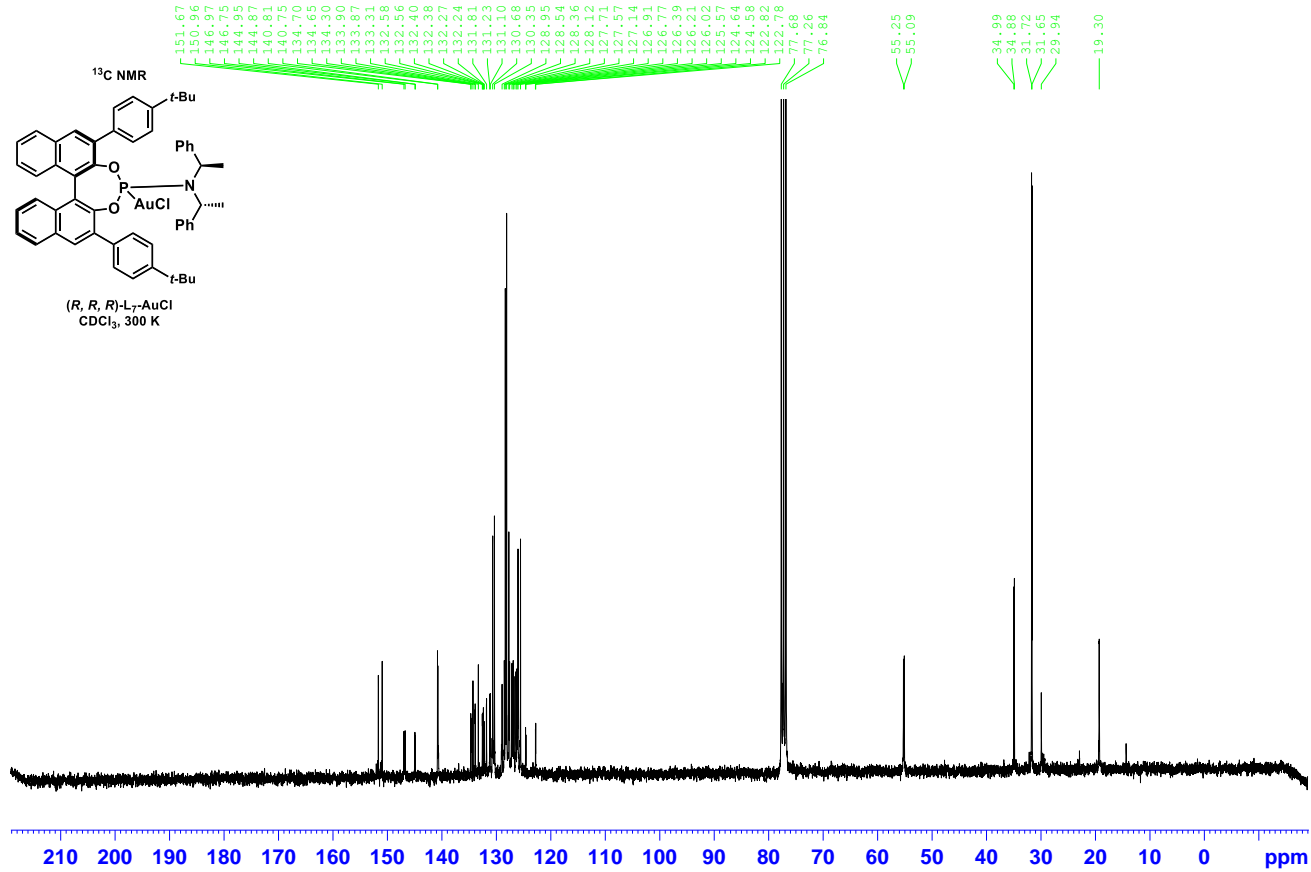
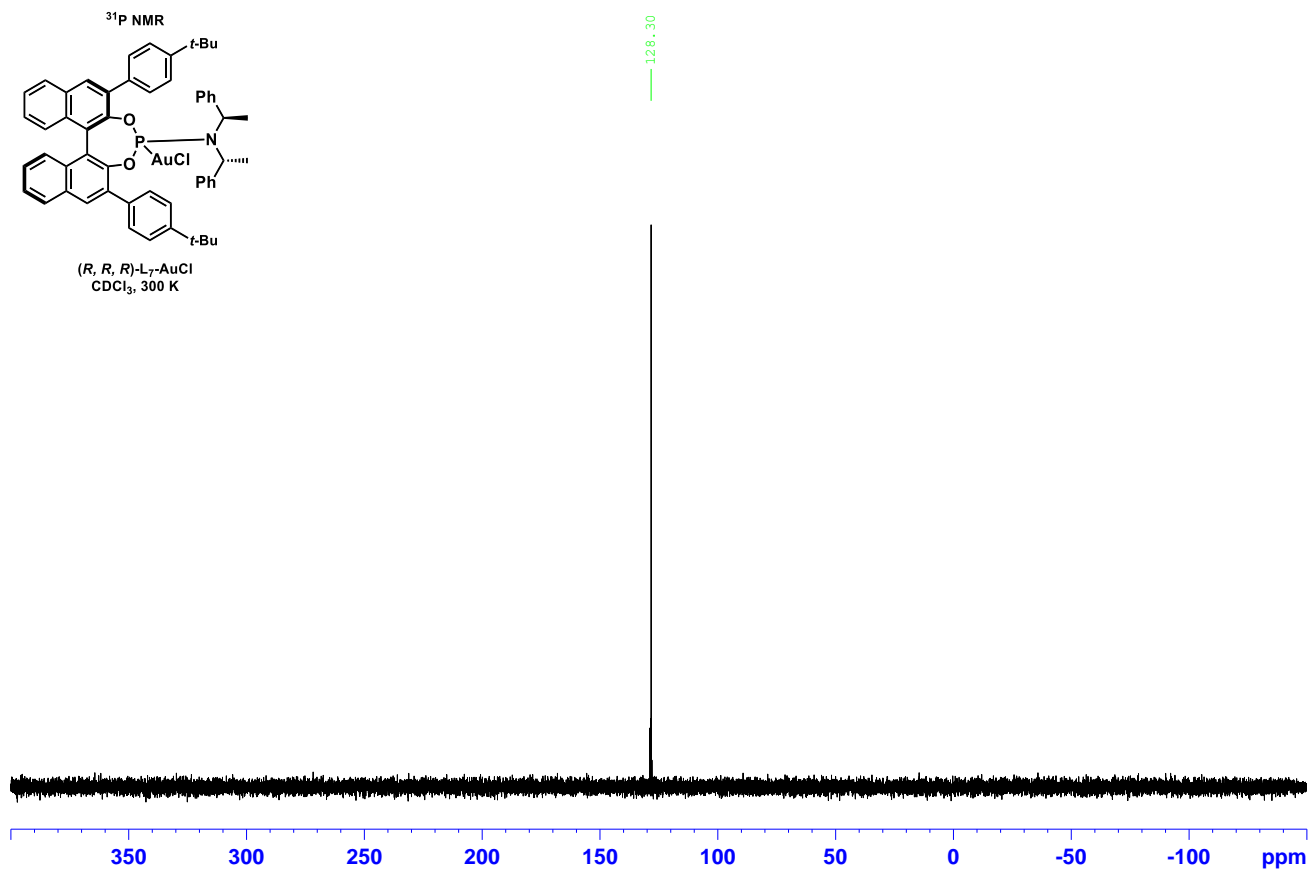


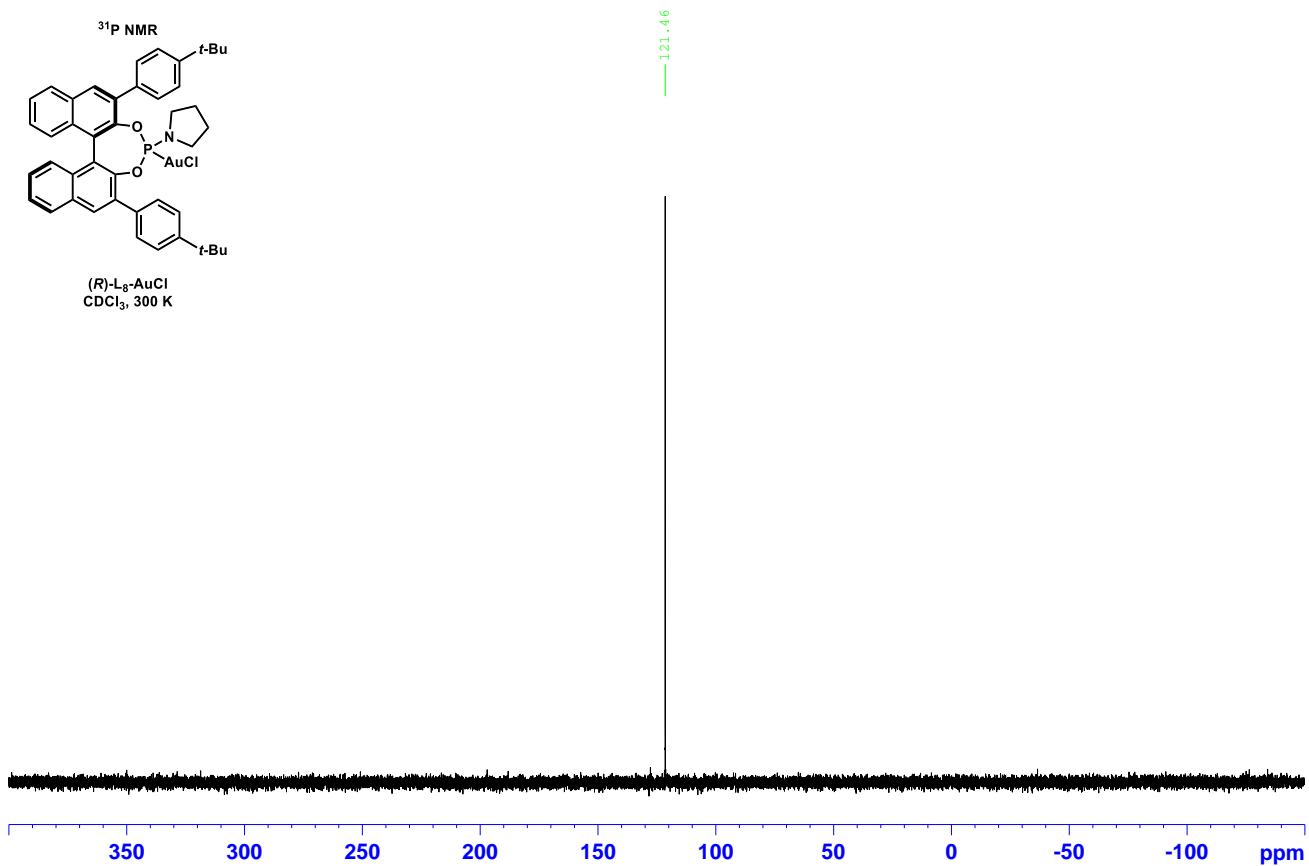
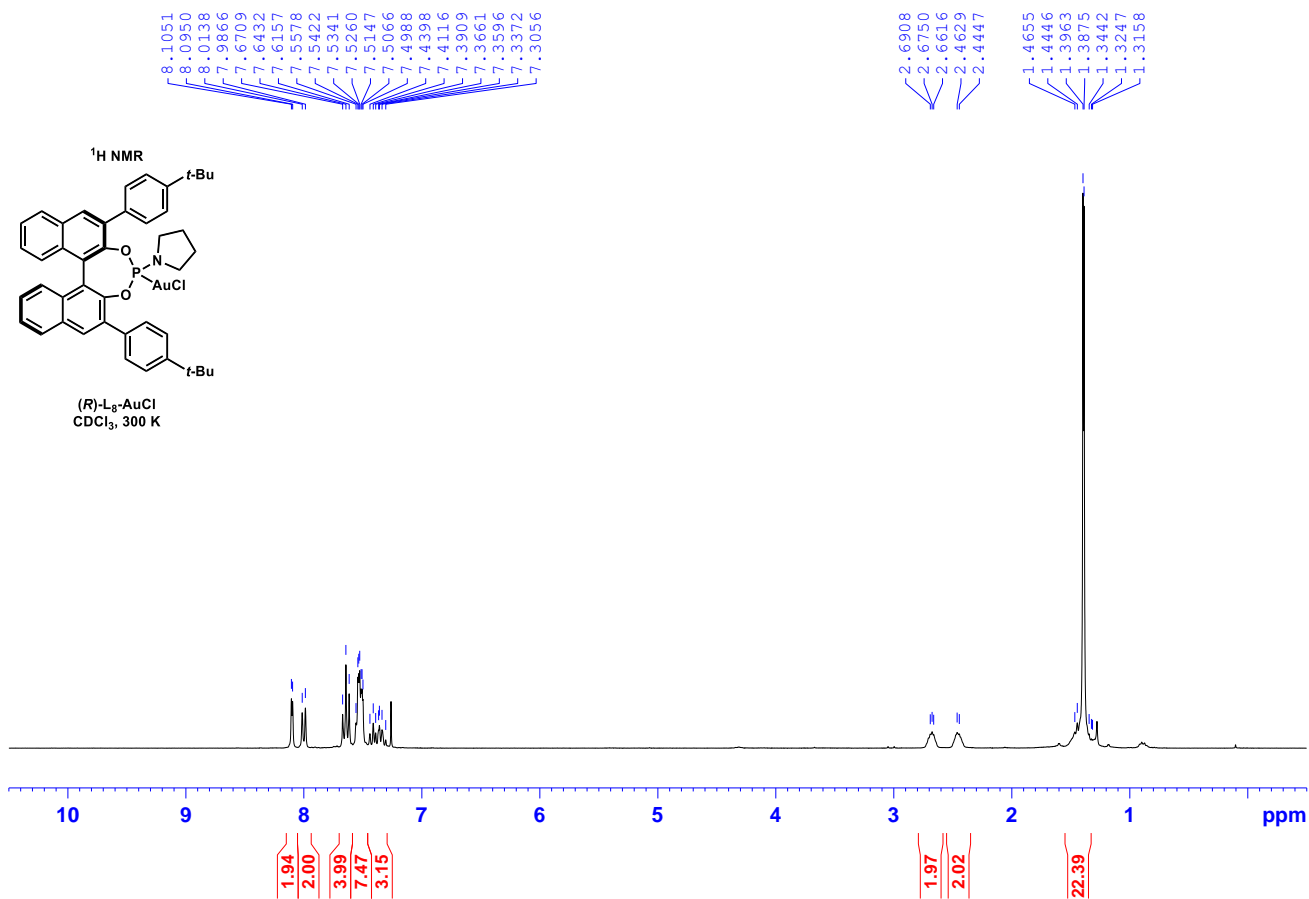


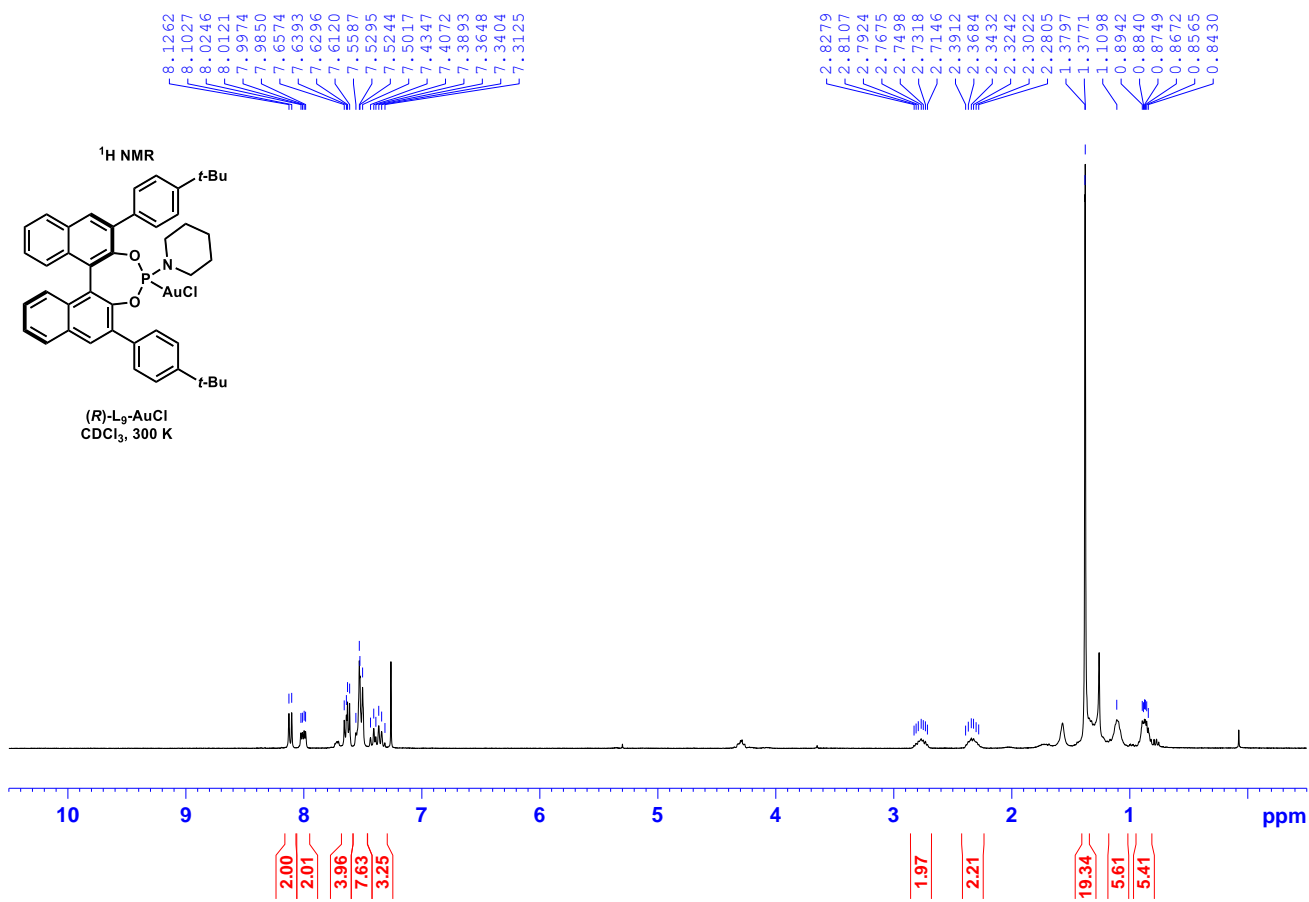
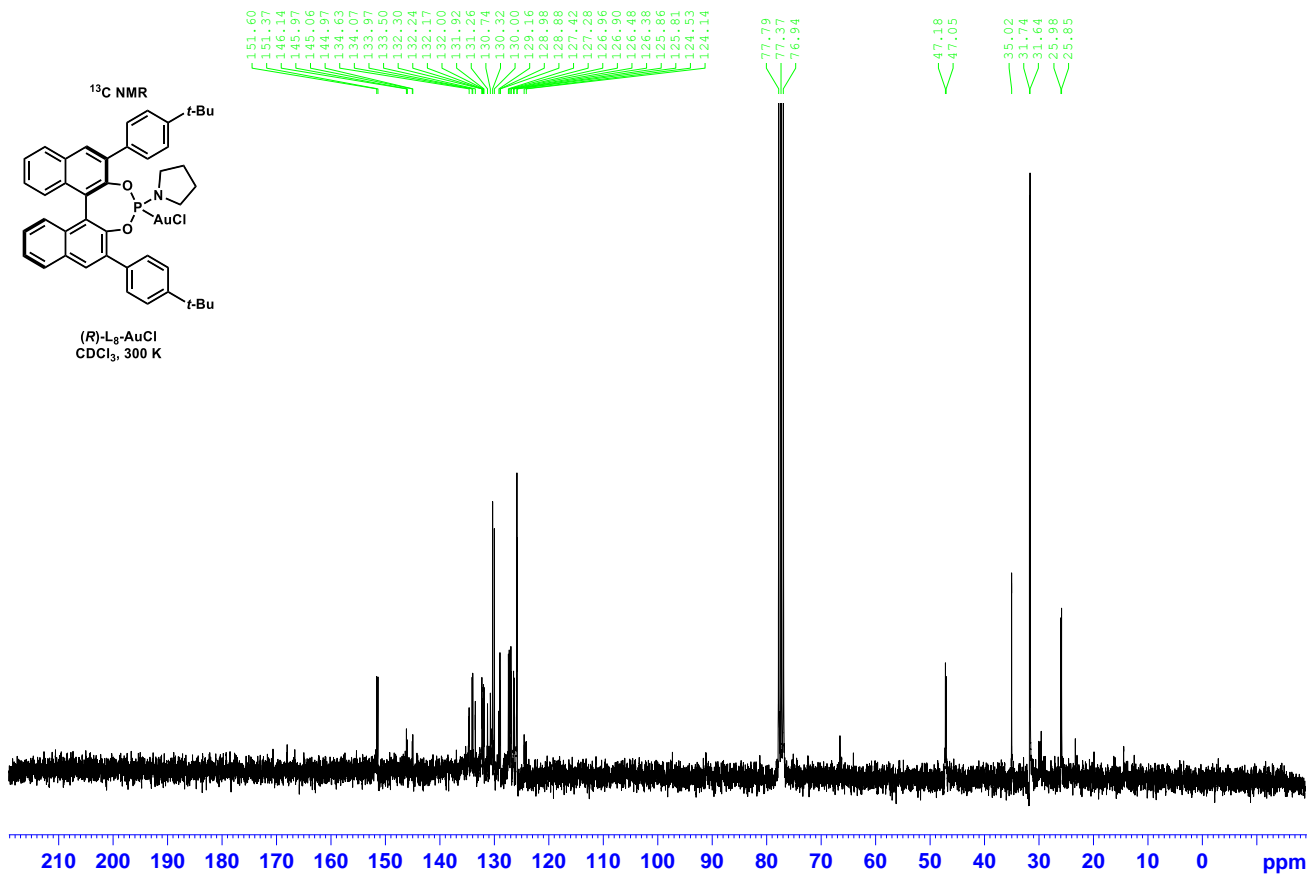


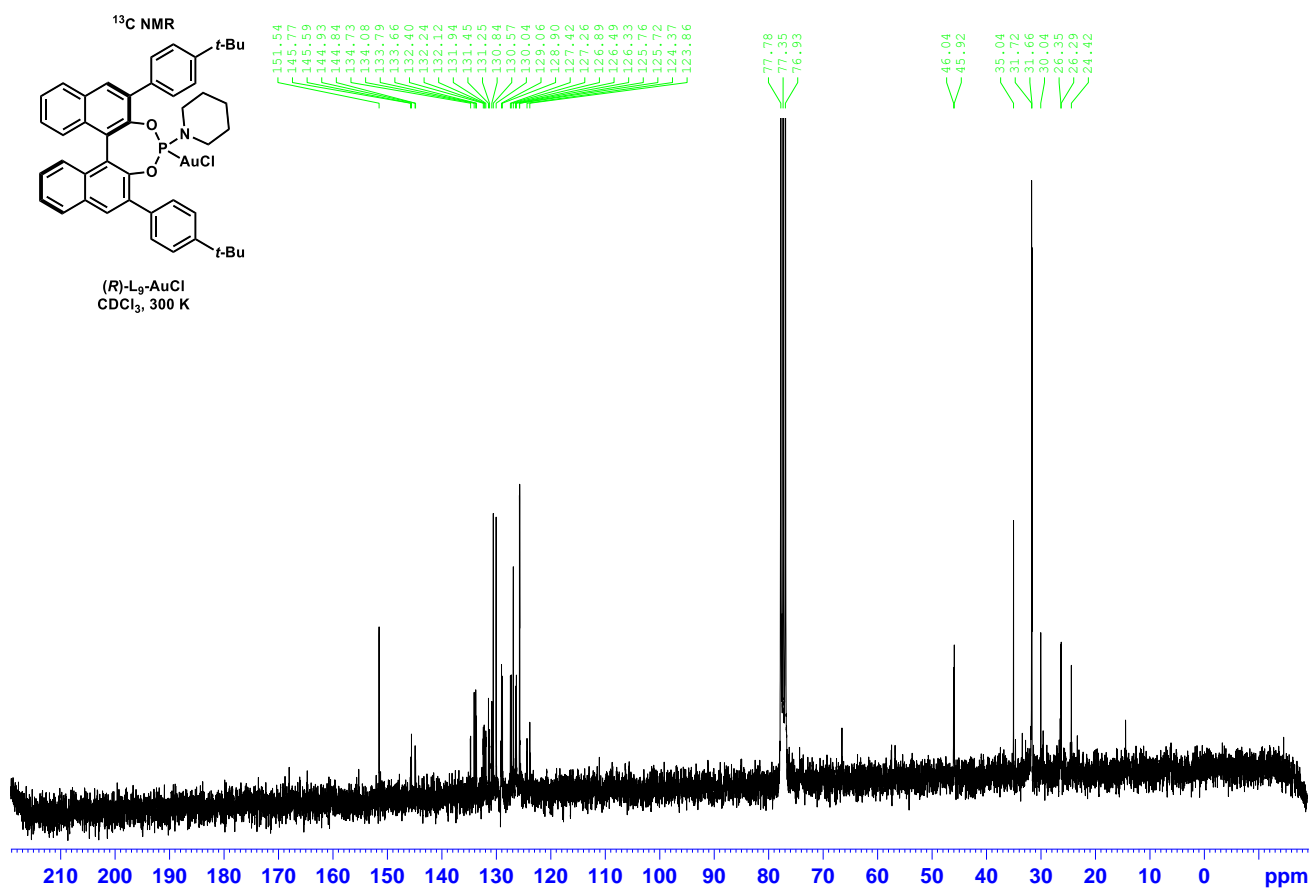
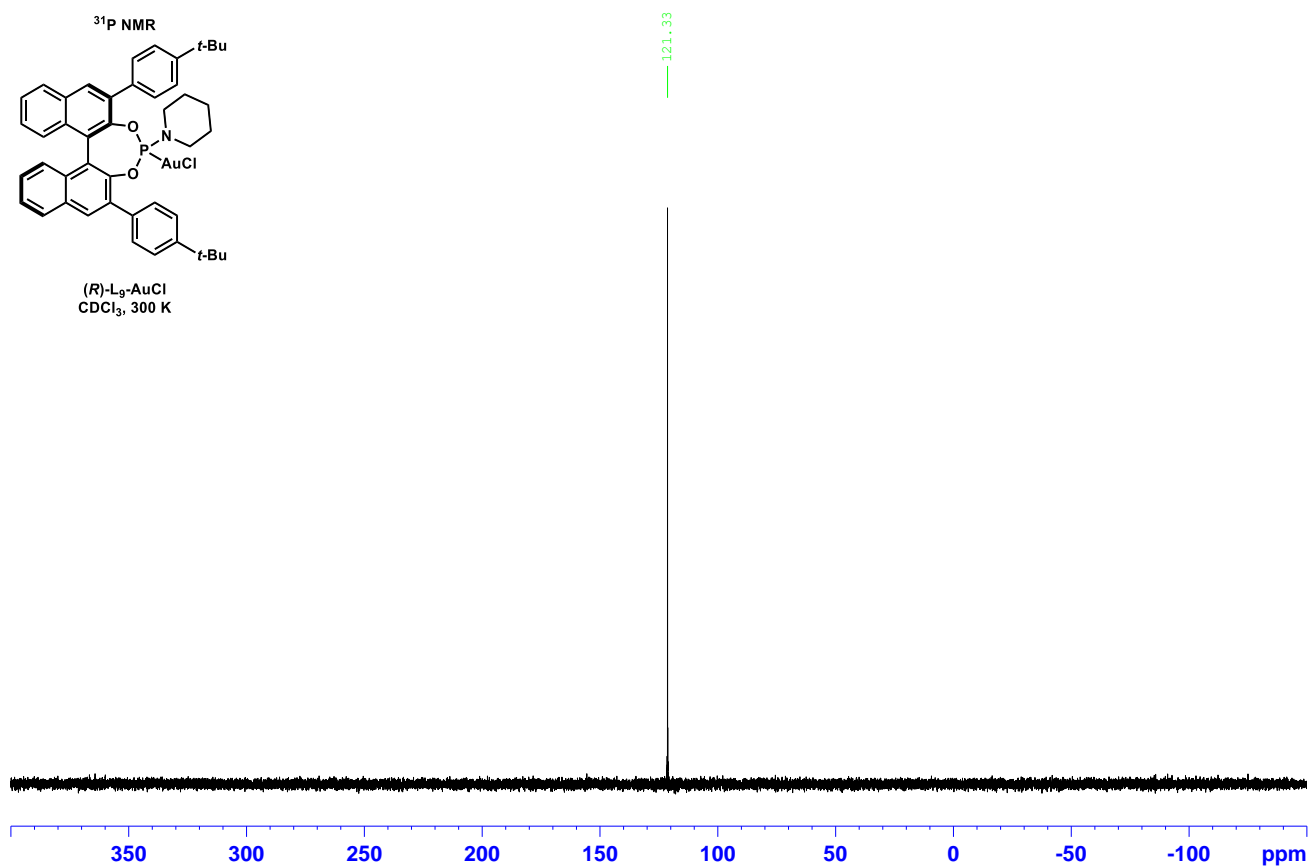


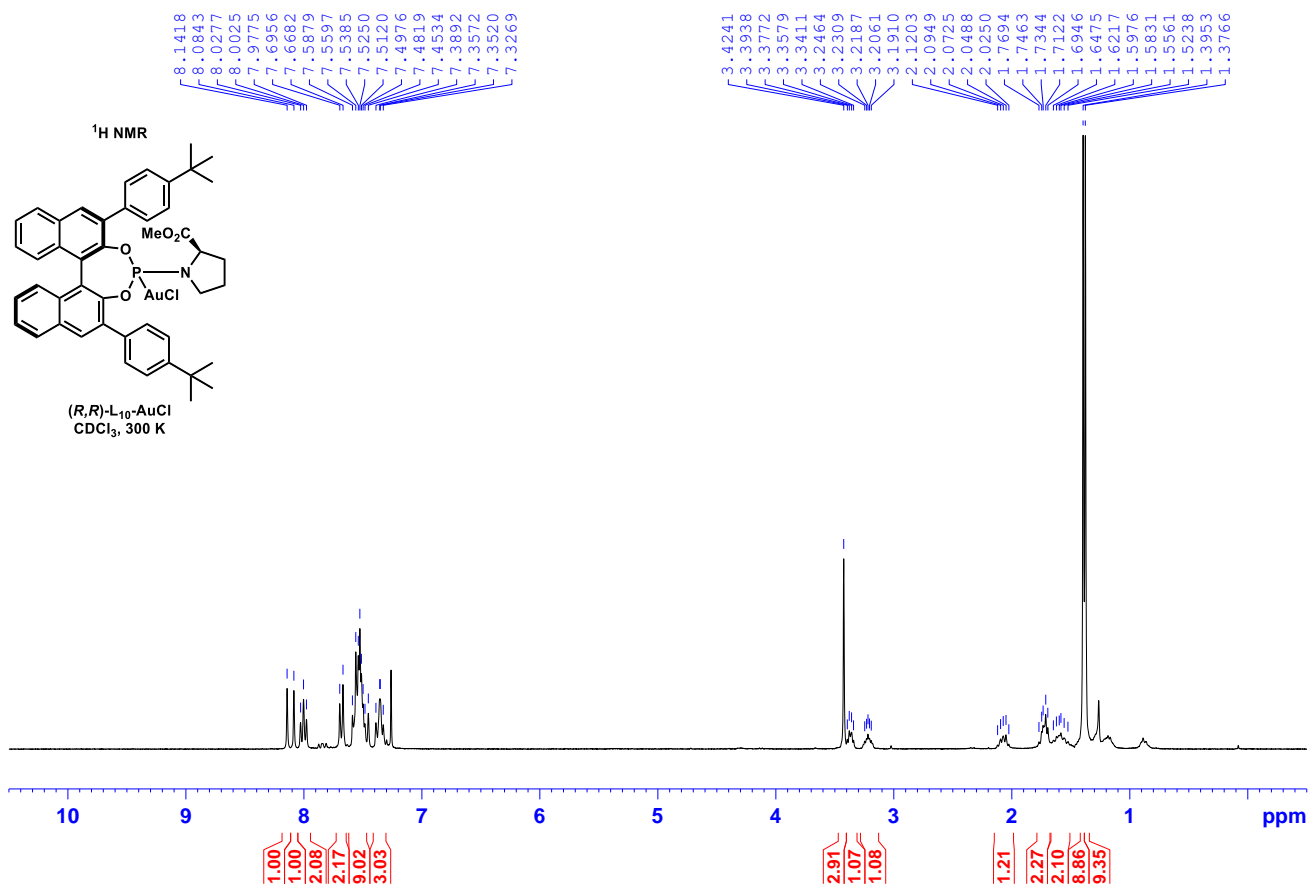




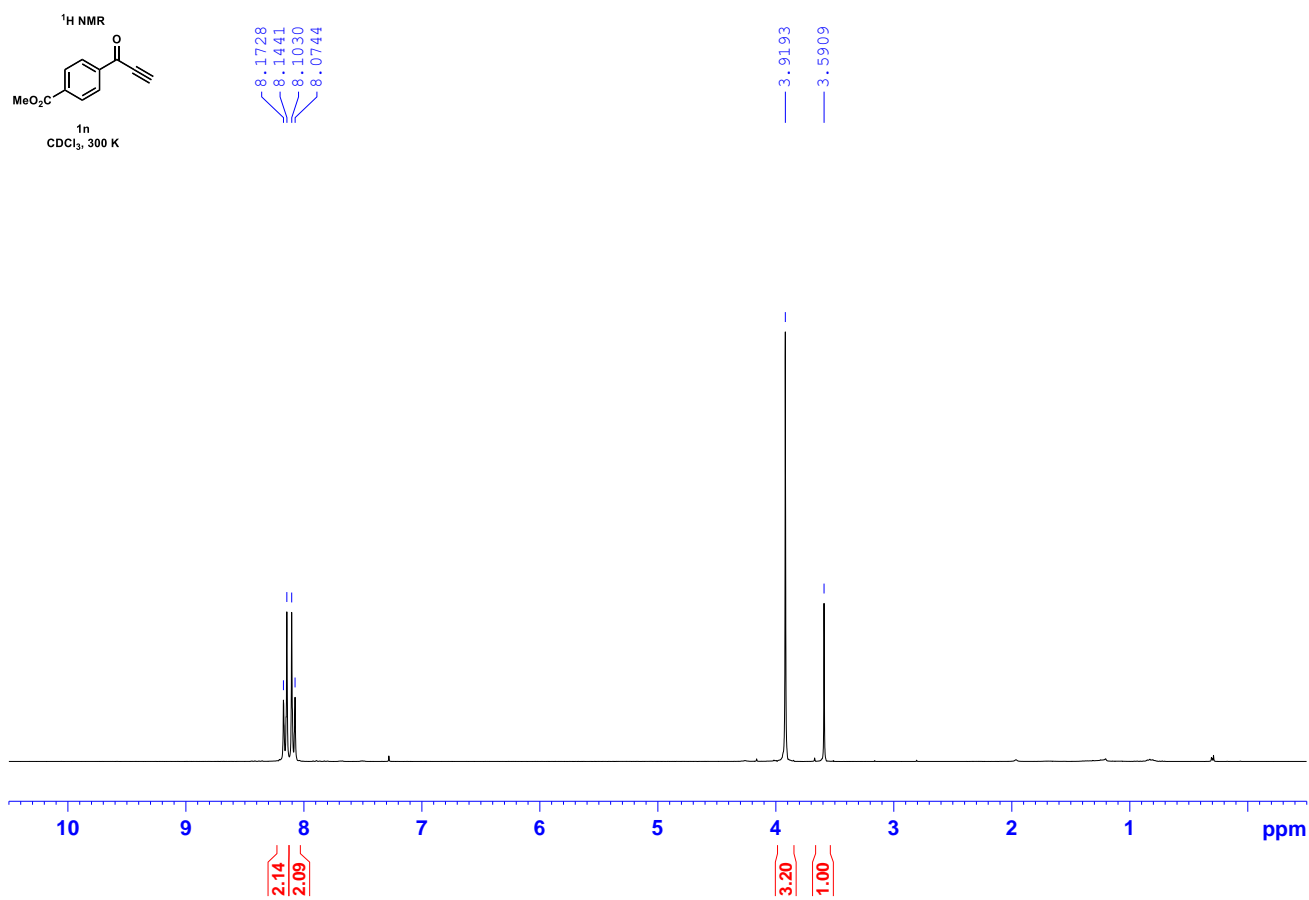
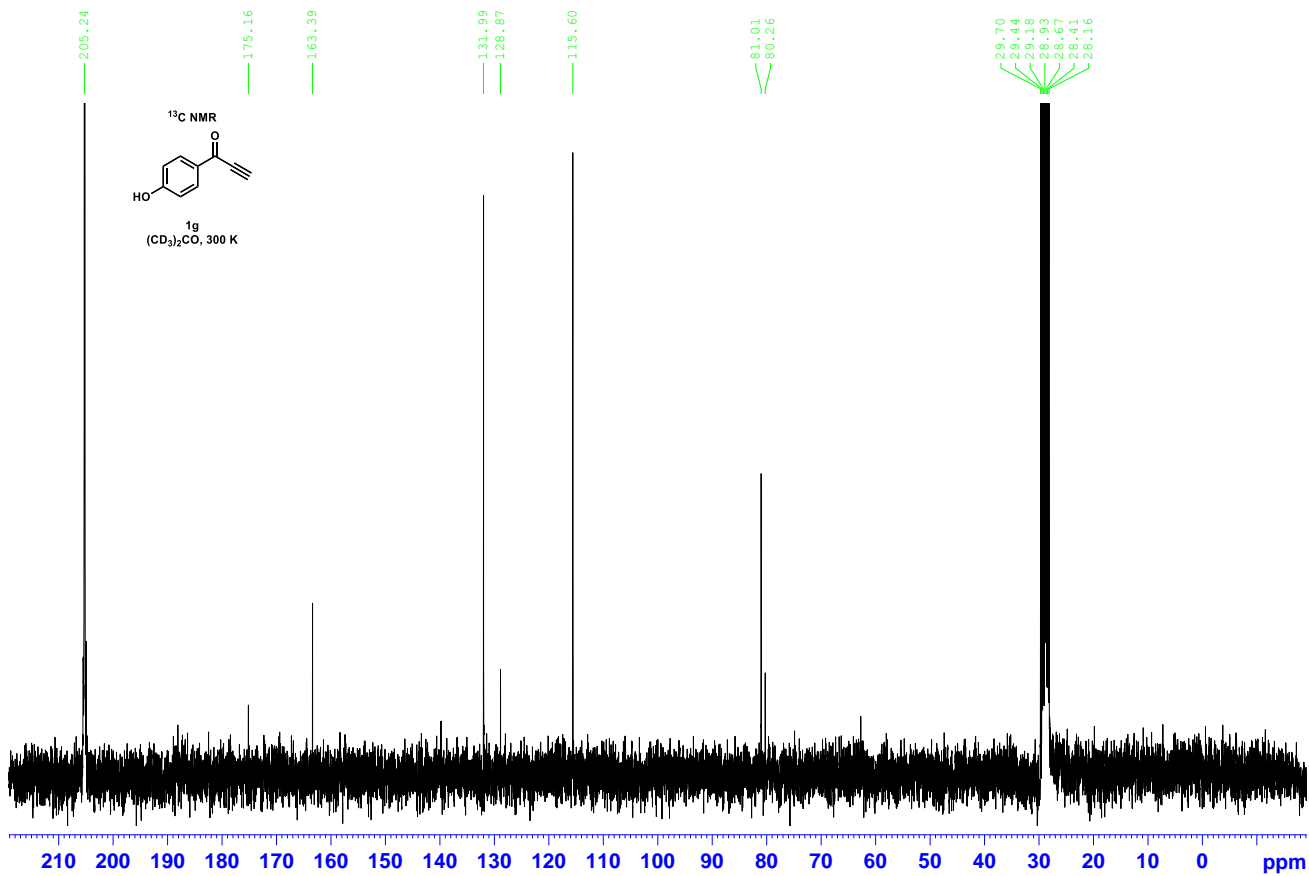


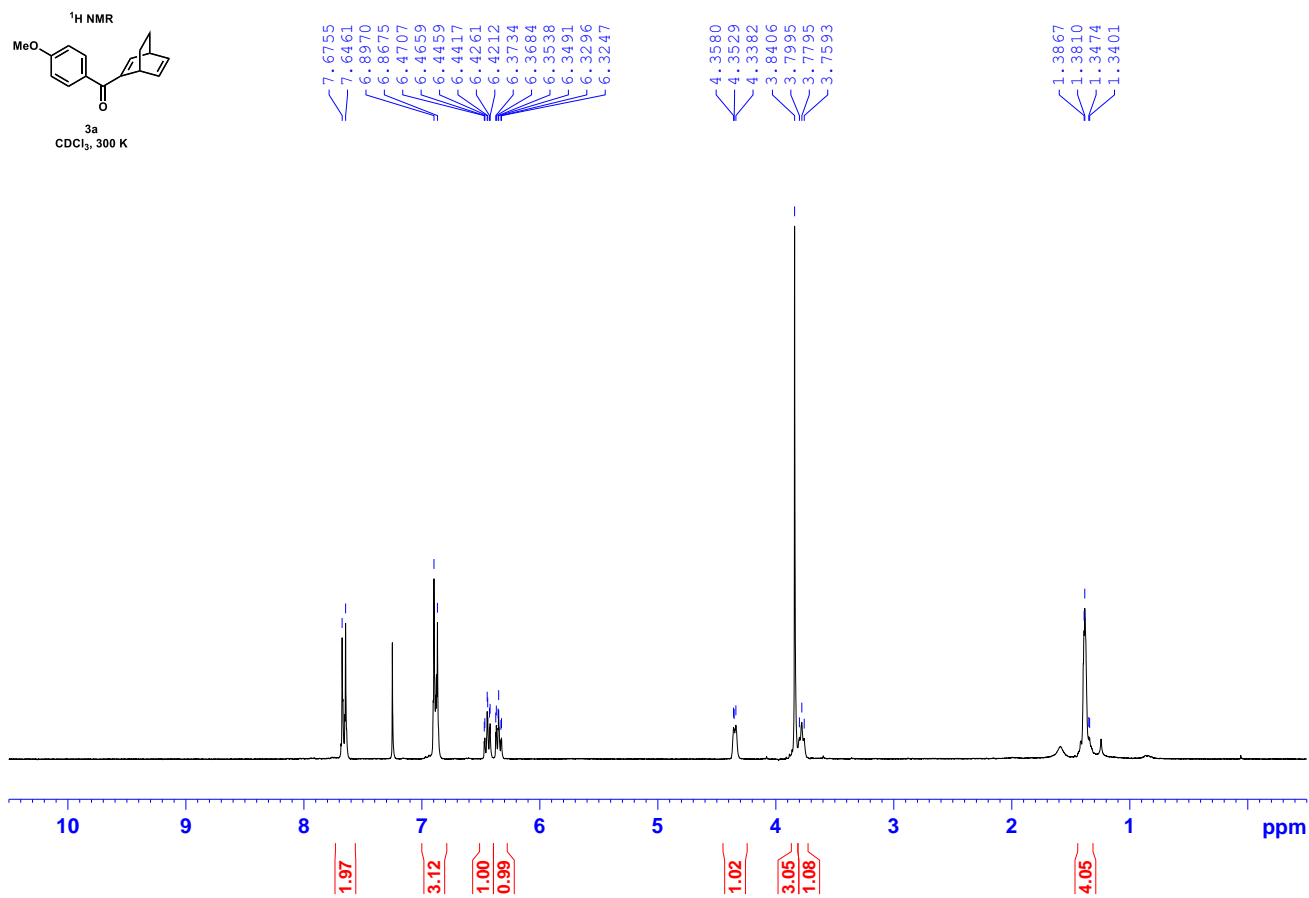
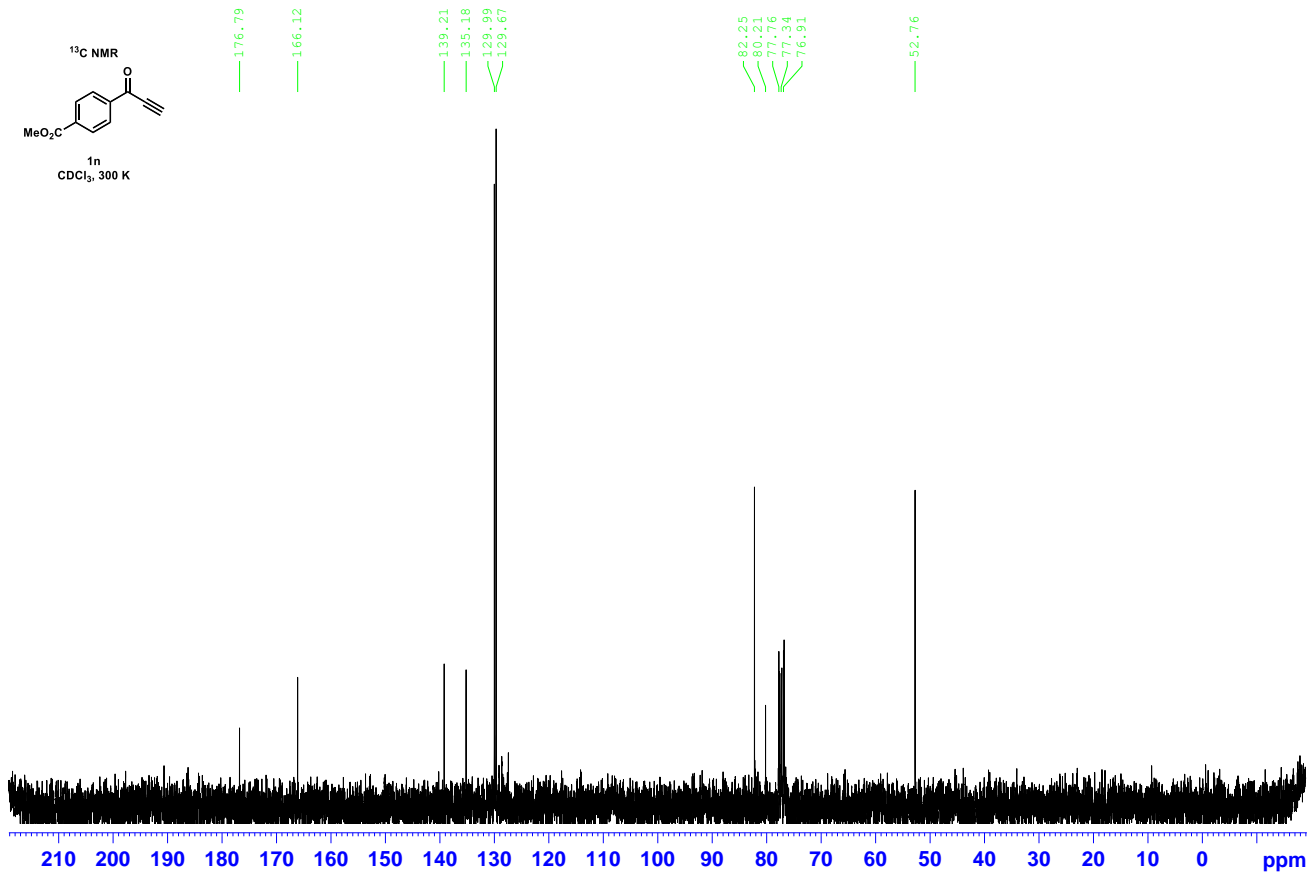


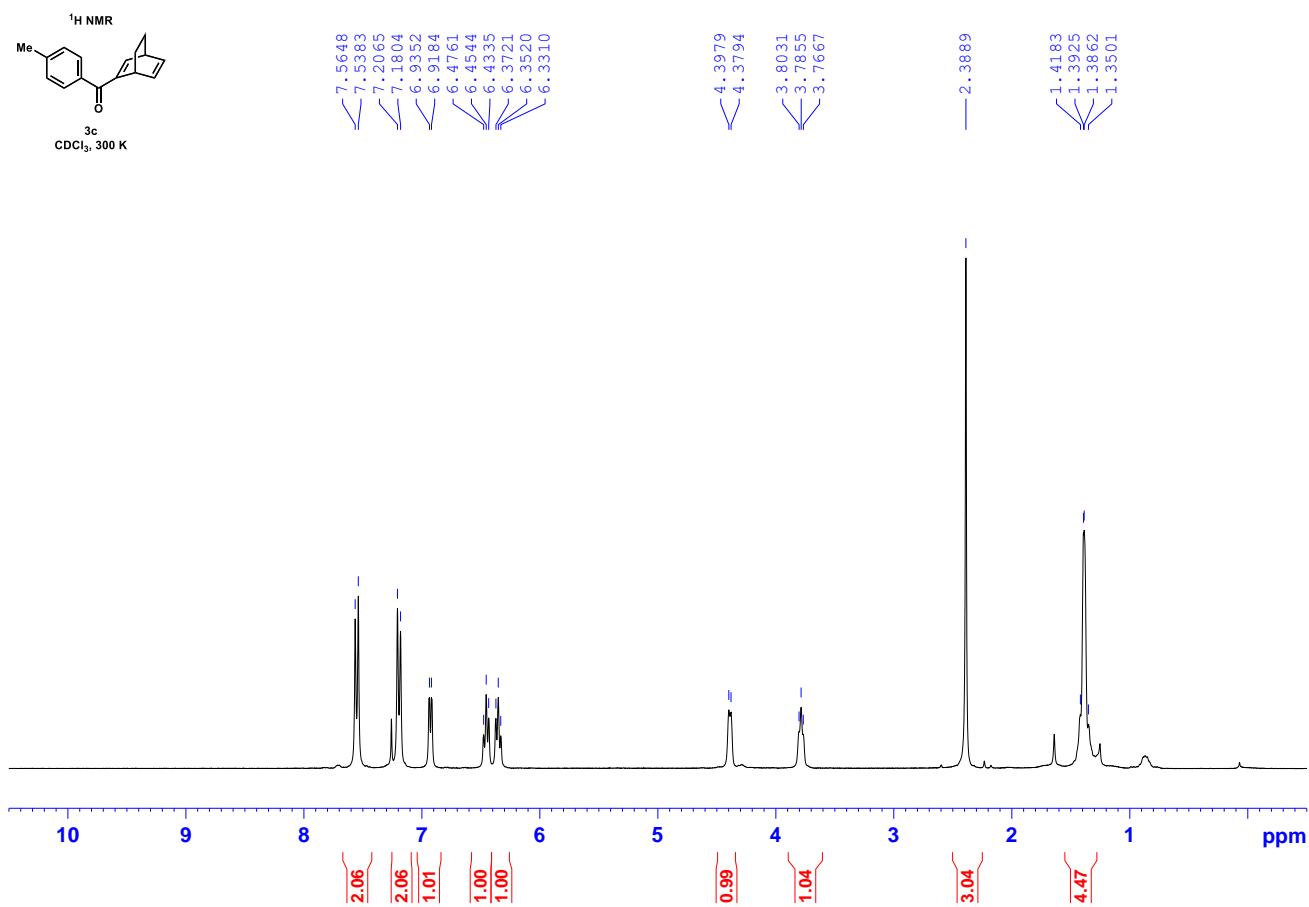
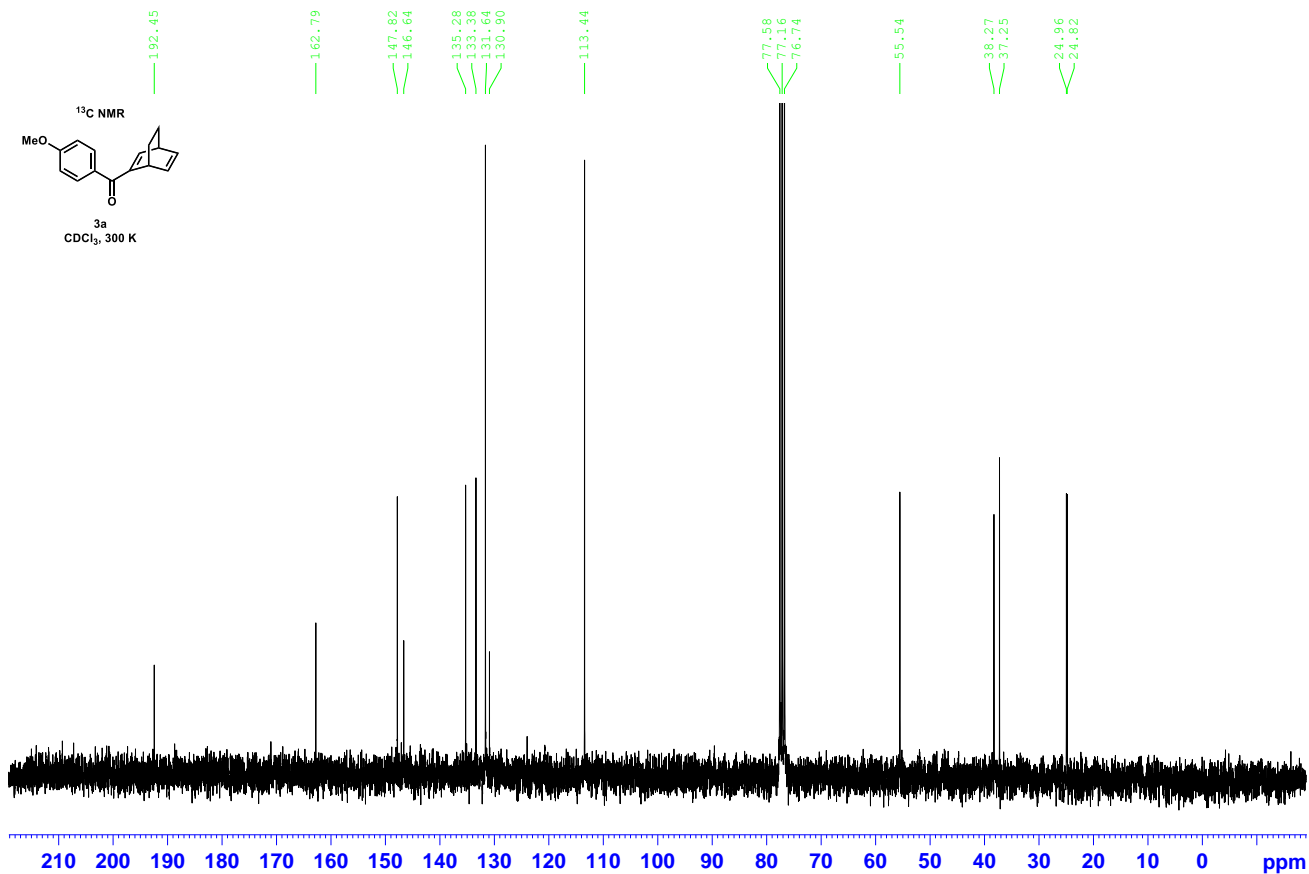


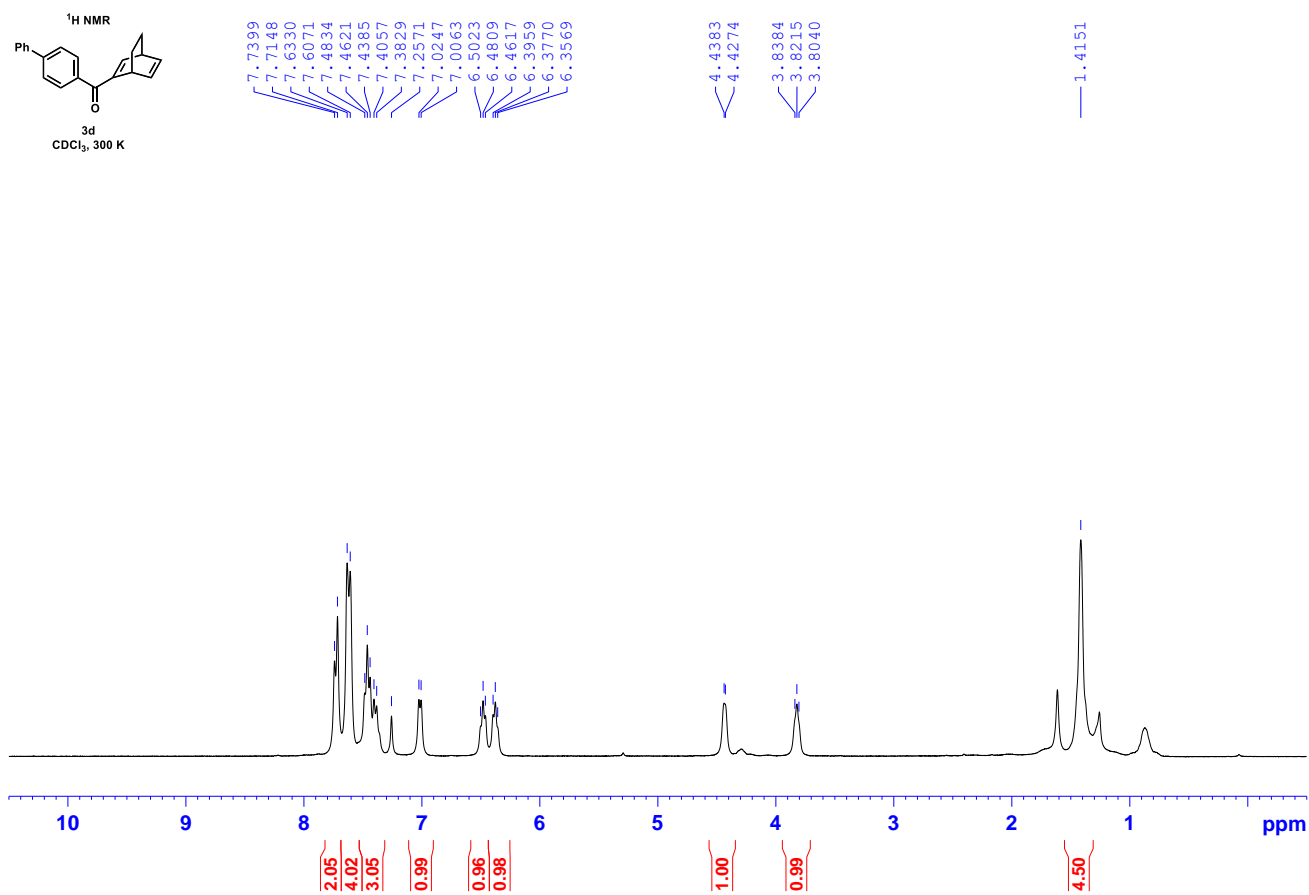
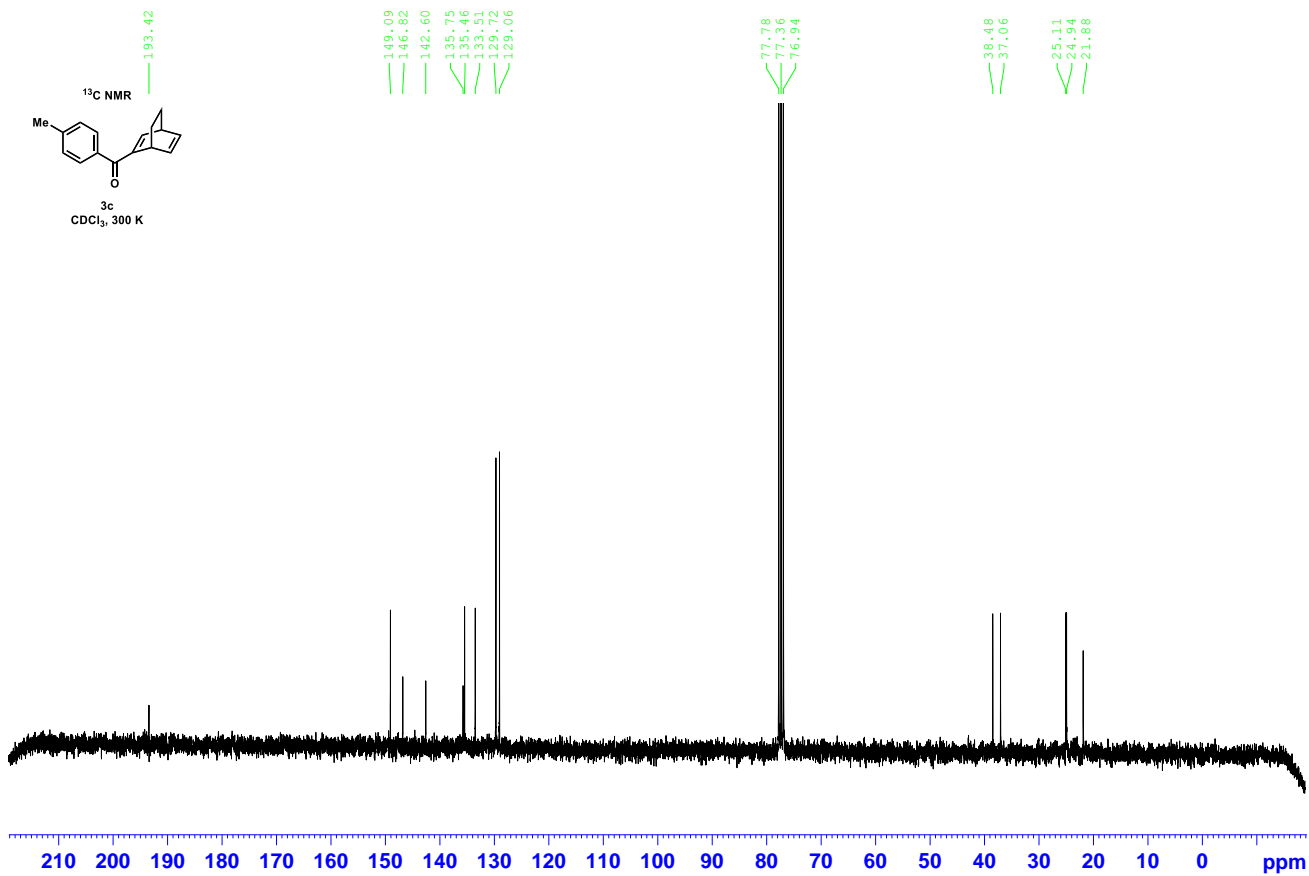


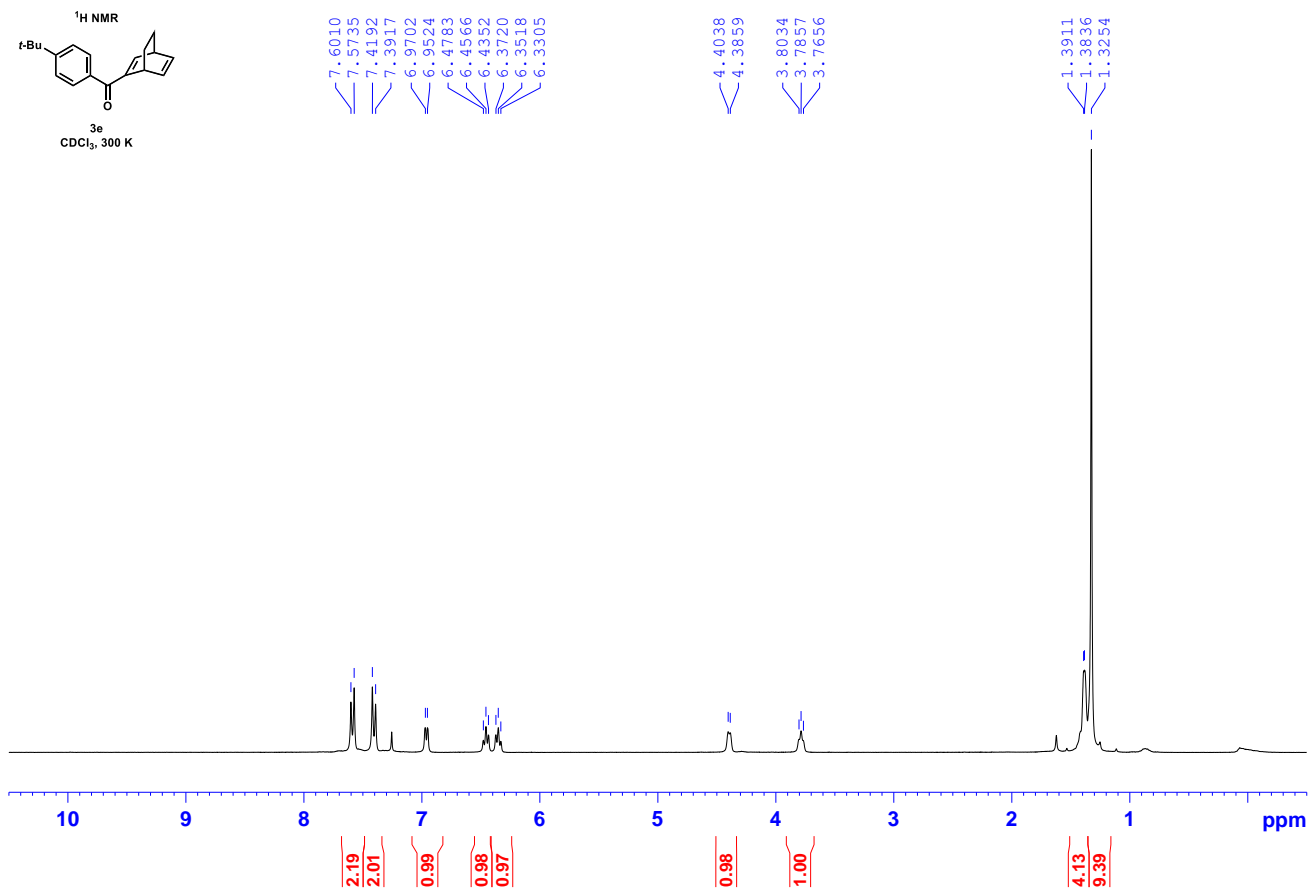
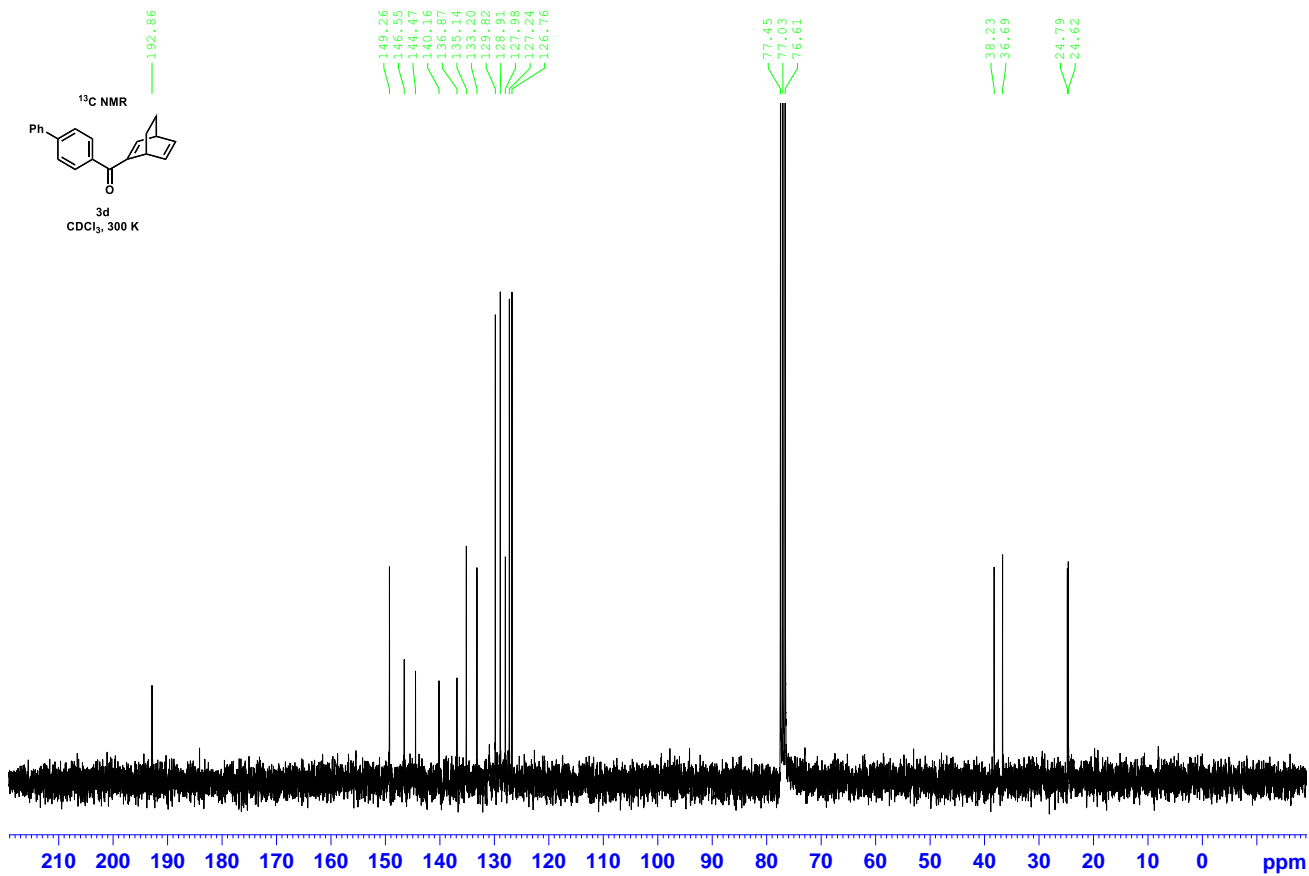


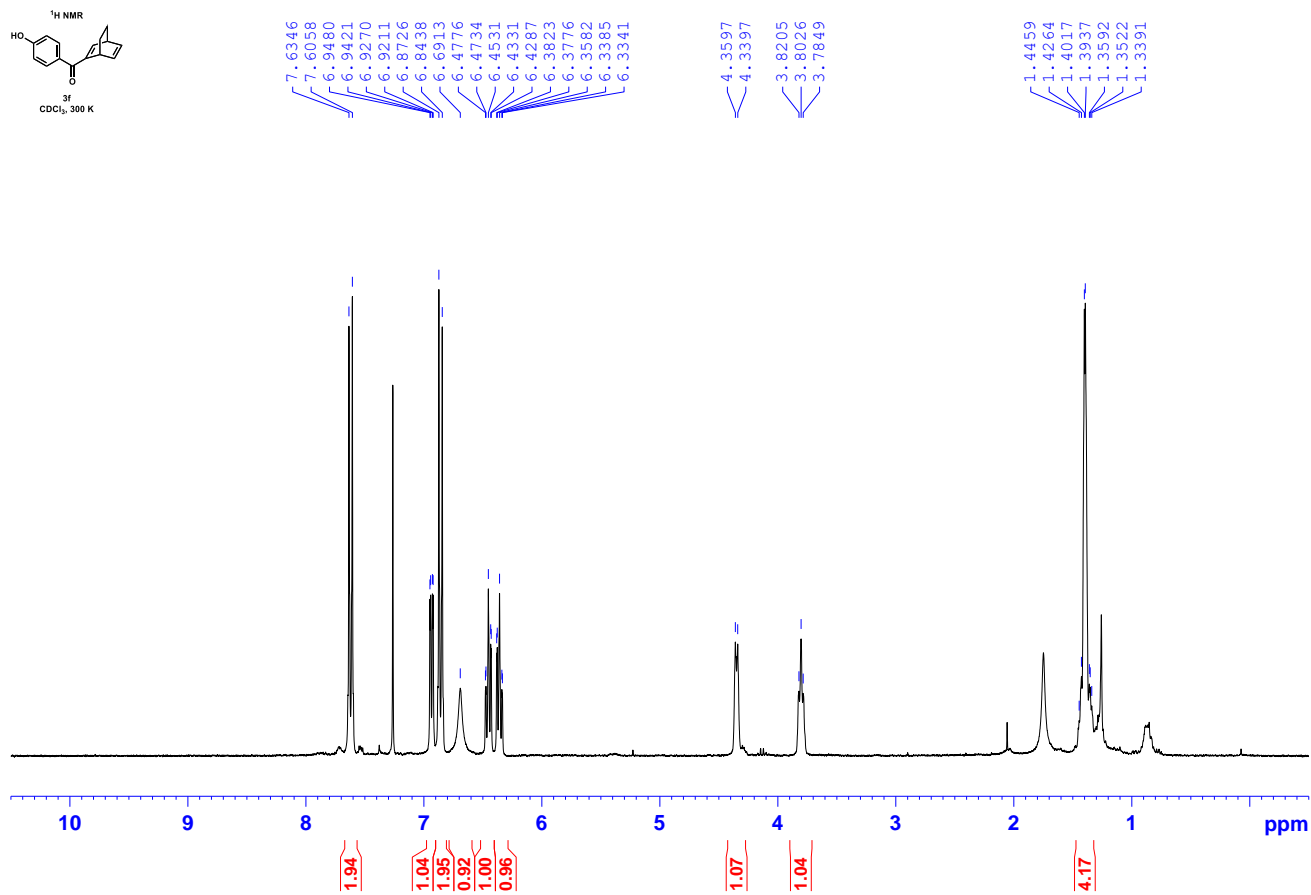
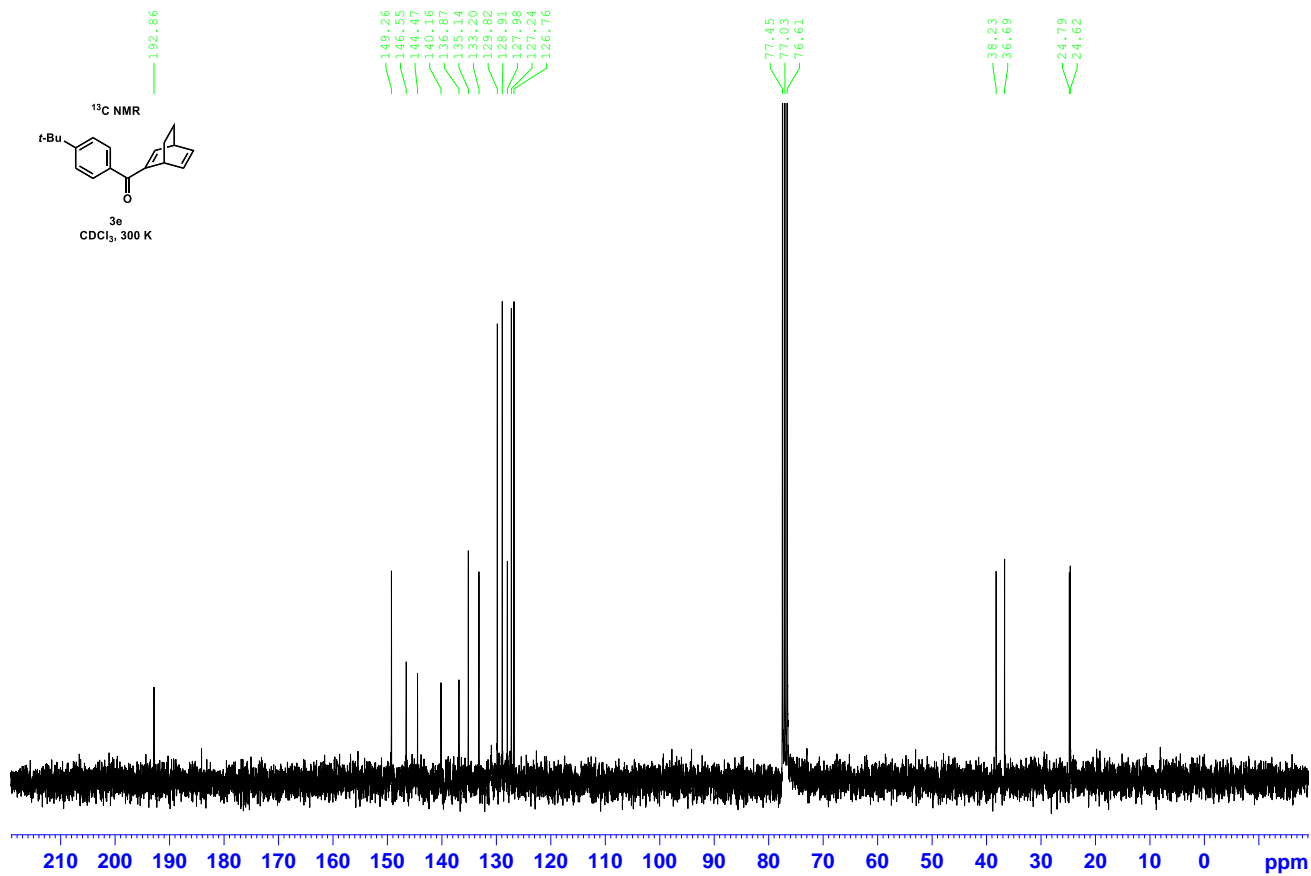


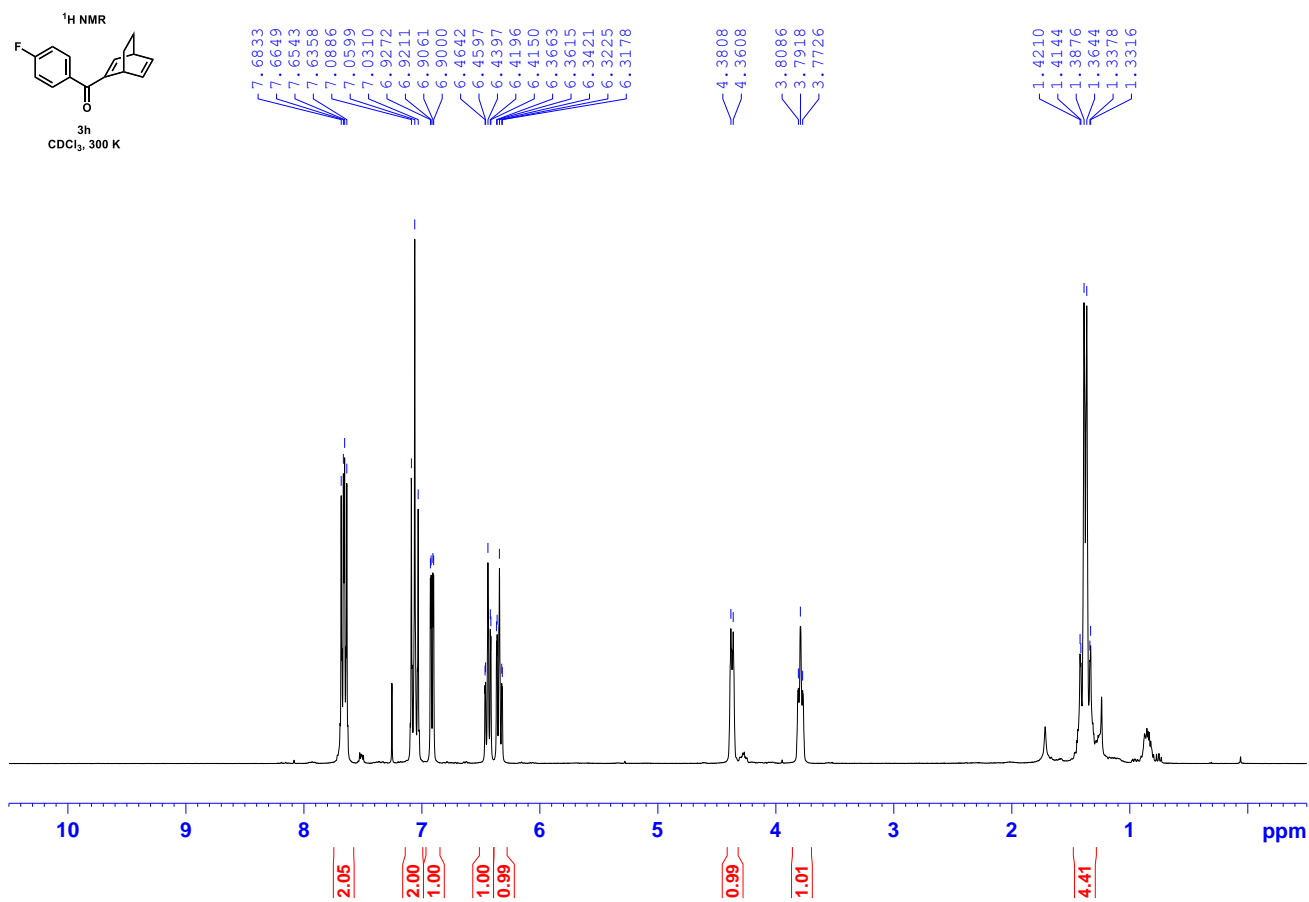
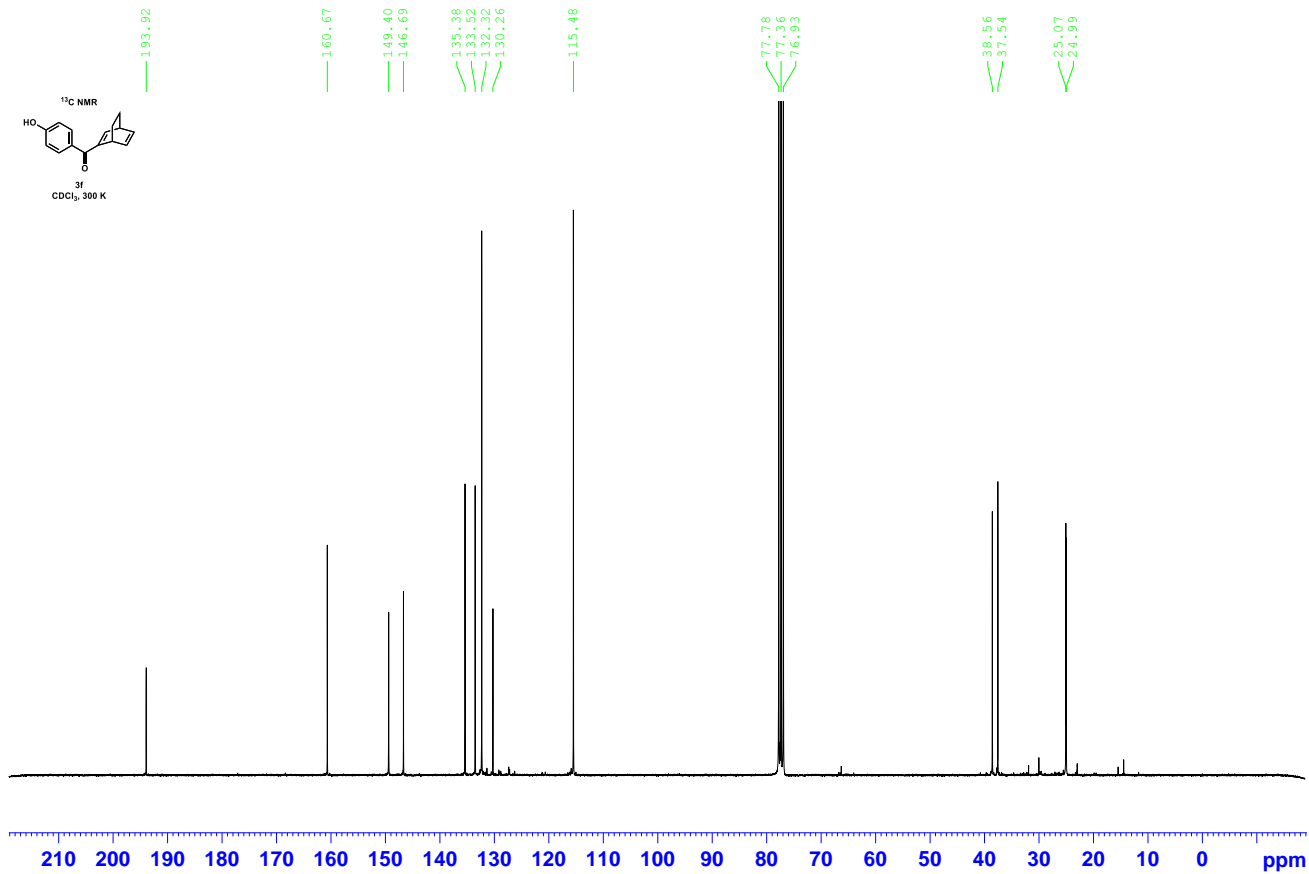


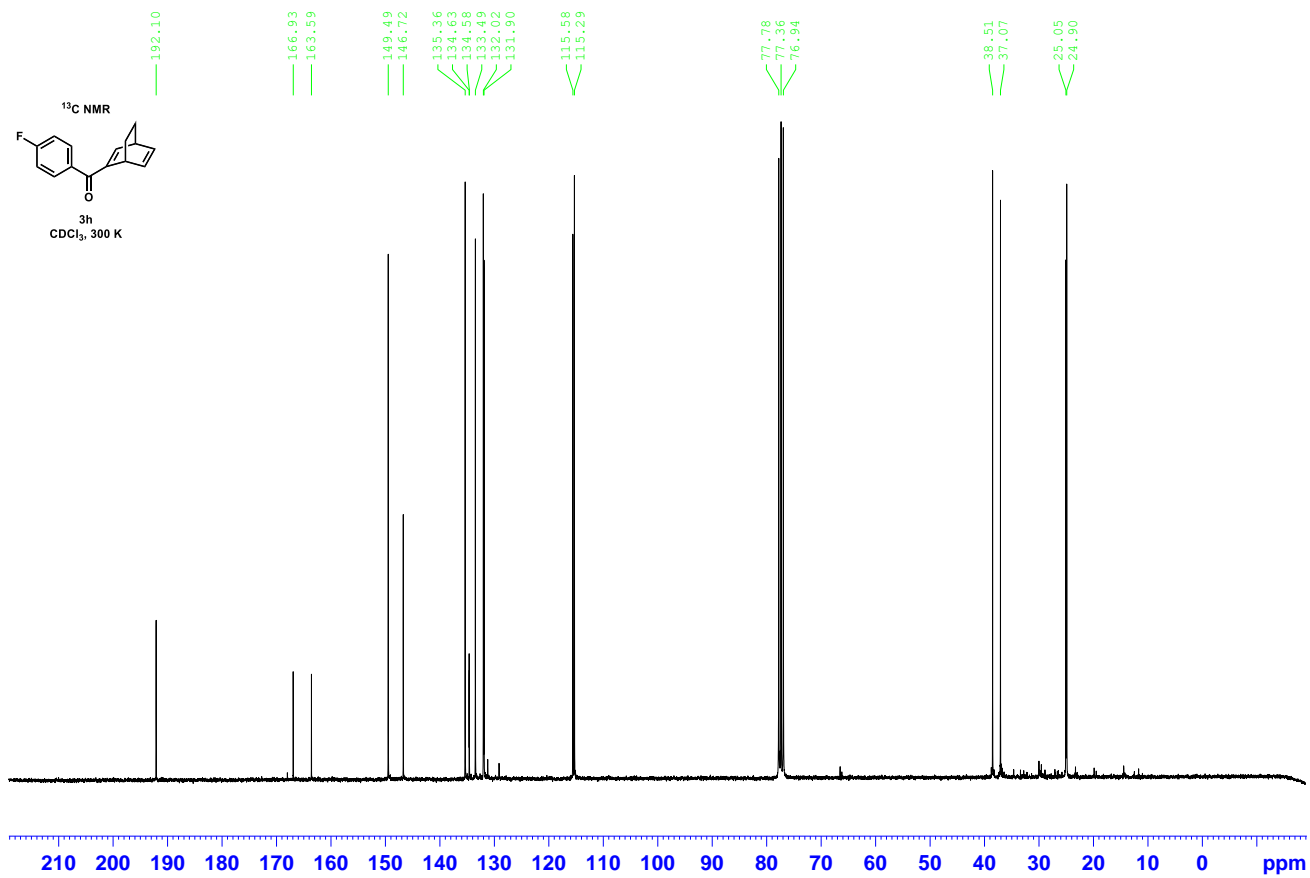
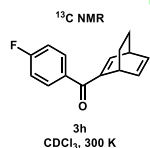
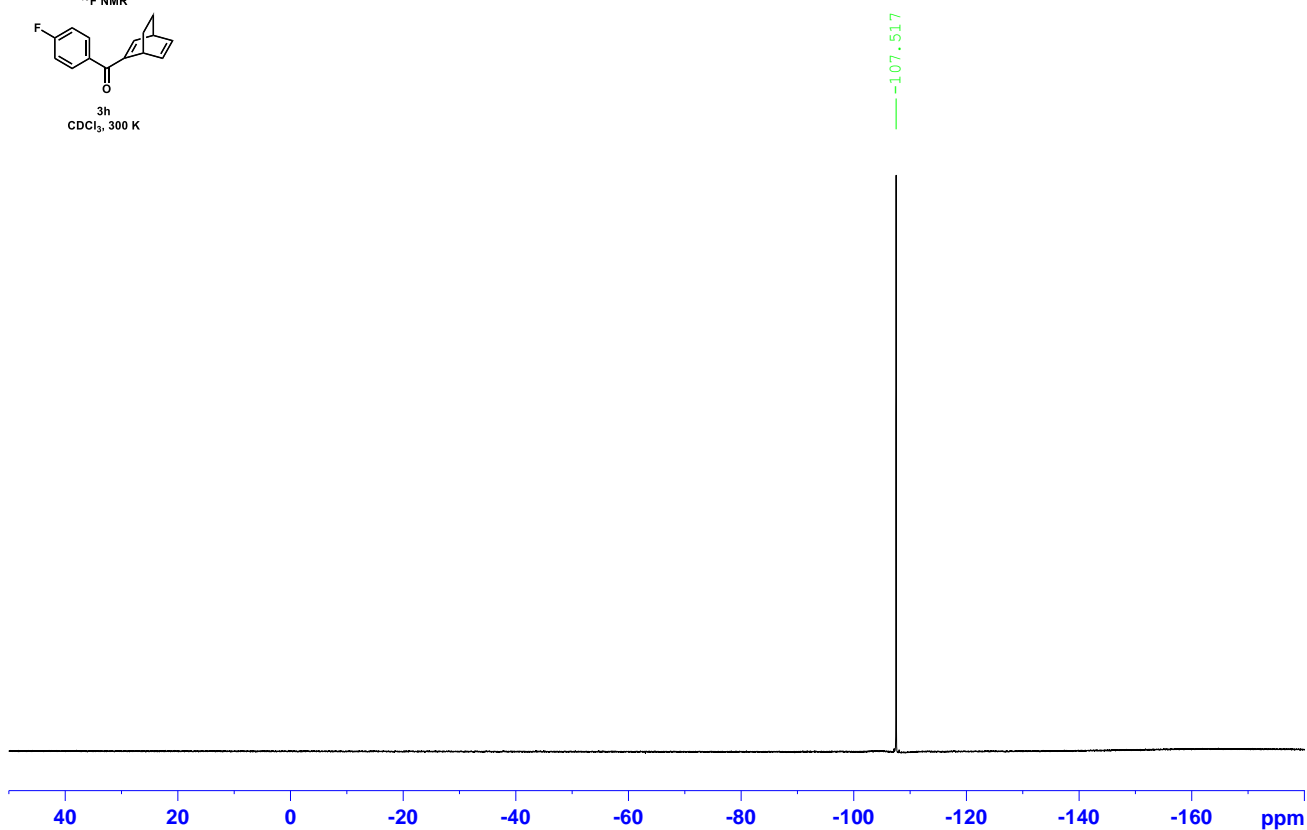
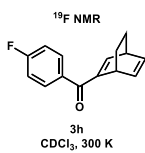


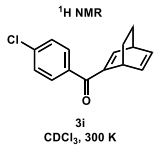








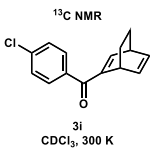
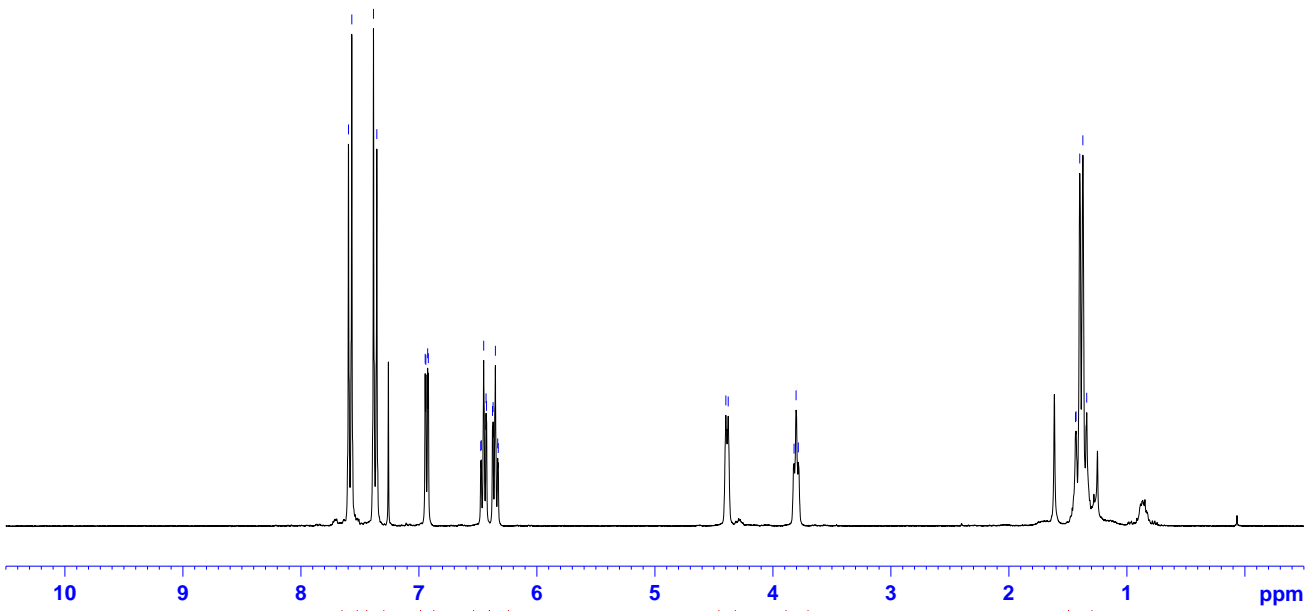




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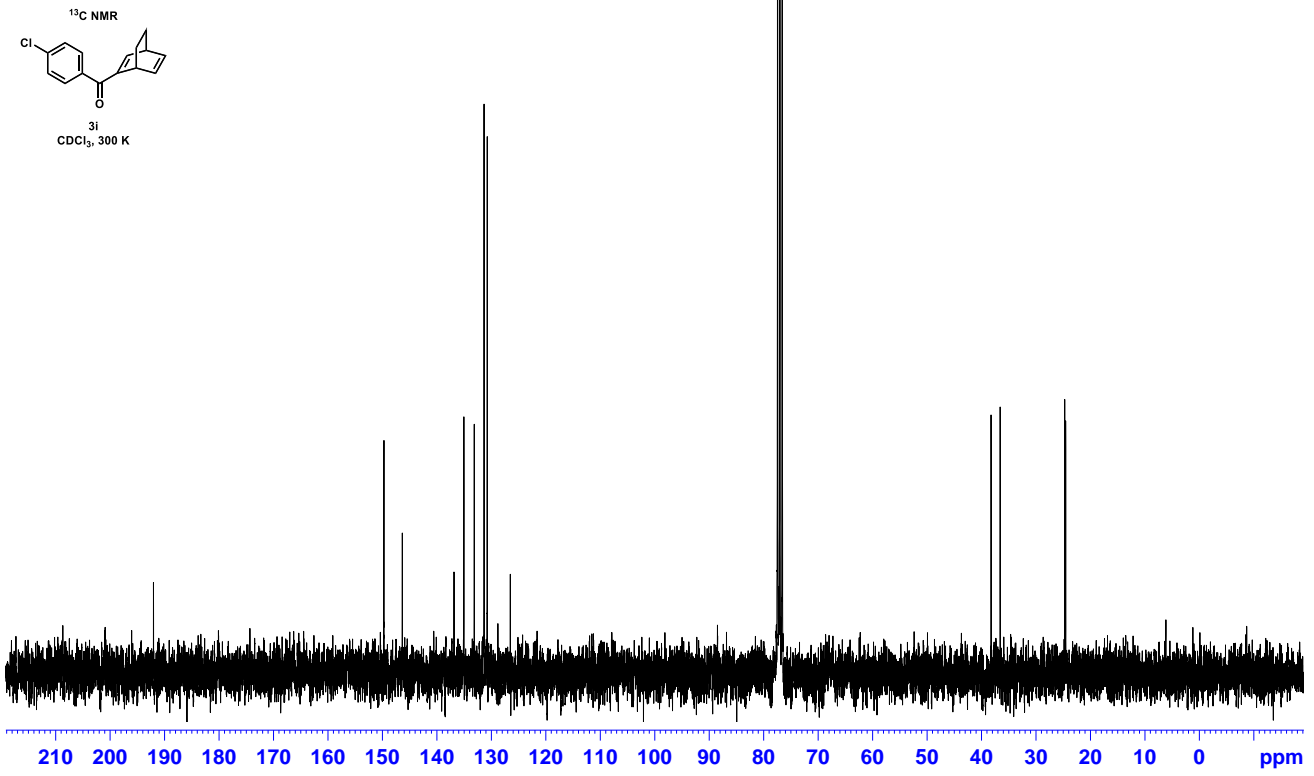
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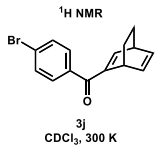
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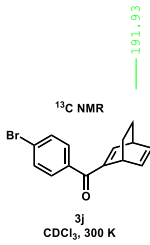
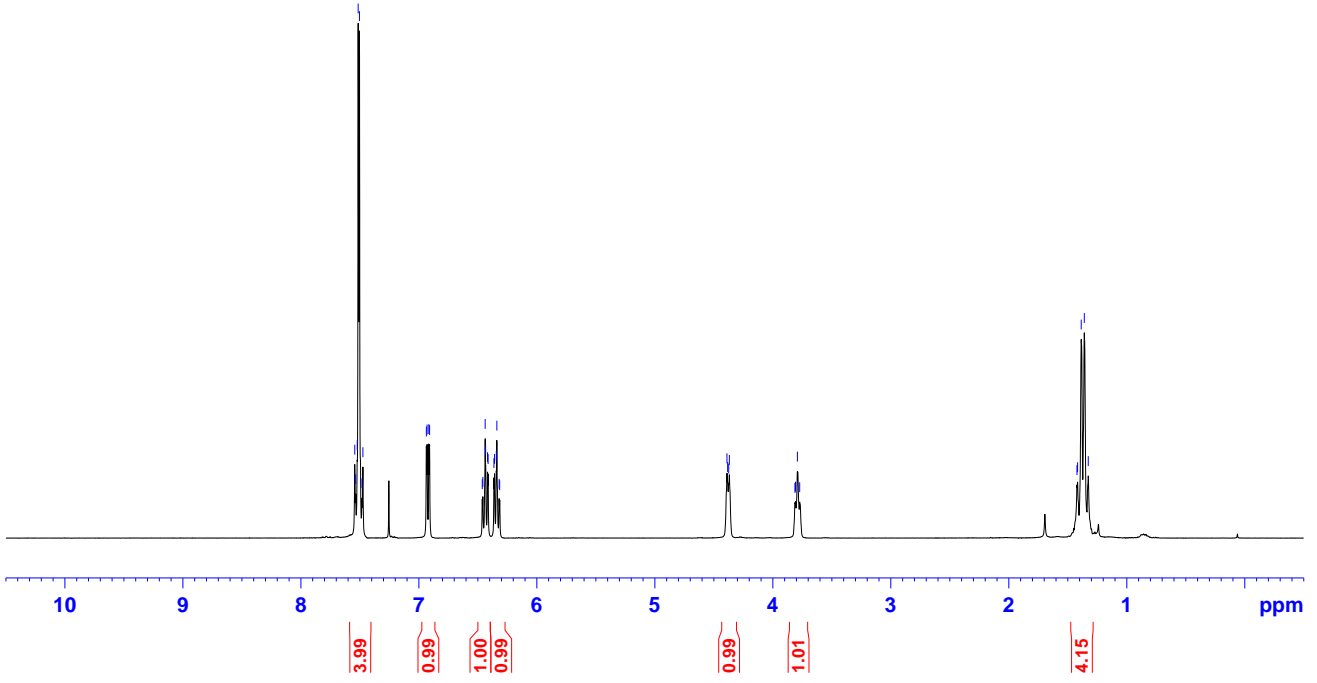




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