Electronic Supplementary Information

Fe-BPsalan complexes catalyzed highly enantioselective Diels-Alder reaction of alkylidene β-ketoesters

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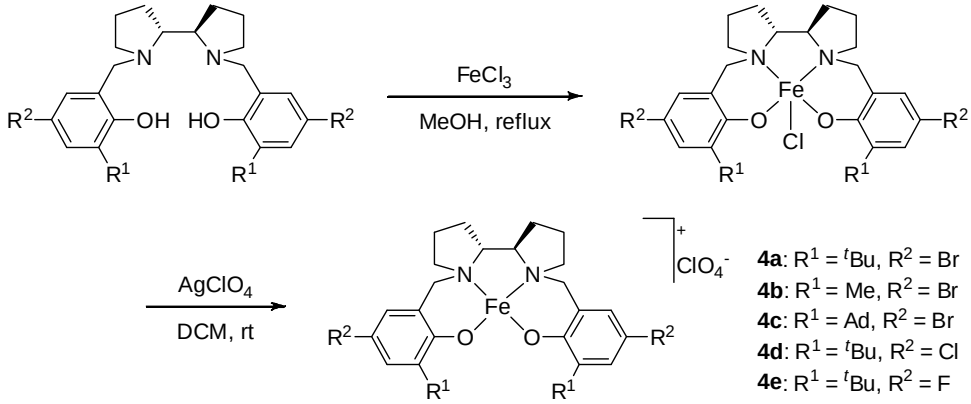
1. General experimental information

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were refluxed over magnesium (methanol, ethanol), sodium (toluene, THF, Et_2O), or calcium hydride (DCM, DCE, EA, MeCN) under an argon atmosphere and collected by distillation. Flash column chromatography was performed with Huanghai silica gel (300-400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 400 (400 MHz) spectrometer. ^1H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. HPLC analyses were conducted on an Agilent 1100 Series chromatograph. Infrared spectra were prepared as KBr pellets or neat and were recorded on a Nicolet iN10 MX spectrometer. Optical rotations were measured with a Perkin-Elmer 241 polarimeter in a 1 dm cuvette. Mass spectra were recorded by the mass spectrometry service of Shanghai Institute of Organic Chemistry.

2. Generel procedure for the synthesis of Fe-BPsalan complexes and starting materials

Generel procedure for the synthesis of Fe-BPsalan complexes.

Fe-BPsalan complexes (**4a-e**) with (*R*,*R*)-bipyrrolidine backbone BPsalan ligands were prepared by the corresponding literature procedures reported by our group.[1] Iron(III) complexes (**5**, **6**) were prepared by the corresponding literature procedures.[2]



Complex 4a: IR (KBr): ν_{max} 3418, 2957, 1622, 1575, 1539, 1463, 1430, 1407, 1295, 1250, 1168, 1096, 931, 879, 815, 734, 596, 497 cm^{-1}. **HRMS** (MALDI) For $[C_{30}H_{40}N_2O_2{}^{79}Br_2{}^{54}Fe]^+$ ($[M\text{-}ClO_4]^+$): Calcld.: 672.0847, Found: 672.0839.

Complex 4b: IR (KBr): ν_{max} 2957, 2922, 2852, 1607, 1475, 1443, 1204, 1089, 867, 800, 726, 622 cm^{-1}. **HRMS** (MALDI) For $[C_{24}H_{28}N_2O_2{}^{79}Br_2{}^{54}Fe]^+$ ($[M\text{-}ClO_4]^+$): Calcld.: 587.9908, Found: 587.9880.

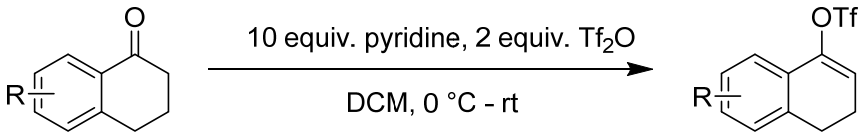
Complex 4c: IR (KBr): ν_{max} 2900, 2846, 1571, 1428, 1406, 1248, 1228, 1099, 1077, 867, 804, 717, 651, 580, 494 cm^{-1}. **HRMS** (MALDI) For $[C_{42}H_{52}N_2O_2{}^{79}Br_2{}^{54}Fe]^+$ ($[M\text{-}ClO_4]^+$): Calcld.: 828.1786, Found: 828.1799.

Complex 4d: IR (KBr): ν_{max} 2956, 1581, 1432, 1411, 1293, 1249, 1090, 928, 874, 815, 753, 623, 598, 507 cm^{-1}. **HRMS** (MALDI) For $[C_{30}H_{40}N_2O_2{}^{35}Cl_2{}^{54}Fe]^+$ ($[M\text{-}ClO_4]^+$): Calcld.: 584.1858, Found: 584.1839.

Complex 4e: IR (KBr): ν_{max} 2959, 1597, 1422, 1296, 1203, 1094, 994, 871, 823, 797, 623, 548 cm^{-1}. **HRMS** (MALDI) For $[C_{30}H_{40}N_2O_2{}^{19}F_2{}^{54}Fe]^+$ ($[M\text{-}ClO_4]^+$): Calcld.: 552.2449, Found: 552.2431.

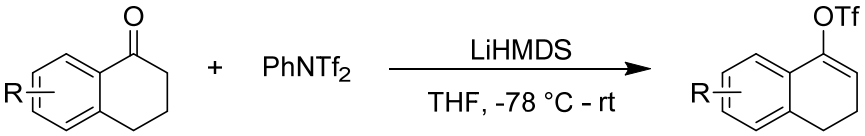
General procedure of trifluoromethanesulfonate

Method 1[3]:



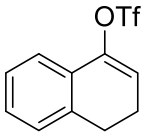
To a solution of 1-tetralone (1 equiv.) in DCM, Tf_2O (2 equiv.) and pyridine (10 equiv.) were sequentially added at 0 ºC. The mixture was allowed to warm to room temperature and stirred overnight. H_2O was added and the aqueous layer was extracted by DCM 3 times, and the combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography.

Method 2[4]:



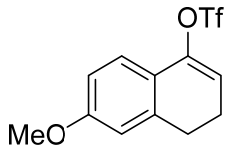
To a solution of 1-tetralone (1 equiv.) in dry THF, 1 M LiHMDS (1.5 equiv.) was added at -78 ºC. After stirring for 1 h, $PhNTf_2$ (1 equiv.) was added and stirred at the same temperature for another hour. The reaction mixture was allowed to warm to room temperature and stirred overnight. Saturated NH_4Cl solution was added to quench the reaction, and the reaction mixture was extracted with Et_2O 3 times. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography.

3,4-Dihydronaphthalen-1-yl trifluoromethanesulfonate[3]



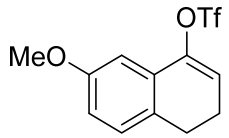
Method 1, prepared from 34.2 mmol of 1-tetralone to afford 9.05 g (32.5 mmol, 95% yield) of desired product as a yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.39-7.31 (m, 1H), 7.31-7.22 (m, 2H), 7.22-7.13 (m, 1H), 6.02 (t, J = 4.8 Hz, 1H), 2.87 (t, J = 8.2 Hz, 2H), 2.51 (td, J = 8.1, 4.8 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -74.09.

6-Methoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate[3]



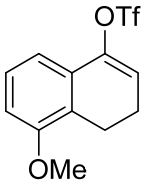
Method 1, prepared from 11.3 mmol of 6-methoxy-1-tetralone to afford 2.22 g (7.2 mmol, 63% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 9.3 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 2H), 6.72 (s, 1H), 5.85 (t, *J* = 4.8 Hz, 1H), 3.80 (s, 3H), 2.82 (q, *J* = 8.1 Hz, 2H), 2.55-2.33 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.76.

7-Methoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate[5]



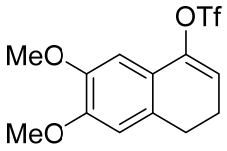
Method 1, prepared from 11.4 mmol of 7-methoxy-1-tetralone to afford 2.59 g (8.4 mmol, 74% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.92 (d, *J* = 2.6 Hz, 1H), 6.81 (dd, *J* = 8.2, 2.2 Hz, 2H), 6.04 (t, *J* = 4.8 Hz, 1H), 3.81 (s, 3H), 2.80 (q, *J* = 8.2 Hz, 2H), 2.54-2.44 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.7, 146.3, 129.6, 128.8, 128.3, 118.74 (t, *J* = 321.2 Hz), 118.5, 114.5, 107.2, 55.4, 26.0, 22.8. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.78.

5-Methoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate[6]



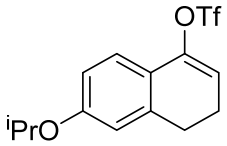
Method 1, prepared from 11.4 mmol of 5-methoxy-1-tetralone to afford 2.18 g (7.1 mmol, 62% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22 (t, *J* = 8.3 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.00 (t, *J* = 4.6 Hz, 1H), 3.83 (s, 3H), 2.86 (t, *J* = 8.4 Hz, 2H), 2.47 (tdd, *J* = 8.2, 4.8, 1.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.2, 146.4, 129.7, 127.3, 124.3, 118.7 (q, *J* = 322.2 Hz), 118.0, 113.9, 111.8, 55.6, 21.9, 19.2. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.78.

6,7-Dimethoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate[7]



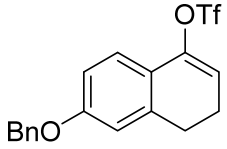
Method 1, prepared from 4.9 mmol of 6,7-dimethoxy-1-tetralone to afford 0.71 g (2.1 mmol, 43% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.88 (s, 1H), 6.71 (s, 1H), 5.88 (t, *J* = 4.8 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.79 (t, *J* = 8.3 Hz, 2H), 2.48 (ddd, *J* = 9.3, 7.6, 4.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.56, 147.77, 146.24, 129.36, 121.26, 118.68 (q, *J* = 320.5 Hz), 115.13, 111.46, 105.24, 56.09, 26.67, 22.58. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.79.

6-Isopropoxy-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate



Method 1, prepared from 4.9 mmol of 6-isopropoxy-1-tetralone to afford 1.47 g (4.4 mmol, 89% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.69-6.59 (m, 2H), 5.75 (tt, *J* = 4.9, 1.4 Hz, 1H), 4.52-4.42 (m, 1H), 2.72 (t, *J* = 8.1 Hz, 2H), 2.37 (td, *J* = 8.1, 4.8, 2H), 1.25 (dd, *J* = 6.0, 1.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.8, 146.5, 138.4, 122.8, 121.4, 118.7 (q, *J* = 320.1 Hz), 115.9, 114.7, 113.0, 70.0, 27.4, 22.4, 22.1. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.81. **IR** (KBr): ν_{max} 2979, 2940, 1654, 1609, 1568, 1497, 1419, 1249, 1212, 1142, 1008, 911, 886, 845, 605 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 336 (M^+), 294 (68.87), 161 (65.82), 133 (100), 115 (28.46), 105 (27.43). **HRMS** (EI) For $[C_{14}H_{15}O_4F_3S]^+$ (M^+): Calcl.: 336.0643, Found: 336.0645.

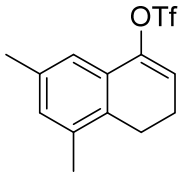
6-(Benzyloxy)-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate[8]



Method 1, prepared from 6.1 mmol of 6-benzyloxy-1-tetralone to afford 0.91 g (2.4 mmol, 39% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50-7.33 (m, 5H), 7.30 (d, *J* = 8.3 Hz, 1H), 6.92-6.83 (m, 2H), 5.89 (t, *J* = 4.8 Hz, 1H), 5.09 (s, 2H), 2.85 (t, *J* = 8.1

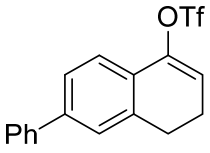
Hz, 2H), 2.49 (ddd, J = 9.3, 7.4, 4.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 159.5, 146.4, 138.4, 136.7, 128.8, 128.2, 127.5, 122.8, 122.0, 118.7 (q, J = 320.2 Hz), 115.2, 115.1, 112.3, 70.1, 27.4, 22.3. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.72.

5,7-Dimethyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate



Method 1, prepared from 11.5 mmol of 5,7-dimethyl-1-tetralone to afford 2.35 g (7.7 mmol, 67% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.12 (s, 1H), 7.03 (s, 1H), 6.04 (t, J = 4.8 Hz, 1H), 2.82 (t, J = 8.3 Hz, 2H), 2.53 (td, J = 8.3, 4.8 Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 146.9, 135.8, 135.4, 132.1, 131.6, 128.5, 120.3, 119.9, 118.8 (q, J = 321 Hz), 117.1, 117.0, 22.6, 22.1, 21.1, 19.4. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.83. **IR** (KBr): ν_{max} 2956, 2942, 1659, 1605, 1412, 1249, 1226, 1142, 1091, 902, 605 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 306 (M^+), 173 (91.53), 145 (100), 130 (52.96), 115 (40.73), 105 (22.9), 91 (16.88), 69 (19.18). **HRMS** (EI) For $[C_{13}H_{13}F_3O_3S]^+$ (M^+): Calcld.: 306.0538, Found: 306.0539.

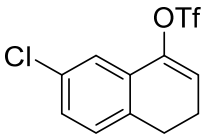
6-Phenyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate



Method 1, prepared from 2.8 mmol of 6-phenyl-1-1-tetralone to afford 0.94 g (2.7 mmol, 94% yield) of desired product as a viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.4 Hz, 2H), 7.55-7.48 (m, 2H), 7.48-7.44 (m, 2H), 7.43 (d, J = 2.0 Hz, 1H), 7.42-7.34 (m, 1H), 6.06 (t, J = 4.8 Hz, 1H), 2.95 (t, J = 8.2 Hz, 2H), 2.57 (td, J = 8.2, 4.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 146.4, 142.1, 140.3, 136.8, 129.0, 127.8, 127.7, 127.1, 126.7, 125.7, 121.8, 118.7 (q, J = 320.2 Hz), 117.8 (t, J = 3.6 Hz), 27.1, 22.5. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.64. **IR** (KBr): ν_{max} 2076, 2831, 1404, 1200, 1139, 1003, 901, 759 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 354

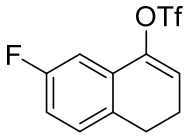
(M^+), 221 (39.88), 193 (60.41), 178 (100), 165 (49.43), 115 (16.37). **HRMS** (EI) For $[C_{17}H_{13}F_3O_3S]^+$ (M^+): Calcld.: 354.0537, Found: 354.0541.

7-Chloro-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate[9]



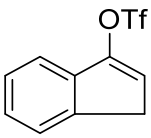
Method 2, prepared from 8.3 mmol of 7-chloro-1-tetralone to afford 0.89 g (2.8 mmol, 34% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 (s, 1H), 7.29-7.20 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.09 (q, *J* = 3.6 Hz, 1H), 2.84 (t, *J* = 8.3 Hz, 2H), 2.57-2.47 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 145.3, 134.5, 133.0, 130.3, 129.1, 121.6, 117.1 (q, *J* = 320.2 Hz), 119.2, 117.1, 26.4, 22.4. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.54.

7-Fluoro-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate[10]



Method 2, prepared from 3.1 mmol of 7-fluoro-1-tetralone to afford 0.35 g (1.2 mmol, 39% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.14 (dd, *J* = 8.1, 5.8 Hz, 1H), 7.06 (dd, *J* = 9.2, 2.6 Hz, 1H), 6.95 (td, *J* = 8.4, 2.0 Hz, 2H), 6.10 (t, *J* = 4.8 Hz, 1H), 2.83 (t, *J* = 8.2 Hz, 2H), 2.52 (td, *J* = 8.2, 4.9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.1, 160.6, 145.5 (d, *J* = 2.4 Hz), 131.7 (d, *J* = 3.4 Hz), 130.4 (d, *J* = 8.2 Hz), 129.2 (d, *J* = 7.9 Hz), 119.3, 118.7 (q, *J* = 320.2 Hz), 115.7 (d, *J* = 21.4 Hz), 108.8 (d, *J* = 24.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.69 (s, 1F), -114.90 (q, *J* = 8.5 Hz, 3F).

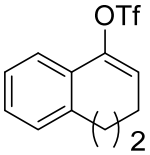
1*H*-Inden-3-yl trifluoromethanesulfonate[11]



Method 1, prepared from 37.8 mmol of 1-indanone to afford 8.90 g (33.7 mmol, 89% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50-7.44 (m, 1H), 7.41 (ddd, *J* = 8.7, 7.4, 1.4 Hz, 1H), 7.38-7.28 (m, 2H), 6.37 (t, *J* = 2.3 Hz, 1H), 3.47 (d, *J* = 2.4 Hz, 2H). **^{13}C**

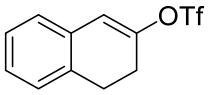
NMR (101 MHz, $CDCl_3$): δ 148.1, 141.3, 136.7, 127.1, 127.0, 124.6, 118.8 (q, *J* = 322.19 Hz), 118.3, 118.2, 34.9. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.15.

6,7-Dihydro-5*H*-benzo[7]annulen-9-yl trifluoromethanesulfonate[12]



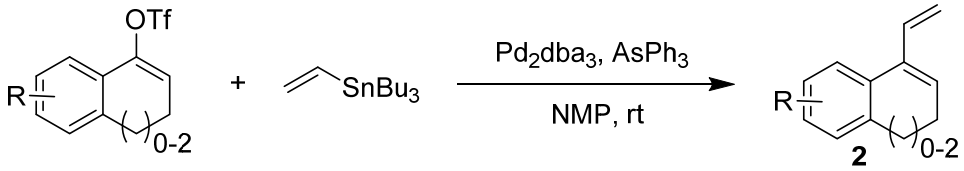
Method 1, prepared from 12.5 mmol of 1-benzosuberone to afford 3.46 g (11.9 mmol, 95% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 - 7.52 (m, 1H), 7.32 - 7.29 (m, 2H), 7.25 - 7.23 (m, 1H), 6.24 (t, *J* = 6.3, 1H), 2.79 - 2.77 (m, 2H), 2.25 (q, *J* = 7.0, 2H), 2.12 - 2.06 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 146.3, 141.8, 132.2, 129.6, 129.4, 126.6, 126.5, 123.5, 118.7 (q, *J* = 318.6 Hz), 33.6, 30.7, 25.5. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -74.2 (t, *J* = 4.7 Hz).

3,4-Dihydronaphthalen-2-yl trifluoromethanesulfonate[13]



Method 1, prepared from 13.7 mmol of 2-tetralone to afford 3.23 g (11.6 mmol, 82% yield) of desired product as a yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.24-7.20 (m, 2H), 7.18-7.13 (m, 1H), 7.11-7.06 (m, 1H), 6.50 (s, 1H), 3.07 (t, *J*= 8.4 Hz, 2H), 2.71 (td, *J* = 8.4, 1.3 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.59.

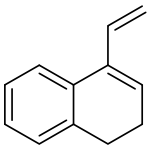
General procedure of diene[3]



Pd_2dba_3 (3 mol%) and $AsPh_3$ (10 mol%) were placed in 20 mL NMP under Ar atmosphere. After degassing for 20 min, corresponding trifluoromethanesulfonate (1 equiv.) and vinyl tributyltin (1.5 equiv.) were added and the reaction mixture was stirred at room temperature for 5 h. Adding of 2 M KF (5 equiv.) solution and H_2O (100 mL) resulted in the formation of a precipitate.

The reaction mixture was stirred vigorously for 30 min, filtered through a pad of Celite, extracted with EtOAc (50 mL × 3). The combined organic layer was dried over $MgSO_4$, concentrated in vacuo. The residue was purified by flash column chromatography.

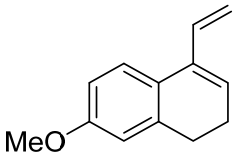
4-Vinyl-1,2-dihydronaphthalene (2a)[3]



2a

Prepared from 3.6 mmol of corresponding trifluoromethanesulfonate to afford 0.47 g (3.0 mmol, 84% yield) of **2a** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.3 Hz, 1H), 7.27-7.16 (m, 1H), 7.19-7.11 (m, 2H), 6.69-6.57 (m, 1H), 6.19 (t, *J* = 4.9 Hz, 1H), 5.53 (d, *J* = 17.4 Hz, 1H), 5.20 (d, *J* = 11.0 Hz, 1H), 2.75 (t, *J* = 7.9 Hz, 2H), 2.30 (td, *J* = 7.9, 5.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 136.7, 136.6, 135.6, 134.2, 127.7, 127.1, 126.5, 126.4, 123.9, 115.3, 28.3, 23.3. **MS** (EI): (relative intensity): *m/z* 156 (M^+), 141 (99.53), 128 (100), 115 (77.39).

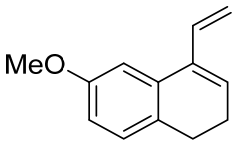
7-Methoxy-4-vinyl-1,2-dihydronaphthalene (2b)[3]



2b

Prepared from 3.2 mmol of corresponding trifluoromethanesulfonate to afford 0.48 g (2.6 mmol, 79% yield) of **2b** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26 (s, 1H), 6.74 (s, 1H), 6.66-6.54 (m, 2H), 6.07 (t, *J* = 4.7 Hz, 1H), 5.51 (dd, *J* = 17.4, 1.9 Hz, 1H), 5.17 (dd, *J* = 10.8, 1.9 Hz, 1H), 3.81 (s, 3H), 2.73 (t, *J* = 7.9 Hz, 2H), 2.34-2.24 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.6, 138.6, 136.3, 135.8, 127.3, 125.1, 124.2, 115.0, 113.9, 110.9, 55.3, 28.8, 23.2. **MS** (EI): (relative intensity): *m/z* 186 (M^+), 171 (69.44), 128 (69.26), 115 (73.56).

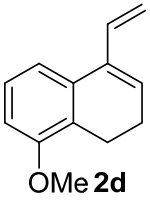
6-Methoxy-4-vinyl-1,2-dihydronaphthalene (2c)[14]



2c

Prepared from 7.8 mmol of corresponding trifluoromethanesulfonate to afford 1.07 g (5.7 mmol, 74% yield) of **2c** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.0 Hz, 1H), 7.00-6.95 (m, 2H), 6.75 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.65 (dd, *J* = 16.8, 11.0 Hz, 1H), 6.24 (t, *J* = 4.9 Hz, 1H), 5.58 (d, *J* = 17.3 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H), 3.83 (s, 3H), 2.72 (t, *J* = 7.9 Hz, 2H), 2.32 (td, *J* = 7.8, 5.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.3, 136.6, 135.5, 135.1, 128.8, 128.3, 127.1, 115.4, 111.7, 110.4, 55.4, 27.3, 23.6.

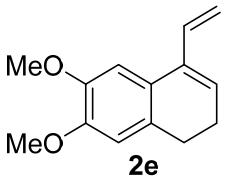
8-Methoxy-4-vinyl-1,2-dihydronaphthalene (2d)



2d

Prepared from 7.1 mmol of corresponding trifluoromethanesulfonate to afford 1.10 g (5.9 mmol, 84% yield) of **2d** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.12 (t, *J* = 7.9 Hz, 1H), 6.74 (dd, *J* = 10.3, 7.9 Hz, 2H), 6.56 (dd, *J* = 17.4, 10.7 Hz, 1H), 6.41 (s, 1H), 5.40-5.28 (m, 1H), 5.15 (d, *J* = 10.9 Hz, 1H), 3.84 (s, 3H), 2.87 (t, *J* = 8.4 Hz, 2H), 2.46 (dd, *J* = 9.1, 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.1, 138.6, 137.7, 135.6, 128.1, 126.8, 123.3, 119.6, 113.0, 109.8, 55.6, 21.8, 20.0. **IR** (KBr): ν_{max} 2935, 2834, 1597, 1570, 1460, 1438, 1336, 1261, 1143, 1082, 1038, 913, 830, 790, 782, 729 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 186 (M^+), 171 (59.4), 155 (68.16), 141 (37.85), 128 (54.55), 115 (70.07). **HRMS** (EI) For $[C_{13}H_{14}O]^+$ (M^+): Calcld.: 186.1045, Found: 186.1043.

6,7-Dimethoxy-4-vinyl-1,2-dihydronaphthalene (2e)

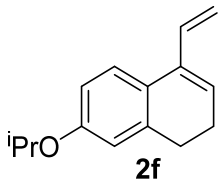


2e

Prepared from 1.9 mmol of corresponding trifluoromethanesulfonate to afford 0.26 g (1.2 mmol, 62% yield) of **2e** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.90 (s, 1H), 6.71 (s, 1H), 6.58 (ddd, *J* = 17.4, 10.9, 1.2 Hz, 1H), 6.07 (t, *J* = 4.7 Hz, 1H), 5.51 (dd, *J* = 17.4, 1.8 Hz, 1H), 5.18 (dd, *J* = 10.9, 1.9 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 2.66 (t, *J* = 8.0 Hz, 2H), 2.33-2.11 (m,

2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 147.9, 147.2, 136.4, 135.9, 129.5, 126.9, 124.7, 115.3, 111.6, 108.5, 56.3, 56.1, 28.0, 23.5. **IR** (KBr): ν_{max} 2929, 2831, 1602, 1569, 1509, 1402, 1355, 1273, 1264, 1234, 1143, 1032, 997, 911, 866, 799 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 216 (M^+), 201 (32.24), 185 (8.36), 158 (25.57), 141 (32.95), 128 (55.46), 115 (69.98). **HRMS** (ESI) For $[C_{14}H_{17}O_2]^+$ ($[M+H]^+$): Calcld.: 217.1233, Found: 217.1221.

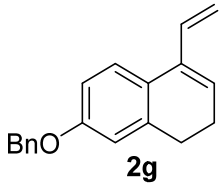
7-Isopropoxy-4-vinyl-1,2-dihydronaphthalene (2f)



2f

Prepared from 1.8 mmol of corresponding trifluoromethanesulfonate to afford 0.24 g (1.1 mmol, 64% yield) of **2f** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 7.9 Hz, 1H), 6.71-6.60 (m, 2H), 6.53 (ddd, *J* = 17.4, 10.9, 1.2 Hz, 1H), 5.98 (t, *J* = 4.7 Hz, 1H), 5.44 (dd, *J* = 17.4, 1.9 Hz, 1H), 5.09 (dd, *J* = 10.9, 1.9 Hz, 1H), 4.48 (p, *J* = 6.1 Hz, 1H), 2.64 (t, *J* = 7.9 Hz, 2H), 2.26-2.16 (m, 2H), 1.26 (d, *J* = 6.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.6, 133.2, 130.9, 130.5, 121.7, 119.7, 118.7, 110.4, 109.6, 107.5, 72.0, 71.7, 71.4, 64.5, 23.4, 17.9, 16.9, 16.8. **IR** (KBr): ν_{max} 2976, 2932, 1606, 1496, 1383, 1275, 1249, 1115, 983, 823 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 214 (M^+), 186 (85.87), 172 (72.54), 157 (100), 145 (67.26), 133 (42.45), 128 (52.09), 115 (50.58). **HRMS** (EI) For $[C_{15}H_{18}O]^+$ (M^+): Calcl.: 214.1358, Found: 214.1354.

7-(Benzyloxy)-4-vinyl-1,2-dihydronaphthalene (2g)

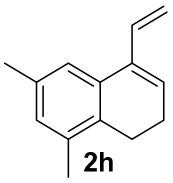


2g

Prepared from 5.2 mmol of corresponding trifluoromethanesulfonate to afford 1.11 g (4.2 mmol, 81% yield) of **2g** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.29 (m, 6H), 6.99-6.75 (m, 2H), 6.73-6.56 (m, 1H), 6.12 (ddp, *J* = 1.5, 3.3, 4.9, 1H), 5.57 (dp, *J* = 17.4, 2.3 Hz, 1H), 5.23 (dp, *J* = 10.9, 2.2 Hz, 1H), 5.11 (s, 2H), 2.78 (t, *J* = 7.9, 2H), 2.32 (dt, *J* = 7.9, 4.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 138.6, 137.2, 136.2, 135.8, 128.6, 128.0, 127.5, 125.1,

124.3, 115.0, 114.9, 111.9, 70.0, 28.8, 23.2. **IR** (KBr): ν_{max} 3031, 2933, 2882, 2828, 1606, 1567, 1497, 1249, 1140, 1028, 912, 827, 735, 695 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 262 (M^+), 128 (12.06), 91 (100). **HRMS** (ESI) For $[C_{19}H_{19}O]^+$ ($[M+H]^+$): Calcld.: 263.1436, Found: 263.1429.

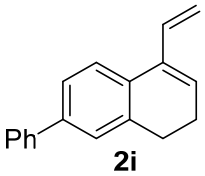
6,8-Dimethyl-4-vinyl-1,2-dihydronaphthalene (2h)



2h

Prepared from 3.3 mmol of corresponding trifluoromethanesulfonate to afford 0.49 g (2.9 mmol, 88% yield) of **2h** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.09 (s, 1H), 6.95 (s, 1H), 6.69 (ddq, *J* = 17.3, 10.8, 1.3 Hz, 1H), 6.24 (td, *J* = 4.8, 1.2 Hz, 1H), 5.57 (dd, *J* = 17.3, 2.0 Hz, 1H), 5.24 (dd, *J* = 10.9, 2.0 Hz, 1H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.38-2.34 (m, 4H), 2.34-2.31 (m, 4H).. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 137.0, 136.2, 135.0, 134.8, 134.0, 131.8, 130.0, 125.8, 122.7, 115.1, 23.6, 23.1, 21.2, 19.8. **IR** (KBr): ν_{max} 2922, 2830, 1606, 1474, 1443, 1014, 911, 853 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 184 (M^+), 169 (100), 154 (33.19), 141 (20.99). **HRMS** (EI) For $[C_{14}H_{16}]^+$ (M^+): Calcld.: 184.1252, Found: 184.1254.

7-Phenyl-4-vinyl-1,2-dihydronaphthalene (2i)

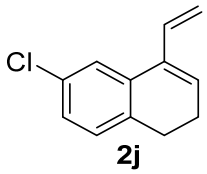


2i

Prepared from 1.7 mmol of corresponding trifluoromethanesulfonate to afford 0.29 g (1.3 mmol, 75% yield) of **2i** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.3 Hz, 2H), 7.53-7.45 (m, 5H), 7.39 (t, *J* = 6.9 Hz, 1H), 6.72 (dt, *J* = 16.5, 8.1 Hz, 1H), 6.27 (t, *J* = 5.0 Hz, 1H), 5.62 (dd, *J* = 17.4, 5.9 Hz, 1H), 5.29 (d, *J* = 10.0 Hz, 1H), 2.87 (q, *J* = 6.2, 4.8 Hz, 2H), 2.41 (td, *J* = 7.8, 4.4 Hz, 2H).. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.0, 139.8, 137.1, 136.4, 135.5, 133.3, 128.8, 127.2, 127.0, 126.6, 126.5, 125.1, 124.4, 115.4, 28.5, 23.4. **IR** (KBr): ν_{max} 2931, 1736, 1593, 1479, 1264, 1241, 1099, 880, 813, 738 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 232 (M^+), 217 (48.53), 215 (31.85), 202 (35.57). **HRMS** (EI) For $[C_{18}H_{16}]^+$ (M^+): Calcl.: 232.1252, Found:

232.1247.

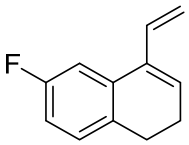
6-Chloro-4-vinyl-1,2-dihydronaphthalene (2j)



2j

Prepared from 2.7 mmol of corresponding trifluoromethanesulfonate to afford 0.37 g (1.9 mmol, 70% yield) of **2j** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 2.1 Hz, 1H), 7.13 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.57 (ddq, *J* = 17.3, 10.9, 1.3 Hz, 1H), 6.23 (t, *J* = 4.8 Hz, 1H), 5.53 (dd, *J* = 17.3, 1.7 Hz, 1H), 5.23 (dd, *J* = 10.9, 1.7 Hz, 1H), 2.71 (t, *J* = 7.9 Hz, 2H), 2.35-2.25 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 136.0, 135.8, 135.0, 134.9, 132.1, 128.8, 127.6, 126.7, 124.1, 116.0, 27.6, 23.2. **IR** (KBr): ν_{max} 2931, 2835, 1611, 1574, 1486, 1425, 1249, 1161, 910, 872, 807 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 190 (M^+), 178 (26.09), 155 (100), 128 (34.84), 115 (24.73), 84 (24.62), 49 (26.07), 43 (31.23). **HRMS** (EI) For $[C_{12}H_{11}{}^{35}Cl]^+$ (M^+): Calcl.: 190. 0549, Found: 190.0548.

6-Fluoro-4-vinyl-1,2-dihydronaphthalene (2k)

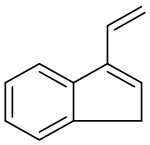


2k

Prepared from 1.2 mmol of corresponding trifluoromethanesulfonate to afford 0.11 g (0.6 mmol, 52% yield) of **2k** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10 (t, *J* = 7.1 Hz, 1H), 7.05 (dd, *J* = 10.4, 2.7 Hz, 1H), 6.84 (td, *J* = 8.4, 2.8 Hz, 1H), 6.56 (dd, *J* = 17.4, 10.9 Hz, 1H), 6.23 (t, *J* = 4.9 Hz, 1H), 5.53 (d, *J* = 17.3 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 2.71 (t, *J* = 7.9 Hz, 2H), 2.30 (td, *J* = 7.9, 4.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 161.8 (d, *J* = 242.2 Hz), 136.1 (d, *J* = 2.2 Hz), 135.9 (d, *J* = 7.5 Hz), 135.1, 132.0 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 8.0 Hz), 127.6, 115.8, 113.2 (d, *J* = 21.4 Hz), 111.1 (d, *J* = 22.6 Hz), 27.4, 23.4. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -116.72 (q, *J* = 9.1 Hz). **IR** (KBr): ν_{max} 2929, 1610, 1578, 1490, 1429, 1262, 1247, 1163, 904, 869, 810 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 174 (M^+), 159 (100), 146 (53.61), 133 (35.43). **HRMS**

(EI) For $[C_{12}H_{11}F]^+$ (M^+): Calcl.: 174.0845, Found: 174.0842.

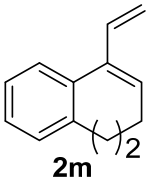
3-Vinyl-1*H*-indene (2l)[15]



2l

Prepared from 3.8 mmol of corresponding trifluoromethanesulfonate to afford 0.33 g (2.3 mmol, 61% yield) of **2l** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 6.80 (dd, *J* = 17.9, 11.3 Hz, 1H), 6.56 (s, 1H), 5.85 (d, *J* = 17.8 Hz, 1H), 5.35 (d, *J* = 11.3 Hz, 1H), 3.42 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 144.7, 143.5, 131.6, 130.7, 126.2, 125.0, 124.1, 120.2, 115.9, 37.9. **MS** (EI): (relative intensity): *m/z* 142 (M^+), 141 (100), 115 (46.83).

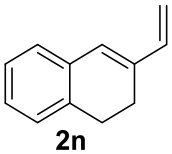
9-Vinyl-6,7-dihydro-5*H*-benzo[7]annulene (2m)[16]



2m

Prepared from 5.1 mmol of corresponding trifluoromethanesulfonate to afford 0.79 g (4.6 mmol, 90% yield) of **2m** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48-7.39 (m, 1H), 7.39-7.25 (m, 3H), 6.72-6.58 (m, 1H), 6.28 (q, *J* = 7.4, 6.8 Hz, 1H), 5.34-5.23 (m, 1H), 5.17 (t, *J* = 8.9 Hz, 1H), 2.71-2.60 (m, 2H), 2.23-2.10 (m, 2H), 2.04-1.91 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.4, 141.2, 138.2, 137.4, 131.1, 128.8, 128.6, 127.1, 125.6, 114.2, 34.2, 31.9, 24.7.

3-Vinyl-1,2-dihydronaphthalene (2n)[17]

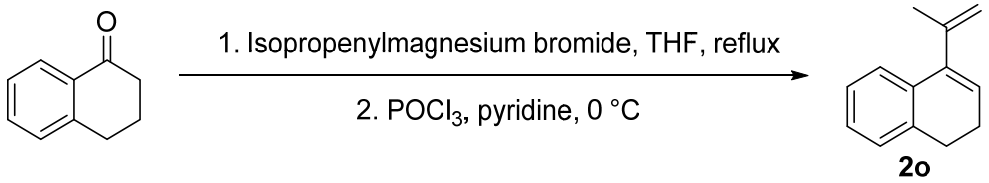


2n

Prepared from 3.6 mmol of corresponding trifluoromethanesulfonate to afford 0.49 g (3.2 mmol, 87% yield) of **2n** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 - 7.10 (m, 3H), 7.05 (ddd, *J* = 6.8, 1.5, 1.0 Hz, 1H), 6.55 (ddd, *J* = 17.5, 10.5, 1.0 Hz, 1H), 6.43 (dd, *J* = l.3, 1.0 Hz,

1H), 5.34 (dd, *J* = l7.5, 1.2 Hz, 1H), 5.14 (dd, *J* = 10.5, 1.2Hz, 1H), 2.89 (t, *J* = 7.5Hz, 2H), 2.48 (dd, *J* = 7.5, 1.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 138.5, 137.8, 135.7, 134.5, 128.2, 127.2, 127.0, 126.5, 112.7, 27.7, 22.3.

4-(Prop-1-en-2-yl)-1,2-dihydronaphthalene (2o)[18]



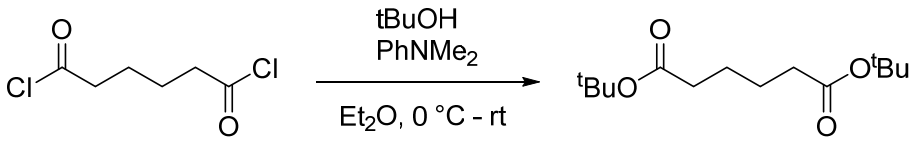
Step1:

To a solution of 1-tetralone (2.0 g, 13.7 mmol) in 20 mL dry THF, 2-propylmagnesium bromide (1.5 equiv.) was added dropwise. The reaction mixture was refluxed for 2 h. After cooling to room temperature, 30 mL saturated NH_4Cl solution was added to quench the reaction. The aqueous layer was extracted with Et_2O (15 mL × 3). The combined organic layer was dried over $MgSO_4$, concentrated in vacuo. The crude product was used without further purification.

Step2:

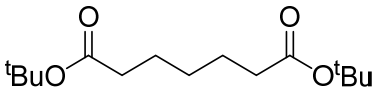
To a solution of the crude alcohol in 20 mL pyridine, $POCl_3$ (1.5 equiv.) was added dropwise at 0 ºC. the reaction mixture was allowed to warm to room temperature and stirred overnight. Ice water was carefully added to quench the reaction and the reaction mixture was extracted with Et_2O. The combined organic layer was dried over $MgSO_4$, concentrated in vacuo. The residue was purified by flash column chromatography to afford the desired product (1.1 g, 51% yield, 2 steps) as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28-7.12 (m, 4H), 6.02 (t, *J* = 4.6 Hz, 1H), 5.12 (s, 1H), 5.07 (s, 1H), 2.78 (t, *J* = 7.9 Hz, 2H), 2.35-2.25 (m, 2H), 2.01-1.97 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 144.6, 141.5, 136.9, 134.0, 127.6, 126.8, 126.3, 125.2, 125.0, 114.5, 28.4, 23.2, 22.9.

di-*tert*-butyl adipate[19]



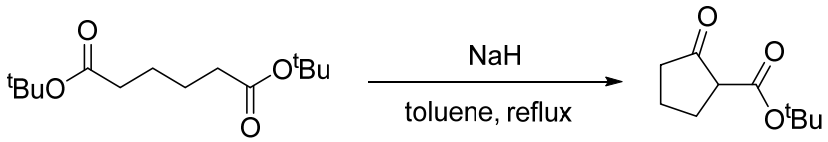
To a solution of ^{t}BuOH (41 mL, 437 mmol, 4 equiv.) and *N*,*N*-dimethylaniline (44 mL, 349 mmol, 4 equiv.) in Et_2O (120 mL), adipoyl chloride (20 g, 109 mmol) in Et_2O (20 mL) was added dropwise at 0 °C. The mixture was allowed to warm slowly to room temperature and stirred for 24 h. H_2O (100 mL) was added and the aqueous layer was extracted with Et_2O (30 mL × 3). The combined organic layer was washed sequentially with 1 M HCl (100 mL), 2 M NaOH (100 mL) and brine (100 mL), then dried over $MgSO_4$ and concentrated in vacuo. The residue was distilled in vacuo to give the desired product as a colorless liquid (20.5 g, 72% yield). **B.P.**: 103-105 °C (at 2.7 mbar).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.27-2.21 (m, 4H), 1.66-1.59 (m, 4H), 1.45 (s, 18H).

di-*tert*-Butyl heptanedioate[20]



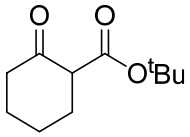
Prepared from 25.4 mmol of heptanedioyl dichloride to afford 5.34 g (19.6 mmol, 77% yield) of desired product as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.35-2.31 (m, 4H), 1.72-1.68 (m, 6H), 1.52 (s, 18H).

tert-Butyl 2-oxocyclopentanecarboxylate[20]



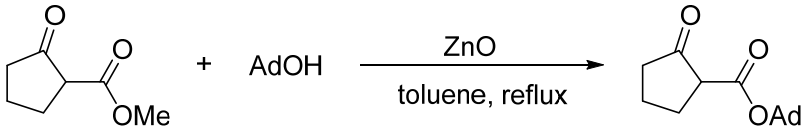
NaH (60% suspension in mineral oil, 6.7 g, 166.3 mmol) was suspended in toluene (80 mL). A solution of di-*tert*-butyladipate (1.3 g) in ^{t}BuOH (0.4 mL) and benzene (25 mL) was added. After refluxed for 30 min, more di-*tert*-butyladipate (19.2 g) a in benzene (40 mL) was added dropwise over 30 min. After the completion of the reaction, the reaction mixture was allowed to cool to room temperature before being cooled to 0 °C; AcOH (aq, 10%, 100 mL) was carefully added to the reaction mixture. The organic layer was separated, dried over $MgSO_4$ and concentrated in vacuo. The residue was distilled in vacuo to give the desired product as a colorless liquid (12.7 g, 87% yield). **B.P.**: 72-74 °C (at 2.7 mbar). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.03 (td, J = 8.8, 0.6 Hz, 1H), 2.33-2.19 (m, 4H), 2.17-2.03 (m, 1H), 1.92-1.76 (m, 1H), 1.50 (s, 9H).

tert-Butyl 2-oxocyclohexanecarboxylate[21]



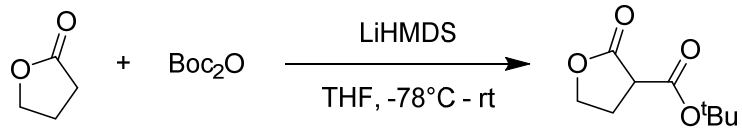
Prepared from 20.3 mmol of di-*tert*-butyl heptanedioate to afford 3.69 g (18.6 mmol, 92% yield) of desired product as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.28 (s, 1H), 2.26-2.18 (m, 2H), 2.13 (d, *J* = 6.1 Hz, 2H), 1.70-1.59 (m, 2H), 1.55 (d, *J* = 6.3 Hz, 2H), 1.47 (s, 9H) ppm。

Adamantan-1-yl 2-oxocyclopentanecarboxylate[22]



A solution of methyl 2-oxocyclopentanecarboxylate (2.7 g, 19.2 mmol), ZnO (2.33 g, 28.8 mmol, 1.5 equiv.) and 1-adamantanol (29.3 g, 96.0 mmol, 5 equiv.) in toluene (50 mL) was refluxed for 8 h. The reaction mixture was filtered and filtrate was concentrated, and was purified by flash column chromatography to give the desired product as a colorless liquid (3.5 g, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.02 (t, *J* = 8.7 Hz, 1H), 2.31-2.18 (m, 4H), 2.19-2.02 (m, 10H), 1.82 (dp, *J* = 12.7, 8.3 Hz, 1H), 1.70-1.56 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 213.1, 168.5, 81.8, 55.9, 41.2, 38.2, 36.2, 30.9, 27.5, 21.0.

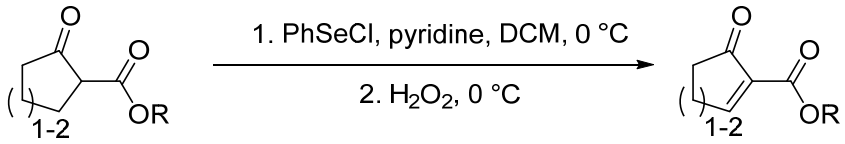
tert-Butyl 2-oxotetrahydrofuran-3-carboxylate[23]



To a solution of γ-butyrolactone (3.0 g, 34.85 mmol) in 100 mL THF, LiHMDS (2 M, 26 mL, 1.5 equiv.) was added dropwise over 30 min at -78 ºC. After stirring for 2 h at -78 ºC, di-*tert*-butyl decarbonate was added in one portion, and the reaction mixture was allowed to warm to room temperature and stirred overnight. NH_4Cl (50 mL) was added to the reaction mixture and the aqueous layer was extracted with Et_2O (25 mL × 3). The combined organic layer was washed with brine (50 mL), then dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by

flash column chromatography to give the desired product as a colorless liquid (5.32 g, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.44 (td, *J* = 5.7, 8.4 Hz, 1H), 4.35-4.24 (m, 1H), 3.43 (dd, *J* = 7.3, 9.4 Hz, 1H), 2.67-2.54 (m, 1H), 2.46 (dddd, *J* = 5.7, 7.7, 9.4, 13.2 Hz, 1H), 1.49 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8, 166.9, 82.8, 67.2, 46.9, 27.8, 26.4.

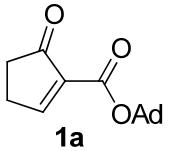
Synthesis of unsaturated *β*-keto esters



General procedure[24]

To a solution of PhSeCl (1.1 equiv.) and pyridine (1.5 equiv.) in DCM (50 mL), 2-oxocyclopentane-1-carboxylate (1 equiv.) was added dropwise at 0 °C. After stirring for 5 h, 1 M HCl (50 mL) was added to quench the reaction. The separated organic layer was washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. The solution was placed in round-bottom flask and cooled to 0 °C, and 35% H_2O_2 (aq, 3 equiv.) was added dropwise. After stirring at the same temperature for another 5 h, the resulting mixture was washed with H_2O (50 mL) and saturated aqueous $NaHCO_3$ (50 mL) and dried over $MgSO_4$ and concentrated in vacuo. The crude product was used without further purification.

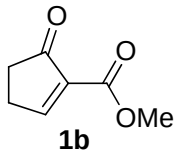
Adamantan-1-yl 5-oxocyclopent-1-enecarboxylate (1a)



1a

Prepared from 6.8 mmol of adamantan-1-yl 2-oxocyclopentane-1-carboxylate to afford 1.56 g (6.0 mmol, 88% yield) of **1a** as a viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.26 (td, *J* = 2.7, 1.1, 1H), 2.72-2.64 (m, 2H), 2.55-2.48 (m, 2H), 2.18 (s, 9H), 1.73-1.65 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 203.3, 170.7, 160.8, 138.6, 82.0, 41.4, 36.2, 35.8, 30.9, 26.3. **IR** (KBr): ν_{max} 2908, 2854, 1700, 1611, 1279, 1050, 825, 784 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 260 (M^+), 135 (100), 109 (32.2), 92 (63.49), 79 (24.85), 53 (15.76). **HRMS** (ESI) For $[C_{16}H_{24}NO_3]^+$ ($[M+NH_4]^+$): Calcld.: 278.1756, Found: 278.1746.

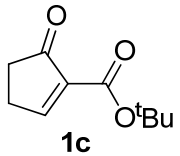
Methyl 5-oxocyclopent-1-enecarboxylate (1b)[25]



1b

Prepared from 7.0 mmol of ethyl 2-oxocyclopentane-1-carboxylate to afford 0.83 g (5.9 mmol, 84% yield) of **1b** as a pale-yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40 (t, *J* = 2.7 Hz, 1H), 3.80 (s, 3H), 2.72 (dt, *J* = 7.3, 2.5 Hz, 2H), 2.53 (dt, *J* = 6.7, 2.2 Hz, 2H).. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 203.0, 172.7, 162.3, 137.1, 52.0, 35.7, 26.7.

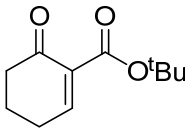
***tert*-Butyl 5-oxocyclopent-1-enecarboxylate (1c)**[25]



1c

Prepared from 14.2 mmol of *tert*-butyl 2-oxocyclopentane-1-carboxylate to afford 2.52 g (13.8 mmol, 97% yield) of **1c** as a viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27 (tq, *J* = 2.5, 1.3 Hz, 1H), 2.74-2.64 (m, 2H), 2.55-2.47 (m, 2H), 1.49 (s, 9H).

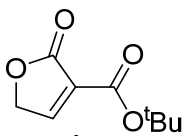
***tert*-Butyl 6-oxocyclohex-1-enecarboxylate (1d)**[26]



1d

Prepared from 3.6 mmol of *tert*-butyl 2-oxocyclohexane-1-carboxylate to afford 0.85 g (3.3 mmol, 90% yield) of **1d** as a pale-yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (s, 1H), 2.50-2.33 (m, 4H), 2.07-1.94 (m, 2H), 1.45 (s, 9H).

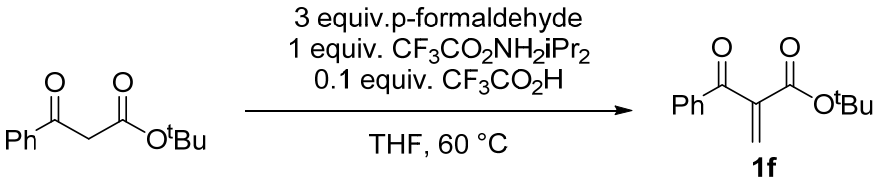
***tert*-Butyl 2-oxo-2,5-dihydrofuran-3-carboxylate (1e)**



1e

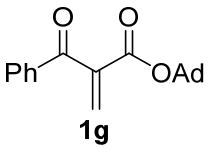
Prepared from 5.4 mmol of *tert*-butyl 2-oxotetrahydrofuran-3-carboxylate to afford 0.98 g (5.3 mmol, 99% yield) of **1e** as a pale-yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.8 Hz, 1H), 4.87 (d, *J* = 1.7 Hz, 2H), 1.50 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 159.0, 158.7, 126.8, 82.9, 69.0, 28.0, 27.8.

tert-Butyl 2-benzoylacrylate (1f)[27]



Unsaturated *β* keto ester **1f** was synthesized by a modified protocol reported in the literature.[27] To a solution of *tert*-butyl 3-oxo-3-phenylpropanoate (1.0 g, 4.5 mmol) and p-formaldehyde (0.41 g, 13.6 mmol, 3 equiv.) in dry THF (20 mL), $CF_3COONH_2{}^iPr_2$ salt (0.98 g, 4.5 mmol, 1 equiv.) and CF_3COOH (34 μL, 0.1 equiv.) were added and the mixture was warmed to 60 °C and stirred overnight. H_2O (30 mL) was added to the mixture, and the aqueous layer was extracted with Et_2O (10 mL × 3). The combined organic layer was washed sequentially with 1 M HCl (50 mL), 1 M NaOH (50 mL) and brine (50 mL), then dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography to give the desired product as a colorless liquid (0.9 g, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.3 Hz, 2H), 7.60-7.55 (m, 1H), 7.48-7.42 (m, 2H), 6.58 (s, 1H), 6.05 (s, 1H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 193.7, 163.4, 143.3, 136.7, 133.3, 130.7, 129.0, 128.4, 82.3, 27.7.

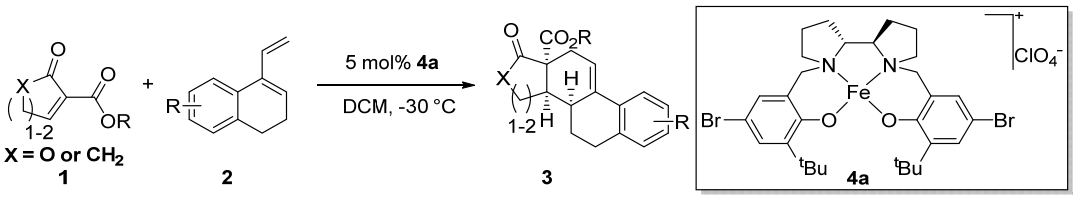
Adamantan-1-yl 2-benzoylacrylate (1g)



Prepared from 3.35 mmol of adamantan-1-yl 3-oxo-3-phenylpropanoate to afford 0.84 g (2.71 mmol, 81% yield) of **1g** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86-7.80 (m, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.56 (s, 1H), 6.02 (s, 1H), 2.16-2.02 (m, 3H), 2.00-1.95 (m, 6H), 1.66-1.49 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 193.8, 163.2, 143.6, 136.9, 133.3, 130.5, 129.2, 128.5, 82.4, 41.1, 36.1, 30.9. **IR** (KBr): ν_{max} 2911, 2854, 1712, 1668, 1329,

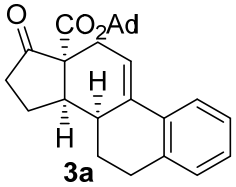
1227, 1156, 1051, 972, 964, 726 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 310 (M^+), 135 (100), 105 (63.1), 92 (34.15), 77 (40.8). **HRMS** (EI) For $[C_{20}H_{22}O_3]^+$ (M^+): Calcl.: 310.1569, Found: 310.1564.

3. General experimental procedure for Fe-BPsalan complexes catalyzed asymmetric Diels-Alder reaction of alkylidene β-ketoesters



The unsaturated β-keto ester (0.2 mmol) and Fe-BPsalan complex (0.01 mmol, 5 mol%) were dissolved in dry DCM under Ar atmosphere at room temperature. After stirring for 30 min, diene (2 equiv.) was added at the given temperature. After the completion of the reaction, the reaction mixture was concentrated, and the product was purified by flash column chromatography. The ee of the product was determined by chiral HPLC.

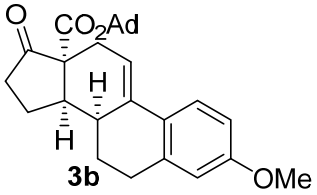
(8*S*,13*R*,14*R*)-Adamantan-1-yl 17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3a)



81 mg, viscous liquid, 97% yield, 8:1 dr, 90%, >99% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 – 7.56 (m, 1H), 7.23 – 7.03(m, 2H), 6.32 (q, *J* = 3.7 Hz, 1H), 3.00 (dt, *J* = 12.3, 6.1 Hz, 1H), 2.92 – 2.81 (m, 3H), 2.65 – 2.54 (m, 1H), 2.54 – 2.21 (m, 4H), 2.21 – 2.07 (m, 9H), 2.07 – 1.90 (m, 3H), 1.73-1.48 (m, 7H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.26, 170.28, 136.83, 133.95, 133.92, 129.26, 127.04, 126.28, 123.31, 116.73, 81.85, 59.90, 44.76, 41.27, 37.10, 36.24, 34.75, 30.95, 30.21, 26.61, 25.47, 21.52. **IR** (KBr): ν_{max} 2911, 2852, 1749, 1723, 1456, 1231, 1054 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 416 (M^+), 135 (100), 93 (8.36), 79 (8.9). **HRMS** (ESI) For $[C_{28}H_{33}O_3]^+$ ($[M+H]^+$): Calcld.: 417.2430, Found: 417.2425. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 99/1, 0.7 mL/min,

214 nm, retention times t_R (*exo* diastereoisomer, minor) = 29.6 min, t_R (*exo* diastereoisomer, major) = 41.5 min, t_R (*endo* diastereoisomer, major) = 46.1 min, t_R (*endo* diastereoisomer, minor) = 65.8 min, 90% ee (*exo*), >99% ee (*endo*), dr (*exo:endo*) = 8:1. $[\alpha]_D^{20}$ = 100.44 (*c* = 0.95, $CHCl_3$).

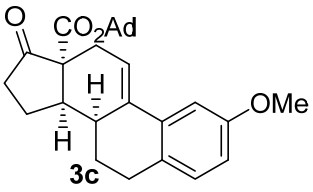
(8*S*,13*R*,14*R*)-Adamantan-1-yl 3-methoxy-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3b)



3b

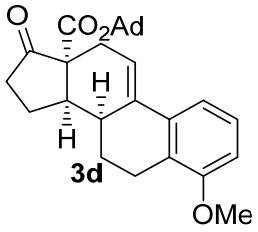
89 mg, viscous liquid, 99% yield, 12:1 dr, 91%, 94% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.8 Hz, 1H), 6.73 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.61 (d, *J* = 2.7 Hz, 1H), 6.16 (q, *J* = 3.7 Hz, 1H), 3.79 (s, 3H), 2.98 (dt, *J* = 12.2, 6.1 Hz, 1H), 2.93 – 2.76 (m, 3H), 2.61 – 2.21 (m, 4H), 2.17 – 2.05 (m, 9H), 2.05 – 1.90 (m, 2H), 1.67 – 1.51 (m, 8H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.19, 170.23, 158.57, 138.14, 133.36, 126.86, 124.65, 114.29, 113.23, 112.77, 81.67, 59.84, 55.29, 44.61, 41.19, 37.00, 36.17, 34.61, 30.87, 30.42, 26.62, 25.22, 21.42. **IR** (KBr): ν_{max} 2908, 2851, 1749, 1717, 1603, 1497, 1456, 1232, 1202, 1167, 1058, 826 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 446 (M^+), 267 (40.2), 135 (100). **HRMS** (ESI) For $[C_{29}H_{35}O_4]^+$ ($[M+H]^+$): Calcld.: 447.2535, Found: 447.2526. **HPLC**: Daicel Chiral IF3, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 214 nm, retention times t_R (*exo* diastereoisomer, minor) = 16.5 min, t_R (*exo* diastereoisomer, major) = 21.2 min, t_R (*endo* diastereoisomer, minor) = 24.6 min, t_R (*endo* diastereoisomer, major) = 26.4 min. 91% ee (*exo*), 94% ee (*endo*), dr (*exo:endo*) = 12:1. $[\alpha]_D^{20}$ = 141.50 (*c* = 1.01, $CHCl_3$).

(8*S*,13*R*,14*R*)-Adamantan-1-yl 2-methoxy-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3c)



78 mg, viscous liquid, 87% yield, 9:1 dr, 90%, 85% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 2.7 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 1H), 6.73 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.30 (q, *J* = 3.8 Hz, 1H), 3.79 (s, 3H), 3.00 (dt, *J* = 12.3, 6.1 Hz, 1H), 2.94 – 2.69 (m, 3H), 2.57 (dd, *J* = 13.1, 5.9 Hz, 1H), 2.52 – 2.35 (m, 2H), 2.29 (dt, *J* = 18.8, 3.6 Hz, 1H), 2.23 – 2.04 (m, 9H), 2.04 – 1.81 (m, 2H), 1.77 – 1.38 (m, 8H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.22, 170.23, 158.07, 134.77, 134.08, 130.10, 129.36, 116.92, 113.87, 107.52, 81.80, 59.84, 55.39, 44.75, 41.21, 37.06, 36.19, 34.67, 30.90, 29.33, 26.85, 25.43, 21.50. **IR** (KBr): ν_{max} 2906, 2849, 1741, 1719, 1610, 1572, 1492, 1282, 1232, 1054 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 446(M^+), 135(100), 93(11.91), 79(12.01), 44(20.82). **HRMS** (ESI) For $[C_{29}H_{35}O_4]^+$ ($[M+H]^+$): Calcld.: 447.2535, Found: 447.2525. **HPLC**: Daicel Chiral IA, Hexane/^{i}PrOH= 85/15, 0.7 mL/min, 214 nm, retention times t_R (*exo* diastereoisomer, minor) = 9.8 min, t_R (*endo* diastereoisomer, minor) = 15.0 min, t_R (*endo* diastereoisomer, major) = 16.0 min, t_R (*exo* diastereoisomer, major) = 18.8 min. 90% ee (*exo*), 85% ee (*endo*), dr (*exo:endo*) = 9:1. $[\alpha]_D^{20}$ = 135.64 (*c* = 1.02, $CHCl_3$).

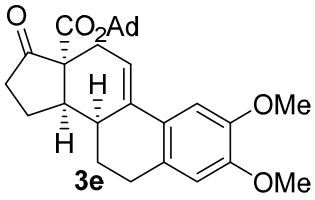
(8*S*,13*R*,14*R*)-Adamantan-1-yl 4-methoxy-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3d)



82 mg, viscous liquid, 92% yield, 6:1 dr, 90%, 78% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.33 (q, *J* = 3.6 Hz, 1H), 3.82 (s, 3H), 3.10 (ddd, *J* = 17.2, 4.9, 2.2 Hz, 1H), 3.00 (dt, *J* = 12.4, 6.2 Hz, 1H), 2.94 – 2.83 (m, 1H), 2.51 (dp, *J* = 17.4, 5.6 Hz, 3H), 2.37 (ddd, *J* = 19.2, 11.5, 8.8 Hz, 1H), 2.22 (dt, *J* = 18.8, 3.4 Hz, 1H), 2.16 – 2.06 (m, 9H), 2.00 (dd, *J* = 19.3, 6.5 Hz, 2H), 1.69 – 1.54 (m, 8H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.09, 170.10, 157.24, 135.08, 133.73, 126.31,

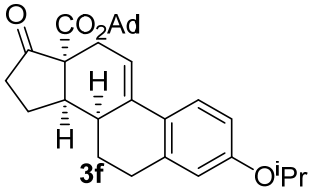
125.74, 116.85, 115.69, 108.09, 81.74, 59.69, 55.51, 44.34, 41.23, 36.84, 36.22, 33.61, 30.92, 26.11, 25.15, 23.03, 21.44. **IR** (KBr): ν_{max} 2910, 2853, 1750, 1724, 1575, 1259, 1055, 781 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 446 (M^+), 340 (34.19), 267 (100), 238 (25.12), 210 (47.39), 171 (25.23), 165 (34.93), 152 (21.52), 97 (22.6), 85 (25.14), 71 (36.81), 57 (54.93). **HRMS** (ESI) For $[C_{29}H_{35}O_4]^+$ ($[M+H]^+$): Calcld.: 447.2535, Found: 447.2528. **HPLC**: Daicel Chiral IG, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 214 nm, retention times t_R (*exo* diastereoisomer, minor) = 11.8 min, t_R (*endo* diastereoisomer, minor) = 14.1 min, t_R (*endo* diastereoisomer, major) = 14.9 min, t_R (*exo* diastereoisomer, major) = 19.9 min. 90% ee (*exo*), 78% ee (*endo*), dr (*exo:endo*) = 6:1. $[\alpha]_D^{20}$ = 122.45 (*c* = 1.05, $CHCl_3$).

(8*S*,13*R*,14*R*)-Adamantan-1-yl 2,3-dimethoxy-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3e)



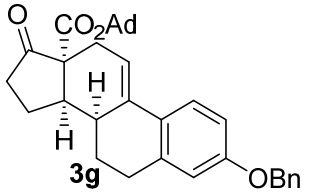
90 mg, viscous liquid, 94% yield, 10:1 dr, 90%, 96% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.07 (s, 1H), 6.56 (s, 1H), 6.13 (q, *J* = 3.7 Hz, 1H), 3.86 (d, *J* = 6.8 Hz, 6H), 2.98 (dt, *J* = 12.2, 6.1 Hz, 1H), 2.92 – 2.70 (m, 3H), 2.44 (dddd, *J* = 50.5, 19.0, 12.1, 7.0 Hz, 3H), 2.25 (dt, *J* = 18.8, 3.4 Hz, 1H), 2.19 – 2.06 (m, 9H), 2.06 – 1.90 (m, 2H), 1.73 – 1.53 (m, 8H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.22, 170.26, 148.52, 147.60, 133.63, 129.54, 126.34, 114.45, 111.41, 105.96, 81.80, 59.85, 55.99, 55.94, 44.67, 41.25, 37.03, 36.21, 34.41, 30.92, 29.75, 26.94, 25.22, 21.50.**MS** (EI): (relative intensity): *m/z* 476 (M^+), 297 (100), 135 (95.46), 93 (28.17), 79 (29.52), 67 (12.96). **HRMS** (ESI) For $[C_{30}H_{37}O_5]^+$ ($[M+H]^+$): Calcld.: 477.2641, Found: 477.2633. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 254 nm, retention times t_R (*exo* diastereoisomer, minor) = 16.6 min, t_R (*endo* diastereoisomer, minor) = 30.9 min, t_R (*endo* diastereoisomer, major) = 33.9 min, t_R (*exo* diastereoisomer, major) = 36.5 min. 90% ee (*exo*), 96% ee (*endo*), dr (*exo:endo*) = 10:1. $[\alpha]_D^{20}$ = 175.33 (*c* = 1.08, $CHCl_3$).

(8*S*,13*R*,14*R*)-Adamantan-1-yl 3-isopropoxy-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3f)



89 mg, viscous liquid, 94% yield, 10:1 dr, 90%, 96% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.8 Hz, 1H), 6.70 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.60 (d, *J* = 2.6 Hz, 1H), 6.15 (q, *J* = 3.8 Hz, 1H), 4.53 (hept, *J* = 6.0 Hz, 1H), 2.98 (dt, *J* = 12.2, 6.2 Hz, 1H), 2.92 – 2.71 (m, 3H), 2.64 – 2.20 (m, 5H), 2.19 – 1.86 (m, 11H), 1.64 (s, 7H), 1.32 (dd, *J* = 6.1, 2.2 Hz, 6H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.28, 170.28, 156.93, 138.19, 133.44, 126.70, 124.66, 115.45, 114.35, 114.21, 81.73, 69.80, 59.90, 44.66, 41.25, 37.05, 36.23, 34.65, 30.93, 30.45, 26.70, 25.27, 22.23, 22.18, 21.47. **IR** (KBr): ν_{max} 2973, 2911, 2853, 1750, 1724, 1605, 1495, 1232, 1115, 1055, 1007, 967 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 474 (M^+), 295 (100), 253 (25.26), 135 (87.96), 107 (10.36), 93 (21.73), 79 (23.81). **HRMS** (ESI) For $[C_{31}H_{39}O_4]^+$ ($[M+H]^+$): Calcld.: 475.2843, Found: 475.2841. **HPLC**: Daicel Chiral IA, Hexane/^{i}PrOH = 98/2, 0.7 mL/min, 214 nm, retention times t_R (*exo* diastereoisomer, minor) = 17.1 min, t_R (*endo* diastereoisomer, minor) = 18.9 min, t_R (*exo* diastereoisomer, major) = 23.0 min, t_R (*endo* diastereoisomer, major) = 26.6 min. 90% ee (*exo*), 96% ee (*endo*), dr (*exo:endo*) = 10:1. $[\alpha]_D^{20}$ = 87.54 (*c* = 0.95, $CHCl_3$).

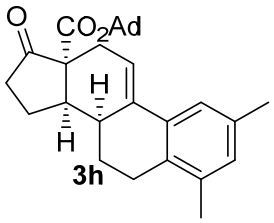
(8*S*,13*R*,14*R*)-Adamantan-1-yl 3-(benzyloxy)-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3g)



74 mg, viscous liquid, 94% yield, 13:1 dr, 90%, 95% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.8 Hz, 1H), 7.51 – 7.28 (m, 5H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.71 (s, 1H), 6.17 (s, 1H), 5.05 (s, 2H), 3.00 (dt, *J* = 12.2, 6.0 Hz, 1H), 2.86 (d, *J* = 17.3 Hz, 3H), 2.44 (ddt, *J* = 66.4, 47.8, 11.9 Hz, 4H), 2.13 (d, *J* = 21.0 Hz, 9H), 2.04 – 1.87 (m, 2H), 1.65 (s, 8H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.23, 170.26, 157.83, 138.21, 137.09, 133.37, 128.66, 128.02, 127.52, 127.15,

124.69, 114.48, 114.35, 113.53, 81.73, 69.99, 59.87, 44.63, 41.22, 37.03, 36.20, 34.62, 30.90, 30.44, 26.63, 25.26, 21.45. **IR** (KBr): ν_{max} 2909, 2851, 1747, 1718, 1606, 1569, 1497, 1455, 1237, 1100, 1061, 804, 696 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 522 (M^+), 343 (91.63), 135 (100), 91 (97.1), 79 (23.59). **HRMS** (ESI) For $[C_{35}H_{39}O_4]^+$ ($[M+H]^+$): Calcld.: 523.2848, Found: 523.2844. **HPLC**: Daicel Chiral IC, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 214 nm, retention times t_R (*exo* diastereoisomer, minor) = 17.1 min, t_R (*endo* diastereoisomer, major) = 19.5 min, t_R (*exo* diastereoisomer, major) = 20.8 min t_R (*endo* diastereoisomer, minor) = 26.8 min, 90% ee (*exo*), 95% ee (*endo*), dr (*exo:endo*) = 13:1. $[\alpha]_D^{20}$ = 130.02 (*c* = 0.96, $CHCl_3$).

(8*S*,13*R*,14*R*)-Adamantan-1-yl 2,4-dimethyl-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3h)

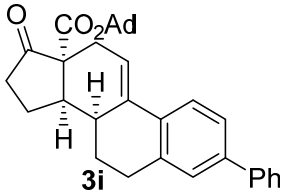


3h

87 mg, viscous liquid, 98% yield, 9:1 dr, 90%, 95% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (s, 1H), 6.88 (s, 1H), 6.31 (d, *J* = 4.6 Hz, 1H), 3.00 (dt, *J* = 12.4, 6.2 Hz, 1H), 2.94 – 2.74 (m, 2H), 2.74 – 2.32 (m, 5H), 2.28 (s, 4H), 2.21 (s, 3H), 2.18 (s, 1H), 2.17 – 1.99 (m, 11H), 1.64 (s, 7H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 214.16, 170.13, 136.37, 135.09, 134.33, 133.83, 132.30, 129.78, 121.87, 116.09, 81.74, 59.77, 44.40, 41.28, 36.92, 36.26, 33.78, 30.96, 26.63, 26.46, 25.30, 21.48, 21.24, 19.83. **IR** (KBr): ν_{max} 2907, 2854, 1749, 1724, 1455, 1325, 1171, 1054, 831, 802 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 444 (M^+), 191 (14.75), 135 (100), 95 (29.71). **HRMS** (ESI) For $[C_{30}H_{37}O_3]^+$ ($[M+H]^+$): Calcld.: 445.2743, Found: 445.2732. **HPLC**: Daicel Chiral IF3, Hexane/^{i}PrOH = 96/4, 0.7 mL/min, 214 nm, retention times t_R (*exo* diastereoisomer, minor) = 10.9 min, t_R (*endo* diastereoisomer, minor) = 12.2 min, t_R (*exo* diastereoisomer, major) = 14.9 min,, t_R (*endo* diastereoisomer, major) = 15.9 min. 90% ee (*exo*), 95% ee (*endo*), dr (*exo:endo*) = 9:1. $[\alpha]_D^{20}$ = 138.25 (*c* = 1.10, $CHCl_3$).

(8*S*,13*R*,14*R*)-Adamantan-1-yl 17-oxo-3-phenyl-7,8,12,13,14,15,16,17-octahydro-

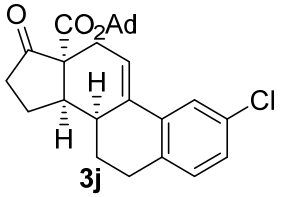
6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3i)



3i

89 mg, viscous liquid, 90% yield, 7:1 dr, 90%, 95% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.42 (q, *J* = 7.5 Hz, 3H), 7.33 (dd, *J* = 7.3, 4.3 Hz, 2H), 6.37 (q, *J* = 3.6 Hz, 1H), 3.02 (dt, *J* = 12.1, 6.1 Hz, 1H), 2.98 – 2.84 (m, 3H), 2.69 – 2.57 (m, 1H), 2.57 – 2.21 (m, 4H), 2.19 – 2.05 (m, 11H), 1.65 (s, 7H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.22, 170.28, 140.83, 139.76, 137.19, 133.65, 133.07, 128.86, 127.80, 127.35, 127.02, 125.13, 123.84, 116.91, 81.90, 59.90, 44.73, 41.29, 37.09, 36.25, 34.77, 30.96, 30.40, 26.66, 25.51, 21.52 **IR** (KBr): ν_{max} 2909, 2852, 1745, 1720, 1483, 1271, 1232, 1205, 1057, 905, 726, 699 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 492 (M^+), 314 (10.79), 135 (100), 95 (13.02), 79 (12.67). **HRMS** (ESI) For $[C_{34}H_{37}O_3]^+$ ($[M+H]^+$): Calcld.: 493.2743, Found: 493.2736. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 214 nm, retention times t_R (*exo* diastereoisomer, minor) = 12.9 min, t_R (*endo* diastereoisomer, minor) = 15.5 min, t_R (*exo* diastereoisomer, major) = 16.9 min, t_R (*endo* diastereoisomer, major) = 19.6 min. 90% ee (*exo*), 95% ee (*endo*), dr (*exo:endo*) = 7:1. $[\alpha]_D^{20}$ = 98.37 (*c* = 1.00, $CHCl_3$).

(8*S*,13*R*,14*R*)-Adamantan-1-yl 2-chloro-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3j)

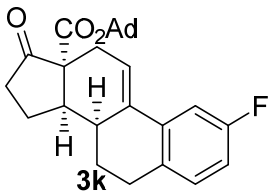


3j

70 mg, viscous liquid, 78% yield, 5:1 dr, 84%, 86% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 2.1 Hz, 1H), 7.07 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.28 (dq, *J* = 14.6, 3.4, 2.9 Hz, 1H), 3.00 (dt, *J* = 12.2, 6.1 Hz, 1H), 2.94 – 2.71 (m, 3H), 2.63 – 2.22 (m, 4H), 2.19 – 1.91 (m, 11H), 1.68 – 1.46 (m, 8H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 213.94, 170.17, 135.14, 133.12, 132.08, 130.54, 126.93, 123.31, 118.15, 81.99, 77.16, 59.75, 44.60, 41.27, 37.03, 36.22, 34.50, 30.95, 29.65, 26.39, 25.46, 21.48. **IR** (KBr): ν_{max} 2912,

2853, 1951, 1705, 1478, 1204, 1053, 800 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 450 (M^+), 135 (100), 93 (10.9), 79 (12.5). **HRMS** (ESI) For $[C_{28}H_{32}{}^{35}ClO_3]^+$ ($[M+H]^+$): Calcld.: 451.2040, Found: 451.2032. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 214 nm, retention times t_R (*exo* diastereoisomer, minor) = 8.8 min, t_R (*endo* diastereoisomer, minor) = 11.6 min, t_R (*endo* diastereoisomer, major) = 12.6 min, t_R (*exo* diastereoisomer, major) = 13.7 min. 84% ee (*exo*), 86% ee (*endo*), dr (*exo:endo*) = 5:1. $[\alpha]_D^{20}$ = 96.4 (*c* = 1.06, $CHCl_3$).

(8*S*,13*R*,14*R*)-Adamantan-1-yl 2-fluoro-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3k)

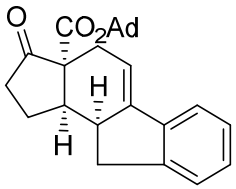


3k

47 mg, viscous liquid, 54% yield, 6:1 dr, 87%, 94% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.21 (m, 1H), 7.04 (dd, *J* = 8.7, 6.1 Hz, 1H), 6.82 (td, *J* = 8.3, 2.8 Hz, 1H), 6.26 (dq, *J* = 11.2, 3.3 Hz, 1H), 3.00 (dt, *J* = 12.2, 6.1 Hz, 1H), 2.94 – 2.71 (m, 3H), 2.60 – 2.23 (m, 4H), 2.22 – 1.84 (m, 11H), 1.75 – 1.41 (m, 8H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 213.95, 170.22, 161.69 (d, *J* = 242.5 Hz), 135.74 (d, *J* = 7.2 Hz), 133.41 (d, *J* = 2.5 Hz), 132.45 (d, *J* = 2.7 Hz), 130.59 (d, *J* = 8.0 Hz), 118.06, 114.14 (d, *J* = 21.5 Hz), 109.51 (d, *J* = 22.1 Hz), 81.98, 59.78, 44.68, 41.30, 37.05, 36.26, 34.51, 30.98, 29.54, 26.64, 25.47, 21.49.**^{19}F NMR** (376 MHz, Chloroform-*d*) δ -117.06 (q, *J* = 8.3 Hz, 1F) **IR** (KBr): ν_{max} 2913, 2857, 1751, 1720, 1490, 1263, 1229, 1203, 1052, 866 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 434 (M^+), 135 (100), 93 (9.12), 79 (9.28). **HRMS** (ESI) For $[C_{28}H_{32}FO_3]^+$ ($[M+H]^+$): Calcld.: 435.2335, Found: 435.2327. **HPLC**: Daicel Chiral IG, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 214 nm, retention times t_R (*exo* diastereoisomer, minor) = 15.2 min, t_R (*endo* diastereoisomer, minor) = 19.1 min, t_R (*endo* diastereoisomer, major) = 22.6 min, t_R (*exo* diastereoisomer, major) = 29.5 min. 87% ee (*exo*), 94% ee (*endo*), dr (*exo:endo*) = 6:1. $[\alpha]_D^{20}$ = 91.33 (*c* = 1.05, $CHCl_3$).

(3a*R*,10a*S*,10b*R*)-Adamantan-1-yl 3-oxo-1,2,3,3a,4,10,10a,10b-octahydro-

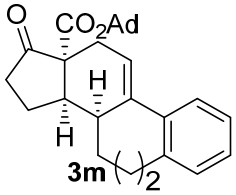
cyclopenta[a]fluorene-3a-carboxylate (3l)



3l

80 mg, viscous liquid, 99% yield, >99:1 dr, 59% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (q, *J* = 4.6 Hz, 1H), 7.27 (d, *J* = 3.3 Hz, 1H), 7.23 – 7.15 (m, 2H), 6.04 (dt, *J* = 5.6, 3.2 Hz, 1H), 3.27 – 3.18 (m, 1H), 3.14 – 3.03 (m, 2H), 2.94 – 2.80 (m, 2H), 2.47 – 2.32 (m, 3H), 2.19 – 1.96 (m, 10H), 1.64 (d, *J* = 3.0 Hz, 6H), 1.39 (qd, *J* = 12.1, 9.4 Hz, 1H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 214.67, 170.81, 144.63, 142.87, 140.28, 128.10, 126.83, 125.39, 120.40, 113.37, 81.98, 60.55, 43.86, 41.29, 39.49, 37.82, 36.26, 33.24, 30.98, 26.08, 21.29.. **IR** (KBr): ν_{max} 2922, 2850, 1734, 1604, 1458, 1263, 736 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 402 (M^+), 238 (27.28), 224 (56.19), 191 (65.55), 181 (41.01), 167 (72.09), 160 (43.06), 152 (44.52), 111 (45.64), 97 (66.37), 83 (76.63), 69 (72.83), 57 (100), 43 (74.17). **HRMS** (ESI) For $[C_{27}H_{31}O_3]^+$ ($[M+H]^+$): Calcld.: 403.2273, Found: 403.2268. **HPLC**: Daicel Chiral PA2, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 214 nm, retention times t_R (*exo* diastereoisomer, minor) = 22.6 min, t_R (*exo* diastereoisomer, major) = 29.6 min, 59% ee (*exo*), dr (*exo:endo*) >99:1. $[\alpha]_D^{20}$ = 113.37 (*c* = 0.98, $CHCl_3$).

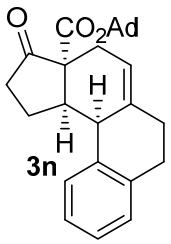
(3a*R*,3b*S*,12a*R*)-Adamantan-1-yl 1-oxo-1,2,3,3a,3b,4,5,6,12,12a-decahydrobenzo-[3,4]cyclohepta[1,2-e]indene-12a-carboxylate (3m)



64 mg, viscous liquid, 74% yield, >99:1 dr, 88% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 (h, *J* = 6.9, 6.2 Hz, 2H), 7.12 – 7.03 (m, 2H), 5.88 (dt, *J* = 6.7, 3.1 Hz, 1H), 2.94 (td, *J* = 8.9, 4.4 Hz, 1H), 2.81 – 2.69 (m, 2H), 2.67 – 2.51 (m, 3H), 2.50 – 2.40 (m, 1H), 2.28 – 2.13 (m, 4H), 2.10 (d, *J* = 2.9 Hz, 6H), 1.89 (ddt, *J* = 18.5, 13.7, 7.6 Hz, 2H), 1.77 (tt, *J* = 12.7, 5.9 Hz, 1H), 1.66 (s, 5H), 1.57 – 1.27 (m, 4H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 216.19, 171.33, 146.42, 141.59,

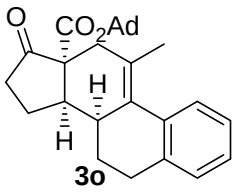
137.88, 128.15, 127.77, 127.14, 126.89, 124.24, 82.11, 60.93, 49.27, 41.23, 38.87, 38.16, 36.20, 31.49, 30.95, 27.64, 26.35, 26.15, 21.86. **IR** (KBr): ν_{max} 2911, 2850, 1742, 1720, 1236, 1199, 1054, 763 cm^{-1}. **MS** (EI): (relative intensity): *m/z*.430 (M^+), 135 (100). **HRMS** (ESI) For $[C_{29}H_{35}O_3]^+$ ($[M+H]^+$): Calcld.: 431.2586, Found: 431.2578. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 99/1, 0.7 mL/min, 254 nm, retention times t_R (*exo* diastereoisomer, major) = 13.6 min, t_R (*exo* diastereoisomer, minor) = 15.1 min, 88% ee (*exo*), dr (*exo:endo*) > 99:1. $[\alpha]_D^{20}$ = 3.26 (*c* = 0.45, $CHCl_3$).

(3a*R*,11b*S*,11c*R*)-Adamantan-1-yl 3-oxo-2,3,3a,4,6,7,11b,11c-octahydro-1*H*-cyclopenta[c]phenanthrene-3a-carboxylate (3n)



47 mg, viscous liquid, 56% yield, >99:1 dr, 99% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 1H), 7.16 – 7.05 (m, 3H), 5.61 (h, *J* = 2.5 Hz, 1H), 4.20 (s, 1H), 2.99 (dq, *J* = 10.3, 5.1 Hz, 1H), 2.67 (dddd, *J* = 18.7, 14.8, 11.3, 4.1 Hz, 2H), 2.47 (dt, *J* = 13.7, 5.2 Hz, 2H), 2.31 (ddd, *J* = 20.5, 10.5, 5.1 Hz, 2H), 2.23 – 2.12 (m, 9H), 2.03 (dtt, *J* = 34.6, 10.6, 6.2 Hz, 3H), 1.69 (d, *J* = 4.4 Hz, 7H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 212.23, 172.91, 140.64, 138.35, 135.90, 128.86, 128.15, 126.05, 125.77, 120.09, 82.88, 66.04, 43.17, 41.54, 41.21, 36.90, 36.17, 33.13, 30.96, 30.81, 28.57, 26.83 **IR** (KBr): ν_{max} 2909, 2849, 1752, 1718, 1227, 1057, 744 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 416 (M^+), 135 (100). **HRMS** (ESI) For $[C_{28}H_{36}NO_3]^+$ ($[M+NH_4]^+$): Calcld.: 434.2695, Found: 434.2681. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 99/1, 0.7 mL/min, 254 nm, retention times t_R (*exo* diastereoisomer, minor) = 24.7 min, t_R (*exo* diastereoisomer, major) = 37.5 min. 99% ee (*exo*), dr (*exo:endo*) > 99:1. $[\alpha]_D^{20}$ = -44.84 (*c* = 1.05, $CHCl_3$).

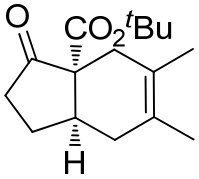
(8*S*,13*R*,14*R*)-Adamantan-1-yl 11-methyl-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3o)



3o

41 mg, viscous liquid, 48% yield, 14:1 dr, 74%, 54% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 1H), 7.19 – 7.06 (m, 3H), 2.85 – 2.72 (m, 2H), 2.68 – 2.49 (m, 2H), 2.43 – 2.30 (m, 3H), 2.23 – 2.02 (m, 6H), 1.97 (dd, *J* = 13.4, 2.2 Hz, 8H), 1.76 (dtd, *J* = 12.5, 10.6, 5.4 Hz, 2H), 1.58 (d, *J* = 3.3 Hz, 7H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 214.04, 169.66, 139.35, 136.65, 130.41, 128.95, 128.68, 127.70, 126.22, 125.05, 81.86, 64.47, 41.23, 40.17, 37.98, 36.20, 35.95, 30.90, 30.17, 25.77, 25.40, 21.87. **IR** (KBr): ν_{max} 2912, 2853, 1745, 1721, 1456, 1234, 1055, 765, 737 cm^{-1}. **MS** (ESI): *m/z* 431 ([M+H]$^+$). **HRMS** (ESI) For $[C_{29}H_{35}O_3]^+$ ([M+H]$^+$): Calcl.: 431.2581, Found: 431.2579. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 99/1, 0.7 mL/min, 254 nm, retention times t_R (*exo* diastereoisomer, major) = 17.3 min. t_R (*endo* diastereoisomer, major) = 19.7 min, t_R (*endo* diastereoisomer, minor) = 22.5 min, t_R (*exo* diastereoisomer, minor) = 25.3 min, 74% ee (*exo*), 54% ee (*endo*), dr (*exo:endo*) 14:1. **$[\alpha]_D^{20}$** = 41.80 (*c* = 0.67, $CHCl_3$, 74% ee).

(3a*R*,7a*R*)-*tert*-Butyl-5,6-dimethyl-3-oxo-2,3,3a,4,7,7a-hexahydro-1H-indene-3a-carboxylate (3p)

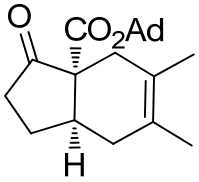


3p

50 mg, colourless liquid, 95%, 92% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 2.86 – 2.75 (m, 1H), 2.46 – 2.32 (m, 3H), 2.31 – 2.17 (m, 1H), 2.07 – 1.95 (m, 2H), 1.79 (d, *J* = 17.8 Hz, 1H), 1.69 – 1.57 (m, 7H), 1.42 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.40, 171.05, 123.44, 122.38, 81.50, 60.48, 38.57, 36.33, 32.56, 30.31, 28.05, 25.90, 19.28, 19.00. **IR** (neat): 2917, 1721, 1451, 1368, 1244, 1147, 1036, 847, 522 cm^{-1}. **HRMS** (ESI) For $[C_{16}H_{24}O_3N]^+$ ([M+NH_4]$^+$): Calcld. 282.2069, Found: 282.2065. **HPLC**: Daicel Chiral ADRH, Acetone/Water = 50/50, 0.5 mL/min, 214 nm, t_R (major) =11.7 min, t_R (minor) = 12.8 min (92% ee). **$[\alpha]_D^{20}$** = 100.04 (c = 0.763,

$CHCl_3$).

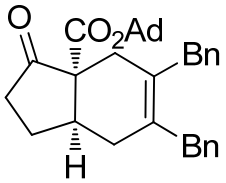
(3a*R*,7a*R*)-Adamantan-1-yl-5,6-dimethyl-3-oxo-2,3,3a,4,7,7a-hexahydro-1H-inden e-3a-carboxylate (3q)



3q

67 mg, colourless liquid, 98%, 96% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 2.79 (dtd, *J* = 10.0, 6.8, 3.5 Hz, 1H), 2.44 – 2.30 (m, 3H), 2.30 – 2.16 (m, 1H), 2.16 – 2.09 (m, 3H), 2.09 – 1.95 (m, 9H), 1.83 – 1.67 (m, 2H), 1.63 (s, 11H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.41, 170.77, 123.39, 122.41, 81.52, 60.55, 41.24, 38.63, 36.31, 36.23, 32.59, 30.91, 30.32, 25.89, 19.26, 18.98. **IR** (neat): 2911, 1751, 1457, 1369, 1238, 1155, 1057, 804, 519 cm^{-1}. **HRMS** (ESI) For $[C_{22}H_{30}O_3Na]^+$ ($[M+Na]^+$): Calcld. 365.2093, Found: 365.2082. **HPLC**: Daicel Chiral ADRH, Acetone/Water = 60/40, 0.7 mL/min, 214 nm, t_R (major) =33.3 min, t_R (minor) = 51.0 min (96% ee). $[\alpha]_D^{20}$ = 75.13 (c = 0.948, $CHCl_3$).

(3a*R*,7a*R*)-Adamantan-1-yl-5,6-dibenzyl-3-oxo-2,3,3a,4,7,7a-hexahydro-1H-inden e-3a-carboxylate (3r)

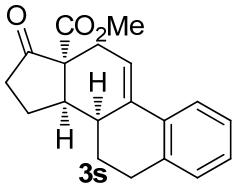


3r

22 mg, colourless liquid, 22%, 72% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.23 (m, 4H), 7.17 (ddt, *J* = 18.2, 11.1, 4.3 Hz, 6H), 3.63 (dd, *J* = 15.2, 6.4 Hz, 2H), 3.48 (t, *J* = 13.9 Hz, 2H), 2.77 (dtd, *J* = 10.2, 6.9, 3.5 Hz, 1H), 2.53 (d, *J* = 17.3 Hz, 1H), 2.36 – 2.20 (m, 3H), 2.14 (s, 3H), 2.07 – 1.95 (m, 8H), 1.88 (d, *J* = 18.2 Hz, 1H), 1.70 – 1.52 (m, 7H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.22, 170.46, 139.93, 139.80, 128.95, 128.71, 128.57, 128.54, 128.43, 126.18, 81.71, 60.57, 41.18, 39.35, 38.97, 38.71, 36.53, 36.24, 30.95, 30.88, 29.85, 29.06, 25.98. **IR** (neat): 2912, 2851, 1746, 1717, 1453, 1053, 1015, 698 cm^{-1}. **HRMS** (ESI) For $[C_{32}H_{38}O_3Na]^+$ ($[M+Na]^+$): Calcld. 517.2719, Found: 517.2709. **HPLC**: Daicel Chiral AD-H, Hexane/iPrOH = 96/4, 0.7

mL/min, 214 nm, t_R (major) =18.8 min, t_R (minor) = 15.4 min (72% ee). $[\alpha]_D^{20}$ = 29.77(c = 0.55, $CHCl_3$, 72% ee).

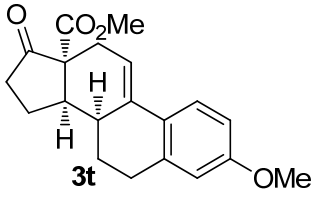
(8*S*,13*R*,14*R*)-Methyl 17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[*a*]phenanthrene-13-carboxylate (3s)



3s

61 mg, viscous liquid, 98% yield, 5:1 dr, 11%, 39% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 – 7.47 (m, 1H), 7.20 – 7.03 (m, 3H), 6.30 (dq, *J* = 20.5, 3.5, 3.0 Hz, 1H), 3.73 (d, *J* = 15.9 Hz, 3H), 3.17 – 2.69 (m, 4H), 2.67 – 2.20 (m, 4H), 2.18 – 2.03 (m, 1H), 2.02 – 1.83 (m, 1H), 1.70 – 1.53 (m, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 213.40, 171.81, 136.76, 133.88, 133.65, 129.38, 127.19, 126.27, 123.29, 115.94, 59.20, 52.92, 44.15, 36.83, 34.34, 30.17, 26.63, 25.42, 21.29. **IR** (KBr): ν_{max} 2952, 2912, 2834, 1749,1728, 1605, 1498, 1234, 1166, 1036, 803 cm^{-1}. MS (EI): (relative intensity): *m/z* 326 (M^+), 267 (100), 238 (29.61), 210 (57.69), 171 (31.63), 165 (37.66). **HRMS** (ESI) For $[C_{20}H_{23}O_4]^+$ ($[M+H]^+$): Calcld.: 327.1591, Found: 327.1587. **HPLC**: Daicel Chiral IG, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 214 nm, retention times t_R (*endo* diastereoisomer, major) = 20.9 min, t_R (*endo* diastereoisomer, minor) = 22.8 min, t_R (*exo* diastereoisomer, minor) = 23.8 min, t_R (*exo* diastereoisomer, major) = 26.2 min. 11% ee (*exo*), 39% ee (*endo*), dr (*exo:endo*) = 5:1. $[\alpha]_D^{20}$ = 29.58 (*c* = 1.01, $CHCl_3$).

(8*S*,13*R*,14*R*)-Methyl 3-methoxy-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3t)

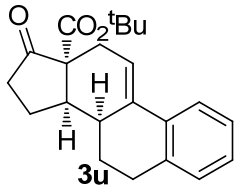


3t

64 mg, viscous liquid, 98% yield, 6:1 dr, 13%, 24% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (dd, *J* = 39.4, 8.8 Hz, 1H), 6.73 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.61 (d, *J* = 2.8 Hz, 1H), 6.16 (q, *J* = 3.7 Hz, 1H), 3.84 – 3.67 (m, 6H), 3.05 (dt, *J* = 12.2, 6.1 Hz, 1H), 2.99 – 2.76 (m, 3H), 2.54 (dd,

J = 19.1, 8.8 Hz, 2H), 2.46 – 2.24 (m, 2H), 2.12 – 1.87 (m, 2H), 1.70 – 1.55 (m, 2H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 213.43, 171.85, 158.76, 138.19, 133.43, 126.69, 124.72, 113.67, 113.38, 112.92, 59.25, 55.38, 52.89, 44.12, 36.83, 34.33, 30.47, 26.71, 25.31, 21.27.**IR** (KBr): ν_{max} 2952, 2912, 2834, 1749,1728, 1605, 1498, 1234, 1166, 1036, 803 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 326 (M^+), 267 (100), 238 (29.61), 210 (57.69), 171 (31.63), 165 (37.66). **HRMS** (ESI) For $[C_{20}H_{23}O_4]^+$ ($[M+H]^+$): Calcld.: 327.1591, Found: 327.1587. **HPLC**: Daicel Chiral IE3, Hexane/^{i}PrOH = 85/15, 0.7 mL/min, 214 nm, retention times t_R (*endo* diastereoisomer, minor) = 29.5 min, t_R (*exo* diastereoisomer, minor) = 31.3 min, t_R (*exo* diastereoisomer, major) = 33.0 min, t_R (*endo* diastereoisomer, major) = 35.1 min. 13% ee (*exo*), 24% ee (*endo*), dr (*exo:endo*) = 6:1. $[\alpha]_D^{20}$ = 29.58 (*c* = 0.90, $CHCl_3$).

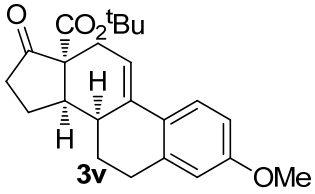
(8*S*,13*R*,14*R*)-*tert*-Butyl 17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3u)



3u

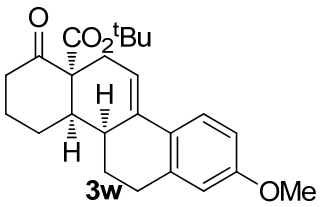
65 mg, viscous liquid, 96% yield, 14:1 dr, 89%, 88% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 – 7.57 (m, 1H), 7.12 (tdd, *J* = 14.1, 9.4, 6.0 Hz, 3H), 6.33 (q, *J* = 3.7 Hz, 1H), 3.01 (dt, *J* = 12.2, 6.1 Hz, 1H), 2.88 (dt, *J* = 10.3, 4.8 Hz, 3H), 2.61 (dd, *J* = 17.8, 10.1 Hz, 1H), 2.54 – 2.34 (m, 2H), 2.29 (dt, *J* = 19.2, 3.5 Hz, 1H), 2.10 – 1.92 (m, 2H), 1.69 – 1.52 (m, 2H), 1.44 (d, *J* = 5.5 Hz, 9H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 214.16, 170.58, 136.83, 133.96, 133.91, 129.28, 127.07, 126.29, 123.32, 116.67, 81.82, 59.83, 44.65, 37.04, 34.74, 30.21, 28.10, 26.63, 25.46, 21.51. **IR** (KBr): ν_{max} 2973, 2935, 1746, 1705, 1367, 1326, 1269, 1153, 850, 743 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 338 (M^+), 282 (51.73), 237 (100), 218 (26.65), 193 (30.19), 179 (47.02), 165 (42,69), 141 (39.55), 128 (30.38), 115 (20.61), 109 (13.52), 57 (58.01). **HRMS** (ESI) For $[C_{22}H_{30}NO_3]^+$ ($[M+NH_4]^+$): Calcld.: 356.2226, Found: 356.2215. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 98/2, 0.7 mL/min, 254 nm, retention times t_R (*exo* diastereoisomer, minor) = 11.9 min, t_R (*endo* diastereoisomer, minor) = 15.7 min, t_R (*endo* diastereoisomer, major) = 16.6 min, t_R (*exo* diastereoisomer, major) = 18.0 min. 89% ee (*exo*), 88% ee (*endo*), dr (*exo:endo*) = 14:1. $[\alpha]_D^{20}$ = 130.81 (*c* = 0.99, $CHCl_3$).

(8*S*,13*R*,14*R*)-*tert*-Butyl 3-methoxy-17-oxo-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (3v)



61 mg, viscous liquid, 83% yield, >99:1 dr, 89% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.8 Hz, 1H), 6.72 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.61 (d, *J* = 2.8 Hz, 1H), 6.15 (q, *J* = 3.6 Hz, 1H), 3.77 (s, 3H), 2.99 (dt, *J* = 12.2, 6.1 Hz, 1H), 2.93 – 2.74 (m, 3H), 2.62 – 2.18 (m, 4H), 2.09 – 1.88 (m, 2H), 1.60 (ddt, *J* = 25.9, 12.4, 6.9 Hz, 2H), 1.44 (s, 9H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 214.04, 170.47, 158.54, 138.07, 133.25, 126.75, 124.60, 114.13, 113.18, 112.74, 81.58, 59.69, 55.22, 44.41, 36.86, 34.50, 30.36, 27.97, 26.59, 25.11, 21.34. **IR** (KBr): ν_{max} 2973, 2910, 2834, 1749, 1724, 1604, 1499, 1231, 1151, 846 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 368 (M^+), 267 (100), 211 (32.19), 171 (23.27), 165 (33.53), 115 (19.51), 57 (26.18), 44 (31.6). **HRMS** (ESI) For $[C_{23}H_{32}NO_4]^+$ ($[M+NH_4]^+$): Calcld.: 386.2331, Found: 386.2321. **HPLC**: Daicel Chiral IF3, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 214 nm, retention times t_R (*endo* diastereoisomer, minor) = 9.2 min, t_R (*endo* diastereoisomer, minor) = 10.2 min, t_R (*exo* diastereoisomer, minor) = 10.8 min, t_R (*exo* diastereoisomer, major) = 12.9 min. 89% ee (*exo*), dr (*exo:endo*) > 99:1. **$[\alpha]_D^{20}$** = 147.27 (*c* = 0.94, $CHCl_3$).

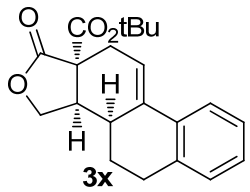
(6a*R*,10a*R*,10b*S*)-*tert*-Butyl 2-methoxy-7-oxo-6,6a,7,8,9,10,10a,10b,11,12-decahydrochrysene-6a-carboxylate (3w)



65 mg, viscous liquid, 85% yield, >99:1 dr, 90% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.8 Hz, 1H), 6.72 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 6.18 (d, *J* = 5.5 Hz, 1H), 3.78 (s, 3H), 3.00 – 2.87 (m, 1H), 2.87 – 2.76 (m, 2H), 2.72 – 2.56 (m, 2H), 2.55 – 2.43 (m, 1H), 2.43 – 2.32 (m, 2H), 2.10 (s, 1H), 1.89 – 1.62 (m, 5H), 1.44 (s, 9H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 210.01, 170.82, 158.57, 138.15, 132.38, 126.68, 124.71, 113.34, 112.88, 81.38,

62.48, 55.37, 43.07, 37.33, 36.69, 31.19, 29.85, 28.08, 27.97, 27.60, 24.66, 21.07.**IR** (KBr): ν_{max} 2931, 2831, 1732, 1703, 1604, 1497, 1456, 1366, 1298, 1234, 1164, 1139, 852, 804 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 382 (M^+), 326 (22.72), 281 (100), 211 (16.84), 123 (17.79), 165 (33.53), 115 (19.51), 57 (26.18), 44 (31.6). **HRMS** (EI) For $[C_{24}H_{30}O_4]^+$ (M^+): Calcld.: 382.2144, Found: 382.2151. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, retention times t_R (*exo* diastereoisomer, minor) = 9.1 min, t_R (*exo* diastereoisomer, major) = 14.0 min. 90% ee (*exo*), dr (*exo:endo*) > 99:1. $[\alpha]_D^{20}$ = 71.16 (*c* = 1.01, $CHCl_3$).

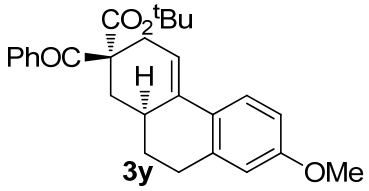
tert-Butyl (3a*R*,3b*S*,11a*R*)-1-oxo-3,3a,3b,4,5,11-hexahydrophenanthro[1,2-c]furan-11a(1*H*)-carboxylate (3x)



3x

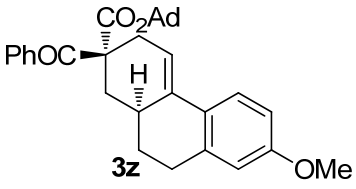
72 mg, viscous liquid, 97% yield, >99:1 dr, 87% ee. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.7 Hz, 1H), 6.75 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.62 (d, *J* = 2.7 Hz, 1H), 6.26 (s, 1H), 4.35 (t, *J* = 8.9 Hz, 1H), 3.91 (dd, *J* = 9.0, 7.8 Hz, 1H), 3.79 (s, 3H), 3.34 (ddd, *J* = 9.0, 7.8, 5.1 Hz, 1H), 2.83 – 2.71 (m, 4H), 2.62 (d, *J* = 13.2 Hz, 1H), 1.98 (dd, *J* = 12.7, 4.3 Hz, 1H), 1.49 (s, 9H), 1.38 (ddd, *J* = 12.7, 8.5, 4.2 Hz, 1H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 176.98, 169.32, 159.01, 138.57, 135.66, 126.66, 124.89, 116.39, 113.26, 112.97, 83.02, 68.82, 55.84, 55.41, 44.30, 35.75, 30.13, 28.22, 27.99, 25.58. **IR** (neat): ν_{max} 2963, 2921, 2844, 1765, 1735, 1632, 1598, 1567, 1486, 1368, 1247, 1147, 1098, 1027, 895, 849, 809, 768, 711, 624, 547, 460 cm^{-1}. **MS** (ESI): *m/z* 393.1 ($[M+Na]^+$). **HRMS** (ESI) For $[C_{22}H_{27}O_5]^+$ ($[M+H]^+$): Calcld.: 371.1858, Found: 371.1854. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 97/3, 0.7 mL/min, 254 nm, retention times t_R (*exo* diastereoisomer, major) = 32.2 min, t_R (*exo* diastereoisomer, minor) = 33.7 min. 87% ee (*exo*), dr (*exo:endo*) > 99:1. $[\alpha]_D^{20}$ = 116.34 (*c* = 0.92, $CHCl_3$).

(2*R*,10a*S*)-*tert*-Butyl 2-benzoyl-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene-2-carboxylate (3y)



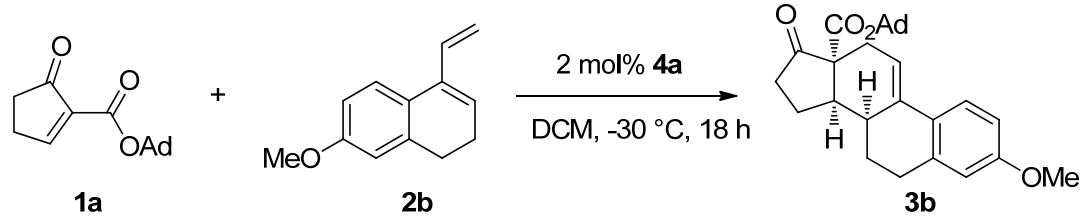
42 mg, viscous liquid, 97% yield, 2:1 dr, 67%, 72% ee. **Mixture of two isomers**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 29.2, 7.8 Hz, 2H), 7.61 – 7.48 (m, 2H), 7.43 (td, *J* = 7.6, 3.9 Hz, 2H), 6.71 (ddd, *J* = 16.9, 7.9, 3.7 Hz, 1H), 6.58 (dd, *J* = 26.8, 2.8 Hz, 1H), 6.20 – 6.11 (m, 1H), 3.78 (d, *J* = 10.5 Hz, 3H), 3.11 (ddd, *J* = 22.2, 18.5, 5.4 Hz, 1H), 2.98 – 2.15 (m, 5H), 1.96 (ddt, *J* = 34.0, 25.0, 13.5 Hz, 2H), 1.60 – 1.31 (m, 5H), 1.26 (s, 5H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.98, 195.96, 173.12, 171.93, 158.59, 158.53, 137.88, 137.65, 136.24, 135.37, 135.22, 134.33, 132.79, 132.62, 128.84, 128.72, 128.52, 128.45, 126.83, 126.79, 125.07, 125.05, 115.23, 114.84, 113.26, 113.19, 112.80, 112.71, 82.22, 81.83, 57.52, 57.10, 55.33, 55.30, 36.85, 36.75, 32.99, 32.91, 32.62, 30.84, 30.24, 30.00, 27.75, 27.69.**IR** (KBr): ν_{max} 2930, 2836, 1728, 1682, 1607, 1499, 1449, 1369, 1253, 1152, 1038, 843, 811, 700 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 418 (M^+), 318 (18.28), 239 (37.1), 105 (100), 77 (51.27), 57 (26.66). **HRMS** (ESI) For $[C_{27}H_{31}NO_4]^+$ ($[M+H]^+$): Calcl.: 419.2217, Found: 419.2214. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 214 nm, retention times t_R (*exo* diastereoisomer, minor) = 7.4 min, t_R (*endo* diastereoisomer, major) = 8.5 min, t_R (*exo* diastereoisomer, major) = 9.5 min, t_R (*endo* diastereoisomer, minor) = 11.3 min. 67% ee (*exo*), 72% ee (*endo*), dr (*exo:endo*) = 2:1. $[\alpha]_D^{20}$ = 6.73 (*c* = 1.08, $CHCl_3$).

(3*S*,5*S*,7*S*)-Adamantan-1-yl (2*R*,10*aS*)-2-benzoyl-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene-2-carboxylate (3z)



93 mg, viscous liquid, 94% yield, 1.6:1 dr, 68%, 78% ee. **Mixture of two isomers**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 31.4, 7.7 Hz, 2H), 7.54 (dt, *J* = 13.5, 9.0 Hz, 2H), 7.43 (q, *J* = 7.0 Hz, 2H), 6.78 – 6.67 (m, 1H), 6.58 (dd, *J* = 26.7, 2.7 Hz, 1H), 6.24 – 6.06 (m, 1H), 3.77 (d, *J* = 10.5 Hz, 3H), 3.10 (td, *J* = 15.7, 13.3, 5.0 Hz, 1H), 2.82 (dddd, *J* = 62.4, 28.1, 16.6, 5.0 Hz, 2H), 2.60 (ddt, *J* = 17.0, 10.1, 5.9 Hz, 1H), 2.53 – 2.26 (m, 2H), 2.16 – 1.84 (m, 11H), 1.58 (d, *J* = 23.4 Hz, 7H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.94, 196.04, 172.82, 171.65, 158.55, 158.50, 137.85, 137.63, 136.19, 135.41, 135.19, 134.30, 132.77, 132.56, 128.85, 128.76, 128.50, 128.42, 126.84, 126.79, 125.07, 125.04, 115.28, 114.86, 113.23, 113.17, 112.77, 112.69, 82.23, 81.84, 57.52, 57.16, 55.31, 55.29, 40.95, 40.87, 36.86, 36.71, 36.09, 36.06, 33.01, 32.96, 32.61, 30.83, 30.76, 30.25, 30.00.**IR** (KBr): ν_{max} 2913, 2853, 1725, 1683, 1606, 1498, 1449, 1235, 1052, 965, 736, 701 cm^{-1} **MS** (EI): (relative intensity): *m/z* 496 (M^+), 317 (14.59), 239 (38.59) 135 (100), 105 (36.94). **HRMS** (ESI) For $[C_{33}H_{37}NO_4]^+$ ($[M+H]^+$): Calcl.: 497.2686, Found: 497.2685. **HPLC**: Daicel Chiral AD-H, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, retention times t_R (*exo* diastereoisomer, minor) = 10.4 min, t_R (*endo* diastereoisomer, minor) = 15.8 min, t_R (*endo* diastereoisomer, major) = 17.0 min, t_R (*exo* diastereoisomer, major) = 20.0 min. 67% ee (*exo*), 72% ee (*endo*), dr: (*exo:endo*) = 2:1. $[\alpha]_D^{20}$ = 31.11 (*c* = 0.90, $CHCl_3$).

Gram scale and transformation of products:



1a
1.0 g 3.84 mmol

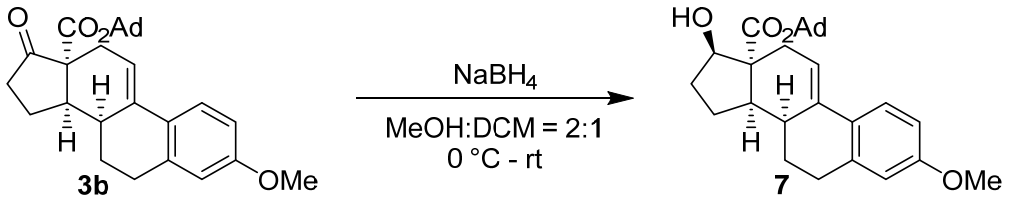
2b
2 eq.

3b
1.67g, 97% yield
13:1 dr, 92% ee

The unsaturated *β*-keto ester **1a** (1.0 g, 3.8 mmol) and **4a** (60 mg, 2 mol%) were dissolved in dry DCM (38 mL, 0.1 M) under Ar atmosphere at room temperature. After stirring for 30 min, diene **2b** (2 equiv.) was added at -30 ºC. After the completion of the reaction (18 h), the reaction mixture

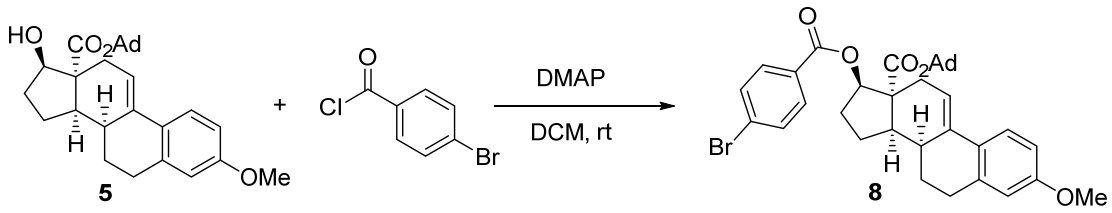
was concentrated, and the product was purified by flash column chromatography to afford the desired product (1.67 g, 97% yield, 13:1 dr, 92% ee) as viscous liquid.

(8*S*,13*R*,14*R*,17*R*)-Adamantan-1-yl 17-hydroxy-3-methoxy-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (7)[28]



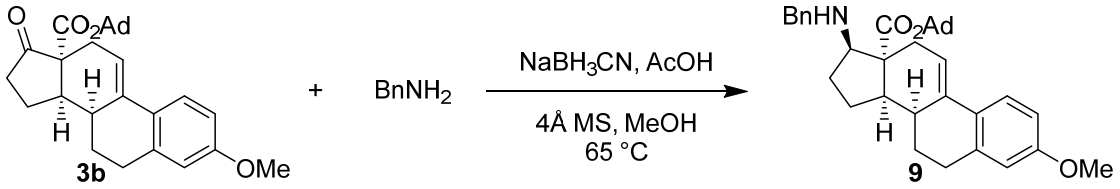
$NaBH_4$ (12.2 mg, 0.32 mmol, 2 equiv.) was suspended in 2 mL dry MeOH, and the solution was cooled to 0 ºC. Then **3b** (72 mg, 0.16 mmol, in 1 mL DCM) was added. The reaction mixture was allowed to warm to room temperature, stirred overnight. H_2O (5 mL) was added to quench the reaction, and MeOH was evaporated in vacuo. The mixture was neutralized by 1 M AcOH, and extracted by DCM (5 mL × 3). The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. the product was purified by flash column chromatography to afford a viscous liquid (68 mg, 94%).**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.8 Hz, 1H), 6.72 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 6.21 (q, *J* = 3.7 Hz, 1H), 4.40 (t, *J* = 8.3 Hz, 1H), 3.78 (s, 3H), 2.93 – 2.73 (m, 2H), 2.67 (ddt, *J* = 13.0, 6.0, 3.1 Hz, 1H), 2.54 – 2.39 (m, 3H), 2.19 – 2.11 (m, 4H), 2.08 (d, *J* = 3.0 Hz, 7H), 1.87 – 1.75 (m, 1H), 1.69 – 1.55 (m, 8H), 1.48 (dddt, *J* = 15.9, 12.9, 7.9, 3.8 Hz, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.70, 158.27, 138.08, 132.30, 127.35, 124.58, 114.90, 113.26, 112.67, 80.98, 78.43, 55.27, 53.68, 43.08, 41.39, 36.19, 35.29, 30.86, 30.78, 28.92, 27.29, 24.54, 22.33.**IR** (KBr): ν_{max} 3482, 2910, 2852, 1708, 1607, 1497, 1233, 1054, 803 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 448 (M^+), 313 (70.0), 135 (100). **HRMS** (ESI) For $[C_{29}H_{37}O_4]^+$ ($[M+H]^+$): Calcld.: 449.2692, Found: 449.2681. $[\alpha]_D^{20}$ = 32.52 (*c* = 1.00, $CHCl_3$).

(8*S*,13*R*,14*R*,17*R*)-Adamantan-1-yl 17-((4-bromobenzoyl)oxy)-3-methoxy-7,8,12,13,14,15,16,17-octahydro-6H-cyclopenta[a]phenanthrene-13-carboxylate (8)[29]



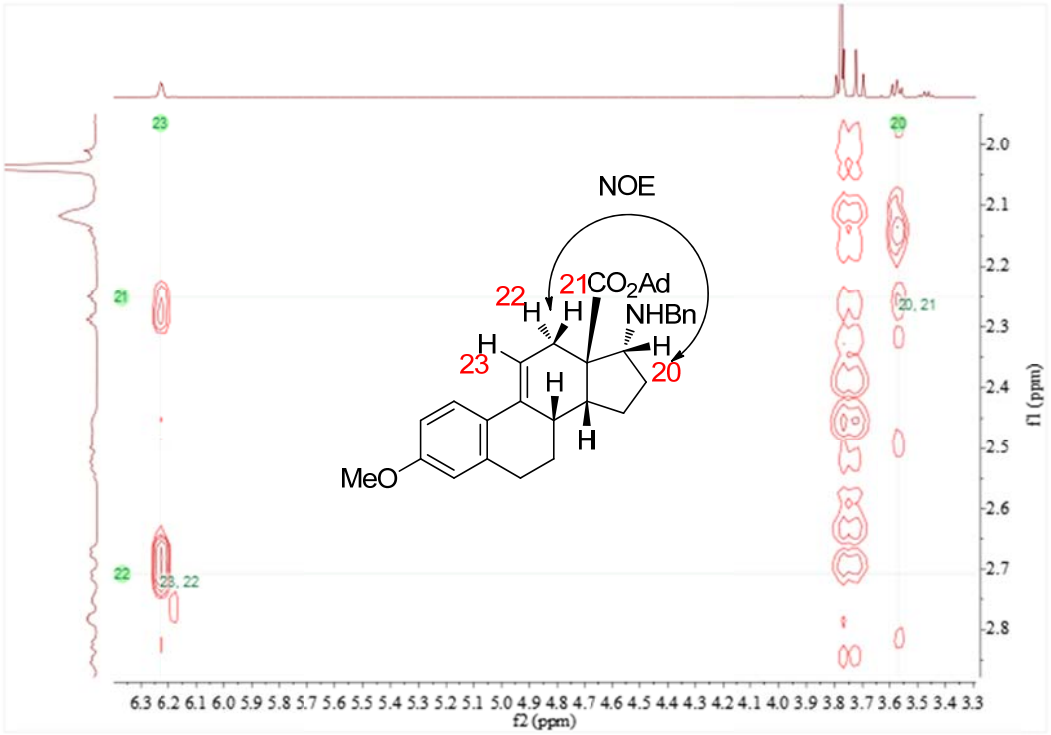
To a solution of **4-6** (55 mg, 0.12 mmol), DMAP (1.5 mg, 10% mol), and pyridine (20 μL, 0.24 mmol, 2 equiv.) in 2 mL DCM, 4-bromobenzoyl chloride (40.4 mg, 0.18 mmol, 1.5 equiv.) was added at 0 ºC. the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by H_2O and extracted by DCM (5 mL × 3). The combined organic layer was dried by $MgSO_4$, concentrated in vacuo. The product was purified by flash column chromatography to afford a viscous liquid (69 mg, 89%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 – 7.80 (m, 2H), 7.59 (d, *J* = 8.5 Hz, 3H), 6.74 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.60 (d, *J* = 2.7 Hz, 1H), 6.23 (dt, *J* = 5.2, 2.8 Hz, 1H), 5.65 (dd, *J* = 9.4, 6.3 Hz, 1H), 3.79 (s, 3H), 2.95 – 2.71 (m, 3H), 2.64 (dd, *J* = 12.2, 6.5 Hz, 1H), 2.59 – 2.50 (m, 1H), 2.42 (ddt, *J* = 25.9, 17.5, 6.1 Hz, 2H), 2.07 (dd, *J* = 24.2, 3.1 Hz, 9H), 1.93 – 1.72 (m, 3H), 1.69 – 1.47 (m, 8H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.65, 165.22, 158.37, 137.94, 131.84, 131.78, 131.25, 129.32, 128.11, 127.16, 124.66, 114.95, 113.26, 112.77, 80.96, 80.86, 55.30, 53.74, 44.73, 41.17, 36.21, 34.69, 30.84, 30.68, 28.38, 27.41, 24.68, 23.30.**IR** (KBr): ν_{max} 2915, 2852, 1720, 1606, 1590, 1497, 1274, 1116, 1103, 1055, 1012, 757, 737 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 630 (M^+), 495 (13.3), 251 (40.9), 183 (21.6), 135 (100), 93 (21.5), 79 (20.0). **HRMS** (EI) For $[C_{36}H_{39}O_5Br]^+$ (M^+): Calcld.: 630.1981, Found: 630.1988. **$[\alpha]_D^{20}$** = 32.79 (*c* = 1.10, $CHCl_3$).

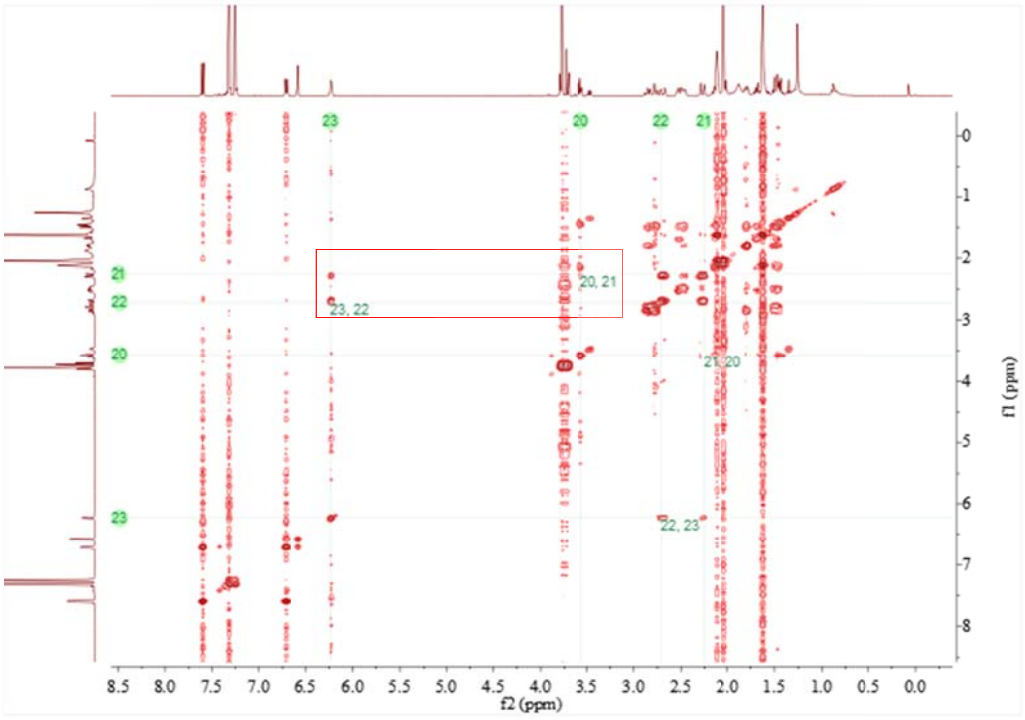
(8*S*,13*R*,14*R*,17*R*)-Adamantan-1-yl 17-(benzylamino)-3-methoxy-7,8,12,13,14,15,16,17-octahydro-6*H*-cyclopenta[a]phenanthrene-13-carboxylate (9)[30]



200 mg pre-activated 4 Å Molecular sieves, **3b** (44.7 mg, 0.1 mmol), benzylamine (22 μL, 0.2 mmol, 2 equiv.) and 2 mL MeOH were placed to a dry Schlenk tube, and the reaction mixture was heated to 65 ºC and stirred overnight. $NaBH_3CN$ (25.1 mg, 0.4 mmol, 4 equiv.) and acetic acid (23 μL, 0.4 mmol, 4 equiv.) were added sequentially. The reaction mixture was stirred overnight, and then filtered and concentrated in vacuo. The product was purified by flash column chromatography to afford a viscous liquid (44 mg, 82%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.9 Hz, 1H), 7.33 (d, *J* = 4.4 Hz, 4H), 6.72 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.58 (d, *J* = 2.7 Hz, 1H), 6.23 (dd, *J* = 5.3, 2.7 Hz, 1H), 3.78 (s, 4H), 3.71 (d, *J* = 13.1 Hz, 1H), 3.58 (t, *J* = 8.3 Hz, 1H), 2.93 – 2.63 (m, 3H), 2.50 (dd, *J* = 18.8, 12.1 Hz, 2H), 2.33 – 2.22 (m, 1H), 2.12 (d, *J* = 5.1 Hz, 4H), 2.03 (d, *J* = 2.9 Hz, 6H), 1.89 – 1.65 (m, 5H), 1.62 (d, *J* = 3.1 Hz, 5H), 1.49 (ddt, *J* = 12.4, 9.6, 5.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.79, 158.23, 140.54, 137.81, 131.38, 128.47, 128.20, 127.40, 127.02, 124.74, 115.43, 113.27, 112.68, 80.39, 65.93, 55.29, 53.13, 52.44, 46.32, 41.27, 36.25, 34.93, 30.85, 30.79, 29.16, 27.62, 23.95, 22.94. **IR** (KBr): ν_{max} 2915, 28531709, 1607, 1496, 1456, 1279, 1233, 1210, 1175, 1057, 754 cm^{-1}. **MS** (EI): (relative intensity): *m/z* 537 (M^+), 251 (100), 135 (69.82), 91 (49.31). **HRMS** (ESI) For $[C_{36}H_{44}NO_3]^+$ ($[M+H]^+$): Calcld.: 538.3321, Found: 538.3305. **$[\alpha]_D^{20}$** = 55.27 (*c* = 1.10, $CHCl_3$).

The absolute configuration of 9 was confirmed by NOE





4. High resolution ESI-MS spectrum

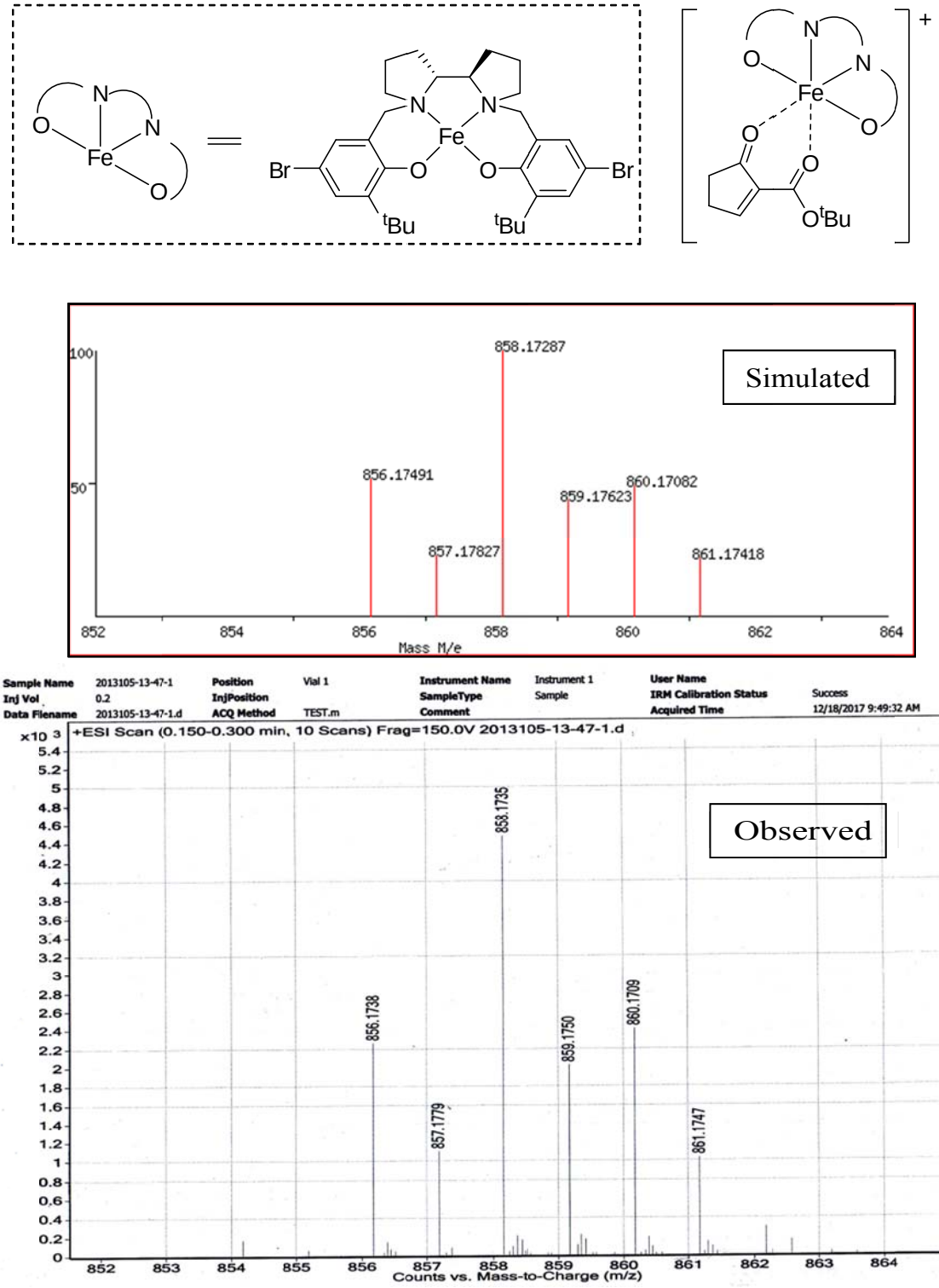


Fig. S1 Upper: Simulated isotopic distribution pattern for the adduct formed between the deprotonated form of substrate **1c** with catalyst **4a** (with ClO_4 as counter anion). Lower: Observed isotopic distribution pattern for the peak at m/z 858.2 detected by high-resolution ESI-MS analysis of a reaction mixture of **1c** and **4a** in DCM/MeOH.

5. IR spectra

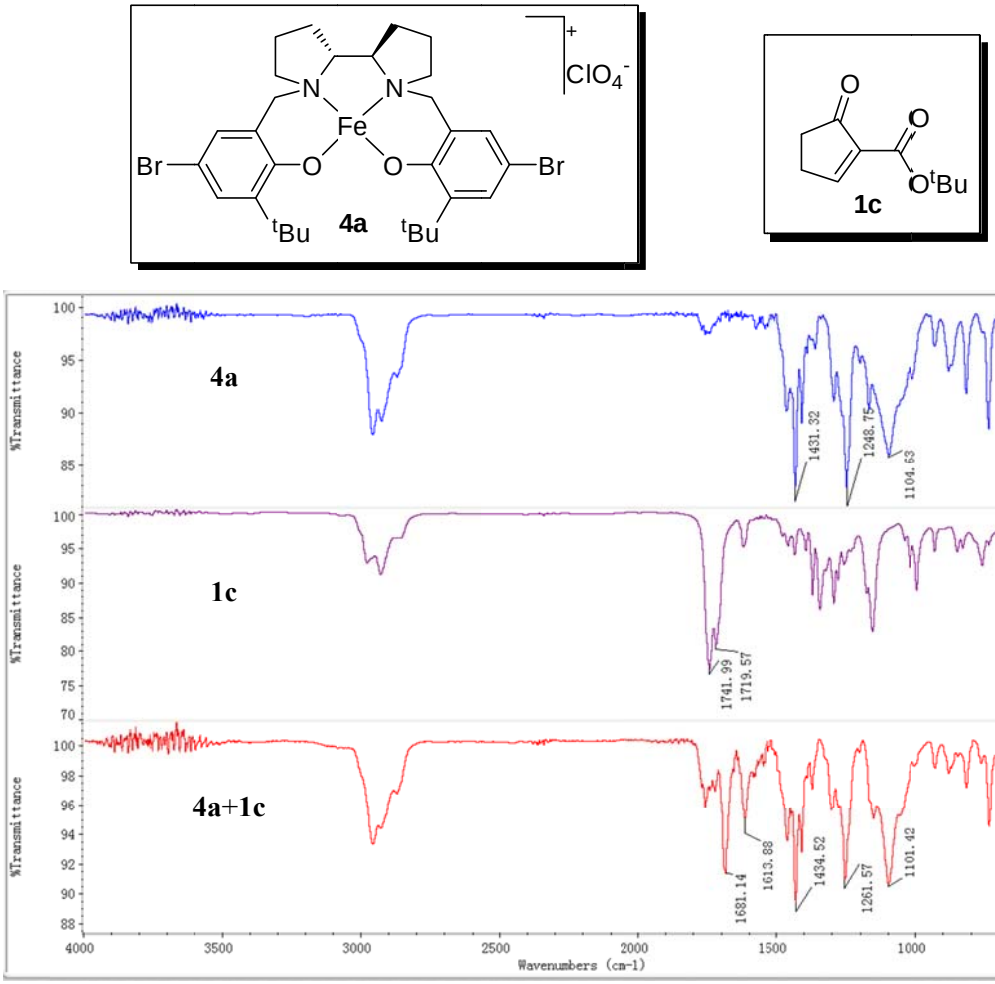
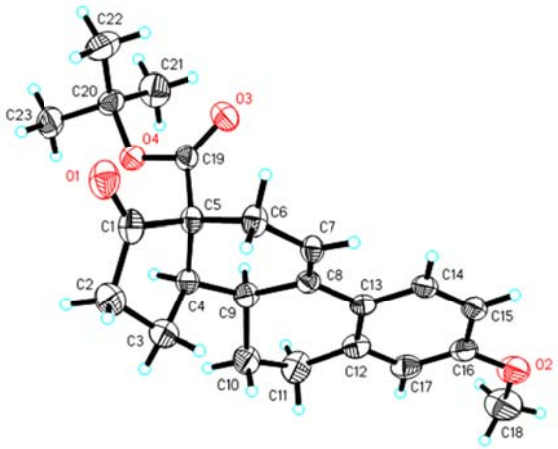
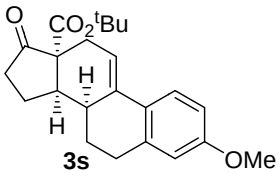


Fig. S2 Upper: IR spectrum of catalyst **4a**. Middle: IR spectrum of substrate **1c**. Lower: IR spectrum of the adduct formed between catalyst **4a** and substrate **1c**.

6. Crystal data of 3s (CCDC 1948562)



≡



Identification code	cu_d8v17496_0m	
Empirical formula	$C_{23}H_{28}O_4$	
Formula weight	368.45	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.98190(10) Å	α= 90°.
	b = 11.9988(2) Å	β= 90°.
	c = 18.9538(3) Å	γ = 90°.
Volume	2042.69(5) $Å^3$	
Z	4	
Density (calculated)	1.198 Mg/m^3	
Absorption coefficient	0.647 mm^{-1}	
F(000)	792	
Crystal size	0.180 x 0.150 x 0.120 mm^3	
Theta range for data collection	4.666 to 65.974°.	
Index ranges	-10<=h<=10, -11<=k<=14, -22<=l<=19	
Reflections collected	15052	
Independent reflections	3529 [R(int) = 0.0341]	
Completeness to theta = 67.679°	95.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5750	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3529 / 0 / 249	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0867	

R indices (all data)	R1 = 0.0346, wR2 = 0.0887
Absolute structure parameter	0.08(8)
Extinction coefficient	0.0110(19)
Largest diff. peak and hole	0.132 and -0.086 e.Å^{-3}

7. Computational details

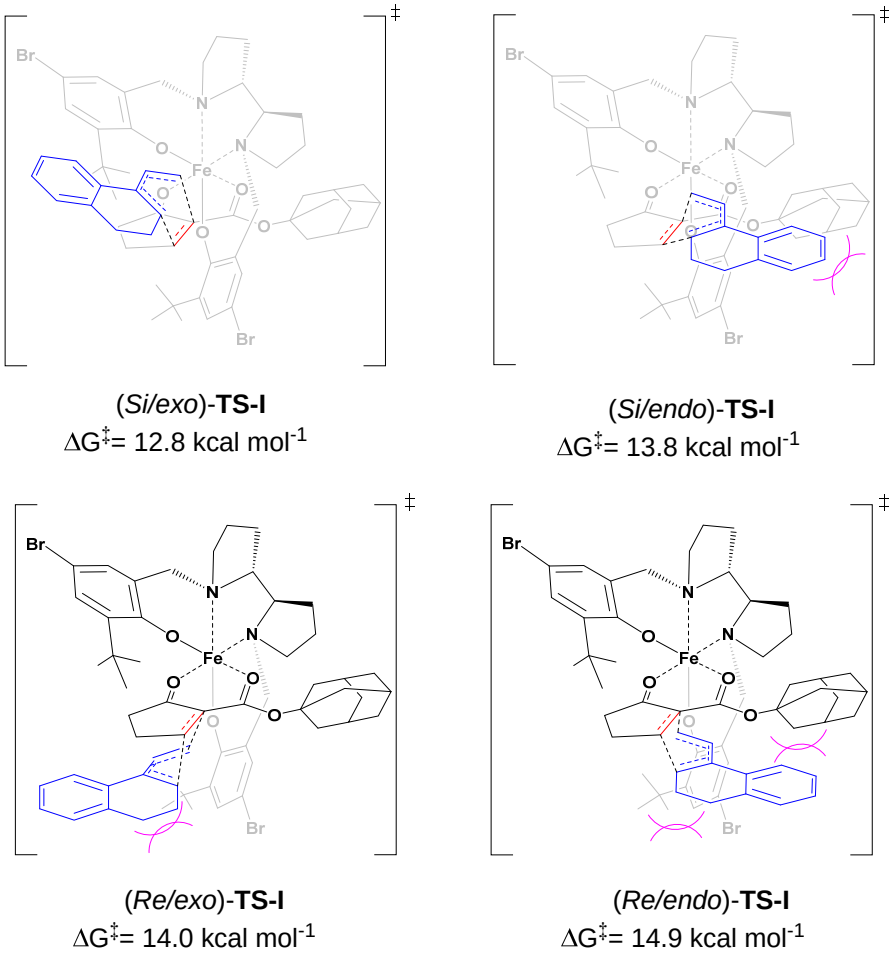


Fig. S3 Structures and corresponding energies at transition state that account for the stereoselectivity and enantioselectivity in the reaction between **1a** and **2a** using intermediate **I** as catalytic precursor. Steric hindrance was shown in purple.

In this work, all DFT calculations were performed using GAUSSIAN09.[31] Geometries were optimized using the B3LYP functional[32] in combination with def2-SVP basis set.[33] Dispersion correction with Grimme's D3 version was employed.[34, 35] Frequency calculations were carried out for these optimized structures to verify the stationary points or transition states at the same level. Solvent effect was considered by means of the polarizable continuum model (PCM). [36] An alternative set of single-point energies was refined with the triple-ζ basis set def2-TZVP. The method employed has been proved successful in treating the Fe-catalyzed systems.[37,38] The open-shell unrestricted U-B3LYP is adopted by default in the calculations of doublet ($S = 1/2$), quartet ($S = 3/2$), and sextet ($S = 5/2$) spin states. The stereoselectivity and enantioselectivity was evaluated by

$$ee \text{ or } de = \frac{\exp(-\Delta\Delta G^{\neq} / RT) - 1}{\exp(-\Delta\Delta G^{\neq} / RT) + 1} \qquad (1)$$

where $\Delta\Delta G^{\neq}$ is given by

$$\Delta\Delta G^{\neq} = \Delta G^{\neq}_{favored} - \Delta G^{\neq}_{disfavored} \qquad (2)$$

$\Delta G^{\neq}$ is the activation Gibbs free energy, R is the gas constant (8.317 J mol^{-1} K^{-1}), and T is temperature (298 K) in Kelvin.

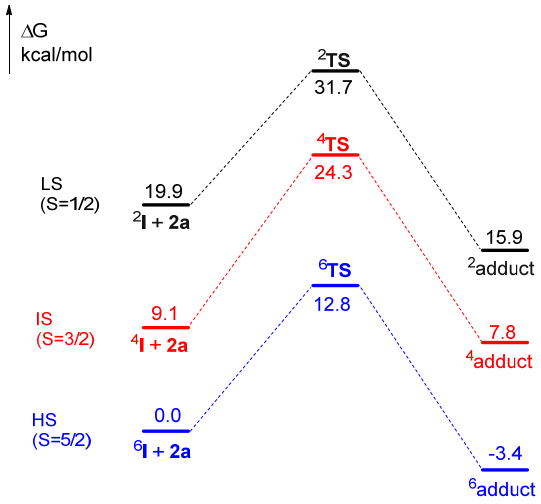


Fig. S4 The examination of multi-state reactivity for the Fe-BPsalan catalyzed Diels-Alder reaction. HS, high-spin; IS, intermediate-spin; LS, low-spin.

Cartesian coordinates of DFT-calculated structures

(*Si/exo*)-**TS-I**

Fe	1.093228000	11.807471000	5.212583000
Br	7.633456000	14.326922000	3.825484000
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O	2.671091000	11.966302000	6.301632000
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H	2.235241000	14.551516000	6.486393000
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C	6.071567000	13.591654000	4.655971000
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(*Si/endo*)-**TS-I**

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C	-1.799120000	12.486002000	6.219583000
H	-2.058403000	11.488807000	6.589667000
H	-1.994539000	12.505974000	5.142650000
C	2.631145000	8.589114000	2.425605000
C	1.588011000	7.632790000	1.819236000
C	0.396960000	8.524207000	1.497275000
C	0.510548000	9.687862000	2.292201000
C	1.812752000	9.779135000	2.880610000
H	3.379417000	8.921516000	1.684581000
H	1.252748000	6.910315000	2.582379000
H	1.960510000	7.045734000	0.970721000
H	-0.586215000	8.096841000	1.301118000
H	3.194006000	8.167053000	3.269249000
O	2.229393000	10.657675000	3.663636000
C	-0.565967000	10.601469000	2.611378000
O	-1.659773000	10.353713000	1.916584000
O	-0.473780000	11.500141000	3.467387000
C	-3.914716000	10.246866000	1.189780000
C	-2.989616000	10.900834000	2.220012000
C	-3.019106000	12.424687000	2.064328000
C	-4.461355000	12.914596000	2.292650000
C	-4.906871000	12.517607000	3.711535000
C	-4.870783000	10.985556000	3.859827000
C	-5.817221000	10.351439000	2.826292000
C	-5.355577000	10.738780000	1.410971000
C	-5.395218000	12.269163000	1.254883000
C	-3.436718000	10.472179000	3.620485000

H	-3.573638000	10.493923000	0.177213000
H	-3.853292000	9.152623000	1.300257000
H	-2.335899000	12.893109000	2.784503000
H	-2.671832000	12.694688000	1.054467000
H	-4.485370000	14.010971000	2.187464000
H	-4.249487000	12.989791000	4.459295000
H	-5.926950000	12.887703000	3.903787000
H	-5.181539000	10.702460000	4.878005000
H	-5.819444000	9.254547000	2.937724000
H	-6.849747000	10.697939000	2.996218000
H	-6.011079000	10.269825000	0.660176000
H	-6.424928000	12.636860000	1.393480000
H	-5.082139000	12.554193000	0.236447000
H	-3.406627000	9.373929000	3.683772000
H	-2.752964000	10.861424000	4.380838000
H	2.423801000	13.937598000	2.518896000
C	-3.461959000	9.896447000	-3.354299000
C	-2.542551000	8.844229000	-3.344181000
C	-1.409748000	8.886512000	-2.527470000
C	-1.197710000	10.013291000	-1.688896000
C	-2.124837000	11.075487000	-1.728106000
C	-3.248130000	11.019026000	-2.547230000
H	0.428970000	8.105953000	-3.275349000
H	-4.343879000	9.842810000	-3.996472000
H	-2.702062000	7.976330000	-3.988383000
C	-0.365777000	7.800474000	-2.569841000
C	0.023220000	10.059174000	-0.874263000
H	-1.984357000	11.948186000	-1.091844000
H	-3.962485000	11.844570000	-2.548708000
C	0.692340000	8.867919000	-0.555012000
C	0.236031000	7.564277000	-1.186601000
H	1.759368000	8.966218000	-0.352592000
H	1.077805000	6.861000000	-1.249269000
H	-0.797230000	6.870418000	-2.967269000
H	-0.529017000	7.084397000	-0.551715000
C	0.516091000	11.332784000	-0.396483000
H	-0.105388000	12.210504000	-0.578397000
C	1.672890000	11.515961000	0.276599000
H	2.401768000	10.720798000	0.427537000
H	1.962297000	12.505670000	0.629431000

(*Re/exo*)-**TS-I**

Fe	0.971229000	11.519556000	5.262822000
Br	7.910574000	13.070123000	3.861138000
Br	-1.274925000	10.804240000	12.349571000
O	2.578710000	11.669578000	6.300739000
O	0.128804000	10.346009000	6.489795000
N	1.565933000	13.411539000	4.206828000
N	-0.317795000	13.049837000	6.298204000
C	2.713338000	14.032433000	4.935231000
H	2.377177000	14.269916000	5.951556000
C	3.910709000	13.131687000	5.035581000
C	5.132186000	13.472606000	4.455721000
H	5.227351000	14.385555000	3.865254000
C	6.224790000	12.632075000	4.656746000
C	6.114776000	11.478220000	5.436459000
H	6.999901000	10.860550000	5.572300000
C	4.901239000	11.106768000	6.030918000
C	3.774592000	11.949230000	5.804975000
C	4.782577000	9.823893000	6.870774000
C	4.197363000	10.148879000	8.262812000
H	3.194635000	10.584561000	8.180132000
H	4.846511000	10.858439000	8.800823000
H	4.130874000	9.227708000	8.864132000
C	3.862275000	8.823907000	6.140129000
H	3.768932000	7.896929000	6.728246000
H	4.274495000	8.566491000	5.151867000
H	2.862814000	9.244869000	5.994550000
C	6.147250000	9.147335000	7.081550000

H	6.860036000	9.810545000	7.596012000
H	6.601552000	8.822341000	6.132882000
H	6.014619000	8.250996000	7.706490000
C	0.186755000	12.989945000	7.697540000
H	-0.204785000	13.841548000	8.277123000
H	1.279529000	13.102250000	7.646735000
C	-0.170368000	11.713023000	8.422577000
C	-0.500681000	11.811952000	9.777757000
H	-0.491881000	12.787202000	10.267746000
C	-0.846160000	10.669921000	10.489616000
C	-0.914148000	9.428212000	9.856569000
H	-1.220297000	8.563644000	10.440773000
C	-0.611929000	9.288261000	8.498631000
C	-0.189308000	10.446204000	7.771890000
C	-0.751808000	7.926344000	7.798688000
C	0.627486000	7.473732000	7.277132000
H	1.058345000	8.214540000	6.595852000
H	0.542484000	6.508812000	6.751223000
H	1.330658000	7.341785000	8.113967000
C	-1.764697000	8.058195000	6.638653000
H	-2.758923000	8.330241000	7.027576000
H	-1.862962000	7.098890000	6.104832000
H	-1.455534000	8.828879000	5.924102000
C	-1.271978000	6.834236000	8.747599000
H	-0.586430000	6.658220000	9.590538000
H	-1.364030000	5.887527000	8.193420000
H	-2.265313000	7.078891000	9.154099000
C	1.842040000	13.411102000	2.749739000
H	1.169559000	12.685594000	2.276282000
H	3.000407000	14.981346000	4.458255000
C	1.518458000	14.850389000	2.267326000
H	2.432743000	15.447113000	2.142041000
H	1.017315000	14.822564000	1.289941000
C	0.604064000	15.446098000	3.372895000
H	-0.325341000	15.870118000	2.970749000
H	1.112993000	16.244843000	3.932948000
C	0.325541000	14.233765000	4.270810000
H	-0.437181000	13.622637000	3.762649000
C	-0.159573000	14.421490000	5.697252000
H	0.576299000	14.979165000	6.289379000
C	-1.548622000	15.110141000	5.765944000
H	-1.490644000	16.091970000	6.253568000
H	-1.935111000	15.272489000	4.748744000
C	-2.445291000	14.116357000	6.519464000
H	-3.491749000	14.147027000	6.185067000
H	-2.440864000	14.313245000	7.602590000
C	-1.780357000	12.777732000	6.217562000
H	-2.060062000	11.966025000	6.896623000
H	-2.003227000	12.450531000	5.196306000
C	2.926823000	9.430683000	1.837280000
C	2.216485000	9.342344000	0.474985000
C	0.729533000	9.405094000	0.810138000
C	0.614359000	9.972010000	2.121126000
C	1.890278000	10.026570000	2.762044000
H	3.841983000	10.040030000	1.837682000
H	2.497298000	8.454809000	-0.107797000
H	2.465736000	10.220626000	-0.142079000
H	0.038353000	9.758409000	0.040779000
H	3.207311000	8.439472000	2.230656000
O	2.156930000	10.493548000	3.887736000
C	-0.573334000	10.516206000	2.730016000
O	-1.678427000	10.216087000	2.071212000
O	-0.562420000	11.192055000	3.776651000
C	-3.938231000	9.964203000	1.428139000
C	-3.032783000	10.610751000	2.481418000
C	-3.198281000	12.133851000	2.435762000
C	-4.666385000	12.478671000	2.754734000
C	-5.025610000	11.939456000	4.151382000
C	-4.851230000	10.410473000	4.180042000

C	-5.772709000	9.769573000	3.129126000
C	-5.406851000	10.306610000	1.734328000
C	-5.586940000	11.834498000	1.704347000
C	-3.384148000	10.055593000	3.867070000
H	-3.650626000	10.330714000	0.430064000
H	-3.782196000	8.873570000	1.440783000
H	-2.527820000	12.614323000	3.160000000
H	-2.921974000	12.498714000	1.433504000
H	-4.784858000	13.573693000	2.736065000
H	-4.387425000	12.408906000	4.916057000
H	-6.066916000	12.202752000	4.397902000
H	-5.099229000	10.026052000	5.181976000
H	-5.669826000	8.671966000	3.153218000
H	-6.825554000	10.001807000	3.358255000
H	-6.049704000	9.838902000	0.972061000
H	-6.637111000	12.094926000	1.914029000
H	-5.349407000	12.224924000	0.700805000
H	-3.247355000	8.962321000	3.866415000
H	-2.717251000	10.471521000	4.631113000
H	2.873330000	13.089822000	2.561382000
C	3.429569000	4.189444000	-0.772783000
C	2.191510000	4.573529000	-1.294782000
C	1.353102000	5.438197000	-0.587979000
C	1.766262000	5.919286000	0.684274000
C	3.016976000	5.516854000	1.200566000
C	3.845491000	4.666502000	0.476186000
H	-0.778203000	5.230167000	-0.651333000
H	4.075390000	3.518870000	-1.343998000
H	1.870851000	4.196747000	-2.268768000
C	0.005350000	5.856449000	-1.115373000
C	0.845730000	6.783891000	1.425272000
H	3.358994000	5.892049000	2.165618000
H	4.816881000	4.376820000	0.881254000
C	-0.066328000	7.594486000	0.699373000
C	-0.242401000	7.328336000	-0.788309000
H	-0.972711000	7.895339000	1.229470000
H	-1.249082000	7.640491000	-1.100792000
H	-0.051053000	5.683067000	-2.199474000
H	0.472464000	7.934450000	-1.370137000
C	0.938793000	6.889974000	2.853852000
H	1.773532000	6.389954000	3.348732000
C	0.095211000	7.623950000	3.620391000
H	-0.836278000	8.032601000	3.233076000
H	0.275499000	7.747622000	4.686773000

(*Re/endo*)-**TS-I**

Fe	1.004734000	11.394984000	5.201835000
Br	7.932333000	13.087981000	3.940172000
Br	-1.554142000	10.465575000	12.173053000
O	2.590429000	11.548883000	6.273810000
O	0.163841000	10.171216000	6.385134000
N	1.583263000	13.333263000	4.206773000
N	-0.334313000	12.873976000	6.247315000
C	2.709251000	13.947858000	4.973239000
H	2.353755000	14.148929000	5.990583000
C	3.917934000	13.062084000	5.065347000
C	5.141489000	13.435558000	4.510668000
H	5.231027000	14.365924000	3.947169000
C	6.243065000	12.604502000	4.701793000
C	6.139096000	11.427810000	5.447461000
H	7.030468000	10.817964000	5.576743000
C	4.923634000	11.024231000	6.016583000
C	3.788917000	11.858160000	5.801509000
C	4.812098000	9.718644000	6.821136000
C	4.230767000	10.007194000	8.222854000
H	3.227159000	10.443526000	8.152591000
H	4.880046000	10.703932000	8.777099000
H	4.166148000	9.071031000	8.800800000

C	3.890384000	8.734500000	6.070907000
H	3.814229000	7.788326000	6.630147000
H	4.289007000	8.513256000	5.068599000
H	2.884810000	9.150188000	5.955185000
C	6.179618000	9.041171000	7.007606000
H	6.892418000	9.691614000	7.538053000
H	6.630551000	8.745814000	6.047628000
H	6.052984000	8.126744000	7.606985000
C	0.132185000	12.776971000	7.658358000
H	-0.275220000	13.612720000	8.249682000
H	1.225872000	12.890484000	7.638510000
C	-0.246762000	11.481588000	8.335902000
C	-0.649669000	11.543914000	9.673199000
H	-0.673430000	12.506163000	10.187608000
C	-1.026169000	10.381934000	10.335503000
C	-1.051946000	9.157474000	9.667159000
H	-1.383792000	8.275873000	10.210346000
C	-0.675118000	9.054553000	8.324424000
C	-0.221723000	10.232951000	7.651137000
C	-0.761624000	7.708858000	7.586413000
C	0.652461000	7.277280000	7.148157000
H	1.131640000	8.044727000	6.531873000
H	0.609830000	6.335092000	6.578051000
H	1.292061000	7.111828000	8.028967000
C	-1.701943000	7.857184000	6.368042000
H	-2.719679000	8.116303000	6.700421000
H	-1.761244000	6.904464000	5.817334000
H	-1.357271000	8.643025000	5.685773000
C	-1.334031000	6.591636000	8.474608000
H	-0.702233000	6.398371000	9.354845000
H	-1.383960000	5.658027000	7.893421000
H	-2.352674000	6.821451000	8.823106000
C	1.884128000	13.384681000	2.755489000
H	1.232388000	12.664548000	2.245866000
H	2.990450000	14.914879000	4.530533000
C	1.545819000	14.833688000	2.313898000
H	2.452786000	15.447564000	2.223543000
H	1.061199000	14.829793000	1.327856000
C	0.604417000	15.379668000	3.422106000
H	-0.324695000	15.802114000	3.017714000
H	1.091678000	16.167481000	4.015802000
C	0.329612000	14.135182000	4.275489000
H	-0.414278000	13.530004000	3.734000000
C	-0.179380000	14.267840000	5.699649000
H	0.544359000	14.808082000	6.321892000
C	-1.574715000	14.943140000	5.777414000
H	-1.533705000	15.892244000	6.327555000
H	-1.939301000	15.170153000	4.764628000
C	-2.483192000	13.901697000	6.449956000
H	-3.516928000	13.934557000	6.078280000
H	-2.522098000	14.048455000	7.540201000
C	-1.789934000	12.585611000	6.114029000
H	-2.077058000	11.744059000	6.752198000
H	-1.978649000	12.294706000	5.075253000
C	3.093666000	9.472383000	1.744994000
C	2.388828000	9.363331000	0.379610000
C	0.892029000	9.363423000	0.702773000
C	0.759385000	9.916958000	2.017845000
C	2.025050000	10.006619000	2.672455000
H	3.969041000	10.137913000	1.749668000
H	2.714345000	8.496312000	-0.210003000
H	2.601729000	10.256777000	-0.229478000
H	0.192786000	9.703539000	-0.061044000
H	3.444518000	8.497421000	2.127009000
O	2.258875000	10.455704000	3.812942000
C	-0.447757000	10.463137000	2.590430000
O	-1.507549000	10.259837000	1.833225000
O	-0.482961000	11.081722000	3.671883000
C	-3.695920000	10.268857000	0.935481000

C	-2.869985000	10.717498000	2.144996000
C	-2.937382000	12.243937000	2.265477000
C	-4.408112000	12.655557000	2.480868000
C	-4.943772000	11.988118000	3.760699000
C	-4.864918000	10.457720000	3.621692000
C	-5.703311000	10.006167000	2.413456000
C	-5.164845000	10.676616000	1.137274000
C	-5.252873000	12.205800000	1.276985000
C	-3.396534000	10.038483000	3.413626000
H	-3.281520000	10.731527000	0.025765000
H	-3.610706000	9.181475000	0.822085000
H	-2.322418000	12.589377000	3.104245000
H	-2.535811000	12.699685000	1.346178000
H	-4.455536000	13.751342000	2.584565000
H	-4.362612000	12.318991000	4.635681000
H	-5.987441000	12.296558000	3.934105000
H	-5.241779000	9.979897000	4.539828000
H	-5.660321000	8.909511000	2.309974000
H	-6.760484000	10.278304000	2.565667000
H	-5.749422000	10.343417000	0.265181000
H	-6.301669000	12.514420000	1.417187000
H	-4.890523000	12.692575000	0.356326000
H	-3.327761000	8.947357000	3.291802000
H	-2.785238000	10.317261000	4.281832000
H	2.923920000	13.087357000	2.575262000
C	-4.611686000	6.608341000	-0.375615000
C	-3.522858000	7.000769000	-1.157679000
C	-2.259749000	7.193345000	-0.592322000
C	-2.088623000	7.002876000	0.804453000
C	-3.195332000	6.582892000	1.576916000
C	-4.443014000	6.386520000	0.996226000
H	-1.093136000	8.749297000	-1.469768000
H	-5.590444000	6.463854000	-0.838066000
H	-3.654559000	7.160591000	-2.230433000
C	-1.095331000	7.645176000	-1.436012000
C	-0.779792000	7.238275000	1.416088000
H	-3.077569000	6.389756000	2.642595000
H	-5.284339000	6.060039000	1.610145000
C	0.365880000	7.436852000	0.595614000
C	0.231553000	7.133560000	-0.879475000
H	1.301955000	7.101368000	1.048641000
H	1.075640000	7.558546000	-1.441464000
H	-1.233411000	7.313248000	-2.475007000
H	0.291731000	6.038325000	-1.012526000
C	-0.666241000	7.371459000	2.838461000
H	-1.583677000	7.425899000	3.423038000
C	0.500044000	7.595733000	3.494509000
H	1.472759000	7.460534000	3.025473000
H	0.504375000	7.833323000	4.557350000

8. References

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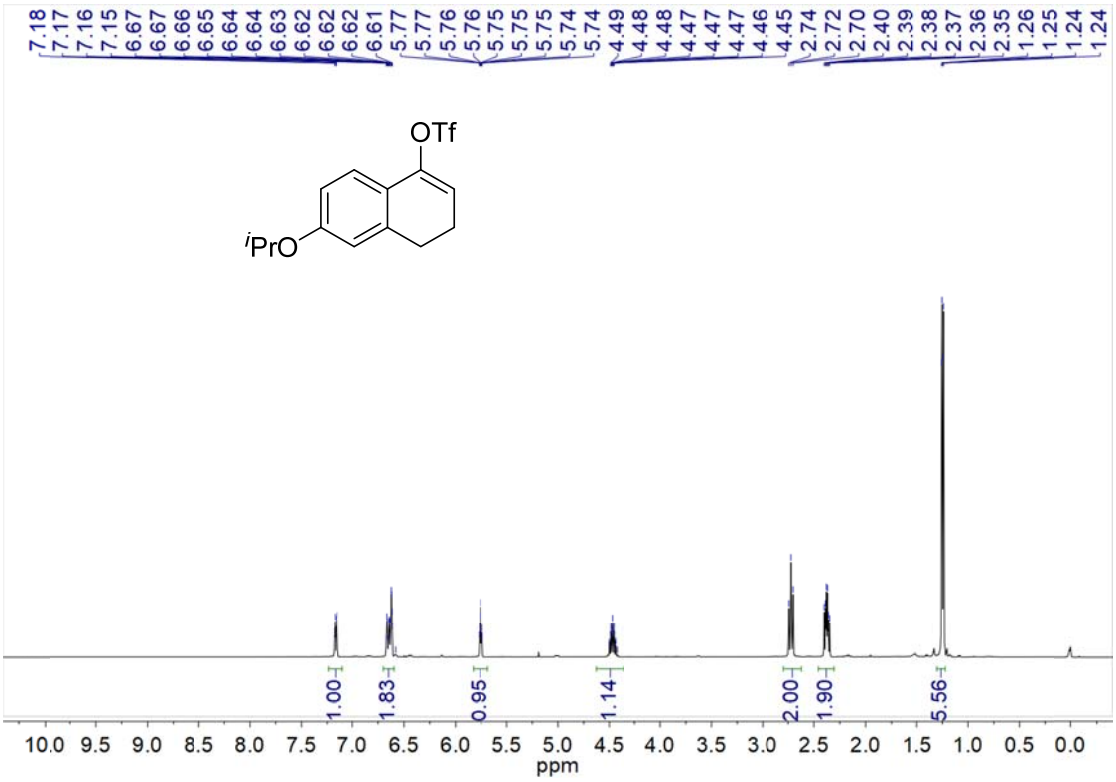
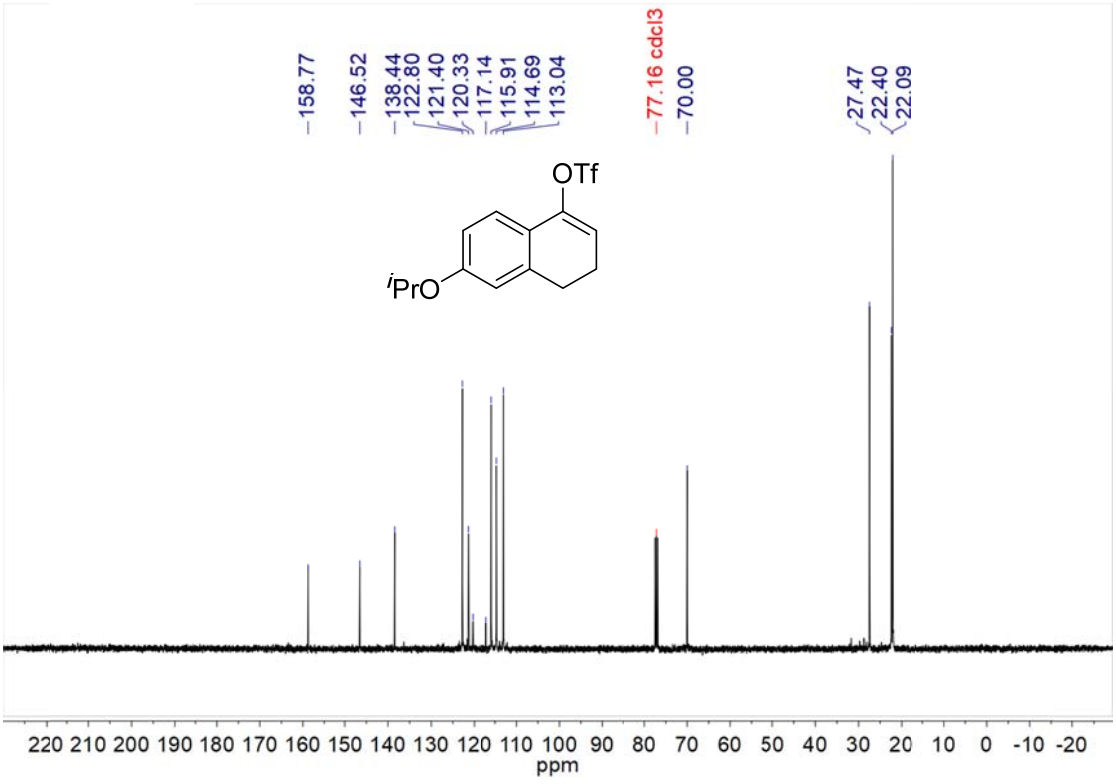
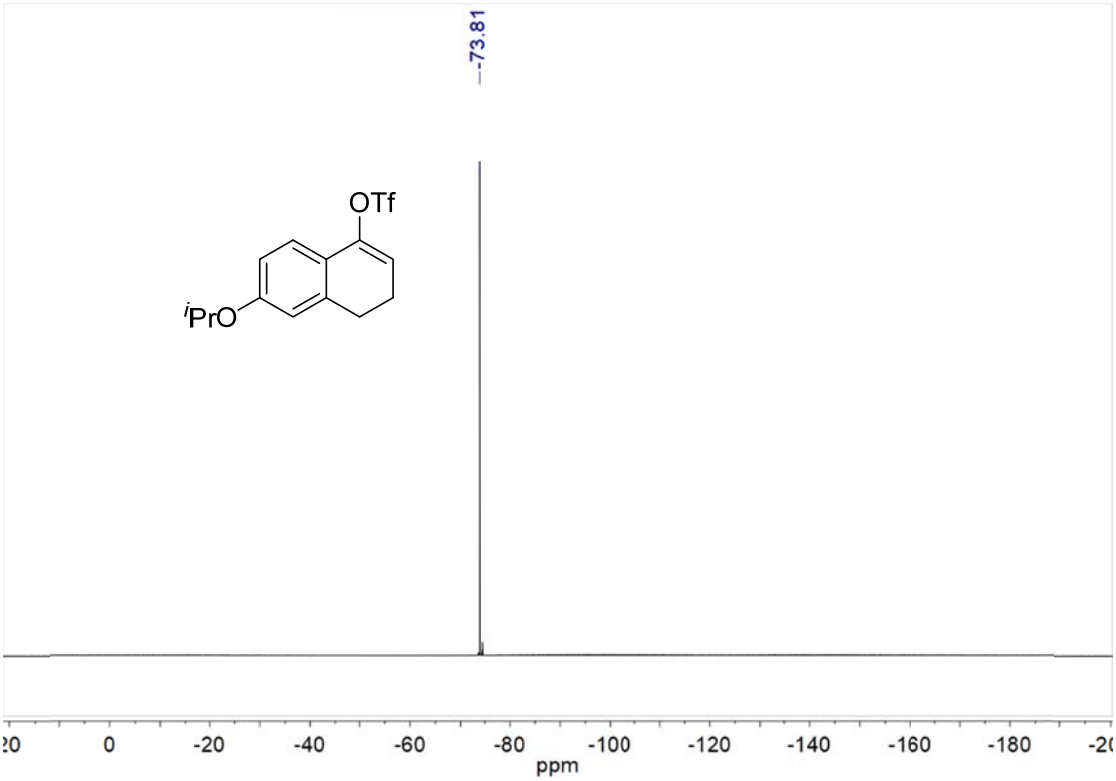
9. NMR spectra



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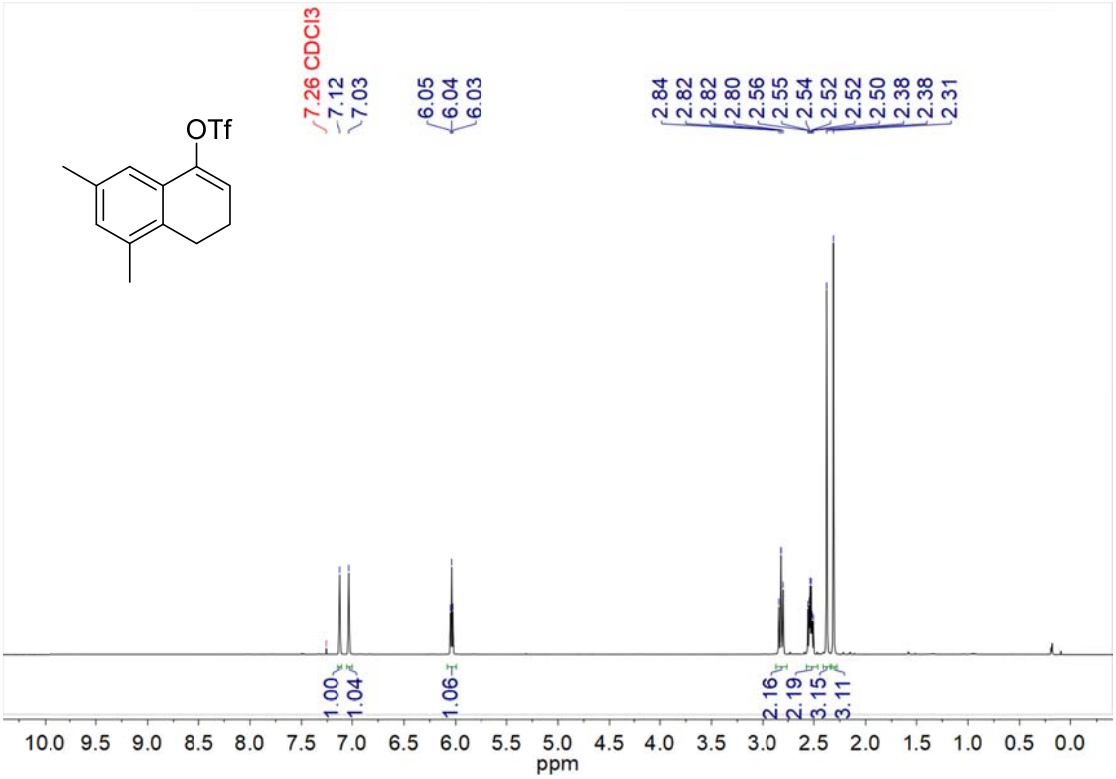
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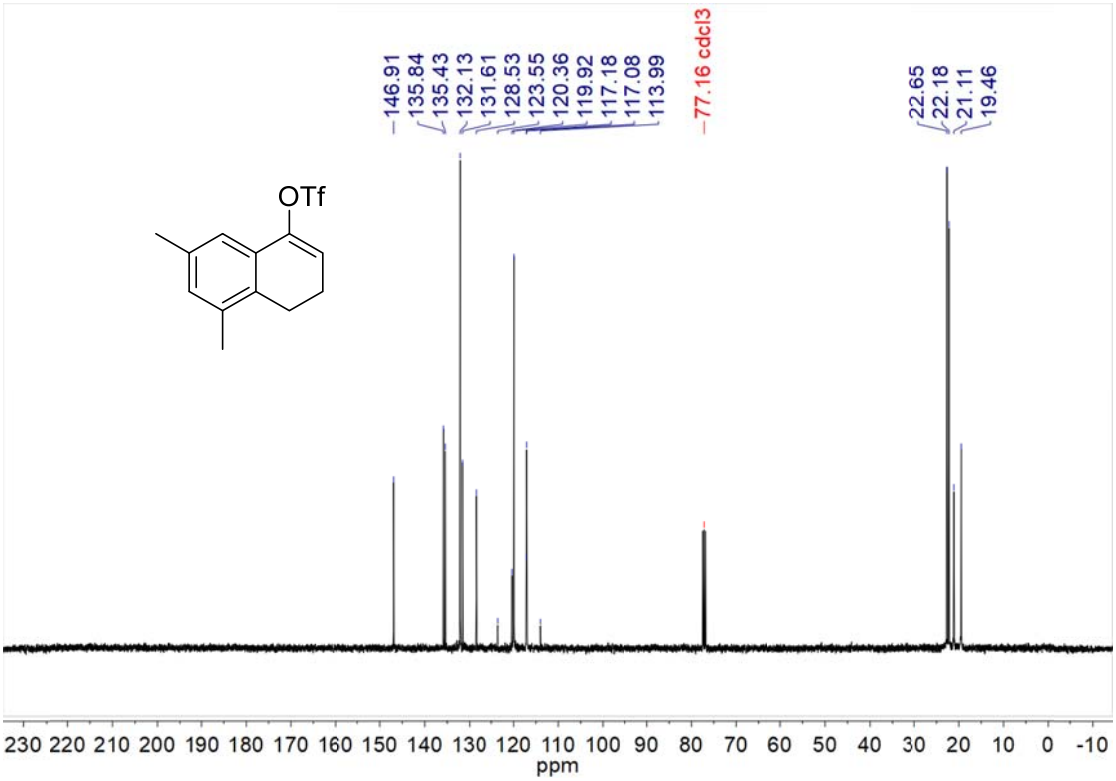
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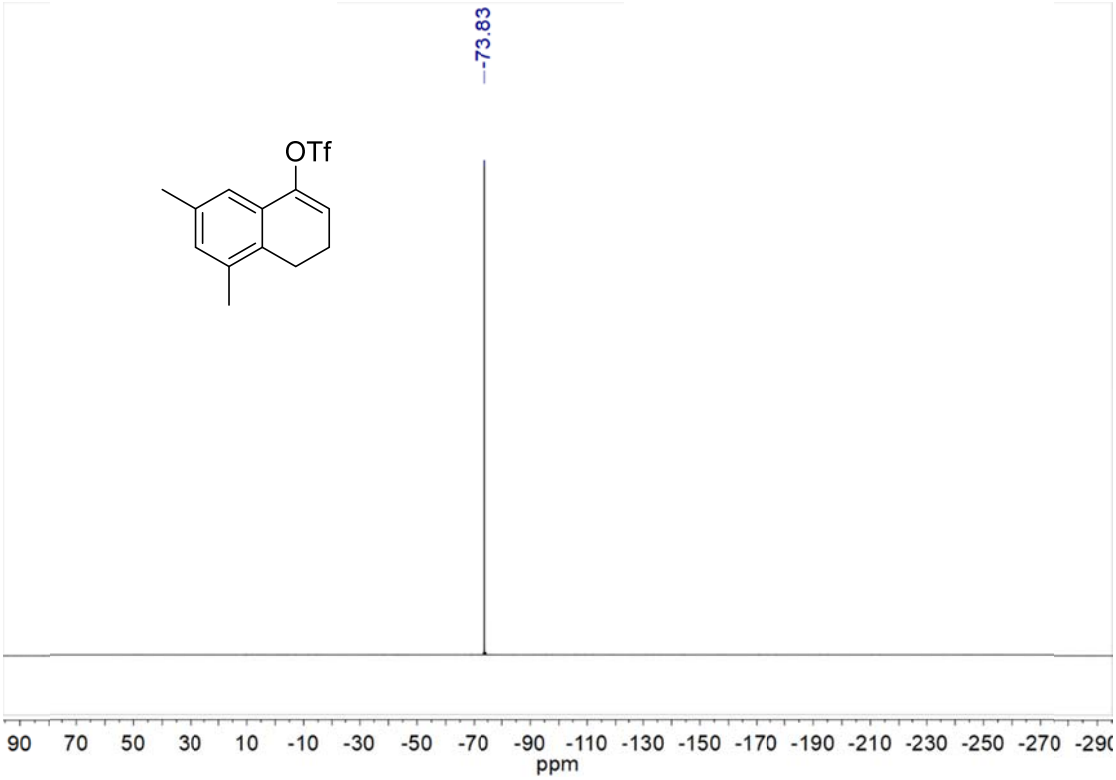
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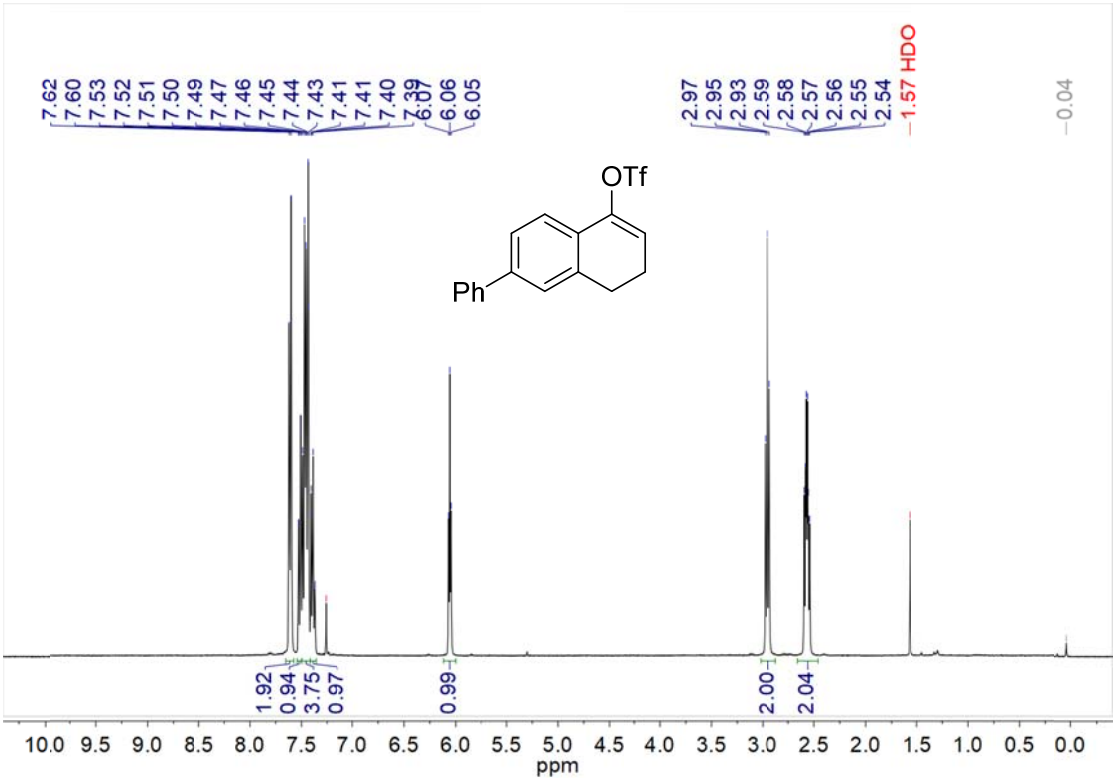
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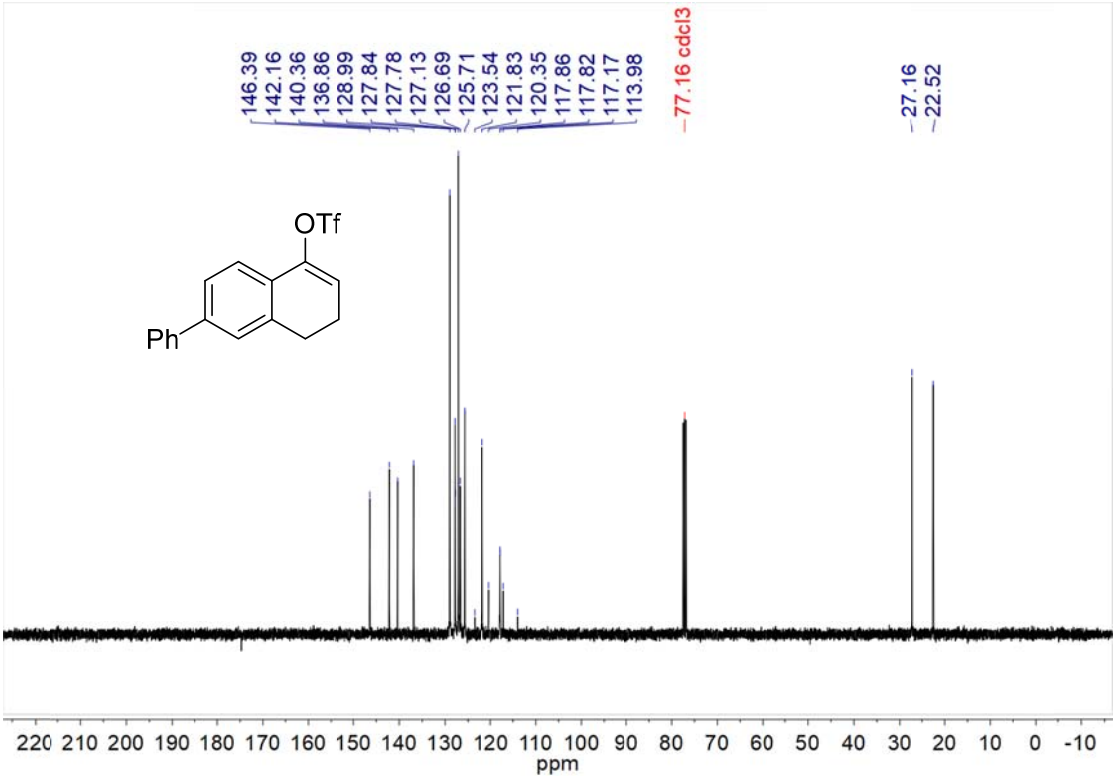
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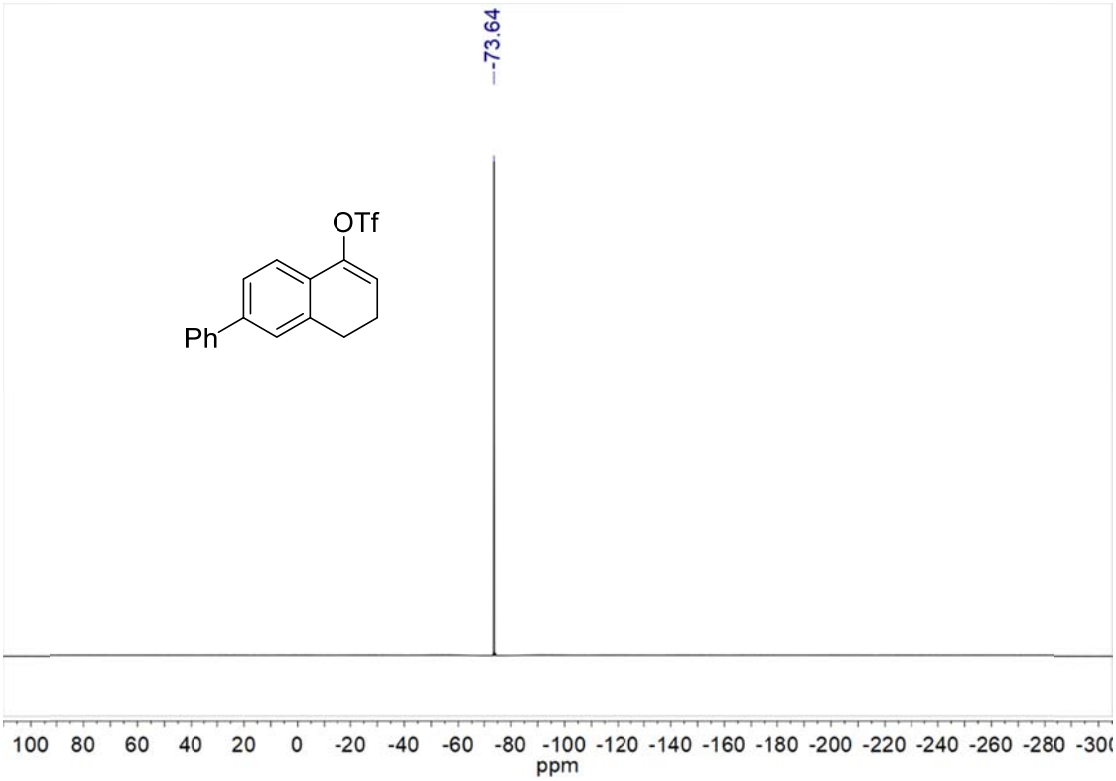
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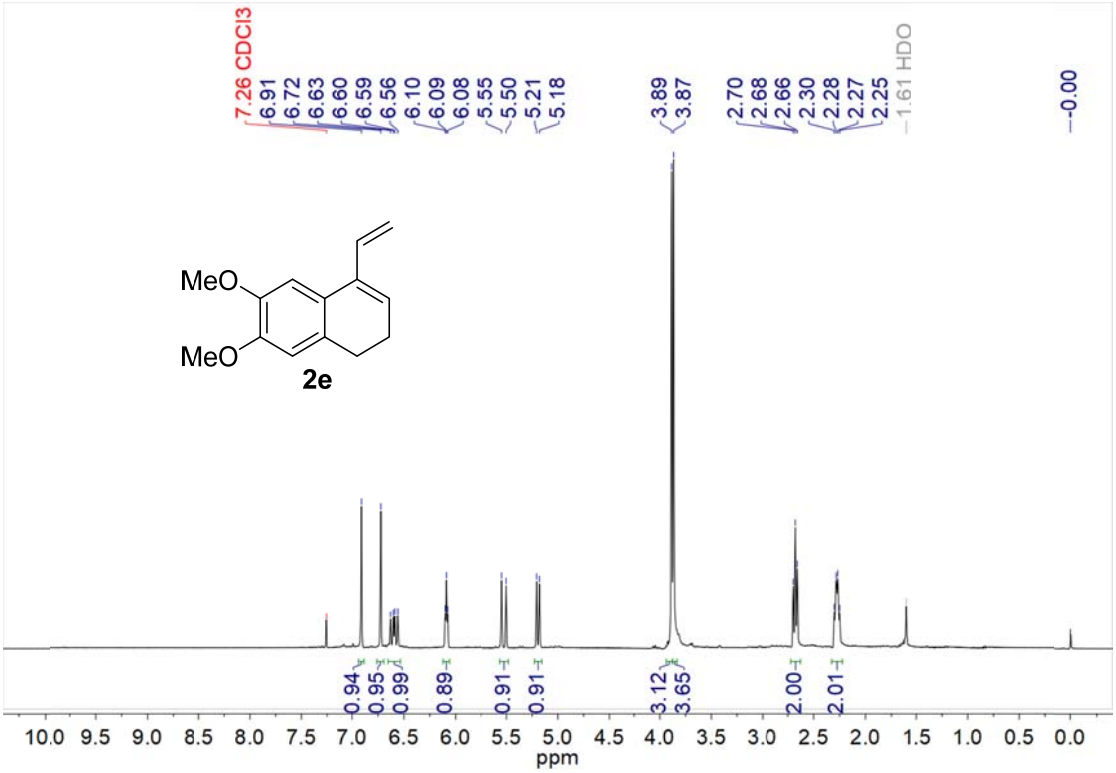
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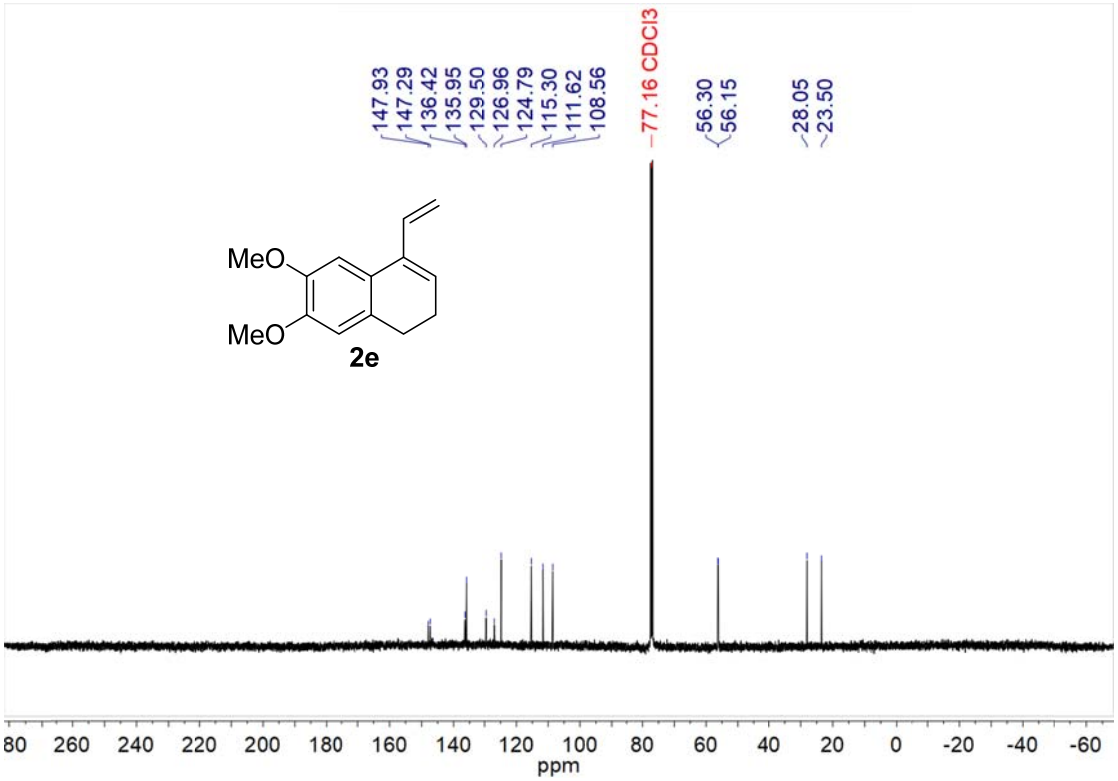
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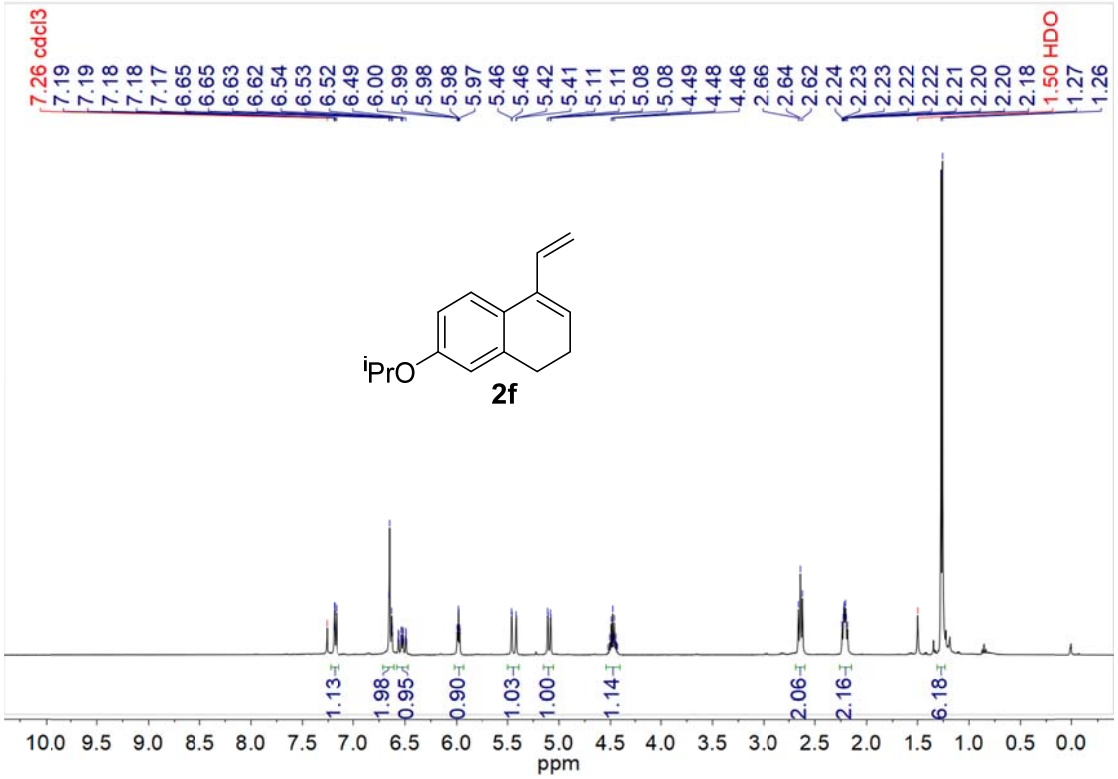
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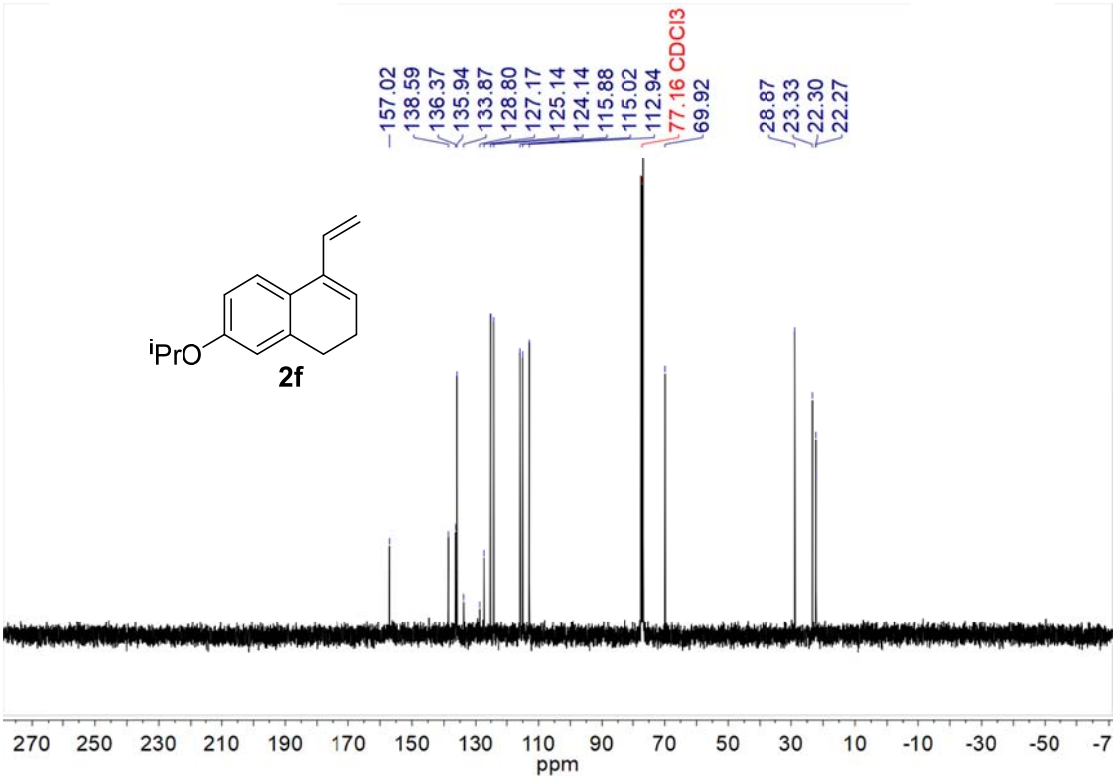
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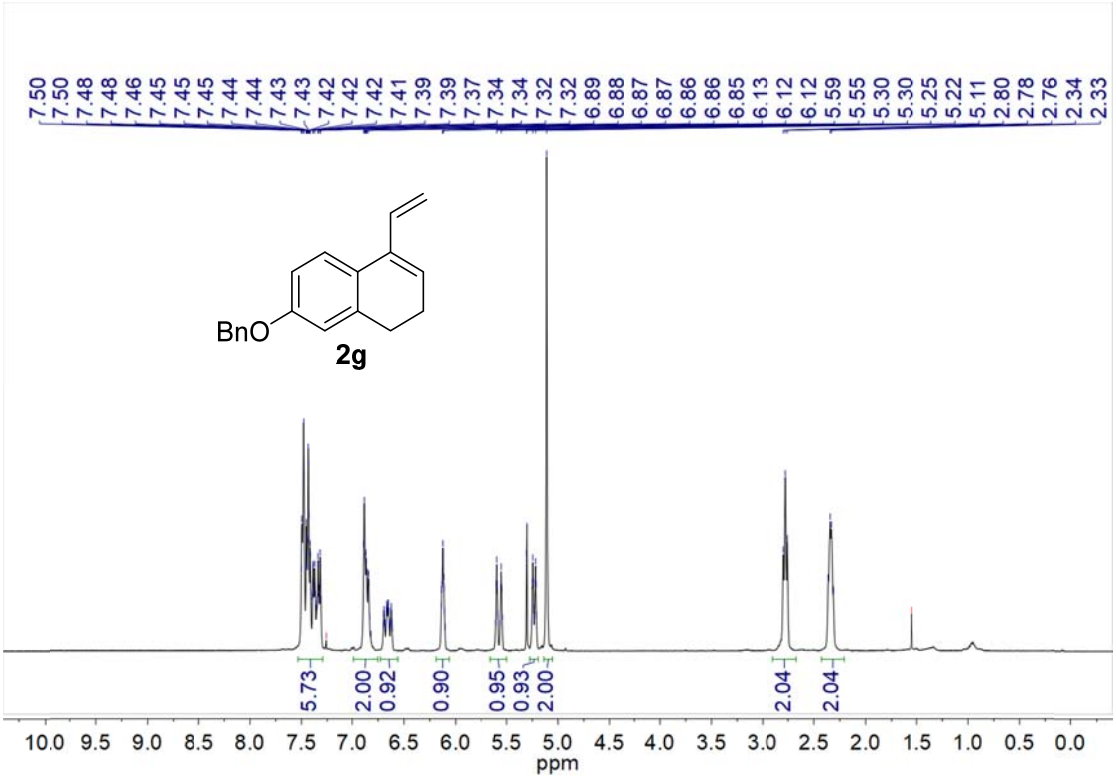
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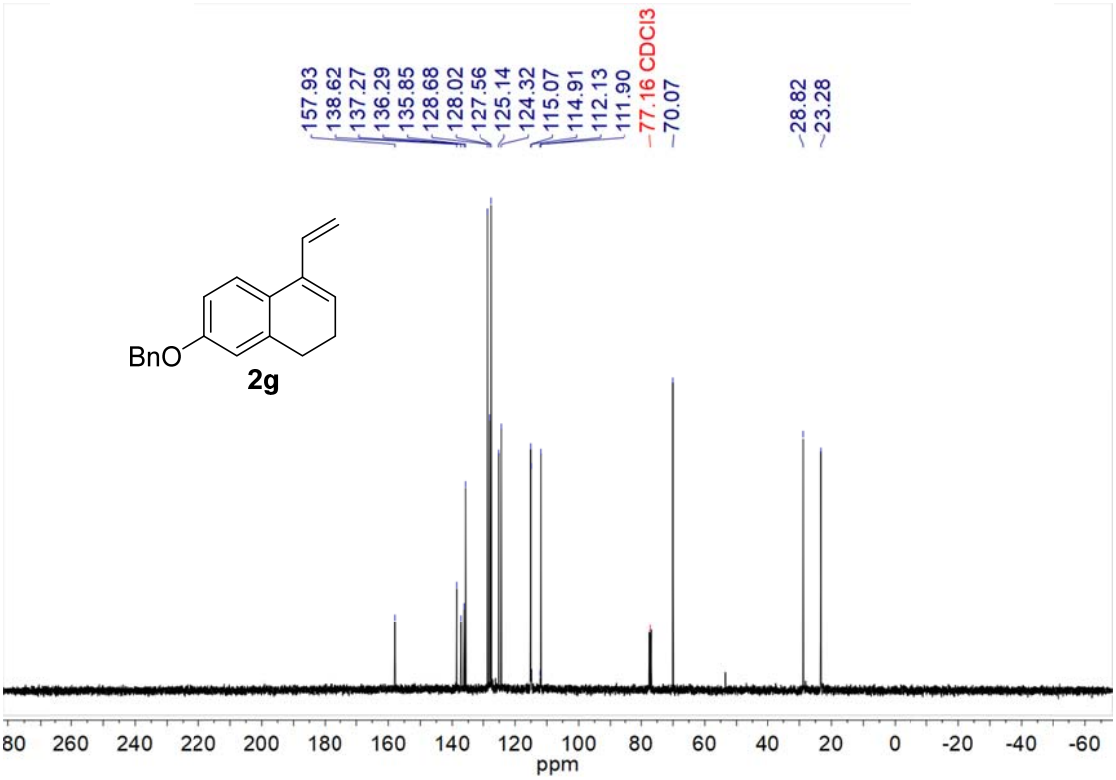
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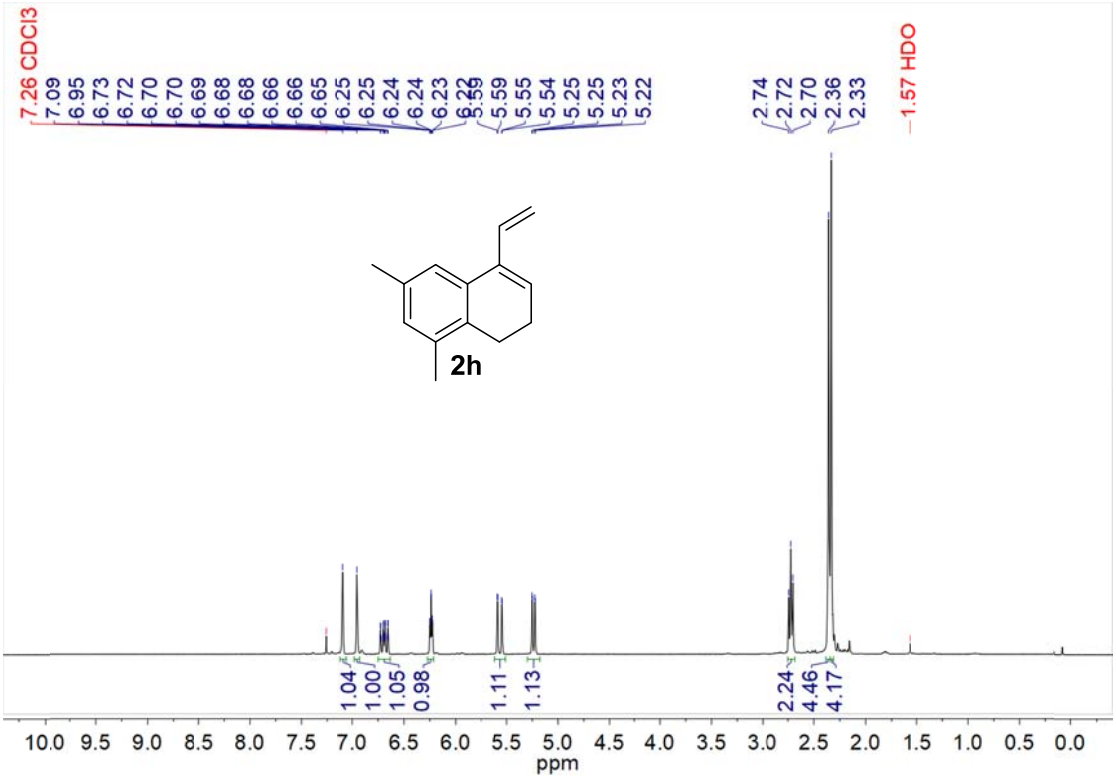
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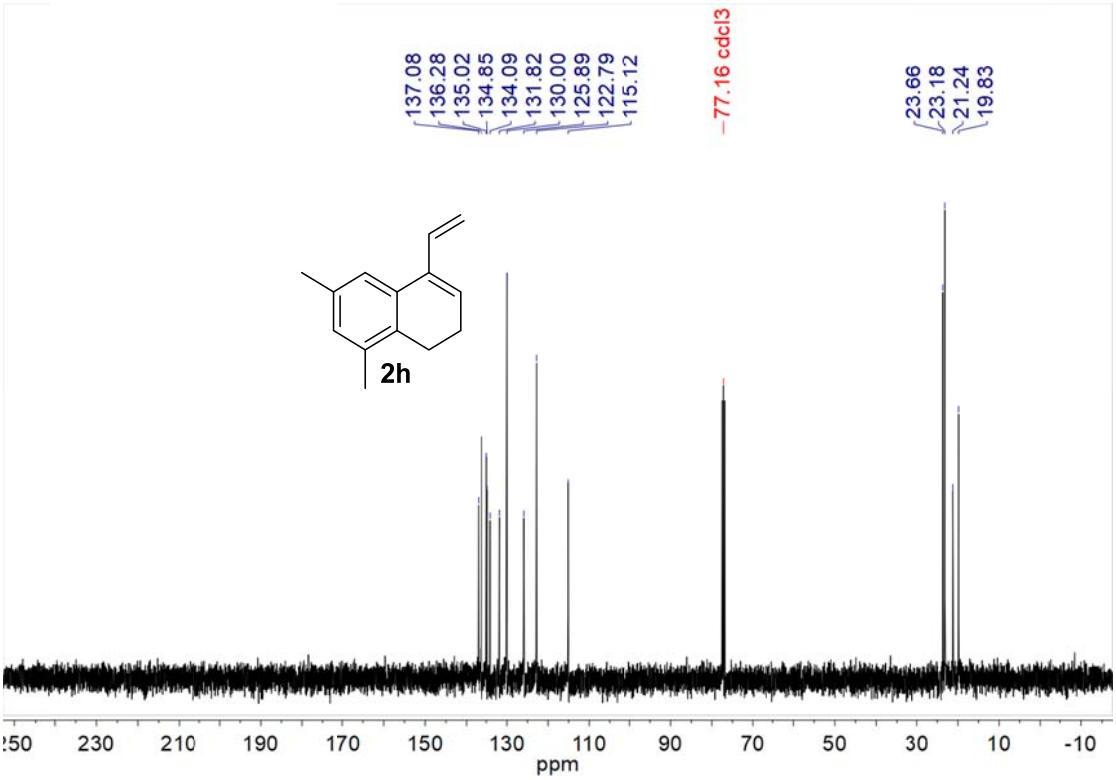
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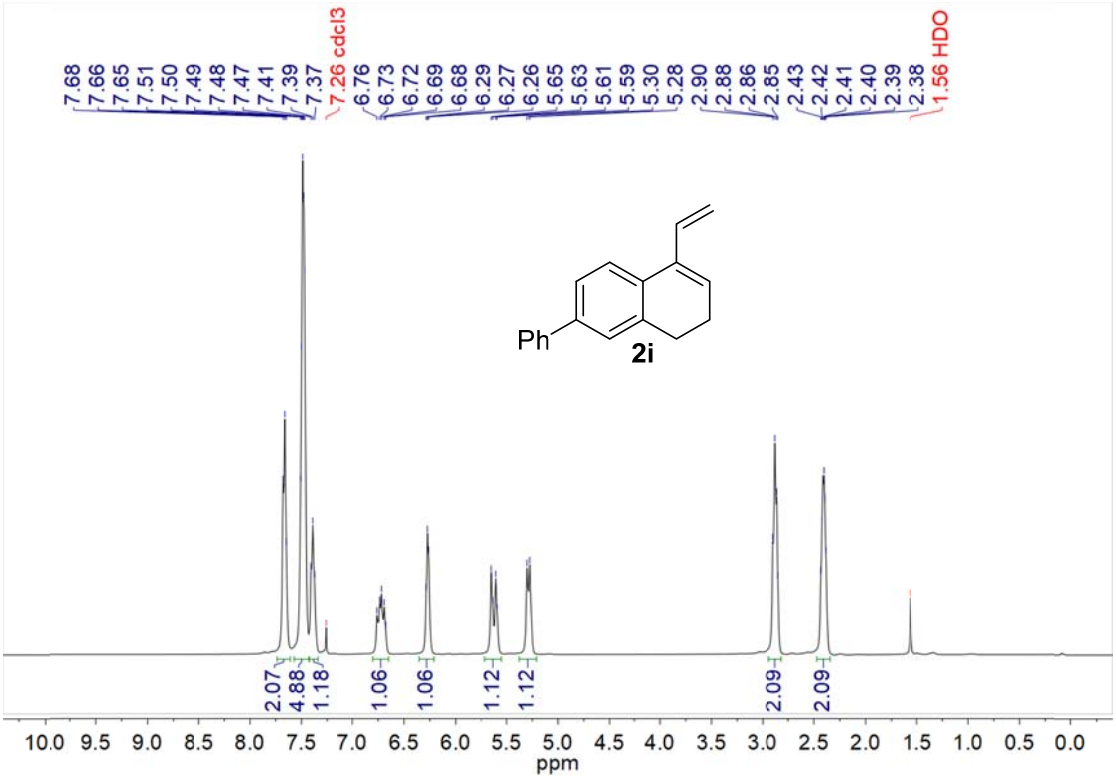
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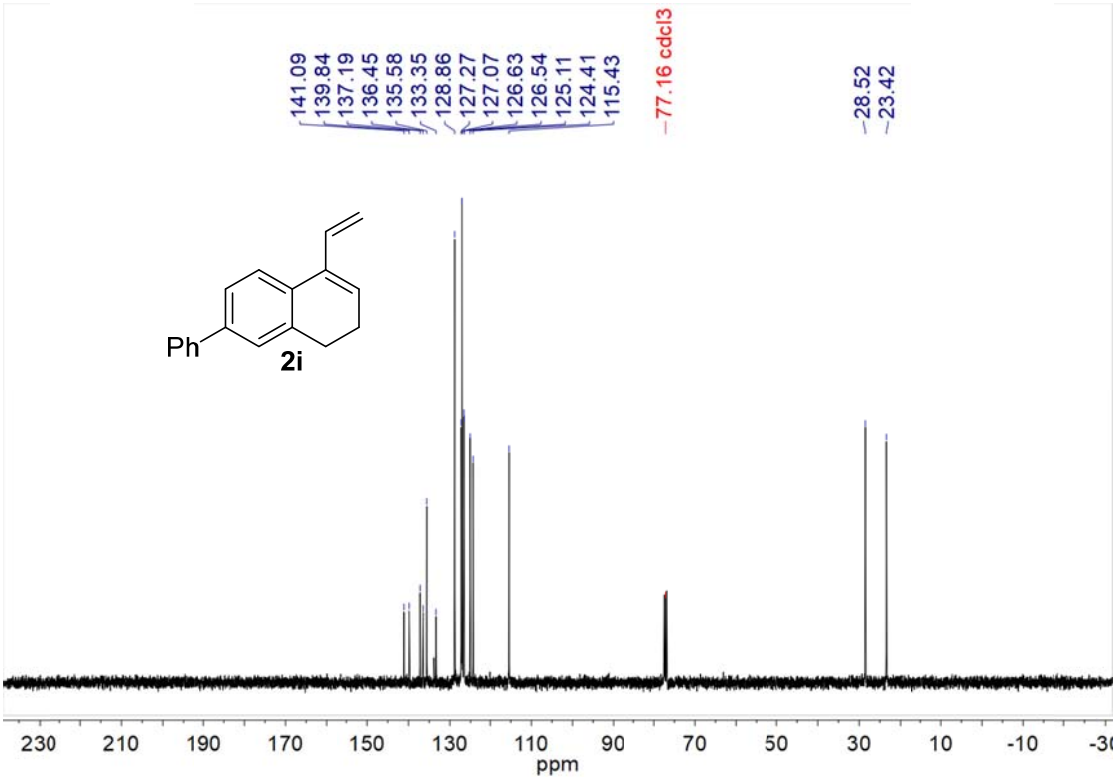
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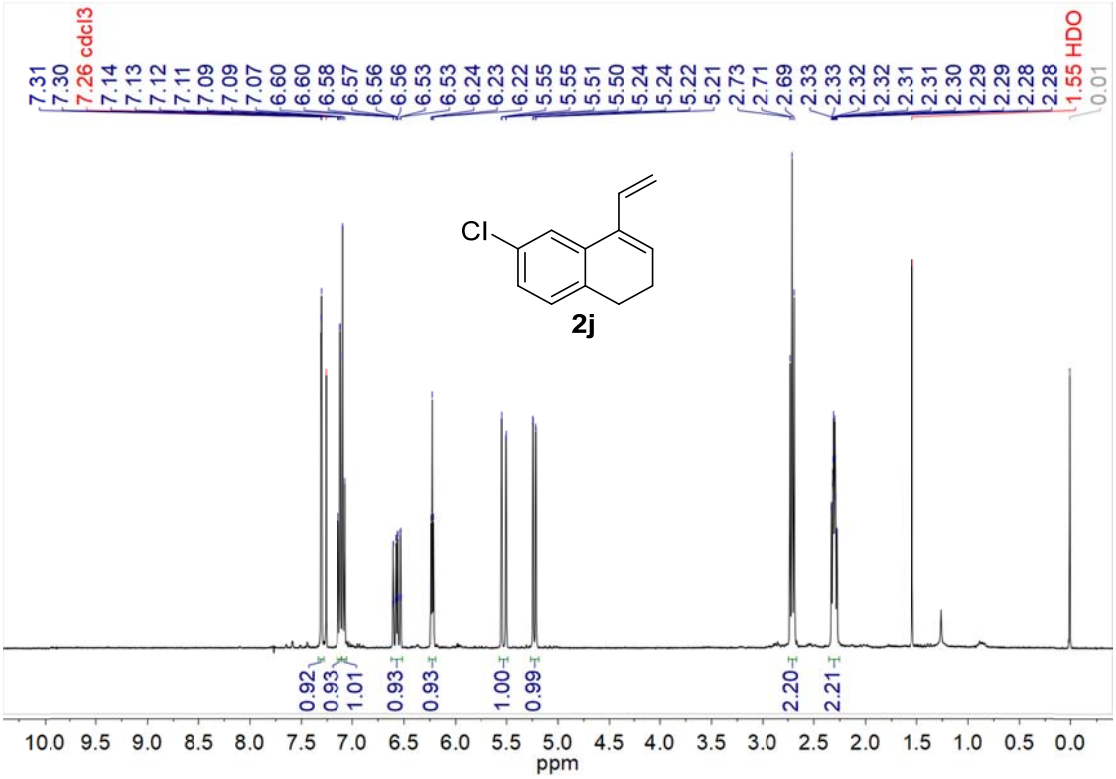
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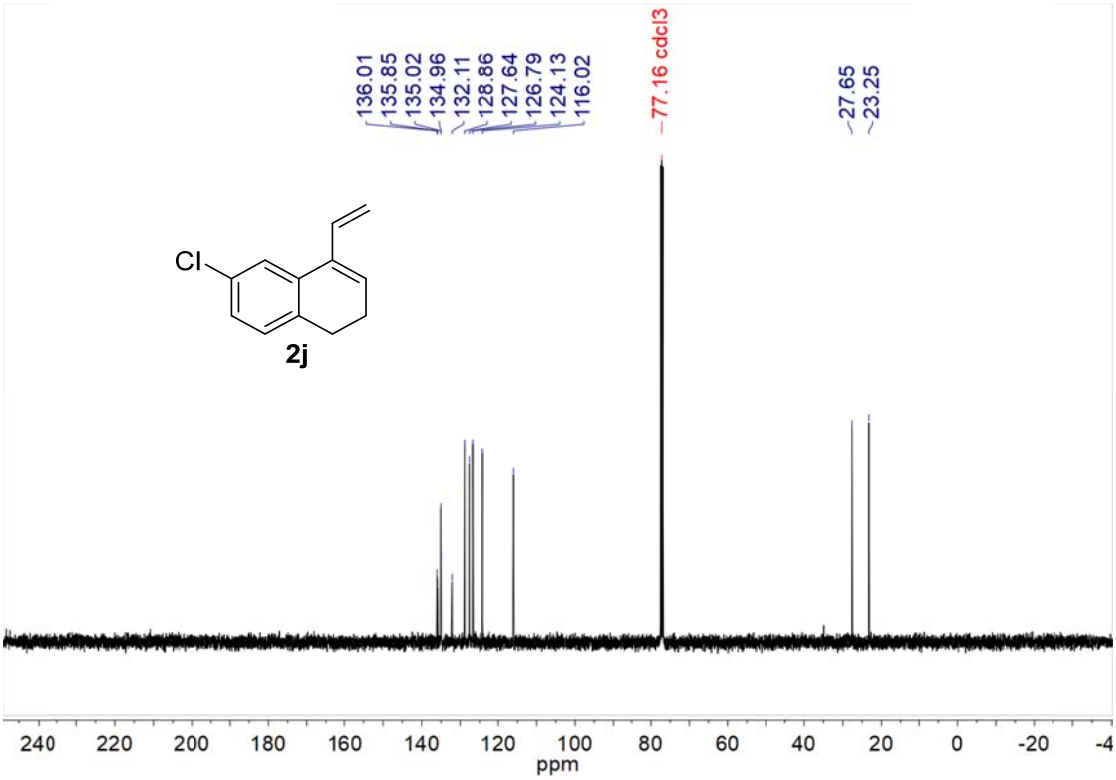
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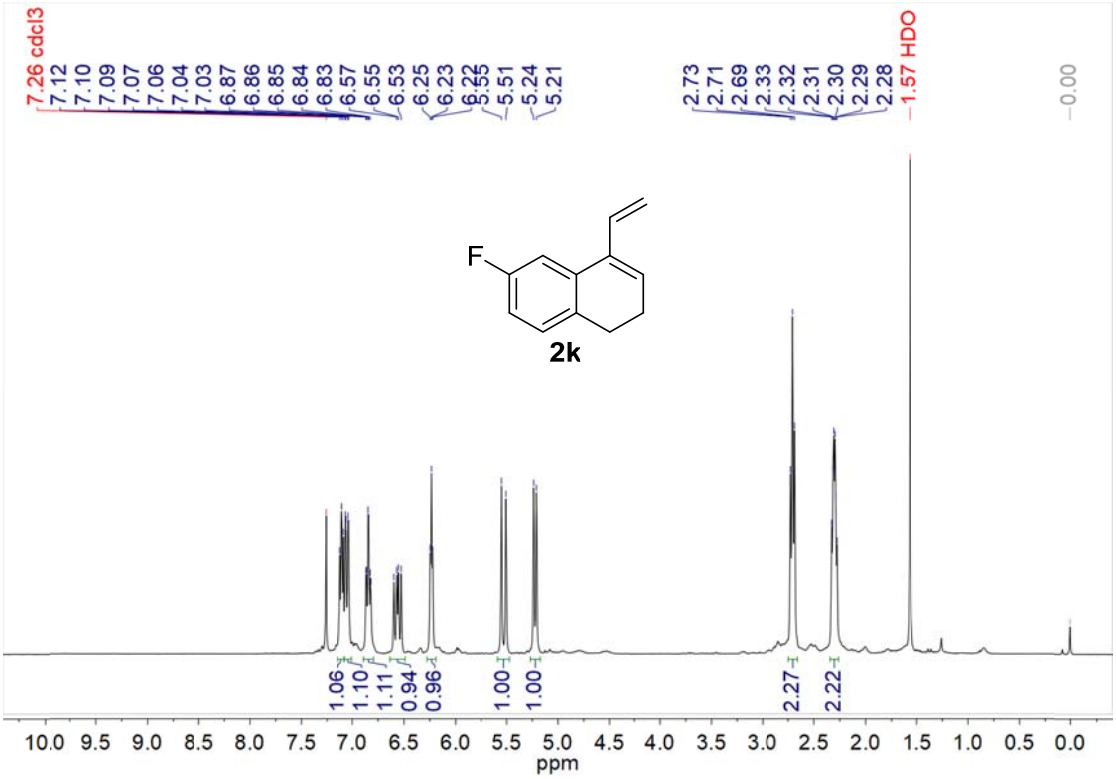
124.13
116.02
77.16 cdcl3
27.65
23.25
Cl
2j
240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -4
ppm


7.26 cdcl3
7.12
7.10
7.09
7.07
7.06
7.04
7.03
6.87
6.86
6.85
6.84
6.83
6.57
6.55
6.53
6.25
6.23
5.51
5.24
5.21
2.73
2.71
2.69
2.33
2.32
2.31
2.30
2.29
2.28
1.57 HDO
0.00
F
2k
1.06
1.10
1.11
0.94
0.96
1.00
1.00
2.27
2.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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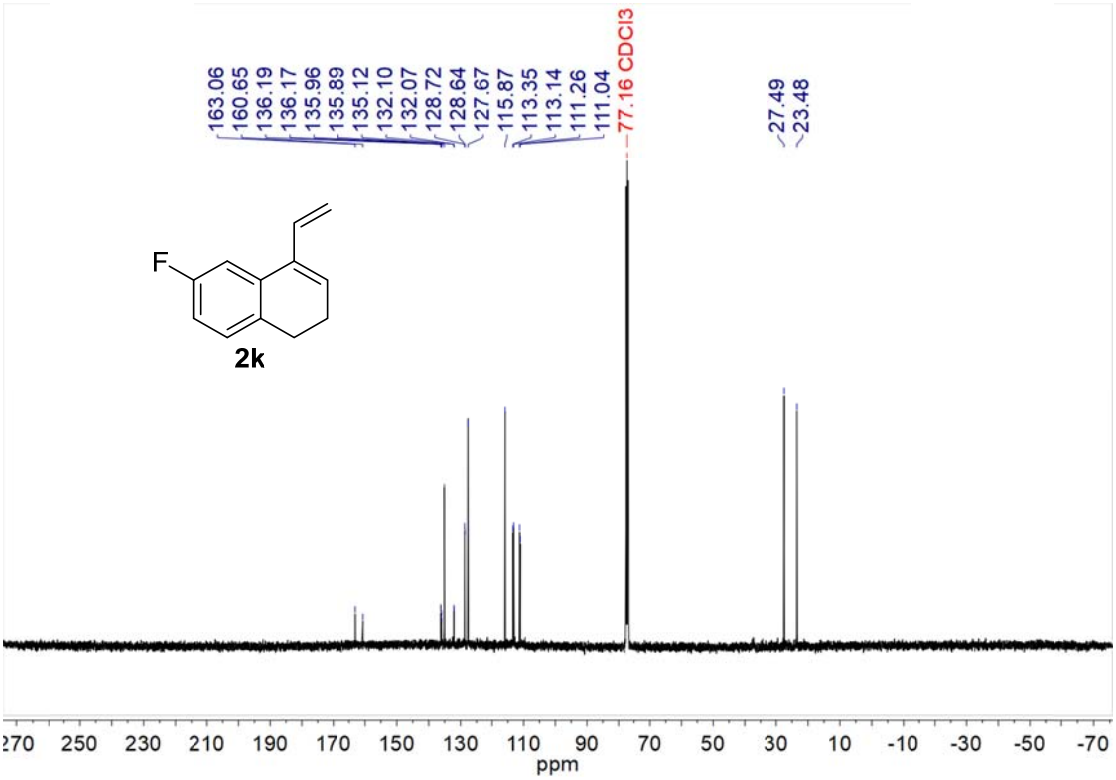
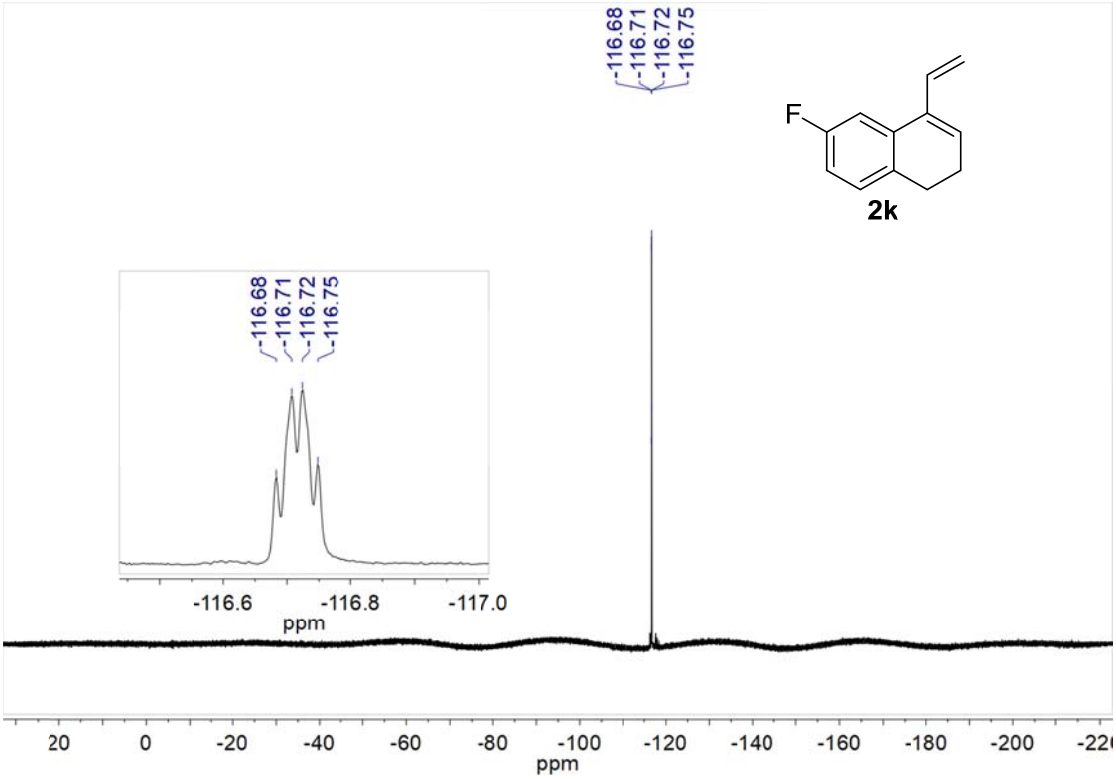
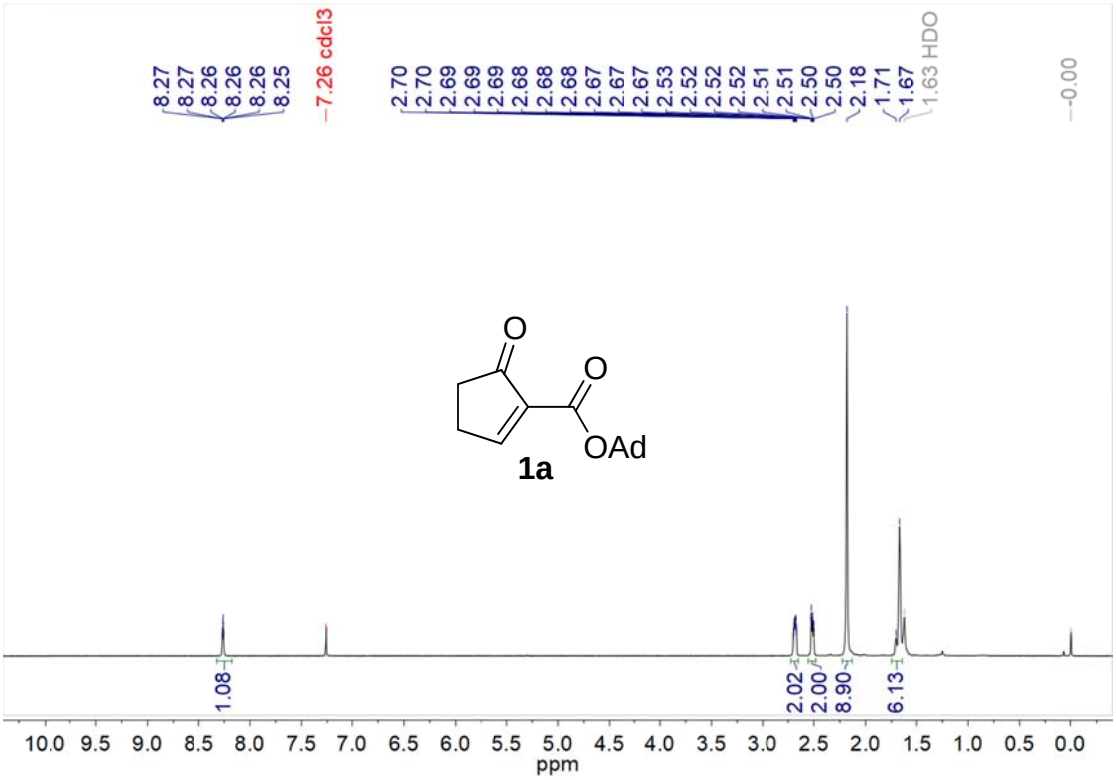
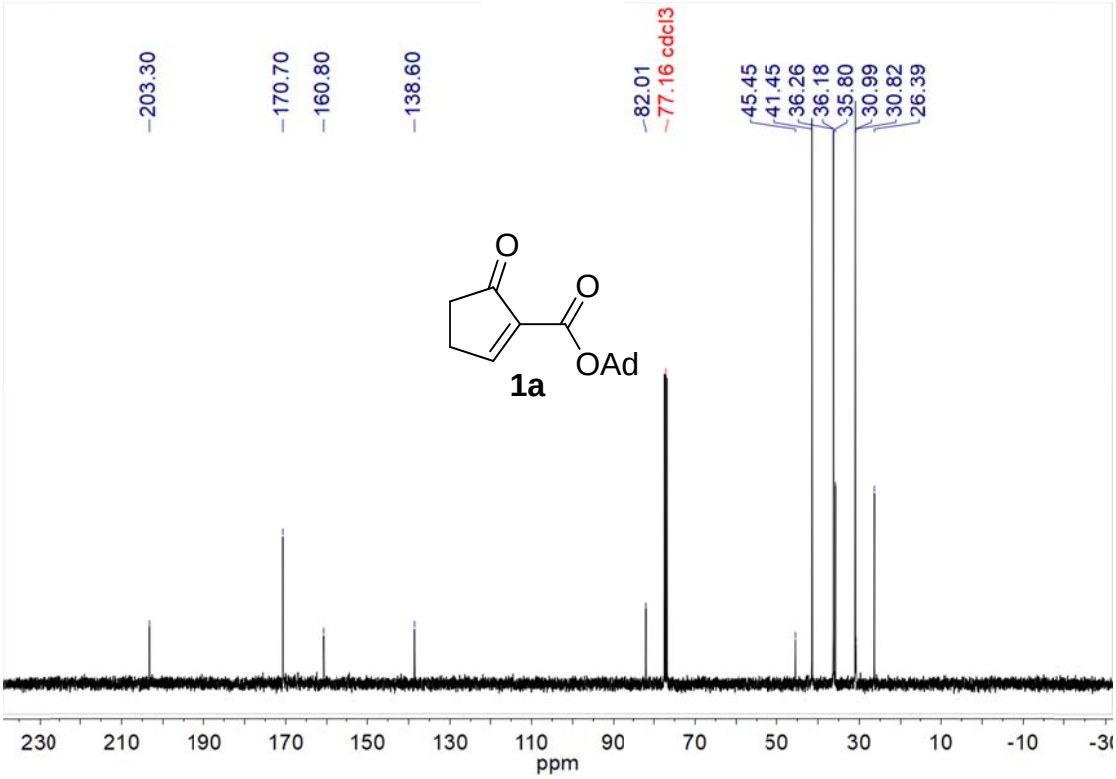
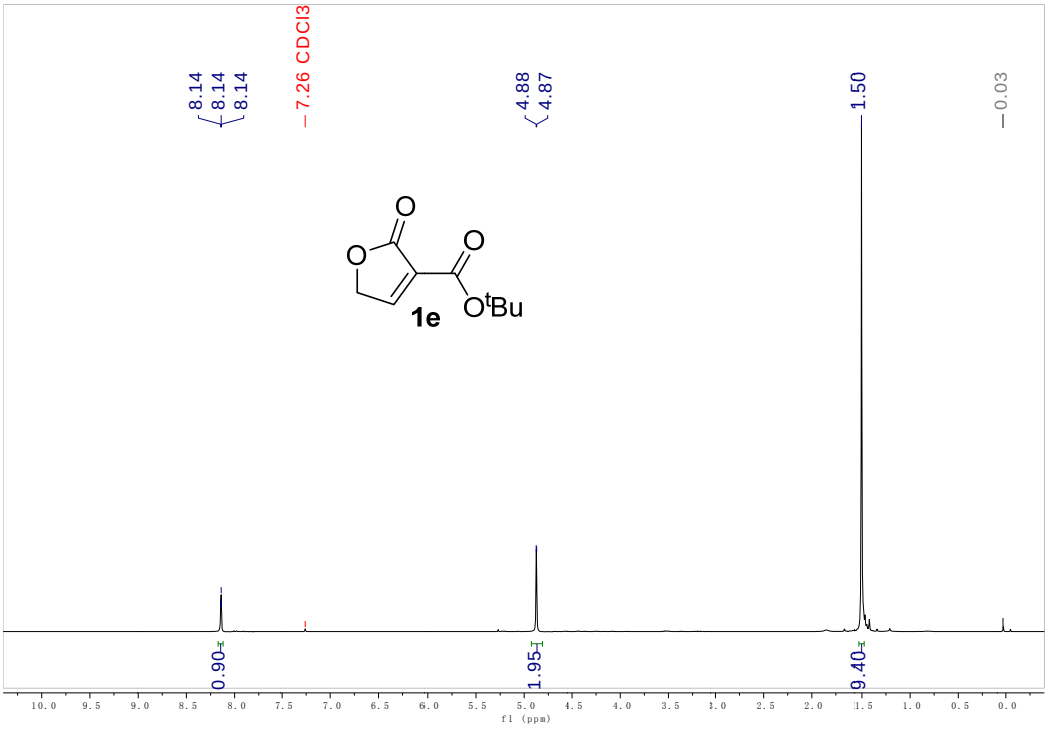
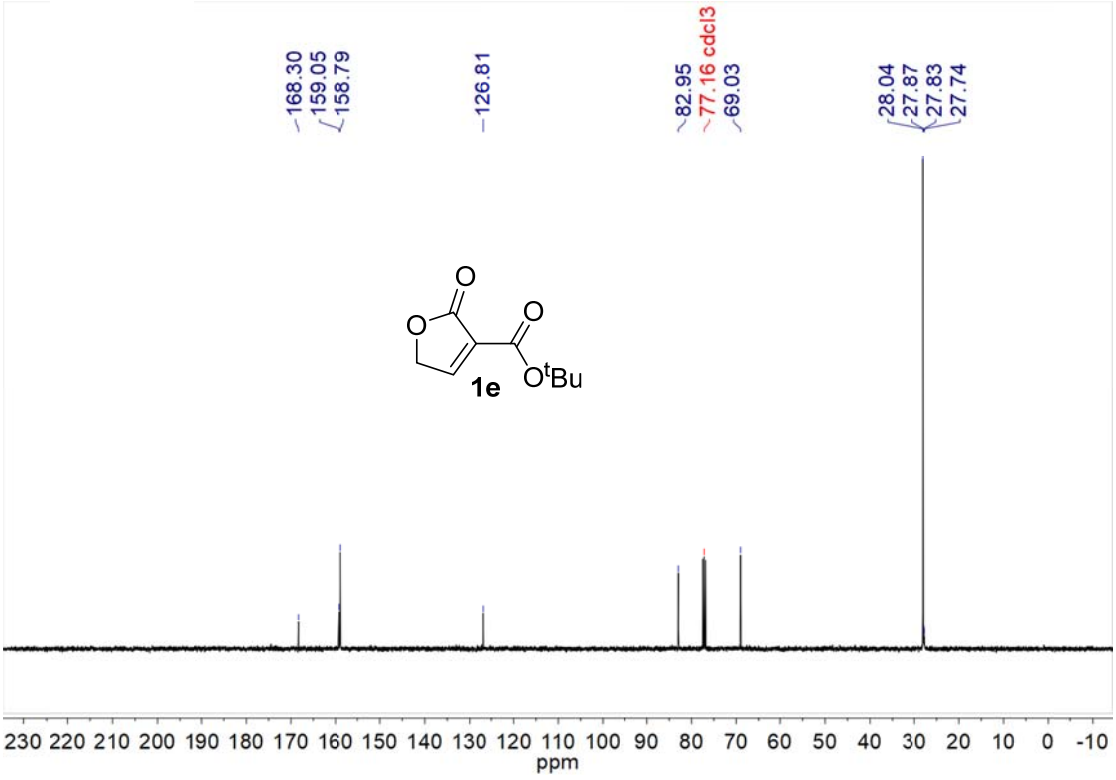

163.06
160.65
136.19
136.17
135.96
135.89
135.12
132.10
132.07
128.72
128.64
127.67
115.87
113.35
113.14
111.26
111.04
77.16 CDCl3
27.49
23.48
F
2k
270 250 230 210 190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70
ppm

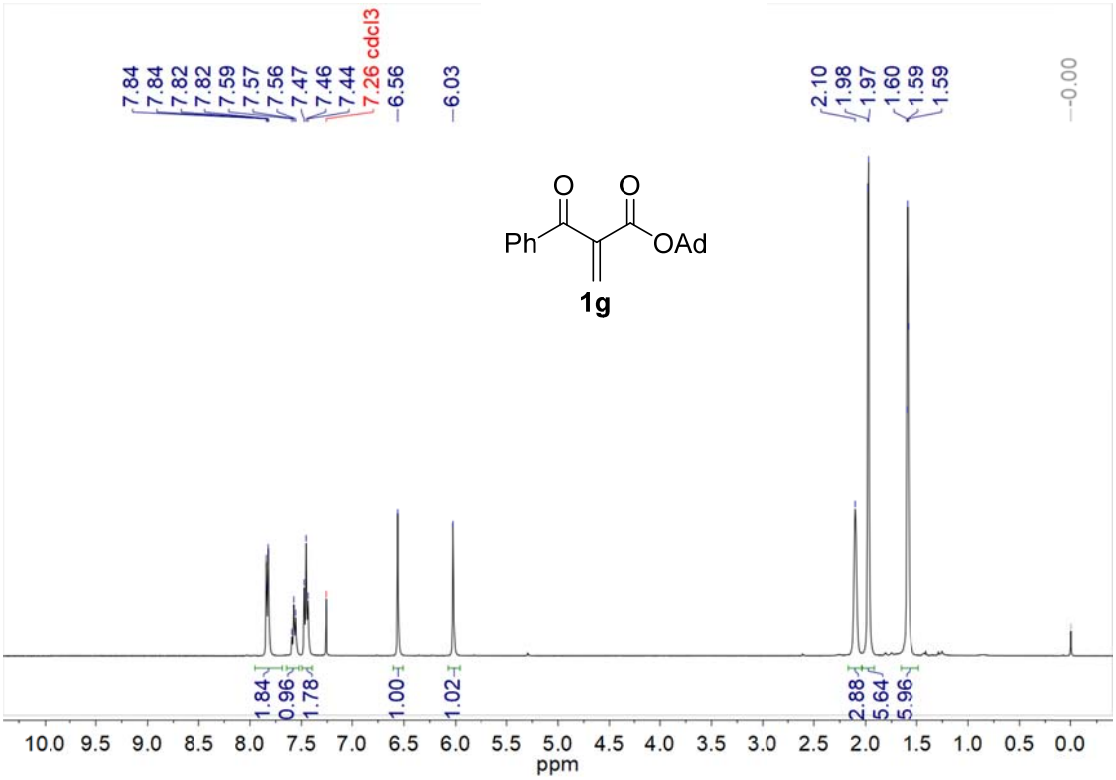

116.68
116.71
116.72
116.75
F
2k
116.68
116.71
116.72
116.75
-116.6 -116.8 -117.0
ppm
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
ppm

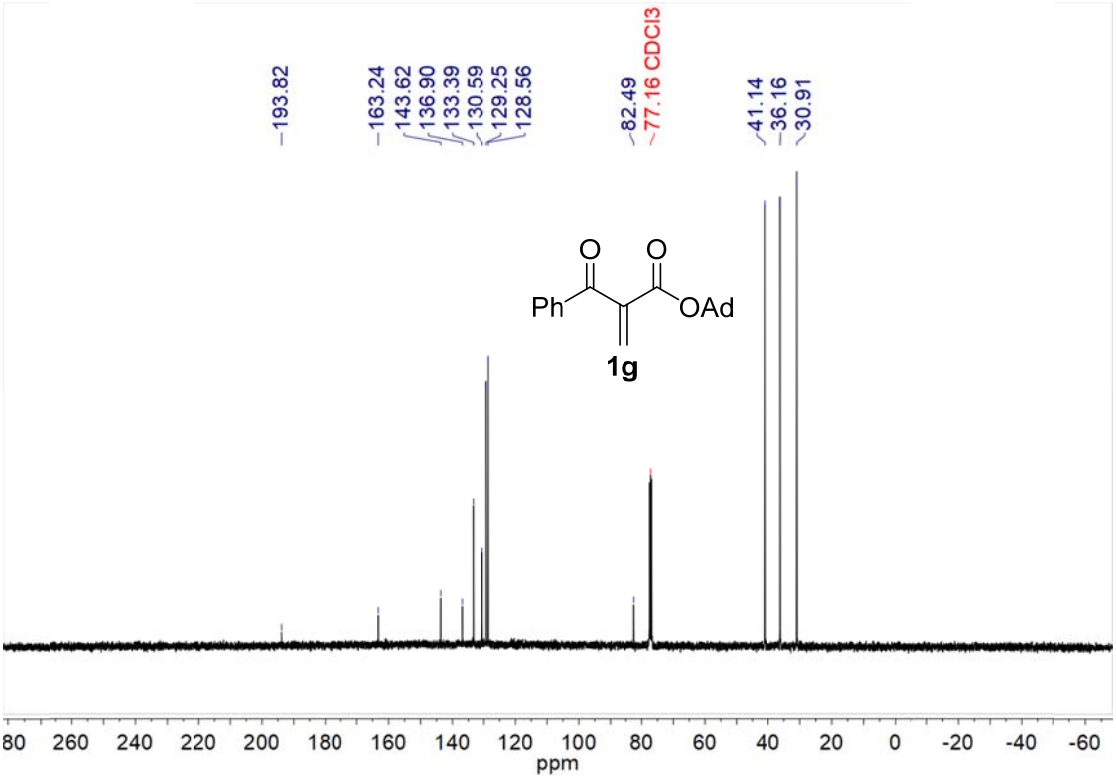

8.27
8.27
8.26
8.26
8.26
8.25
7.26 cdcl3
2.70
2.70
2.69
2.69
2.69
2.68
2.68
2.68
2.67
2.67
2.67
2.53
2.52
2.52
2.52
2.51
2.51
2.50
2.50
2.18
1.71
1.67
1.63 HDO
0.00
O
O
OAd
1a
1.08
2.02
2.00
8.90
6.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


203.30
170.70
160.80
138.60
82.01
77.16 cdcl3
45.45
41.45
36.26
36.18
35.80
30.99
30.82
26.39
O
O
OAd
1a
230 210 190 170 150 130 110 90 70 50 30 10 -10
ppm

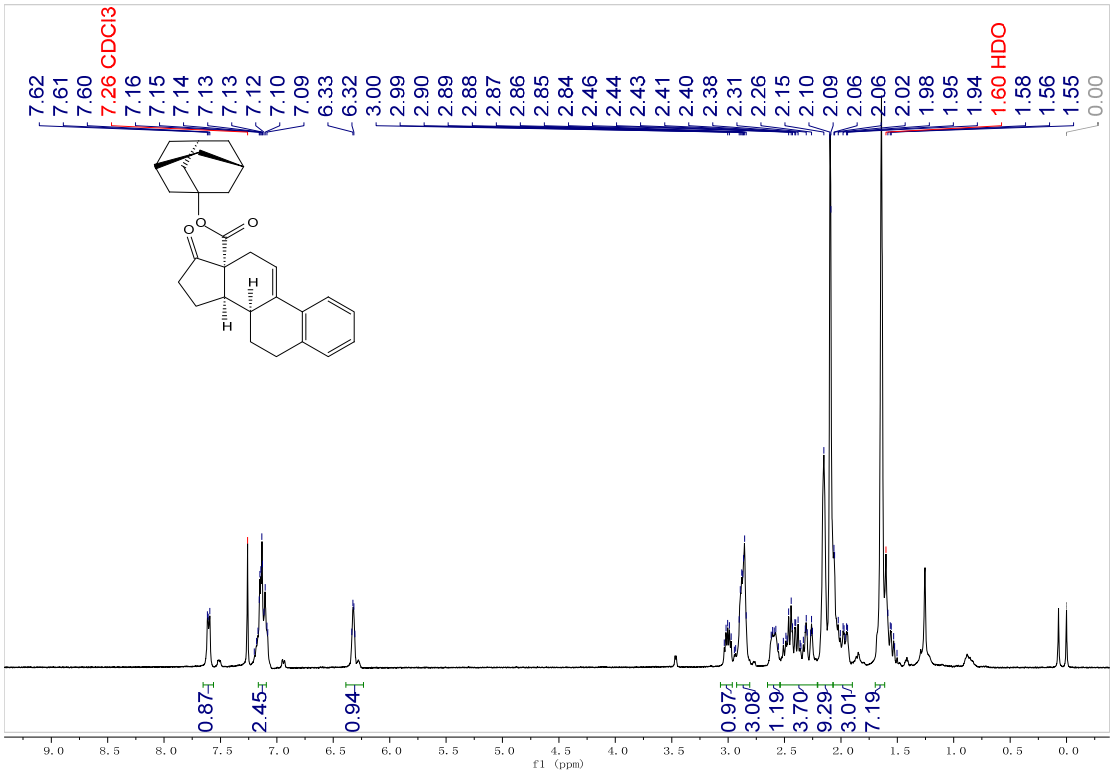

8.14
8.14
8.14
7.26 CDCl3
4.88
4.87
1.50
0.03
O
O
O
O
tBu
1e
0.90
1.95
9.40
f1 (ppm)

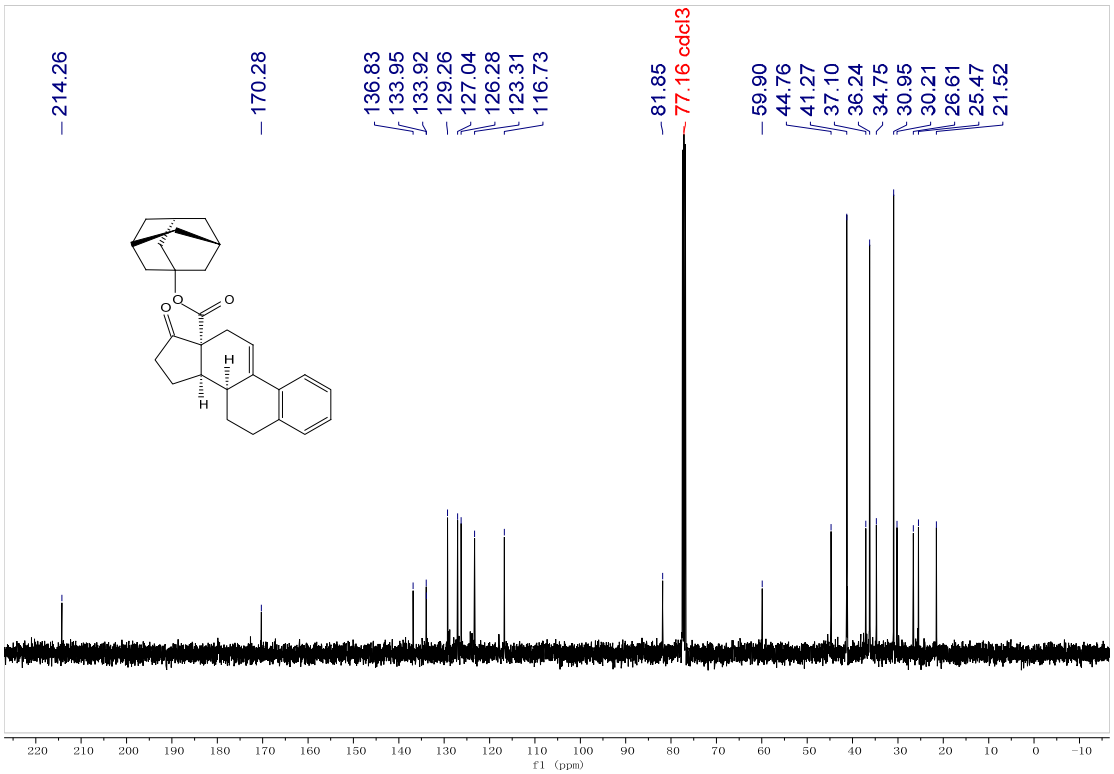

168.30
159.05
158.79
126.81
82.95
77.16 cdcl3
69.03
28.04
27.87
27.83
27.74
O
O
O
O
tBu
1e
ppm


7.84
7.84
7.82
7.82
7.59
7.57
7.56
7.47
7.46
7.44
7.26 cdcl3
6.56
6.03
2.10
1.98
1.97
1.60
1.59
1.59
0.00
O
O
Ph
OAd
1g
1.84
0.96
1.78
1.00
1.02
2.88
5.64
5.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

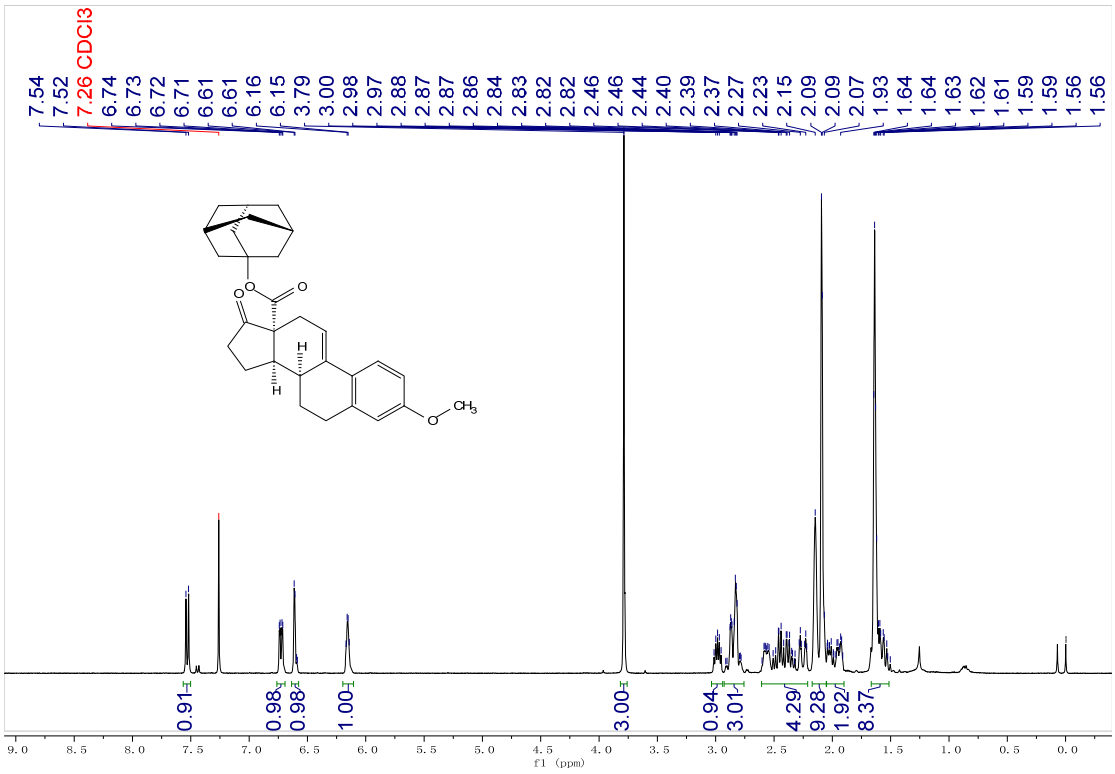

193.82
163.24
143.62
136.90
133.39
130.59
129.25
128.56
82.49
77.16 CDCl3
41.14
36.16
30.91
O
O
Ph
OAd
1g
80 260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60
ppm

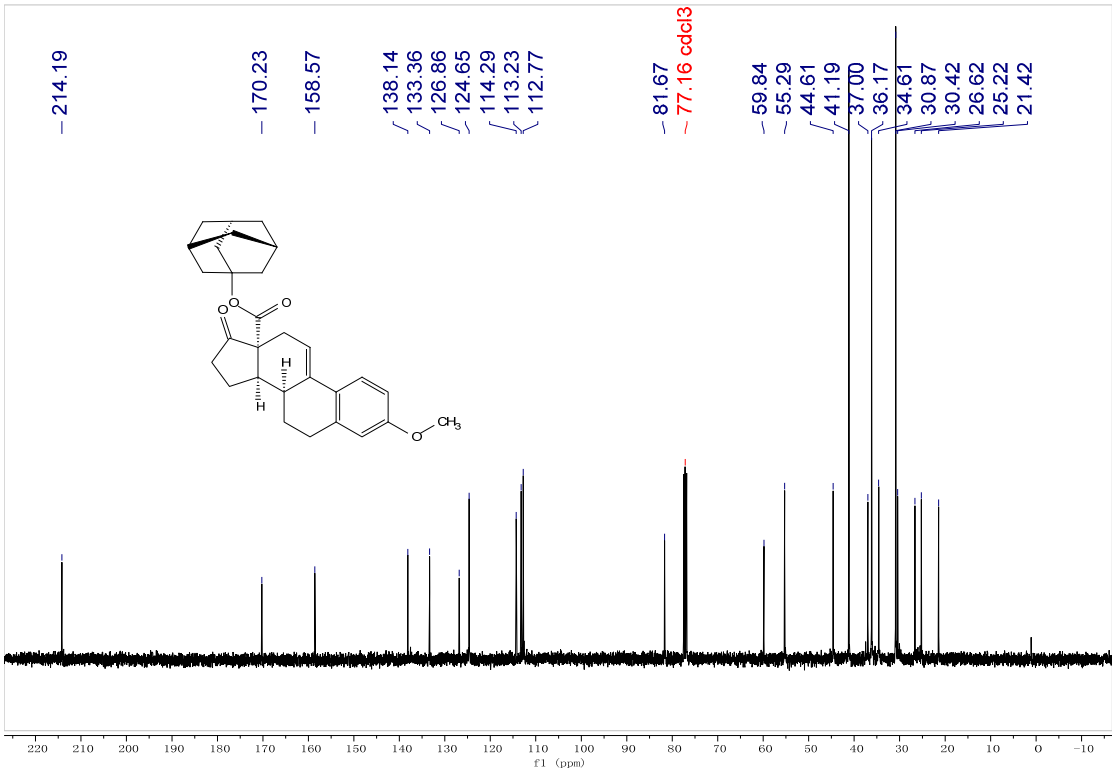
3a


7.62
7.61
7.60
7.26 CDCl3
7.16
7.15
7.14
7.13
7.13
7.12
7.10
7.09
6.33
6.32
3.00
2.99
2.90
2.89
2.88
2.87
2.86
2.85
2.84
2.46
2.44
2.43
2.41
2.40
2.38
2.31
2.26
2.15
2.10
2.09
2.06
2.06
2.02
1.98
1.95
1.94
1.60 HDO
1.58
1.56
1.55
0.00
0.87
2.45
0.94
0.97
3.08
1.19
3.70
9.29
3.01
7.19
f1 (ppm)

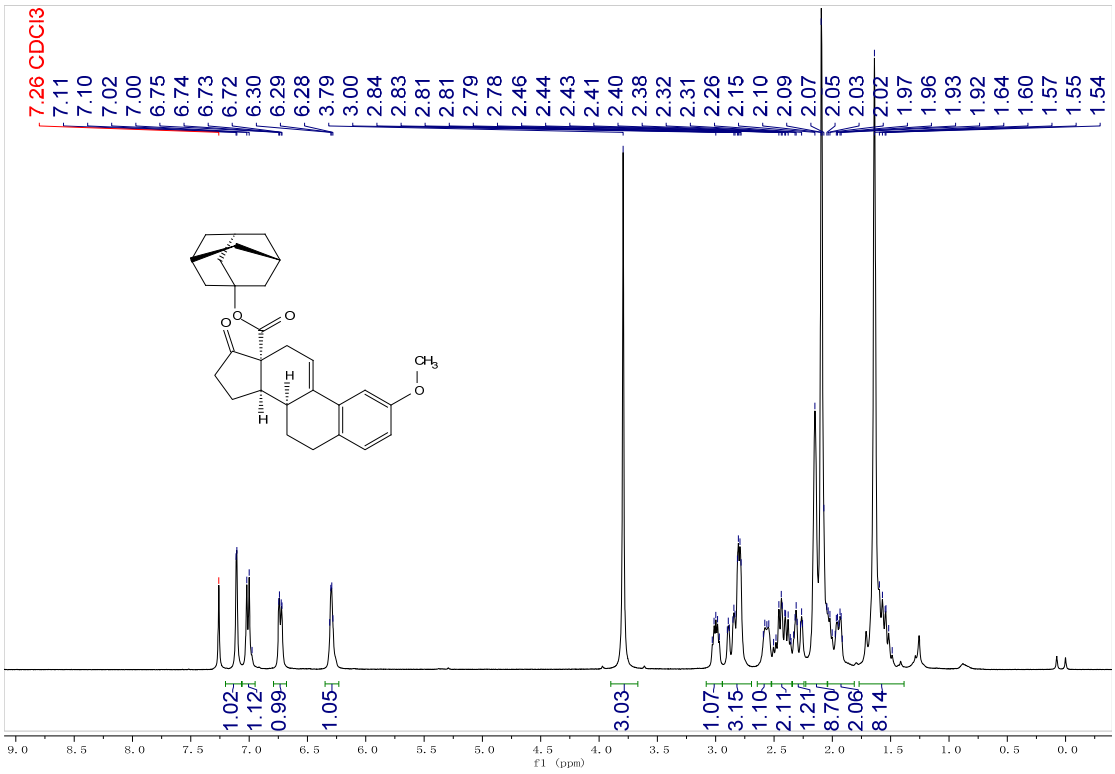

214.26
170.28
136.83
133.95
133.92
129.26
127.04
126.28
123.31
116.73
81.85
77.16 cdcl3
59.90
44.76
41.27
37.10
36.24
34.75
30.95
30.21
26.61
25.47
21.52
f1 (ppm)

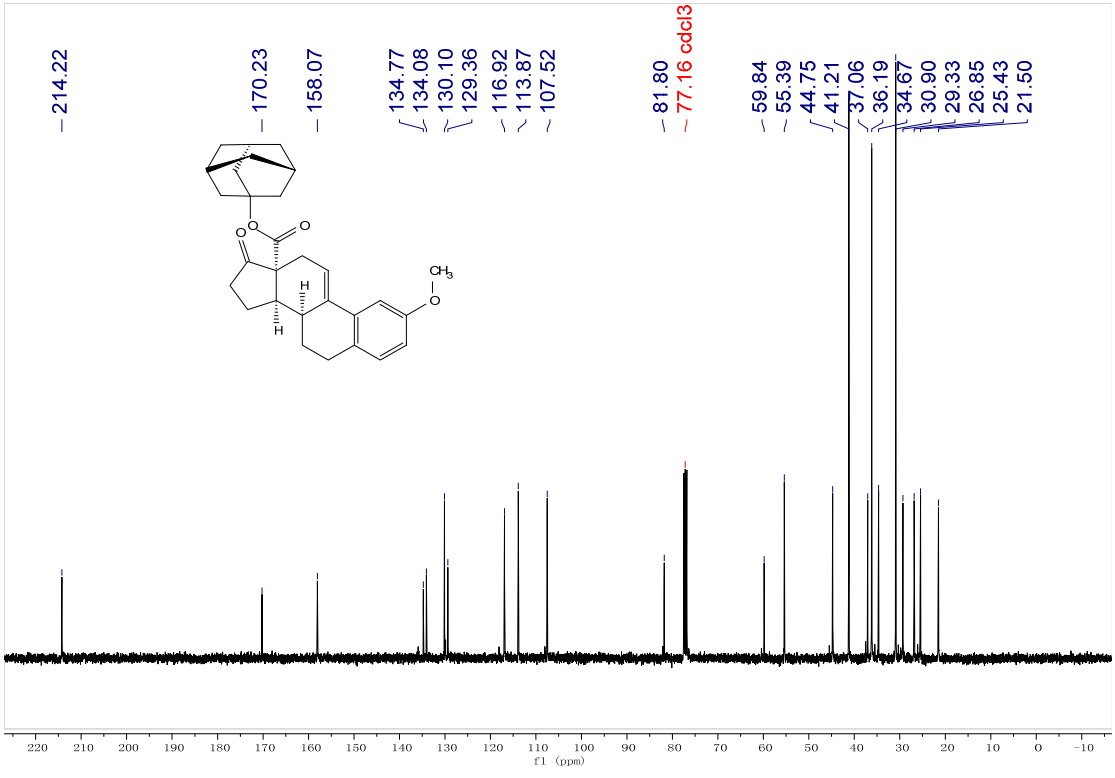
3b


7.54
7.52
7.26 CDCl3
6.74
6.73
6.72
6.71
6.61
6.61
6.16
6.15
3.79
3.00
2.98
2.97
2.88
2.87
2.87
2.86
2.84
2.83
2.82
2.82
2.46
2.46
2.44
2.40
2.39
2.37
2.27
2.23
2.15
2.09
2.09
2.07
1.93
1.64
1.64
1.63
1.62
1.61
1.59
1.59
1.56
1.56
0.91
0.98
0.98
1.00
3.00
0.94
3.01
4.29
9.28
1.92
8.37
f1 (ppm)

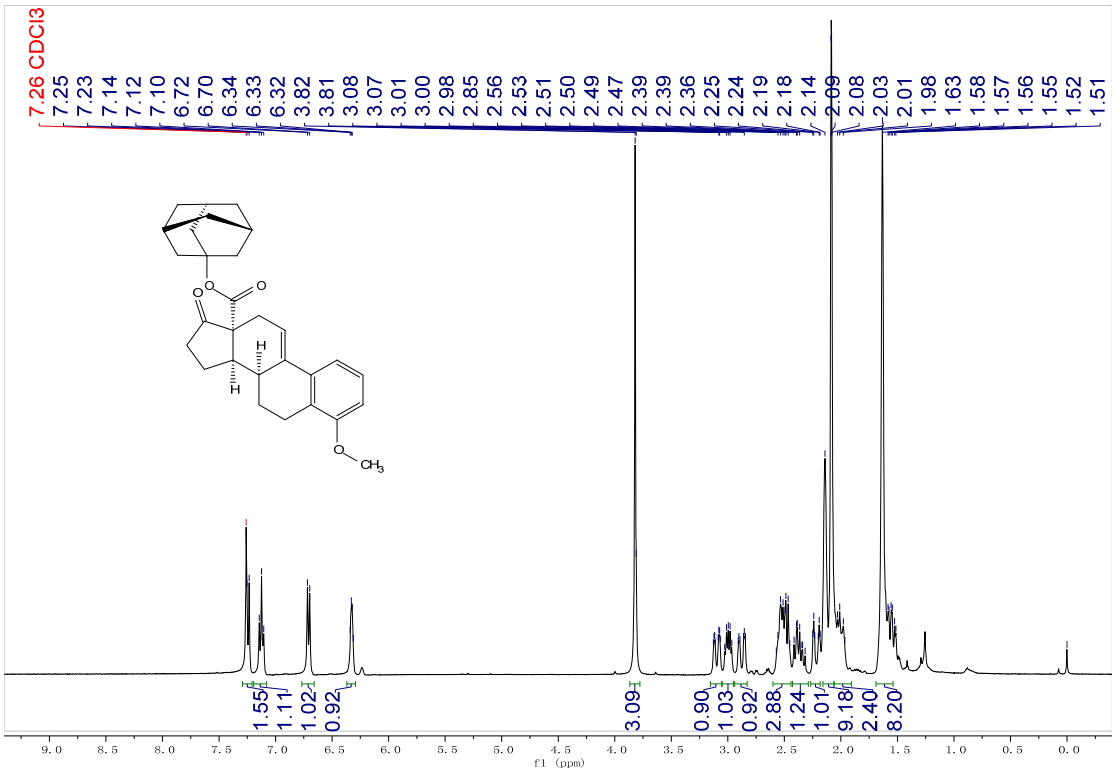

214.19
170.23
158.57
138.14
133.36
126.86
124.65
114.29
113.23
112.77
81.67
77.16 cdcl3
59.84
55.29
44.61
41.19
37.00
36.17
34.61
30.87
30.42
26.62
25.22
21.42
f1 (ppm)

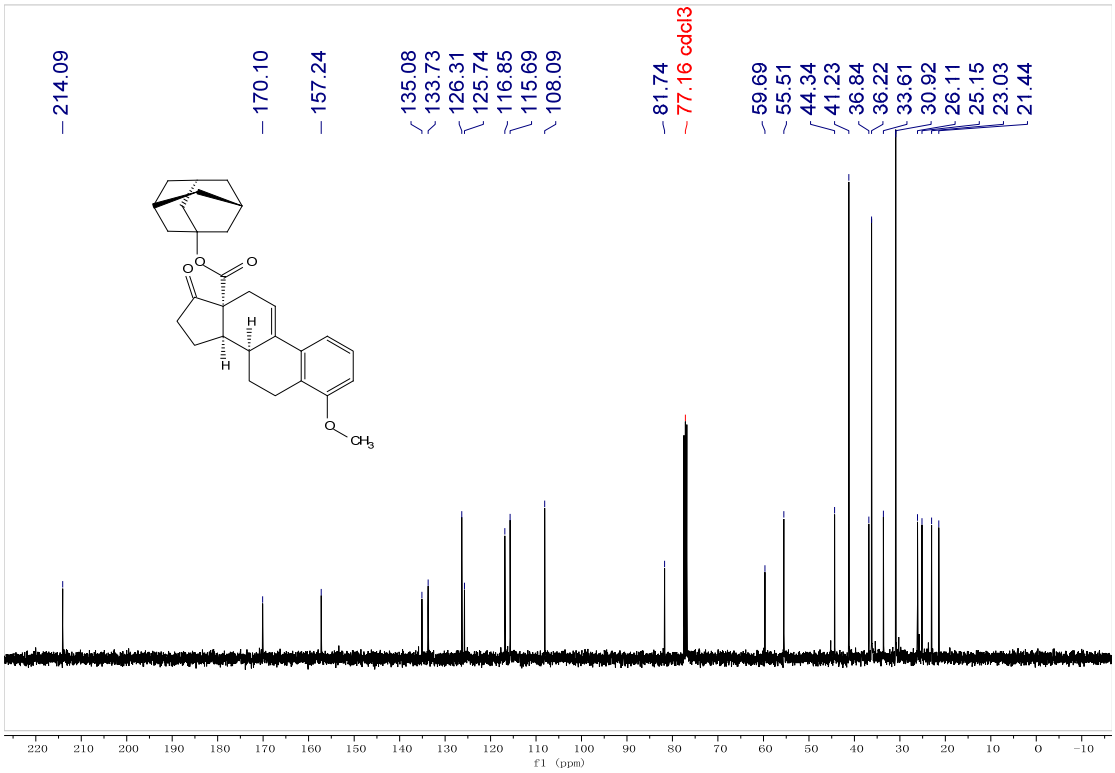
3c


7.26 CDCl3
7.11
7.10
7.02
7.00
6.75
6.74
6.73
6.72
6.30
6.29
6.28
3.79
3.00
2.84
2.83
2.81
2.81
2.79
2.78
2.46
2.44
2.43
2.41
2.40
2.38
2.32
2.31
2.26
2.15
2.10
2.09
2.07
2.05
2.03
2.02
1.97
1.96
1.93
1.92
1.64
1.60
1.57
1.55
1.54
1.02
1.12
0.99
1.05
3.03
1.07
3.15
1.10
2.11
1.21
8.70
2.06
8.14
f1 (ppm)

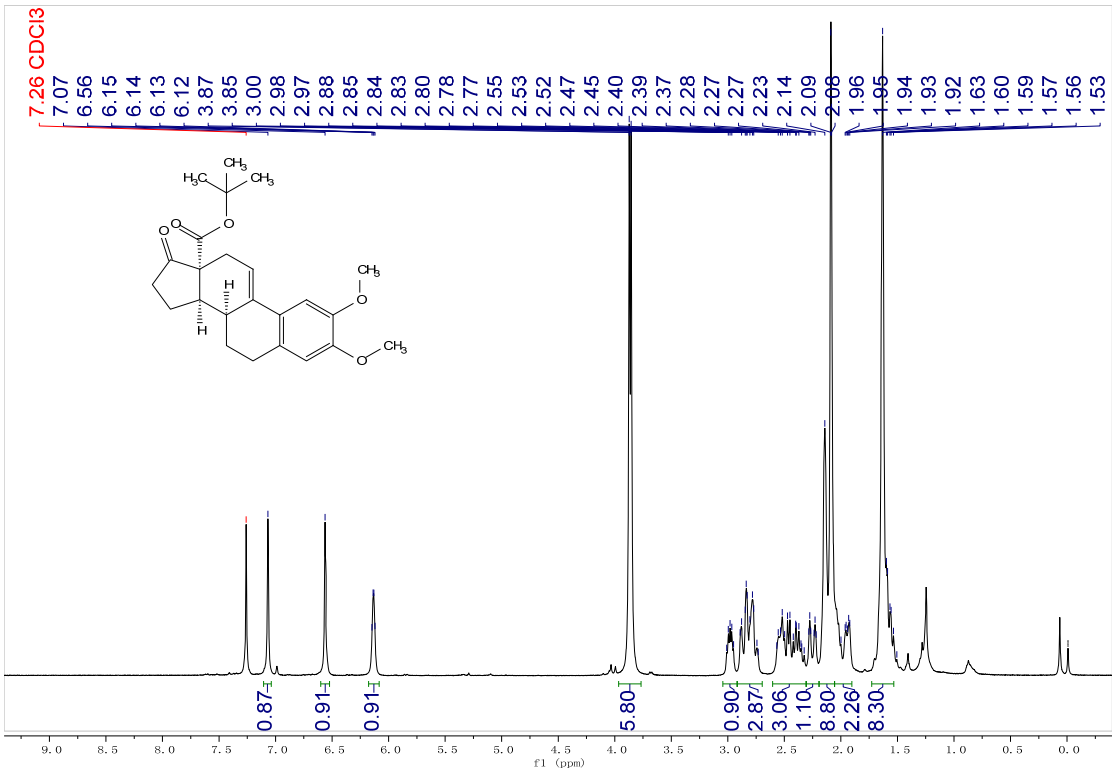

214.22
170.23
158.07
134.77
134.08
130.10
129.36
116.92
113.87
107.52
81.80
77.16 cdcl3
59.84
55.39
44.75
41.21
37.06
36.19
34.67
30.90
29.33
26.85
25.43
21.50
f1 (ppm)

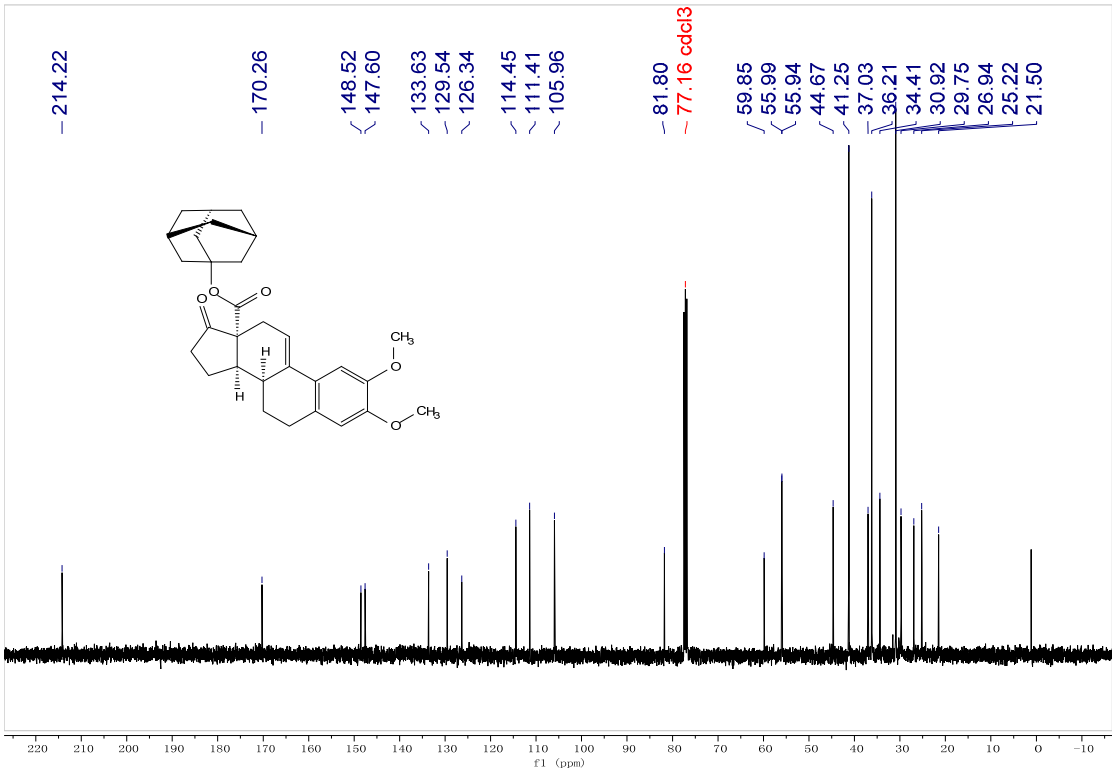
3d


7.26 CDCl3
7.25
7.23
7.14
7.12
7.10
6.72
6.70
6.34
6.33
6.32
3.82
3.81
3.08
3.07
3.01
3.00
2.98
2.85
2.56
2.53
2.51
2.50
2.49
2.47
2.39
2.39
2.36
2.25
2.24
2.19
2.18
2.14
2.09
2.08
2.03
2.01
1.98
1.63
1.58
1.57
1.56
1.55
1.52
1.51
1.55
1.11
1.02
0.92
3.09
0.90
1.03
0.92
2.88
1.24
1.01
9.18
2.40
8.20
f1 (ppm)

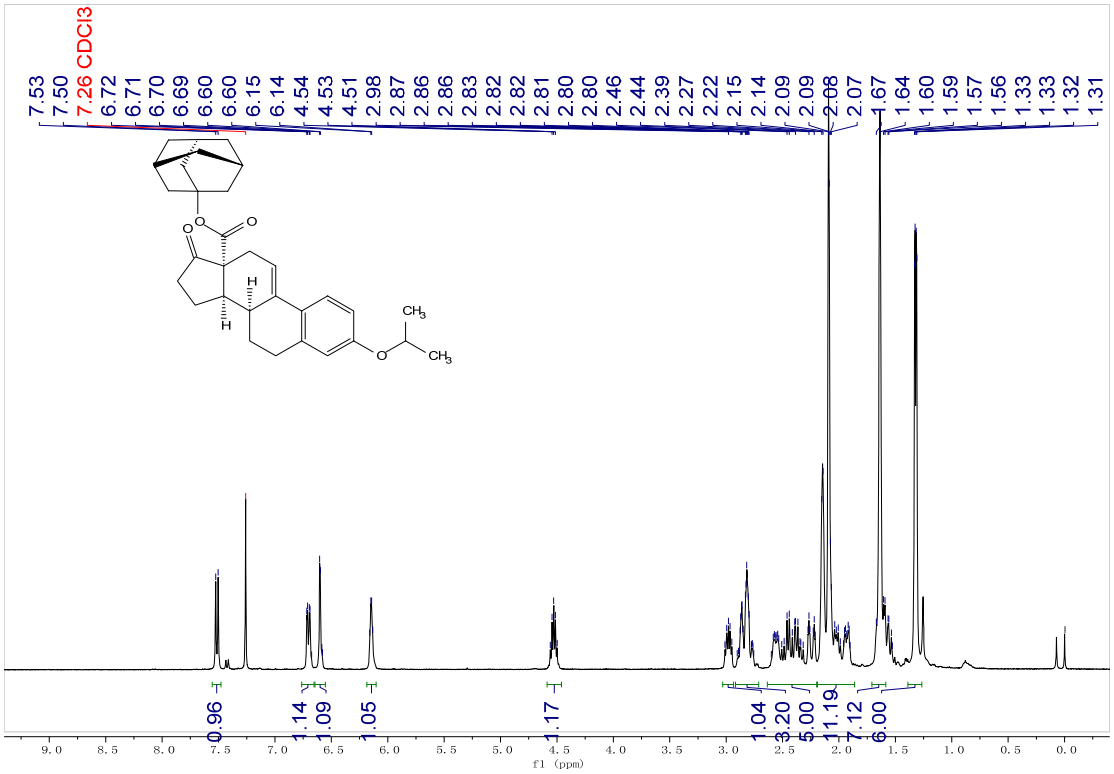

214.09
170.10
157.24
135.08
133.73
126.31
125.74
116.85
115.69
108.09
81.74
77.16 cdcl3
59.69
55.51
44.34
41.23
36.84
36.22
33.61
30.92
26.11
25.15
23.03
21.44
f1 (ppm)

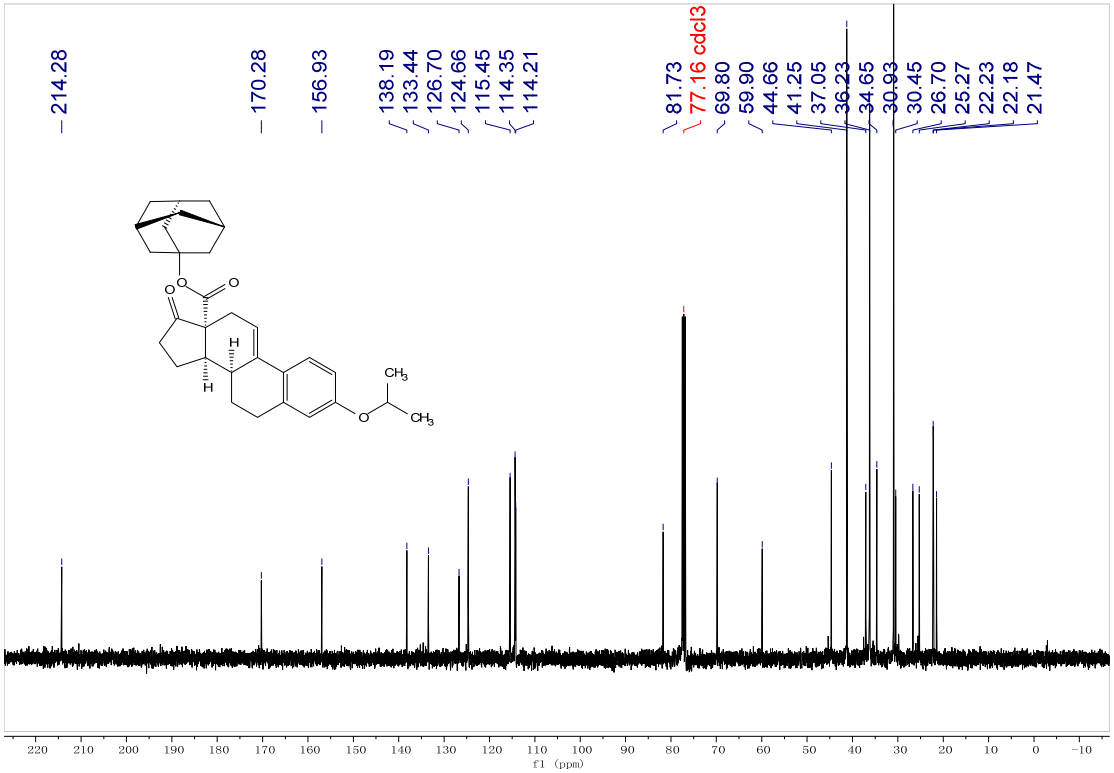
3e


7.26 CDCl3
7.07
6.56
6.15
6.14
6.13
6.12
3.87
3.85
3.00
2.98
2.97
2.88
2.85
2.84
2.83
2.80
2.78
2.77
2.55
2.53
2.52
2.47
2.45
2.40
2.39
2.37
2.28
2.27
2.27
2.23
2.14
2.09
2.08
1.96
1.95
1.94
1.93
1.92
1.63
1.60
1.59
1.57
1.56
1.53
0.87
0.91
0.91
5.80
0.90
2.87
3.06
1.10
8.80
2.26
8.30
f1 (ppm)

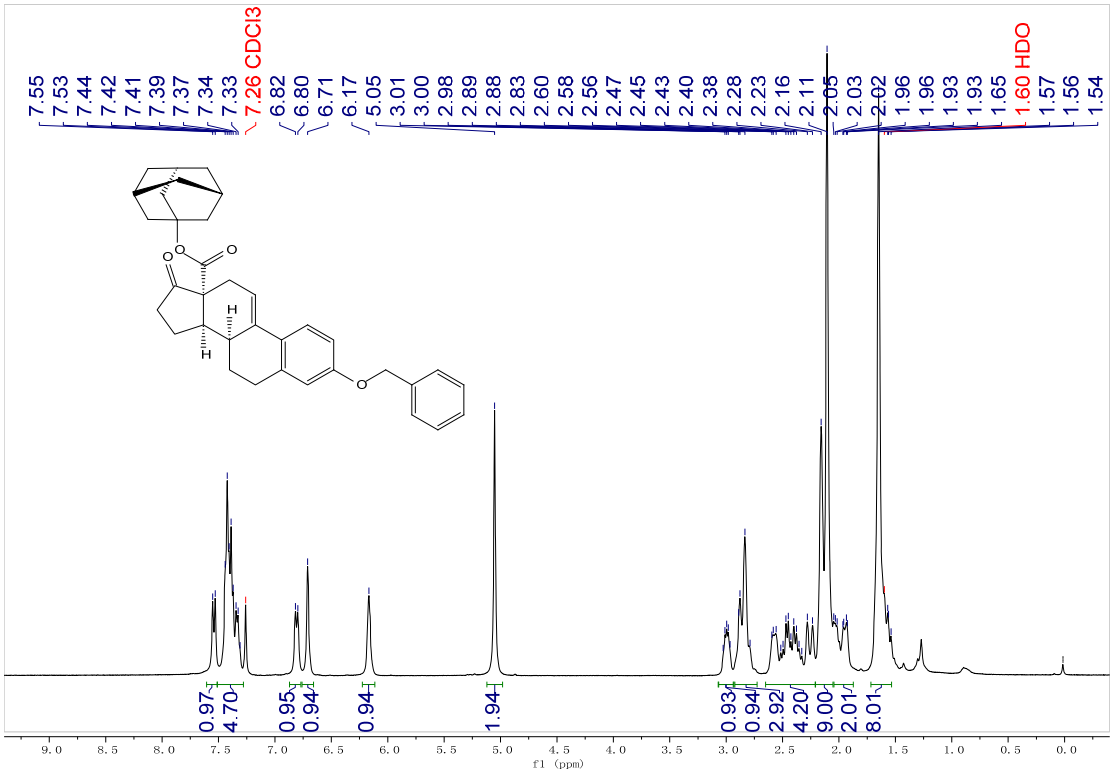

214.22
170.26
148.52
147.60
133.63
129.54
126.34
114.45
111.41
105.96
81.80
77.16 cdcl3
59.85
55.99
55.94
44.67
41.25
37.03
36.21
34.41
30.92
29.75
26.94
25.22
21.50
f1 (ppm)

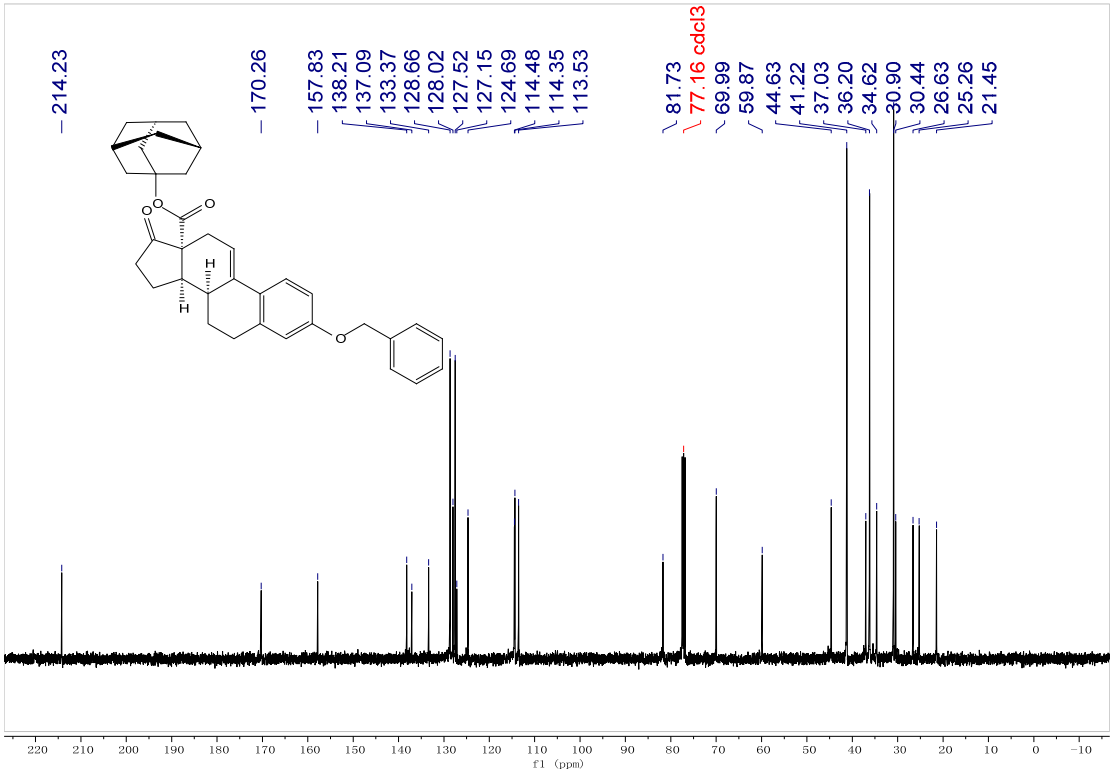
3f


7.53
7.50
7.26 CDCl3
6.72
6.71
6.70
6.69
6.60
6.60
6.15
6.14
4.54
4.53
4.51
2.98
2.87
2.86
2.86
2.83
2.82
2.82
2.81
2.80
2.80
2.46
2.44
2.39
2.27
2.22
2.15
2.14
2.09
2.09
2.08
2.07
1.67
1.64
1.60
1.59
1.57
1.56
1.33
1.33
1.32
1.31
0.96
1.14
1.09
1.05
1.17
1.04
3.20
5.00
11.19
7.12
6.00
f1 (ppm)

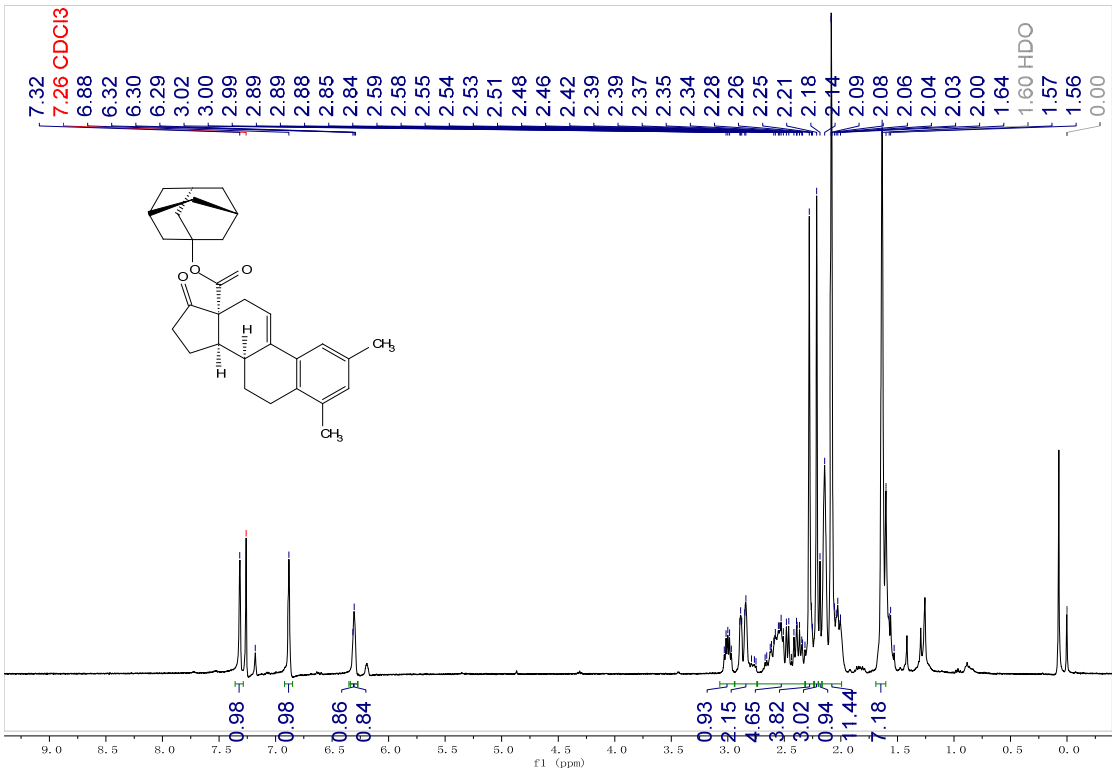

214.28
170.28
156.93
138.19
133.44
126.70
124.66
115.45
114.35
114.21
81.73
77.16 cdcl3
69.80
59.90
44.66
41.25
37.05
36.23
34.65
30.93
30.45
26.70
25.27
22.23
22.18
21.47
f1 (ppm)

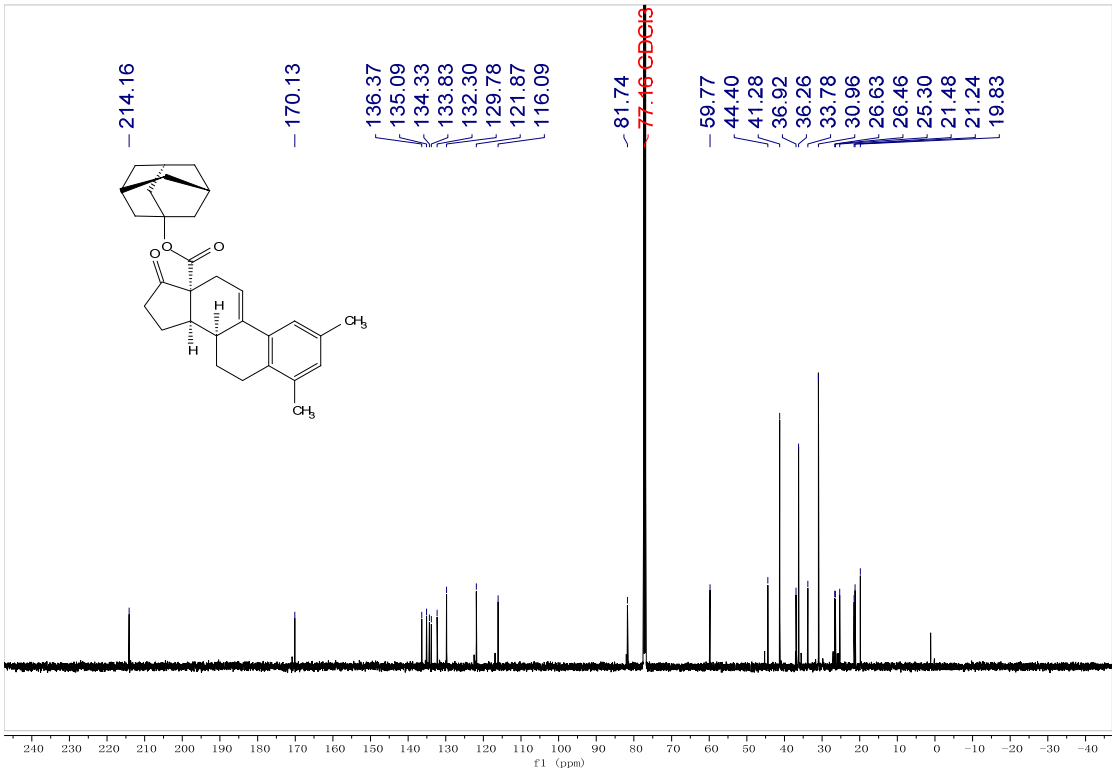
3g


7.55 7.53 7.44 7.42 7.41 7.39 7.37 7.34 7.33 7.26 CDCl3 6.82 6.80 6.71 6.17 5.05 3.01 3.00 2.98 2.89 2.88 2.83 2.60 2.58 2.56 2.47 2.45 2.43 2.40 2.38 2.28 2.23 2.16 2.11 2.05 2.03 2.02 1.96 1.96 1.93 1.93 1.65 1.60 HDO 1.57 1.56 1.54
0.97 4.70 0.95 0.94 0.94 1.94 0.93 0.94 2.92 4.20 9.00 2.01 8.01
f1 (ppm)

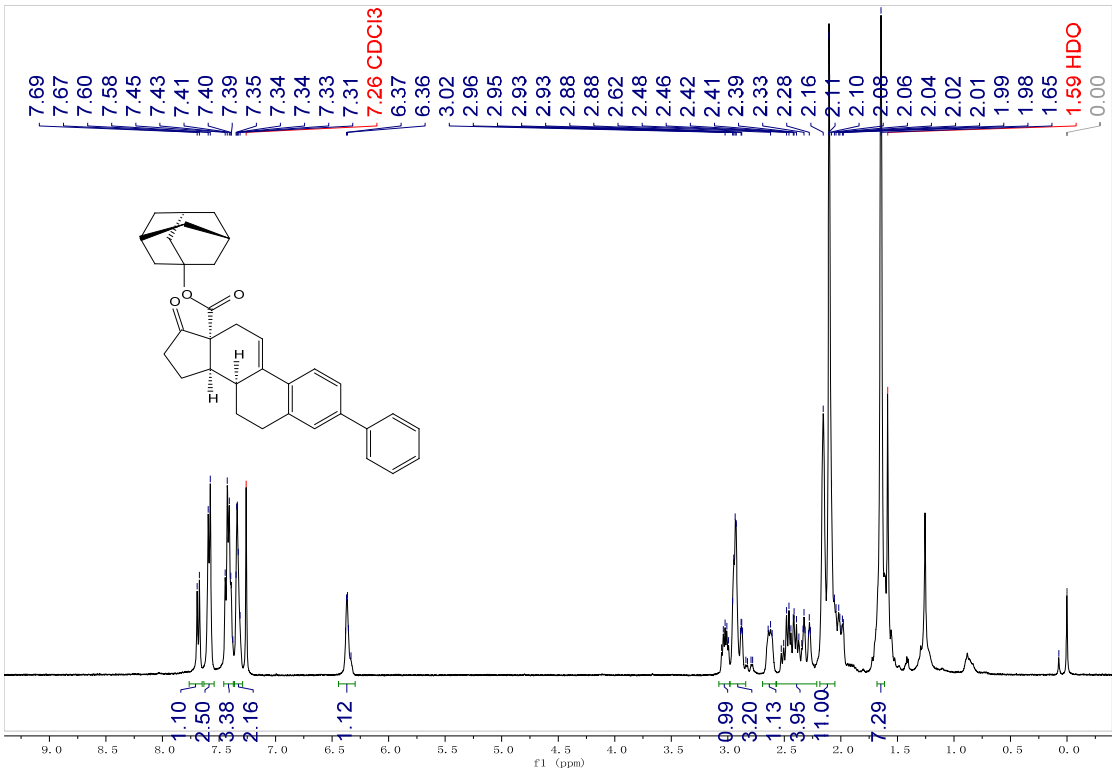

214.23 170.26 157.83 138.21 137.09 133.37 128.66 128.02 127.52 127.15 124.69 114.48 114.35 113.53 81.73 77.16 cdcl3 69.99 59.87 44.63 41.22 37.03 36.20 34.62 30.90 30.44 26.63 25.26 21.45
f1 (ppm)

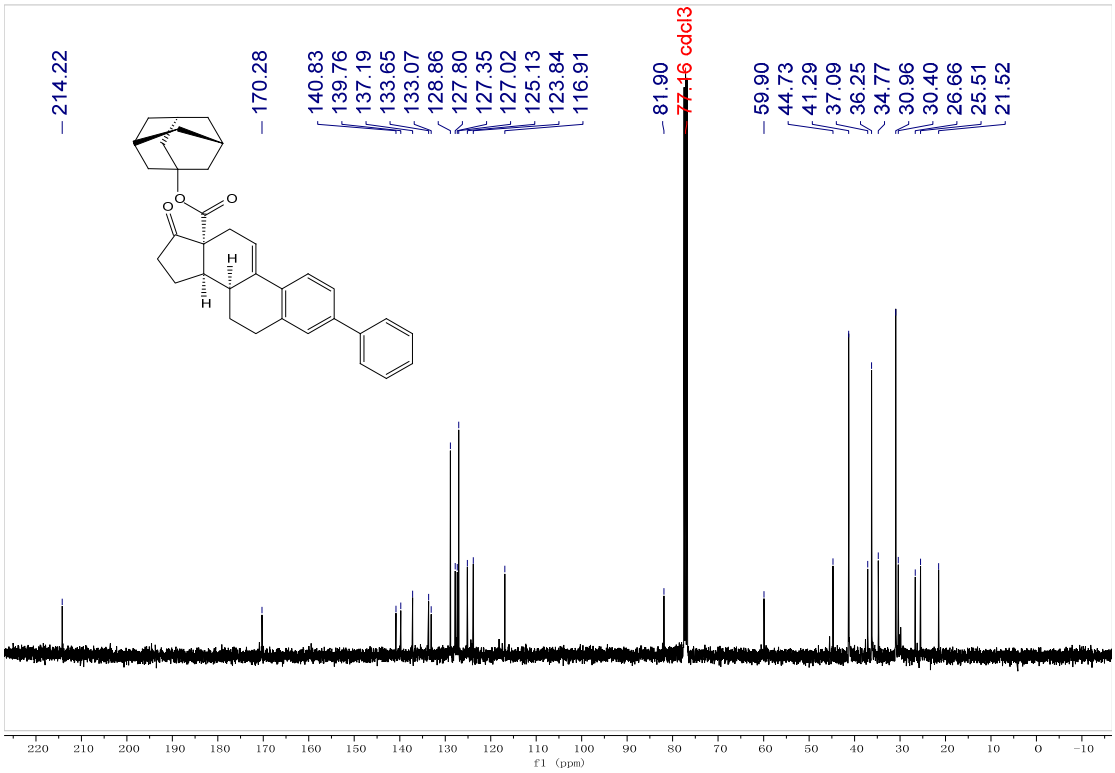
3h


7.32
7.26 CDCl3
6.88
6.32
6.30
6.29
3.02
3.00
2.99
2.89
2.89
2.88
2.85
2.84
2.59
2.58
2.55
2.54
2.53
2.51
2.48
2.46
2.42
2.39
2.39
2.37
2.35
2.34
2.28
2.26
2.25
2.21
2.18
2.14
2.09
2.08
2.06
2.04
2.03
2.00
1.64
1.60 HDO
1.57
1.56
0.00
0.98
0.98
0.86
0.84
0.93
2.15
4.65
3.82
3.02
0.94
11.44
7.18
f1 (ppm)

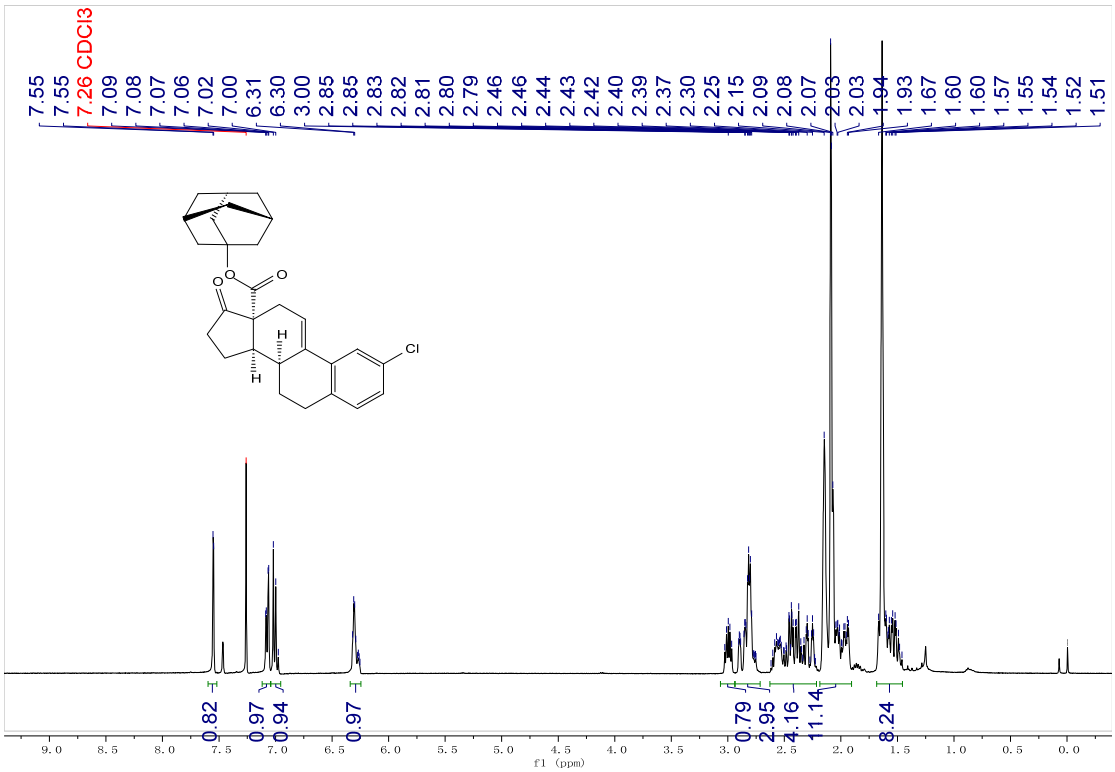

214.16
170.13
136.37
135.09
134.33
133.83
132.30
129.78
121.87
116.09
81.74
77.16 CDCl3
59.77
44.40
41.28
36.92
36.26
33.78
30.96
26.63
26.46
25.30
21.48
21.24
19.83
f1 (ppm)

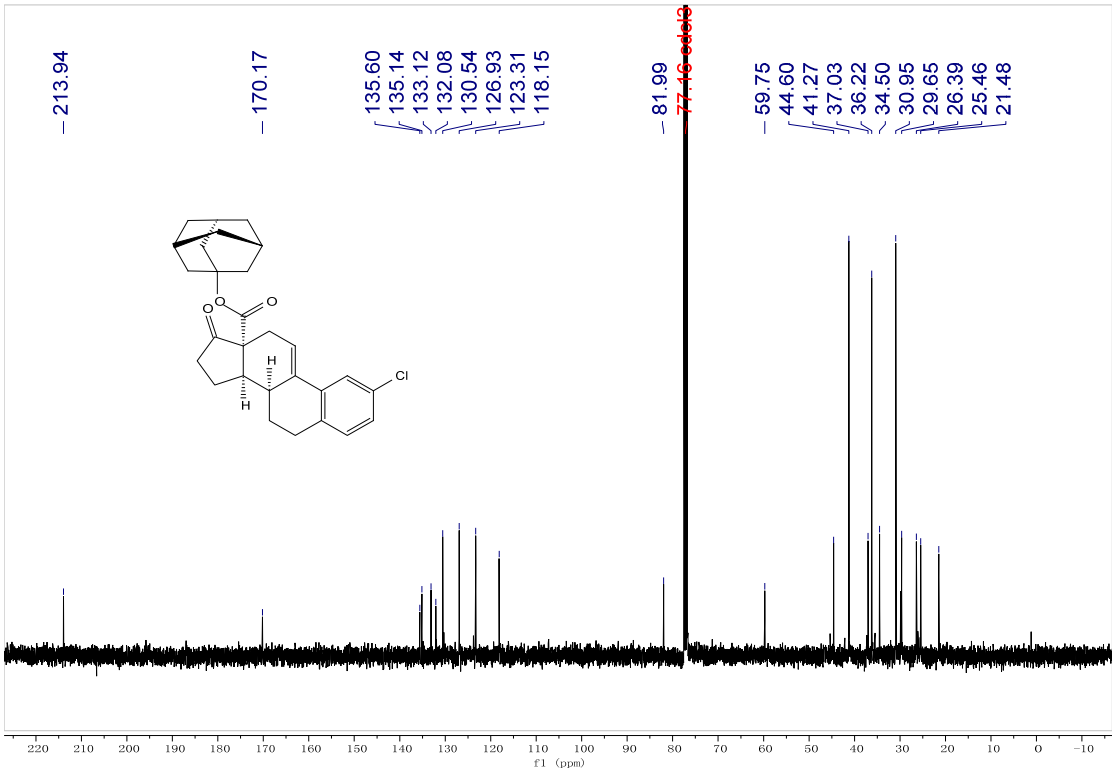
3i


7.69
7.67
7.60
7.58
7.45
7.43
7.41
7.40
7.39
7.35
7.34
7.34
7.33
7.31
7.26 CDCl3
6.37
6.36
3.02
2.96
2.95
2.93
2.93
2.88
2.88
2.62
2.48
2.46
2.42
2.41
2.39
2.33
2.28
2.16
2.11
2.10
2.08
2.06
2.04
2.02
2.01
1.99
1.98
1.65
1.59 HDO
0.00
1.10
2.50
3.38
2.16
1.12
0.99
3.20
1.13
3.95
11.00
7.29
f1 (ppm)

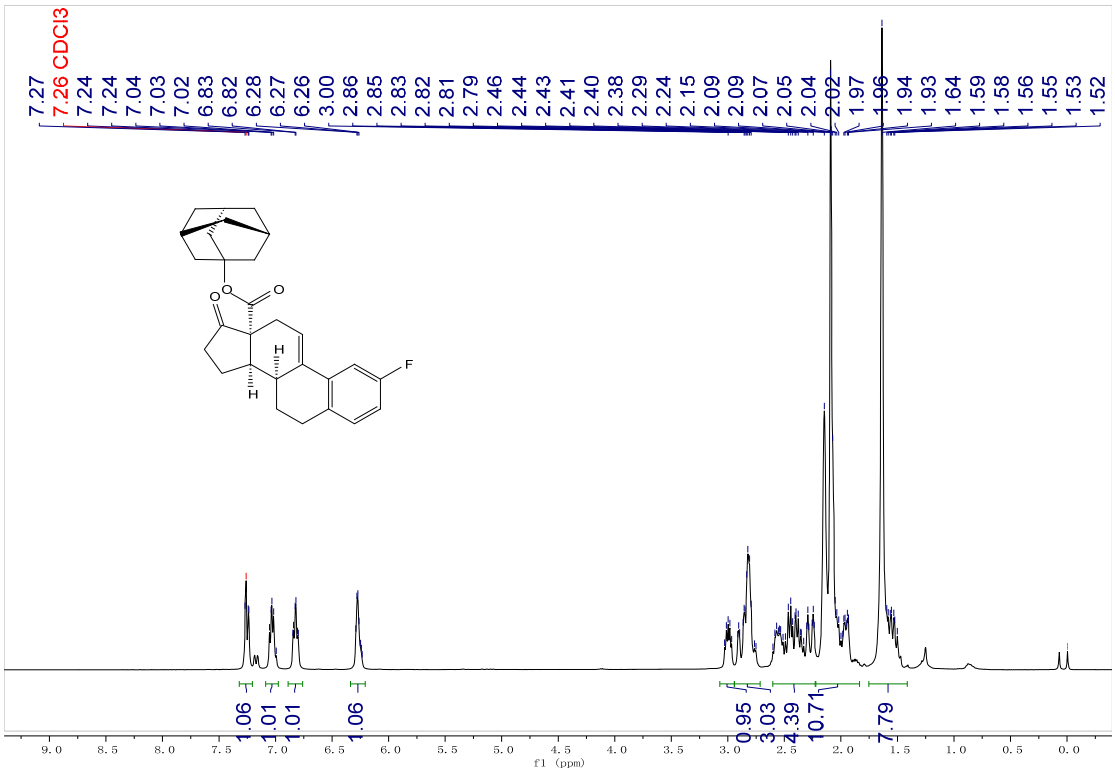

214.22
170.28
140.83
139.76
137.19
133.65
133.07
128.86
127.80
127.35
127.02
125.13
123.84
116.91
81.90
77.46 cdcl3
59.90
44.73
41.29
37.09
36.25
34.77
30.96
30.40
26.66
25.51
21.52
f1 (ppm)

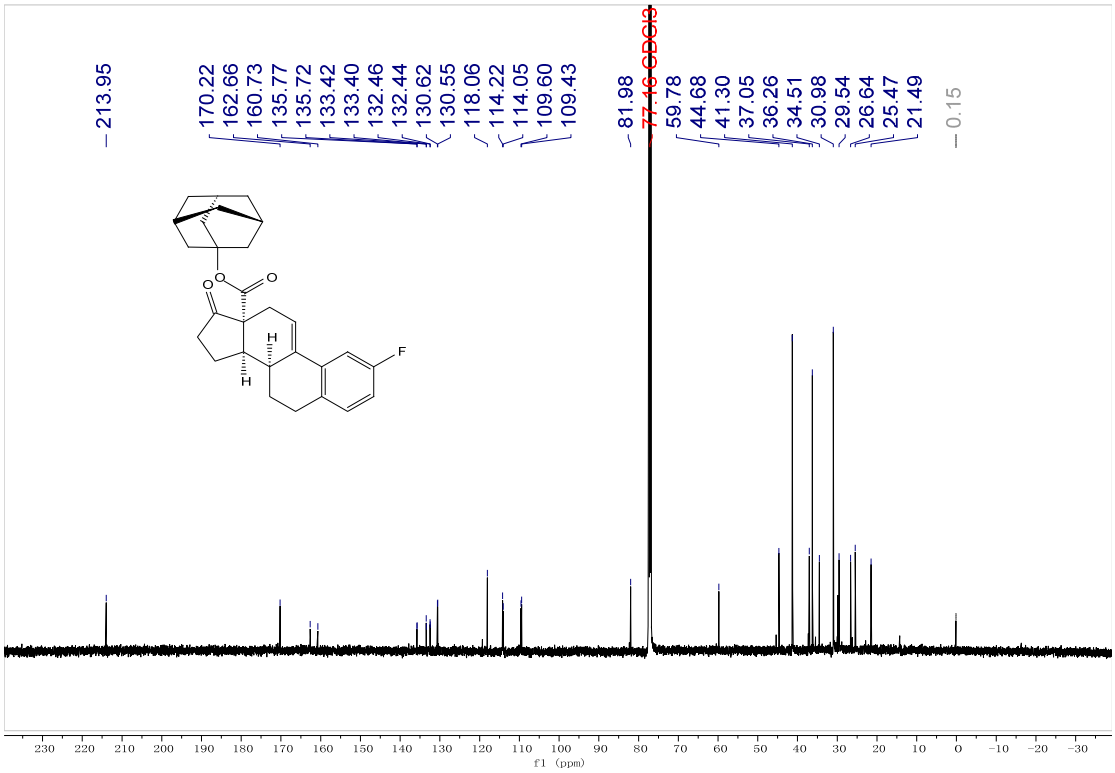
3j

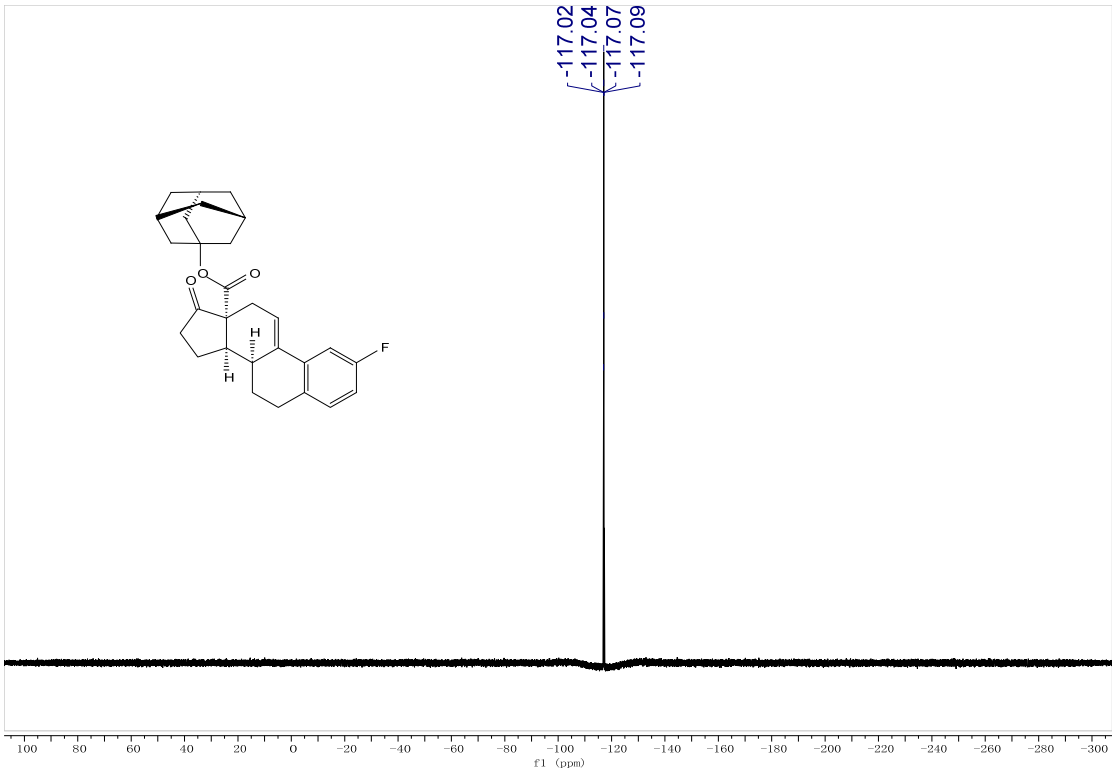

7.55
7.55
7.26 CDCl3
7.09
7.08
7.07
7.06
7.02
7.00
6.31
6.30
3.00
2.85
2.85
2.83
2.82
2.81
2.80
2.79
2.46
2.46
2.44
2.43
2.42
2.40
2.39
2.37
2.30
2.25
2.15
2.09
2.08
2.07
2.03
2.03
1.94
1.93
1.67
1.60
1.60
1.57
1.55
1.54
1.52
1.51
O
O
O
H
H
Cl
0.82
0.97
0.94
0.97
0.79
2.95
4.16
11.14
8.24
f1 (ppm)


213.94
170.17
135.60
135.14
133.12
132.08
130.54
126.93
123.31
118.15
81.99
77.16 cdcl3
59.75
44.60
41.27
37.03
36.22
34.50
30.95
29.65
26.39
25.46
21.48
O
O
O
H
H
Cl
f1 (ppm)

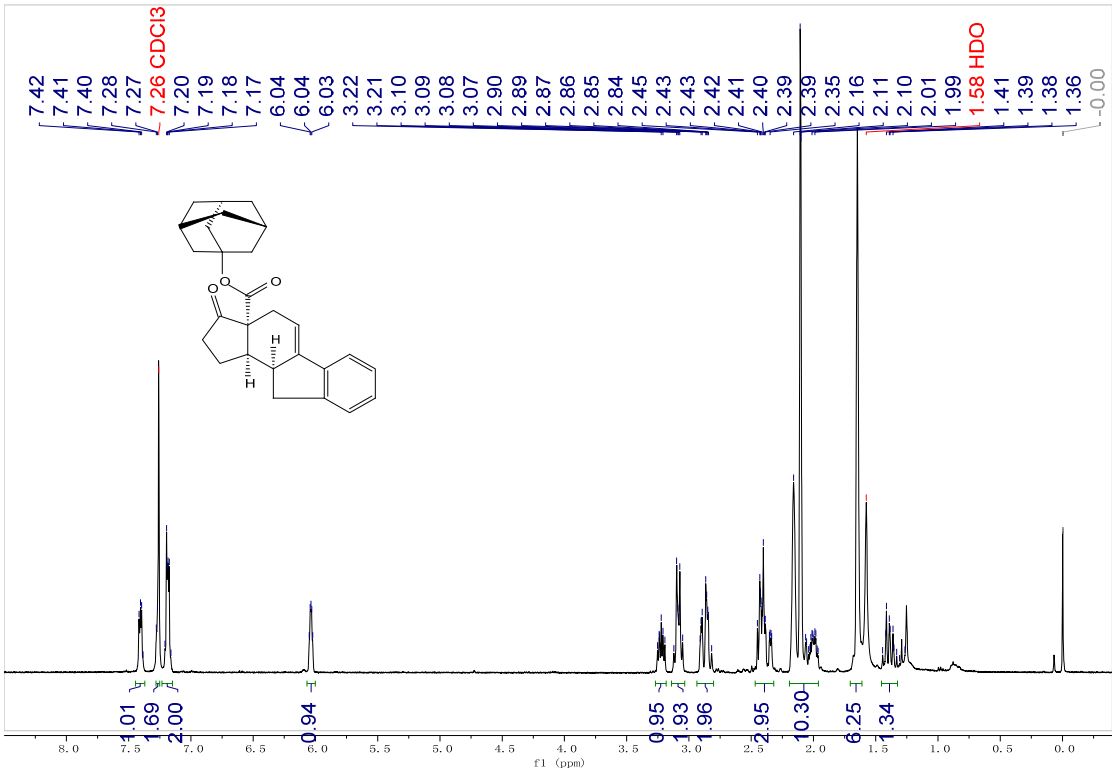
3k

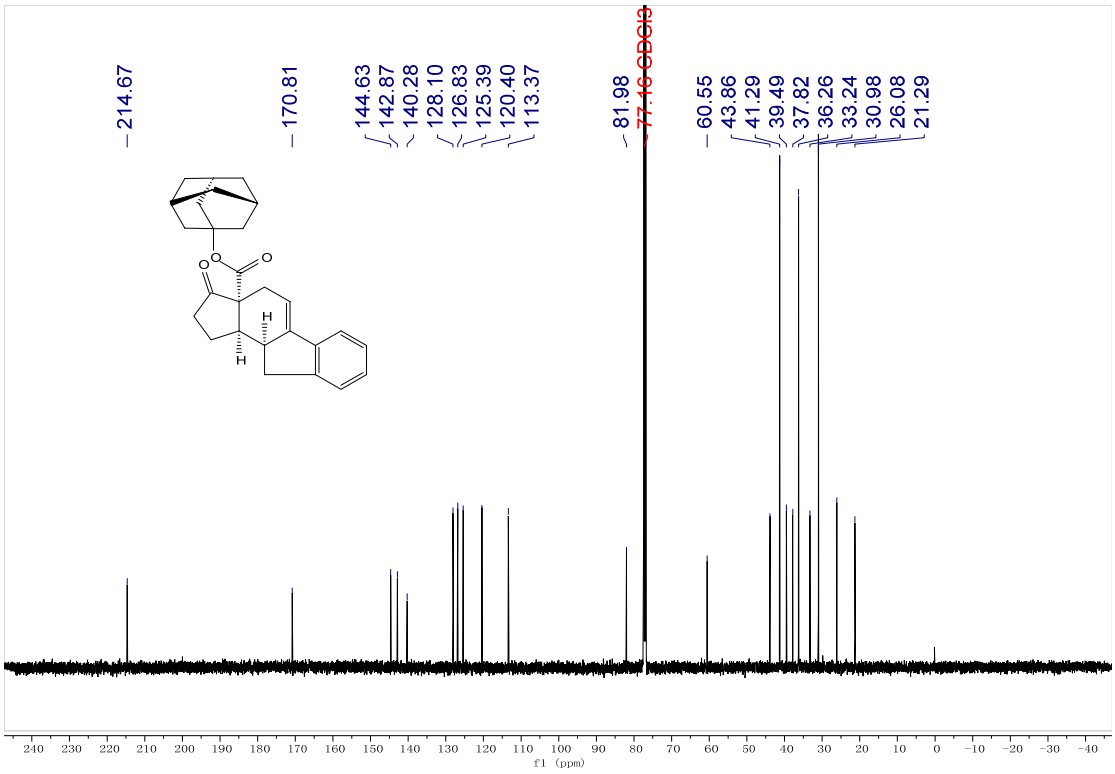

7.27
7.26 CDCl3
7.24
7.24
7.04
7.03
7.02
6.83
6.82
6.28
6.27
6.26
3.00
2.86
2.85
2.83
2.82
2.81
2.79
2.46
2.44
2.43
2.41
2.40
2.38
2.29
2.24
2.15
2.09
2.09
2.07
2.05
2.04
2.02
1.97
1.96
1.94
1.93
1.64
1.59
1.58
1.56
1.55
1.53
1.52
1.06
1.01
1.01
1.06
0.95
3.03
4.39
10.71
7.79
f1 (ppm)


213.95
170.22
162.66
160.73
135.77
135.72
133.42
133.40
132.46
132.44
130.62
130.55
118.06
114.22
114.05
109.60
109.43
81.98
77.16 CDCl3
59.78
44.68
41.30
37.05
36.26
34.51
30.98
29.54
26.64
25.47
21.49
0.15
f1 (ppm)

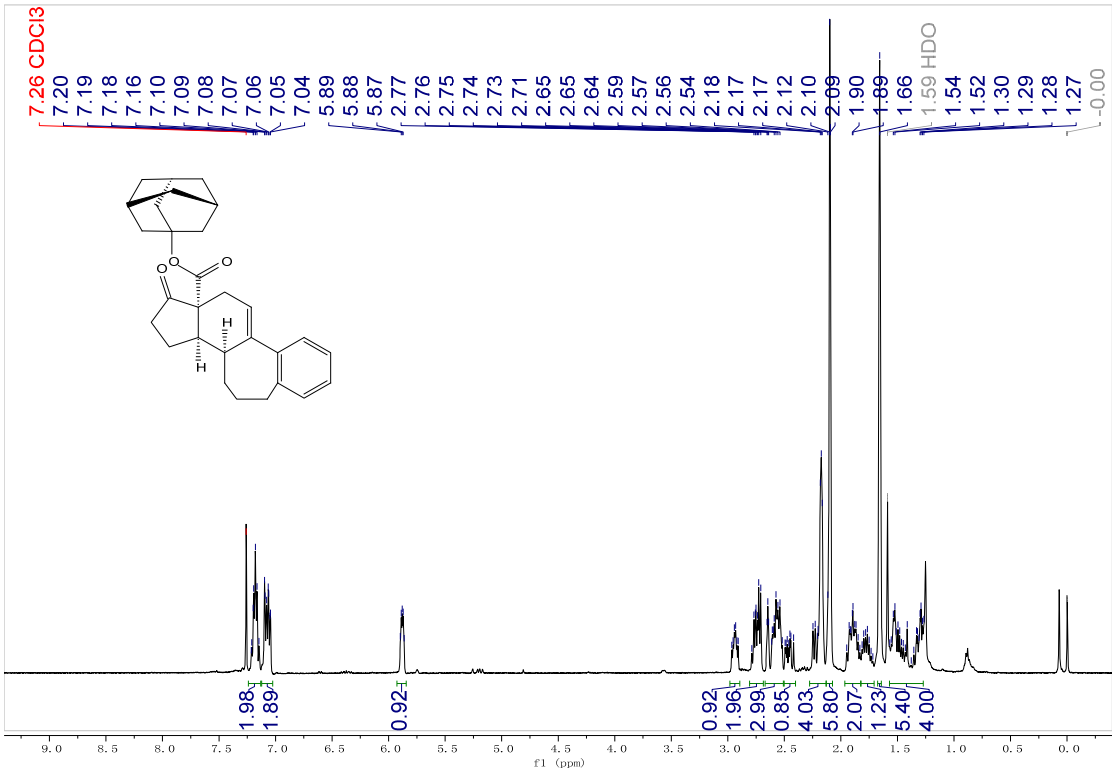

-117.02
-117.04
-117.07
-117.09
O
O
O
H
H
F
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

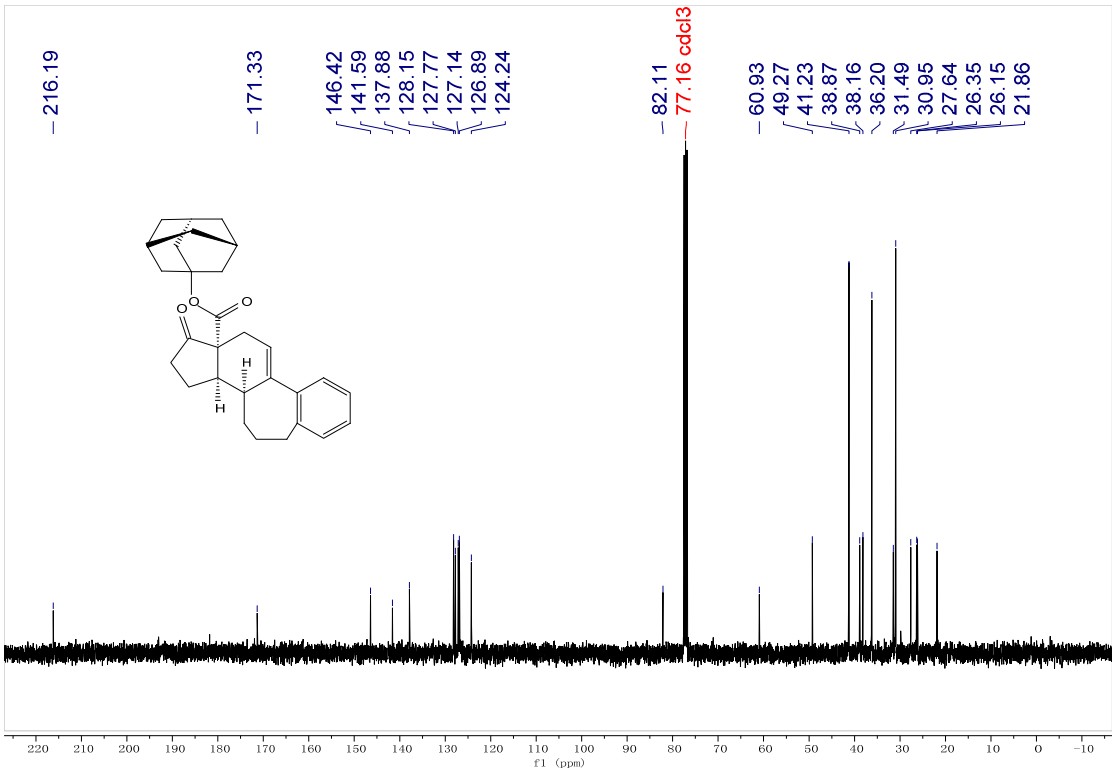
3l


7.42
7.41
7.40
7.28
7.27
7.26 CDCl3
7.20
7.19
7.18
7.17
6.04
6.04
6.03
3.22
3.21
3.10
3.09
3.08
3.07
2.90
2.89
2.87
2.86
2.85
2.84
2.45
2.43
2.43
2.42
2.41
2.40
2.39
2.39
2.35
2.16
2.11
2.10
2.01
1.99
1.58 HDO
1.41
1.39
1.38
1.36
0.00
O
O
O
H
H
1.01
1.69
2.00
0.94
0.95
1.93
1.96
2.95
10.30
6.25
1.34
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

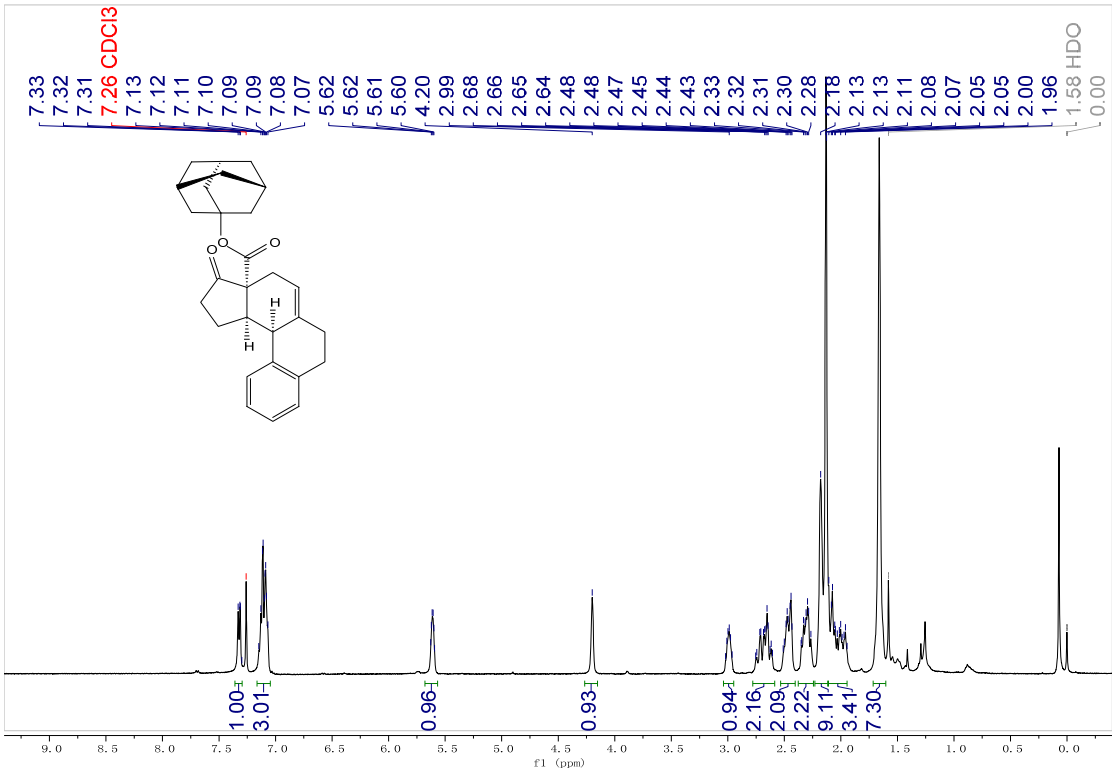

214.67
170.81
144.63
142.87
140.28
128.10
126.83
125.39
120.40
113.37
81.98
77.16 CDCl3
60.55
43.86
41.29
39.49
37.82
36.26
33.24
30.98
26.08
21.29
f1 (ppm)

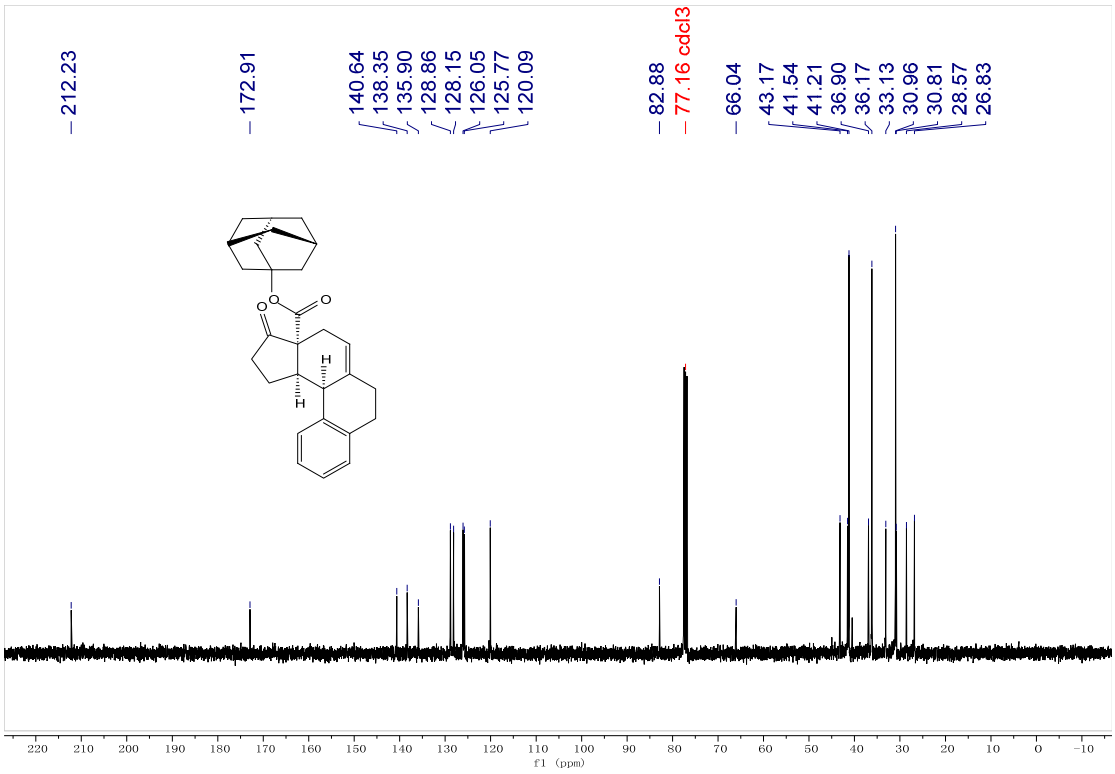
3m


7.26 CDCl3
1.59 HDO
f1 (ppm)

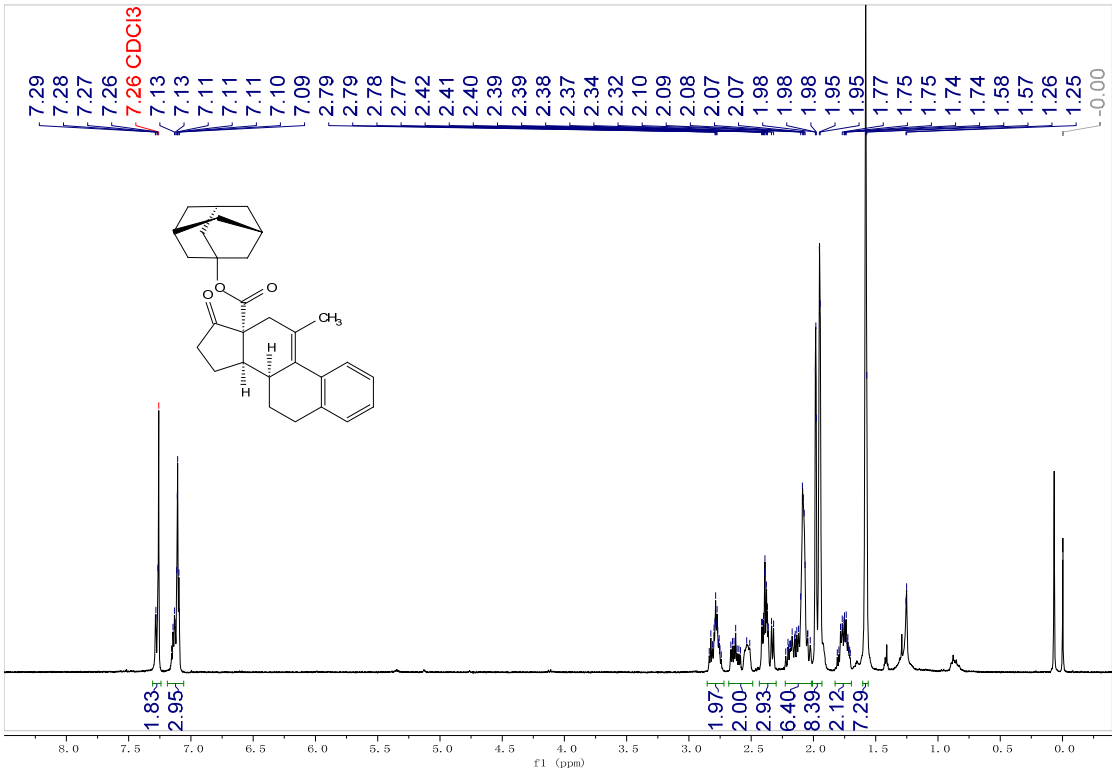

216.19
171.33
146.42
141.59
137.88
128.15
127.77
127.14
126.89
124.24
82.11
77.16 cdcl3
60.93
49.27
41.23
38.87
38.16
36.20
31.49
30.95
27.64
26.35
26.15
21.86
f1 (ppm)

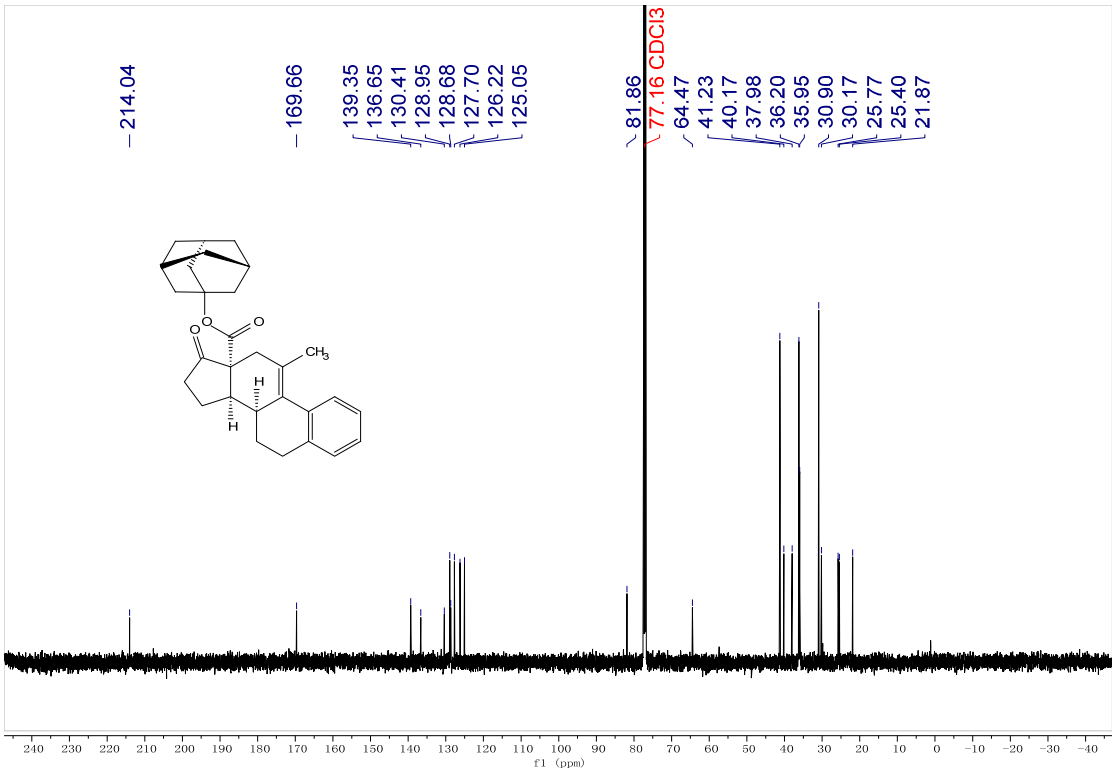
3n


7.33
7.32
7.31
7.26 CDCl3
7.13
7.12
7.11
7.10
7.09
7.09
7.08
7.07
5.62
5.62
5.61
5.60
4.20
2.99
2.68
2.66
2.65
2.64
2.48
2.48
2.47
2.45
2.44
2.43
2.33
2.32
2.31
2.30
2.28
2.18
2.13
2.13
2.11
2.08
2.07
2.05
2.05
2.00
1.96
1.58 HDO
0.00
1.00
3.01
0.96
0.93
0.94
2.16
2.09
2.22
9.11
3.41
7.30
f1 (ppm)

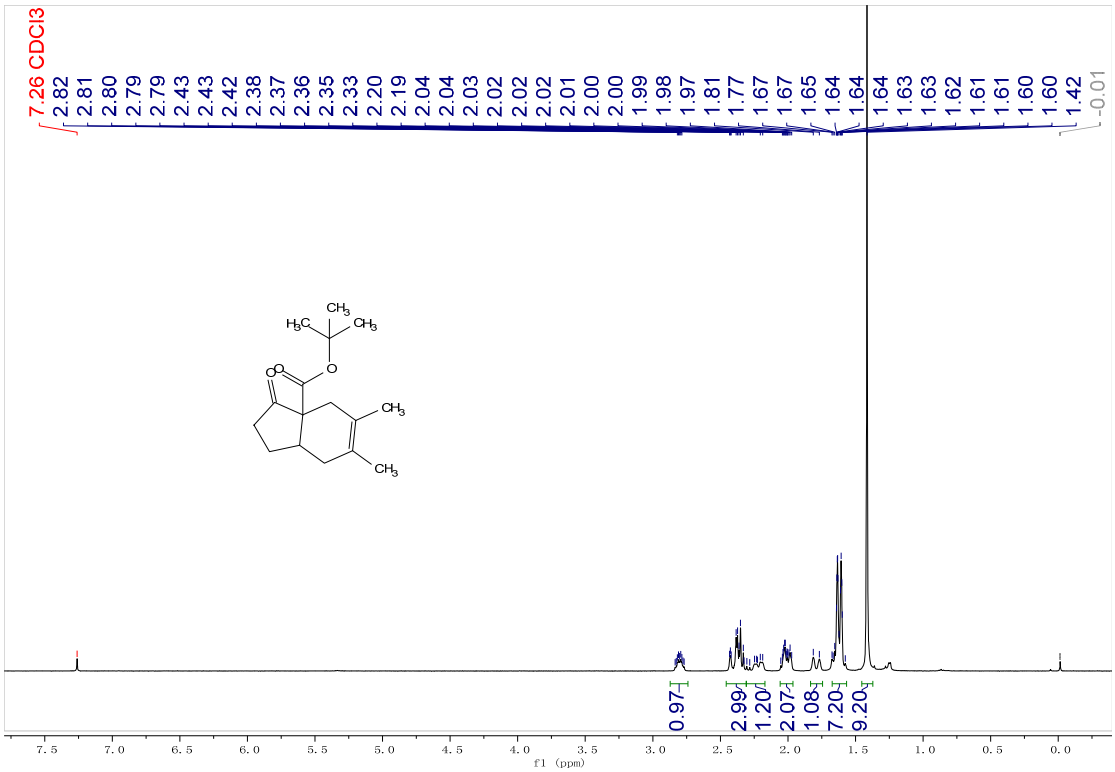

212.23
172.91
140.64
138.35
135.90
128.86
128.15
126.05
125.77
120.09
82.88
77.16 cdcl3
66.04
43.17
41.54
41.21
36.90
36.17
33.13
30.96
30.81
28.57
26.83
f1 (ppm)

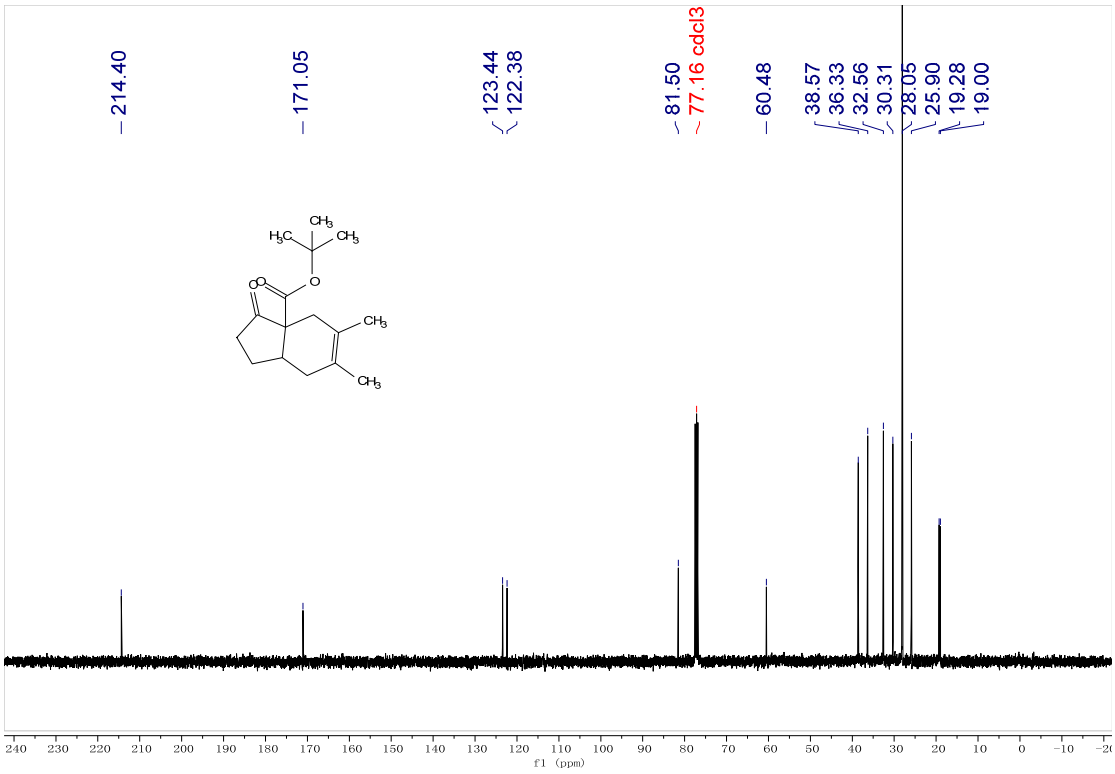
3o


7.29
7.28
7.27
7.26
7.26 CDCl3
7.13
7.13
7.11
7.11
7.11
7.10
7.09
2.79
2.79
2.78
2.77
2.42
2.41
2.40
2.39
2.39
2.38
2.37
2.34
2.32
2.10
2.09
2.08
2.07
2.07
1.98
1.98
1.98
1.95
1.95
1.77
1.75
1.75
1.74
1.74
1.58
1.57
1.26
1.25
-0.00
1.83
2.95
1.97
2.00
2.93
6.40
8.39
2.12
7.29
f1 (ppm)

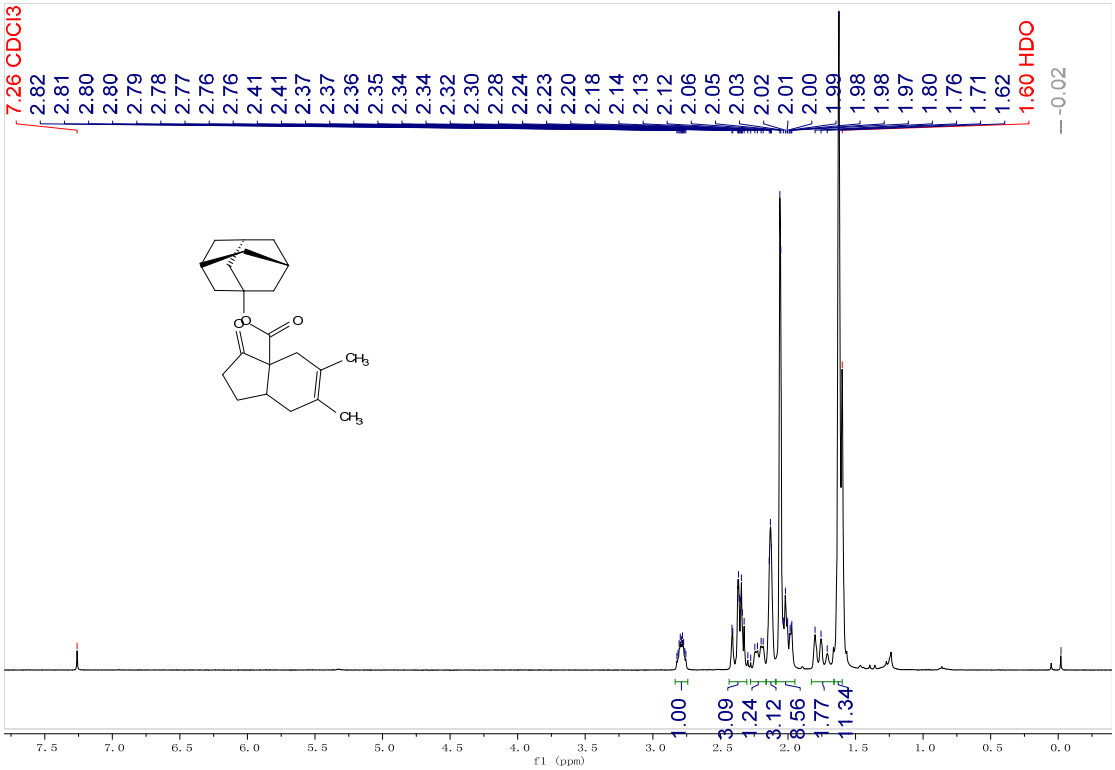

214.04
169.66
139.35
136.65
130.41
128.95
128.68
127.70
126.22
125.05
81.86
77.16 CDCl3
64.47
41.23
40.17
37.98
36.20
35.95
30.90
30.17
25.77
25.40
21.87
f1 (ppm)

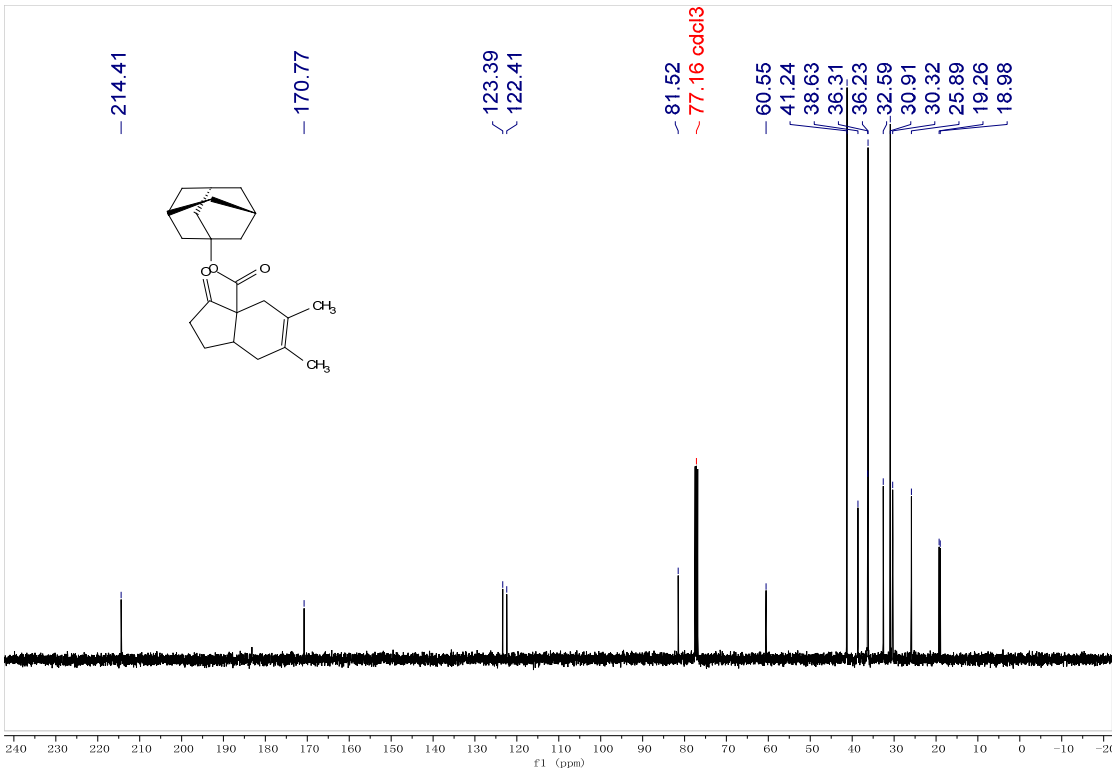
3p


7.26 CDCl3
2.82
2.81
2.80
2.79
2.79
2.43
2.43
2.42
2.38
2.37
2.36
2.35
2.33
2.20
2.19
2.04
2.04
2.03
2.02
2.02
2.02
2.01
2.00
2.00
1.99
1.98
1.97
1.81
1.77
1.67
1.67
1.65
1.64
1.64
1.64
1.63
1.63
1.62
1.61
1.61
1.60
1.60
1.42
-0.01
0.97
2.99
1.20
2.07
1.08
7.20
9.20
f1 (ppm)

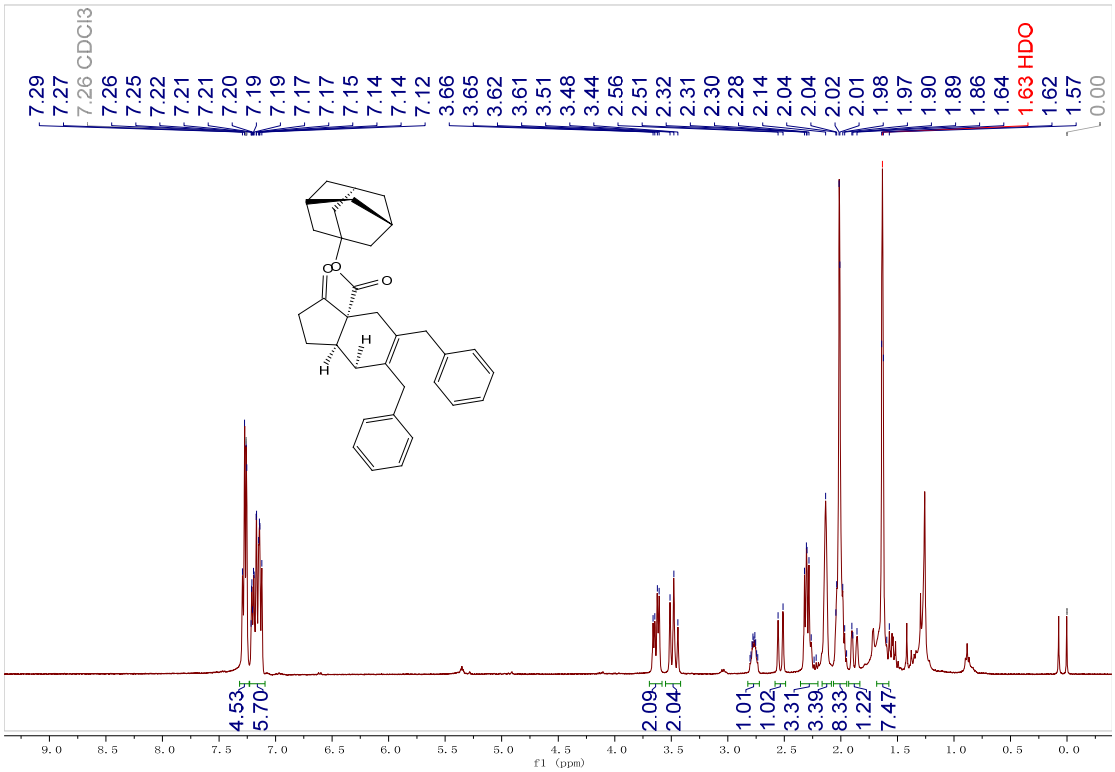

214.40
171.05
123.44
122.38
81.50
77.16 cdcl3
60.48
38.57
36.33
32.56
30.31
28.05
25.90
19.28
19.00
f1 (ppm)

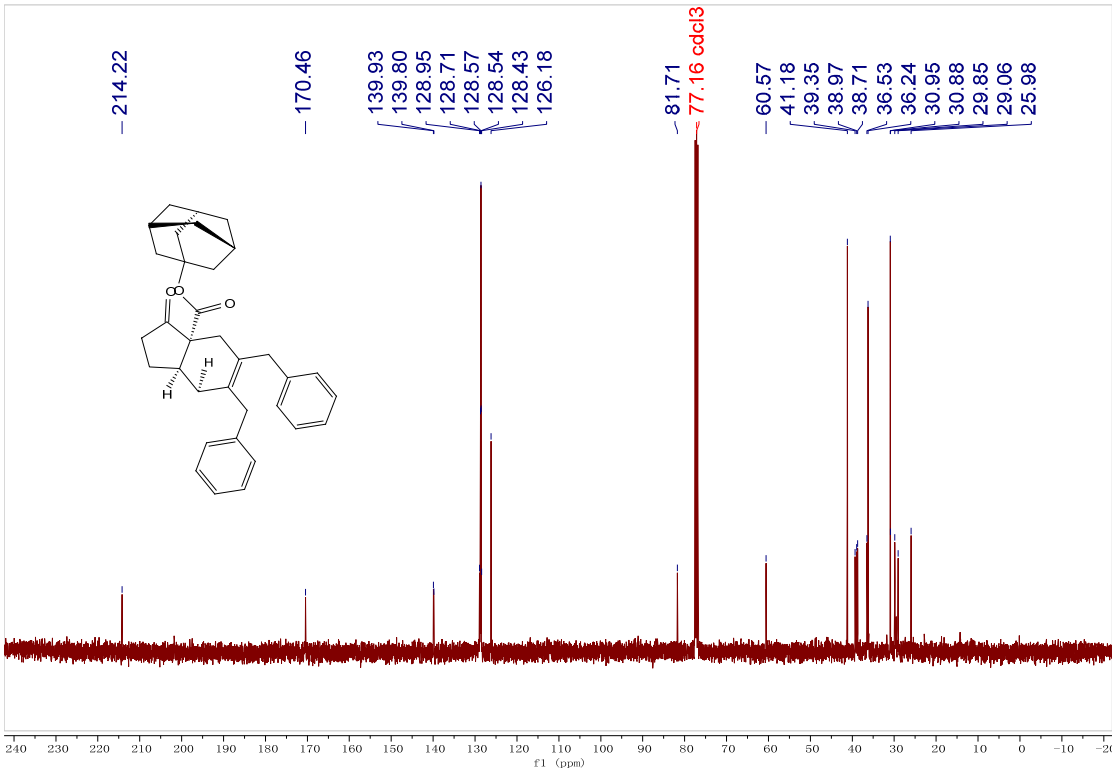
3q


7.26 CDCl3
1.60 HDO
-0.02
1.00
3.09
1.24
3.12
8.56
1.77
11.34
f1 (ppm)

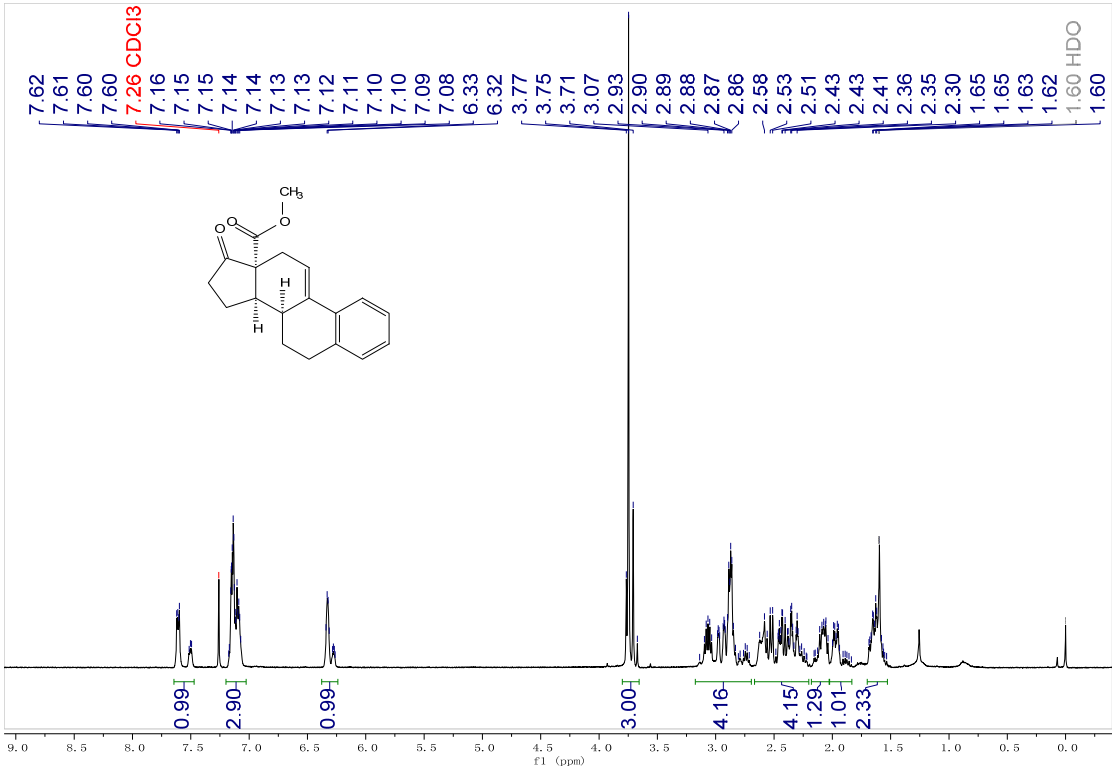

214.41
170.77
123.39
122.41
81.52
77.16 cdcl3
60.55
41.24
38.63
36.31
36.23
32.59
30.91
30.32
25.89
19.26
18.98
f1 (ppm)

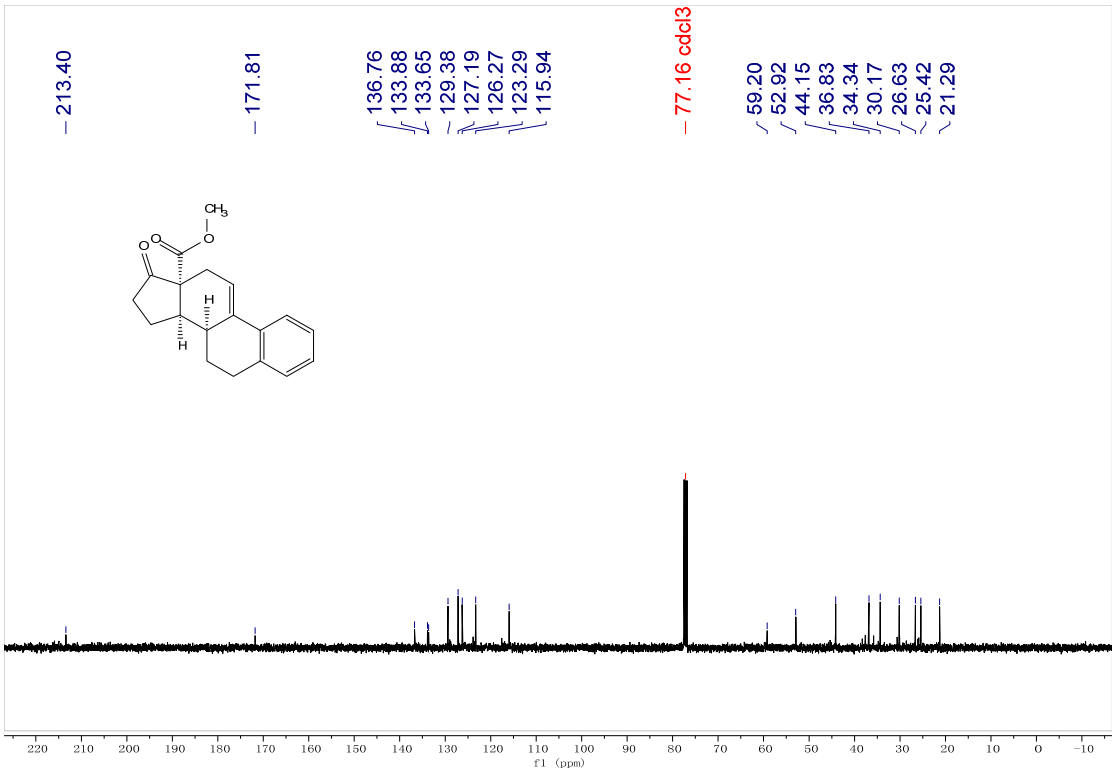
3r


7.29
7.27
7.26 CDCl3
7.26
7.25
7.22
7.21
7.21
7.20
7.19
7.19
7.17
7.17
7.15
7.14
7.14
7.12
3.66
3.65
3.62
3.61
3.51
3.48
3.44
2.56
2.51
2.32
2.31
2.30
2.28
2.14
2.04
2.04
2.02
2.01
1.98
1.97
1.90
1.89
1.86
1.64
1.63 HDO
1.62
1.57
0.00
4.53
5.70
2.09
2.04
1.01
1.02
3.31
3.39
8.33
1.22
7.47
f1 (ppm)

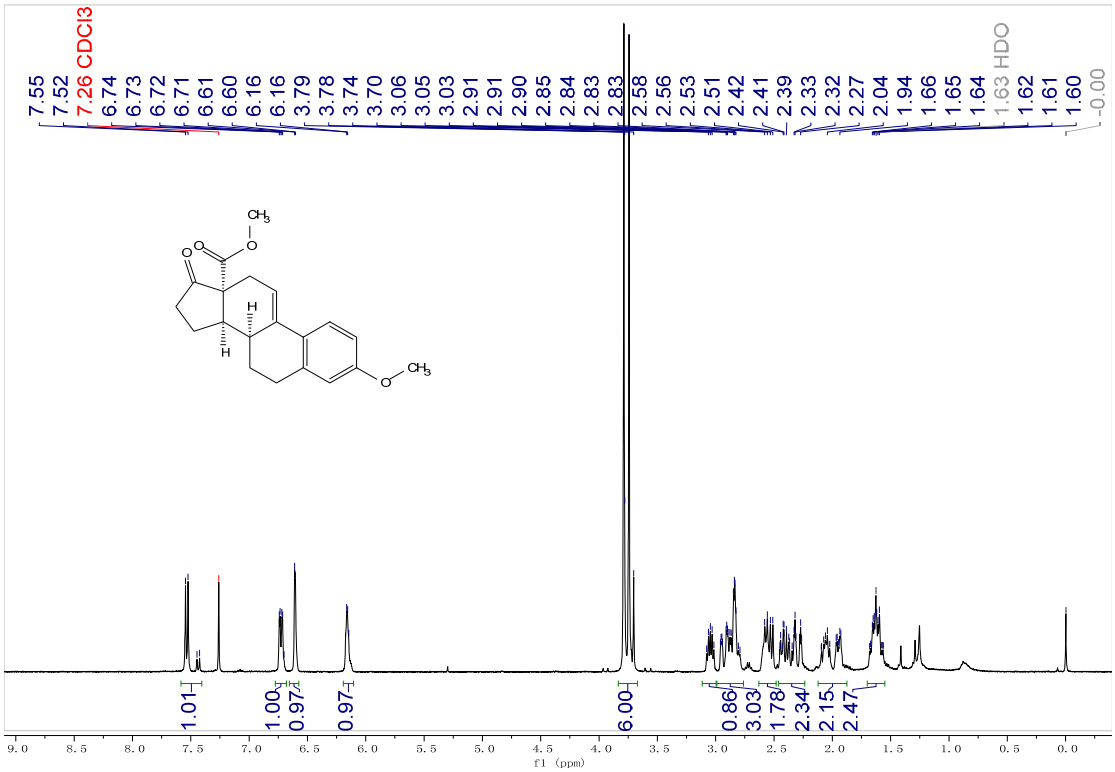

214.22
170.46
139.93
139.80
128.95
128.71
128.57
128.54
128.43
126.18
81.71
77.16 cdcl3
60.57
41.18
39.35
38.97
38.71
36.53
36.24
30.95
30.88
29.85
29.06
25.98
f1 (ppm)

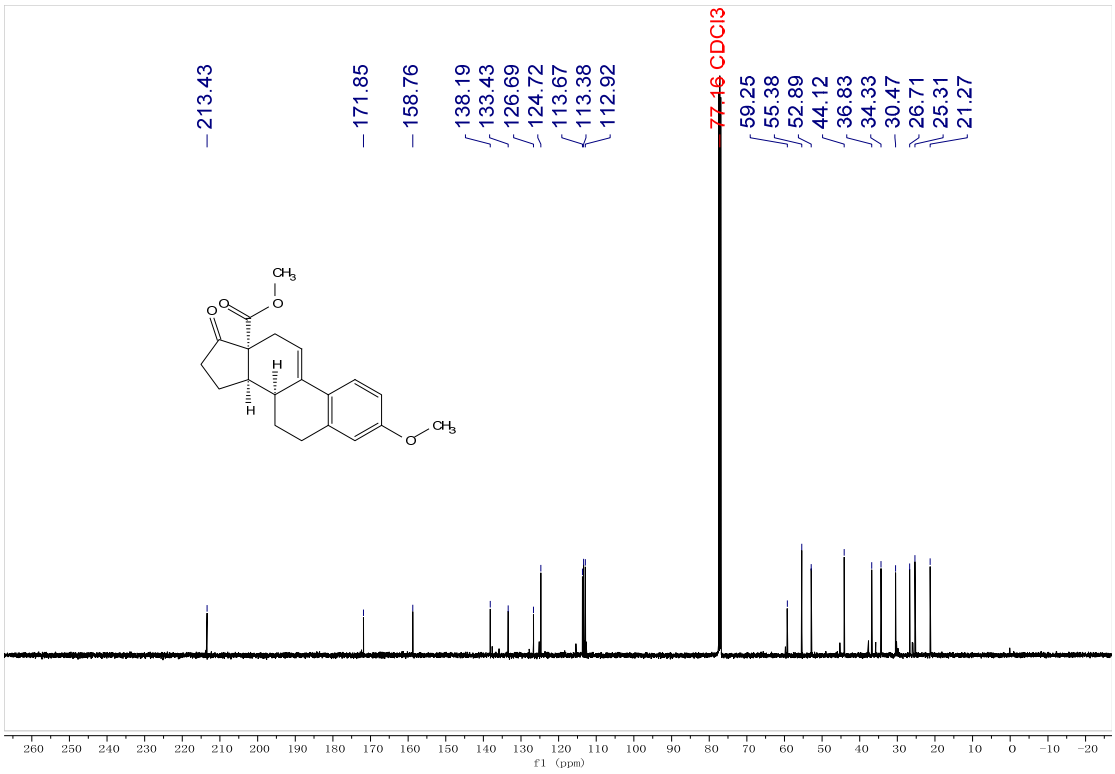
3s


7.62
7.61
7.60
7.60
7.26 CDCl3
7.16
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.11
7.10
7.10
7.09
7.08
6.33
6.32
3.77
3.75
3.71
3.07
2.93
2.90
2.89
2.88
2.87
2.86
2.58
2.53
2.51
2.43
2.43
2.41
2.36
2.35
2.30
1.65
1.65
1.63
1.62
1.60 HDO
1.60
0.99
2.90
0.99
3.00
4.16
4.15
1.29
1.01
2.33
f1 (ppm)

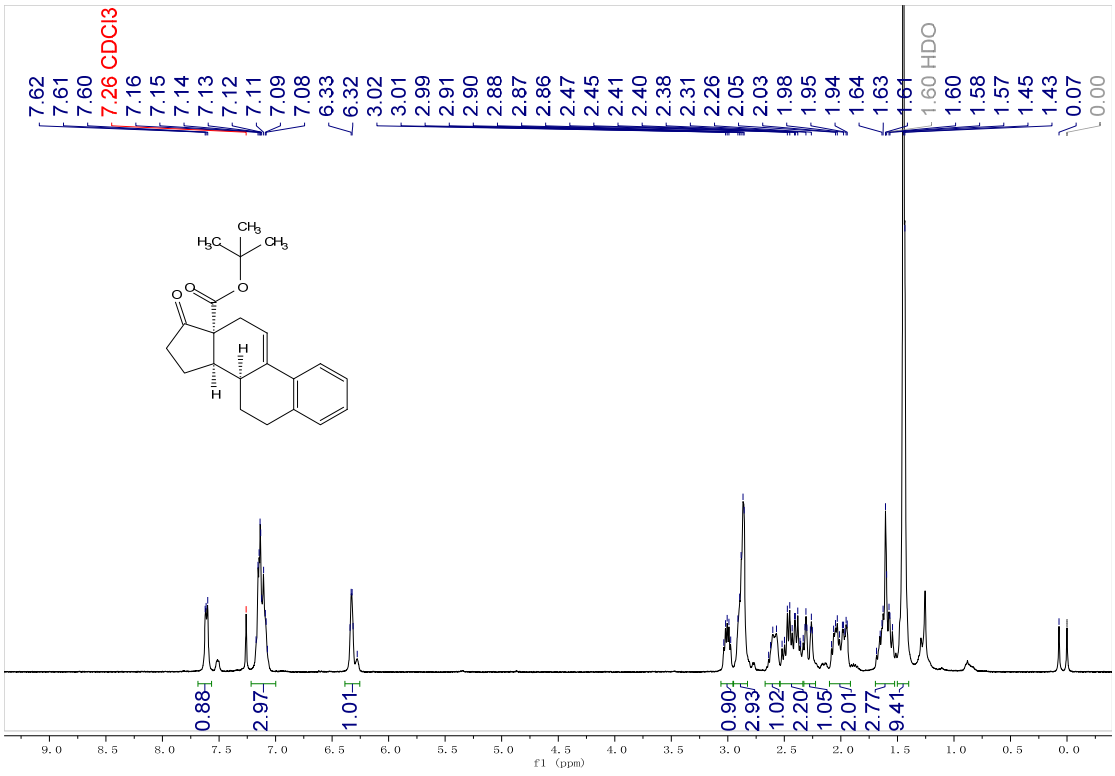

213.40
171.81
136.76
133.88
133.65
129.38
127.19
126.27
123.29
115.94
77.16 cdcl3
59.20
52.92
44.15
36.83
34.34
30.17
26.63
25.42
21.29
f1 (ppm)

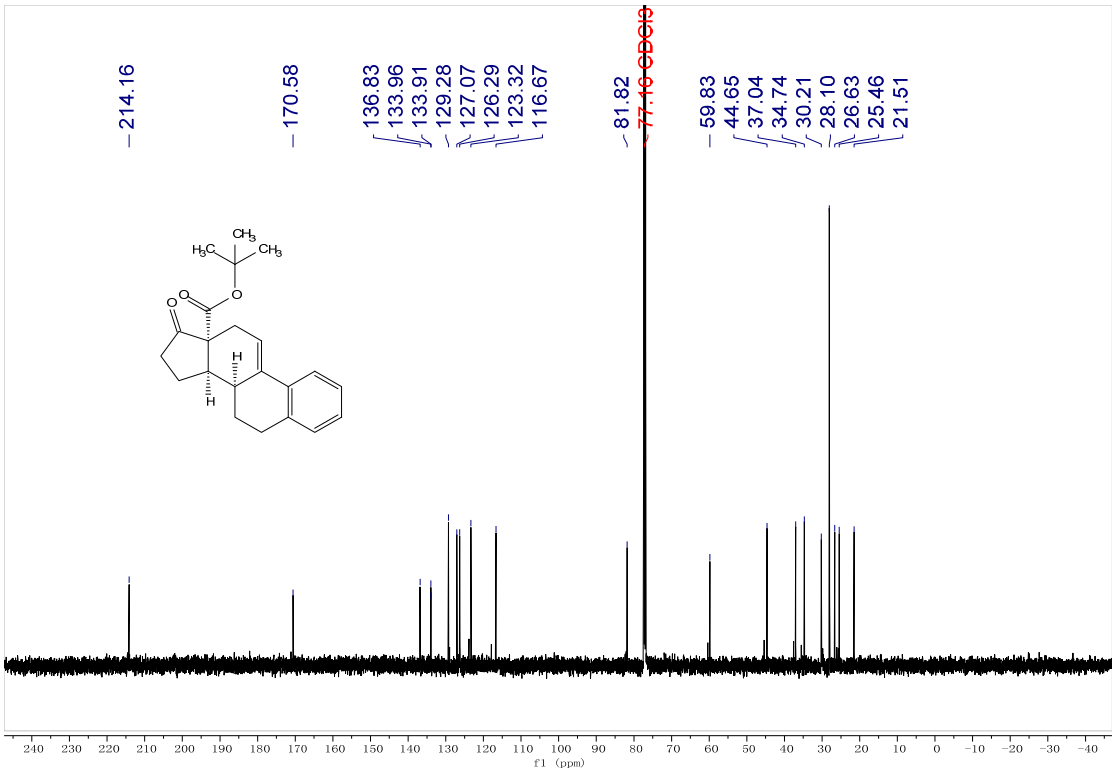
3t


7.55
7.52
7.26 CDCl3
6.74
6.73
6.72
6.71
6.61
6.60
6.16
6.16
3.79
3.78
3.74
3.70
3.06
3.05
3.03
2.91
2.91
2.90
2.85
2.84
2.83
2.83
2.58
2.56
2.53
2.51
2.42
2.41
2.39
2.33
2.32
2.27
2.04
1.94
1.66
1.65
1.64
1.63 HDO
1.62
1.61
1.60
-0.00
1.01
1.00
0.97
0.97
6.00
0.86
3.03
1.78
2.34
2.15
2.47
f1 (ppm)

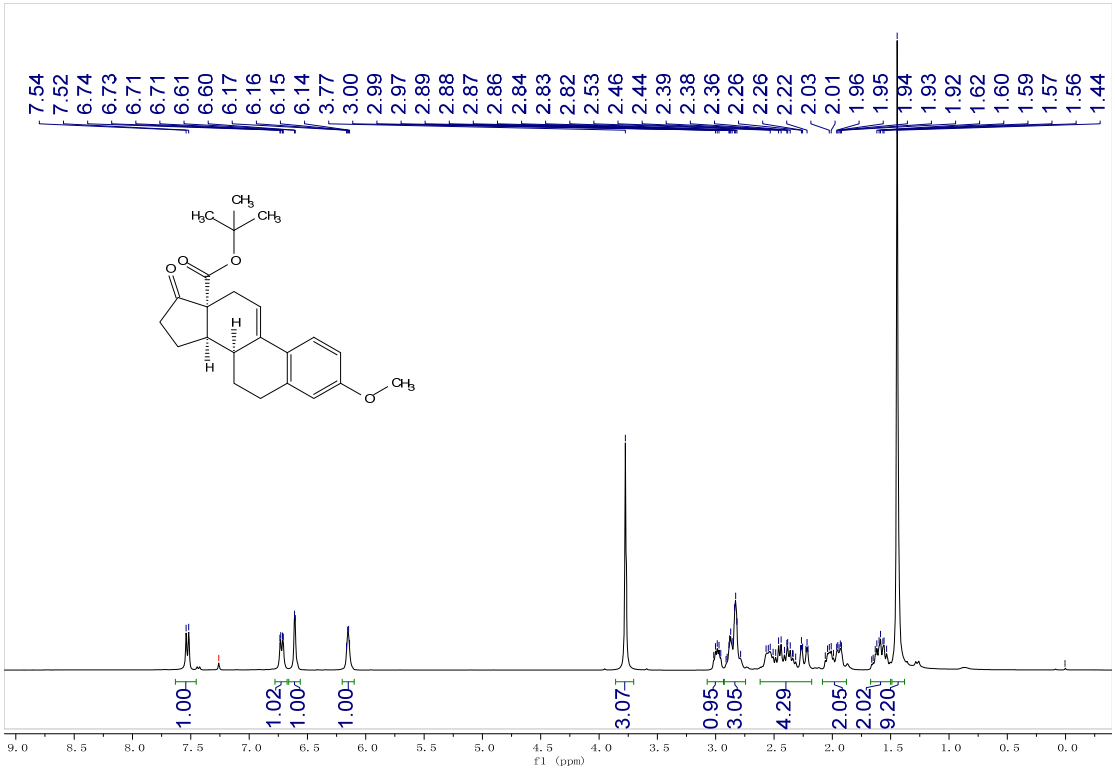

213.43
171.85
158.76
138.19
133.43
126.69
124.72
113.67
113.38
112.92
77.16 CDCl3
59.25
55.38
52.89
44.12
36.83
34.33
30.47
26.71
25.31
21.27
f1 (ppm)

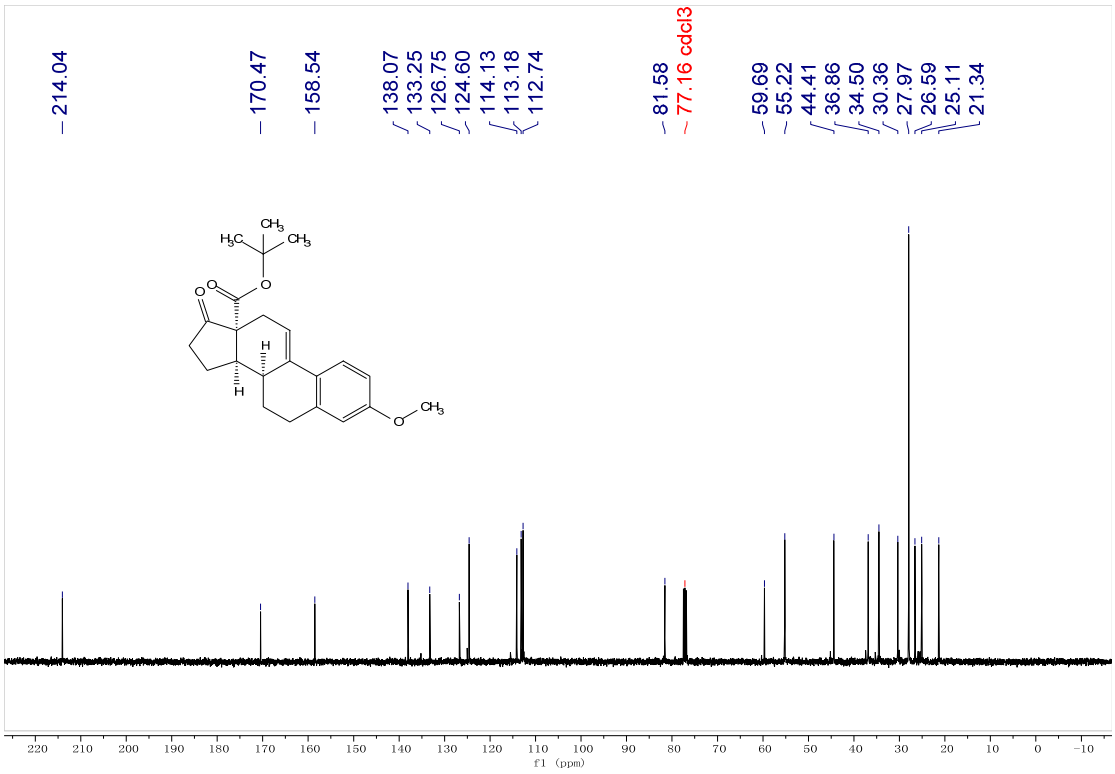
3u


7.62
7.61
7.60
7.26 CDCl3
7.16
7.15
7.14
7.13
7.12
7.11
7.09
7.08
6.33
6.32
3.02
3.01
2.99
2.91
2.90
2.88
2.87
2.86
2.47
2.45
2.41
2.40
2.38
2.31
2.26
2.05
2.03
1.98
1.95
1.94
1.64
1.63
1.61
1.60 HDO
1.60
1.58
1.57
1.45
1.43
0.07
0.00
0.88
2.97
1.01
0.90
2.93
1.02
2.20
1.05
2.01
2.77
9.41
f1 (ppm)


214.16
170.58
136.83
133.96
133.91
129.28
127.07
126.29
123.32
116.67
81.82
77.16 CDCl3
59.83
44.65
37.04
34.74
30.21
28.10
26.63
25.46
21.51
f1 (ppm)

3v


7.54
7.52
6.74
6.73
6.71
6.71
6.61
6.60
6.17
6.16
6.15
6.14
3.77
3.00
2.99
2.97
2.89
2.88
2.87
2.86
2.84
2.83
2.82
2.53
2.46
2.44
2.39
2.38
2.36
2.26
2.26
2.22
2.03
2.01
1.96
1.95
1.94
1.93
1.92
1.62
1.60
1.59
1.57
1.56
1.44
1.00
1.02
1.00
1.00
3.07
0.95
3.05
4.29
2.05
2.02
9.20
f1 (ppm)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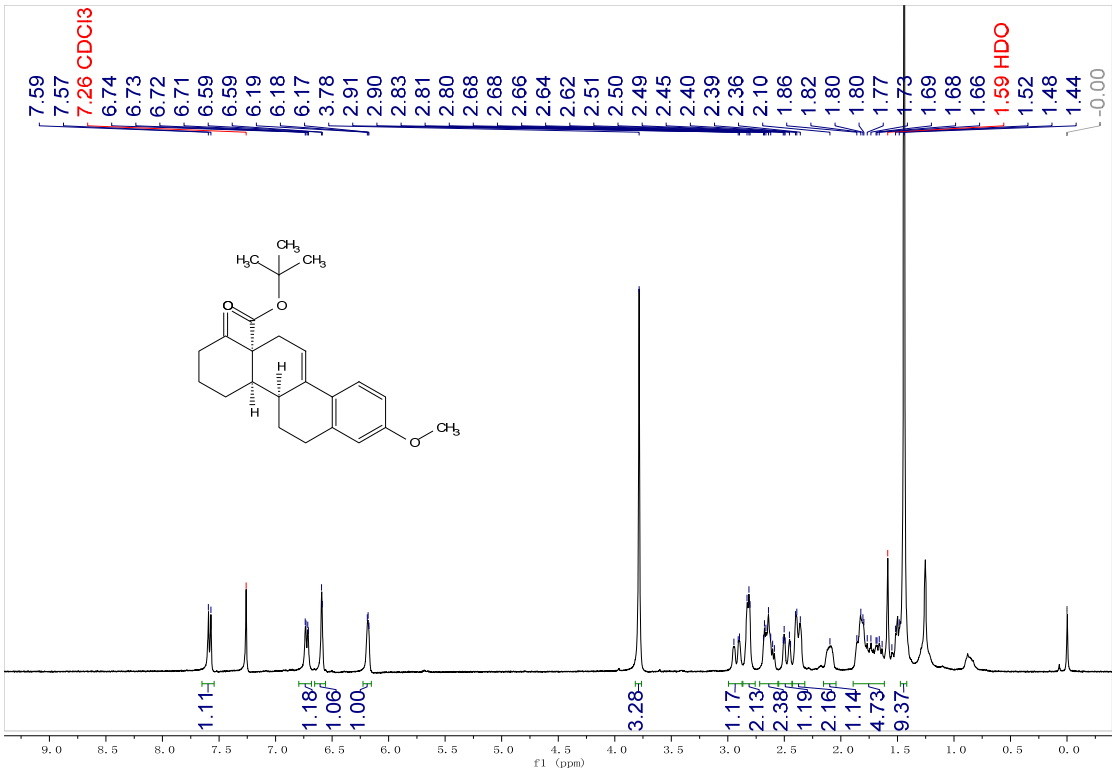
170.47
158.54
138.07
133.25
126.75
124.60
114.13
113.18
112.74
81.58
77.16 cdcl3
59.69
55.22
44.41
36.86
34.50
30.36
27.97
26.59
25.11
21.34
f1 (ppm)

3w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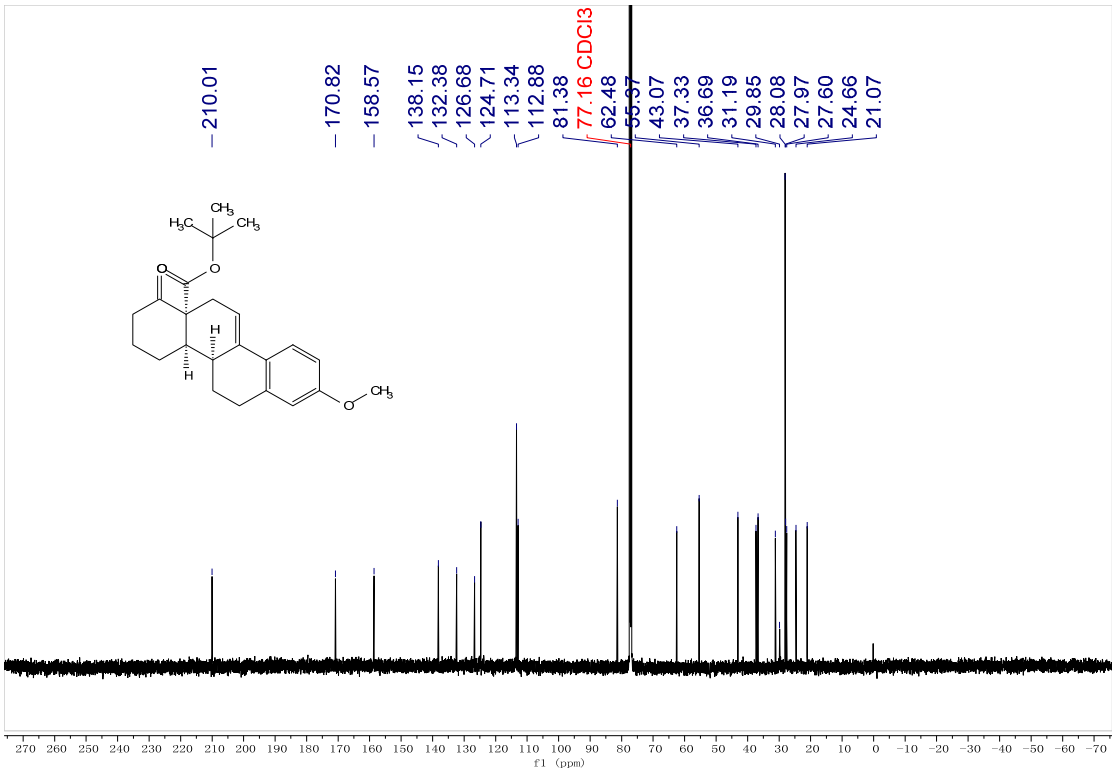
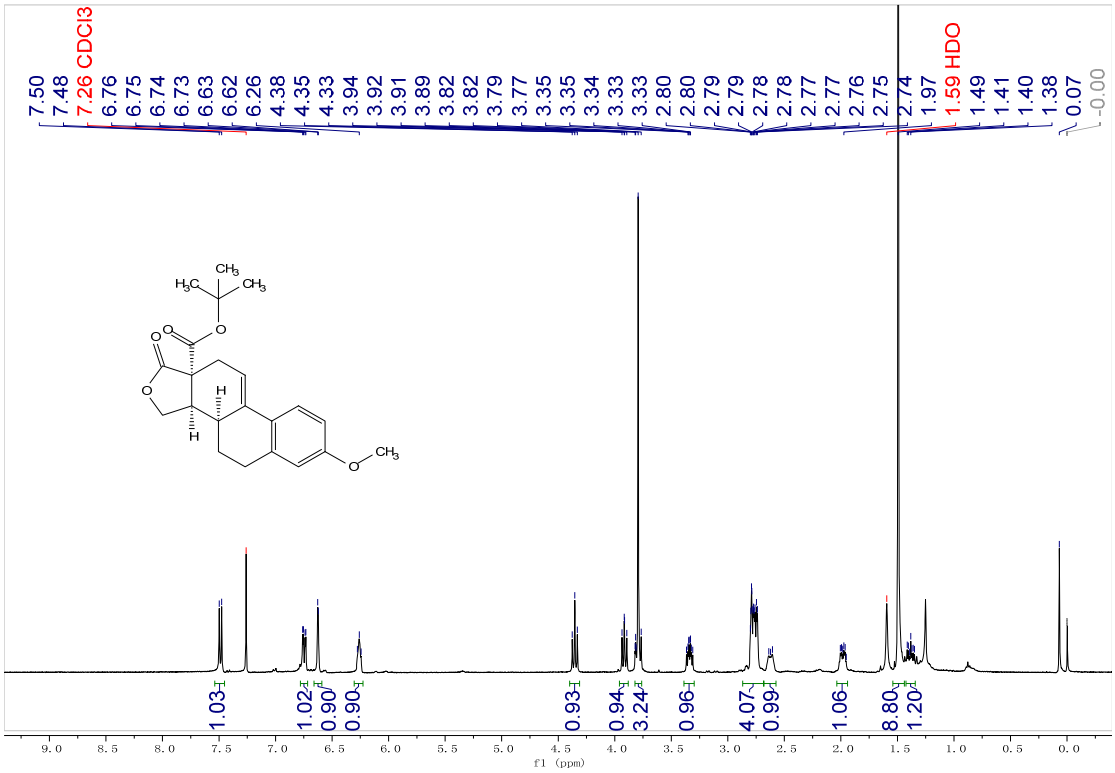
7.57
7.26 CDCl3
6.74
6.73
6.72
6.71
6.59
6.59
6.19
6.18
6.17
3.78
2.91
2.90
2.83
2.81
2.80
2.68
2.68
2.66
2.64
2.62
2.51
2.50
2.49
2.45
2.40
2.39
2.36
2.10
1.86
1.82
1.80
1.80
1.77
1.73
1.69
1.68
1.66
1.59 HDO
1.52
1.48
1.44
0.00
1.11
1.18
1.06
1.00
3.28
1.17
2.13
2.38
1.19
2.16
1.14
4.73
9.37
f1 (ppm)


210.01
170.82
158.57
138.15
132.38
126.68
124.71
113.34
112.88
81.38
77.16 CDCl3
62.48
55.97
43.07
37.33
36.69
31.19
29.85
28.08
27.97
27.60
24.66
21.07
f1 (ppm)

3x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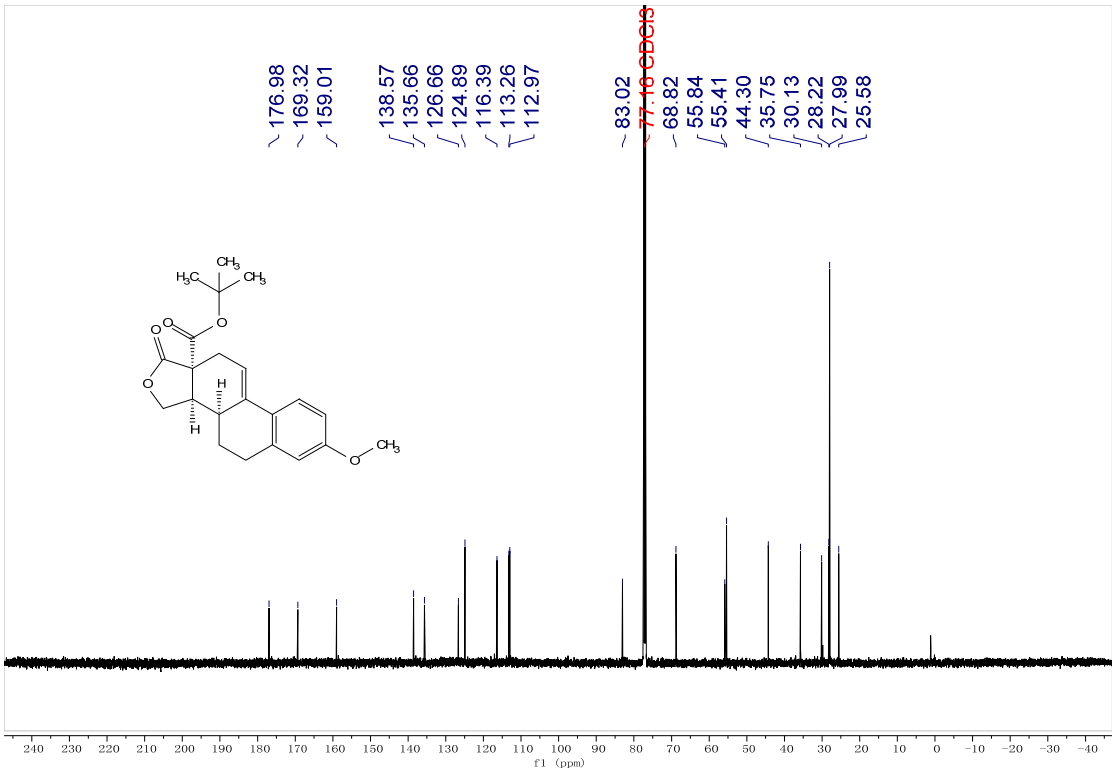
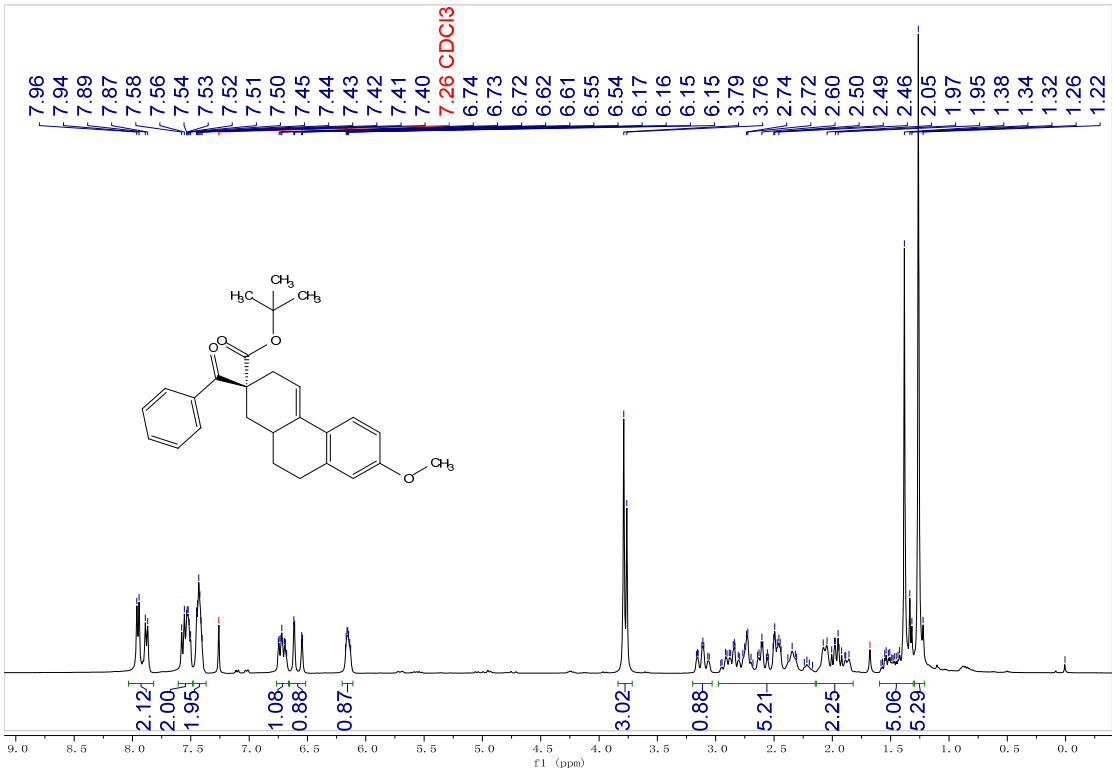
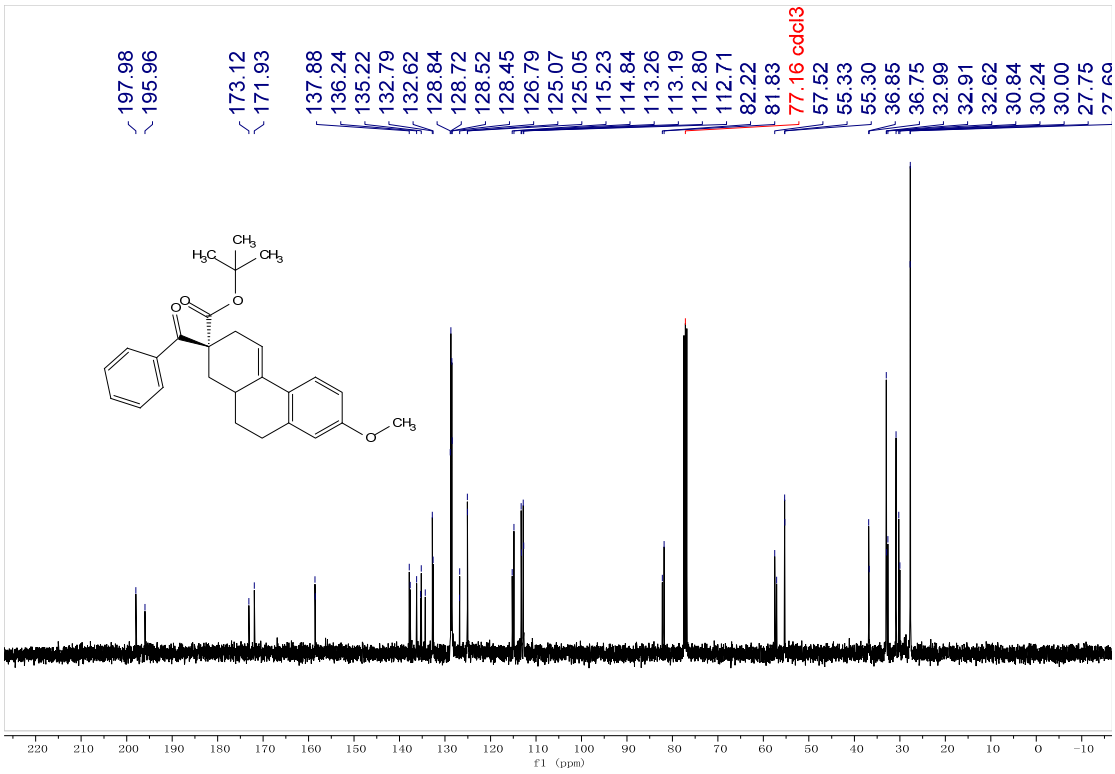
7.48
7.26 CDCl3
6.76
6.75
6.74
6.73
6.63
6.62
6.26
4.38
4.35
4.33
3.94
3.92
3.91
3.89
3.82
3.82
3.79
3.77
3.35
3.35
3.34
3.33
3.33
2.80
2.80
2.79
2.79
2.78
2.78
2.77
2.77
2.76
2.75
2.74
1.97
1.59 HDO
1.49
1.41
1.40
1.38
0.07
-0.00
1.03
1.02
0.90
0.90
0.93
0.94
3.24
0.96
4.07
0.99
1.06
8.80
1.20
f1 (ppm)

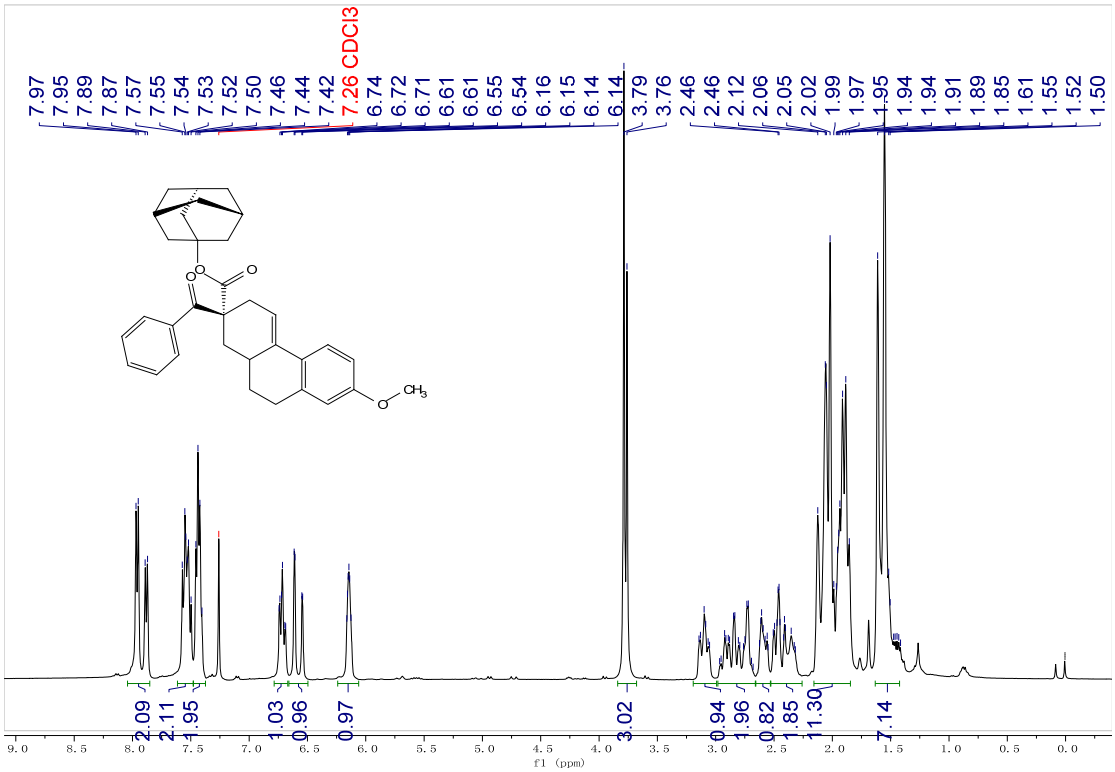

176.98
169.32
159.01
138.57
135.66
126.66
124.89
116.39
113.26
112.97
83.02
77.16 CDCl3
68.82
55.84
55.41
44.30
35.75
30.13
28.22
27.99
25.58
f1 (ppm)

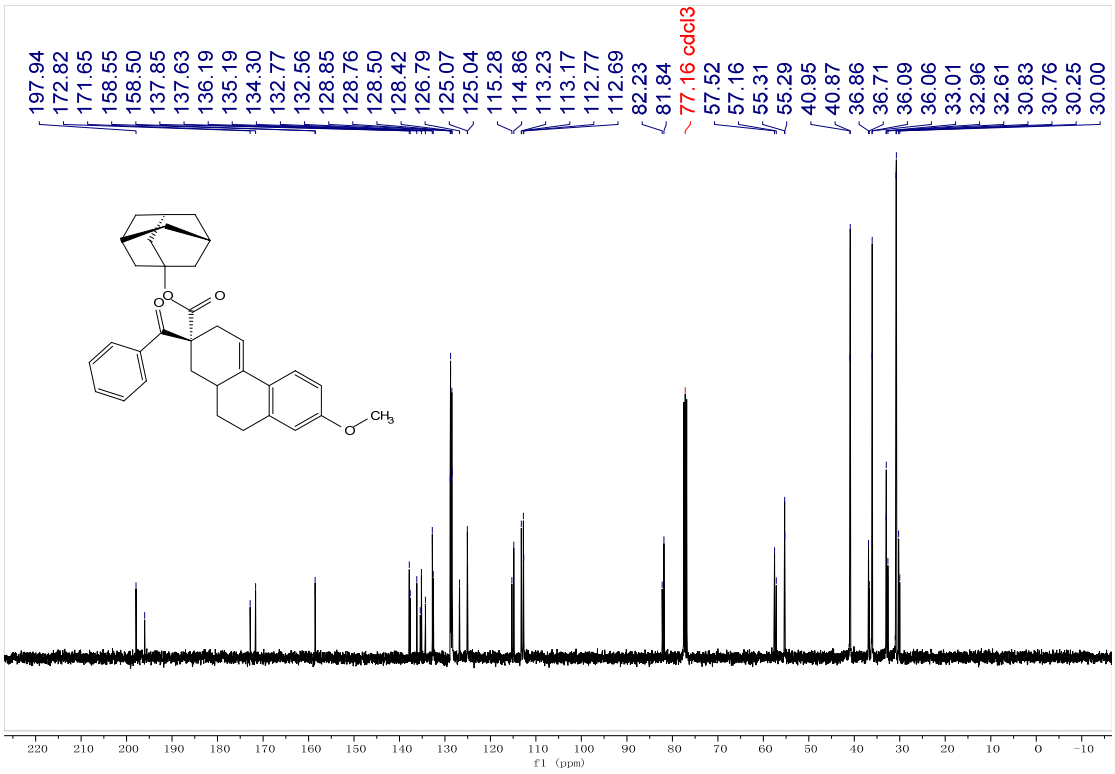
3y


7.96
7.94
7.89
7.87
7.58
7.56
7.54
7.53
7.52
7.51
7.50
7.45
7.44
7.43
7.42
7.41
7.40
7.26 CDCl3
6.74
6.73
6.72
6.62
6.61
6.55
6.54
6.17
6.16
6.15
6.15
3.79
3.76
2.74
2.72
2.60
2.50
2.49
2.46
2.05
1.97
1.95
1.38
1.34
1.32
1.26
1.22
2.12
2.00
1.95
1.08
0.88
0.87
3.02
0.88
5.21
2.25
5.06
5.29
f1 (ppm)


197.98
195.96
173.12
171.93
137.88
136.24
135.22
132.79
132.62
128.84
128.72
128.52
128.45
126.79
125.07
125.05
115.23
114.84
113.26
113.19
112.80
112.71
82.22
81.83
77.16 cdcl3
57.52
55.33
55.30
36.85
36.75
32.99
32.91
32.62
30.84
30.24
30.00
27.75
f1 (ppm)

3z


7.97
7.95
7.89
7.87
7.57
7.55
7.54
7.53
7.52
7.50
7.46
7.44
7.42
7.26 CDCl3
6.74
6.72
6.71
6.61
6.61
6.55
6.54
6.16
6.15
6.14
6.14
3.79
3.76
2.46
2.46
2.12
2.06
2.05
2.02
1.99
1.97
1.95
1.94
1.94
1.91
1.89
1.85
1.61
1.55
1.52
1.50
2.09
2.11
1.95
1.03
0.96
0.97
3.02
0.94
1.96
0.82
1.85
11.30
7.14
f1 (ppm)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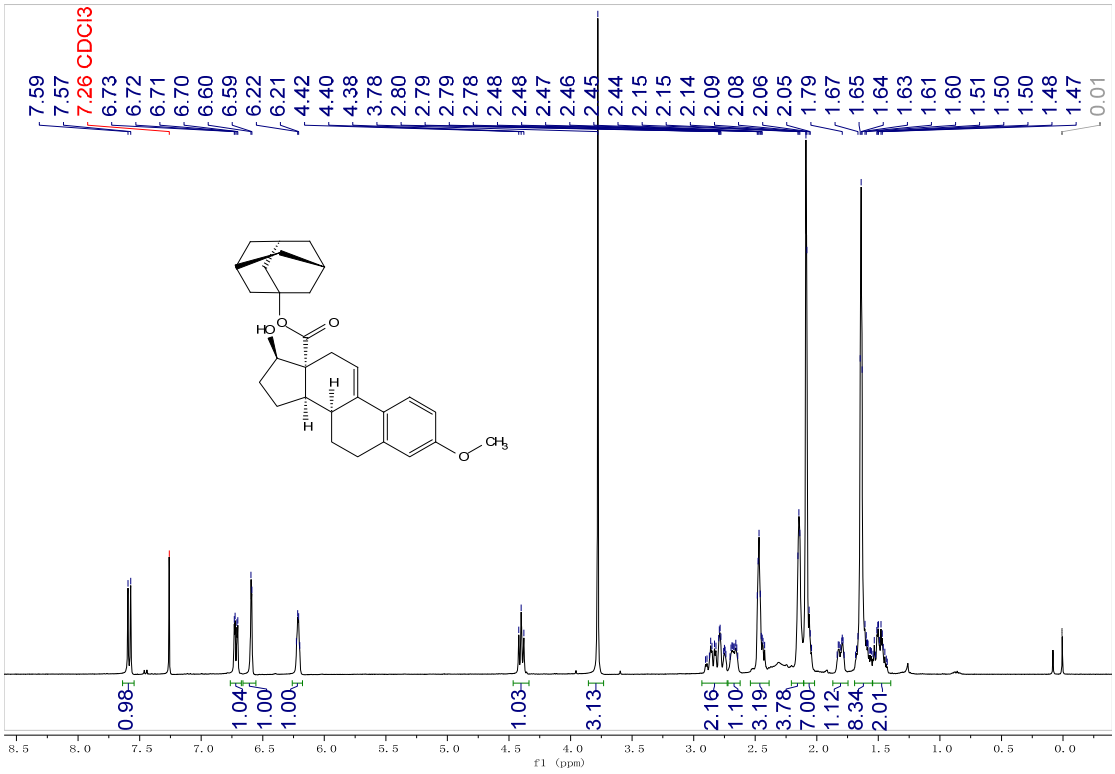
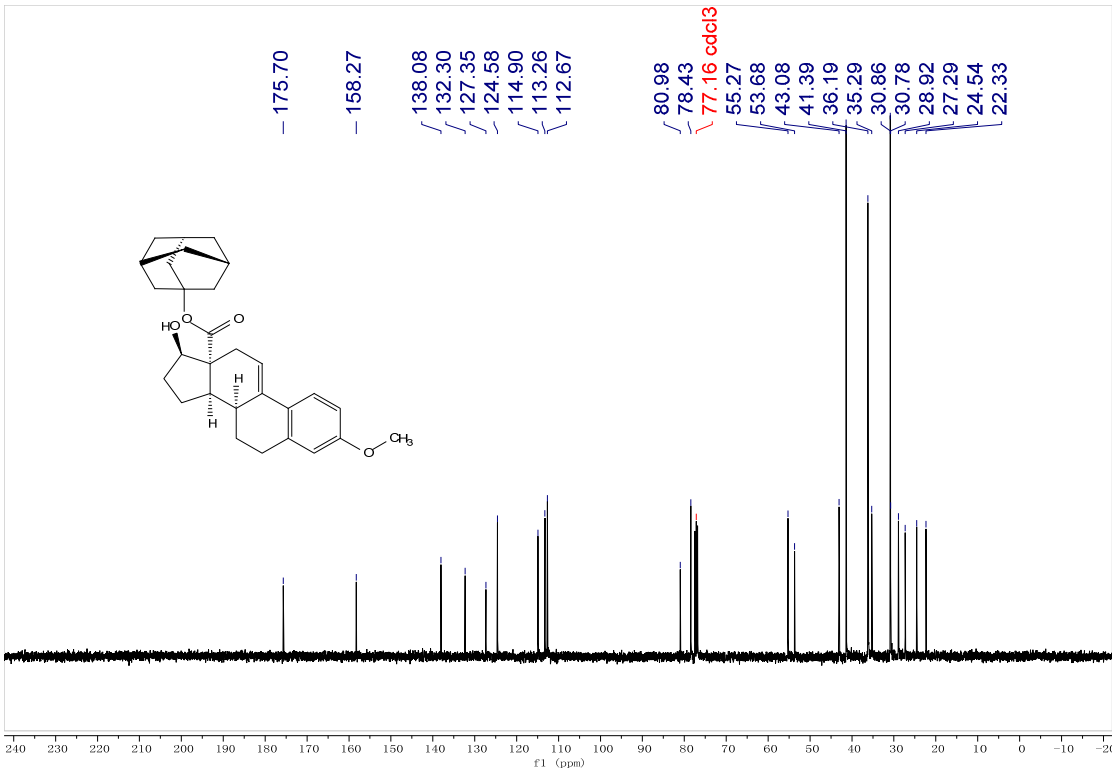
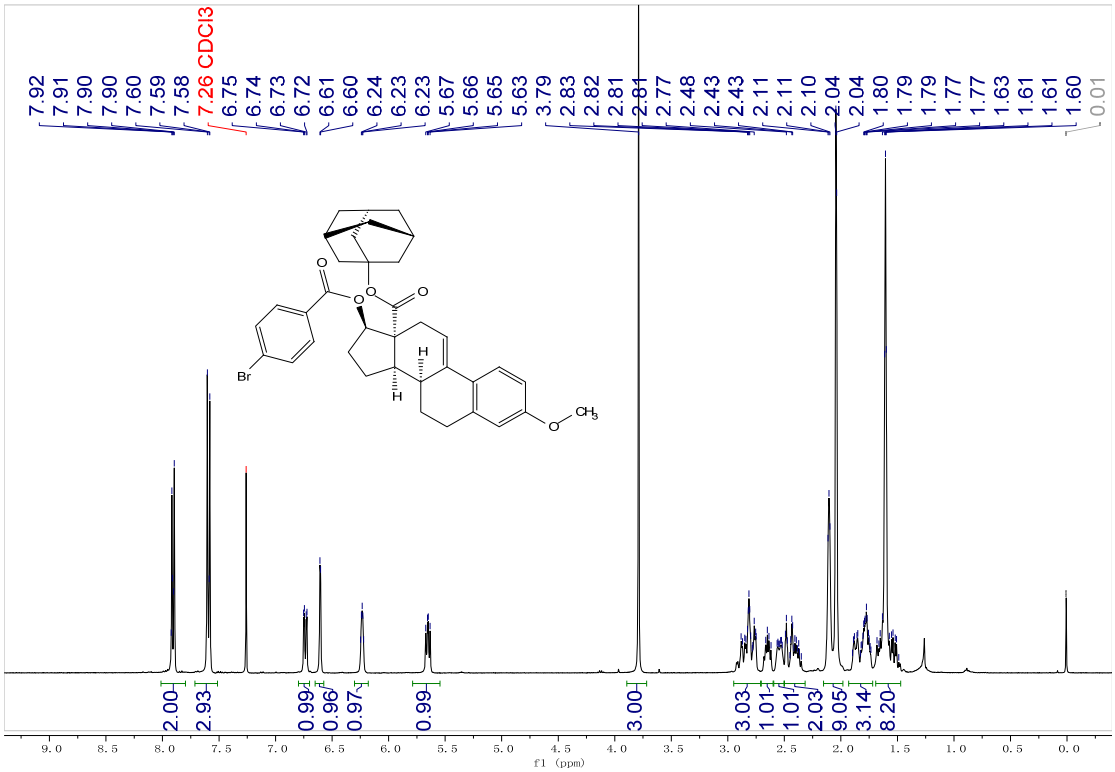
171.65
158.55
158.50
137.85
137.63
136.19
135.19
134.30
132.77
132.56
128.85
128.76
128.50
128.42
126.79
125.07
125.04
115.28
114.86
113.23
113.17
112.77
112.69
82.23
81.84
77.16 cdcl3
57.52
57.16
55.31
55.29
40.95
40.87
36.86
36.71
36.09
36.06
33.01
32.96
32.61
30.83
30.76
30.25
30.00
O
O
O
O
CH3
f1 (ppm)

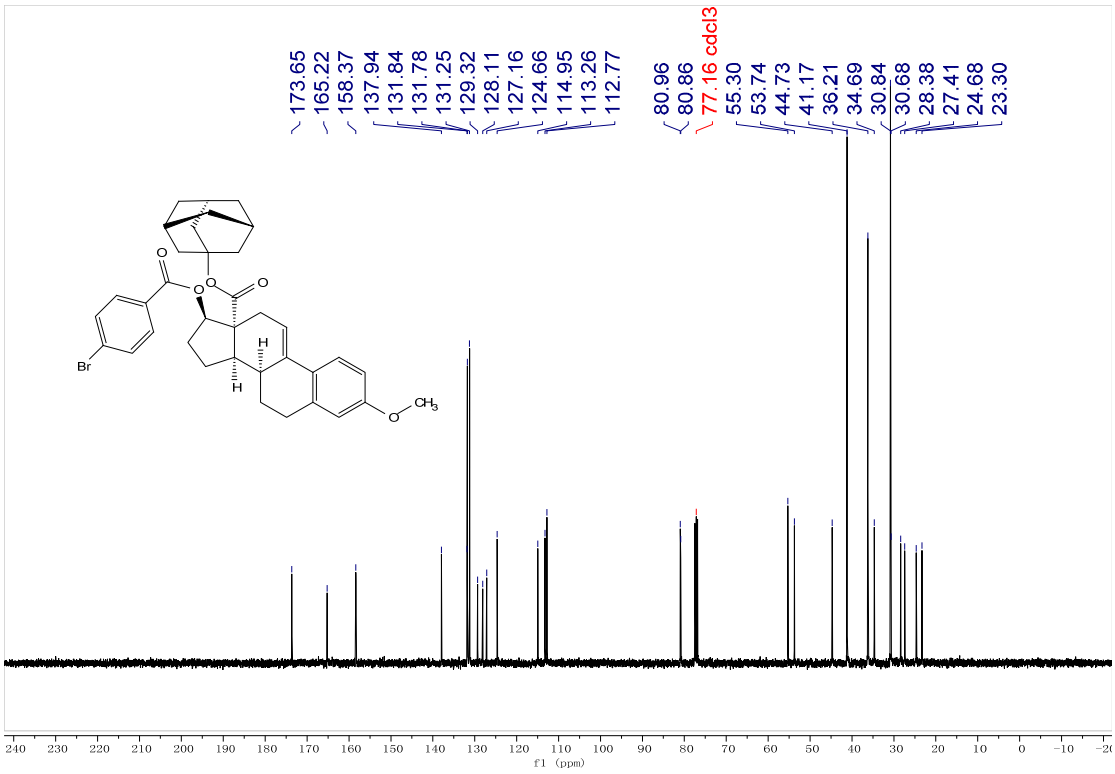
7


7.59
7.57
7.26 CDCl3
6.73
6.72
6.71
6.70
6.60
6.59
6.22
6.21
4.42
4.40
4.38
3.78
2.80
2.79
2.79
2.78
2.48
2.48
2.47
2.46
2.45
2.44
2.15
2.15
2.14
2.09
2.08
2.06
2.05
1.79
1.67
1.65
1.64
1.63
1.61
1.60
1.51
1.50
1.50
1.48
1.47
0.01
HO
O
O
H
H
O
CH3
0.98
1.04
1.00
1.00
1.03
3.13
2.16
1.10
3.19
3.78
7.00
1.12
8.34
2.01
f1 (ppm)


175.70
158.27
138.08
132.30
127.35
124.58
114.90
113.26
112.67
80.98
78.43
77.16 cdcl3
55.27
53.68
43.08
41.39
36.19
35.29
30.86
30.78
28.92
27.29
24.54
22.33
HO
O
O
H
H
O
CH3
f1 (ppm)

8


7.92
7.91
7.90
7.90
7.60
7.59
7.58
7.26 CDCl3
6.75
6.74
6.73
6.72
6.61
6.60
6.24
6.23
6.23
5.67
5.66
5.65
5.63
3.79
2.83
2.82
2.81
2.81
2.77
2.48
2.43
2.43
2.11
2.11
2.10
2.04
2.04
1.80
1.79
1.79
1.77
1.77
1.63
1.61
1.61
1.60
0.01
Br
O
O
O
O
H
H
O
CH3
2.00
2.93
0.99
0.96
0.97
0.99
3.00
3.03
1.01
1.01
2.03
9.05
3.14
8.20
f1 (ppm)


173.65
165.22
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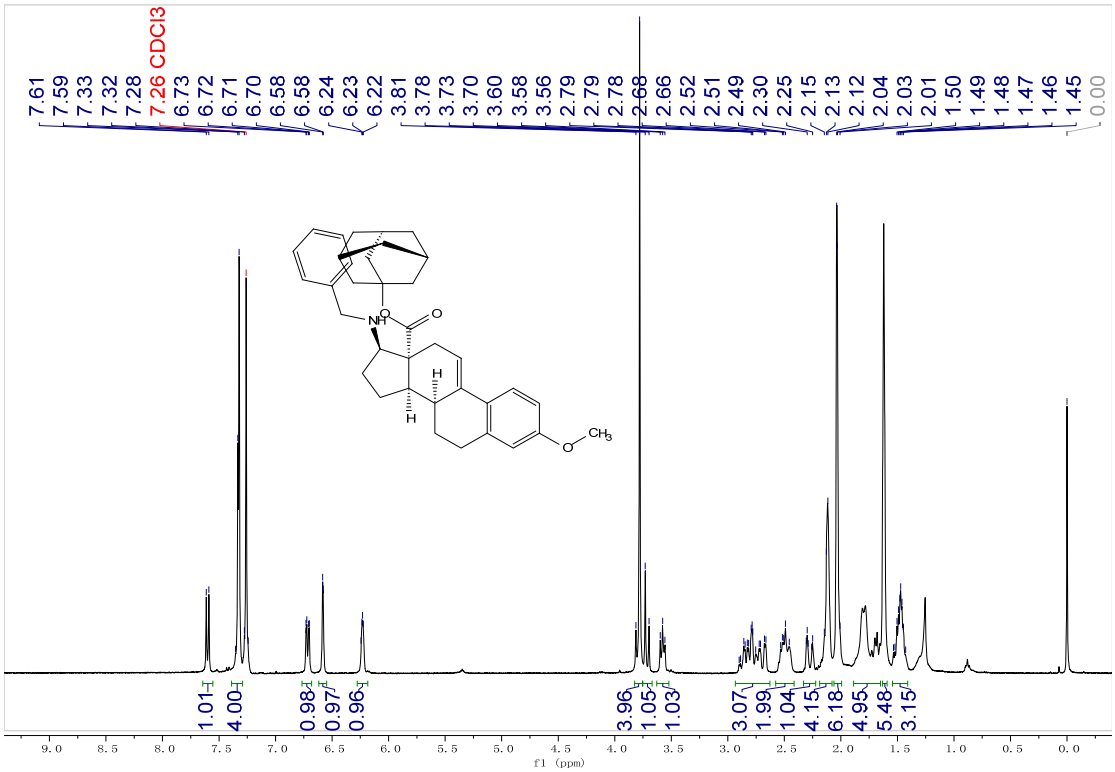
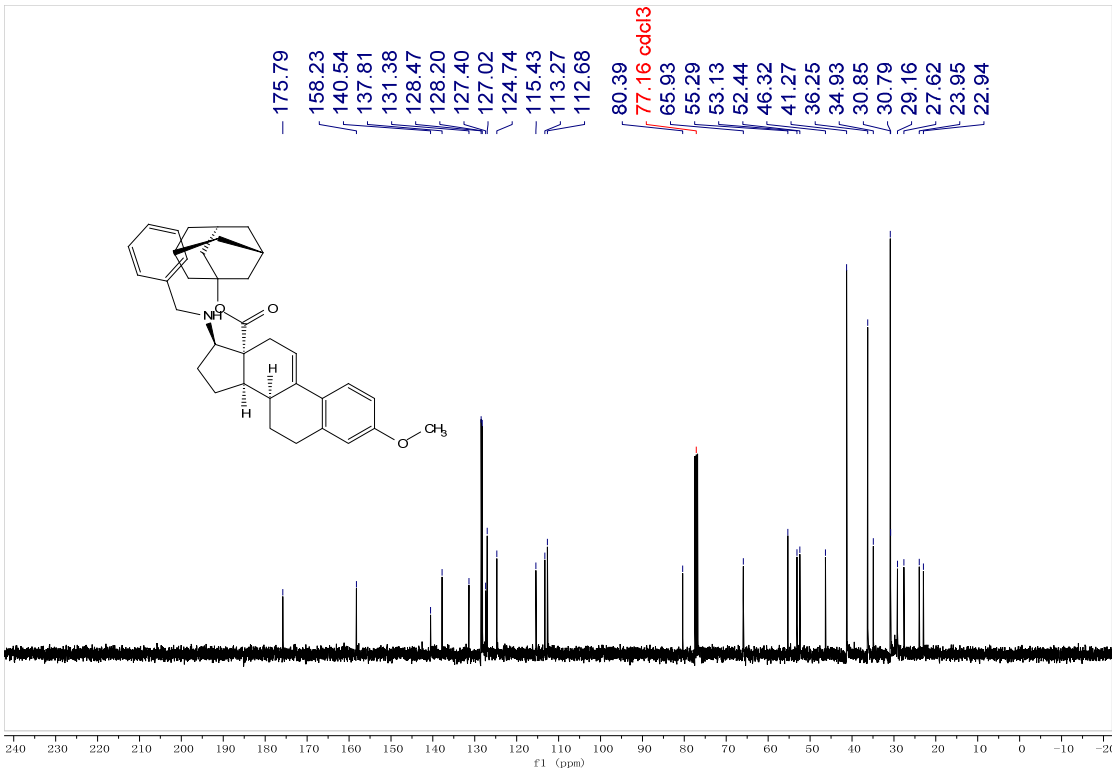
137.94
131.84
131.78
131.25
129.32
128.11
127.16
124.66
114.95
113.26
112.77
80.96
80.86
77.16 cdcl3
55.30
53.74
44.73
41.17
36.21
34.69
30.84
30.68
28.38
27.41
24.68
23.30
Br
O
H
H
CH3
f1 (ppm)

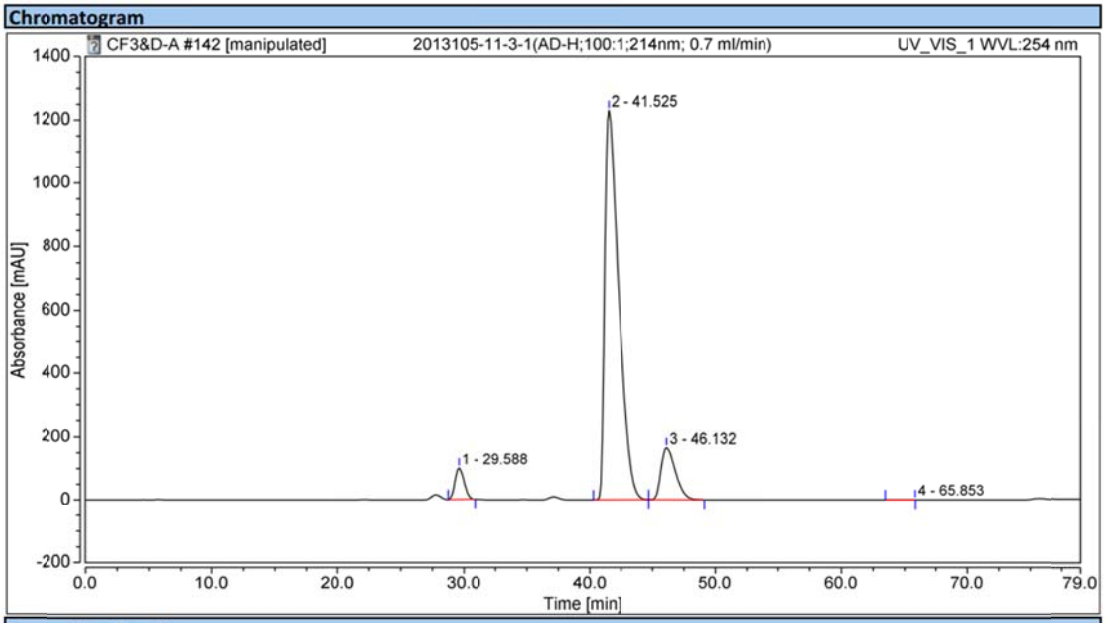
9


7.61
7.59
7.33
7.32
7.28
7.26 CDCl3
6.73
6.72
6.71
6.70
6.58
6.58
6.24
6.23
6.22
3.81
3.78
3.73
3.70
3.60
3.58
3.56
2.79
2.79
2.78
2.68
2.66
2.52
2.51
2.49
2.30
2.25
2.15
2.13
2.12
2.04
2.03
2.01
1.50
1.49
1.48
1.47
1.46
1.45
0.00
1.01
4.00
0.98
0.97
0.96
3.96
1.05
1.03
3.07
1.99
1.04
4.15
6.18
4.95
5.48
3.15
NH
O
H
H
CH3
f1 (ppm)


175.79
158.23
140.54
137.81
131.38
128.47
128.20
127.40
127.02
124.74
115.43
113.27
112.68
80.39
77.16 cdcl3
65.93
55.29
53.13
52.44
46.32
41.27
36.25
34.93
30.85
30.79
29.16
27.62
23.95
22.94
NH
O
O
H
H
O
CH3
f1 (ppm)

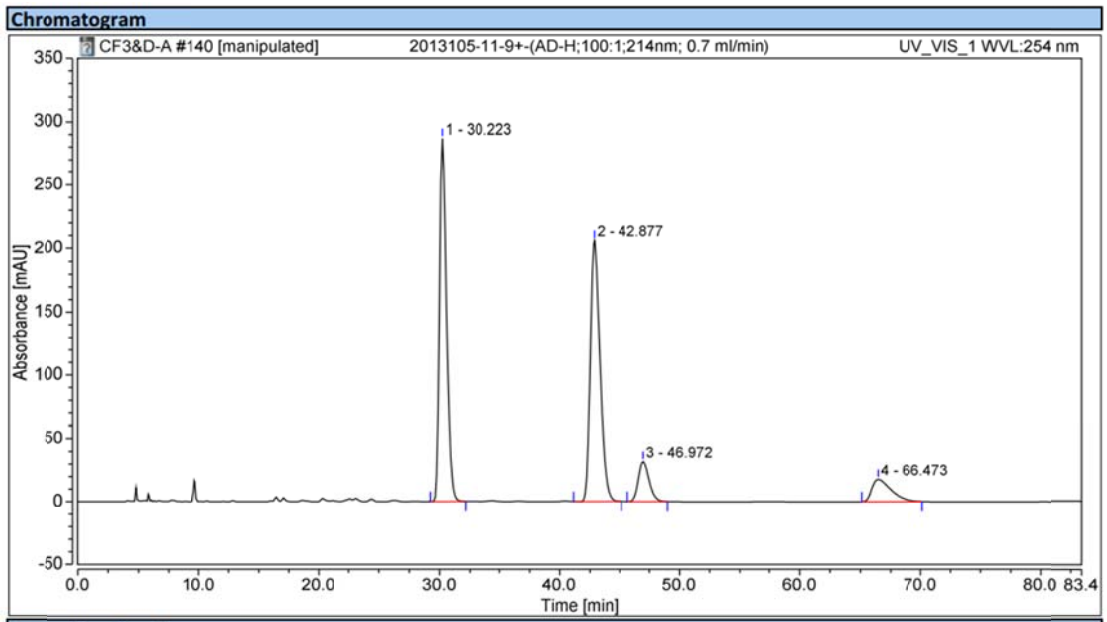
10. HPLC data

HPLC of **3a**



Integration Results

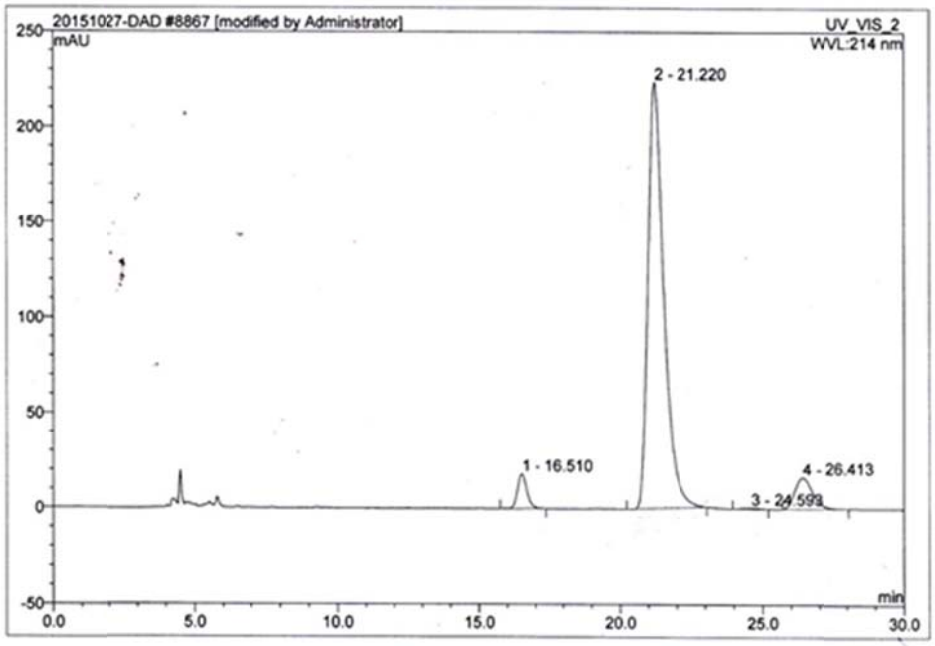
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		29.588	82.980	99.322	4.36	6.65	n.a.
2		41.525	1601.657	1230.031	84.13	82.32	n.a.
3		46.132	219.107	164.891	11.51	11.04	n.a.
4		65.853	0.051	0.004	0.00	0.00	n.a.
Total:			**1903.795**	**1494.248**	**100.00**	**100.00**	



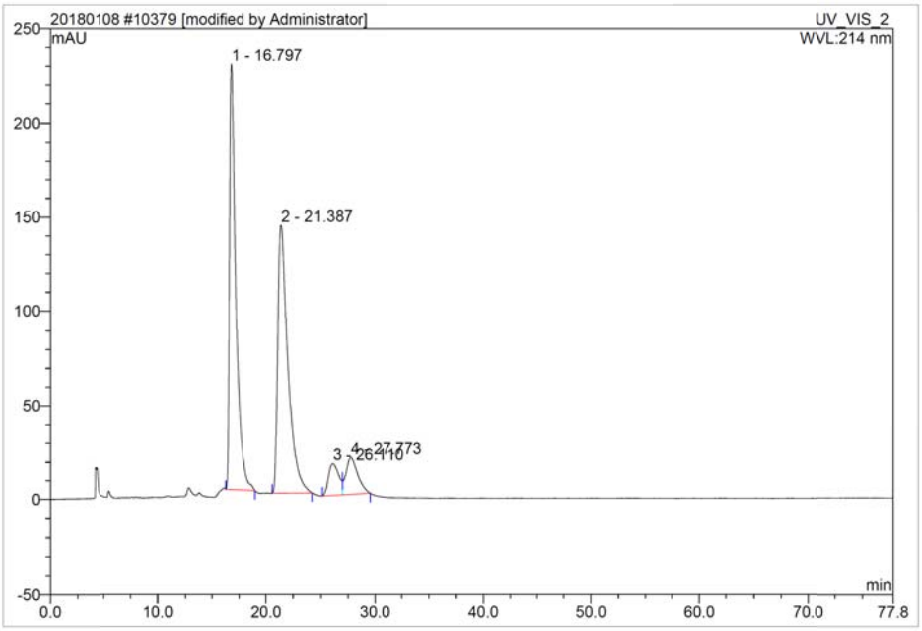
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		30.223	192.944	286.822	42.80	52.89	n.a.
2		42.877	192.199	205.773	42.63	37.95	n.a.
3		46.972	33.000	31.838	7.32	5.87	n.a.
4		66.473	32.672	17.822	7.25	3.29	n.a.
Total:			**450.815**	**542.255**	**100.00**	**100.00**	

HPLC of **3b**

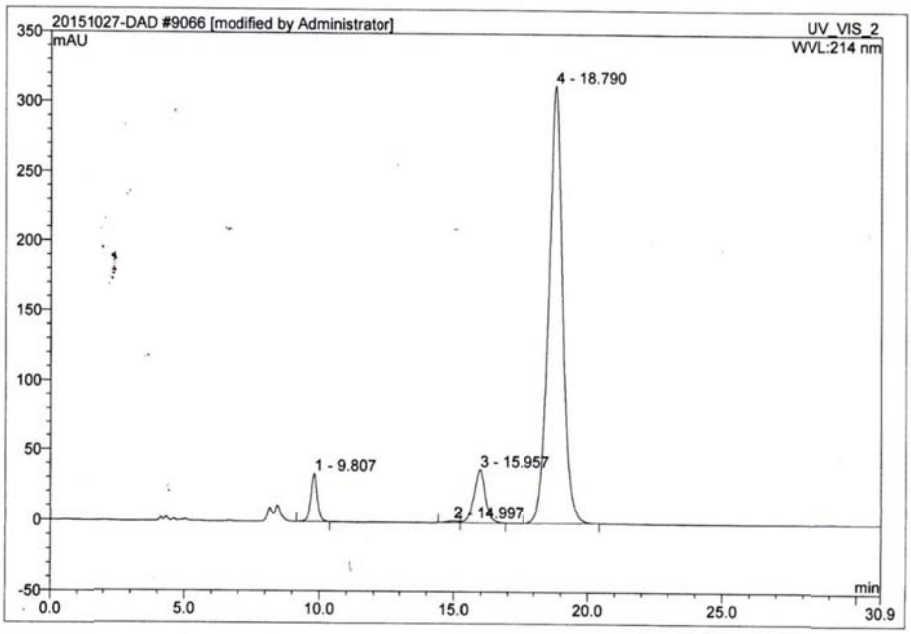


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.51	n.a.	18.293	6.985	4.27	n.a.	BMB*
2	21.22	n.a.	223.548	144.232	88.10	n.a.	BMB*
3	24.59	n.a.	0.534	0.361	0.22	n.a.	BMB*
4	26.41	n.a.	16.725	12.135	7.41	n.a.	BMB*
Total:			259.099	163.713	100.00	0.000	

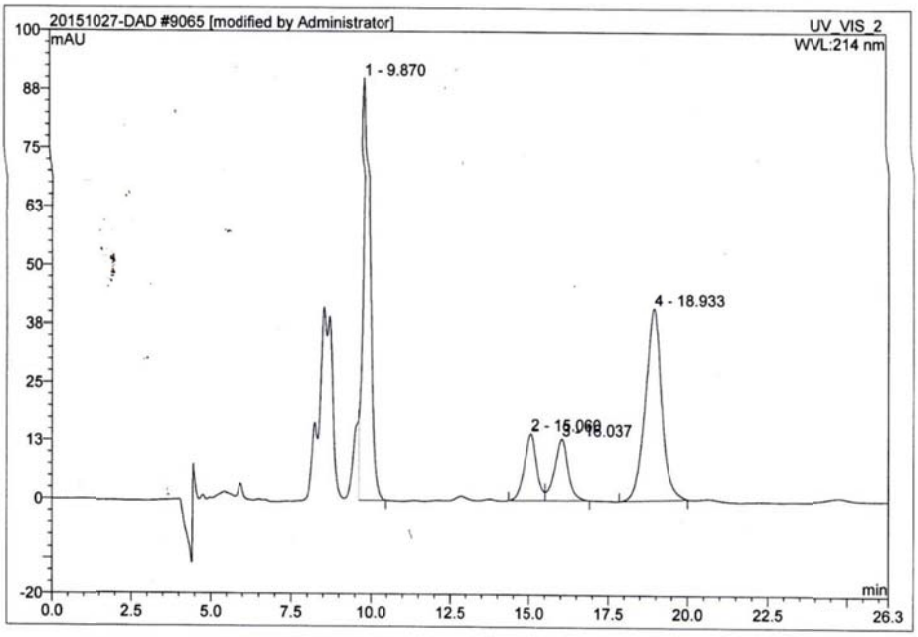


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.80	n.a.	225.936	155.764	43.90	n.a.	BMB*
2	21.39	n.a.	142.321	155.035	43.70	n.a.	BMB
3	26.11	n.a.	17.135	18.892	5.32	n.a.	BM
4	27.77	n.a.	19.785	25.097	7.07	n.a.	MB
Total:			405.177	354.788	100.00	0.000	

HPLC of **3c**

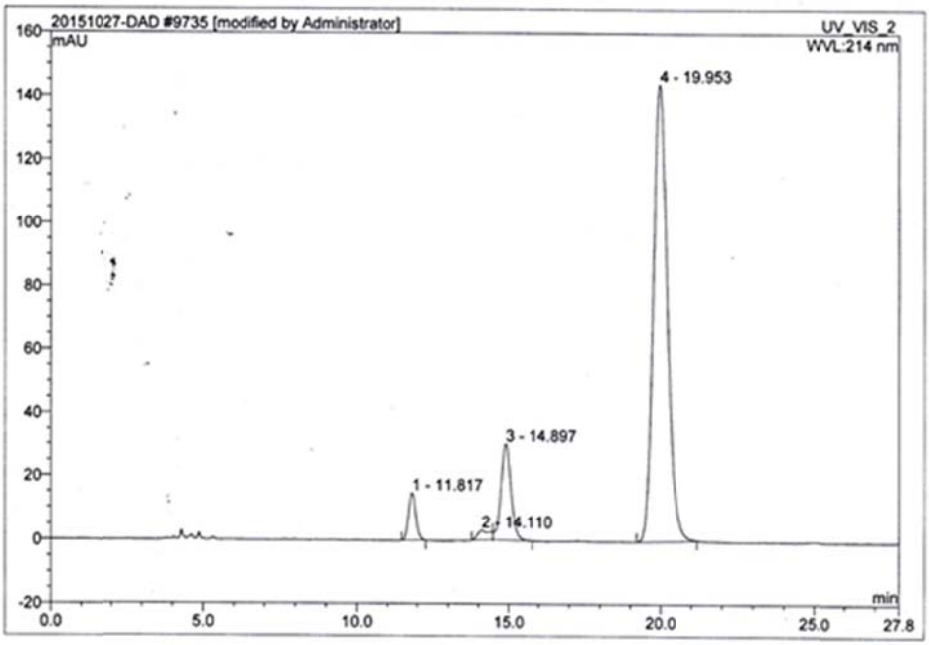


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.81	n.a.	34.591	9.605	4.43	n.a.	BMB*
2	15.00	n.a.	1.290	0.571	0.26	n.a.	BM
3	15.96	n.a.	38.187	18.759	8.65	n.a.	MB
4	18.79	n.a.	313.678	187.899	86.66	n.a.	BMB*
Total:			387.747	216.834	100.00	0.000	

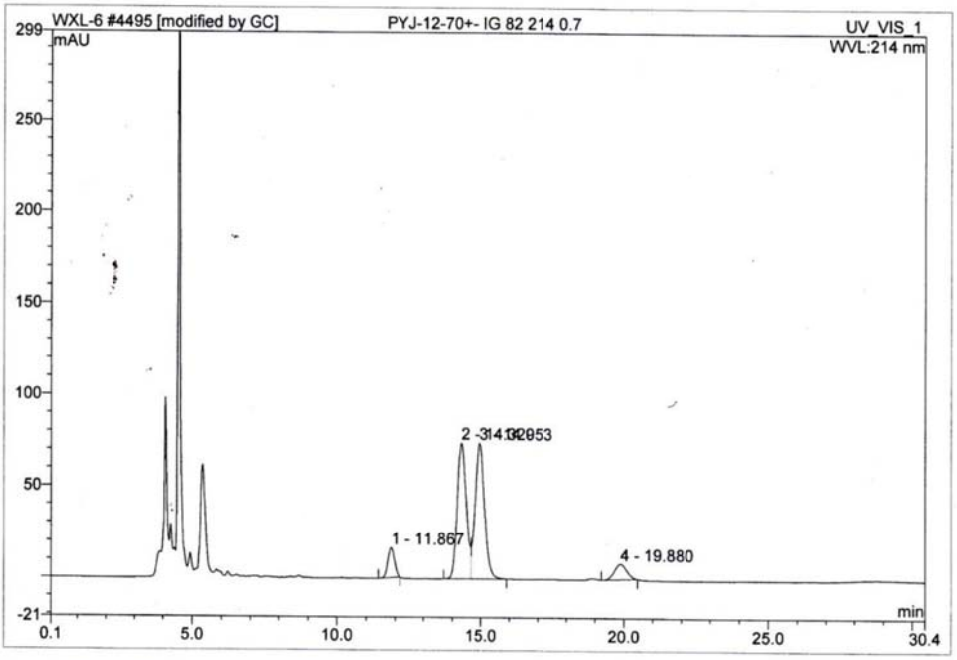


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.87	n.a.	89.906	24.497	39.49	n.a.	MB*
2	15.06	n.a.	14.203	6.487	10.46	n.a.	BM
3	16.04	n.a.	13.164	6.502	10.48	n.a.	MB
4	18.93	n.a.	41.014	24.554	39.58	n.a.	BMB
Total:			158.287	62.040	100.00	0.000	

HPLC of **3d**



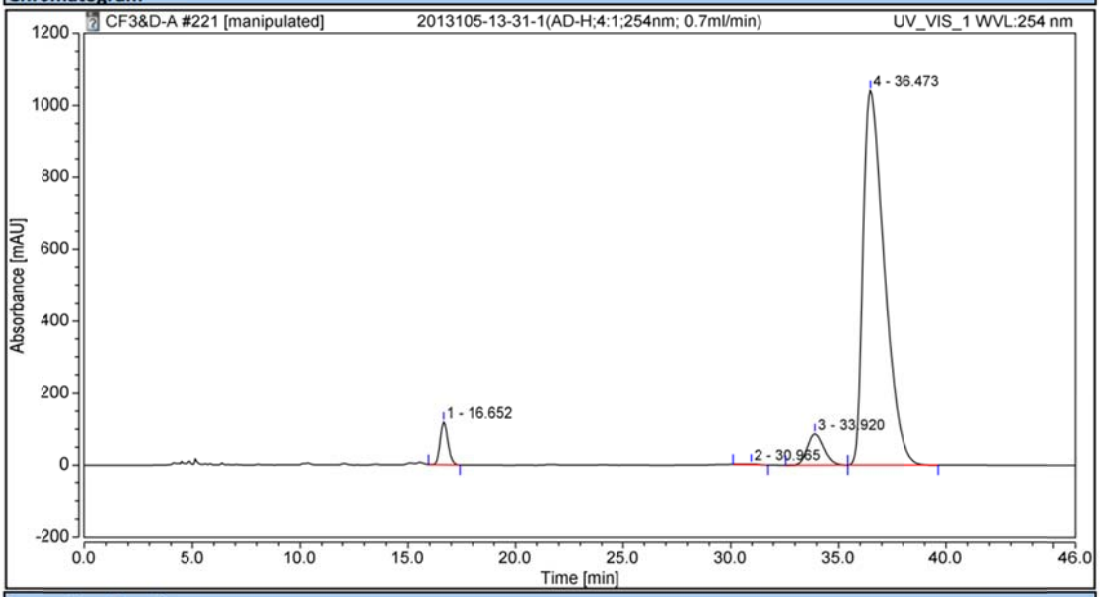
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.82	n.a.	15.000	4.138	4.40	n.a.	BMB
2	14.11	n.a.	3.016	1.418	1.51	n.a.	BM *
3	14.90	n.a.	30.517	11.743	12.49	n.a.	MB*
4	19.95	n.a.	144.195	76.732	81.60	n.a.	BMB
Total:			192.728	94.033	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.87	n.a.	16.451	4.398	6.78	n.a.	BMB*
2	14.32	n.a.	74.468	27.500	42.41	n.a.	BM *
3	14.95	n.a.	74.489	28.723	44.29	n.a.	MB*
4	19.88	n.a.	8.519	4.230	6.52	n.a.	BMB*
Total:			173.926	64.851	100.00	0.000	

HPLC of **3e**

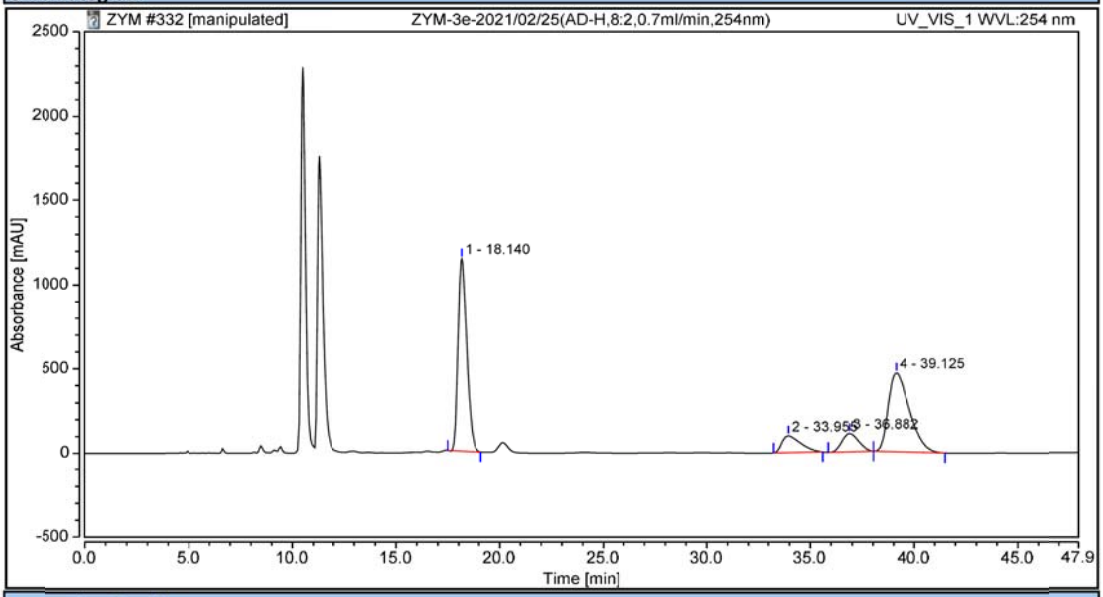
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		16.652	49.227	118.657	3.75	9.51	n.a.
2		30.965	1.096	1.463	0.08	0.12	n.a.
3		33.920	75.843	86.712	5.78	6.95	n.a.
4		36.473	1184.904	1040.827	90.38	83.42	n.a.
Total:			**1311.070**	**1247.660**	**100.00**	**100.00**	

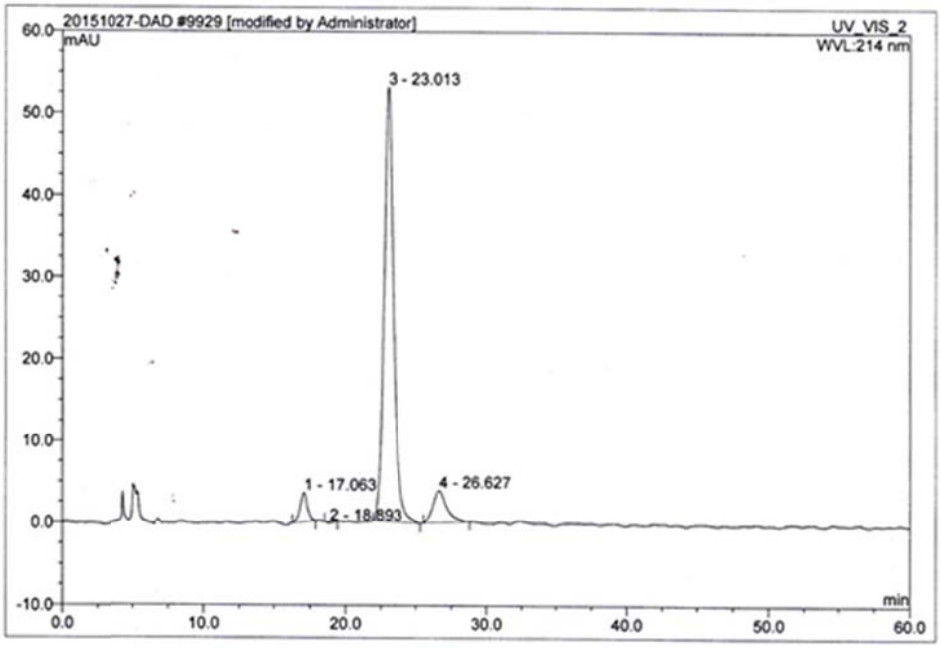
Chromatogram



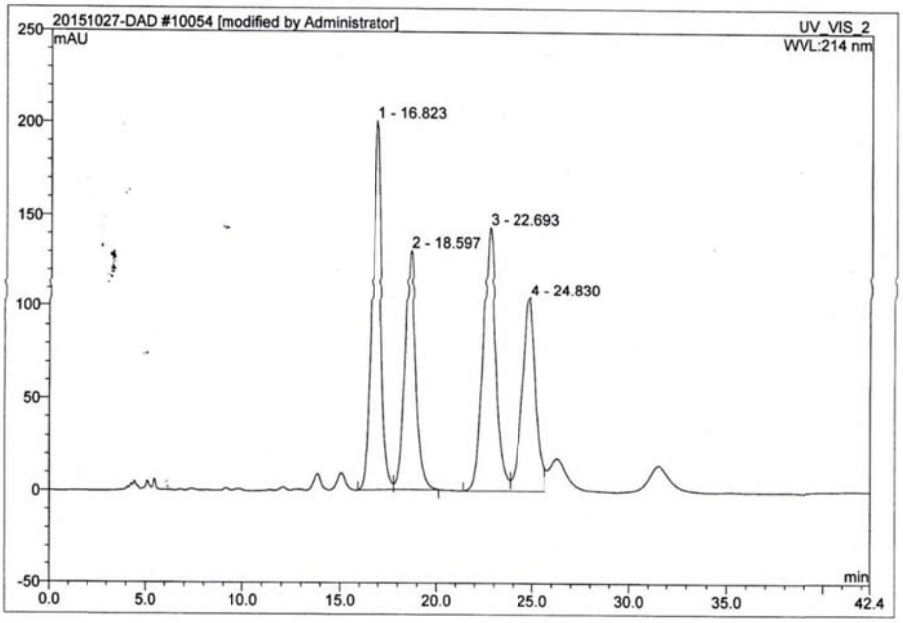
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.140	559.835	1144.161	42.36	62.96	n.a.
2		33.955	103.435	99.079	7.83	5.45	n.a.
3		36.882	100.134	108.797	7.58	5.99	n.a.
4		39.125	558.147	465.209	42.23	25.60	n.a.
Total:			**1321.551**	**1817.245**	**100.00**	**100.00**	

HPLC of **3f**

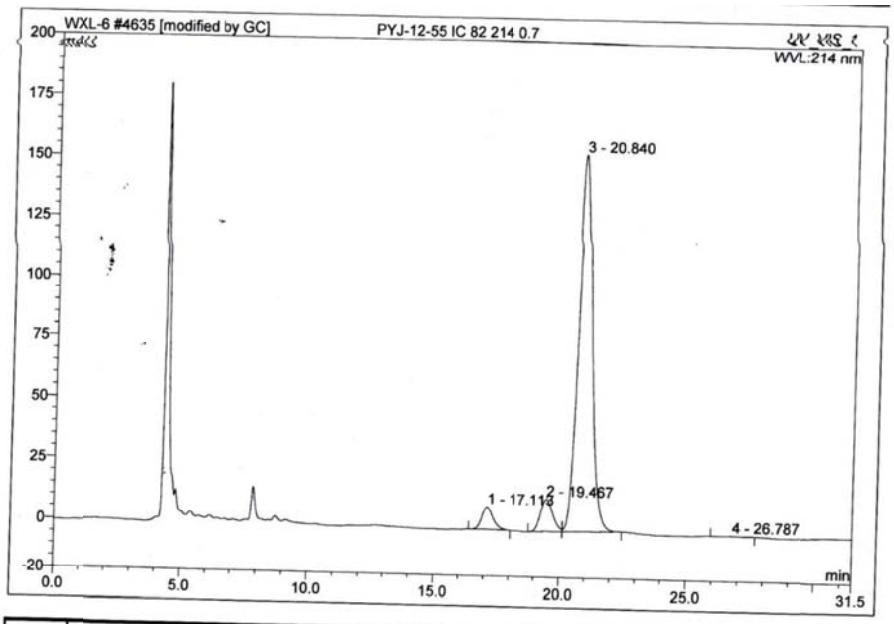


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.06	n.a.	3.638	2.099	4.34	n.a.	BMB*
2	18.89	n.a.	0.211	0.092	0.19	n.a.	BMB*
3	23.01	n.a.	52.978	41.735	86.25	n.a.	BMB*
4	26.63	n.a.	4.000	4.460	9.22	n.a.	BMB*
Total:			60.827	48.387	100.00	0.000	

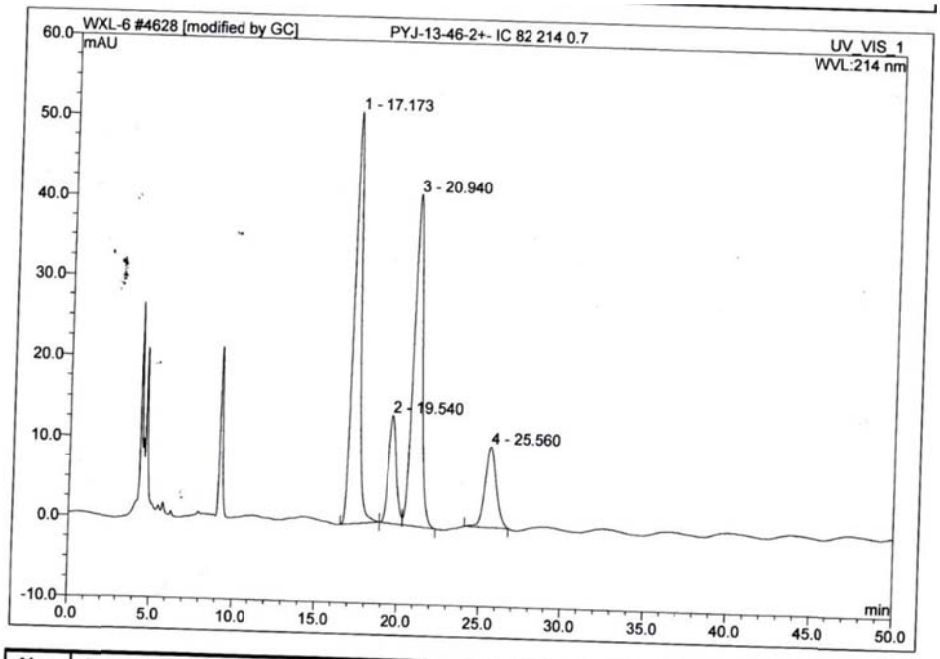


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.82	n.a.	200.807	110.954	28.29	n.a.	BM *
2	18.60	n.a.	130.134	84.646	21.58	n.a.	MB*
3	22.69	n.a.	143.598	111.036	28.31	n.a.	BM *
4	24.83	n.a.	105.343	85.562	21.82	n.a.	M *
Total:			579.882	392.198	100.00	0.000	

HPLC of **3g**

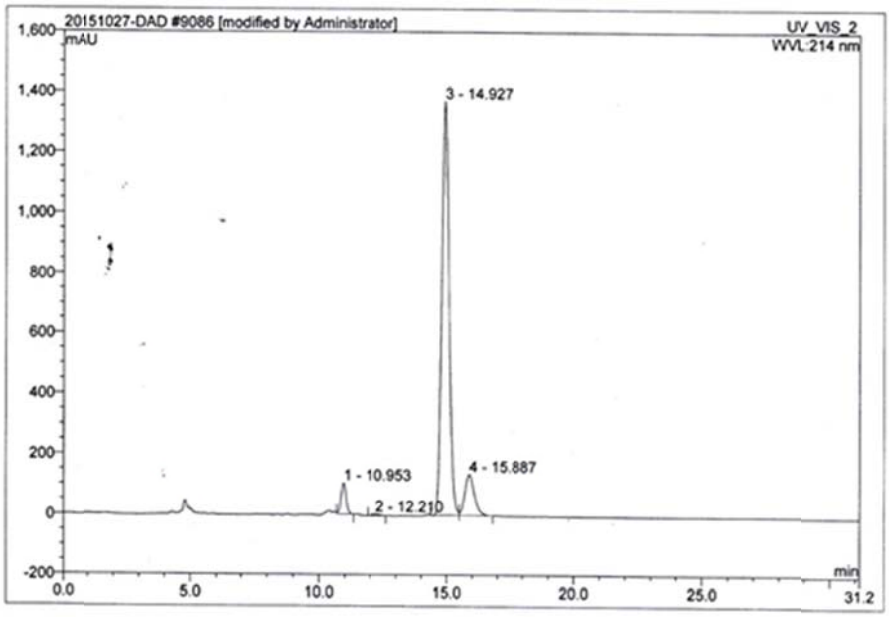


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.11	n.a.	9.299	4.820	4.42	n.a.	BMB*
2	19.47	n.a.	13.419	7.519	6.90	n.a.	BM *
3	20.84	n.a.	155.792	96.460	88.51	n.a.	MB*
4	26.79	n.a.	0.182	0.178	0.16	n.a.	BMB*
Total:			178.691	108.977	100.00	0.000	

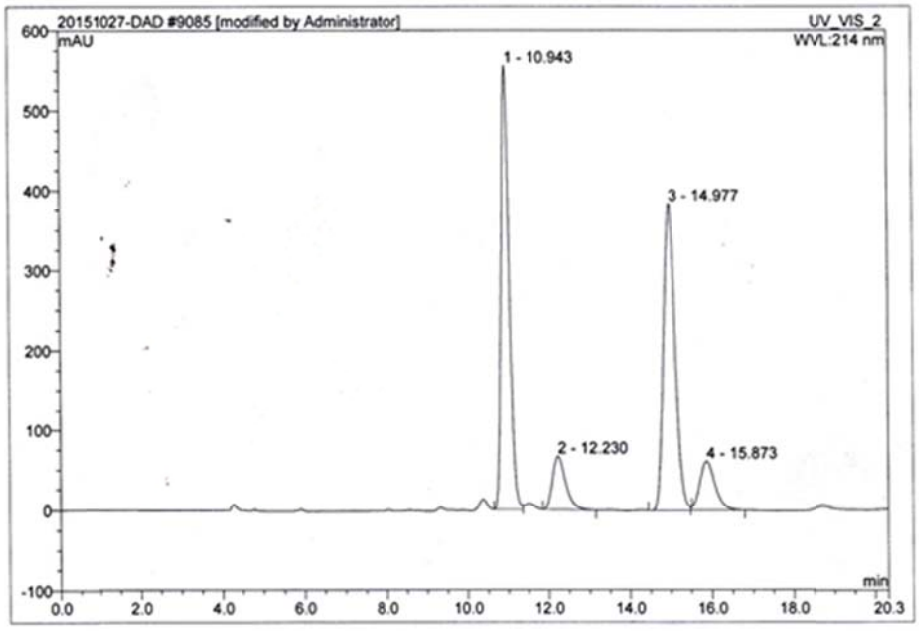


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.17	n.a.	51.177	26.540	39.04	n.a.	BMb*
2	19.54	n.a.	13.413	7.731	11.37	n.a.	bM
3	20.94	n.a.	41.219	25.744	37.87	n.a.	MB*
4	25.56	n.a.	9.995	7.964	11.72	n.a.	BMB*
Total:			115.805	67.979	100.00	0.000	

HPLC of **3h**

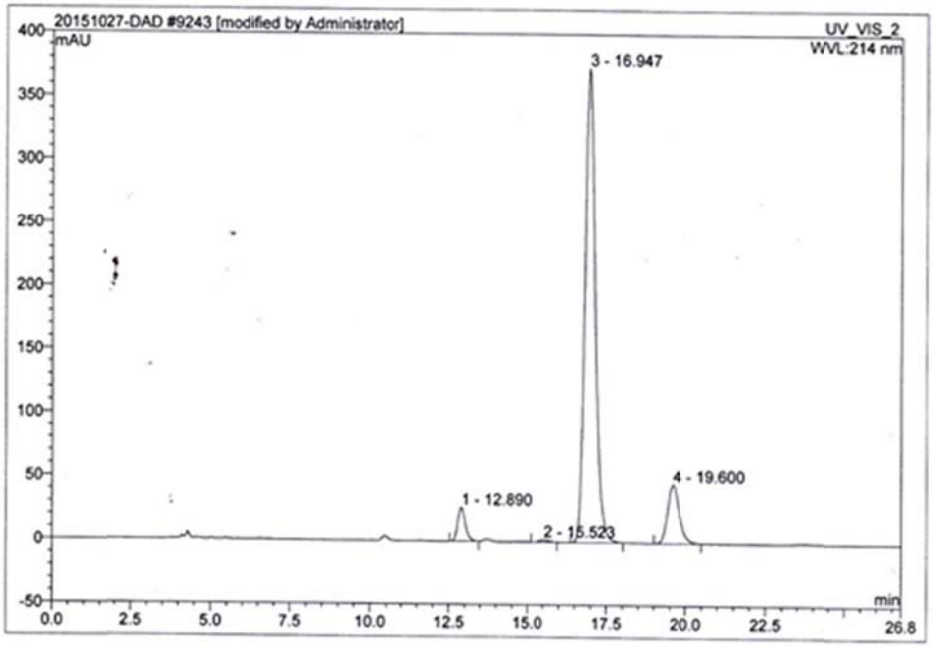


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.95	n.a.	105.337	23.888	4.41	n.a.	MB*
2	12.21	n.a.	3.904	1.510	0.28	n.a.	BMB*
3	14.93	n.a.	1373.411	457.792	84.57	n.a.	BM *
4	15.89	n.a.	136.380	58.140	10.74	n.a.	MB*
Total:			1619.032	541.330	100.00	0.000	

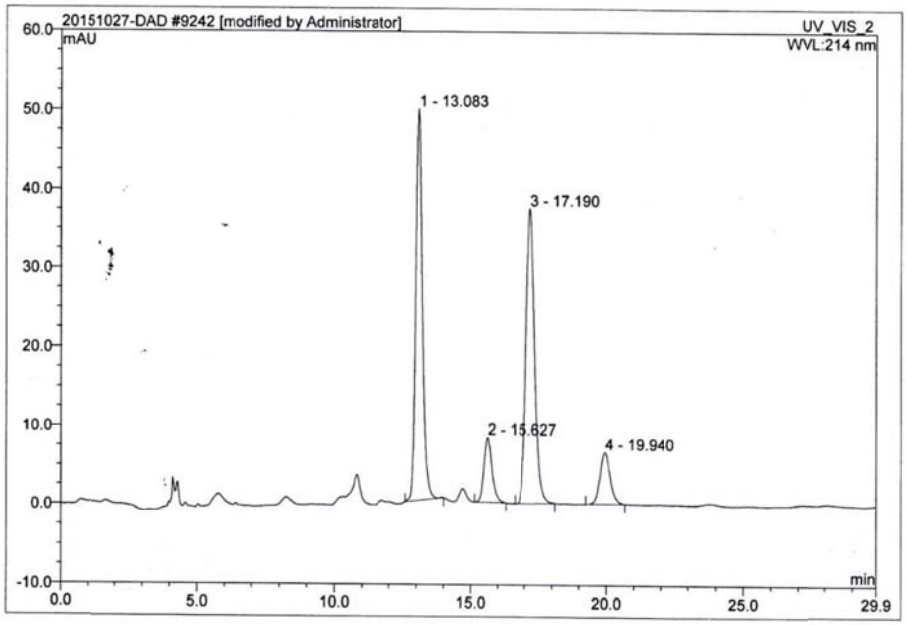


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.94	n.a.	555.458	127.009	41.59	n.a.	BM *
2	12.23	n.a.	67.242	25.062	8.21	n.a.	BMB*
3	14.98	n.a.	383.213	126.879	41.55	n.a.	BM *
4	15.87	n.a.	61.671	26.406	8.65	n.a.	MB*
Total:			1067.583	305.355	100.00	0.000	

HPLC of **3i**

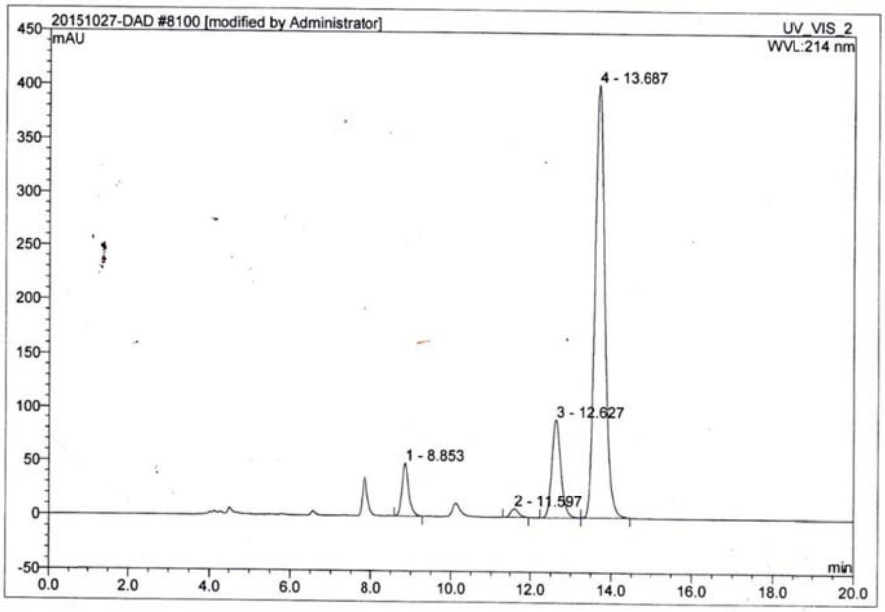


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.89	n.a.	27.307	7.543	4.46	n.a.	BMB*
2	15.52	n.a.	1.692	0.556	0.33	n.a.	BMB*
3	16.95	n.a.	374.290	140.684	83.13	n.a.	BMB
4	19.60	n.a.	47.142	20.442	12.08	n.a.	BMB
Total:			450.430	169.225	100.00	0.000	

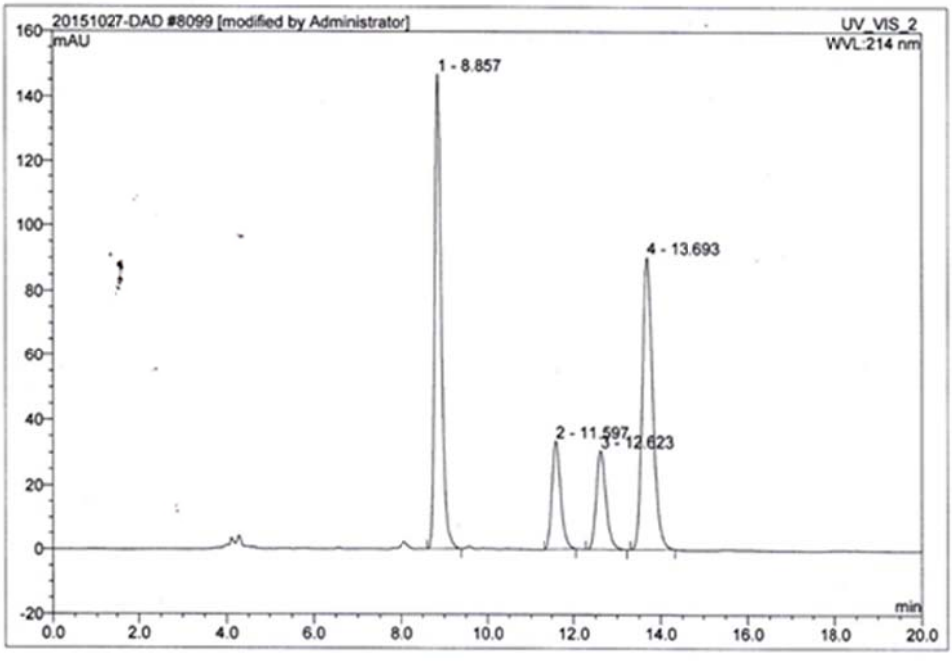


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.08	n.a.	49.621	13.944	41.68	n.a.	BMB*
2	15.63	n.a.	8.251	2.847	8.51	n.a.	BMB*
3	17.19	n.a.	37.351	13.812	41.28	n.a.	BMB*
4	19.94	n.a.	6.634	2.852	8.53	n.a.	BMB*
Total:			101.856	33.456	100.00	0.000	

HPLC of **3j**

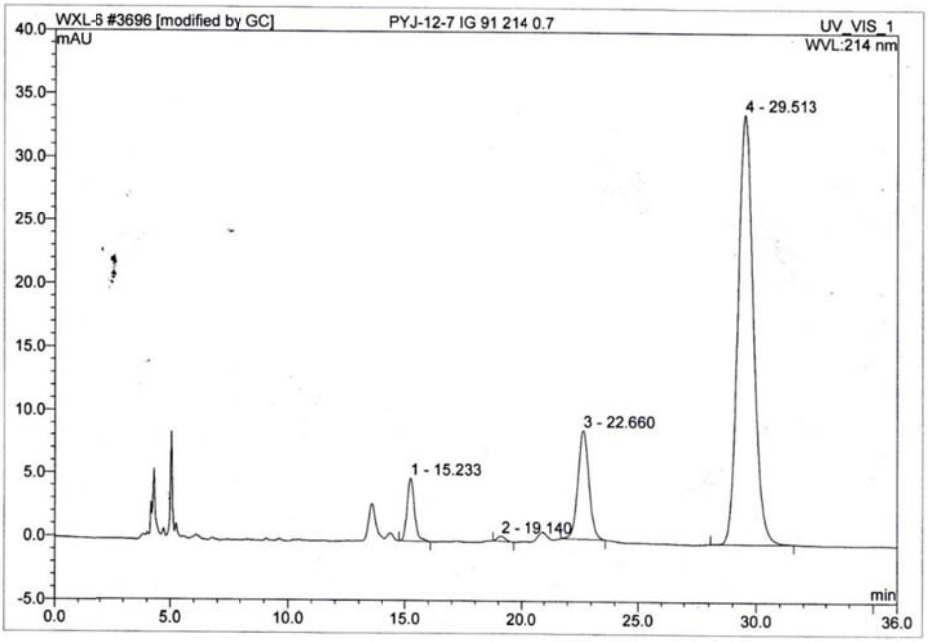


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.85	n.a.	49.588	9.471	6.33	n.a.	BMB
2	11.60	n.a.	7.762	1.808	1.21	n.a.	BMB
3	12.63	n.a.	91.193	23.727	15.87	n.a.	BM
4	13.69	n.a.	402.321	114.534	76.59	n.a.	MB
Total:			550.864	149.540	100.00	0.000	

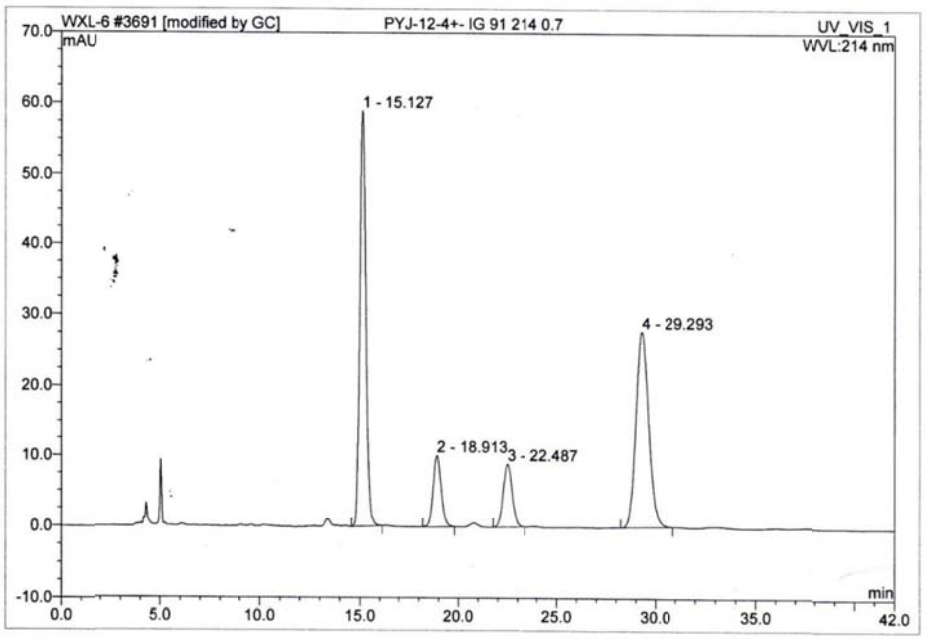


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.86	n.a.	146.634	25.800	38.33	n.a.	BMB
2	11.60	n.a.	33.480	7.932	11.78	n.a.	BMB
3	12.62	n.a.	30.796	8.022	11.92	n.a.	BMB
4	13.69	n.a.	90.337	25.563	37.97	n.a.	BMB
Total:			301.247	67.317	100.00	0.000	

HPLC of **3k**

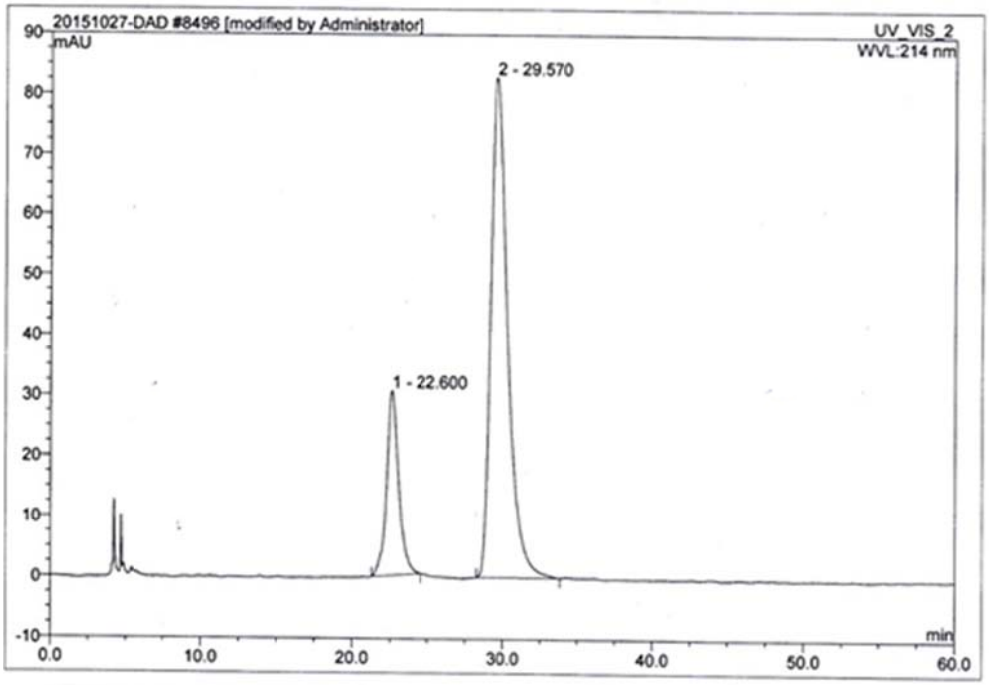


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.23	n.a.	5.046	1.842	5.67	n.a.	BMB*
2	19.14	n.a.	0.390	0.152	0.47	n.a.	BMB*
3	22.66	n.a.	8.665	4.754	14.63	n.a.	BMB*
4	29.51	n.a.	34.100	25.749	79.24	n.a.	BMB*
Total:			48.200	32.497	100.00	0.000	

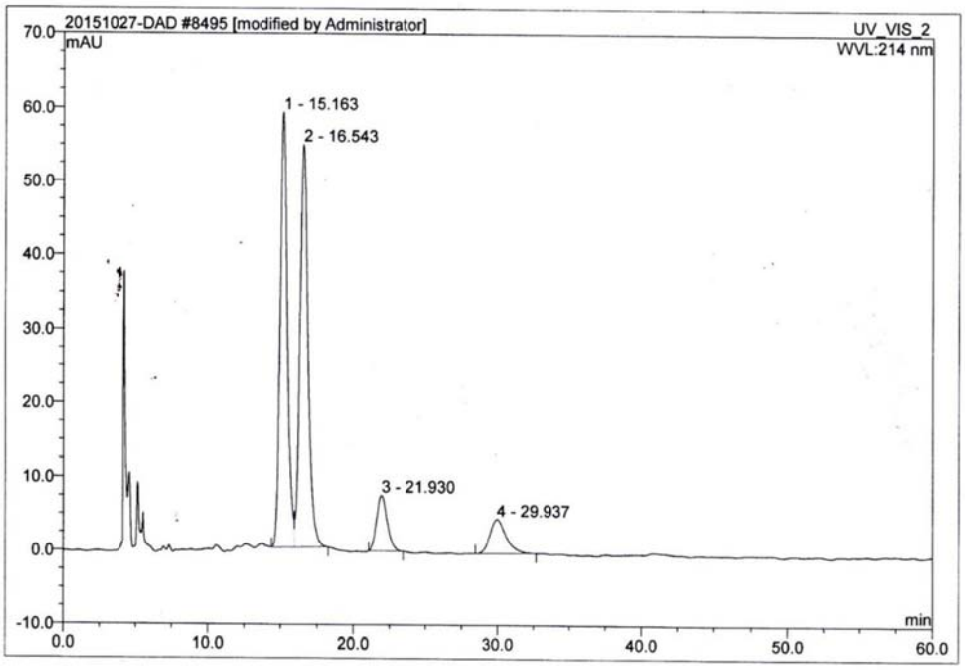


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.13	n.a.	59.022	20.807	40.75	n.a.	BMB*
2	18.91	n.a.	10.248	4.800	9.40	n.a.	BMB*
3	22.49	n.a.	9.073	4.780	9.36	n.a.	BMB*
4	29.29	n.a.	27.844	20.672	40.49	n.a.	BMB*
Total:			106.187	51.059	100.00	0.000	

HPLC of **3l**



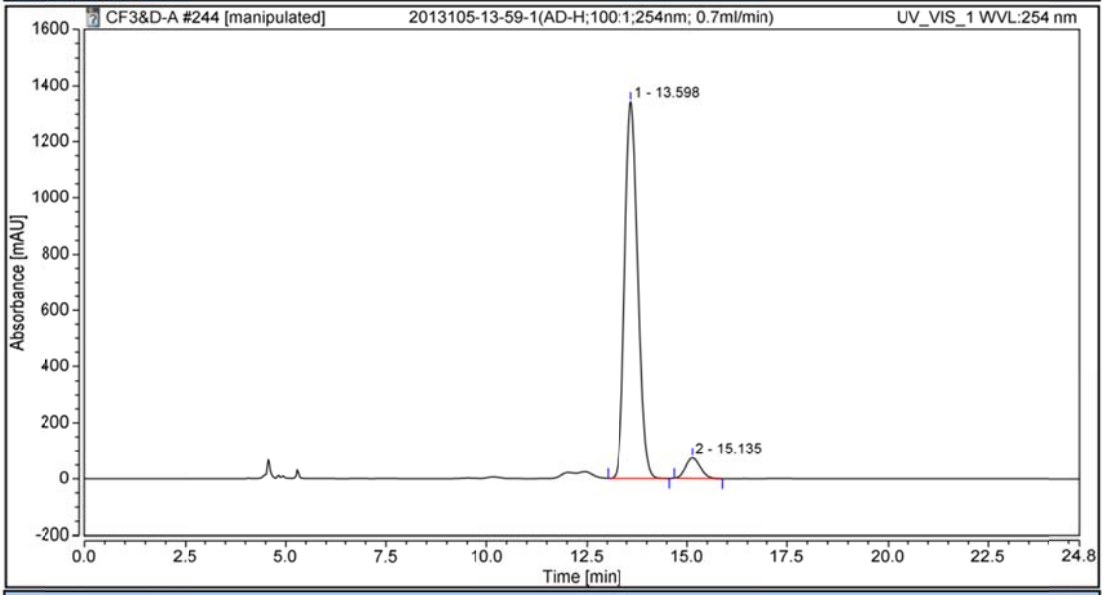
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.60	n.a.	30.544	28.117	20.64	n.a.	BMB*
2	29.57	n.a.	82.832	108.091	79.36	n.a.	BMB*
Total:			113.376	136.208	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.16	n.a.	58.951	33.623	41.40	n.a.	BM *
2	16.54	n.a.	54.523	35.072	43.18	n.a.	MB*
3	21.93	n.a.	7.604	6.465	7.96	n.a.	BMB*
4	29.94	n.a.	4.630	6.057	7.46	n.a.	BMB*
Total:			125.708	81.218	100.00	0.000	

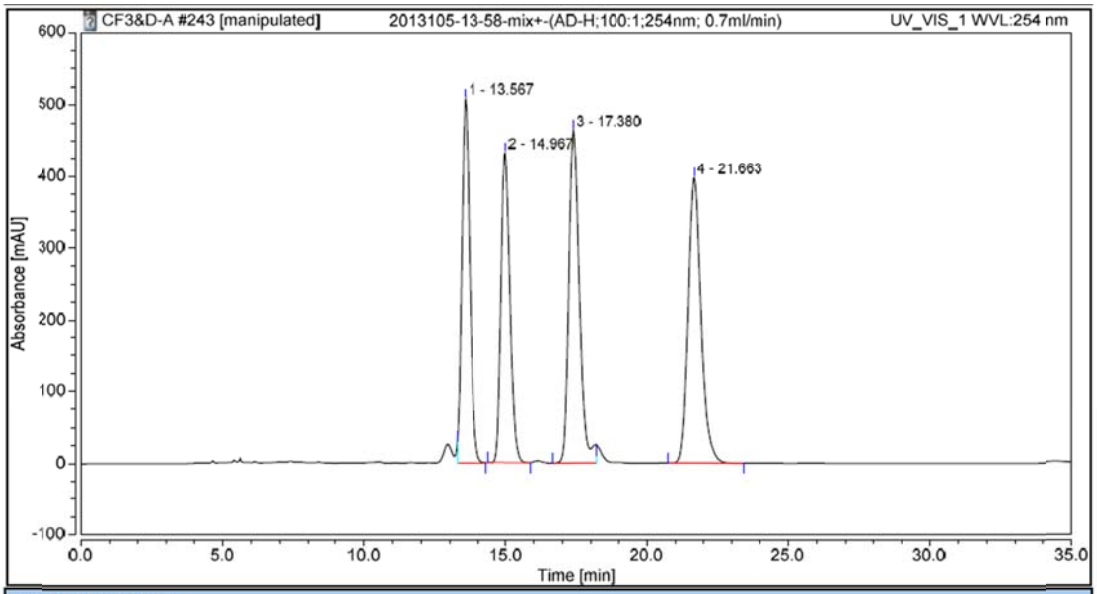
HPLC of **3m**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		13.598	507.828	1341.484	94.32	94.83	n.a.
2		15.135	30.579	73.185	5.68	5.17	n.a.
Total:			**538.406**	**1414.669**	**100.00**	**100.00**	

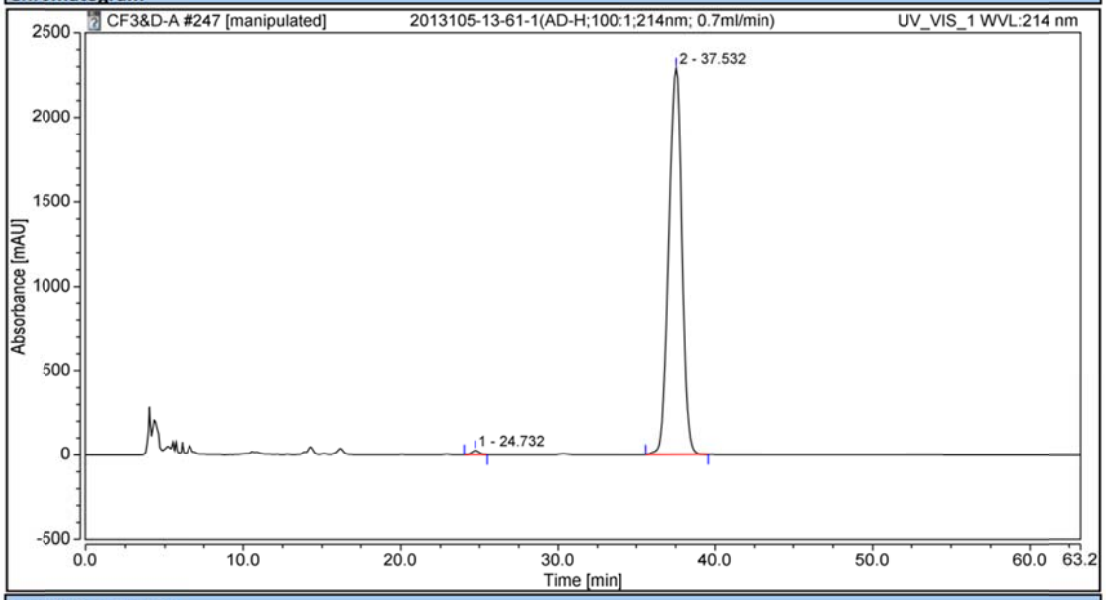


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		13.567	165.895	506.796	22.58	28.17	n.a.
2		14.967	158.636	431.557	21.59	23.99	n.a.
3		17.380	201.123	463.518	27.37	25.77	n.a.
4		21.663	209.046	397.084	28.45	22.07	n.a.
Total:			**734.699**	**1798.954**	**100.00**	**100.00**	

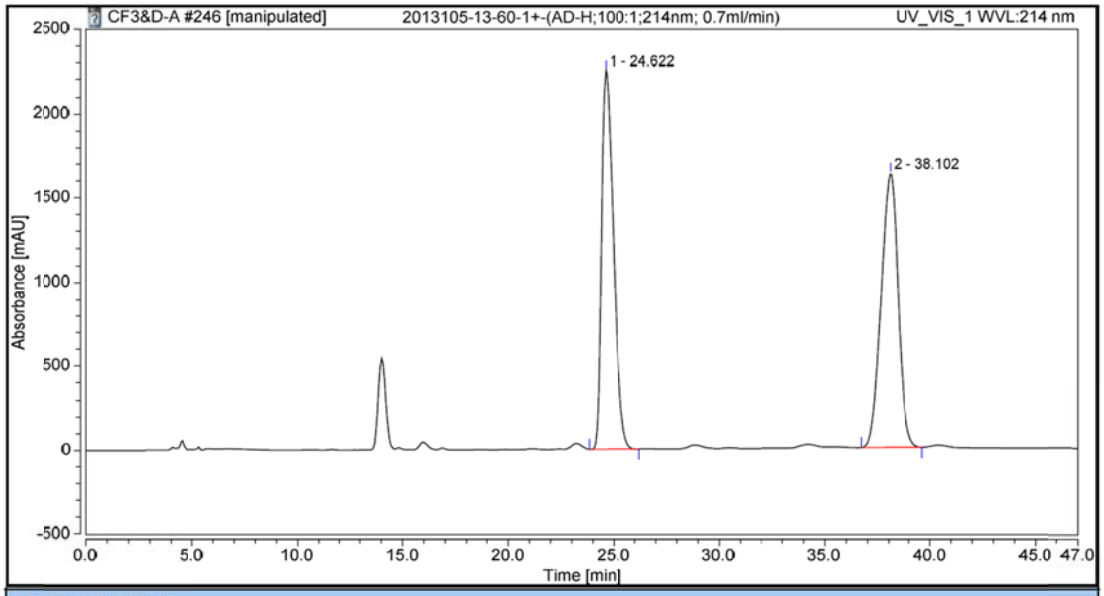
HPLC of **3**n

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		24.732	12.866	23.700	0.58	1.02	n.a.
2		37.532	2211.129	2290.646	99.42	98.98	n.a.
Total:			**2223.996**	**2314.346**	**100.00**	**100.00**	

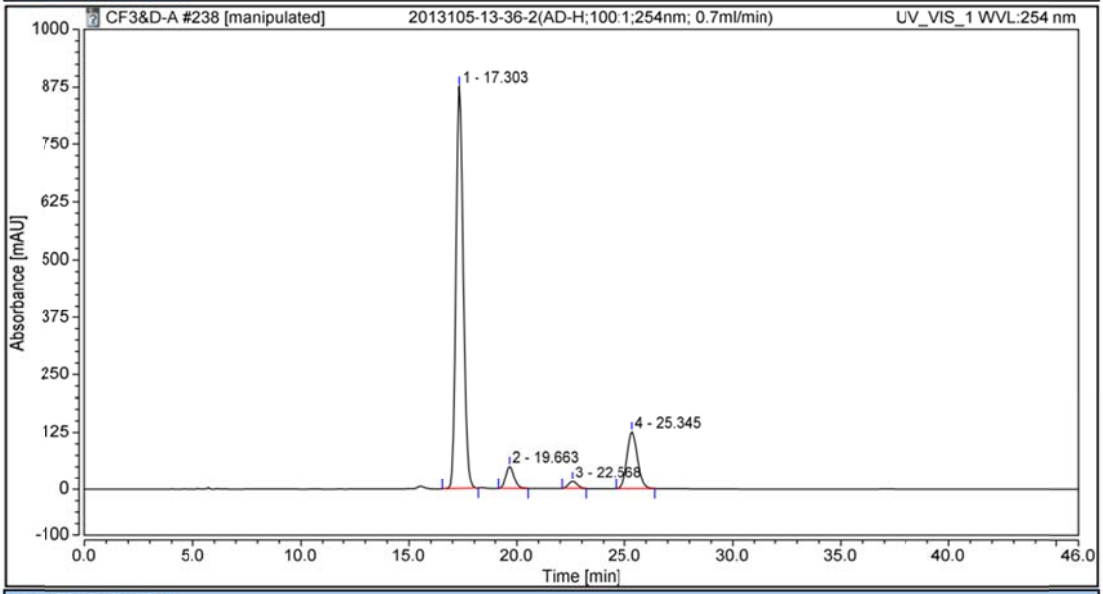


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		24.622	1487.305	2248.167	49.39	58.00	n.a.
2		38.102	1523.997	1628.085	50.61	42.00	n.a.
Total:			**3011.302**	**3876.252**	**100.00**	**100.00**	

HPLC of **3o**

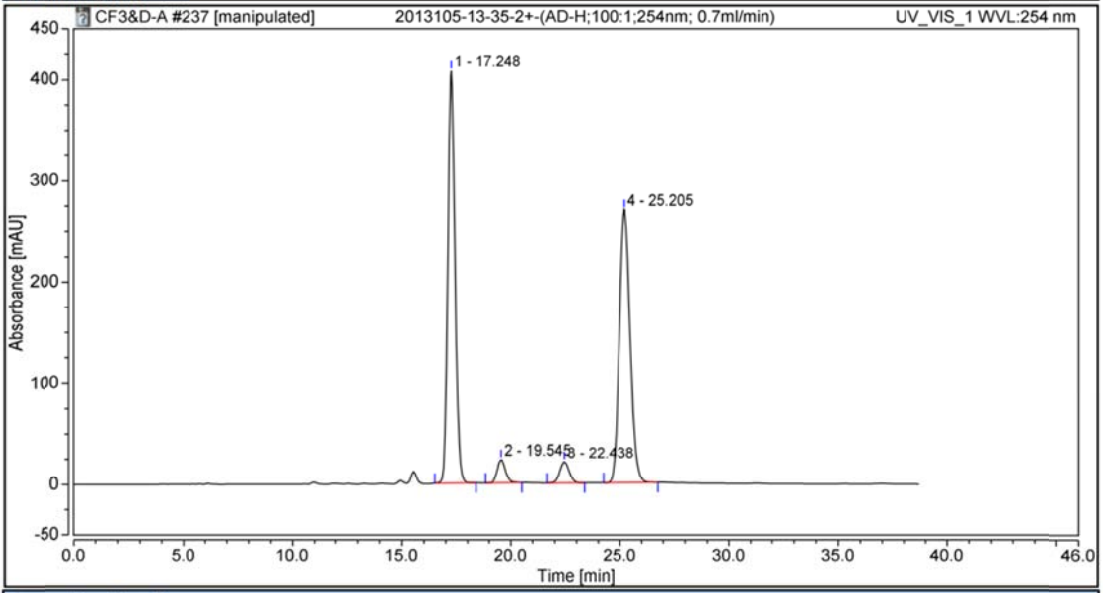
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		17.303	337.410	875.180	77.22	82.26	n.a.
2		19.663	21.613	48.631	4.95	4.57	n.a.
3		22.568	7.335	15.485	1.68	1.46	n.a.
4		25.345	70.616	124.617	16.16	11.71	n.a.
Total:			**436.973**	**1063.913**	**100.00**	**100.00**	

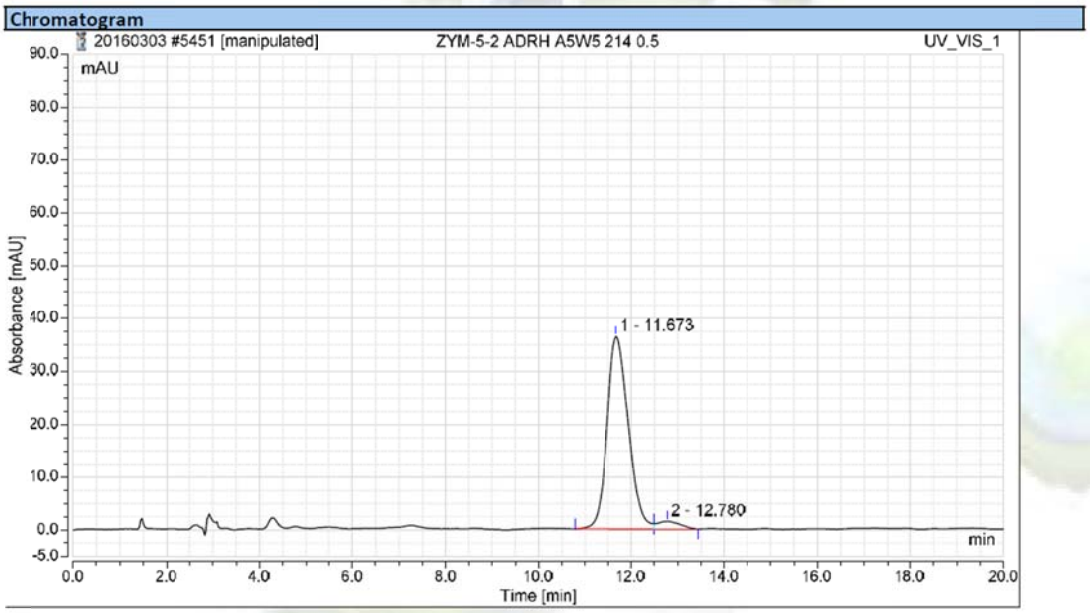
Chromatogram



Integration Results

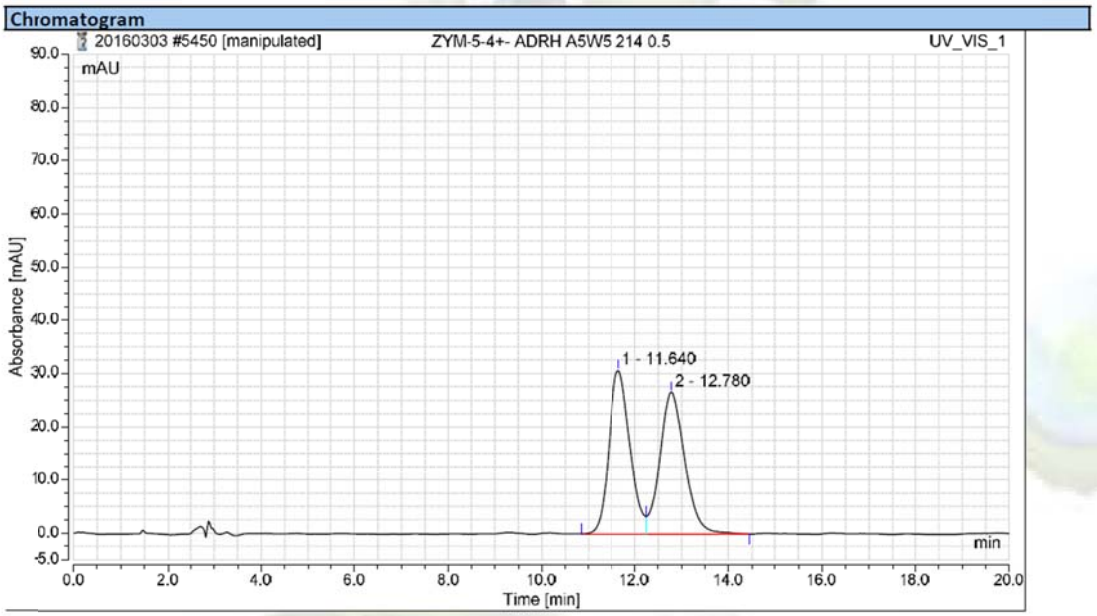
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		17.248	154.595	407.433	46.98	56.50	n.a.
2		19.545	10.152	23.017	3.09	3.19	n.a.
3		22.438	10.451	20.977	3.18	2.91	n.a.
4		25.205	153.857	269.736	46.76	37.40	n.a.
Total:			**329.055**	**721.164**	**100.00**	**100.00**	

HPLC of **3p**



Integration Results

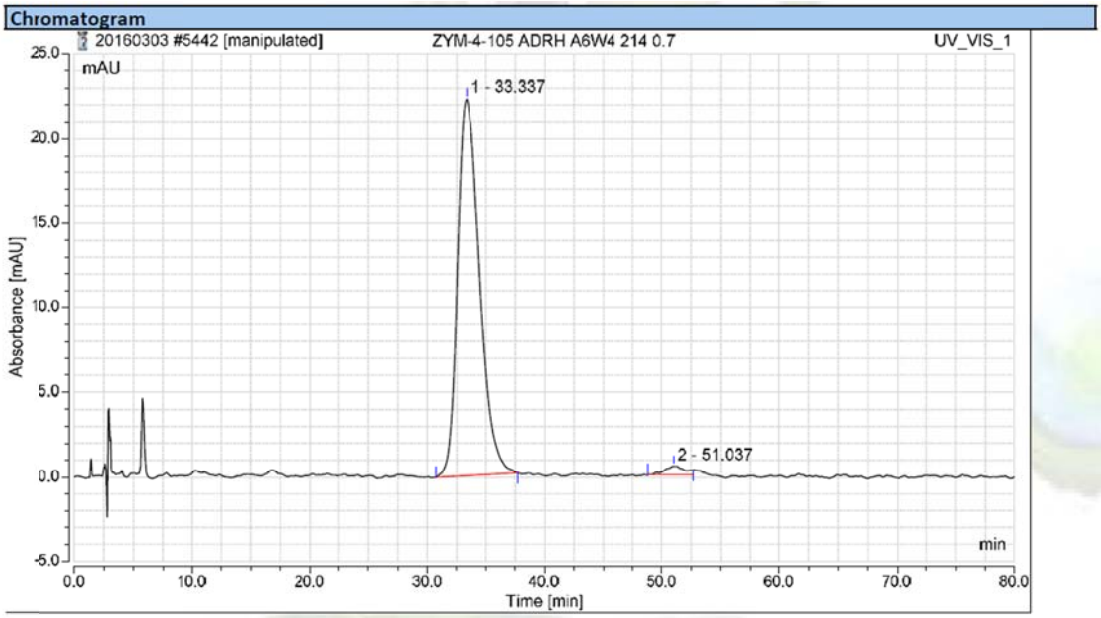
Nc.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	11.673	19.4920	36.4224	95.981
2	12.780	0.8161	1.4592	4.019
Total:		**20.308**	**1401.998**	**100.000**



Integration Results

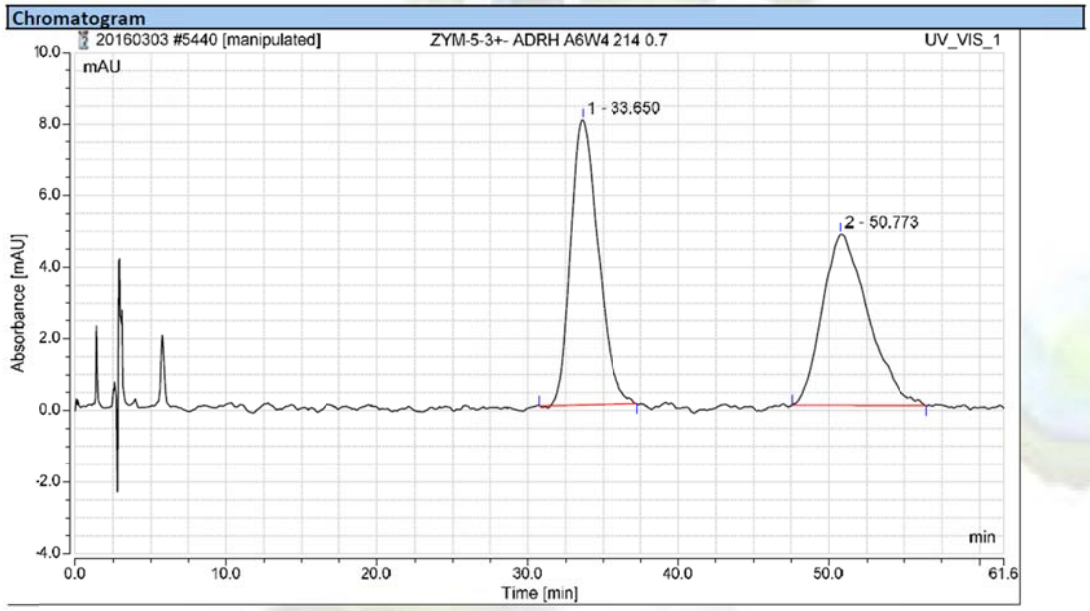
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	11.640	16.3680	30.8136	49.780
2	12.780	16.5130	26.6937	50.220
Total:		**32.881**	**1401.998**	**100.000**

HPLC of **3q**



Integration Results

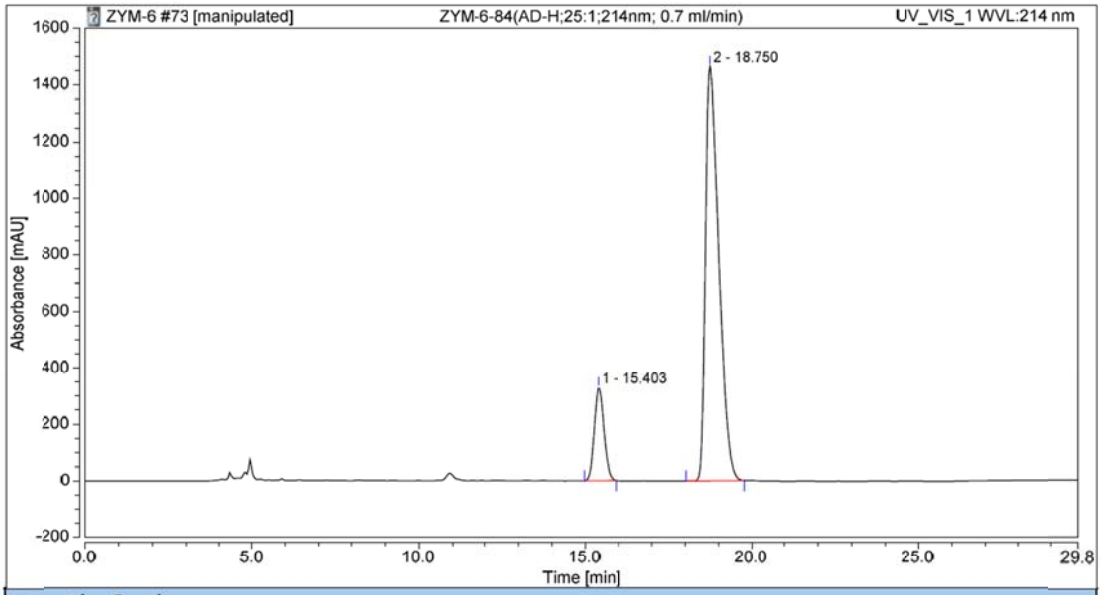
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	33.337	48.2474	22.2994	98.086
2	51.037	0.9414	0.4981	1.914
Total:		**49.189**	**1401.998**	**100.000**



Integration Results

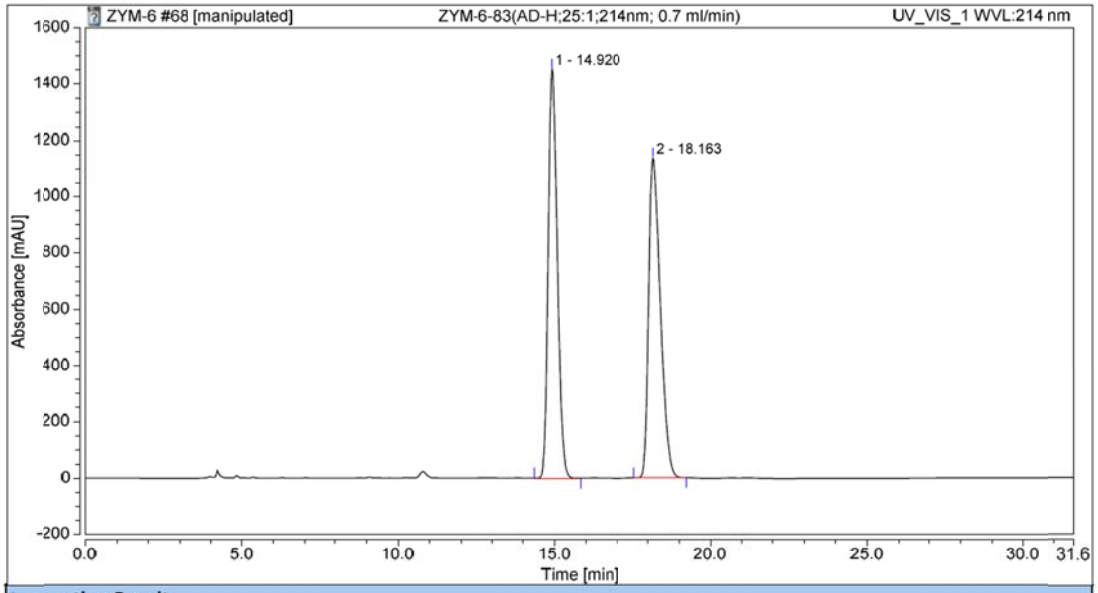
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	33.650	16.8446	7.9743	50.324
2	50.773	16.6274	4.7830	49.676
Total:		**33.472**	**1401.998**	**100.000**

HPLC of **3r**



Integration Results

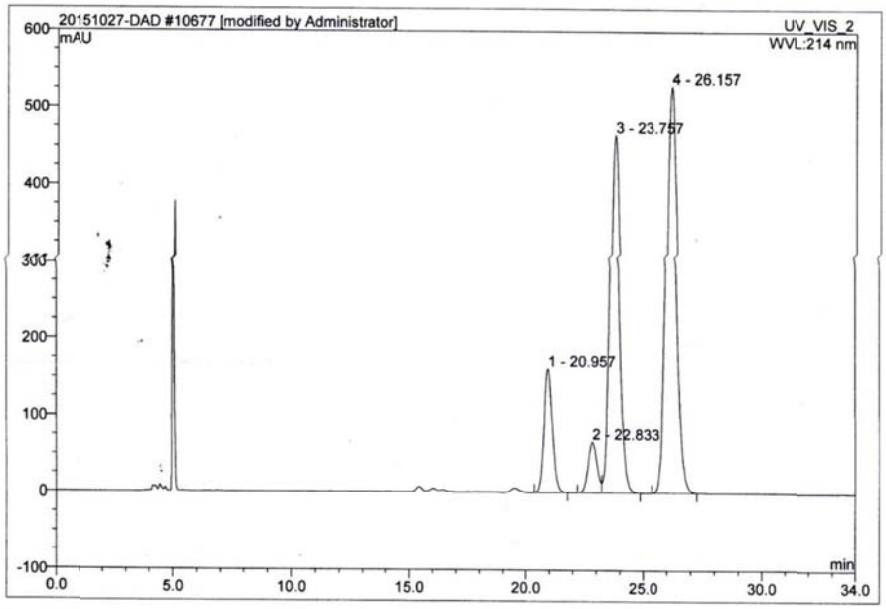
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.403	109.947	329.839	13.94	18.38	n.a.
2		18.750	678.597	1464.847	86.06	81.62	n.a.
Total:			**788.544**	**1794.686**	**100.00**	**100.00**	



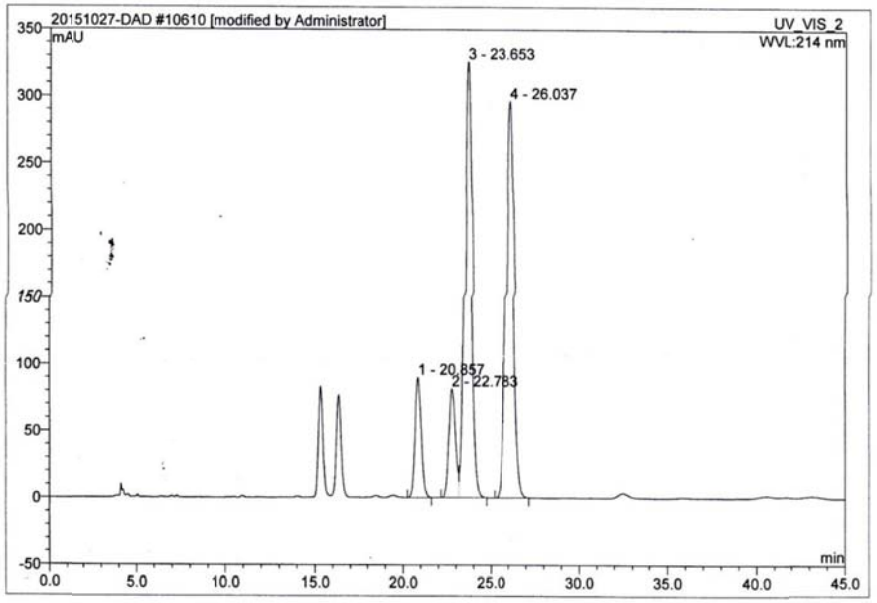
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.920	487.153	1452.212	49.85	56.12	n.a.
2		18.163	490.071	1135.266	50.15	43.88	n.a.
Total:			**977.224**	**2587.478**	**100.00**	**100.00**	

HPLC of **3s**

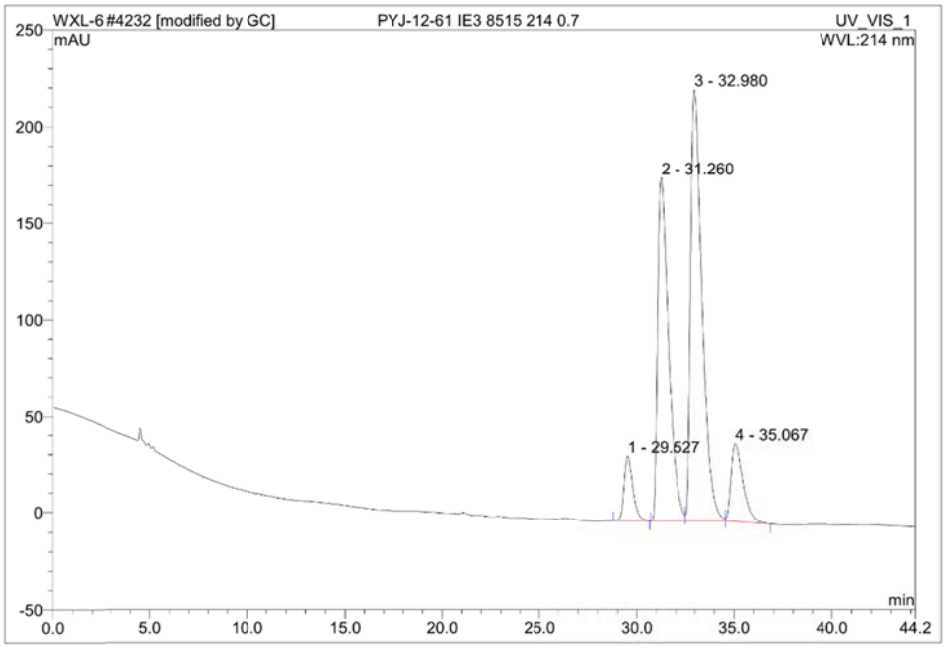


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.96	n.a.	161.814	66.143	11.08	n.a.	BMB
2	22.83	n.a.	67.122	29.365	4.92	n.a.	BM *
3	23.76	n.a.	466.355	223.127	37.38	n.a.	MB*
4	26.16	n.a.	529.620	278.202	46.61	n.a.	BMB
Total:			1224.911	596.838	100.00	0.000	

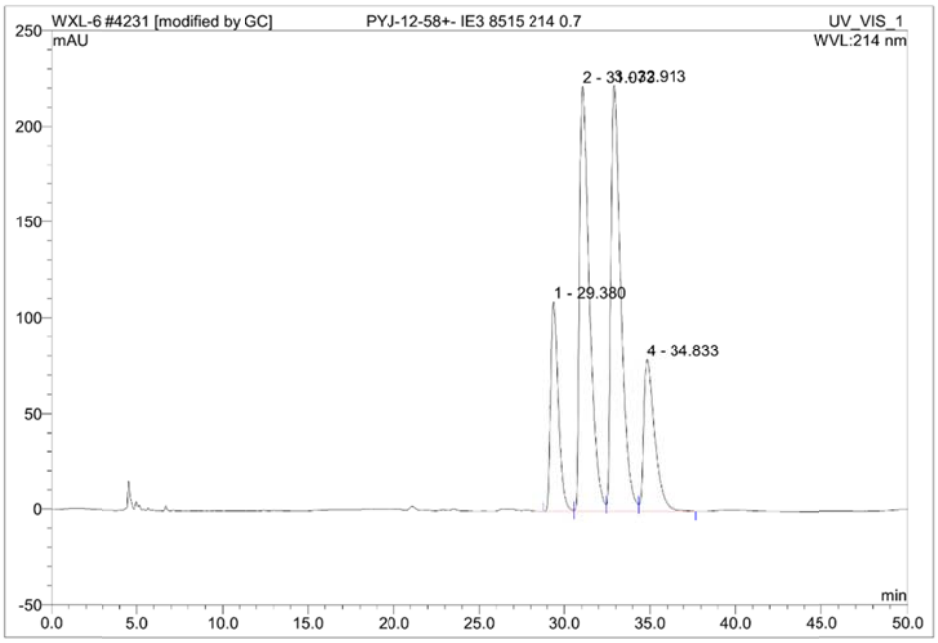


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.86	n.a.	89.412	36.487	9.52	n.a.	BMB
2	22.78	n.a.	80.883	35.550	9.27	n.a.	BM
3	23.65	n.a.	325.814	156.025	40.70	n.a.	MB
4	26.04	n.a.	296.849	155.252	40.50	n.a.	BMB
Total:			792.958	383.313	100.00	0.000	

HPLC of **3t**

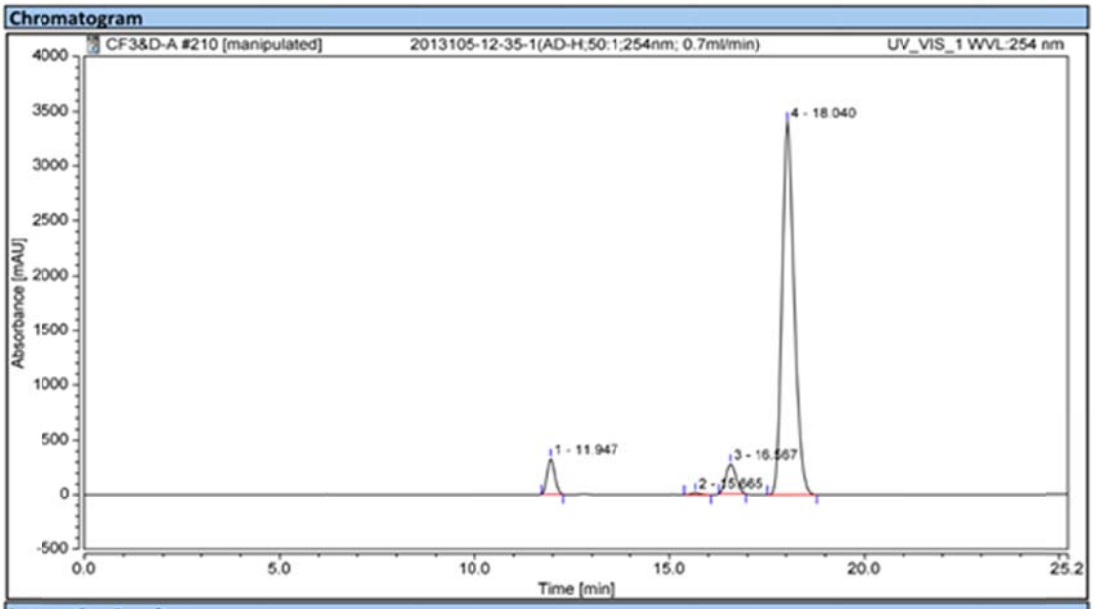


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	29.53	n.a.	33.546	17.584	5.58	n.a.	BMB*
2	31.26	n.a.	177.719	117.170	37.21	n.a.	BM *
3	32.98	n.a.	223.387	151.661	48.16	n.a.	M *
4	35.07	n.a.	40.371	28.512	9.05	n.a.	MB*
Total:			475.023	314.926	100.00	0.000	



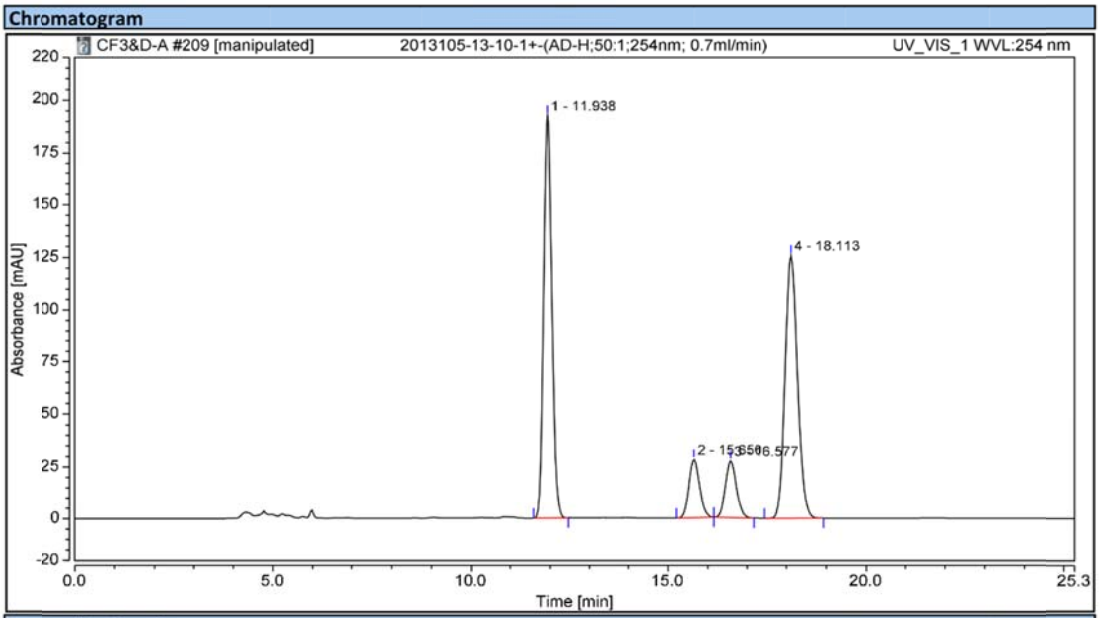
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	29.38	n.a.	109.512	57.209	13.76	n.a.	BM
2	31.07	n.a.	222.033	148.838	35.81	n.a.	M
3	32.91	n.a.	222.552	150.356	36.17	n.a.	M
4	34.83	n.a.	79.187	59.261	14.26	n.a.	MB
Total:			633.284	415.664	100.00	0.000	

HPLC of **3u**



Integration Results

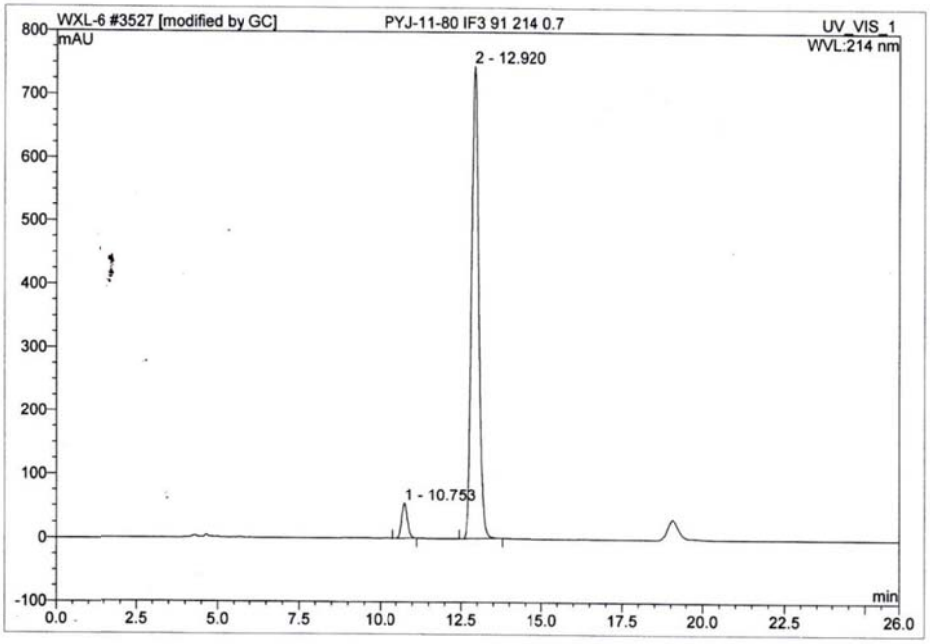
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		11.947	73.774	325.038	5.38	8.09	n.a.
2		15.665	5.301	17.927	0.39	0.45	n.a.
3		16.567	83.581	271.991	6.09	6.77	n.a.
4		18.040	1209.459	3404.112	88.15	84.70	n.a.
Total:			**1372.116**	**4019.068**	**100.00**	**100.00**	



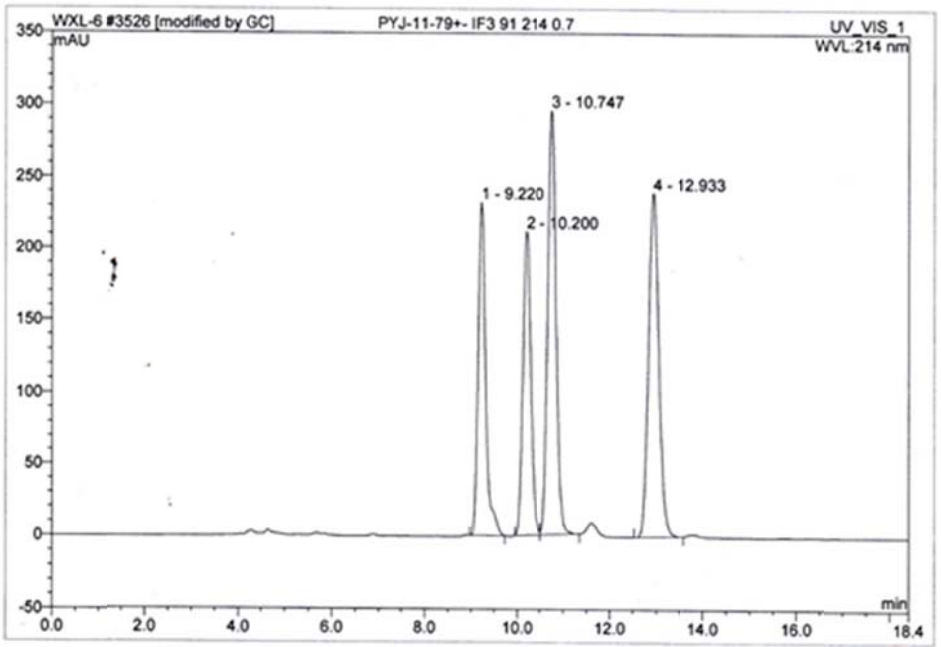
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		11.938	45.452	192.570	41.77	51.51	n.a.
2		15.650	8.843	28.131	8.13	7.52	n.a.
3		16.577	8.906	27.409	8.18	7.33	n.a.
4		18.113	45.615	125.750	41.92	33.64	n.a.
Total:			**108.815**	**373.861**	**100.00**	**100.00**	

HPLC of **3v**

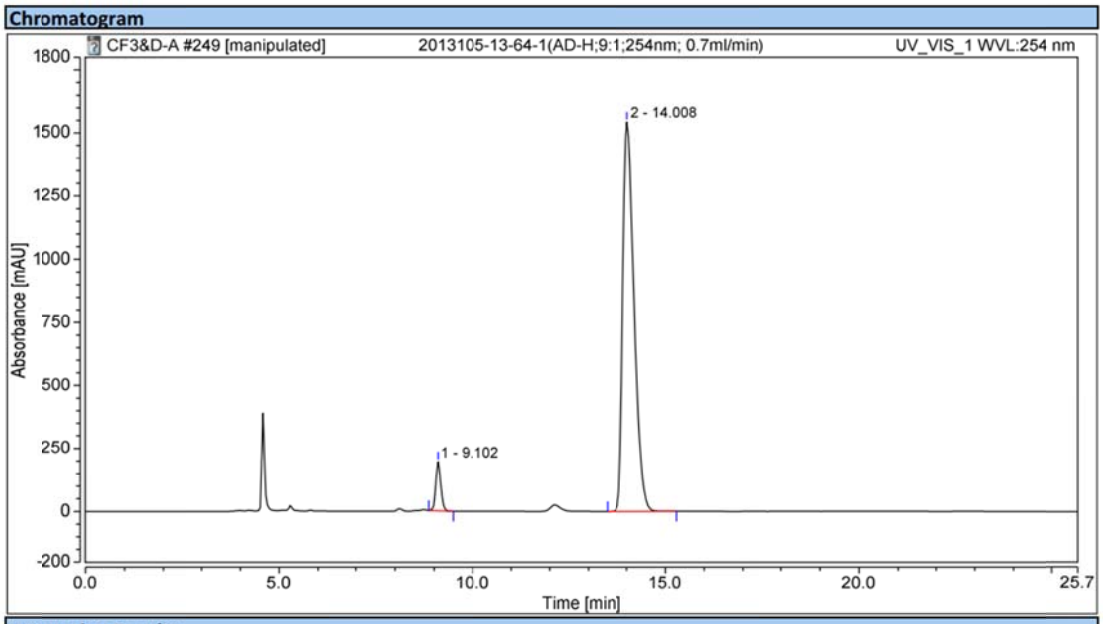


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.75	n.a.	55.361	11.350	5.55	n.a.	BMB*
2	12.92	n.a.	746.316	193.152	94.45	n.a.	BMB*
Total:			801.676	204.502	100.00	0.000	



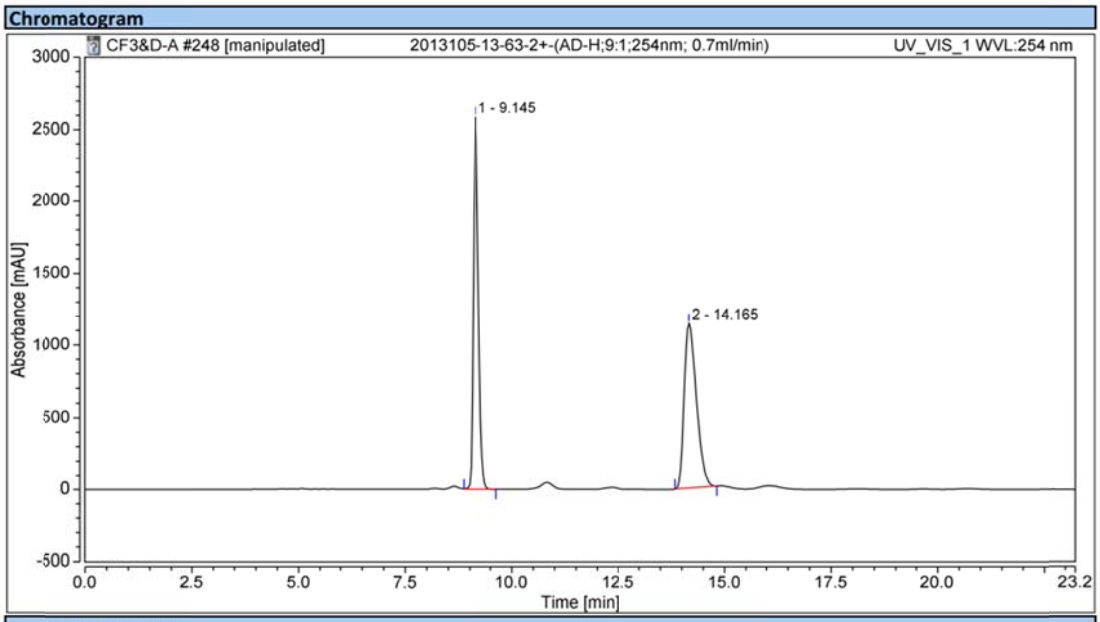
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.22	n.a.	231.630	43.935	21.12	n.a.	BMB*
2	10.20	n.a.	211.126	41.862	20.12	n.a.	BM *
3	10.75	n.a.	295.187	61.016	29.33	n.a.	MB*
4	12.93	n.a.	239.160	61.242	29.44	n.a.	BMB*
Total:			977.103	208.056	100.00	0.000	

HPLC of **3w**



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		9.102	28.861	194.205	5.22	11.17	n.a.
2		14.008	523.601	1544.293	94.78	88.83	n.a.
Total:			**552.462**	**1738.498**	**100.00**	**100.00**	

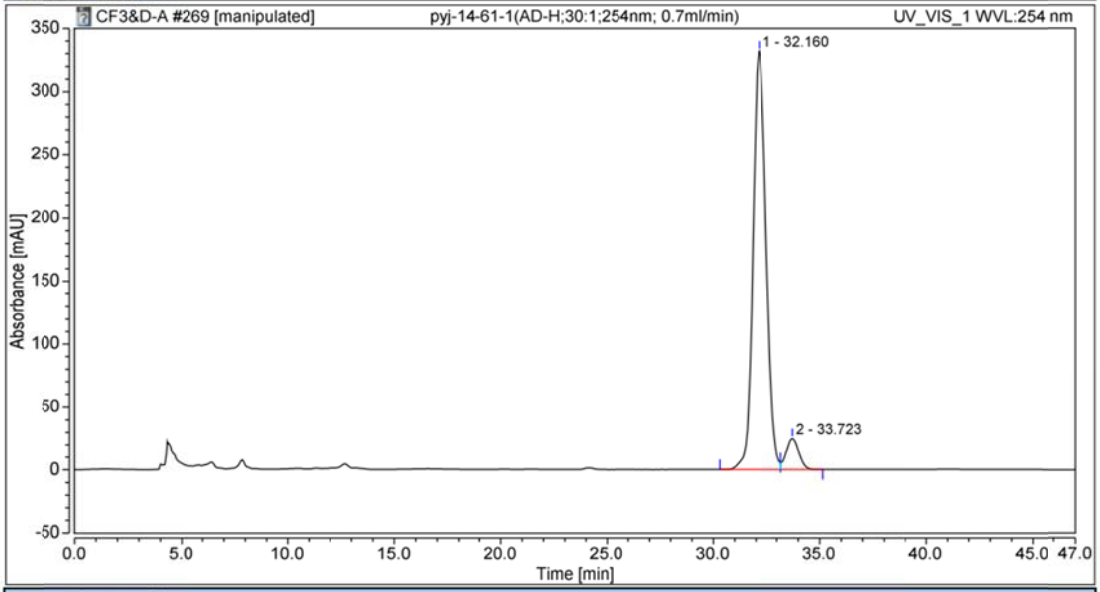


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		9.145	373.783	2590.259	49.70	69.46	n.a.
2		14.165	378.276	1138.944	50.30	30.54	n.a.
Total:			**752.059**	**3729.203**	**100.00**	**100.00**	

HPLC of **3x**

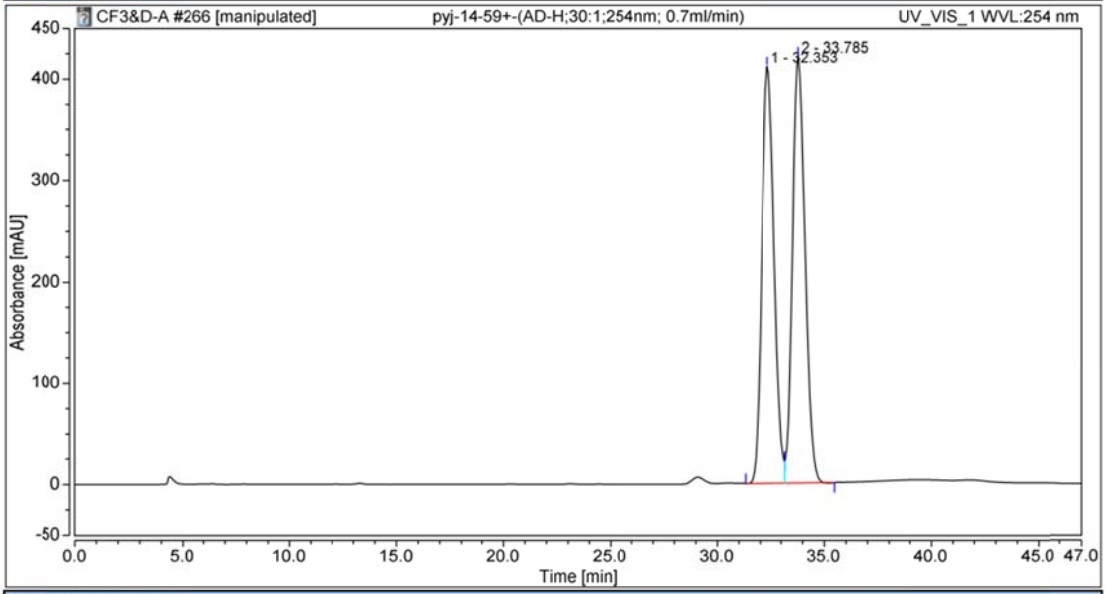
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		32.160	240.097	331.830	93.41	93.05	n.a.
2		33.723	16.949	24.791	6.59	6.95	n.a.
Total:			**257.047**	**356.621**	**100.00**	**100.00**	

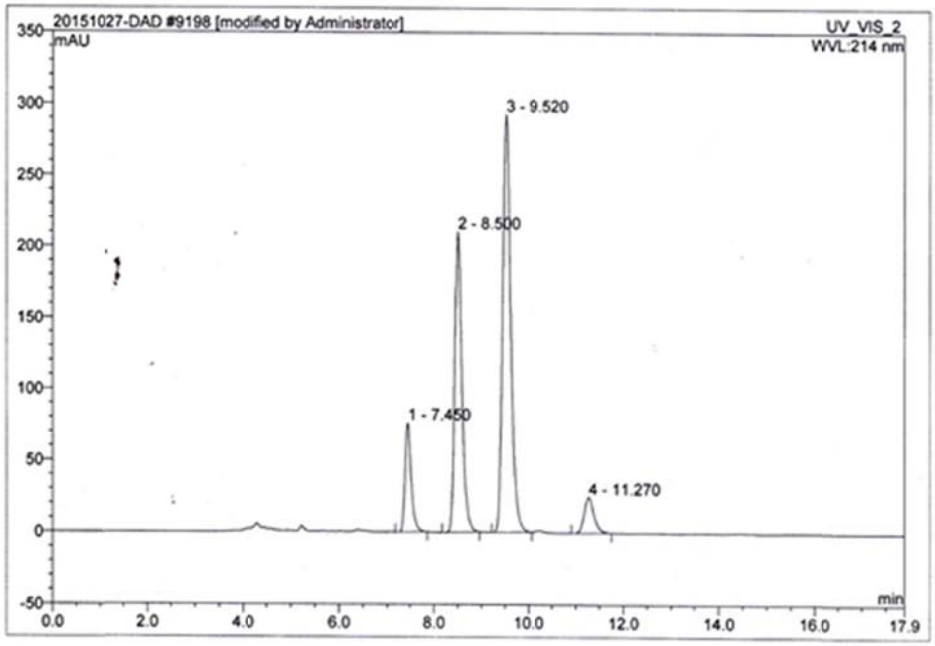
Chromatogram



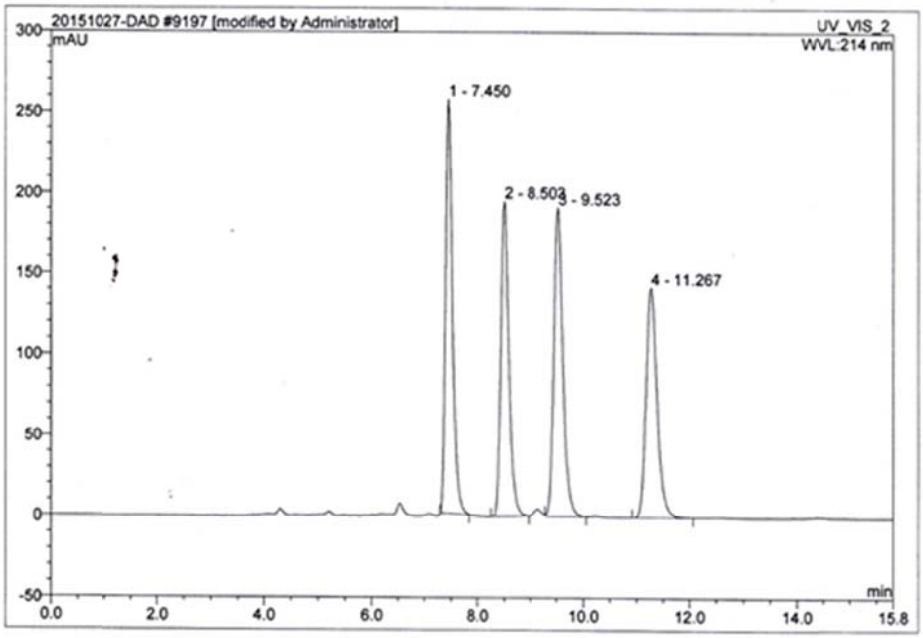
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		32.353	276.373	410.938	49.40	49.44	n.a.
2		33.785	283.031	420.301	50.60	50.56	n.a.
Total:			**559.404**	**831.238**	**100.00**	**100.00**	

HPLC of **3y**



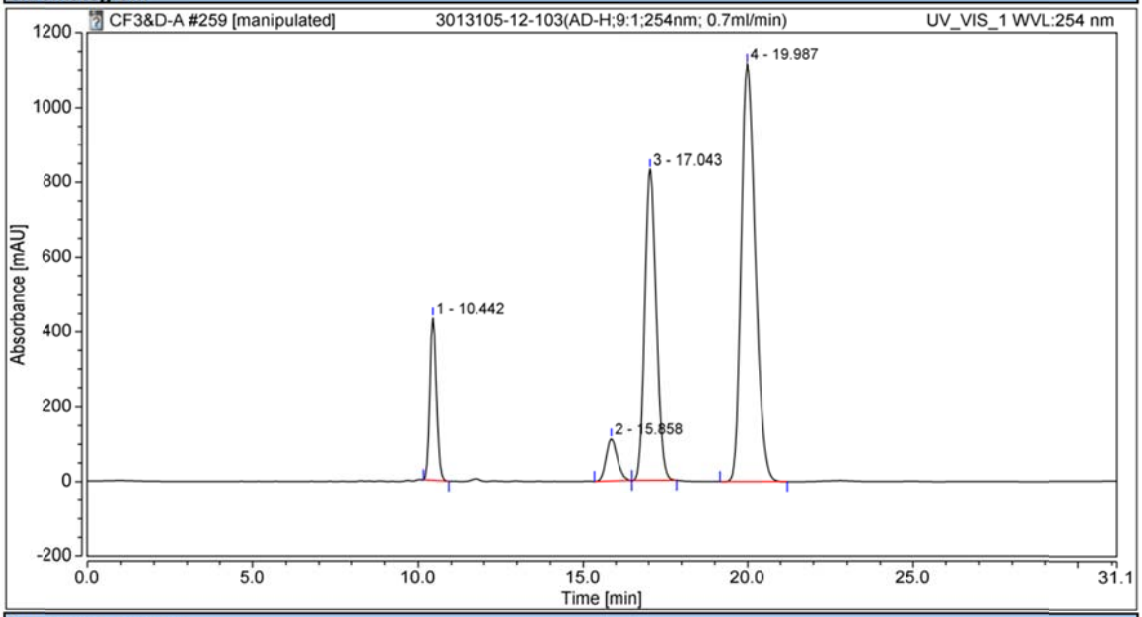
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.45	n.a.	76.351	11.444	10.26	n.a.	BMB*
2	8.50	n.a.	210.385	36.666	32.88	n.a.	BMB*
3	9.52	n.a.	292.917	57.374	51.45	n.a.	BMB*
4	11.27	n.a.	25.540	6.025	5.40	n.a.	BMB*
Total:			605.193	111.509	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.45	n.a.	256.525	38.579	26.80	n.a.	BMB*
2	8.50	n.a.	194.837	33.895	23.54	n.a.	BMB*
3	9.52	n.a.	191.157	37.551	26.08	n.a.	MB*
4	11.27	n.a.	142.404	33.940	23.58	n.a.	BMB
Total:			784.922	143.964	100.00	0.000	

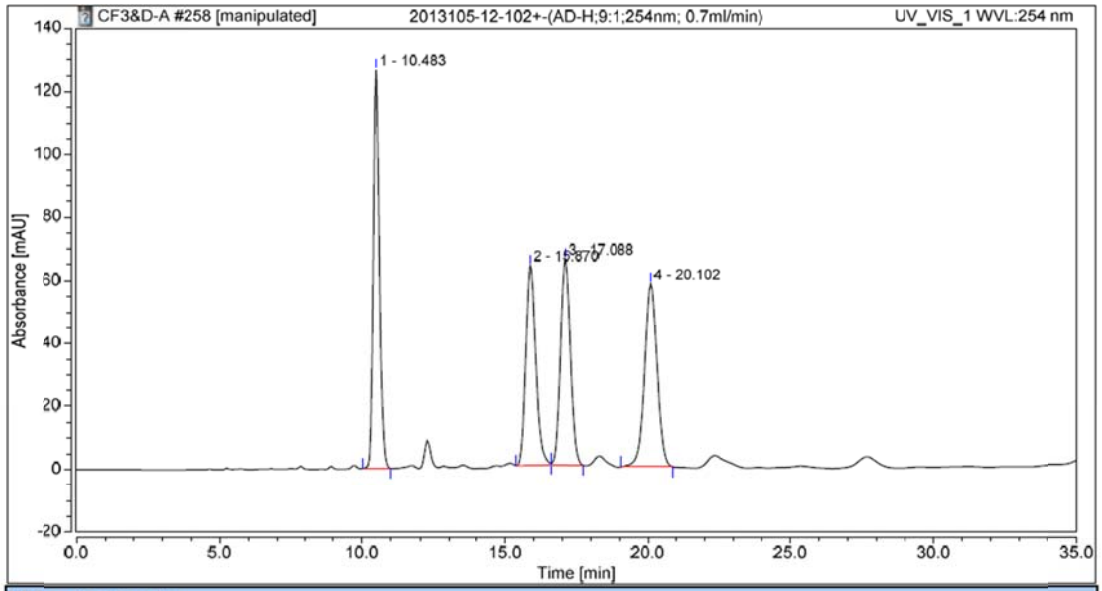
HPLC of **3z**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.442	100.694	434.934	9.66	17.43	n.a.
2		15.858	45.072	112.755	4.33	4.52	n.a.
3		17.043	338.274	830.774	32.47	33.30	n.a.
4		19.987	557.903	1116.383	53.54	44.75	n.a.
Total:			**1041.942**	**2494.846**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.483	30.445	126.475	27.18	40.31	n.a.
2		15.870	25.712	63.518	22.95	20.25	n.a.
3		17.088	26.241	65.507	23.43	20.88	n.a.
4		20.102	29.618	58.218	26.44	18.56	n.a.
Total:			**112.015**	**313.717**	**100.00**	**100.00**	