Supporting Information

Rh-catalyzed intramolecular decarbonylative cyclization of *ortho*-formyl group tethered alkylidenecyclopropanes (ACPs) for the construction of 2-methylindenes

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General Remarks

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz, respectively. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. HRMS spectra were recorded by ESI method. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI, and HRMS was measured on a HP-5989 instrument. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. The employed solvents were dried up by standard methods when necessary. Commercially obtained reagents such as Wilkinson's catalyst, $Rh(CO)Cl(PPh_3)_2$, $Rh(CO)H(PPh_3)_2$, phthalic anhydride derivatives, 2-benzoylbenzoic acid derivatives, $SOCl_2$, IBX, nBuLi et al. were purchased from Admas-beta, TCI and J&K, and used without further purification. All reactions were monitored by TLC with silica gel coated plates (Huanghai GF254). Flash column chromatography was performed by using 300-400 mesh silica gel eluting with ethyl acetate and petroleum ether at increased pressure. Abbreviations are reported as follows: EA = ethyl acetate, DCM = dichloromethane, DCE = 1,2-dichloroethane, MeOH = methanol, THF = tetrahydrofuran, DMF = N,N-dimethylformamide, DIBAL-H = diisobutylaluminium hydride, IBX = 2-iodoxybenzoic acid, rt = room temperature, acac = acetylacetone, Ac = Acetyl.

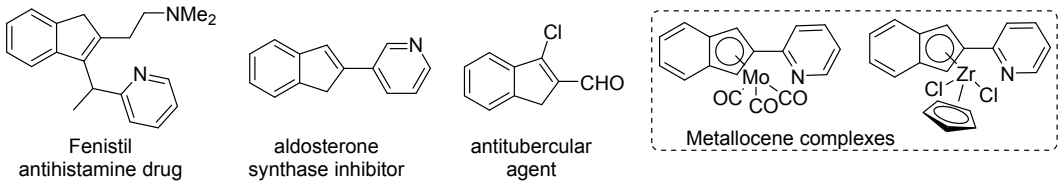
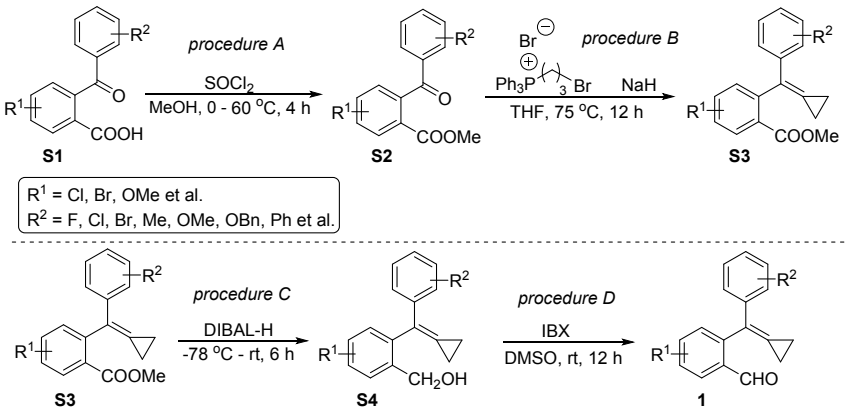


Figure S1. Medicines and metallocene complexes bearing indene structures.

General procedure for the preparation of compounds 1a-1q

Methods 1: For the synthesis of substrates 1a, 1d, 1e, 1f, 1i, 1j, 1k, 1l, 1m, 1n, 1o:



Compounds **S1** and compounds **S2** were commercially available or prepared according to the previous literature.[1]

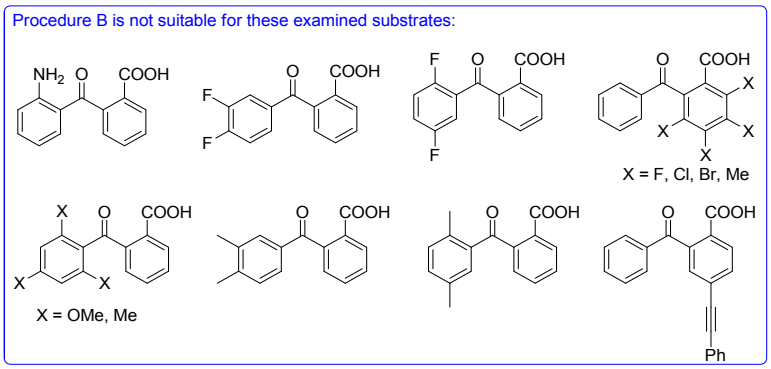
General procedure A: To a solution of **S1** in anhydrous MeOH (0.5 M) at ice-water bath (0 °C), $SOCl_2$ was added dropwise. After completion of addition, the mixture was stirred at 0 °C for 30 min, and then the clear solution was heated at 60 °C for 3 h. After completion of the reaction, the excess solvent was evaporated under vacuum, and the residue was purified by a flash column chromatograph on silica gel using PE/EA (10:1) as the eluent to yield the product **S2** as a white solid.

General procedure B: A solution of (4-bromopropyl)triphenylphosphonium bromide (1.2 eq.) and NaH (2.4 eq.) in ultra-dry THF (25 mL) was stirred at 75 °C under Ar atmosphere for 2 h. Afterwards the solution of compound **S2** in ultra-dry THF (10 mL) was added and the reaction solution was stirred at 75 °C until compound **S2** was consumed completely (2-10 h). Then the reaction mixture was cooled to room temperature, and the mixture was filtered through a celite pad. The filtrate was concentrated under reduced pressure and the residue was purified by a flash column chromatography on silica gel (PE/EA = 50:1-20:1) to afford the product **S3**.

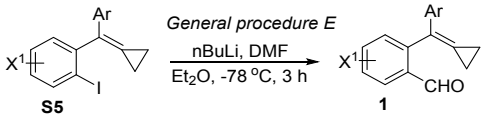
General procedure C: DIBAL-H (1.0M, 2.2 equiv) was added slowly to a solution of **S3** in dry

DCM in a flamed-dried flask at -78 °C under the protection of Ar atmosphere. After completion of addition, the mixture was allowed to stir at rt for 3-6 h. After completion of the reaction, the reaction was quenched with 10 mL of H_2O, 30 mL of 15% NaOH, 10 mL of H_2O sequence and the resulting mixture was stirred at rt for 1 h. Then, the mixture was extracted with EA (3 x 20 mL). The combined extracts were washed with saturated NaCl aq., dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under vacuum, and the residue was purified by a flash column chromatograph on silica gel using PE/EA (5:1) as the eluent to yield the product **S4**.

General procedure D: Compound **S4** was dissolved in DMSO (1.0 M) at rt, IBX (1.1 equiv) was added in one portion, and then the mixture was stirred at rt overnight. The reaction was quenched by addition of water (10 mL) along with the generation of precipitations. Then, the mixture was extracted with EA (3 x 20 mL), and the combined extracts were washed with saturated NaCl, dried over anhydrous Na_2SO_4. After the solution was filtered, the solvent was evaporated under vacuum, and the residue was purified by a flash column chromatography (Al_2O_3, PE/EA = 20:1-10:1) to afford the product **1**.



Methods 2: For the synthesis of substrates 1a, 1b, 1c, 1g, 1h, 1p, 1q, 1r:



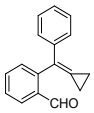
Compounds **S5**[2] and compound **1**[3] were prepared according to the previous literature.

General procedure E: To a solution of **S5** in anhydrous Et_2O (1.0 M) was added nBuLi (1.6 M, 1.3 eq.) at -78 °C over 10 min under Ar atmosphere. The mixture was stirred at -78 °C for 1 h, and then DMF (1.3 eq.) was added by a syringe at -78 °C under Ar atmosphere. Afterwards, the mixture was stirred at rt for 3 h, and then the reaction was quenched with water (10 mL) at rt. The mixture was extracted with EA (3 x 30 mL), and the combined extracts were washed with brine, dried over

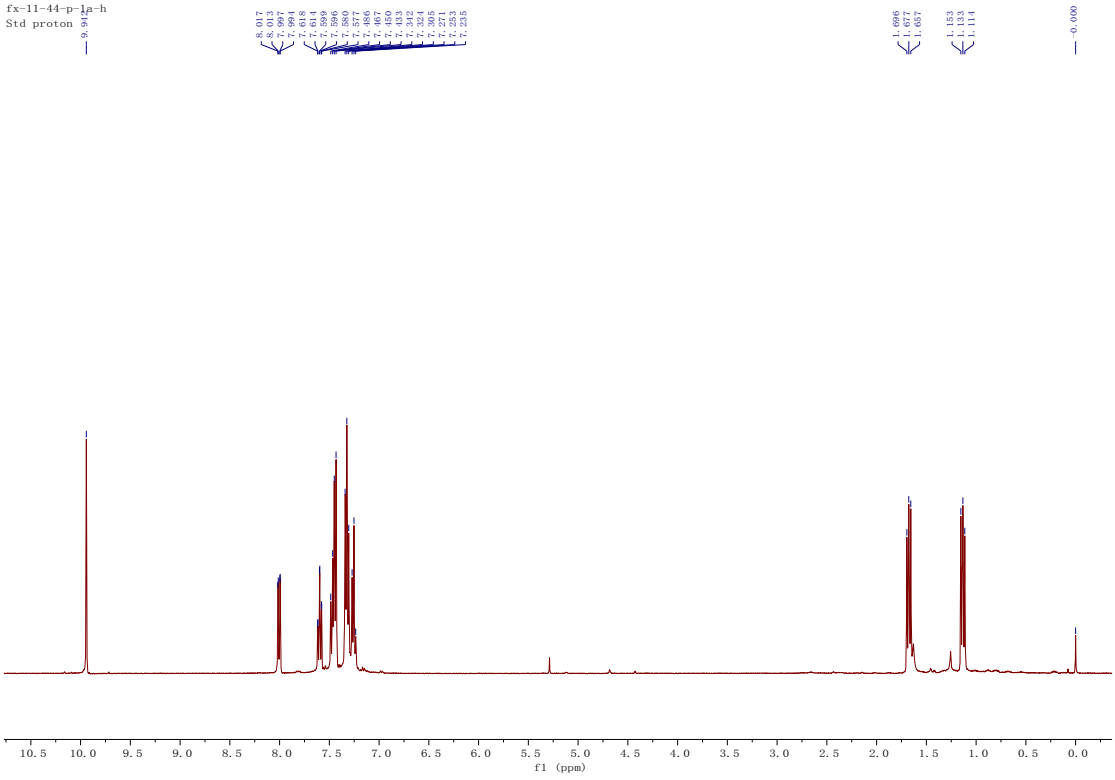
anhydrous Na_2SO_4. After the solution was filtered through a celit pad, the solvent was evaporated under vacuum and the residue was purified by a flash column chromatograph on Al_2O_3 using PE/EA (10:1) as the eluent to yield the product **1**.

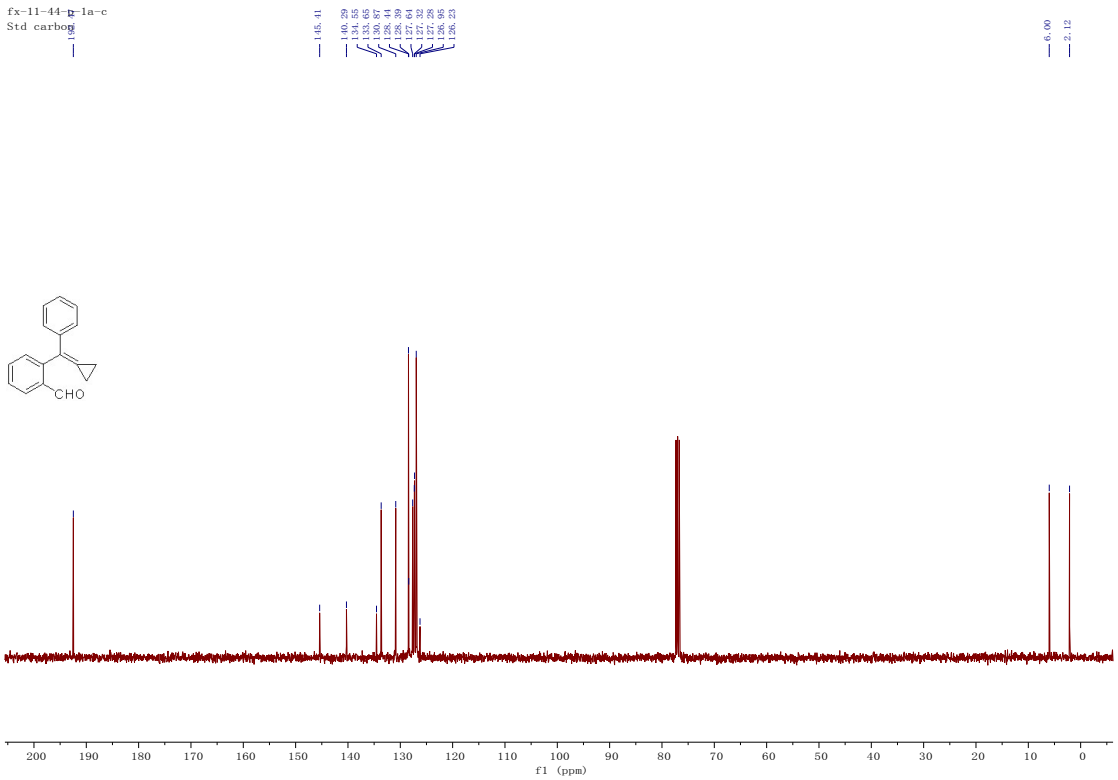
Note: these compounds (compounds 1) are quite labile and sensitive to moisture or acidic media. They should be used for the reaction immediately after preparation.

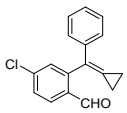
Spectroscopic data for substrates **1a-1r**



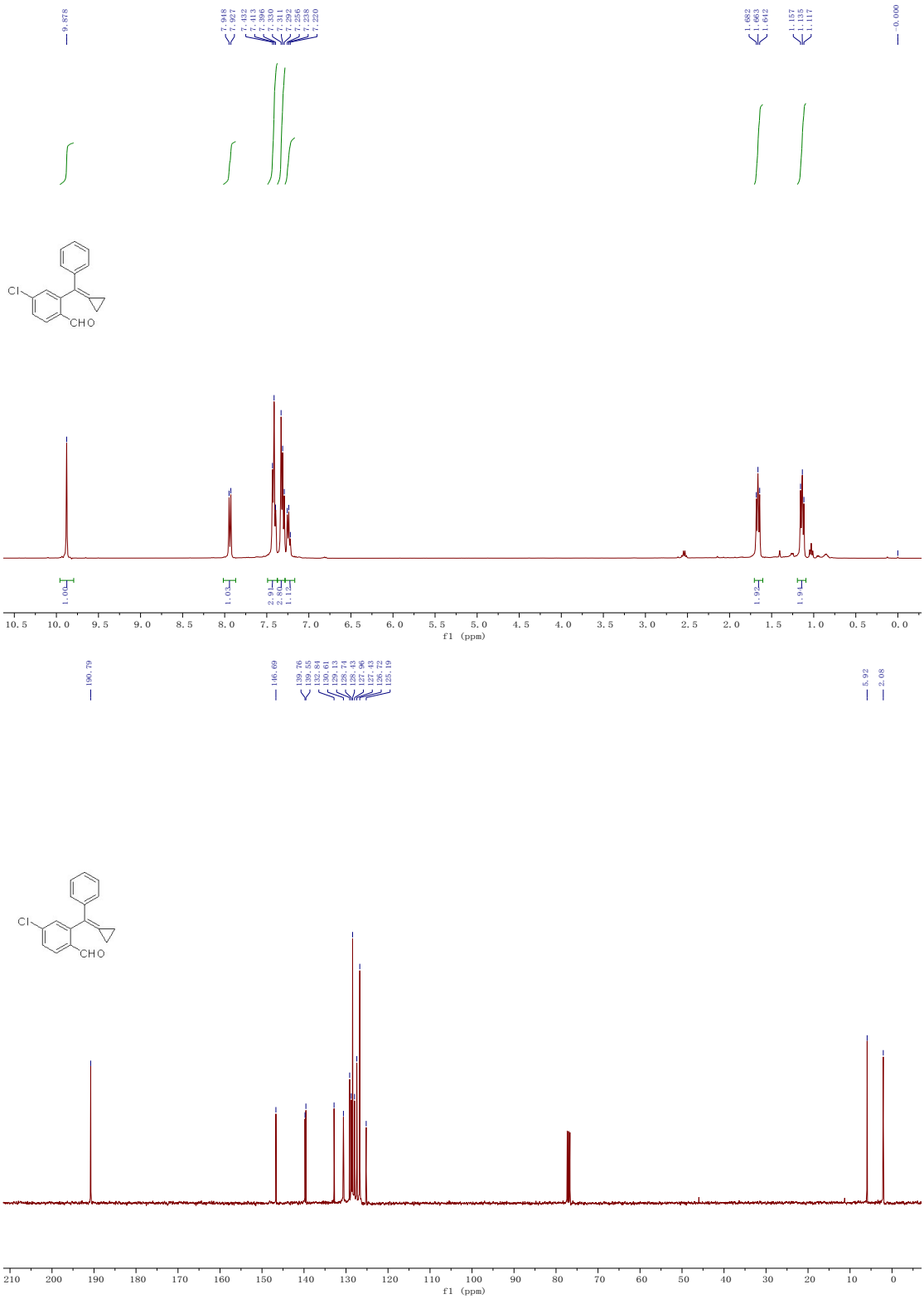
Compound 1a: A pale yellow solid (171.0 mg, 38%); M.p. 63 - 64 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13 (t, 2H), 1.68 (t, 2H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.37 (m, 3H), 7.41 – 7.49 (m, 3H), 7.60 (ddd, *J* = 7.5, 1.5, Hz 1H), 8.01 (dd, *J* = 7.8, 1.4 Hz, 1H), 9.94 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.1, 6.0, 126.2, 127.0, 127.3, 127.3, 127.6, 128.4, 128.4, 130.9, 133.7, 134.5, 140.3, 145.4, 192.5. IR (neat) ν 2964, 2847, 2745, 1686, 1641, 1593, 1493, 1388, 1211, 1192, 823, 769, 758, 697 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{15}O$ requires (M^+): 235.1117, Found: 235.1113.

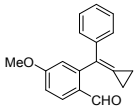






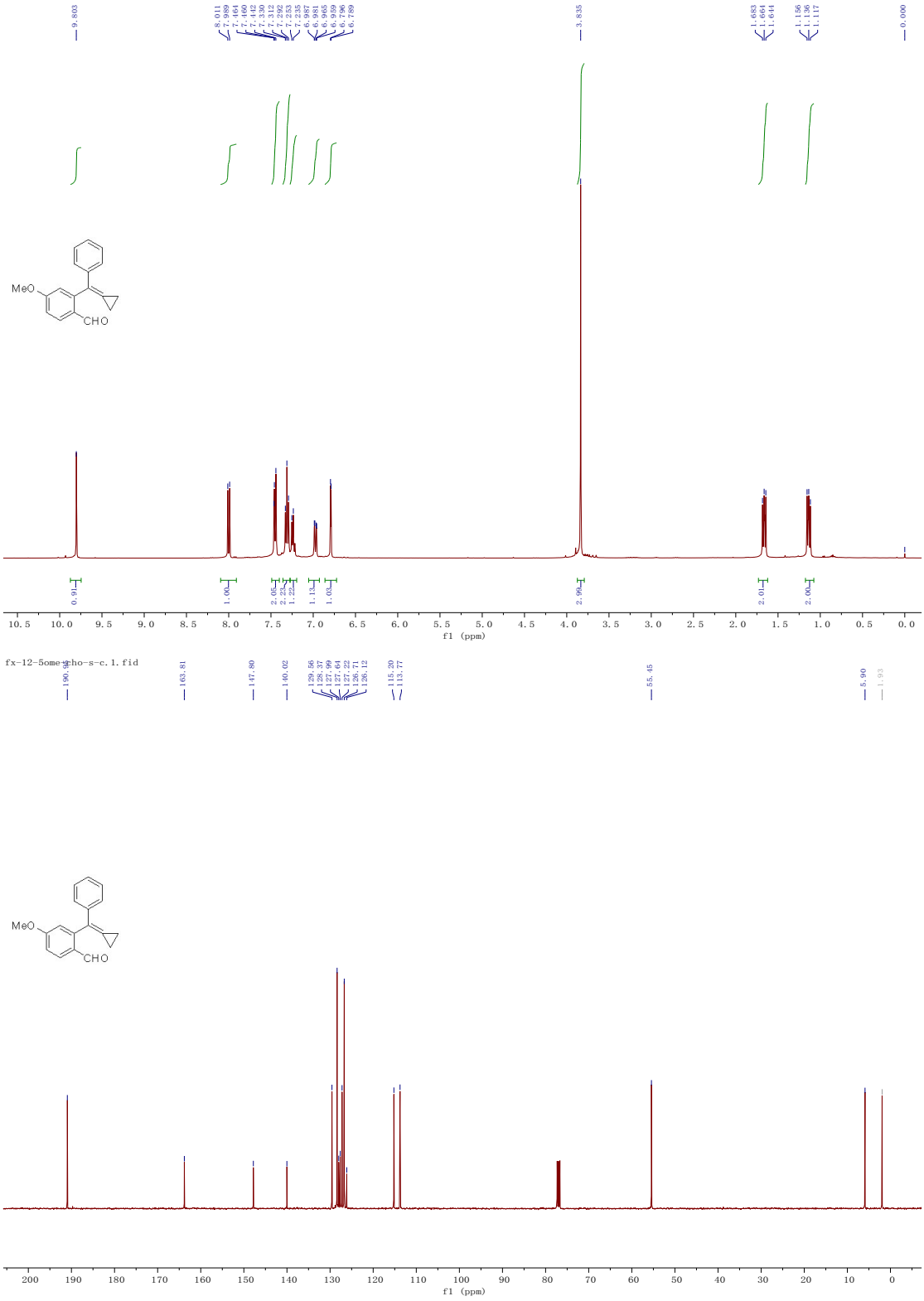
Compound 1b: A yellow oil (156.8 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 – 1.19 (m, 2H), 1.61 – 1.71 (m, 2H), 7.17 – 7.28 (m, 1H), 7.28 – 7.37 (m, 3H), 7.37 – 7.49 (m, 3H), 7.94 (d, *J* = 8.3 Hz, 1H), 9.88 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.1, 5.9, 125.2, 126.7, 127.4, 128.0, 128.4, 128.7, 129.1, 130.6, 132.8, 139.5, 139.8, 146.7, 190.8. IR (neat) ν 2972, 2923, 1772, 1705, 1596, 1447, 1324, 1271, 1237, 1070, 1044, 957, 878, 815, 758, 700 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{13}OCl$ requires (M^+): 268.0655, Found: 268.0653.

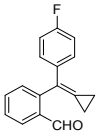




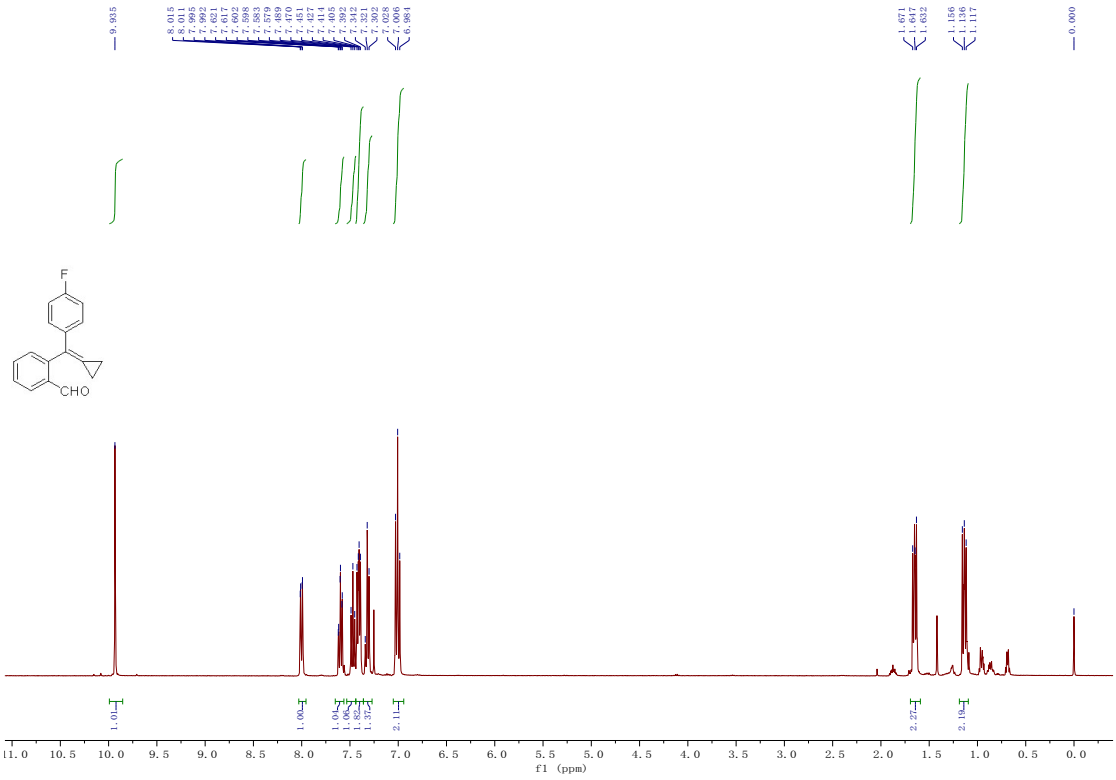
Compound 1c: A yellow oil (88.0 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.08 – 1.18 (m, 2H), 1.62 – 1.73 (m, 2H), 3.84 (s, 3H), 6.79 (d, *J* = 2.6 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.24

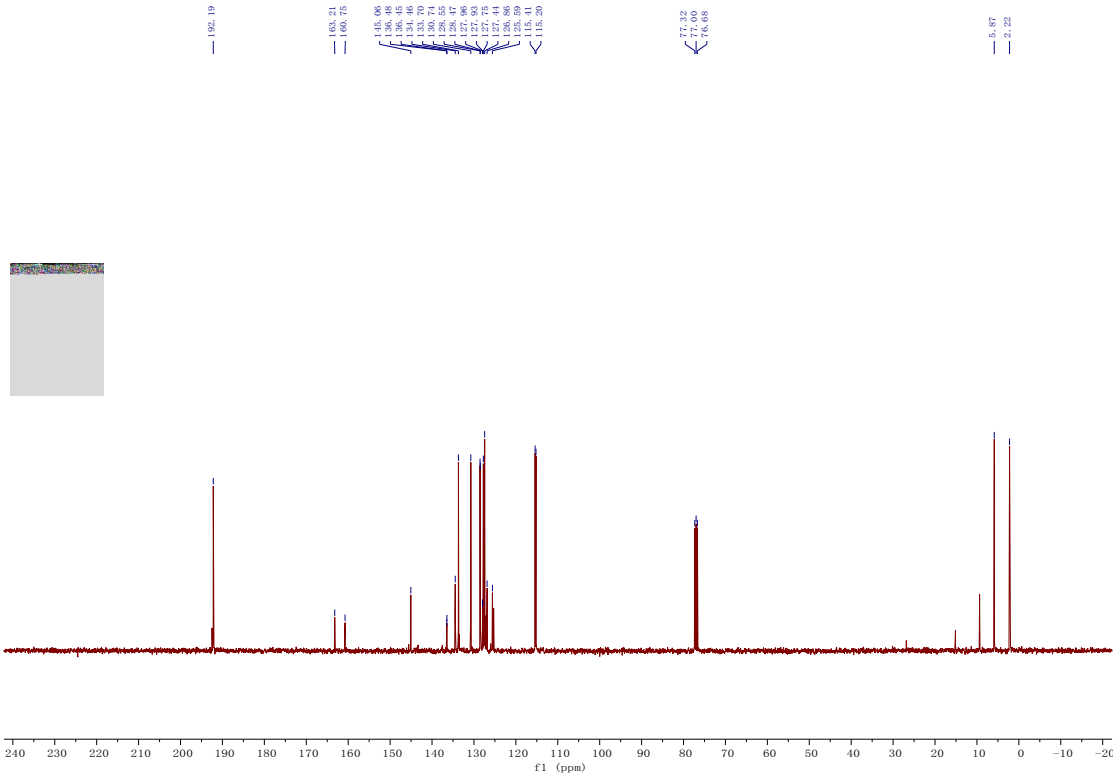
(d, J = 7.2 Hz, 1H), 7.27 – 7.36 (m, 2H), 7.40 – 7.49 (m, 2H), 8.00 (d, J = 8.8 Hz, 1H), 9.80 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.9, 5.9, 55.4, 113.8, 115.2, 126.1, 126.7, 127.2, 127.6, 128.0, 128.4, 129.6, 140.0, 147.8, 163.8, 190.9. IR (neat) ν 3058, 3037, 3001, 2959, 2922, 2849, 2831, 1769, 1683, 1594, 1490, 1446, 1285, 1239, 1170, 1028, 853, 759, 723, 696 cm^{-1}. HRMS (EI) Calcd. for $C_{18}H_{16}O_2$ requires (M^+): 264.1150, Found: 264.1148.





Compound 1d: A yellow oil (773.1 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 – 1.19 (m, 2H), 1.59 – 1.69 (m, 2H), 6.94 – 7.05 (m, 2H), 7.32 (dd, *J* = 7.8 Hz, 1H), 7.36 – 7.44 (m, 2H), 7.47 (dd, *J* = 7.6 Hz, 1H), 7.60 (td, *J* = 7.5, 1.5 Hz, 1H), 8.00 (dd, *J* = 7.8 Hz, 1.5, 1H), 9.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.22, 5.87, 115.30 (d, *J* = 21.5 Hz), 125.59, 126.86, 127.44, 127.75, 127.95 (d, *J* = 2.0 Hz), 128.51 (d, *J* = 8.0 Hz), 130.74, 133.70, 134.46, 136.47 (d, *J*= 3.3 Hz), 145.06, 161.98 (d, *J* = 247.5 Hz), 192.19. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.7. IR (neat) ν 3061, 2975, 2920, 2842, 2750, 1780, 1691, 1596, 1506, 1224, 1193, 1158, 1014, 904, 833, 822, 806, 759, 677 cm^{-1}. HRMS (EI) Calcd. for $C_{16}H_{13}OF$ requires (M^+): 252.0950, Found: 252.0951.

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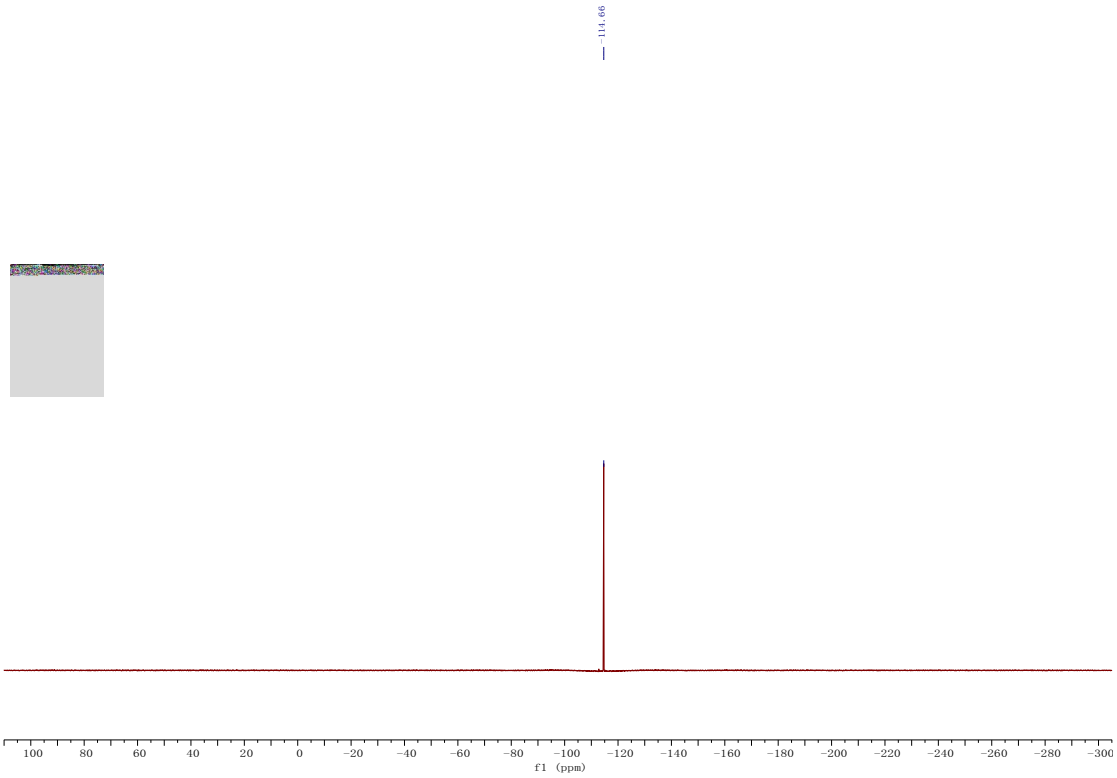
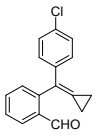
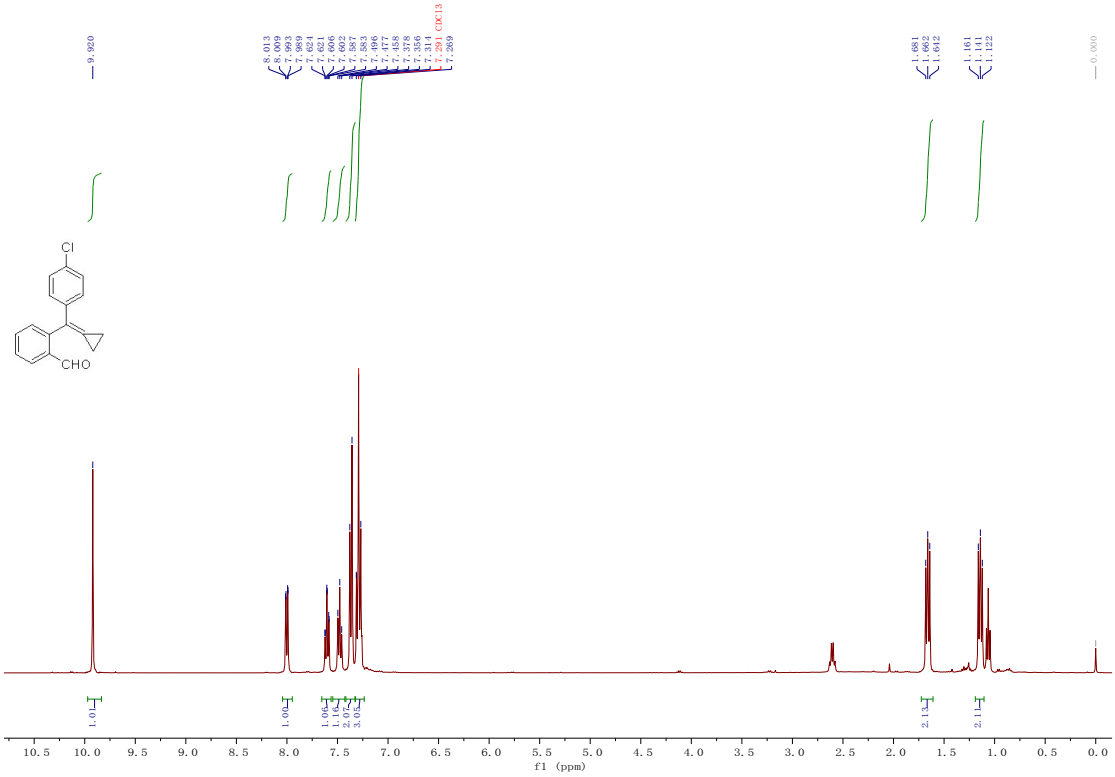
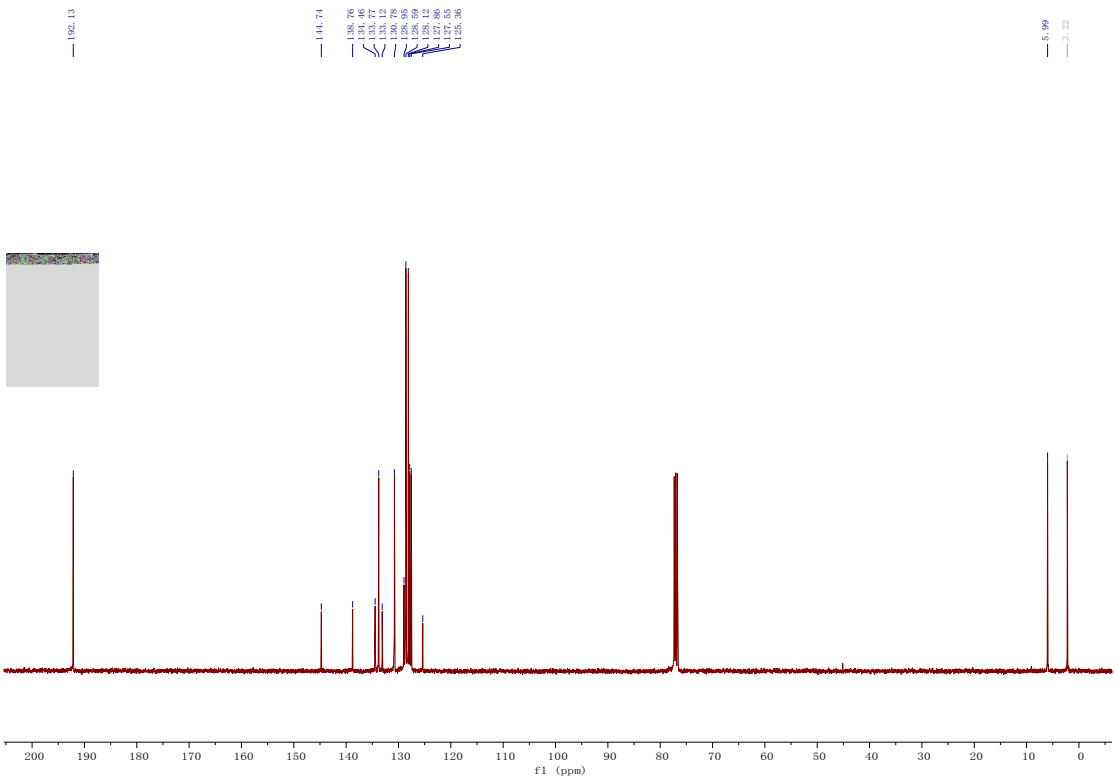
160.75
145.06
136.48
136.45
134.46
133.70
130.74
128.55
128.47
127.96
127.90
127.75
127.44
126.96
126.58
115.41
115.20
77.32
77.00
76.68
5.87
2.22
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

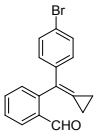

114.66
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300
f1 (ppm)


Cl
CHO

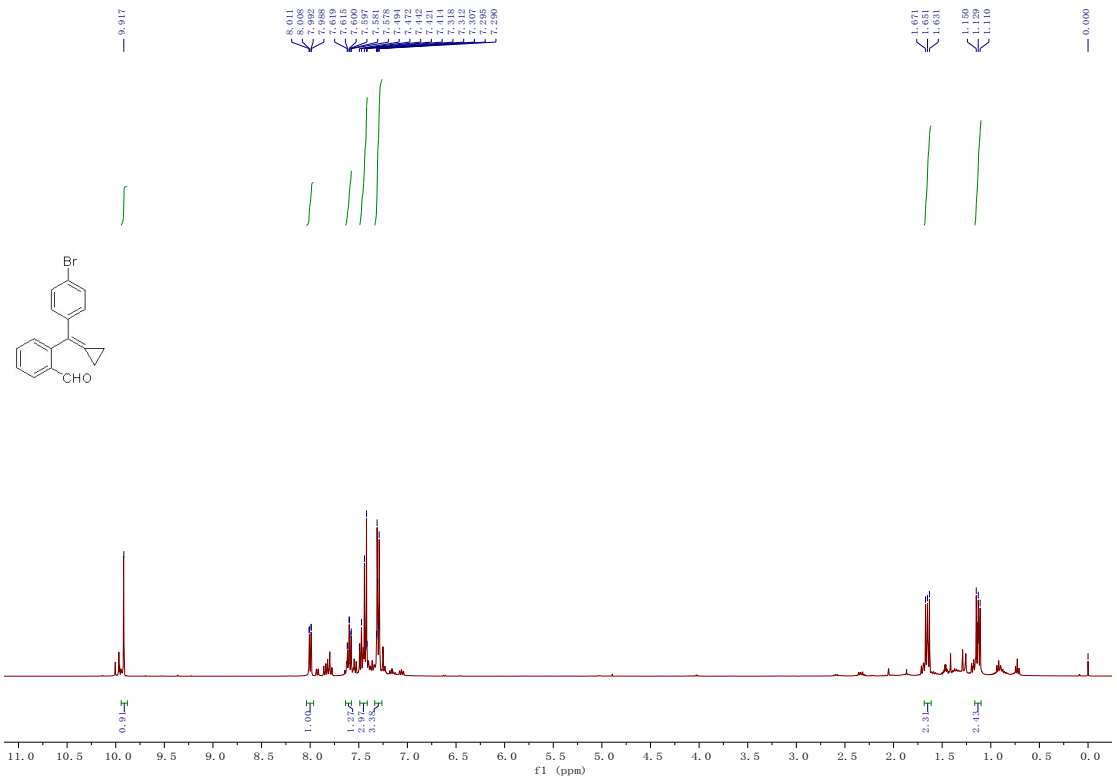
Compound 1e: An orange oil (842.0 mg, 98%). This compound contains some impurities, which are difficult to be purified. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.10 – 1.19 (m, 2H), 1.61 – 1.73 (m, 2H), 7.24 – 7.32 (m, 3H), 7.32 – 7.42 (m, 2H), 7.48 (dd, *J* = 7.6 Hz, 1H), 7.60 (ddd, *J* = 7.5, 1.5 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.5 Hz, 1H), 9.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.2, 6.0, 125.4, 127.6, 127.9, 128.1, 128.6, 128.9, 130.8, 133.1, 133.8, 134.5, 138.8, 144.7, 192.1. IR (neat) ν 3069, 2969, 2831, 1774, 1691, 1595, 1489, 1209, 1090, 1013, 820, 759, 732, 719 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{13}OCl$ requires (M^+): 268.0655, Found: 268.0657.







Compound 1f: A yellow solid (201.1 mg, 41%); This compound contains some impurities, which are difficult to be purified. M.p. 55 - 56 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.10 – 1.16 (m, 2H), 1.61 – 1.69 (m, 2H), 7.26 – 7.34 (m, 3H), 7.41 – 7.49 (m, 3H), 7.60 (ddd, J = 7.5, 1.5 Hz, 1H), 8.00 (dd, J = 7.8, 1.2 Hz, 1H), 9.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.2, 5.9, 121.2, 125.3, 127.5, 127.8, 128.3, 129.0, 130.7, 131.4, 133.7, 134.4, 139.1, 144.5, 191.9. IR (neat) ν 3063, 2972, 2925, 2849, 2745, 1780, 1691, 1596, 1506, 1224, 1193, 1158, 833, 822, 759, 677 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{13}OBr$ requires (M^+): 312.0150, Found: 312.0146.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7.600
7.597
7.581
7.578
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7.442
7.421
7.414
7.318
7.313
7.307
7.295
7.290
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1.631
1.150
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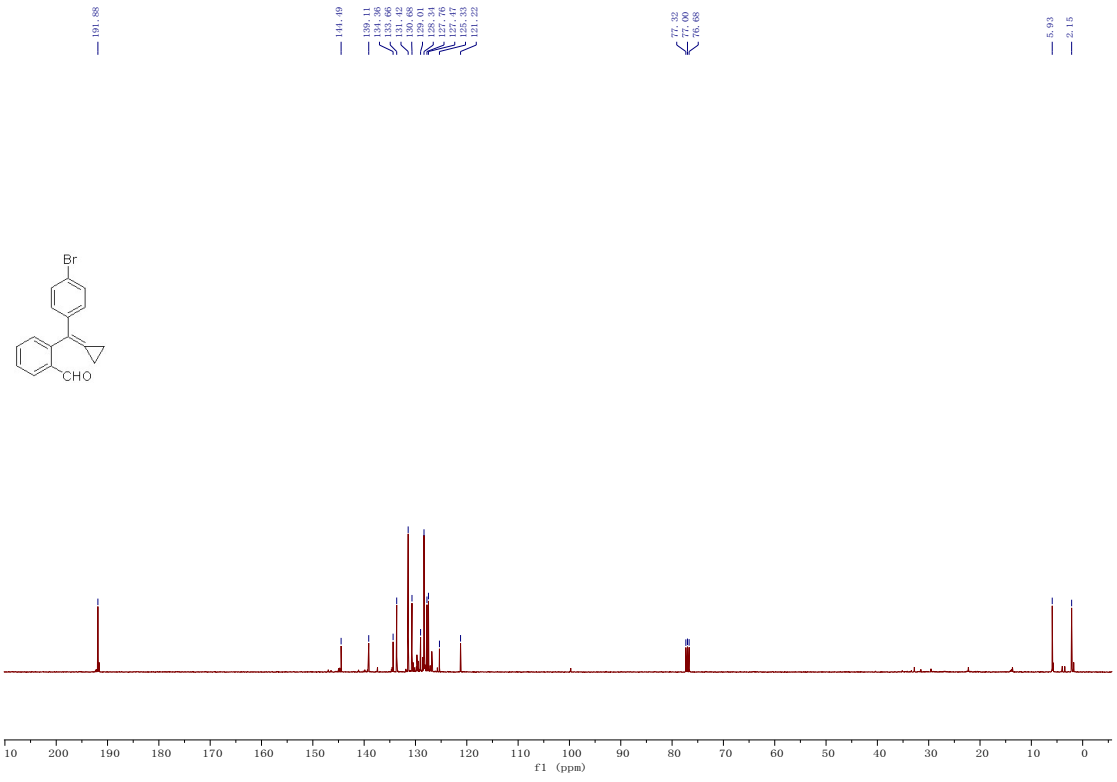
f1 (ppm)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133.66
131.42
130.68
129.01
128.34
127.76
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5.93
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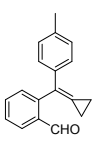
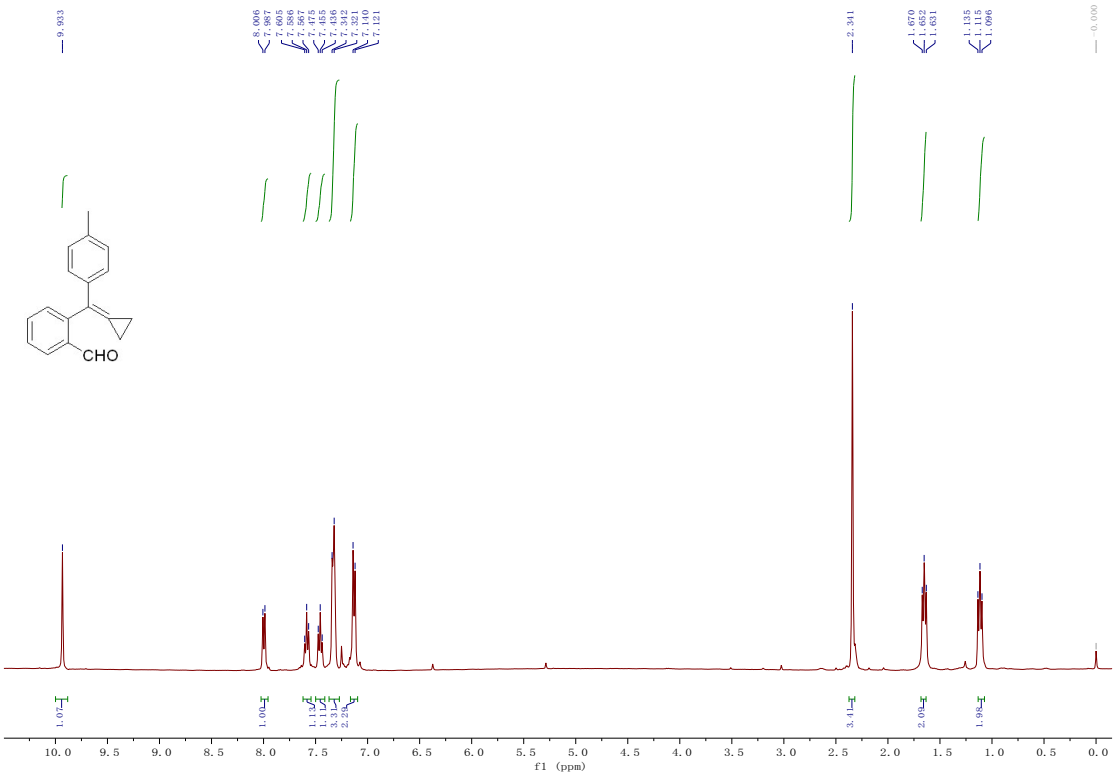
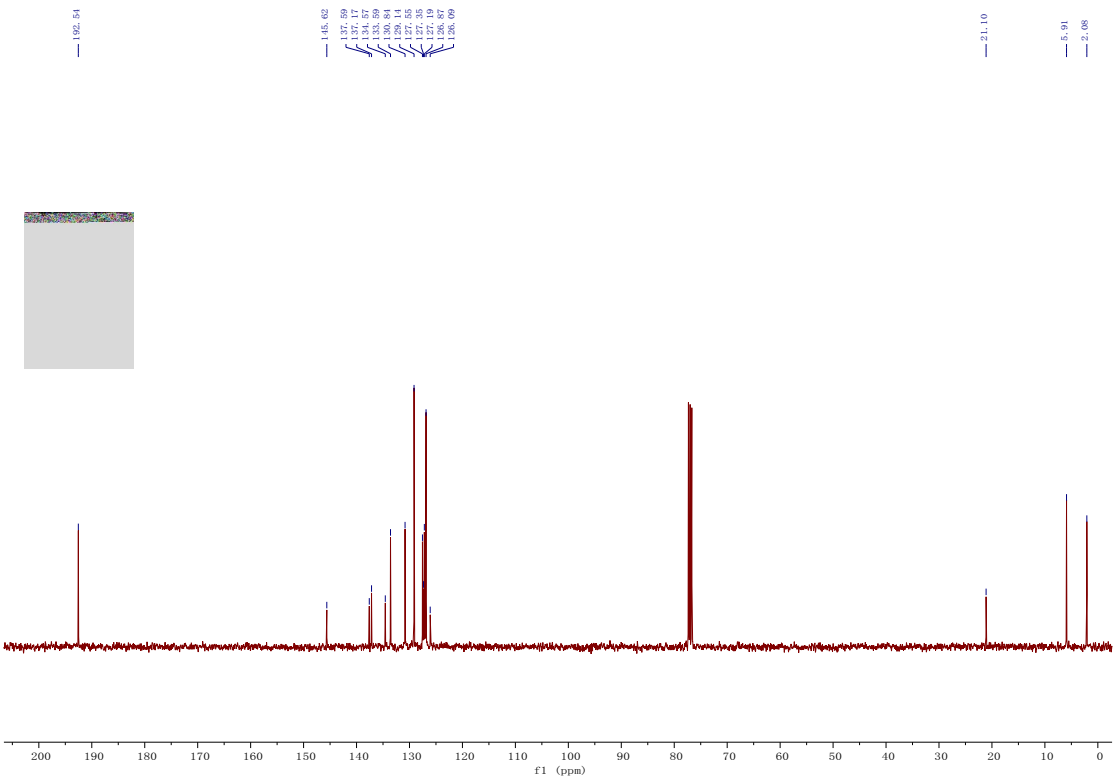
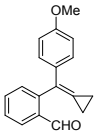
Br
CHO
f1 (ppm)


CHO

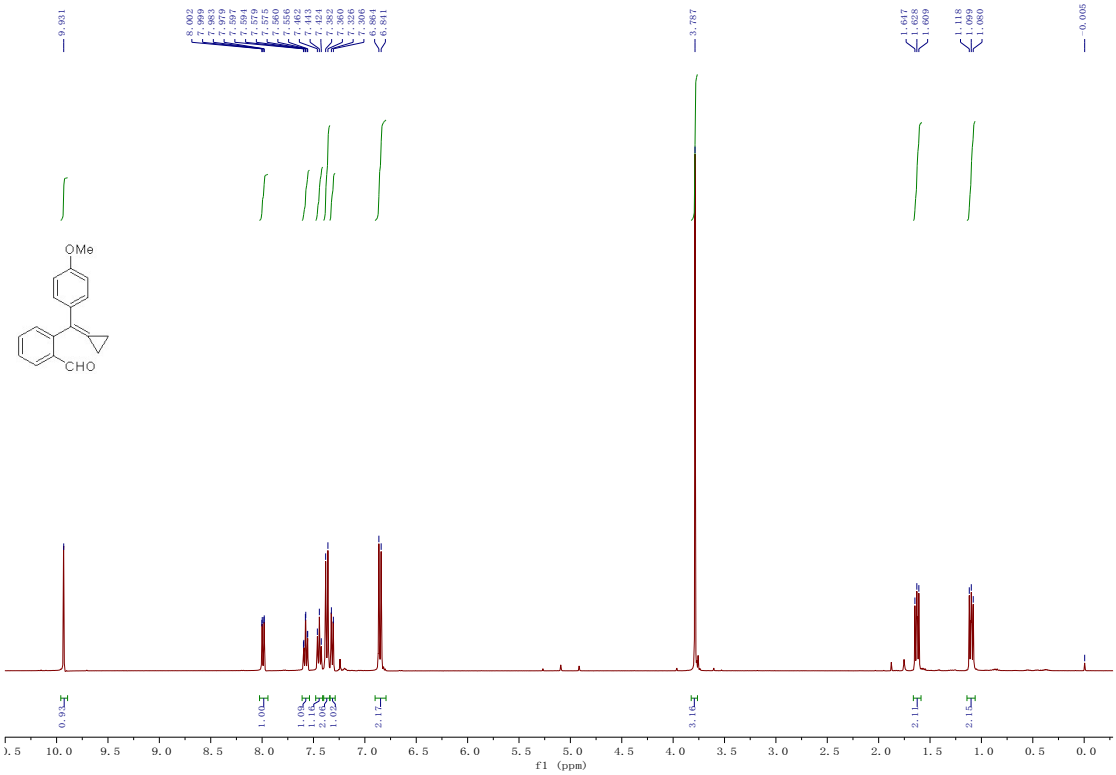
Compound 1g: A yellow solid (490.1 mg, 71%); M.p. 63 - 64 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.11 (t, *J* = 7.7 Hz, 2H), 1.66 (t, *J* = 7.3 Hz, 2H), 2.34 (s, 3H), 7.10 – 7.16 (m, 2H), 7.27 – 7.37 (m, 3H), 7.46 (dd, *J* = 7.6 Hz, 1H), 7.59 (dd, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 9.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.1, 5.9, 21.1, 76.7, 77.0, 77.3, 126.1, 126.9, 127.2, 127.3, 127.6, 129.1, 130.8, 133.6, 134.6, 137.2, 137.6, 145.6, 192.5. IR (neat) ν 3030, 2917, 2857, 1764, 1693, 1602, 1511, 1464, 1326, 1178, 1019, 1002, 956, 807, 755, 703 cm^{-1}. HRMS (EI) Calcd. for $C_{18}H_{16}O$ requires (M^+): 248.1201, Found: 248.1195.







Compound 1h: A orange solid (813.3 mg, 89%); M.p. 53 - 54 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.06 – 1.14 (m, 2H), 1.59 – 1.66 (m, 2H), 3.79 (s, 3H), 6.79 – 6.90 (m, 2H), 7.32 (d, J = 7.7 Hz, 1H), 7.34 – 7.40 (m, 2H), 7.44 (dd, J = 7.6 Hz, 1H), 7.58 (ddd, J = 7.5, 1.5 Hz, 1H), 7.99 (dd, J = 7.8, 1.4 Hz, 1H), 9.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.0, 5.8, 55.2, 113.8, 125.6, 126.1, 127.1, 127.5, 128.1, 130.8, 133.1, 133.5, 134.5, 145.6, 158.8, 192.5. IR (neat) ν 3066, 2998, 2930, 2836, 2737, 1780, 1692, 1596, 1509, 1464, 1300, 1248, 1176, 1032, 908, 825, 759, 731 cm^{-1}. HRMS (EI) Calcd. for $C_{18}H_{16}O_2$ requires (M^+): 264.1150, Found: 264.1157.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7.985
7.979
7.597
7.594
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7.575
7.560
7.556
7.445
7.413
7.424
7.382
7.380
7.358
7.306
6.864
6.841
3.787
1.647
1.638
1.609
1.118
1.089
1.080
-0.005
OMe
CHO
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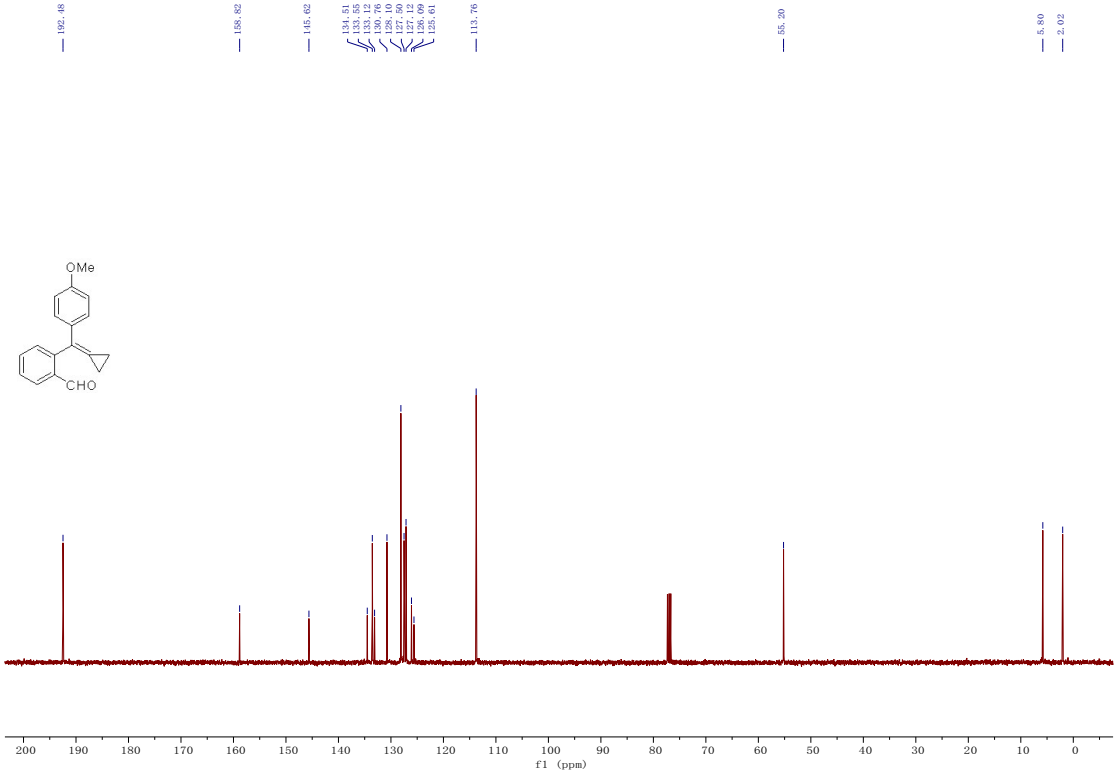
1.00
1.09
1.14
1.05
2.17
3.16
2.11
2.14
f1 (ppm)


192.48
158.82
145.62
134.51
133.55
133.12
130.76
128.10
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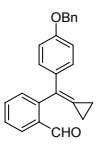
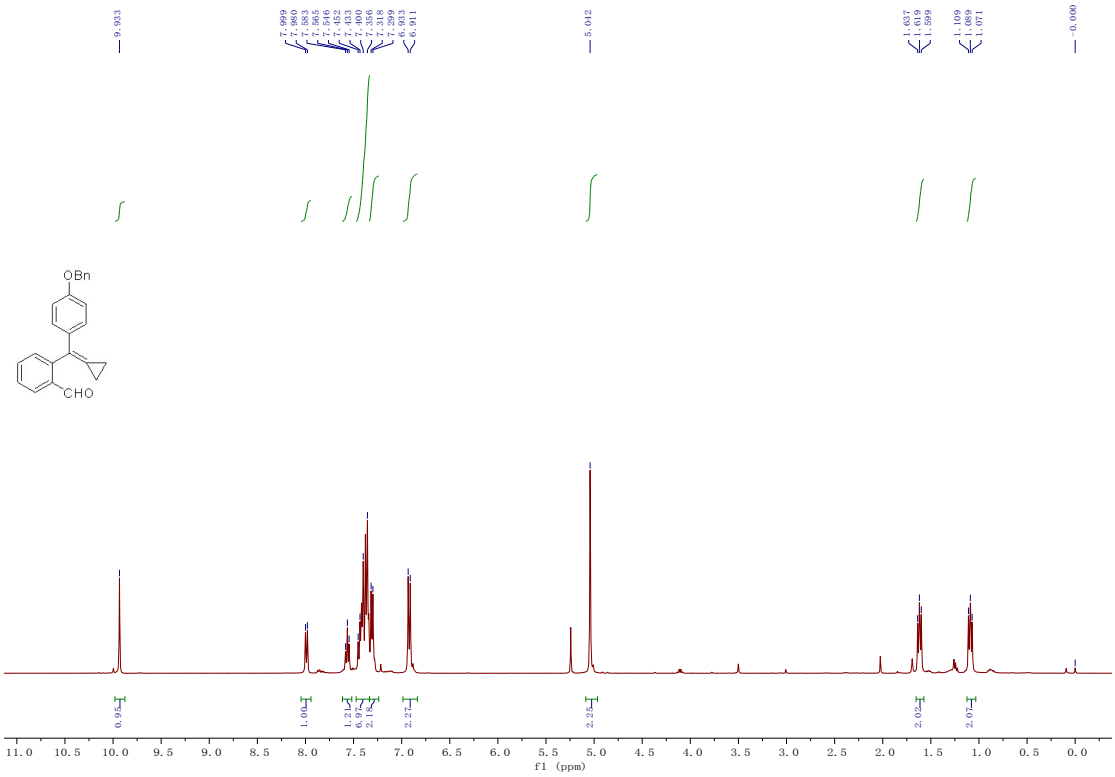
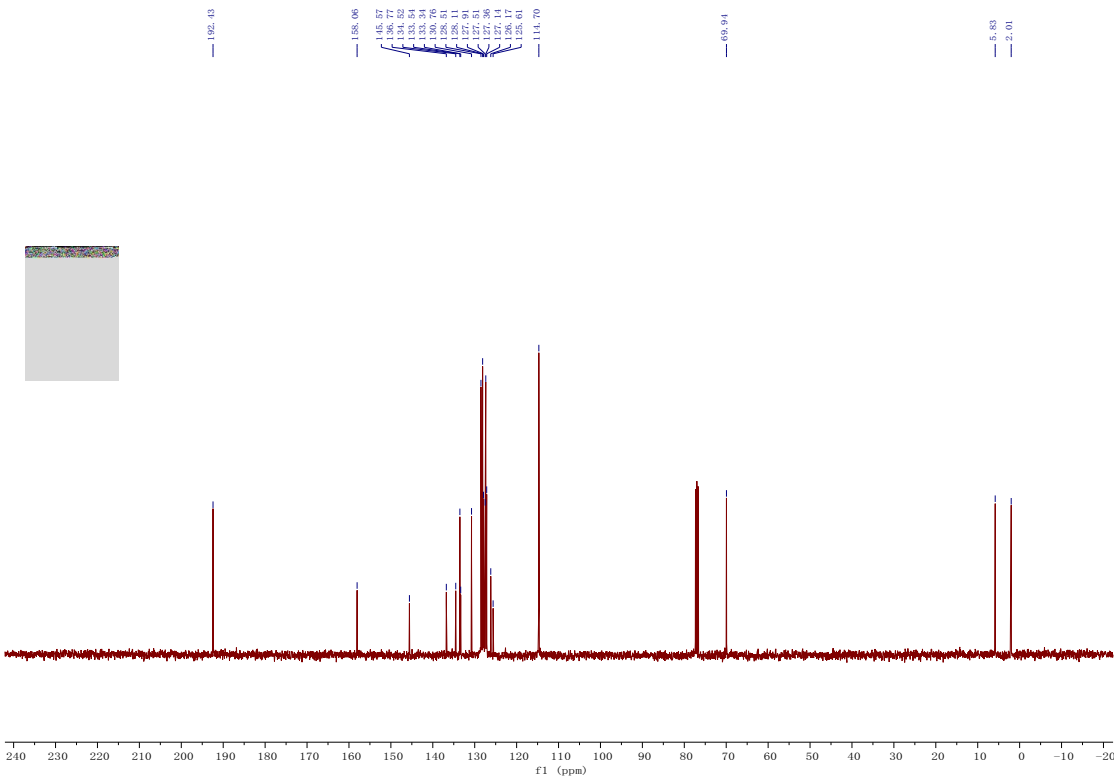
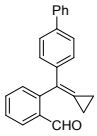
127.12
126.09
125.61
113.76
55.20
5.80
2.02
OMe
CHO
f1 (ppm)


OBn
CHO

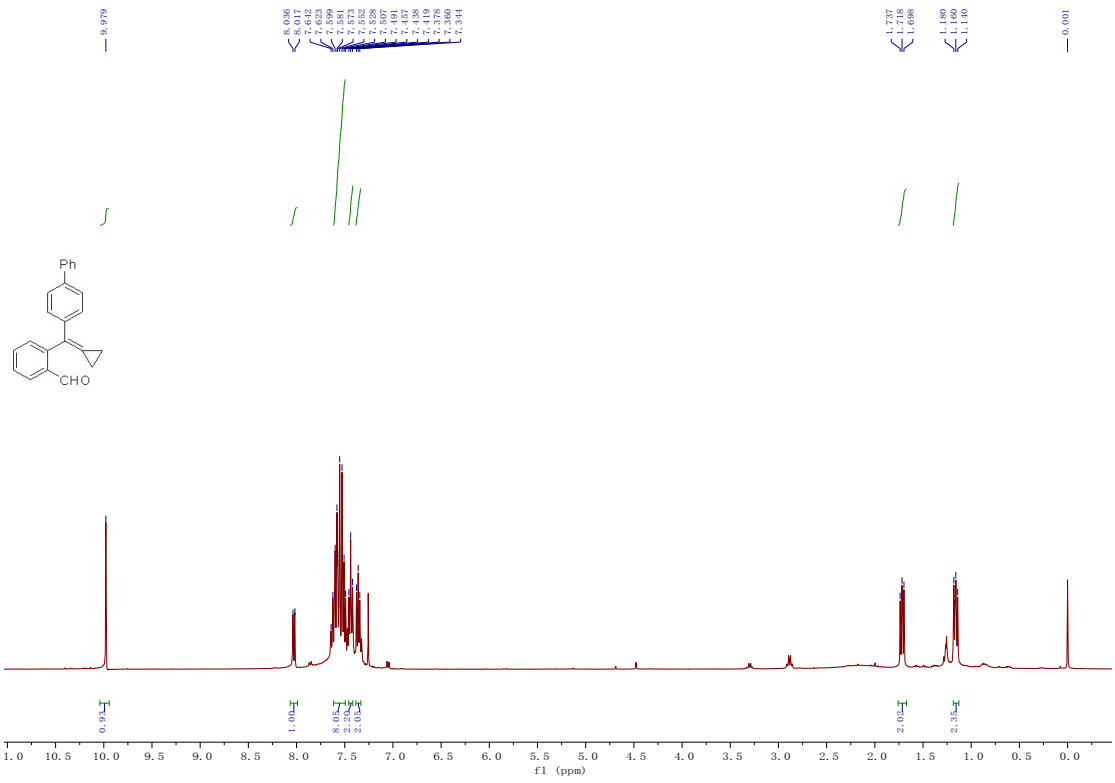
Compound 1i: A pale yellow solid (133.2 mg, 40%); M.p. 74 - 75 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.03 – 1.12 (m, 2H), 1.57 – 1.65 (m, 2H), 5.04 (s, 2H), 6.84 – 6.99 (m, 2H), 7.24 – 7.33 (m, 2H), 7.33 – 7.47 (m, 7H), 7.56 (dd, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 9.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.0, 5.8, 69.9, 114.7, 125.6, 126.2, 127.1, 127.4, 127.5, 127.9, 128.1, 128.5, 130.8, 133.3, 133.5, 134.5, 136.8, 145.6, 158.1, 192.4. IR (neat) ν 3068, 2969, 2834, 2735, 1777, 1693, 1596, 1509, 1459, 1383, 1302, 1249, 1177, 1023, 908, 824, 760, 735 cm^{-1}. HRMS (EI) Calcd. for $C_{24}H_{20}O_2$ requires (M^+): 340.1463, Found: 340.1459.







Compound 1j: A yellow sticky (328.0 mg, 90%). This compound contains some impurities, which are difficult to be purified. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13 – 1.19 (m, 2H), 1.67 – 1.76 (m, 2H), 7.33 – 7.38 (m, 2H), 7.42 – 7.46 (m, 2H), 7.49 – 7.62 (m, 8H), 8.03 (d, J = 7.8 Hz, 1H), 9.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.2, 6.1, 125.9, 127.0, 127.1, 127.3, 127.4, 127.7, 128.5, 128.8, 130.9, 133.7, 134.6, 139.3, 140.1, 140.5, 145.3, 192.5. IR (neat) ν 3055, 3022, 2923, 1769, 1692, 1597, 1486, 1324, 1207, 1036, 1006, 828, 762, 730, 696 cm^{-1}. HRMS (EI) Calcd. for $C_{23}H_{18}O$ requires (M^+): 310.1358, Found: 310.1361.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7.552
7.528
7.507
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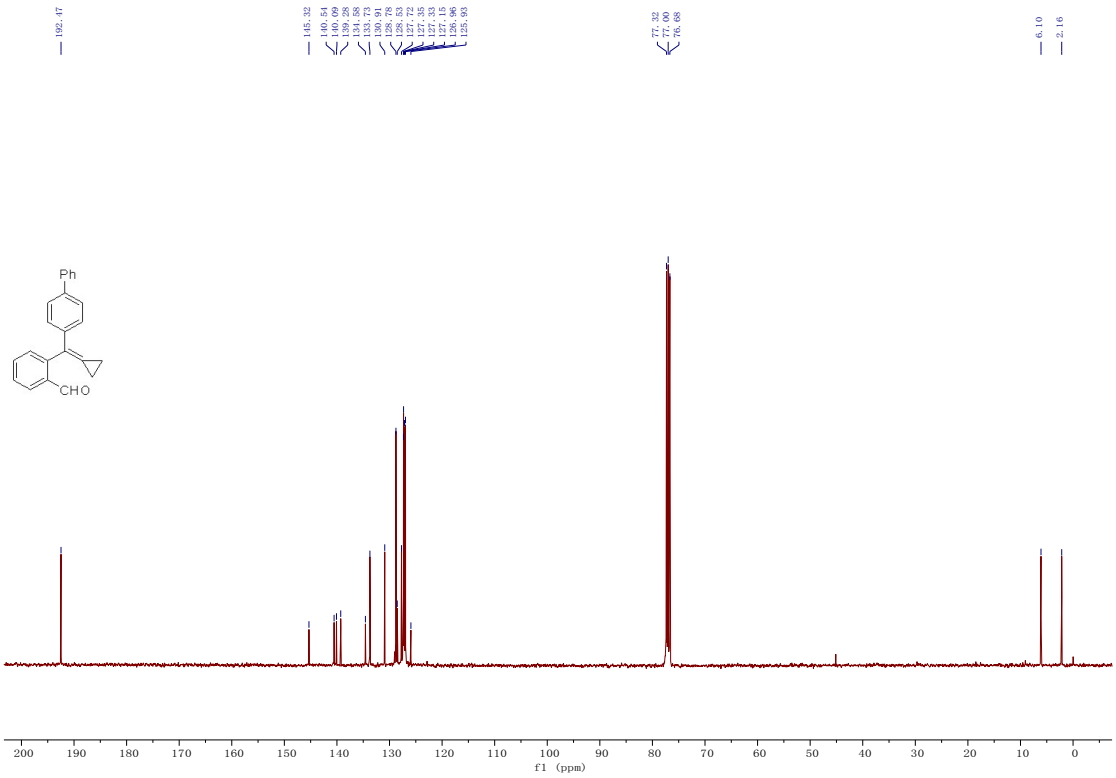
7.457
7.438
7.419
7.378
7.360
7.344
1.737
1.718
1.698
1.180
1.160
1.140
0.001
Ph
CHO
0.93
1.00
8.05
2.24
2.05
2.02
2.35
f1 (ppm)


192.47
145.32
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140.09
139.28
134.58
133.73
130.91
128.78
128.53
127.72
127.55
127.33
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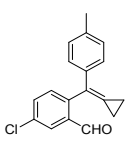
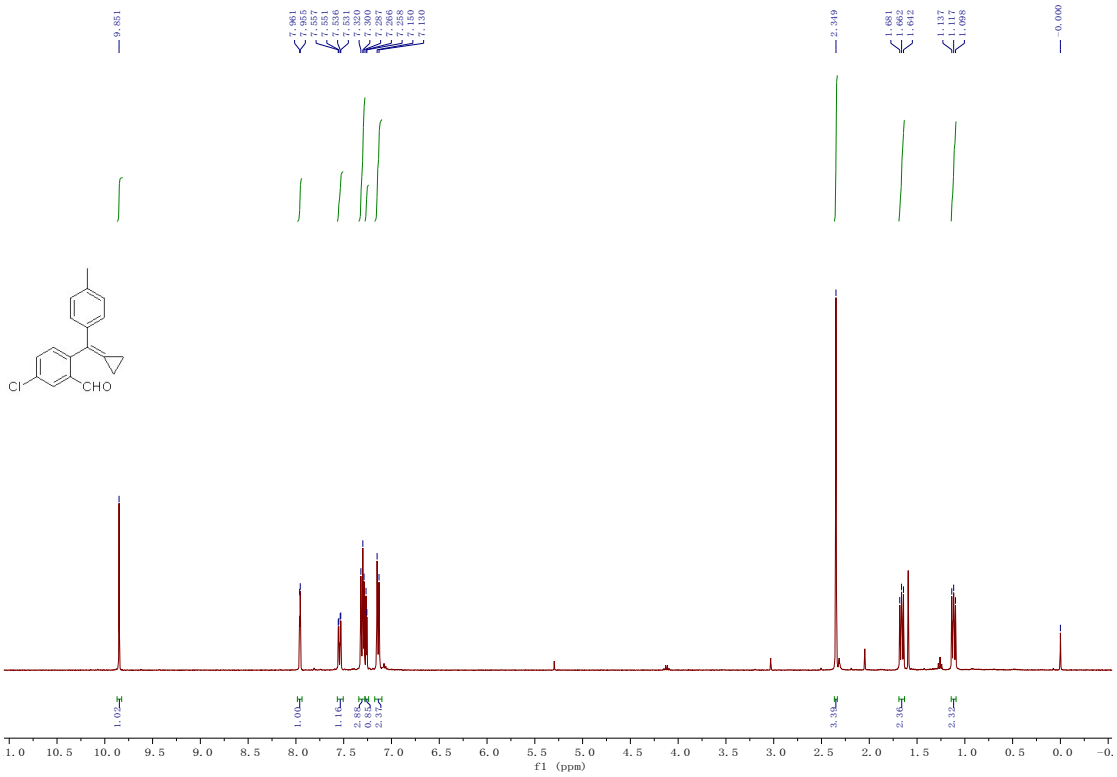
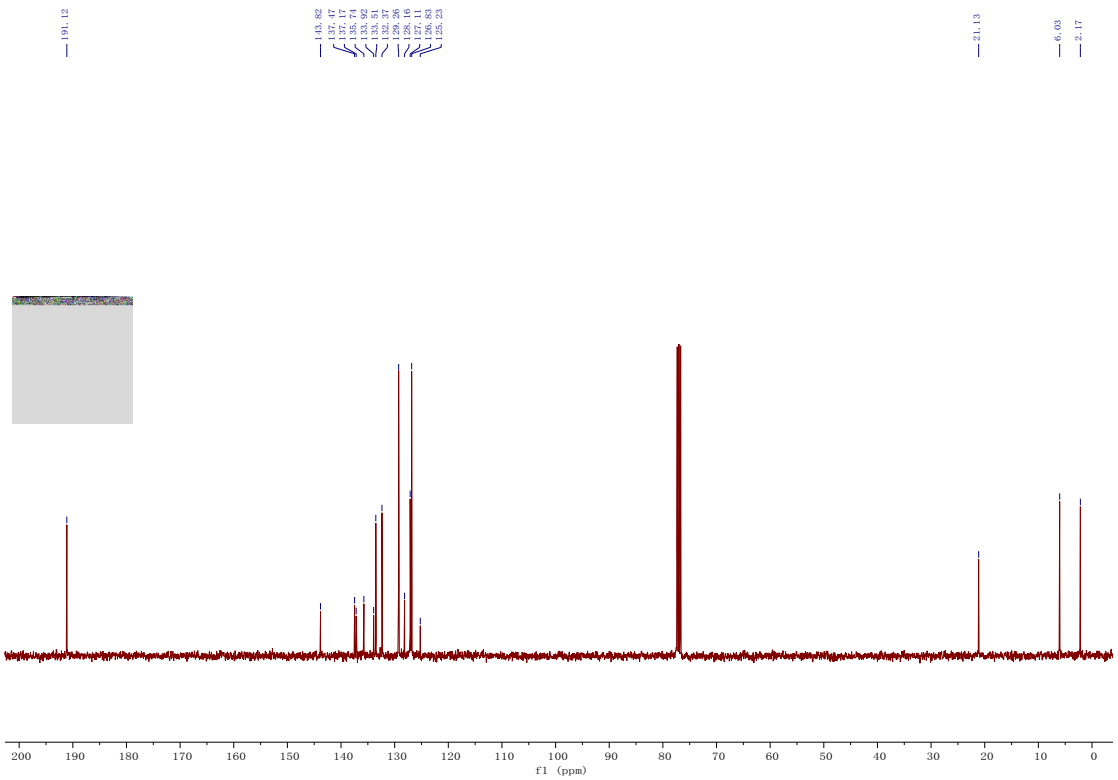
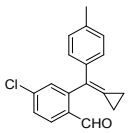
126.96
125.93
77.32
77.00
76.68
6.10
2.16
Ph
CHO
f1 (ppm)


Cl
CHO

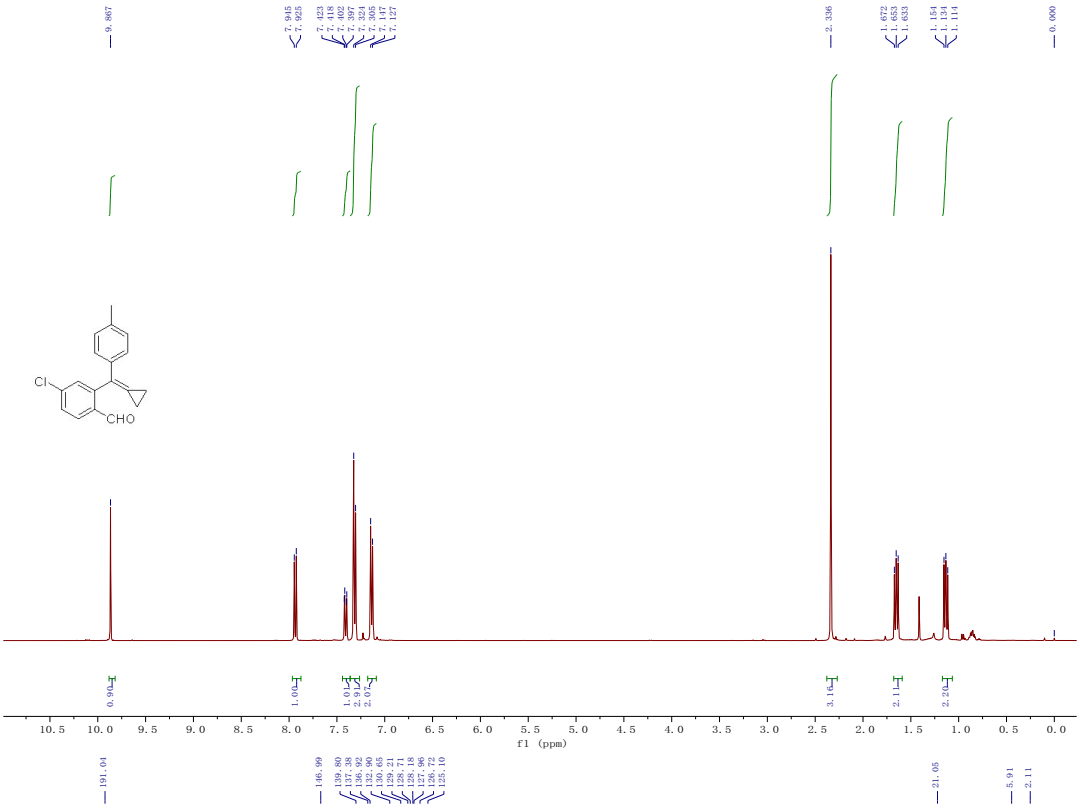
Compound 1k: A yellow oil (343.8 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 – 1.14 (m, 2H), 1.63 – 1.69 (m, 2H), 2.35 (s, 3H), 7.10 – 7.18 (m, 2H), 7.26 (d, *J* = 3.6 Hz, 1H), 7.28 – 7.34 (m, 3H), 7.54 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.96 (d, *J* = 2.3 Hz, 1H), 9.85 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.2, 6.0, 21.1, 125.2, 126.8, 127.1, 128.2, 129.3, 132.4, 133.5, 133.9, 135.7, 137.2, 137.5, 143.8, 191.1. IR (neat) ν 3030, 3001, 2972, 2915, 2860, 1780, 1692, 1581, 1506, 1472, 1183, 1074, 1038, 1019, 909, 808, 730, 706 cm^{-1}. HRMS (EI) Calcd. for $C_{18}H_{15}ClO$ requires (M^+): 282.0811, Found: 282.0817.

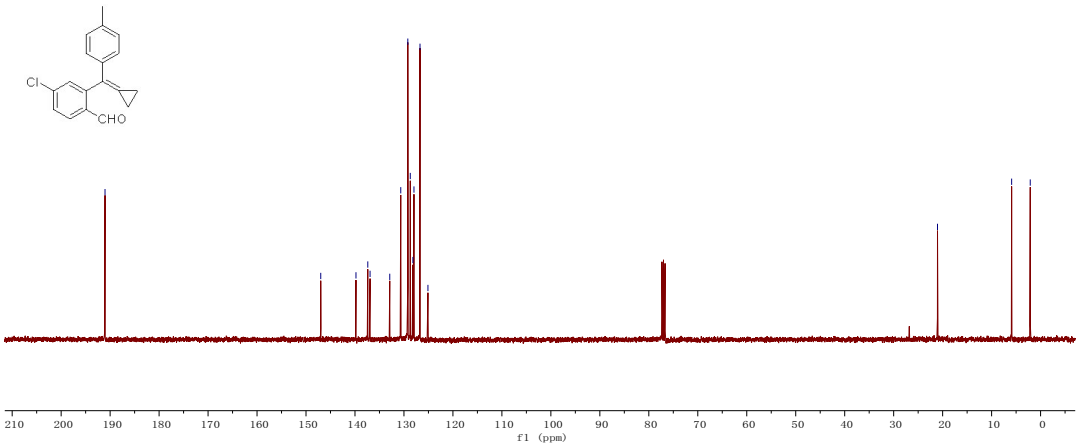


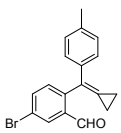




Compound 1l: A yellow oil (773.1 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 – 1.17 (m, 2H), 1.59 – 1.68 (m, 2H), 2.34 (s, 3H), 7.09 – 7.18 (m, 2H), 7.26 – 7.36 (m, 3H), 7.41 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 9.87 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.1, 5.9, 21.0, 125.1, 126.7, 128.0, 128.2, 128.7, 129.2, 130.7, 132.9, 136.9, 137.4, 139.8, 147.0, 191.0. IR (neat) ν 3024, 2975, 2925, 2857, 1780, 1692, 1587, 1510, 1467, 1391, 1250, 1209, 1086, 1018, 908, 850, 816, 730 cm^{-1}. HRMS (EI) Calcd. for $C_{18}H_{15}ClO$ requires (M^+): 282.0811, Found: 282.0813.

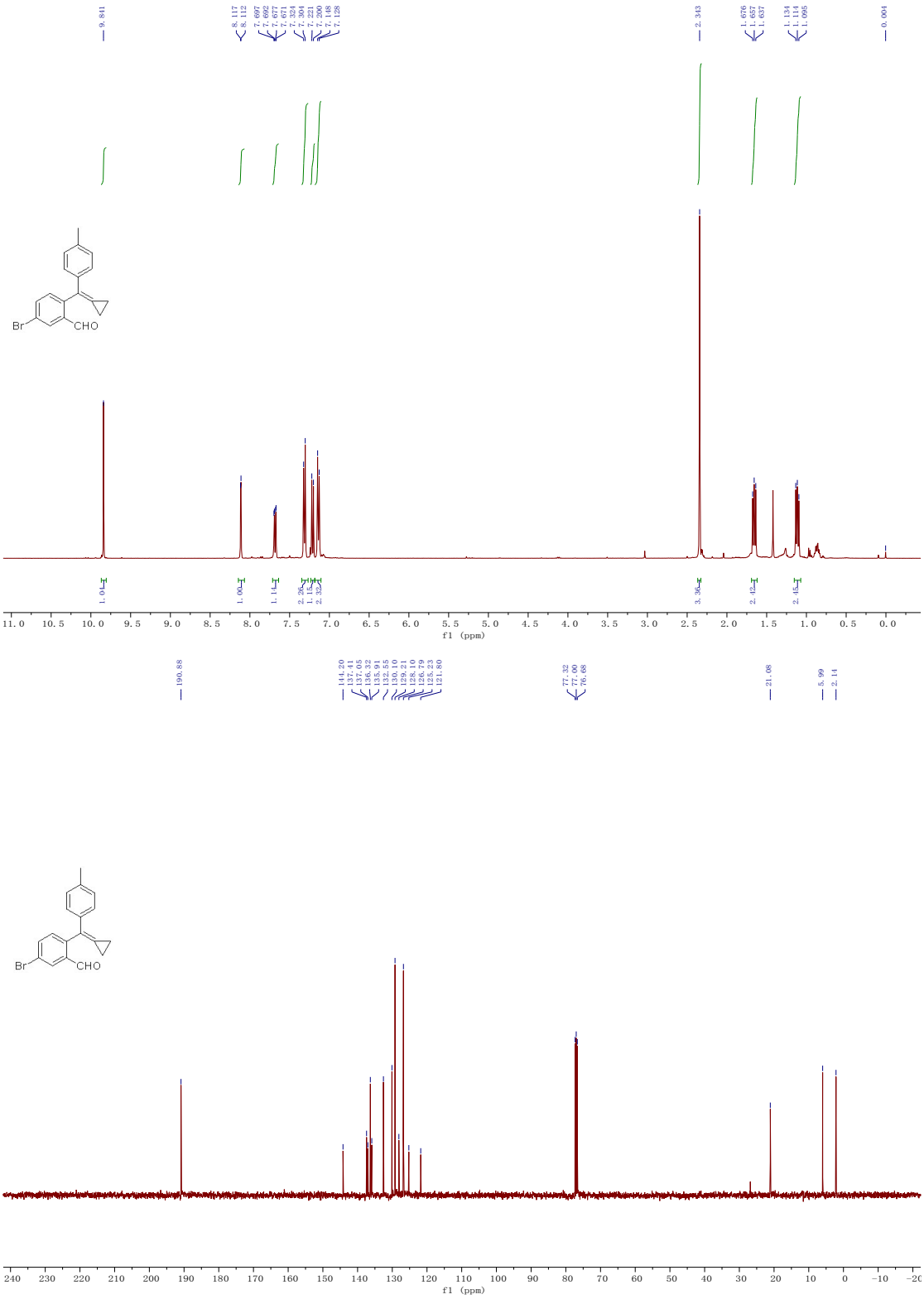


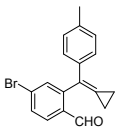




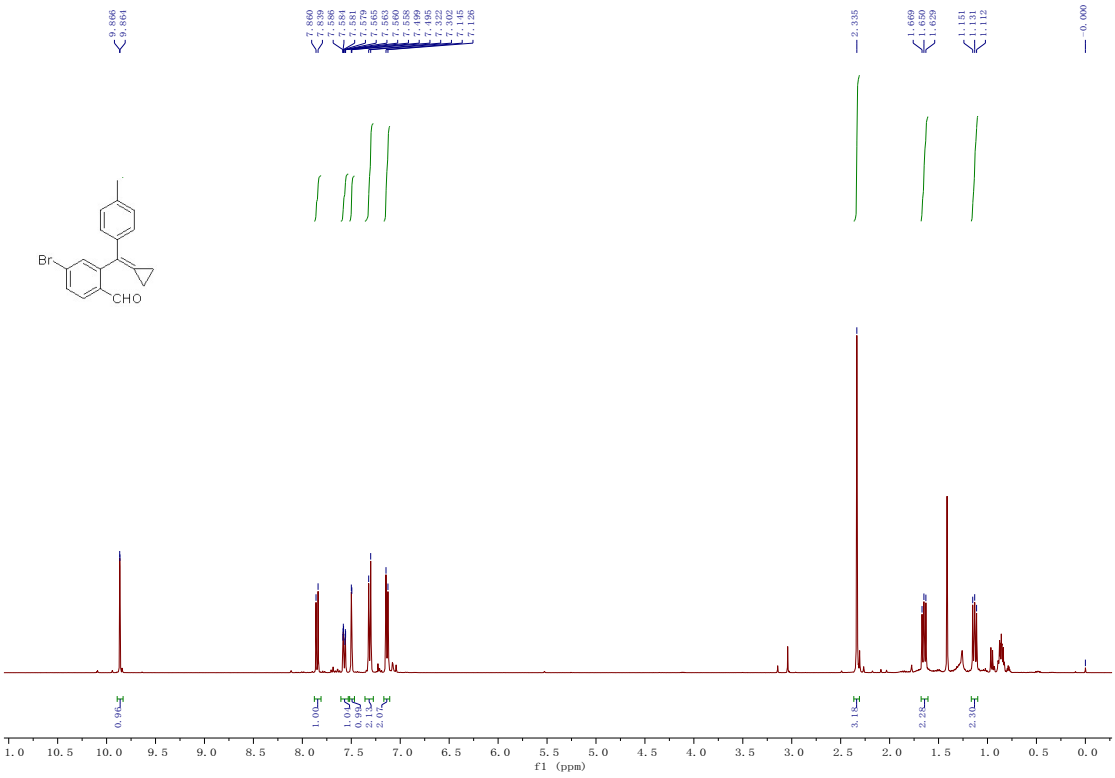
Compound 1m: A white solid (251.3 mg, 94%); M.p. 89 - 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 – 1.15 (m, 2H), 1.62 – 1.69 (m, 2H), 2.34 (s, 3H), 7.11 – 7.18 (m, 2H), 7.21 (d, J = 8.2 Hz, 1H), 7.27 – 7.35 (m, 2H), 7.68 (dd, J = 8.2, 2.2 Hz, 1H), 8.11 (d, J = 2.2 Hz, 1H), 9.84 (s, 1H).

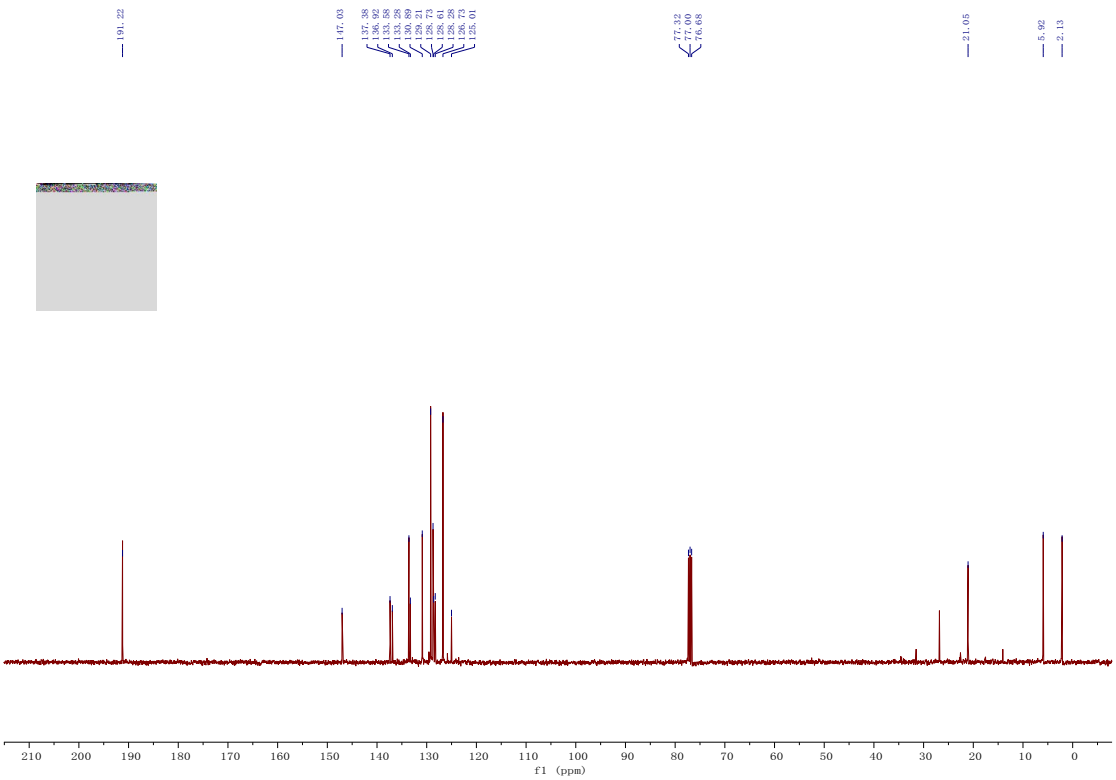
^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.1, 6.0, 21.1, 121.8, 125.2, 126.8, 128.1, 129.2, 130.1, 132.6, 135.9, 136.3, 137.0, 137.4, 144.2, 190.9. IR (neat) ν 2977, 2917, 2842, 1772, 1694, 1582, 1558, 1509, 1386, 1331, 1206, 1075, 1057, 820, 833, 730, 700, 670 cm^{-1}. HRMS (EI) Calcd. for $C_{18}H_{15}BrO$ requires (M^+): 326.0306, Found: 326.0304.

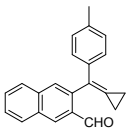




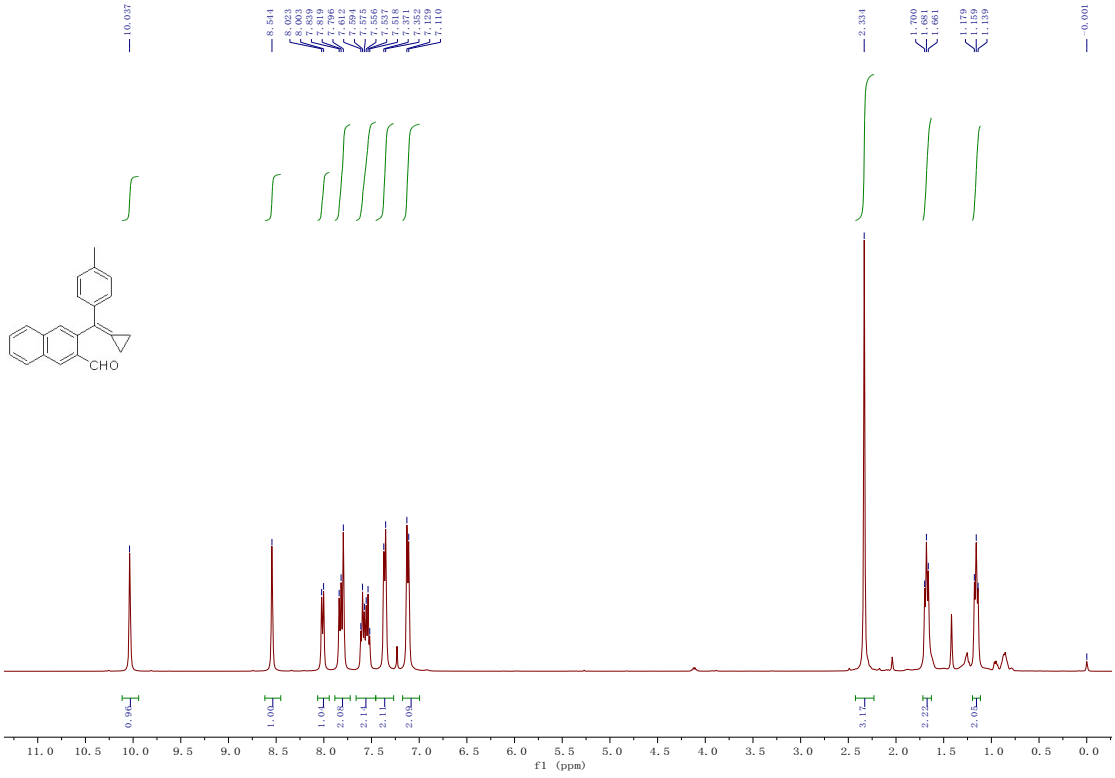
Compound 1n: A white solid (380.3 mg, 87%); M.p. 71 - 72 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.10 – 1.17 (m, 2H), 1.61 – 1.68 (m, 2H), 2.33 (s, 3H), 7.11 – 7.17 (m, 2H), 7.27 – 7.36 (m, 2H), 7.50 (d, J = 2.0 Hz, 1H), 7.57 (ddd, J = 8.4, 2.0, 0.8 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 9.86 (d, J = 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.1, 5.9, 21.1, 125.0, 126.7, 128.3, 128.6, 128.7, 129.2, 130.9, 133.3, 133.6, 136.9, 137.4, 147.0, 191.2. IR (neat) ν 3087, 3024, 2977, 2917, 2844, 1788, 1694, 1581, 1555, 1510, 1387, 1252, 1217, 1208, 1075, 1021, 918, 845, 819, 745, 723, 698 cm^{-1}. HRMS (EI) Calcd. for $C_{18}H_{15}BrO$ requires (M^+): 326.0306, Found: 326.0310.







Compound 1o: A yellow oil (3.87 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (t, *J* = 7.9 Hz, 2H), 1.63 – 1.72 (m, 2H), 2.33 (s, 3H), 7.00 – 7.17 (m, 2H), 7.27 – 7.46 (m, 2H), 7.46 – 7.66 (m, 2H), 7.72 – 7.88 (m, 2H), 8.01 (d, *J* = 8.1 Hz, 1H), 8.54 (s, 1H), 10.04 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.0, 5.9, 21.1, 126.5, 126.7, 126.8, 127.7, 128.8, 129.2, 129.4, 129.8, 129.9, 131.8, 132.6, 135.9, 137.1, 138.0, 140.0, 192.5. IR (neat) ν 3056, 3022, 2967, 2923, 2849, 1782, 1738, 1688, 1624, 1589, 1509, 1443, 1152, 1106, 1045, 1022, 907, 894, 819, 747, 731 cm^{-1}. HRMS (EI) Calcd. for $C_{23}H_{18}O$ requires (M^+): 298.1358, Found: 298.1354.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7.352
7.129
7.110
2.334
1.700
1.681
1.661
1.179
1.159
1.139
-0.001
CHO
0.94
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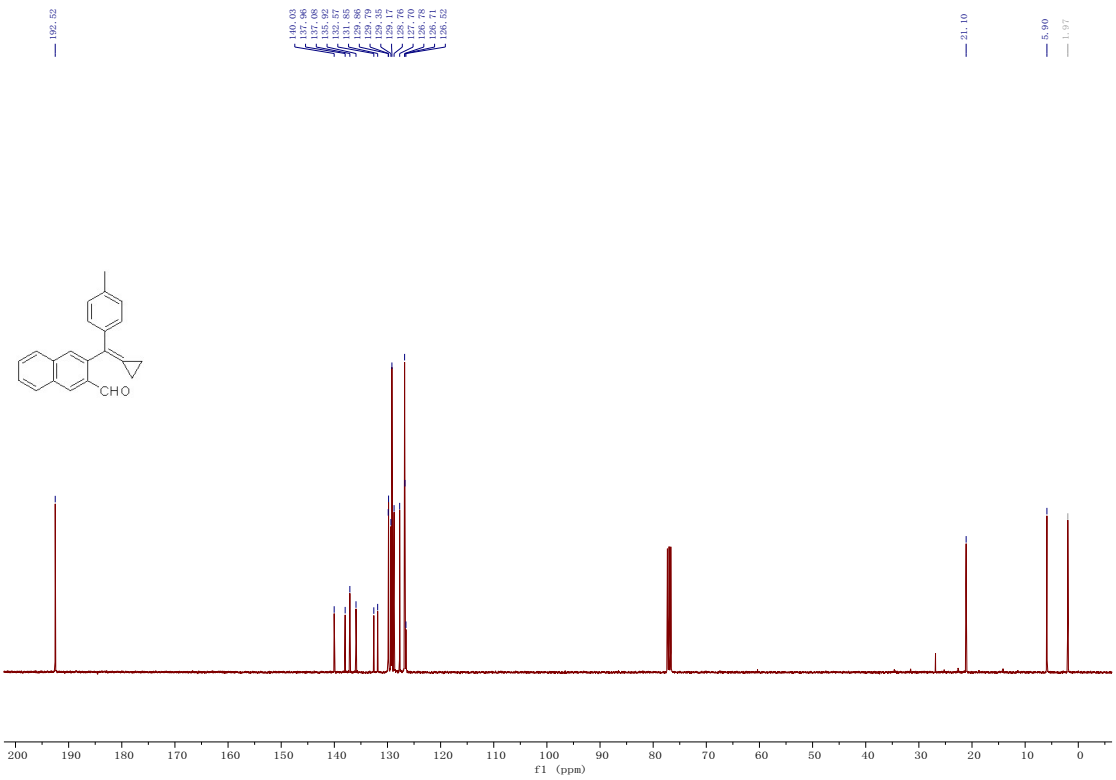
1.04
2.08
2.14
2.11
2.04
3.17
2.22
2.05
f1 (ppm)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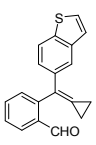
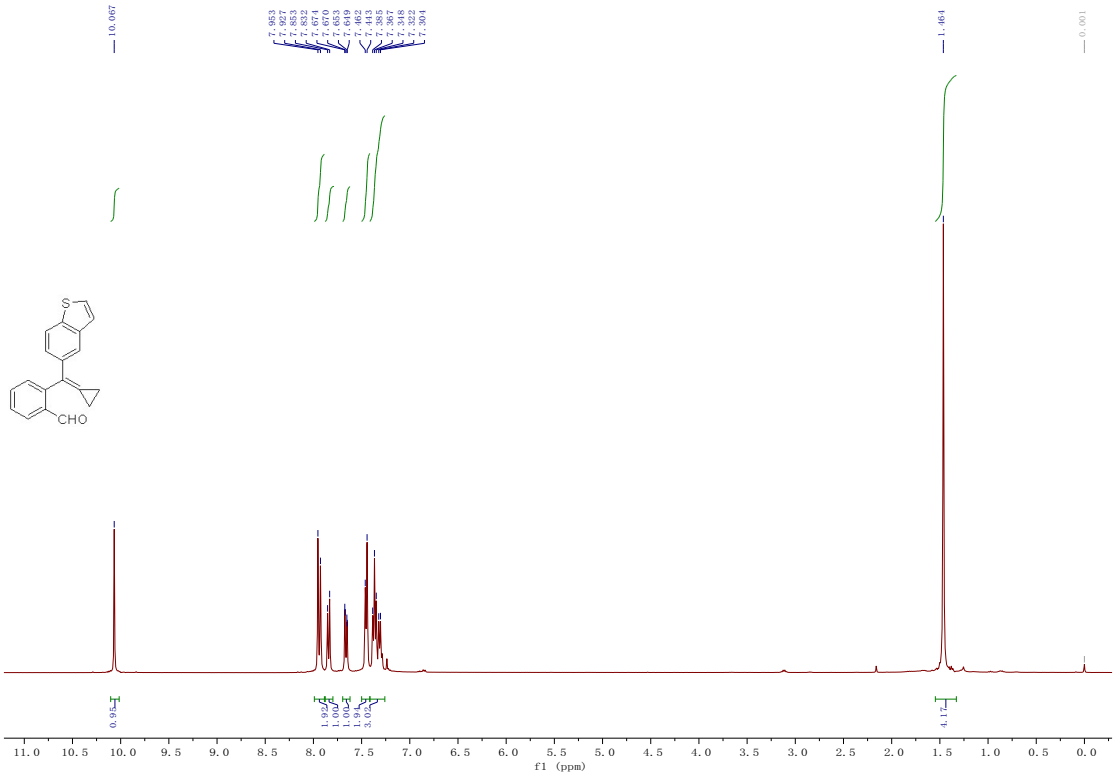
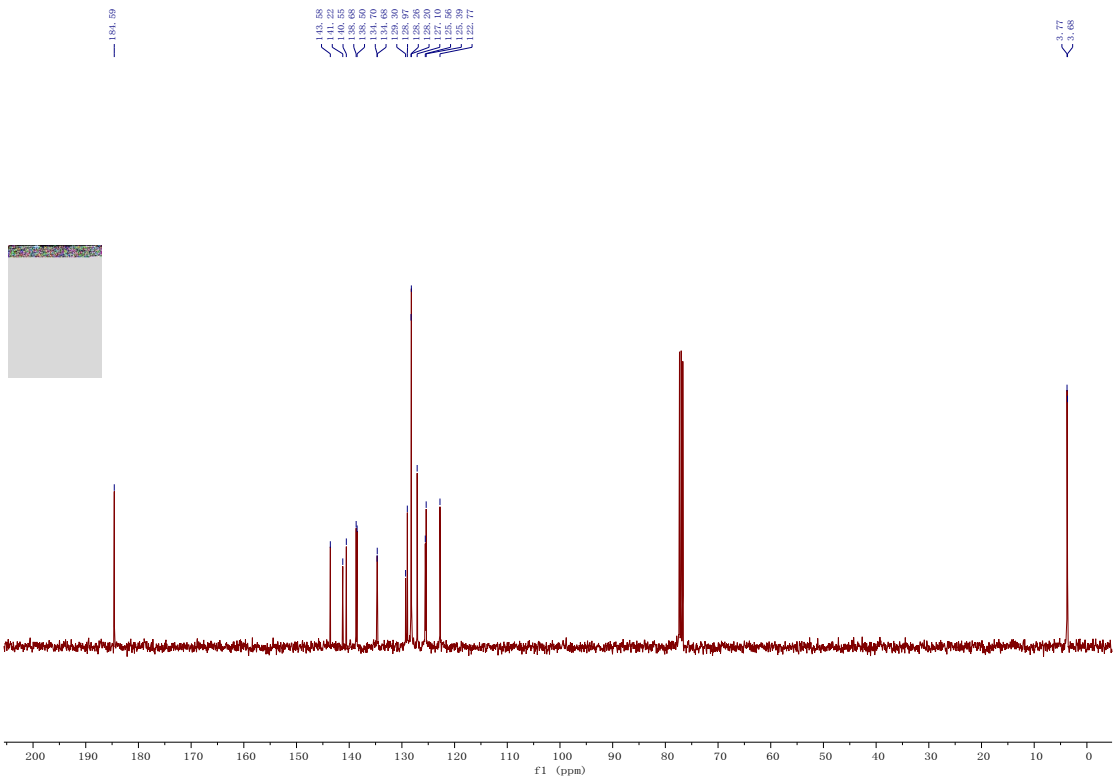
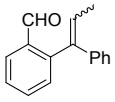
1.97
CHO
f1 (ppm)


S
CHO

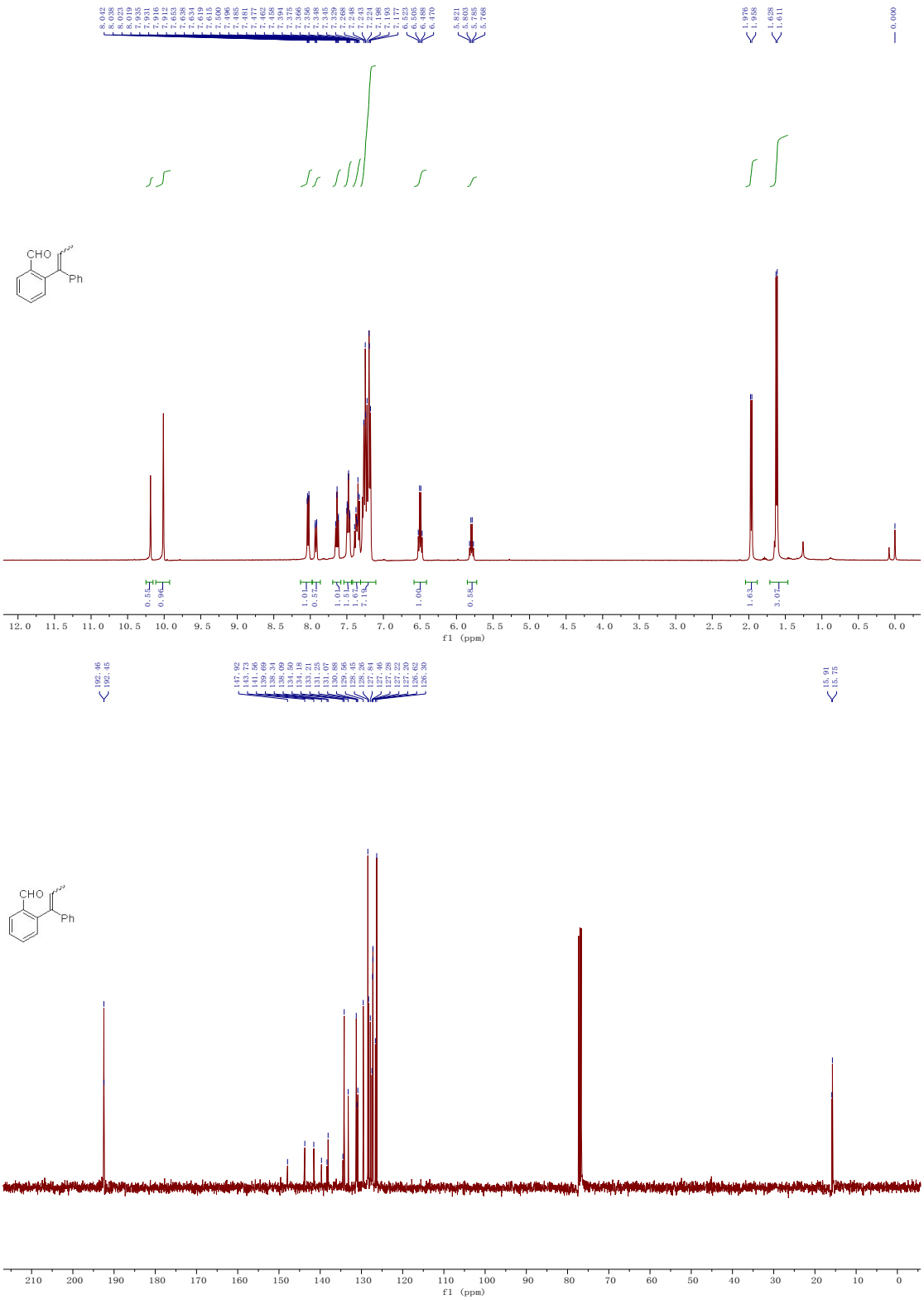
Compound 1p: A white solid (107.9 mg, 61%); M.p. 49 - 51 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.46 (s, 4H), 7.26 – 7.41 (m, 3H), 7.41 – 7.50 (m, 2H), 7.66 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.89 – 7.99 (m, 2H), 10.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 3.7, 3.8, 122.8, 125.4, 125.6, 127.1, 128.2, 128.3, 129.0, 129.3, 134.7, 134.7, 138.5, 138.7, 140.5, 141.2, 143.6, 184.6. IR (neat) ν 2988, 2900, 2226, 1969, 1581, 1434, 1406, 1323, 1208, 1146, 1002, 896, 799, 755, 727, 696, 657 cm^{-1}. HRMS (EI) Calcd. for $C_{19}H_{14}OS$ requires (M^+): 290.0765, Found: 290.0762.

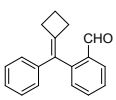






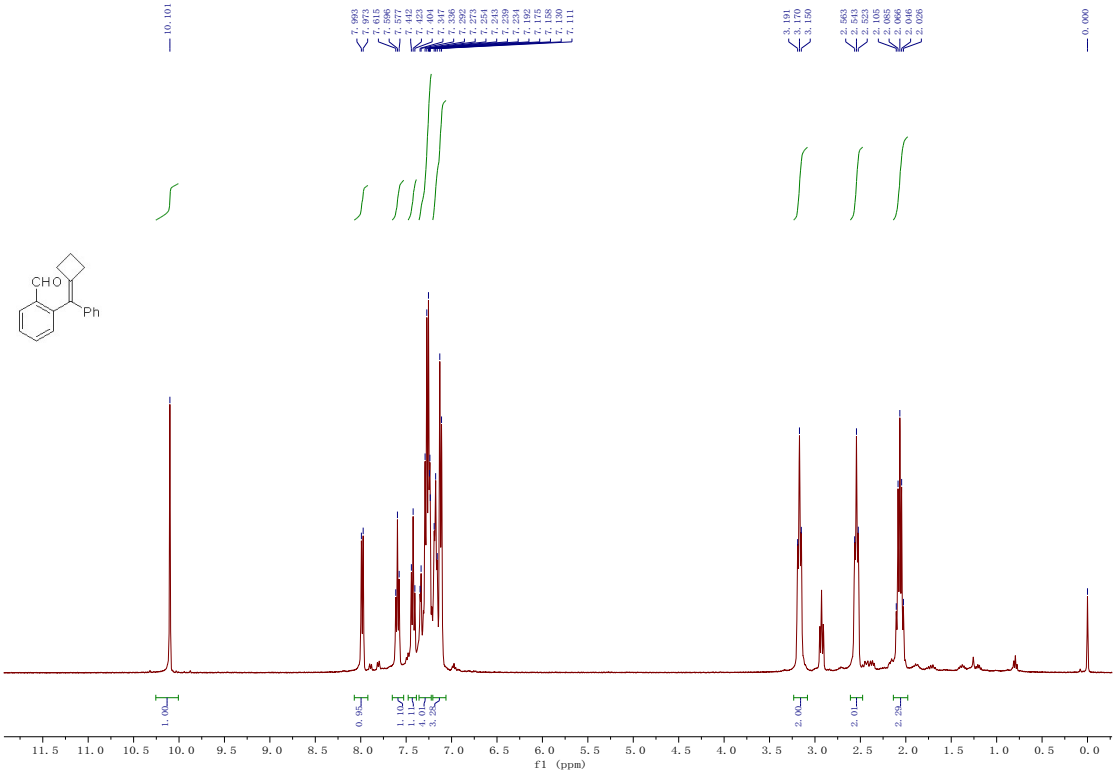
Compound 1q: A colorless oil (180.1 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.6 (d, *J* = 7.0 Hz, 3H), 2.0 (d, *J* = 7.1 Hz, 2H), 5.8 (q, *J* = 7.1 Hz, 1H), 6.5 (q, *J* = 7.0 Hz, 1H), 7.1 – 7.3 (m, 7H), 7.3 – 7.4 (m, 2H), 7.4 – 7.5 (m, 2H), 7.6 – 7.7 (m, 1H), 7.9 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.0 (dd, *J* = 7.8, 1.5 Hz, 1H), 10.0 (s, 1H), 10.2 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.8, 15.9, 126.3, 126.6, 127.2, 127.2, 127.3, 127.5, 127.8, 128.3, 128.4, 129.6, 130.9, 131.1, 131.3, 133.2, 134.2, 134.5, 138.1, 138.3, 139.7, 141.6, 143.7, 147.9, 192.4, 192.5. IR (neat) ν 3060, 3021, 2958, 2927, 2854, 1687, 1641, 1596, 1494, 1442, 1196, 824, 760, 700 cm^{-1}. HRMS (ESI) Calcd. for $C_{16}H_{15}O$ requires (M^+): 222.1117, Found: 222.1118.

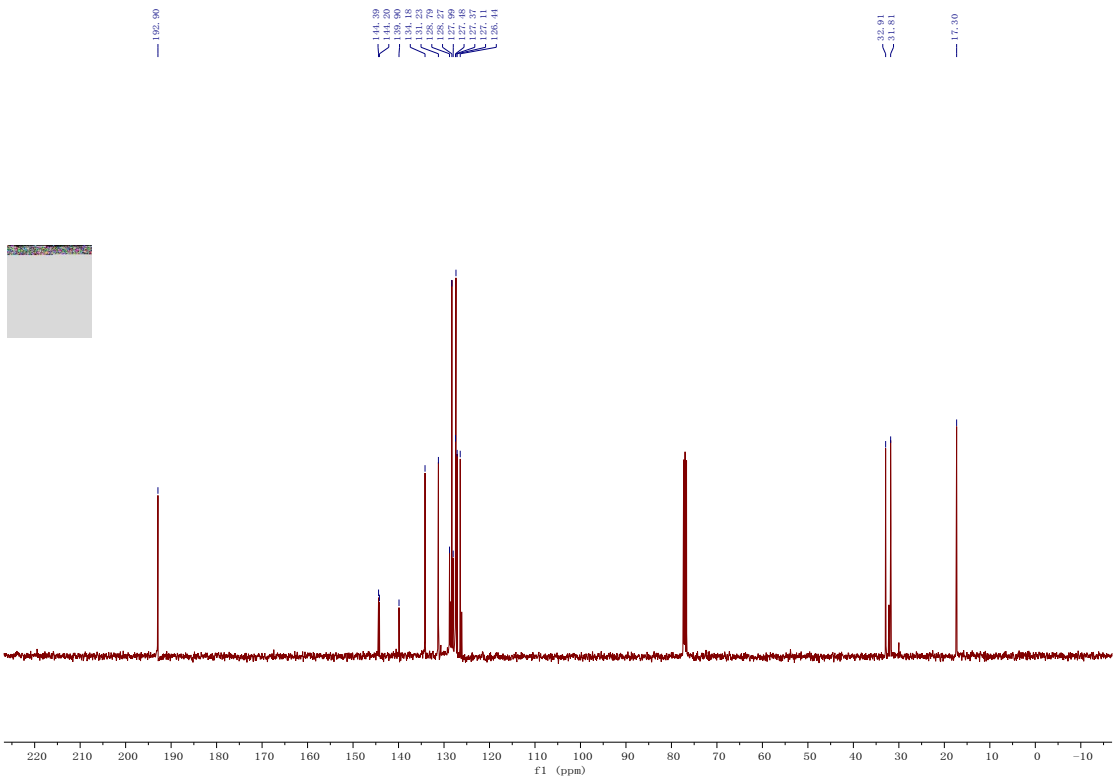




Compound 1r: A colorless oil (173.2 mg, 67%). This compound contains some impurities, which are difficult to be purified. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.1 (p, J = 7.9 Hz, 2H), 2.5 (t, J =

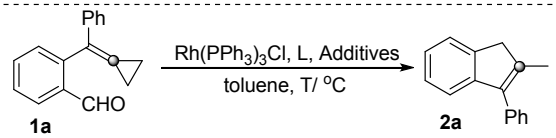
8.0 Hz, 2H), 3.2 (t, J = 8.1 Hz, 2H), 7.1 – 7.2 (m, 3H), 7.2 – 7.4 (m, 4H), 7.4 (dd, J = 7.6 Hz, 1H), 7.6 (dd, J = 7.5 Hz, 1H), 8.0 (d, J = 7.8 Hz, 1H), 10.1 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 17.3, 31.8, 32.9, 126.4, 127.1, 127.4, 127.5, 128.0, 128.3, 128.8, 131.2, 134.2, 139.9, 144.2, 144.4, 192.9. IR (neat) ν 3030, 2985, 2951, 2899, 2839, 2753, 1690, 1647, 1594, 1494, 1440, 1263, 1198, 1148, 824, 772, 762, 732, 693 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{16}O$ requires (M^+): 248.1201, Found: 248.1198.




192.90
144.39
144.20
139.90
131.18
131.23
128.79
128.27
127.99
127.68
127.37
127.11
126.44
32.91
31.81
17.30
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

Optimization of the reaction conditions for the synthesis of product **2a**

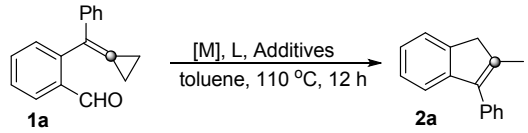
Table S1. Screening of the reaction conditions on temperature and ligand.[a,b,c,d]



Entry[a]	Ligand	Additives	T/°C	Yield/%[b]
1	dppp	--	80	19
2	dppp	--	110	42[c]
3	dppp	--	130	42[d]
4	dppe	--	110	45
5	dppb	--	110	51
6	dppbz	--	110	32
7	dppf	--	110	30
8	DPEPhos	--	110	37
9	XantPhos	--	110	36
10	BINAP	--	110	34
11	$P(O^tBu)_3$	--	110	39
12	JohnPhos	--	110	48
13	$P(4\text{-}FPh)_3$	--	110	13
14	$P(^tBu)_2Ph$	--	110	12
15	$P(C_6F_5)_3$	--	110	56
16	dppb	AgOTf	110	0
17	dppb	$AgNTf_2$	110	0
18	dppb	$AgBF_4$	110	0

[a] All reactions were carried out with **1a** (0.1 mmol), **Rh cat.** (2.5 mol %) and **ligand** (10 mol %) were dissolved in 1.0 mL of solvent for 12 h.
[b] ^1H NMR yields using 1,3,5-trimethoxybenzene as an internal standard.
[c] Isolated yields.
[d] This reaction was performed on a sealed tube.

Table S2. Screening of the reaction conditions on metal catalysts and additives.[a,b,c,d]

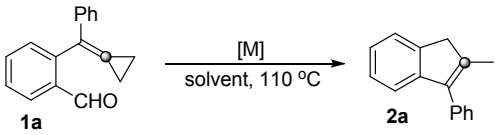


1a **2a**

Entry[a]	*cat*.	Ligand	Additives	Yield/%[b]
1	$[Rh(cod)_2Cl]_2$	$P(C_6F_5)_3$	--	28
2	$[Rh(cod)_2Cl]_2$	-	--	29
3	$Rh(cod)_2BF_4$	$P(C_6F_5)_3$	--	0
4	$Rh(cod)_2BF_4$	-	--	0
5	$[Rh(CO)_2Cl]_2$	$P(C_6F_5)_3$	--	0
6	$[Rh(CO)_2Cl]_2$	-	--	0
7	$[Rh(cod)_2OH]_2$	$P(C_6F_5)_3$	--	32
8	$[Rh(cod)_2OH]_2$	-	--	33
9	$Rh(PPh_3)_3Cl$	-	--	48
10	$Ir(PPh_3)_2(CO)Cl$	-	--	8
11	$Rh(PPh_3)_2(CO)Cl$	-	--	77
12	Rh(acac)(CO)Cl	-	--	49
13	$Rh(P(C_6F_5)_3)_2(CO)Cl$	-	--	16
14	$Au(PPh_3)Cl$	-	--	0
15	$Rh(PPh_3)_3Cl$	-	$TsOH•H_2O$	0
16[c]	$Rh(PPh_3)_3Cl$	-	Na_2CO_3	56
17[c,d]	$Rh(PPh_3)_3Cl$	-	K_2CO_3	29
18[c,d]	$Rh(PPh_3)_3Cl$	-	Cs_2CO_3	0
19[c,d]	$Rh(PPh_3)_3Cl$	-	NMO	0

[a] All reactions were carried out with **1a** (0.1 mmol), **Rh cat.** (2.5 mol %) and **ligand** (10 mol %) were dissolved in 1.0 mL of solvent for 12 h.
[b] ^1H NMR yields using 1,3,5-trimethoxybenzene as an internal standard.
[c] reaction time was prolonged to 28 h.
[d] recovery of **1a**.

Table S3. Screening of the reaction conditions on solvents.[a,b,c]



1a **2a**

Entry[a]	*cat.*	Ligand	solvent	Yield/%[b]
1	$Rh(PPh_3)_2(CO)H$	-	PhMe	83
2	$Rh(PPh_3)_2(CO)H$	-	DCE	24
3	$Rh(PPh_3)_2(CO)H$	-	MeCN	7
4	$Rh(PPh_3)_2(CO)H$	-	DMF	0
5	$Rh(PPh_3)_2(CO)H$	-	xylene	60
6	$Rh(PPh_3)_2(CO)H$	-	PhCl	39
7	$Rh(PPh_3)_2(CO)H$	-	$PhCF_3$	42
8[c]	$Rh(PPh_3)_2(CO)H$	Na_2CO_3	PhMe	77

[a] All reactions were carried out with **1a** (0.1 mmol) and Rh cat. (2.5 mol %) in 1.0 mL solvent.
[b] ^1H NMR yields using 1,3,5-trimethoxybenzene as an internal standard.
[c] reaction time was prolonged to 28 h.

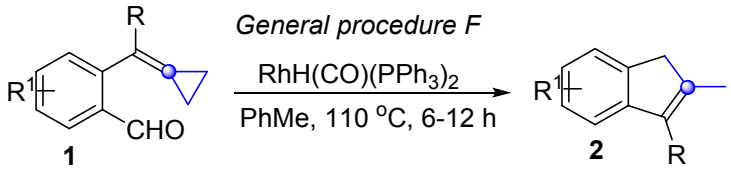
We initially investigated the ligand effect on the intramolecular decarbonylative cyclization reaction of **1a** with Wilkinson's catalyst and found that using dppp as a ligand afforded the desired product **2a** in 19% yield in toluene at 80 °C overnight (Table S1, entry 1). Raising the reaction temperature from 80 °C to 110 °C gave the corresponding cyclized product **2a** in 42% yield, however, when the reaction was carried out at 130 °C in a sealed tube, **2a** was still given in 42% yield (Table S1, entries 2 *vs* 3). Thus, we set up the reaction temperature at 110 °C for the further reaction condition screening.

Next, several other commercially available bisphosphine ligands were used in the reaction. The use of dppe and dppb as external ligands afforded **2a** in 45% and 51% yields, respectively (Table S1, entries 4 - 5). In addition, using dpppz, dppf, DPEphos, Xantphos and BINAP as external ligands did not improve the reaction outcomes (Table S1, entries 6 - 10). Then, we turned our attention to screen several monophosphine ligands such as $P(OtBu)_3$, JohnPhos, $P(4\text{-}FPh)_3$, sterically bulky $P(^tBu)_2C_6H_5$, electron deficient $P(4\text{-}FC_6H_4)_3$ and $P(C_6F_5)_3$ under otherwise identical conditions (Table S1, entries 11 - 15). During these examinations, we identified that using $P(C_6F_5)_3$ as a ligand gave **2a** in the best yield of 56% (Table S1, entry 15). When silver salts were added, the desired product could not be yielded at all (Table S1, entries 16 - 18).

Subsequently, we performed the reactions using $[Rh(cod)Cl]_2$, $[Rh(cod)OH]_2$, in which no phosphine ligand was coordinated to the rhodium metal center and found that the yields of **2a** were

almost identical in the presence or absence of $P(C_6F_5)_3$ ligand (Table S2, entries 1 *vs* 2, 7 *vs* 8). Afterwards, we realized that the yield of **2a** could reach to 48% if using Wilkinson's catalyst alone even without any external phosphine ligand (Table S2, entry 9). These results suggested that the addition of extra phosphine ligand did not significantly improve the yield of **2a** if using Wilkinson's type of Rh catalyst. Moreover, $Rh(cod)BF_4$ and $[Rh(CO)_2Cl]_2$ had no catalytic activity for this reaction (Table S2, entries 3 - 6). Therefore, we started to seek out other rhodium catalyst for this reaction rather than the phosphine ligand. Gratifyingly, when $Rh(CO)Cl(PPh_3)_2$ was used as the catalyst, the yield of **2a** was up to 77% isolated yield (Table S2, entry 11). However, using $Ir(CO)Cl(PPh_3)_2$ as the catalyst only gave **2a** in 8% yield and most of starting materials **1a** were recovered (Table S2, entry 10). Changing the coordinated PPh_3 ligand with other ligands such as acac (acetylacetone) or $P(C_6F_5)_3$, the yields of **2a** were 49% and 16%, respectively (Table S2, entries 12 and 13). Using $Rh(CO)H(PPh_3)_2$ as the catalyst could produce **2a** in 83% isolated yield (Table S3, entry 1). Finally, the examination of solvent effect in DCE, MeCN, DMF, xylene, PhCl and $PhCF_3$ revealed that toluene was the best choice (Table S3, entries 2 - 8).

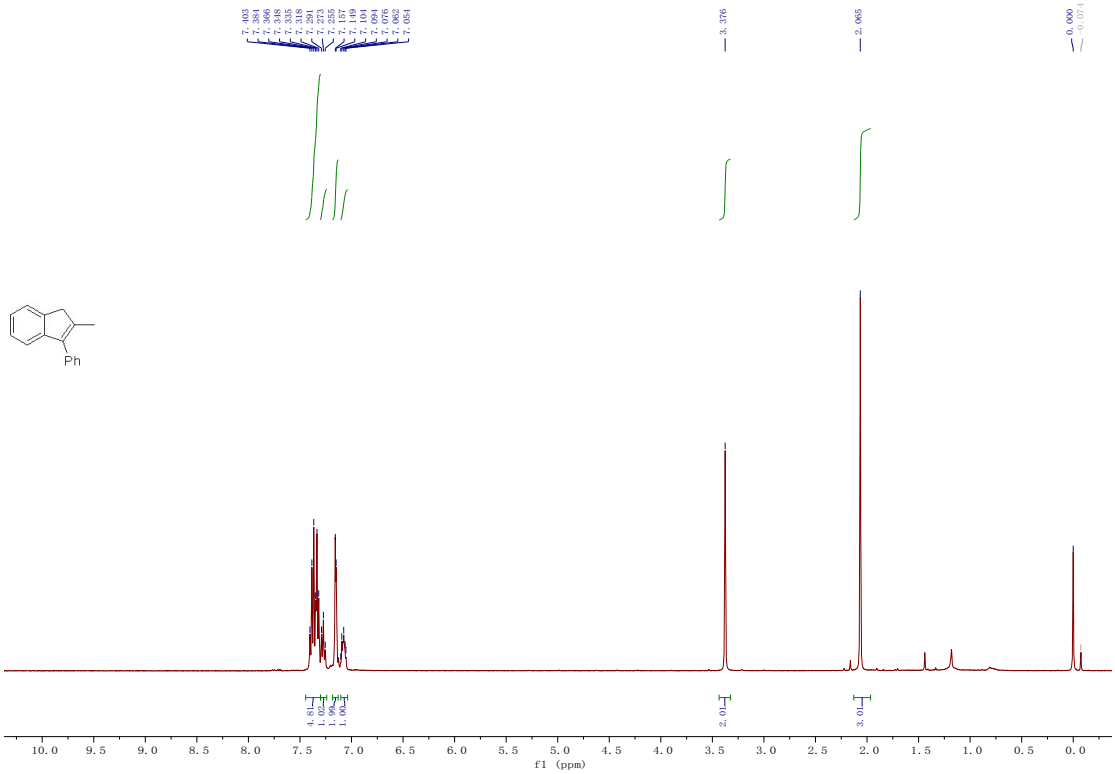
General procedure for the preparation of compounds 2a-2p

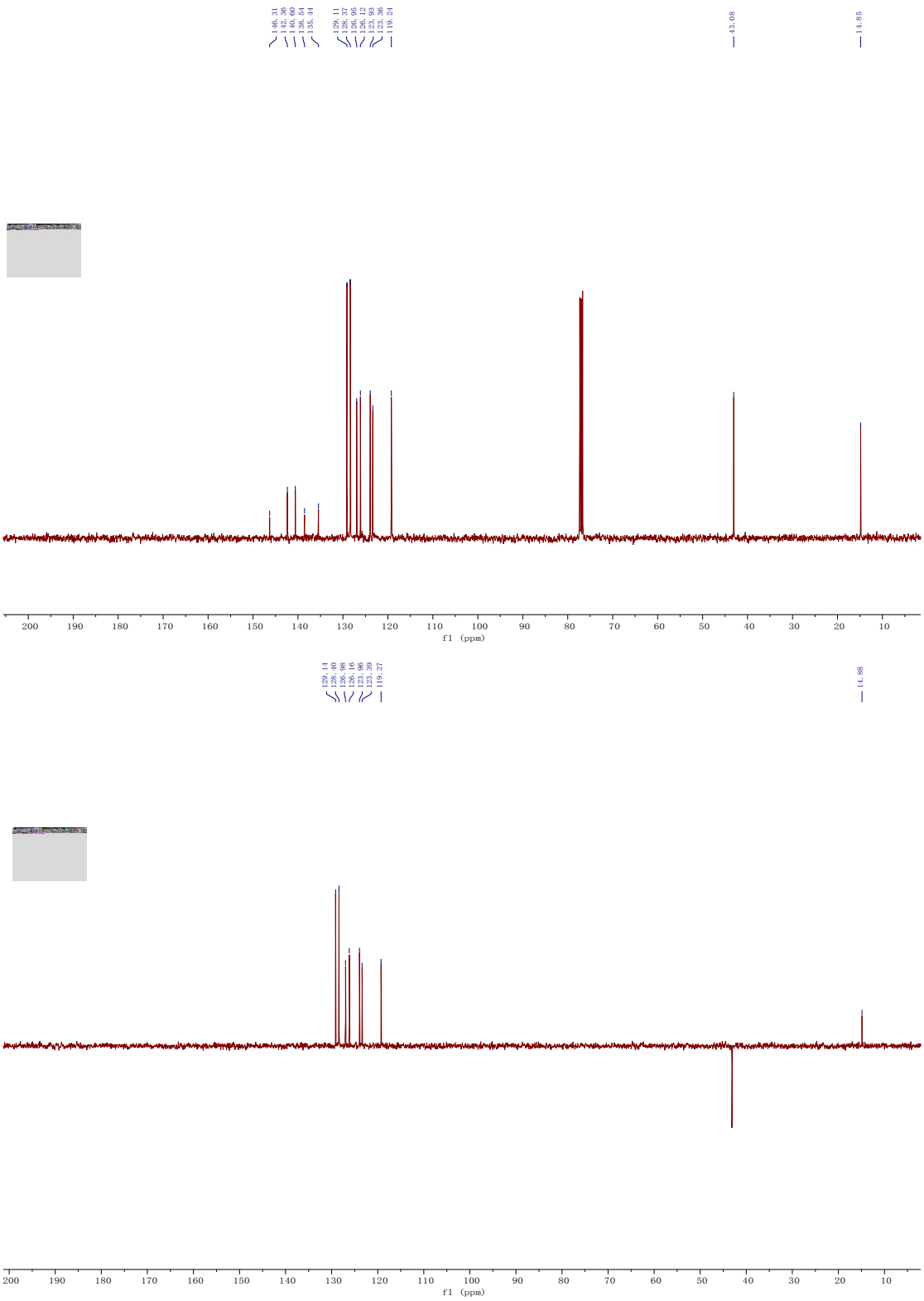


General procedure F: A solution of **1** (0.2 mmol) and $RhH(CO)(PPh_3)_2$ (0.005 mmol, 4.5 mg, 2.5 mol %) in 2 mL anhydrous toluene (0.1 M) was heated at 110 °C for 6-12 h. Then the mixture was concentrated under vacuum, and the residue was purified by a flash column chromatograph on silica gel using PE/EA (100:1) as the eluent to yield the product **2**.

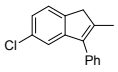
Spectroscopic data for products **2a-2p** as follow:

Compound 2a: This is a known compound.[4] An orange solid (17.1 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.07 (s, 3H), 3.38 (s, 2H), 7.04 – 7.10 (m, 1H), 7.13 – 7.18 (m, 2H), 7.27 (dd, J = 7.2 Hz, 1H), 7.30 – 7.44 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 1.0, 14.8, 43.1, 119.2, 123.4, 123.9, 126.1, 126.9, 128.4, 129.1, 135.4, 138.5, 140.6, 142.4, 146.3.



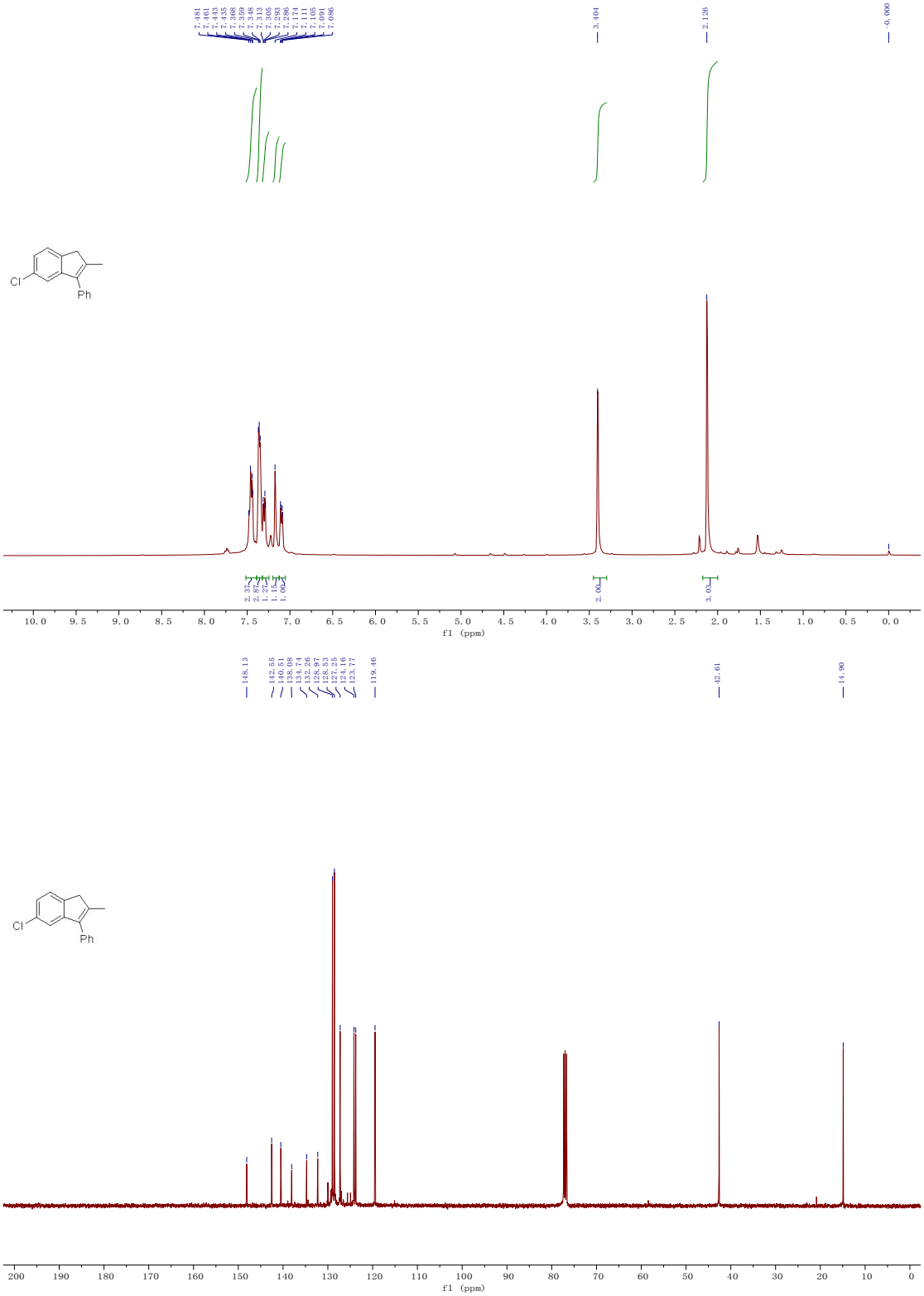


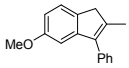
^{13}C NMR-DEPT spectrum of **2a**



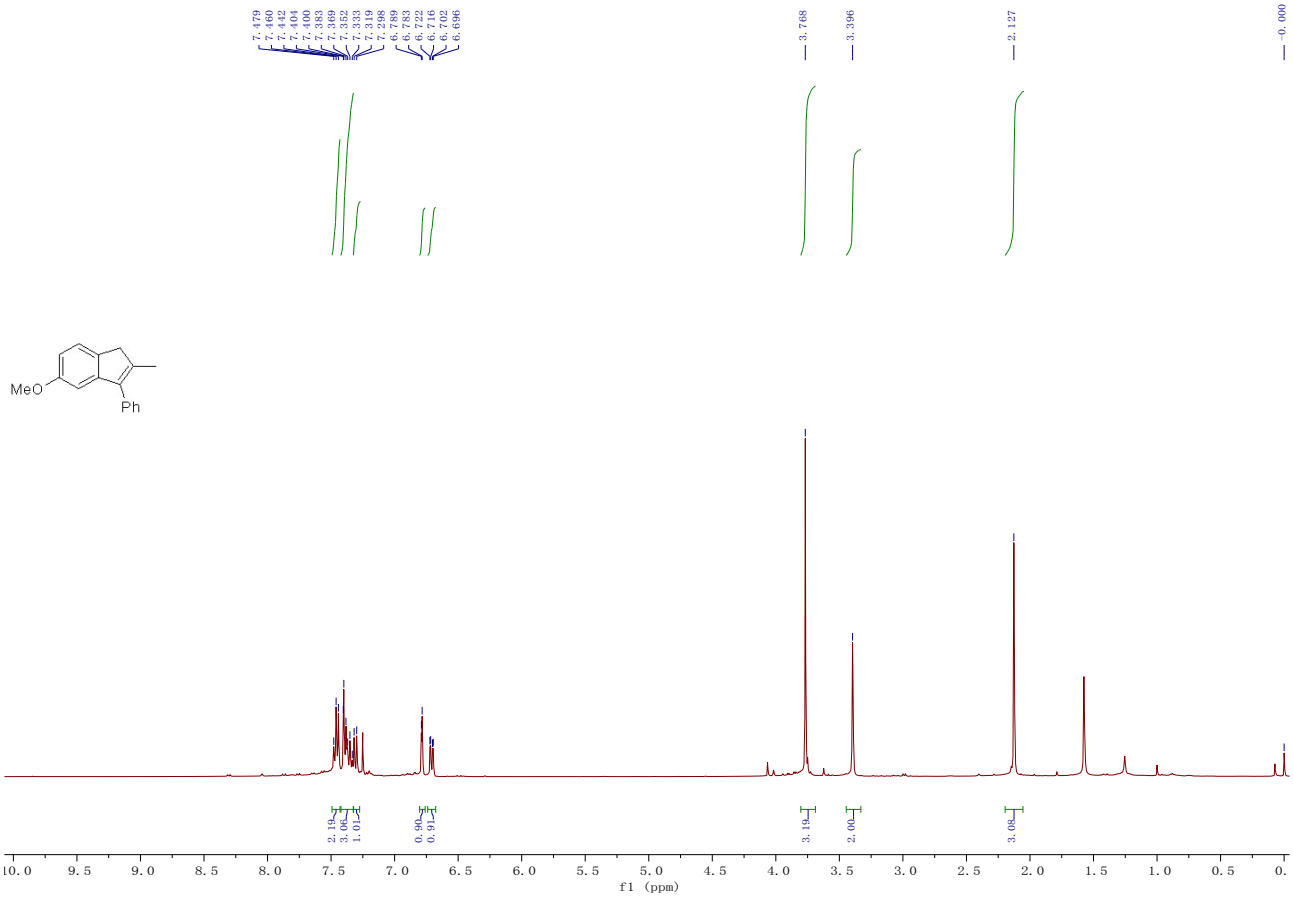
Compound 2b: A yellow oil (33.8 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.13 (s, 3H), 3.40 (s, 2H), 7.10 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.17 (s, 1H), 7.30 (dd, *J* = 7.8, 3.0 Hz, 1H), 7.32 – 7.39

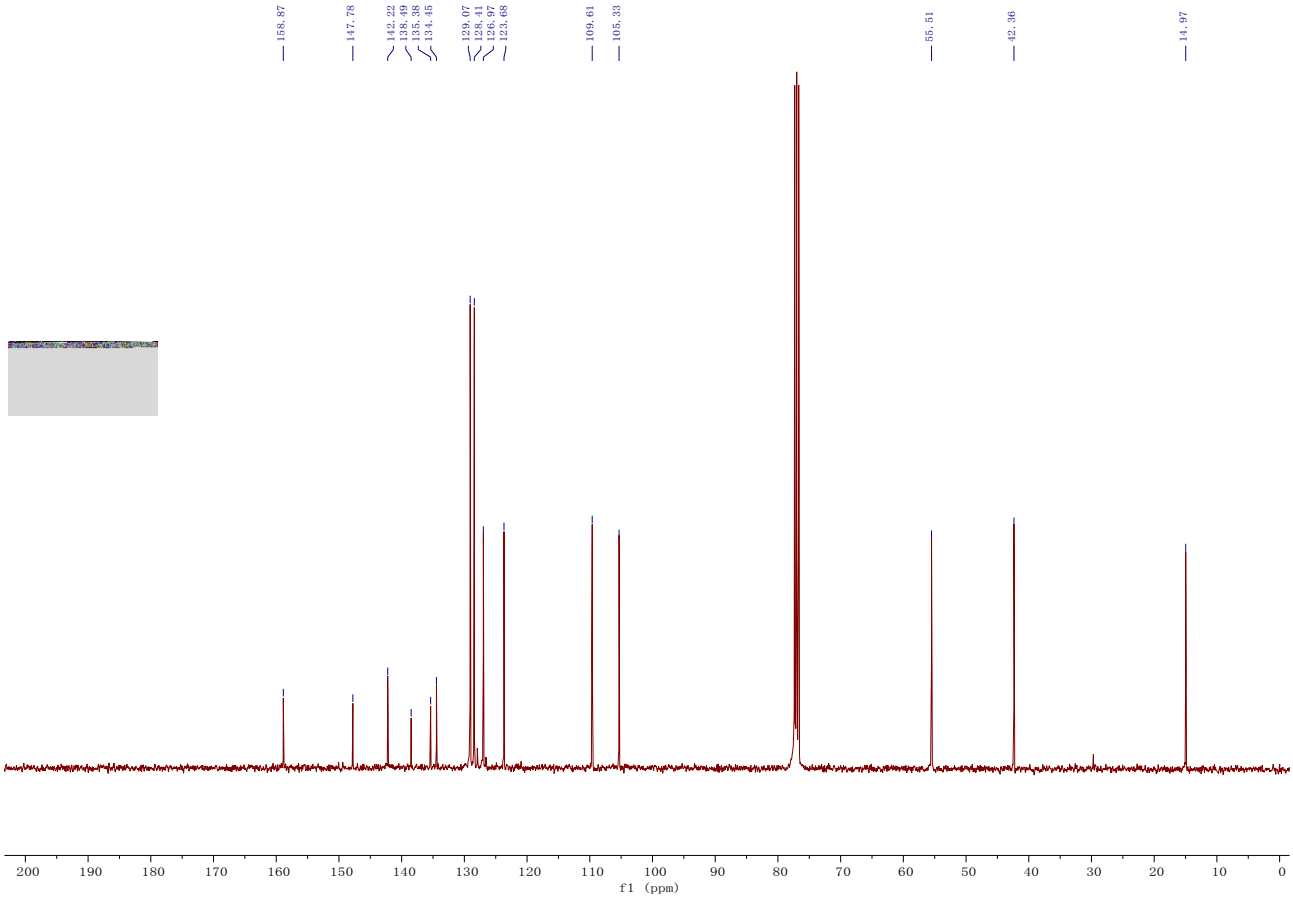
(m, 3H), 7.39 – 7.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.9, 42.6, 119.5, 123.8, 124.2, 127.2, 128.5, 129.0, 132.3, 134.7, 138.1, 140.5, 142.5, 148.1. IR (neat) ν 3063, 2972, 2922, 2844, 1718, 1660, 1587, 1489, 1460, 1400, 1288, 1090, 1063, 1013, 931, 825, 811, 762, 724 cm^{-1}. HRMS (EI) Calcd. for $C_{16}H_{13}Cl$ requires (M^+): 240.0706, Found: 240.0704.

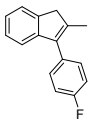




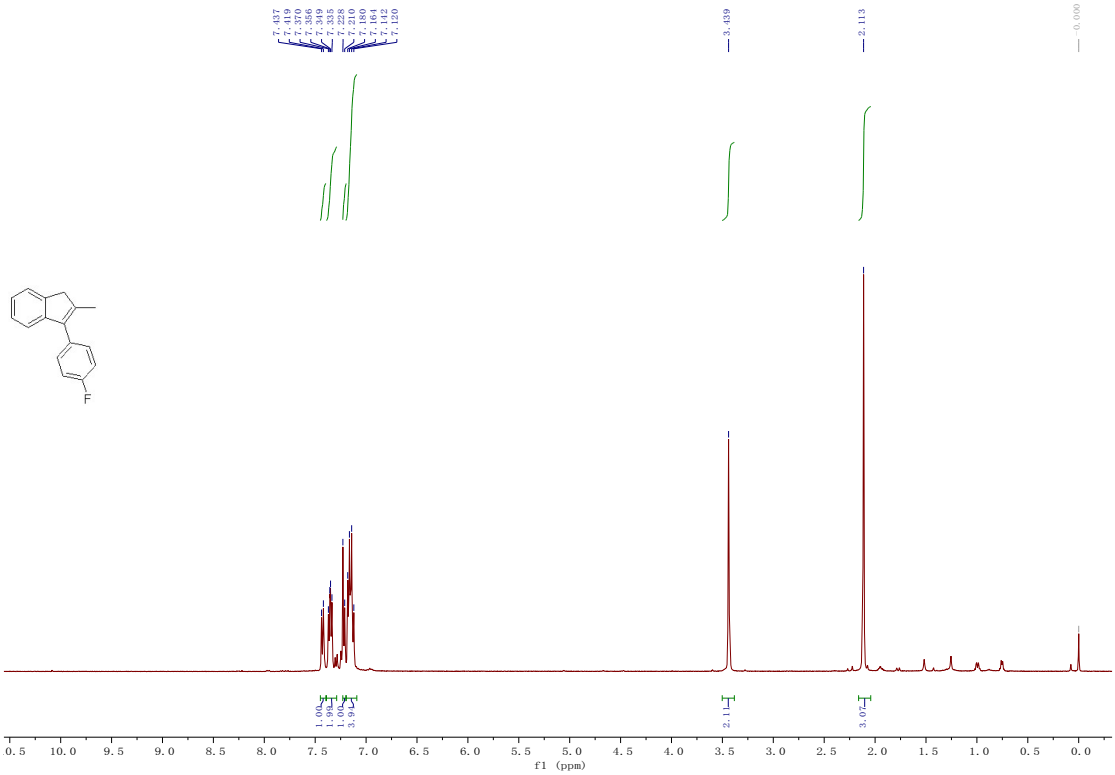
Compound 2c: A pale yellow solid (43.2 mg, 91%); M.p. 104 - 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.13 (s, 3H), 3.40 (s, 2H), 3.77 (s, 3H), 6.71 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.42 (m, 3H), 7.43 – 7.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.0, 42.4, 55.5, 105.3, 109.6, 123.7, 127.0, 128.4, 129.1, 134.5, 135.4, 138.5, 142.2, 147.8, 158.9. IR (neat) ν 3066, 3030, 2956, 2923, 2830, 1717, 1664, 1596, 1488, 1448, 1280, 1224, 1174, 1147, 1056, 1029, 967, 851, 814, 747, 699, 658 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{16}O_2$ requires (M^+): 252.1150, Found: 252.1159.







Compound 2d: A pale yellow oil (32.2 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.11 (s, 3H), 3.44 (s, 2H), 7.09 – 7.20 (m, 4H), 7.22 (d, *J* = 7.1 Hz, 1H), 7.29 – 7.39 (m, 2H), 7.43 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.77, 43.02, 115.33 (d, *J* = 21.1 Hz), 119.04, 123.41, 124.06, 125.56, 126.19, 129.01, 130.68 (d, *J* = 8.0 Hz), 137.63, 140.78, 142.28, 161.84 (d, *J* = 245.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.0. IR (neat) ν 3066, 3024, 2977, 2917, 2852, 1722, 1662, 1588, 1488, 1459, 1440, 1398, 1088, 1012, 931, 837, 812, 761, 722, 662 cm^{-1}. HRMS (EI) Calcd. for $C_{16}H_{13}F$ requires (M^+): 224.1001, Found: 224.1003.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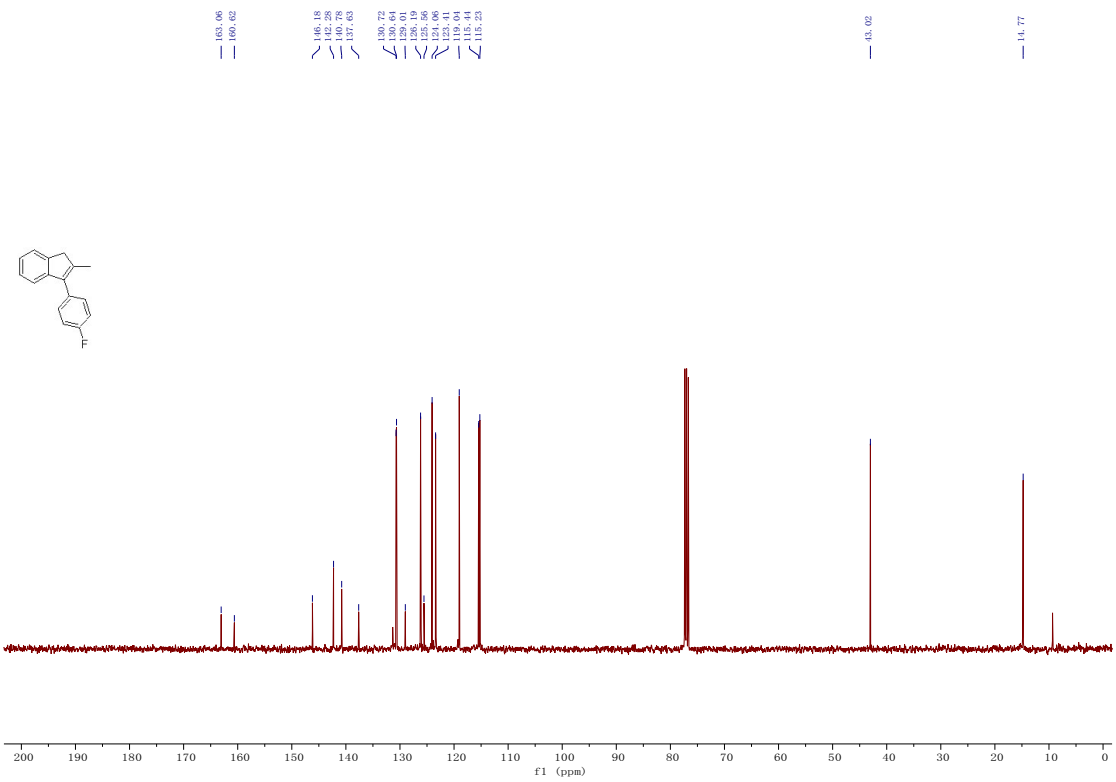
1.00
1.99
1.00
3.91
2.11
3.07
f1 (ppm)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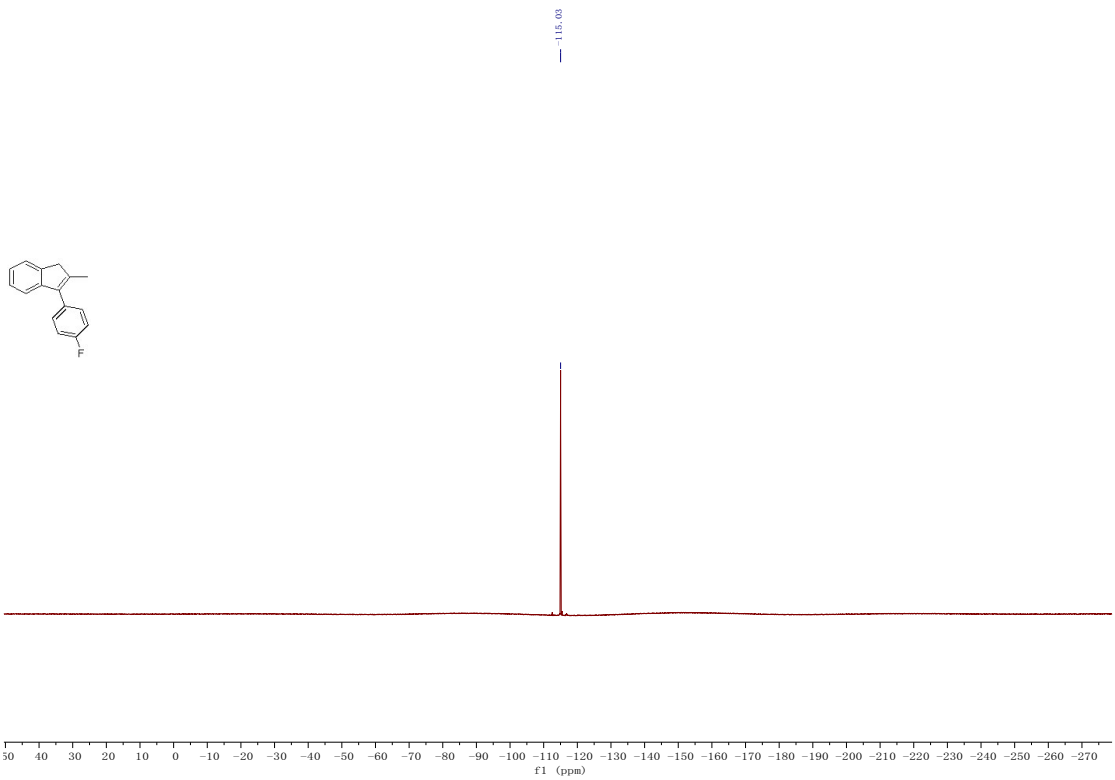
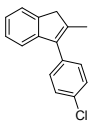
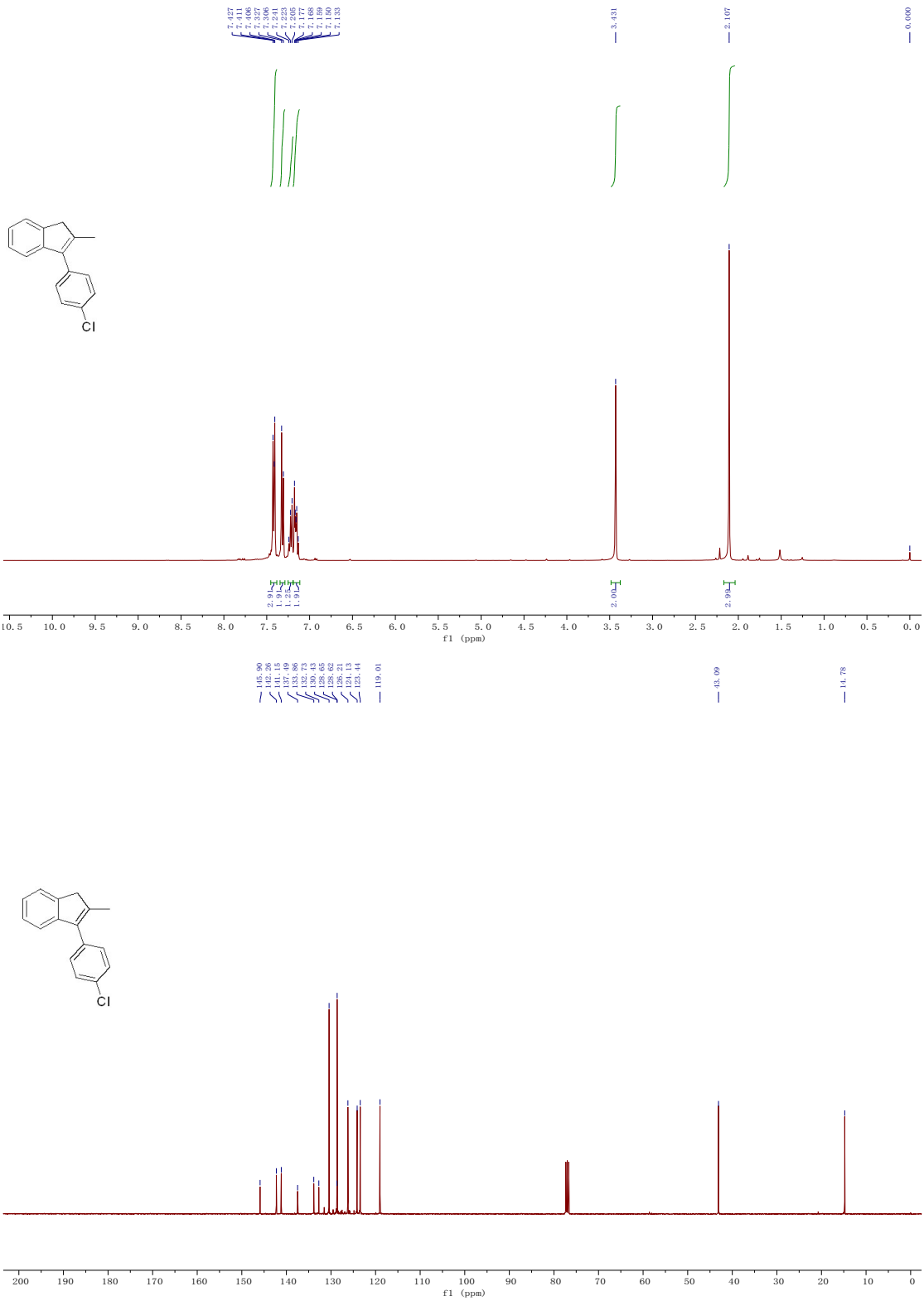
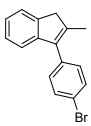




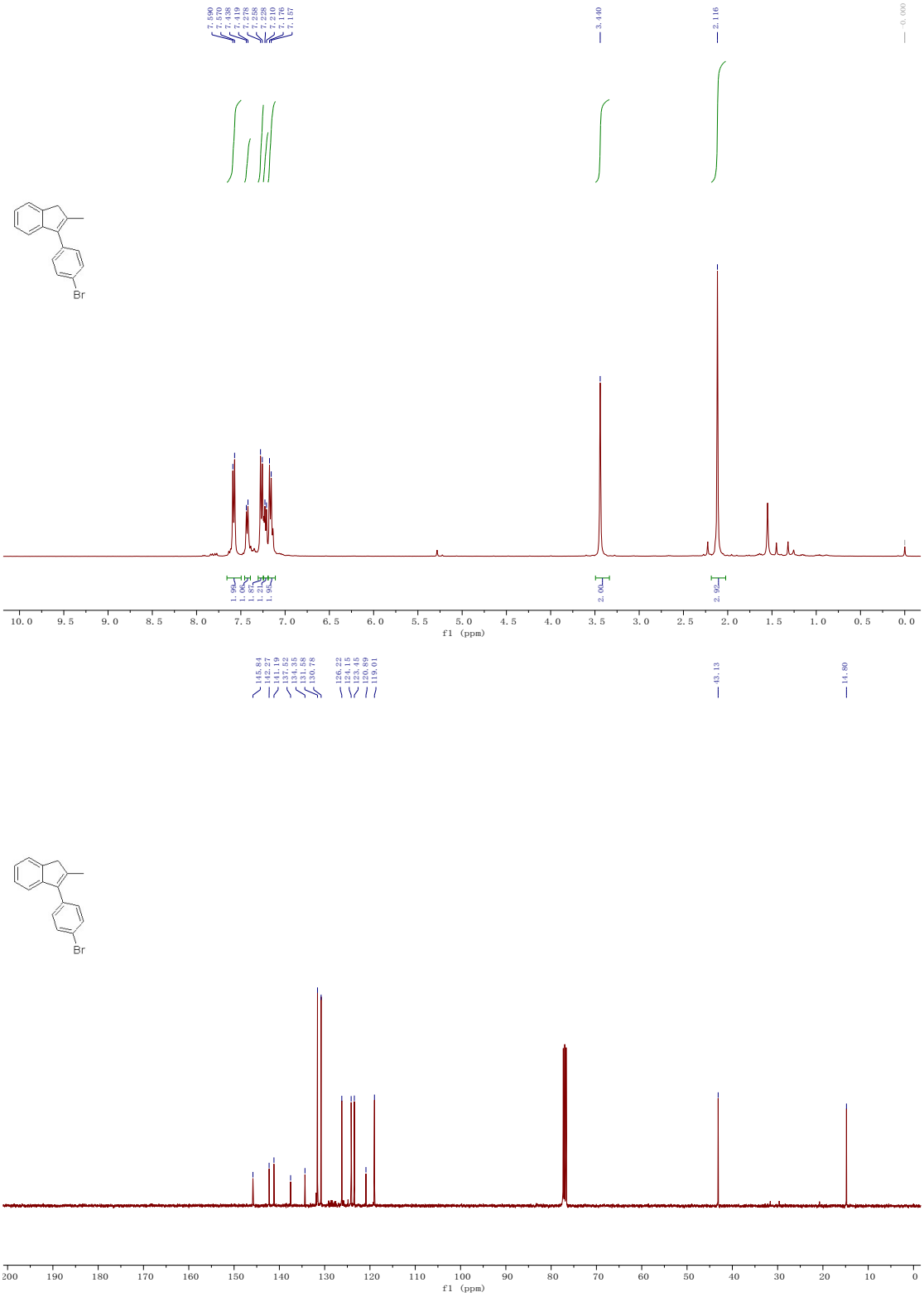
Compound 2e: A yellow solid (34.1 mg, 71%); M.p. 52 - 53 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.11 (s, 3H), 3.43 (s, 2H), 7.11 – 7.19 (m, 2H), 7.19 – 7.25 (m, 1H), 7.29 – 7.34 (m, 2H), 7.38 – 7.45 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.8, 43.1, 119.0, 123.4, 124.1, 126.2, 128.6, 128.6, 130.4, 132.7, 133.9, 137.5, 141.1, 142.3, 145.9. IR (neat) ν 3066, 3016, 2969, 2909, 2852, 1702, 1488, 1460, 1440, 1399, 1089, 1013, 931, 837, 812, 761, 722, 662 cm^{-1}. HRMS (EI) Calcd. for $C_{16}H_{13}Cl$ requires (M^+): 240.0706, Found: 240.0711.

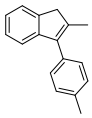




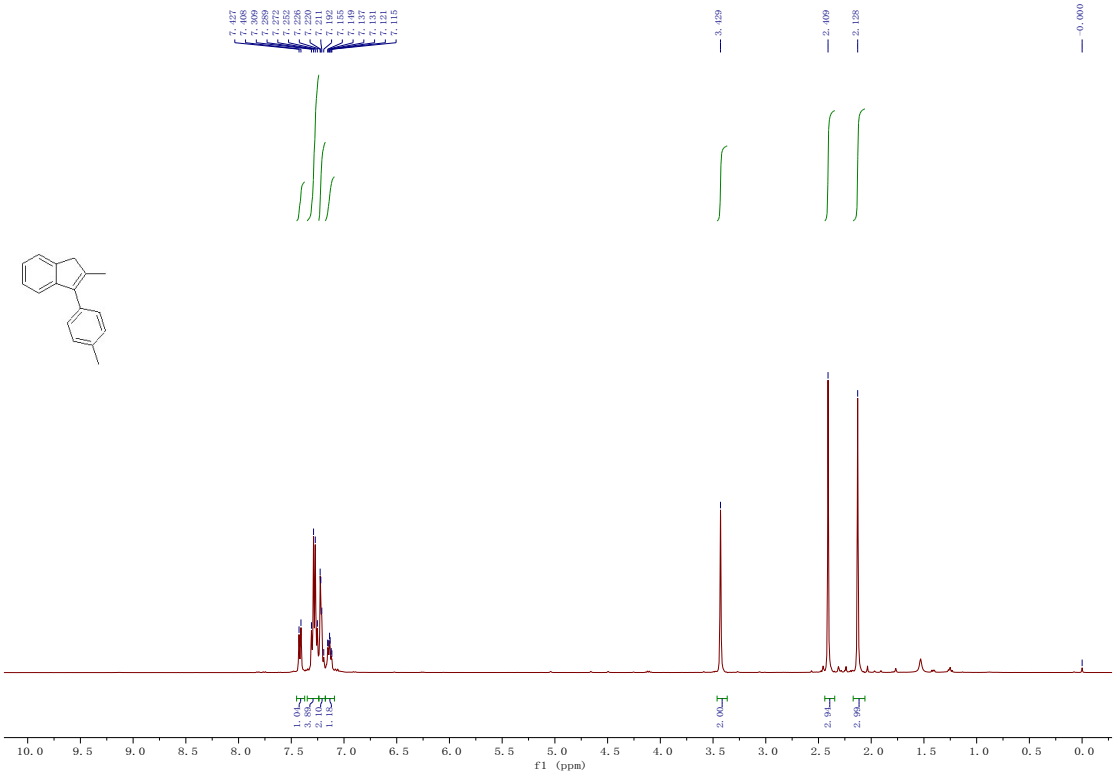
Compound 2f: A yellow solid (22.9 mg, 40%); M.p. 45 - 47 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.12 (s, 3H), 3.44 (s, 2H), 7.11 – 7.19 (m, 2H), 7.22 (d, J = 7.1 Hz, 1H), 7.25 – 7.30 (m, 2H), 7.43

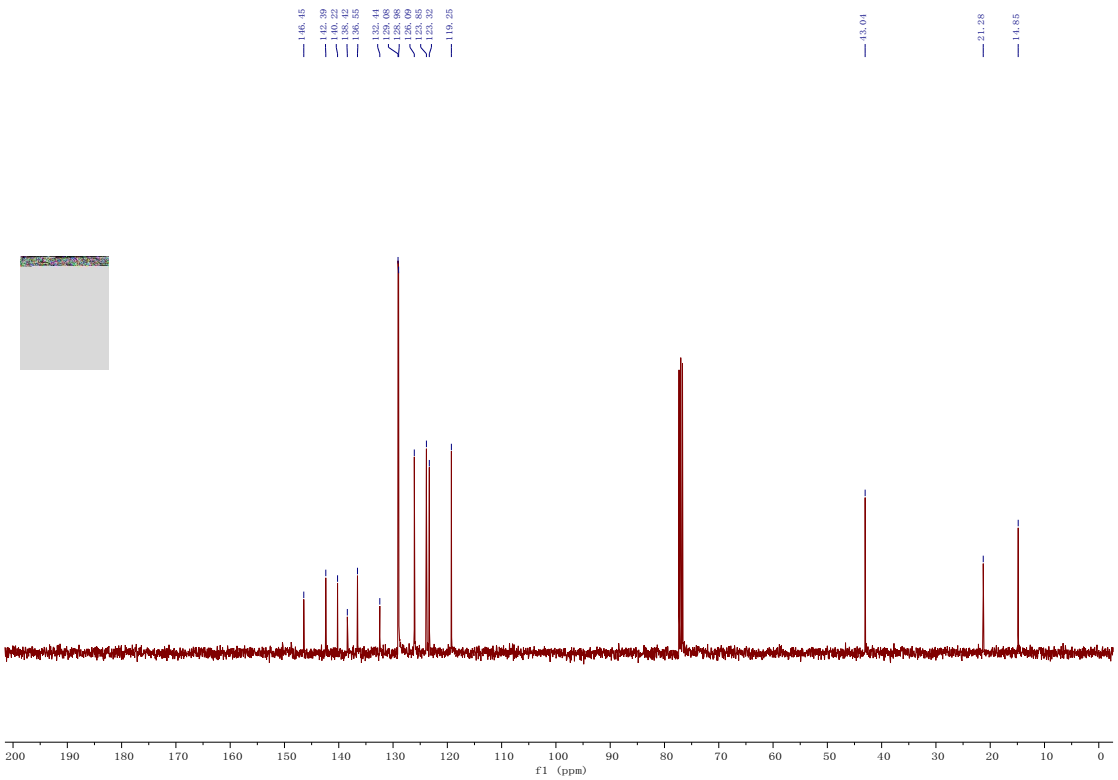
(d, J = 7.3 Hz, 1H), 7.50 – 7.66 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.8, 43.1, 119.0, 120.9, 123.4, 124.2, 126.2, 130.8, 131.6, 134.4, 137.5, 141.2, 142.3, 145.8. IR (neat) ν 3071, 2927, 2850, 1720, 1661, 1585, 1486, 1460, 1495, 1357, 1254, 1159, 1099, 1069, 1009, 959, 930, 809, 762, 738 cm^{-1}. HRMS (EI) Calcd. for $C_{16}H_{13}Br$ requires (M^+): 284.0201, Found: 284.0203.

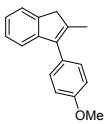




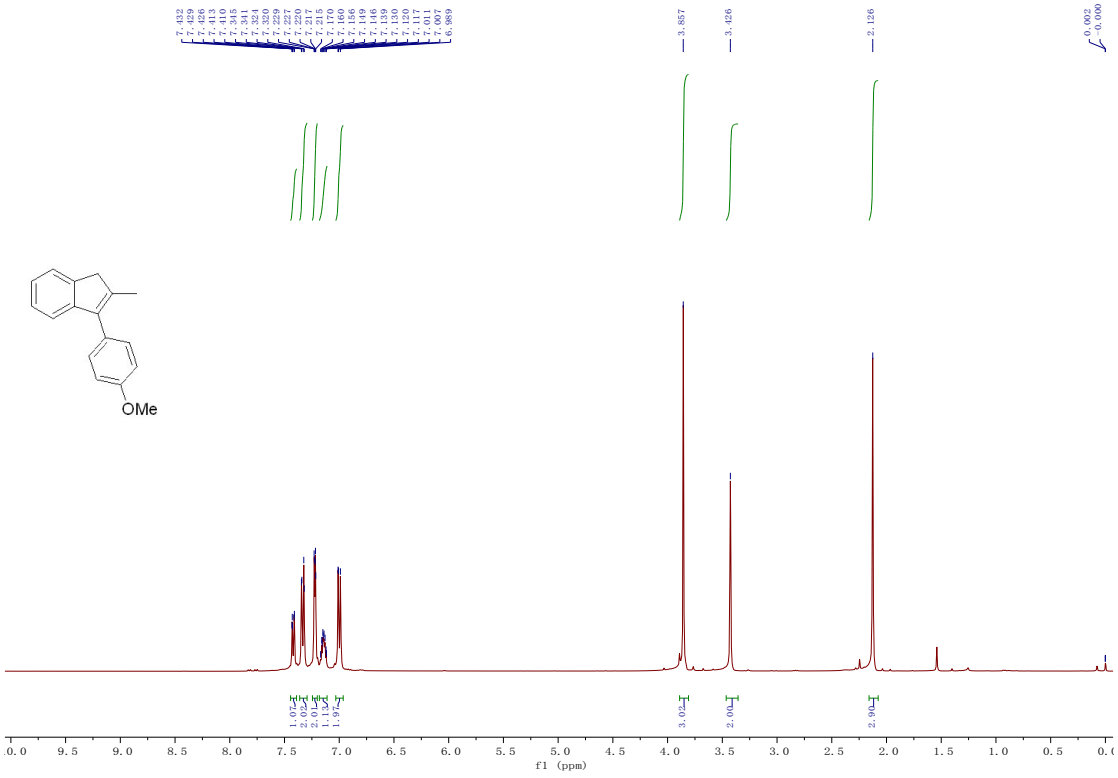
Compound 2g: A pale yellow oil (26.9 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.13 (s, 3H), 2.41 (s, 3H), 3.43 (s, 2H), 7.13 (ddd, J = 6.8, 2.5 Hz, 1H), 7.18 – 7.24 (m, 2H), 7.24 – 7.35 (m, 4H), 7.42 (d, J = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.8, 21.3, 43.0, 119.3, 123.3, 123.9, 126.1, 129.0, 129.1, 132.4, 136.6, 138.4, 140.2, 142.4, 146.4. IR (neat) ν 3068, 3025, 2967, 2922, 2865, 1717, 1655, 1604, 1511, 1477, 1459, 1376, 1273, 1181, 1063, 1020, 931, 823, 805, 758, 726, 670 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{16}$ requires (M^+): 220.1252, Found: 220.1258.

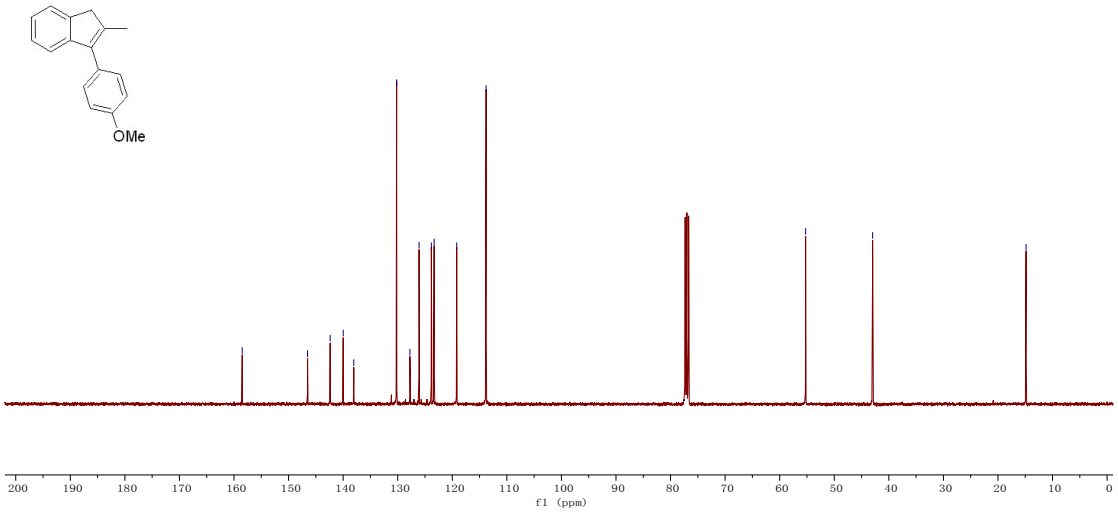


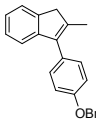




Compound 2h: A pale yellow solid (32.3 mg, 68%); M.p. 66 - 68 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.13 (s, 3H), 3.43 (s, 2H), 3.86 (s, 3H), 6.96 – 7.03 (m, 2H), 7.14 (ddd, *J* = 10.3, 4.0 Hz, 1H), 7.20 – 7.24 (m, 2H), 7.29 – 7.36 (m, 2H), 7.39 – 7.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.8, 43.0, 55.2, 113.8, 119.2, 123.3, 123.8, 126.1, 127.8, 130.2, 138.0, 140.0, 142.4, 146.5, 158.5. IR (neat) ν 3074, 3037, 3003, 2972, 2933, 2904, 2873, 2844, 1728, 1662, 1602, 1509, 1463, 1440, 1300, 1282, 1244, 1176, 1150, 1111, 1026, 1002, 839, 818, 793, 762, 729, 720 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{16}O$ requires (M^+): 236.1201, Found: 236.1210.

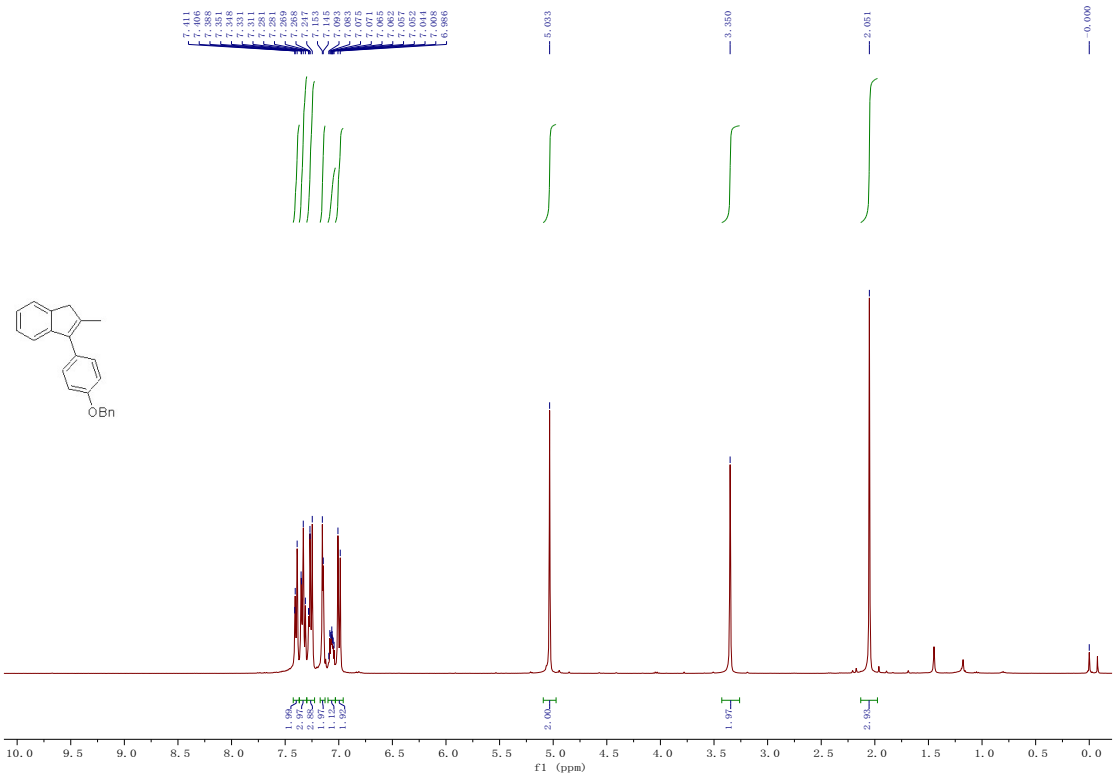


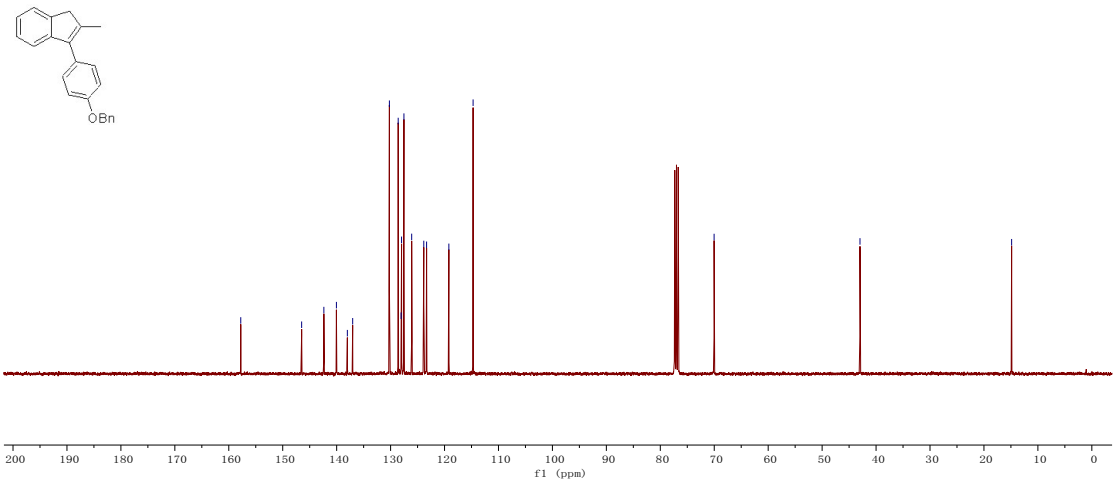


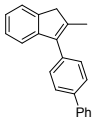


Compound 2i: A yellow solid (37.3 mg, 60%); M.p. 43 - 44 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.05 (s, 3H), 3.35 (s, 2H), 5.03 (s, 2H), 6.96 – 7.03 (m, 2H), 7.06 (ddd, *J* = 7.3, 5.2, 3.4 Hz, 1H),

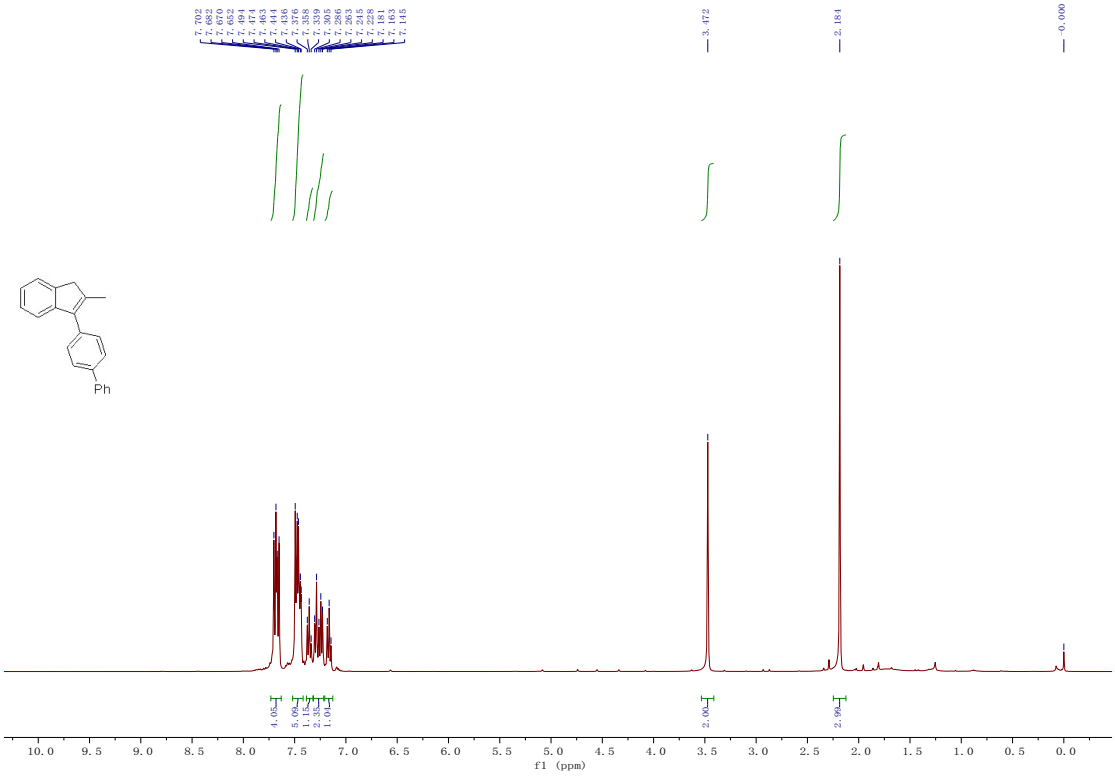
7.13 – 7.17 (m, 2H), 7.23 – 7.30 (m, 3H), 7.30 – 7.37 (m, 3H), 7.37 – 7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.9, 43.0, 70.0, 114.7, 119.2, 123.3, 123.8, 126.1, 127.5, 128.0, 128.0, 128.6, 130.2, 137.0, 138.0, 140.0, 142.4, 146.5, 157.8. IR (neat) ν 3066, 3032, 2971, 2928, 1720, 1651, 1598, 1508, 1454, 1381, 1243, 1175, 1151, 1060, 1016, 932, 829, 763, 733, 697 cm^{-1}. HRMS (EI) Calcd. for $C_{23}H_{20}O$ requires (M^+): 312.1514, Found: 312.1517.

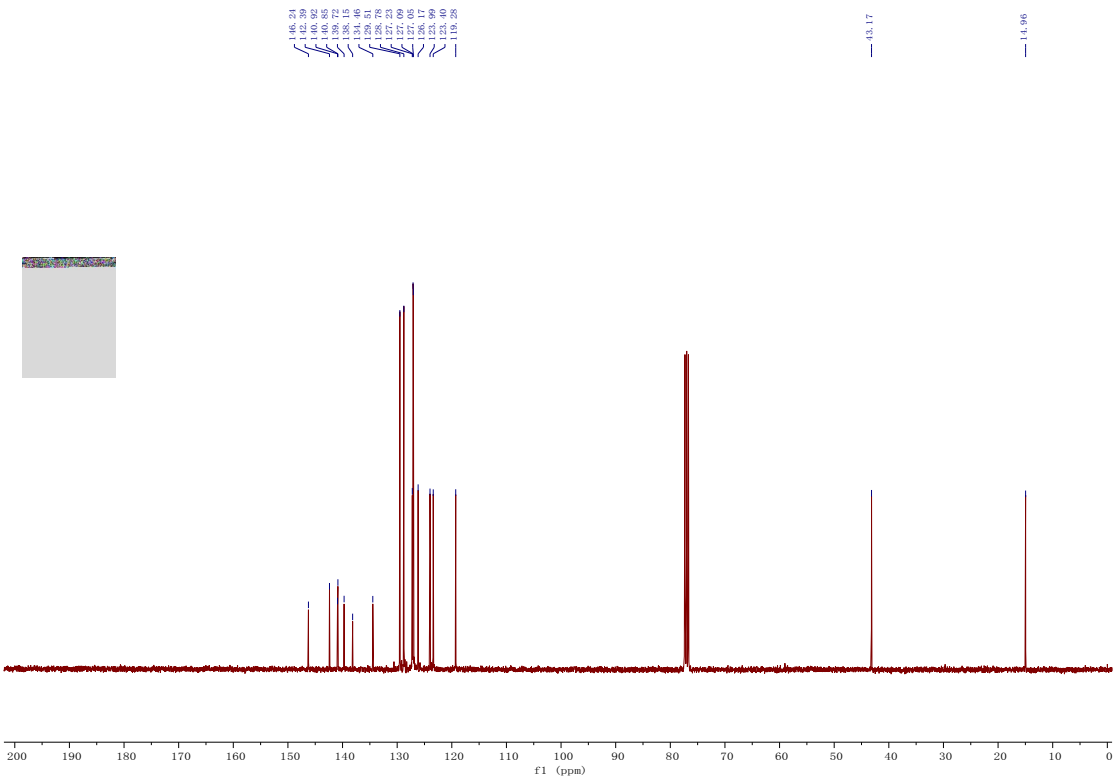


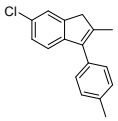




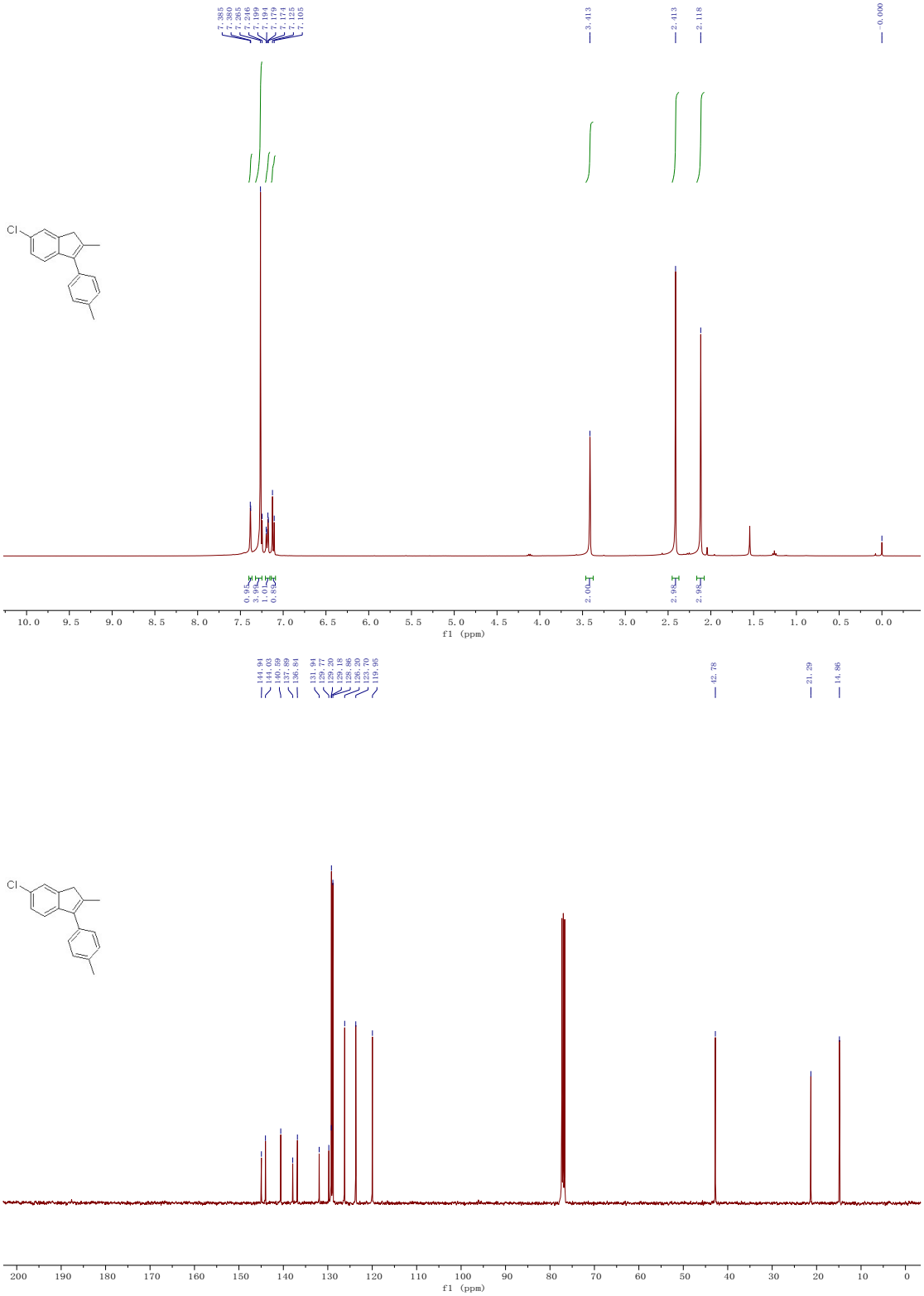
Compound 2j: A yellow solid (23.8 mg, 42%); M.p. 104 - 106 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.18 (s, 3H), 3.47 (s, 2H), 7.16 (dd, *J* = 7.2 Hz, 1H), 7.22 – 7.32 (m, 2H), 7.36 (dd, *J* = 7.5 Hz, 1H), 7.42 – 7.52 (m, 5H), 7.63 – 7.73 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.0, 43.2, 119.3, 123.4, 124.0, 126.2, 127.0, 127.1, 127.2, 128.8, 129.5, 134.5, 138.2, 139.7, 140.8, 140.9, 142.4, 146.2. IR (neat) ν 3053, 3030, 3016, 2961, 2902, 2878, 2849, 1600, 1486, 1609, 1458, 1447, 1393, 1199, 1181, 1111, 1076, 1022, 1006, 936, 840, 813, 759, 725, 693 cm^{-1}. HRMS (EI) Calcd. for $C_{22}H_{18}$ requires (M^+): 282.1409, Found: 282.1415.

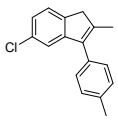






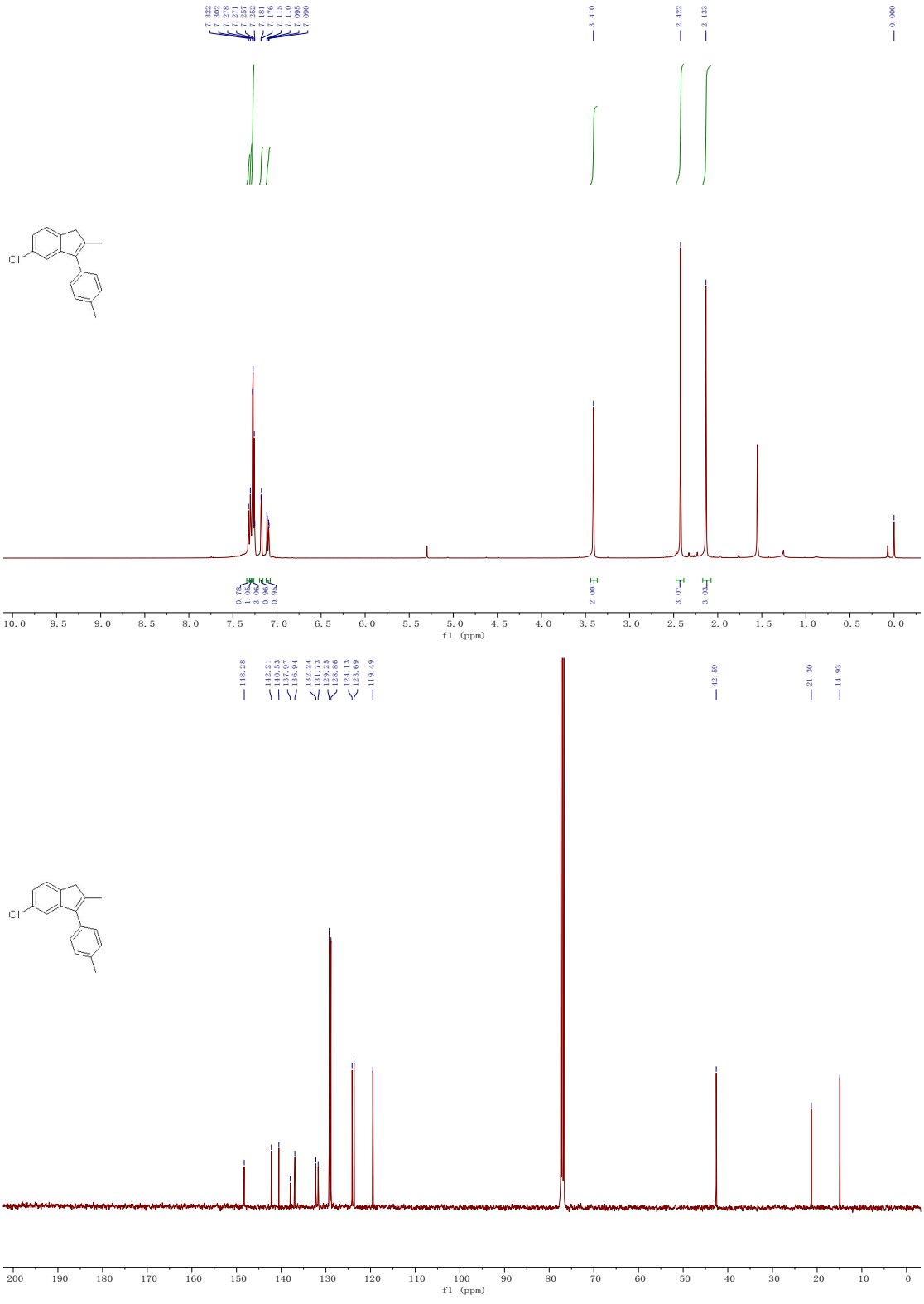
Compound 2k: A white solid (31.3 mg, 61%); M.p. 123 - 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.12 (s, 3H), 2.41 (s, 3H), 3.41 (s, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 7.19 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.25 – 7.32 (m, 4H), 7.38 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.9, 21.3, 42.8, 120.0, 123.7, 126.2, 128.9, 129.2, 129.2, 129.8, 131.9, 136.8, 137.9, 140.6, 144.0, 144.9. IR (neat) ν 3030, 2969, 2923, 2896, 2849, 1563, 1508, 1457, 1414, 1378, 1150, 1112, 1068, 937, 867, 821, 814, 736 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{15}Cl$ requires (M^+): 254.0862, Found: 254.0864.

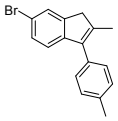




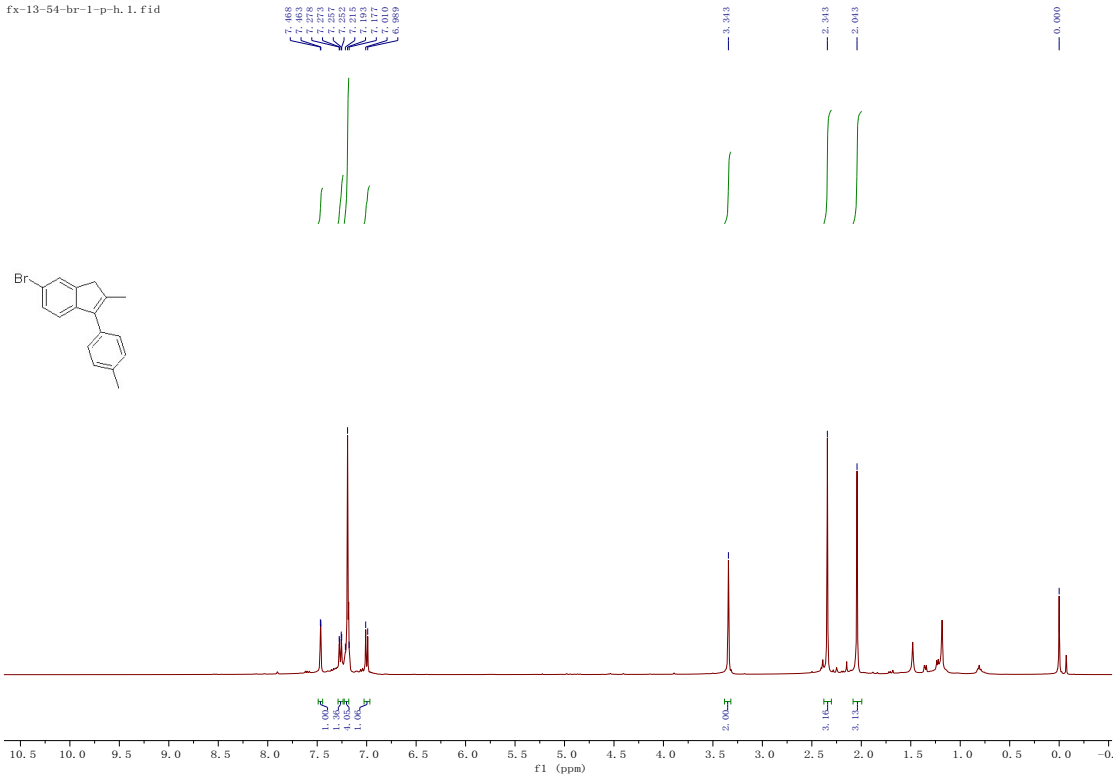
Compound 2l: An orange solid (40.2 mg, 79%); M.p. 71 - 73 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.13 (s, 3H), 2.42 (s, 3H), 3.41 (s, 2H), 7.10 (dd, J = 7.9, 2.0 Hz, 1H), 7.18 (d, J = 2.0 Hz,

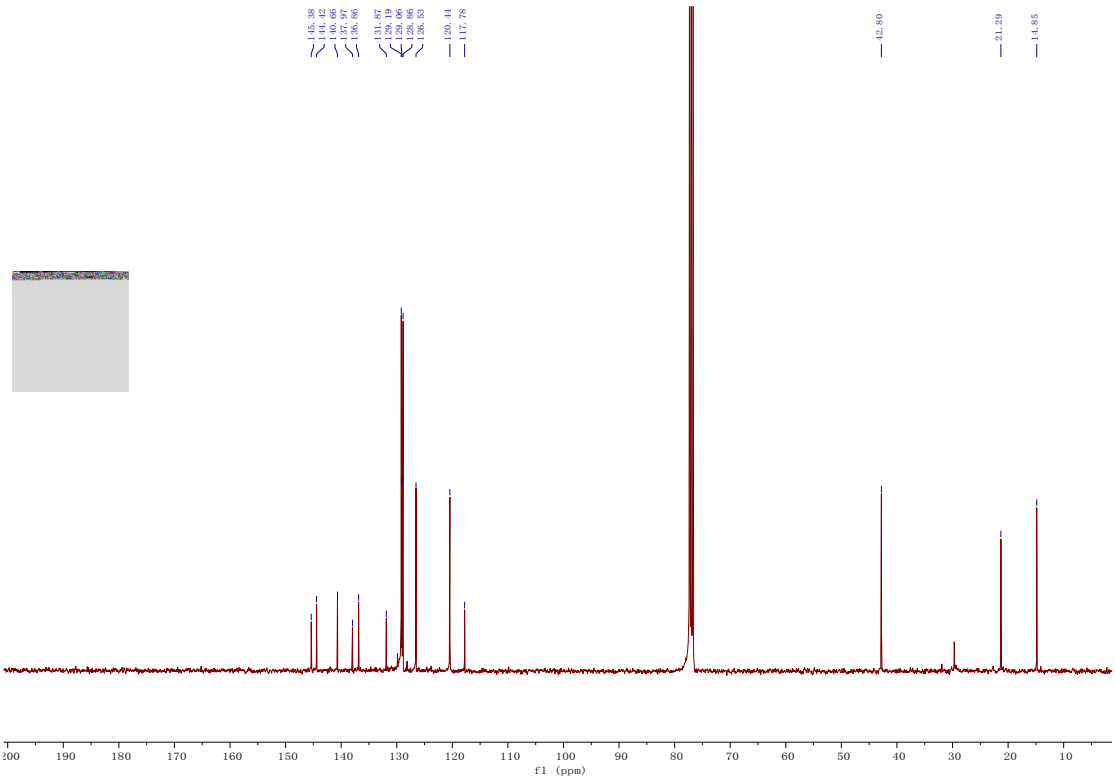
1H), 7.26 – 7.29 (m, 3H), 7.30 (s, 1H), 7.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.9, 21.3, 42.6, 119.5, 123.7, 124.1, 128.9, 129.2, 131.7, 132.2, 136.9, 138.0, 140.5, 142.2, 148.3. IR (neat) ν 3056, 3022, 2959, 2928, 2847, 1671, 1585, 1516, 1494, 1447, 1436, 1301, 1282, 1009, 821, 773, 745, 700 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{15}Cl$ requires (M^+): 254.0862, Found: 254.0868.

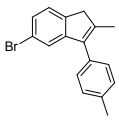




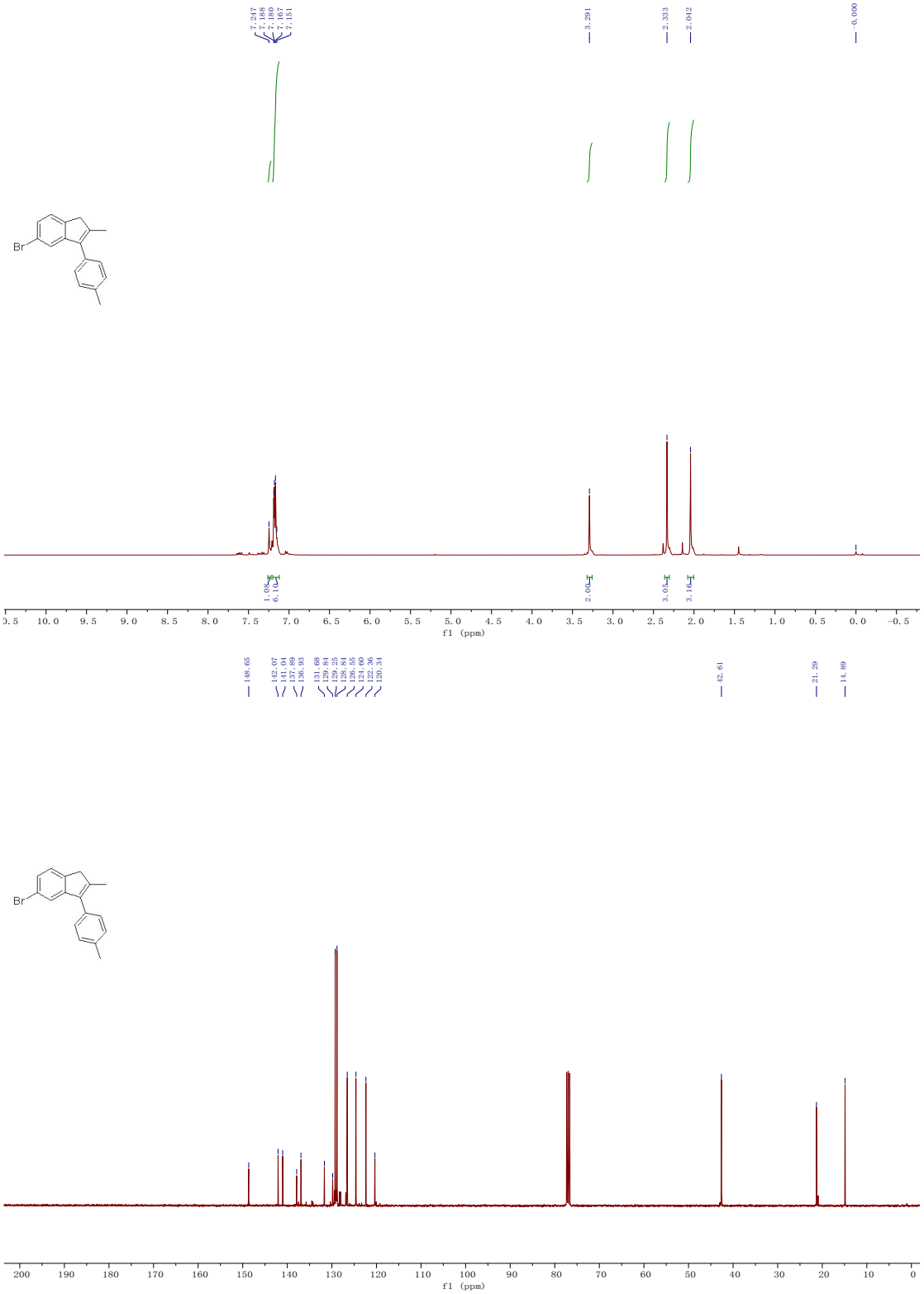
Compound 2m: A yellow solid (13.4 mg, 22%); M.p. 91 - 93 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.04 (s, 3H), 2.34 (s, 3H), 3.34 (s, 2H), 7.00 (d, *J* = 8.1 Hz, 1H), 7.18 – 7.23 (m, 4H), 7.26 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.47 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.8, 21.3, 42.8, 117.8, 120.4, 126.5, 128.9, 129.1, 129.2, 131.9, 136.9, 138.0, 140.7, 144.4, 145.4. IR (neat) ν 3035, 2962, 2920, 2852, 1660, 1602, 1508, 1456, 1412, 1375, 1255, 1112, 1059, 1019, 936, 852, 819, 735 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{15}Br$ requires (M^+): 298.0357, Found: 298.0356.

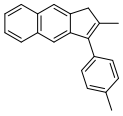






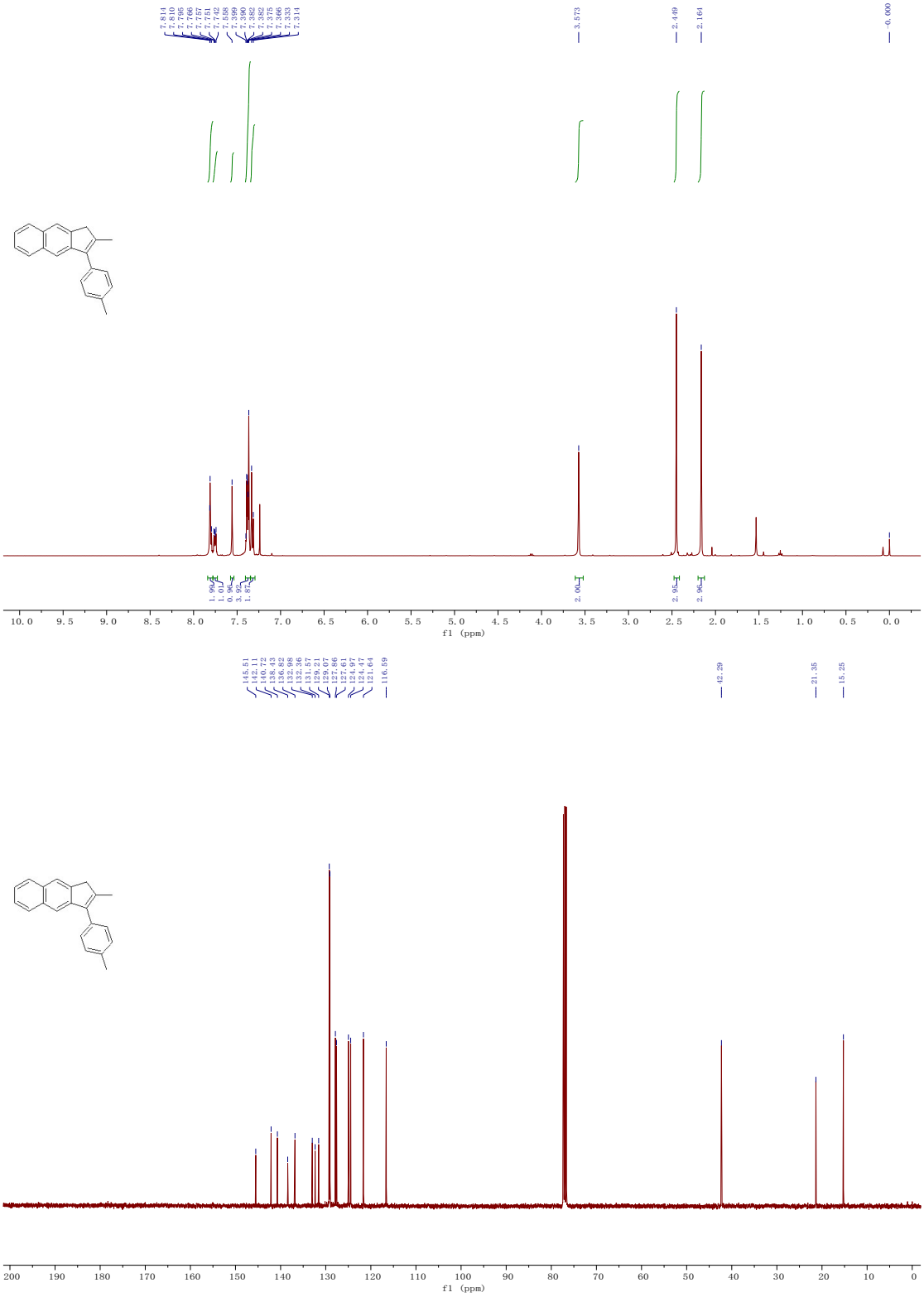
Compound 2n: A pale yellow solid (15.8 mg, 26%); M.p. 67 - 69 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.04 (s, 3H), 2.33 (s, 3H), 3.29 (s, 2H), 7.12 – 7.20 (m, 6H), 7.25 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.9, 21.3, 42.6, 120.3, 122.4, 124.6, 126.5, 128.8, 129.2, 129.8, 131.7, 136.9, 137.9, 141.0, 142.1, 148.6. IR (neat) ν 3027, 2964, 2917, 2860, 1724, 1660, 1604, 1469, 1408, 1311, 1259, 1158, 1062, 1020, 941, 805, 753, 720, 687 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{15}Br$ requires (M^+): 298.0357, Found: 298.0353.

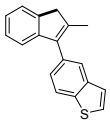




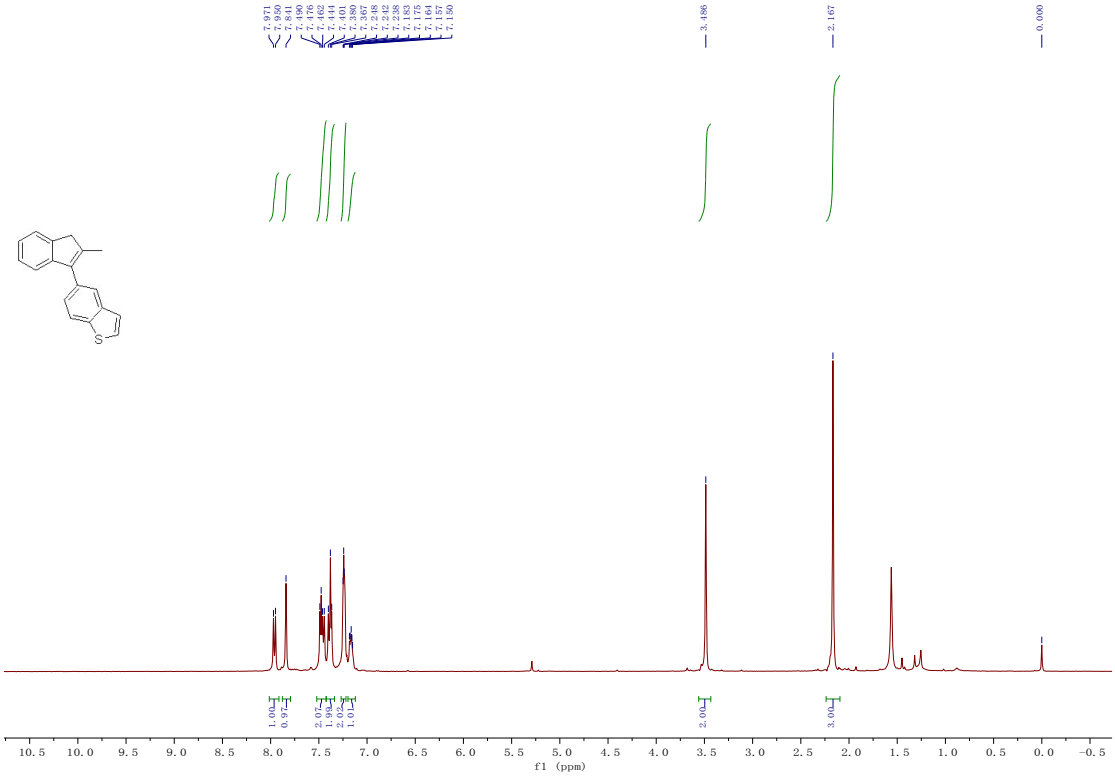
Compound 2o: A pale yellow oil (33.6 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.16 (s, 3H), 2.45 (s, 3H), 3.57 (s, 2H), 7.29 – 7.34 (m, 2H), 7.35 – 7.40 (m, 4H), 7.56 (s, 1H), 7.75 (dd, *J* =

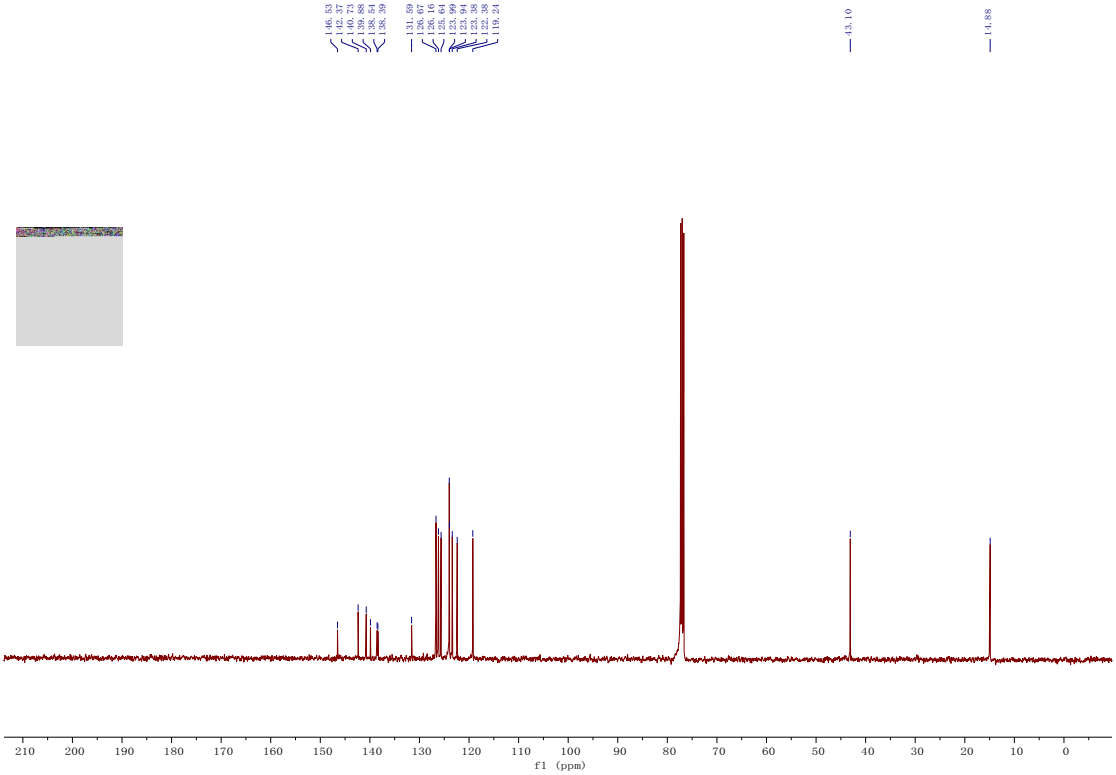
6.1, 3.5 Hz, 1H), 7.78 – 7.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 15.3, 21.3, 42.3, 116.6, 121.6, 124.5, 125.0, 127.6, 127.9, 129.1, 129.2, 131.6, 132.4, 133.0, 136.8, 138.4, 140.7, 142.1, 145.5. IR (neat) ν 2964, 2925, 2863, 1660, 1607, 1518, 1464, 1283, 1259, 1180, 1158, 1110, 1062, 941, 805, 753, 687 cm^{-1}. HRMS (EI) Calcd. for $C_{21}H_{18}$ requires (M^+): 270.1409, Found: 270.1406.





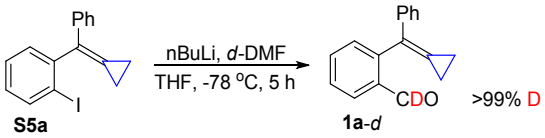
Compound 2p: A pale yellow solid (17.4 mg, 33%); M.p. 94 - 96 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.17 (s, 3H), 3.49 (s, 2H), 7.12 – 7.20 (m, 1H), 7.22 – 7.27 (m, 2H), 7.34 – 7.42 (m, 2H), 7.42 – 7.52 (m, 2H), 7.84 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.9, 43.1, 119.2, 122.4, 123.4, 123.9, 124.0, 125.6, 126.2, 126.7, 131.6, 138.4, 138.5, 139.9, 140.7, 142.4, 146.5. IR (neat) ν 3061, 2962, 2920, 2847, 1704, 1641, 1587, 1490, 1456, 1263, 1152, 1117, 1100, 1027, 814, 752, 721, 700 cm^{-1}. HRMS (EI) Calcd. for $C_{18}H_{14}S$ requires (M^+): 262.0816, Found: 262.0815.




146.53
142.37
140.73
139.88
138.54
138.39
131.89
129.67
126.16
125.64
123.99
123.94
123.38
122.38
119.24
43.10
14.88
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

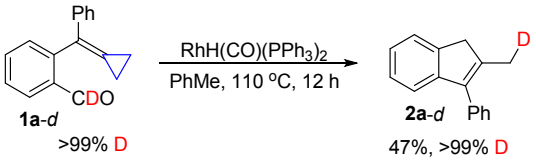
Labeling experiment: for the synthesis of **1a**-*d* and **2a**-*d*

General procedure for the synthesis of compound **1a**-*d*[5]:



To a solution of **S5a** in anhydrous Et_2O (1.0 M) was added nBuLi (1.6 M, 1.3 equiv) at -78 °C over 20 min, then *d*-DMF was added at -78 °C. The reaction mixture was stirred at rt for 1 h, and then the reaction was quenched with 1.0 mL H_2O. After the reaction was completed, the mixture was extracted with EA (3 x 30 mL), and the combined extracts were washed with water and brine, dried over anhydrous Na_2SO_4. After the solution was filtered through a celite pad, the solvent was evaporated under vacuum and the residue was purified by a flash column chromatograph on Al_2O_3 using PE/EA (10:1) as the eluent to yield the product **1a**-*d* as a white solid in 56% yield.

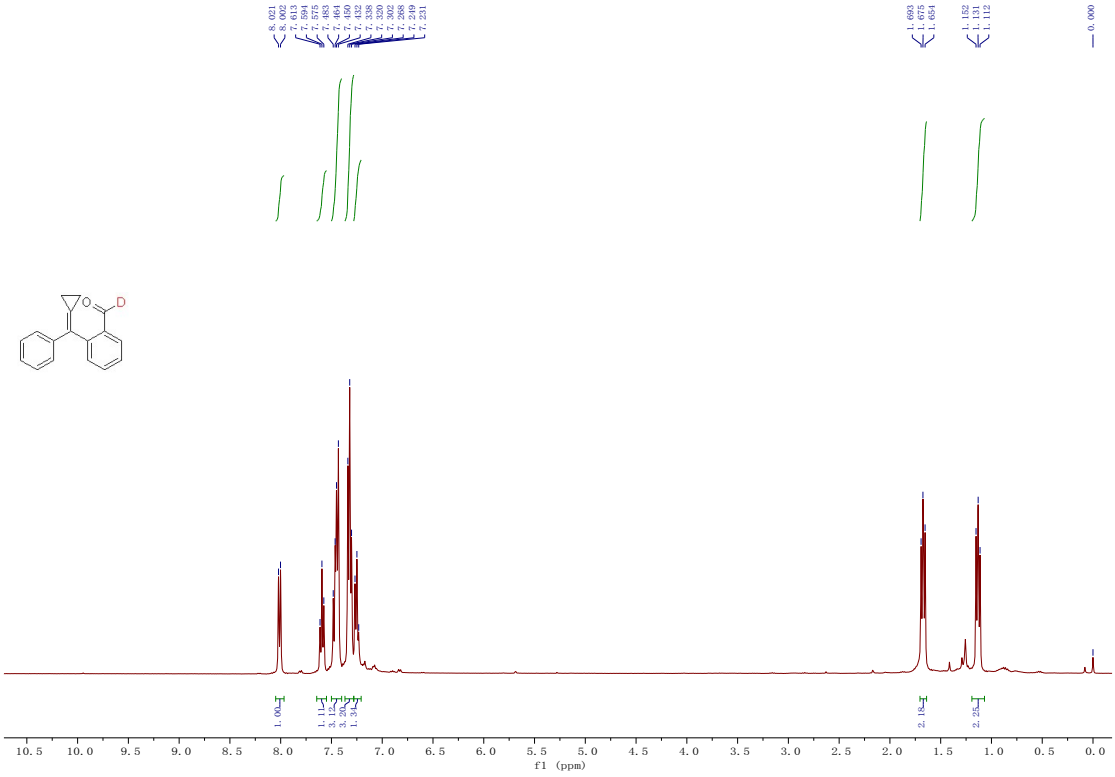
General procedure for the synthesis of compound **2a**-*d*:

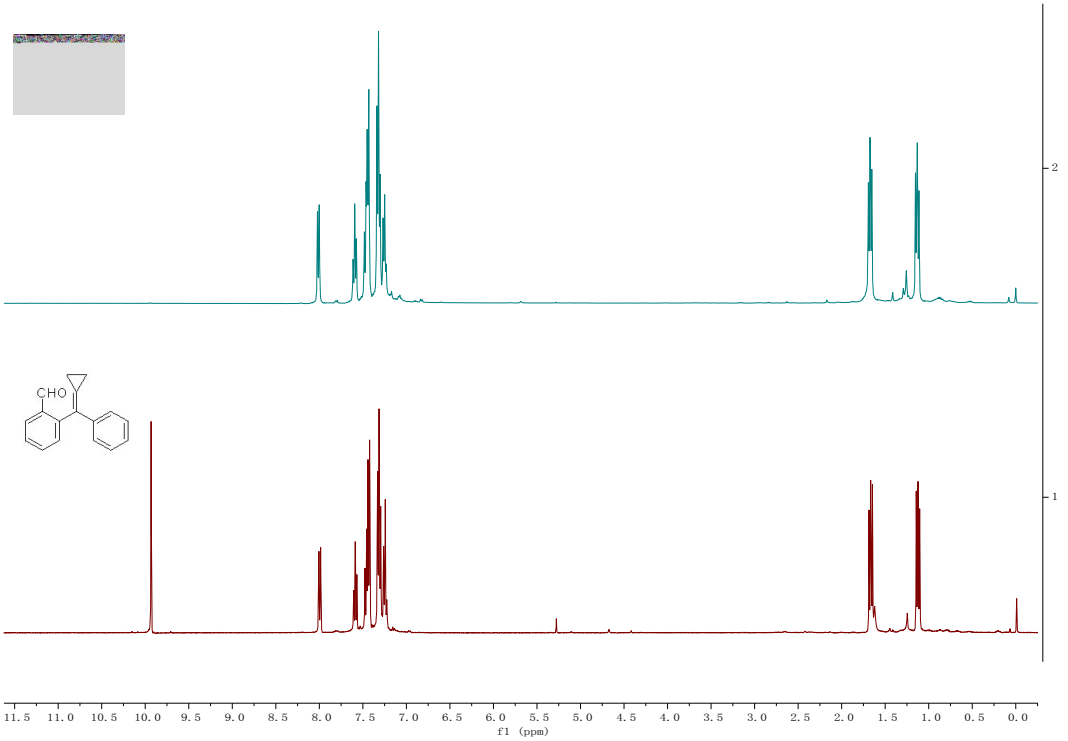


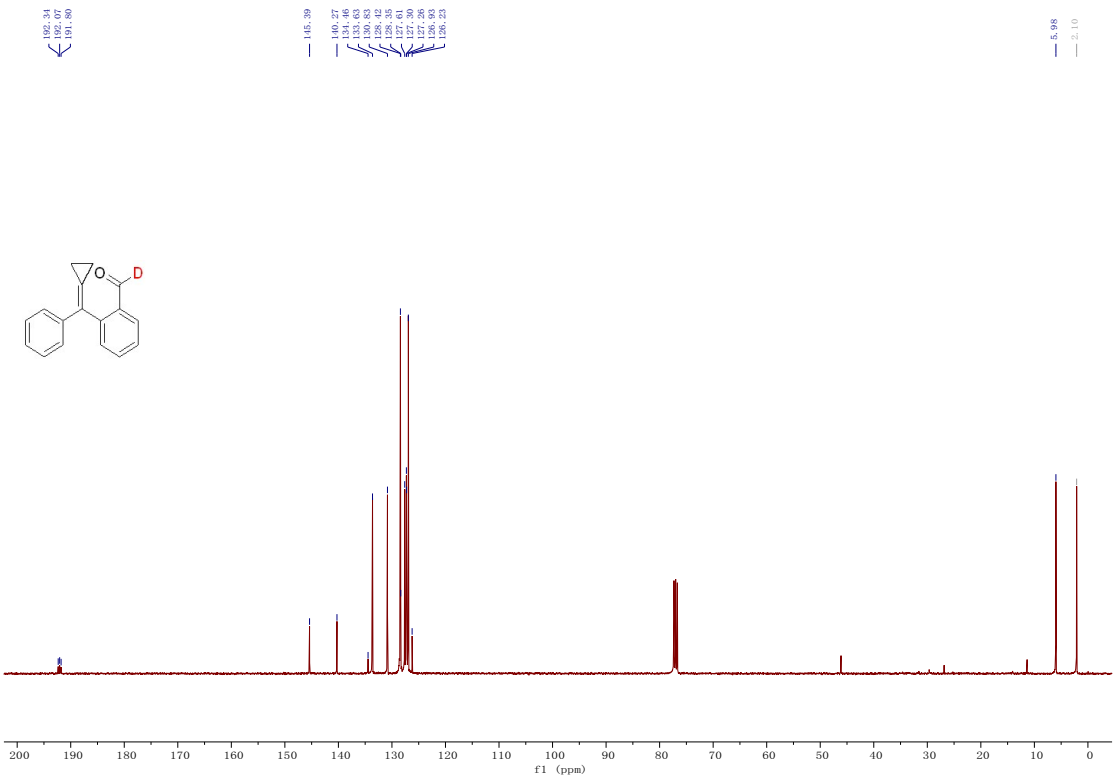
A solution of **1a**-*d* (0.2 mmol) and $RhH(CO)(PPh_3)_2$ (0.005 mmol, 4.5 mg, 2.5 mol %) in 2 mL anhydrous toluene (0.1 M) was heated at 110 °C for 12 h. Then, the mixture was concentrated under vacuum and the residue was purified by a flash column chromatograph on silica gel using PE/EA (100:1) as the eluent to yield the product **2a**-*d* as a white solid in the yield of 56%.

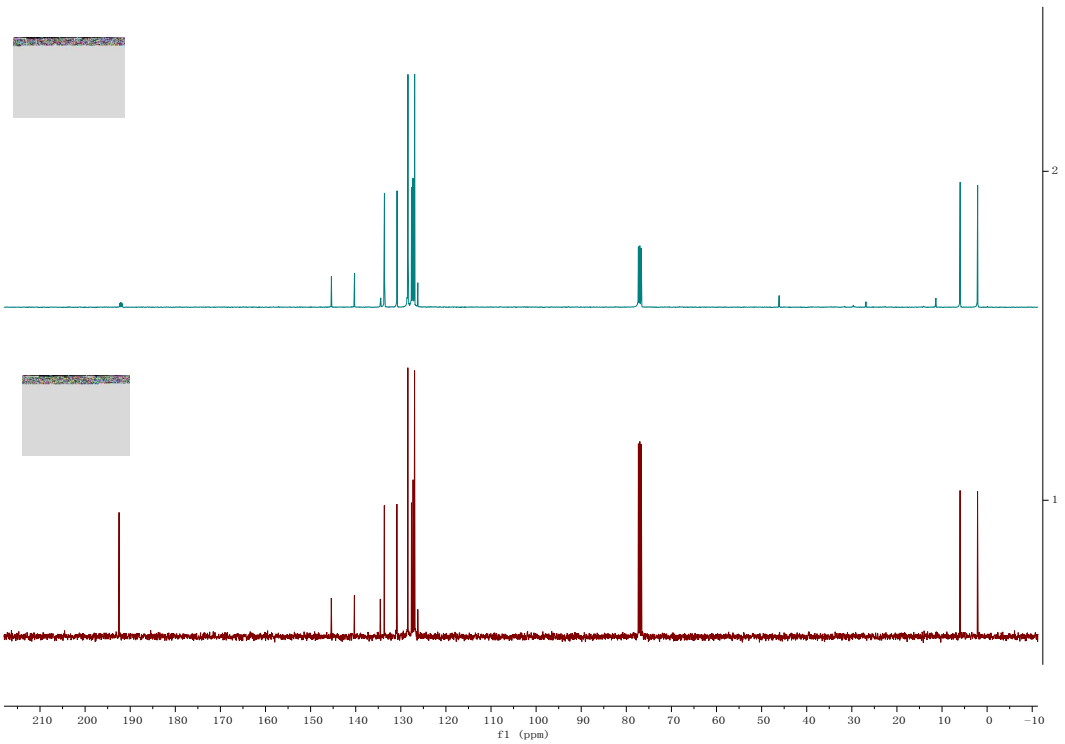
Spectroscopic data for compounds **1a**-*d* and **2a**-*d*

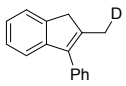
Compound 1a-*d*: A white solid (131.4 mg, 56%); M.p. 54 - 55 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 – 1.19 (m, 2H), 1.64 – 1.70 (m, 2H), 7.25 (dd, *J* = 7.3 Hz, 1H), 7.28 – 7.37 (m, 3H), 7.40 – 7.50 (m, 3H), 7.59 (dd, *J* = 7.5 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 2.10, 5.98, 126.23, 126.93, 127.26, 127.30, 127.61, 128.35, 128.42, 130.83, 133.63, 134.46, 140.27, 145.39, 192.07 (t, *J* = 27.0 Hz). HRMS (EI) Calcd. for $C_{17}H_{13}OD$ requires (M^+): 235.1107, Found: 235.1100.



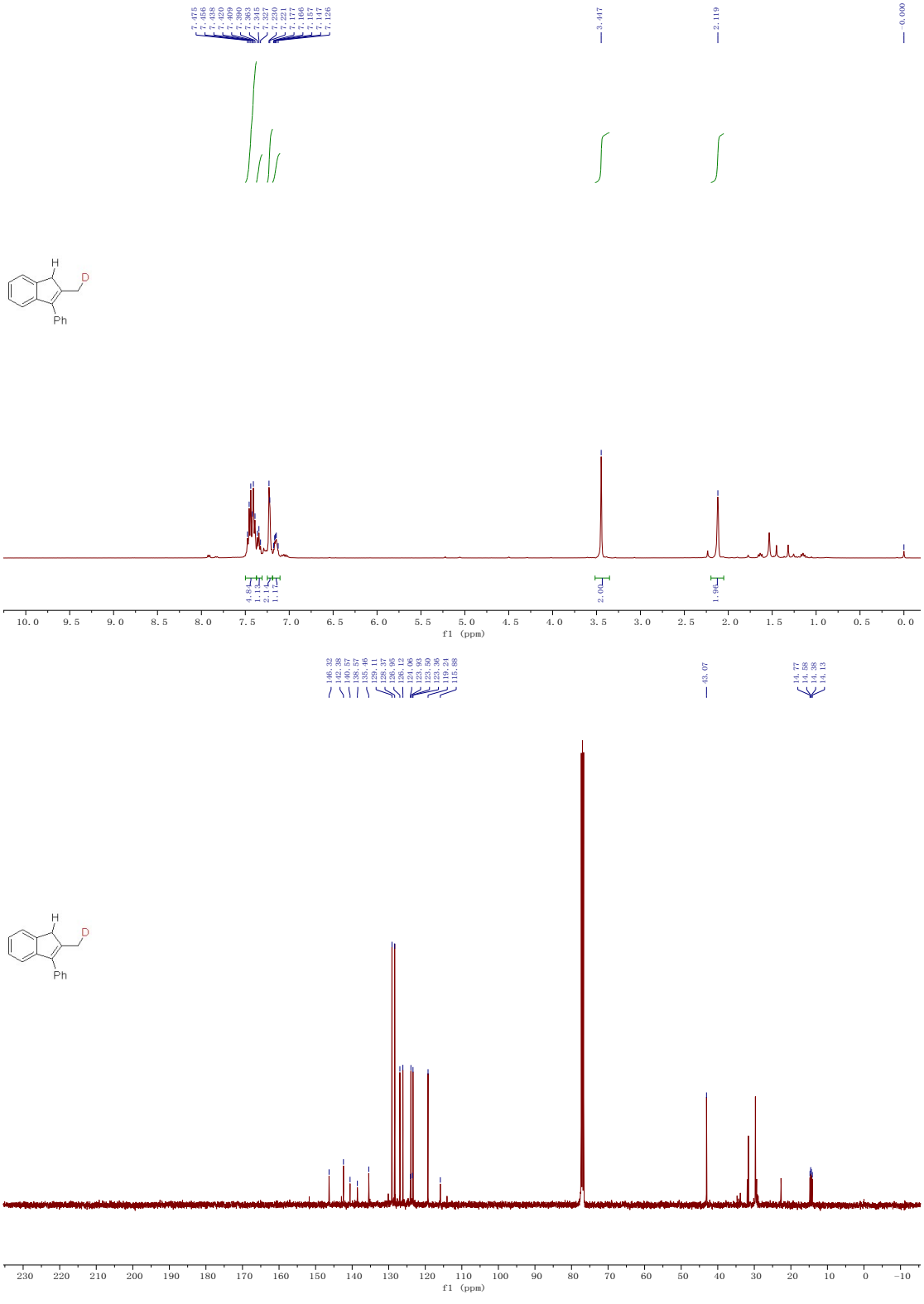

CHO
2
1
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

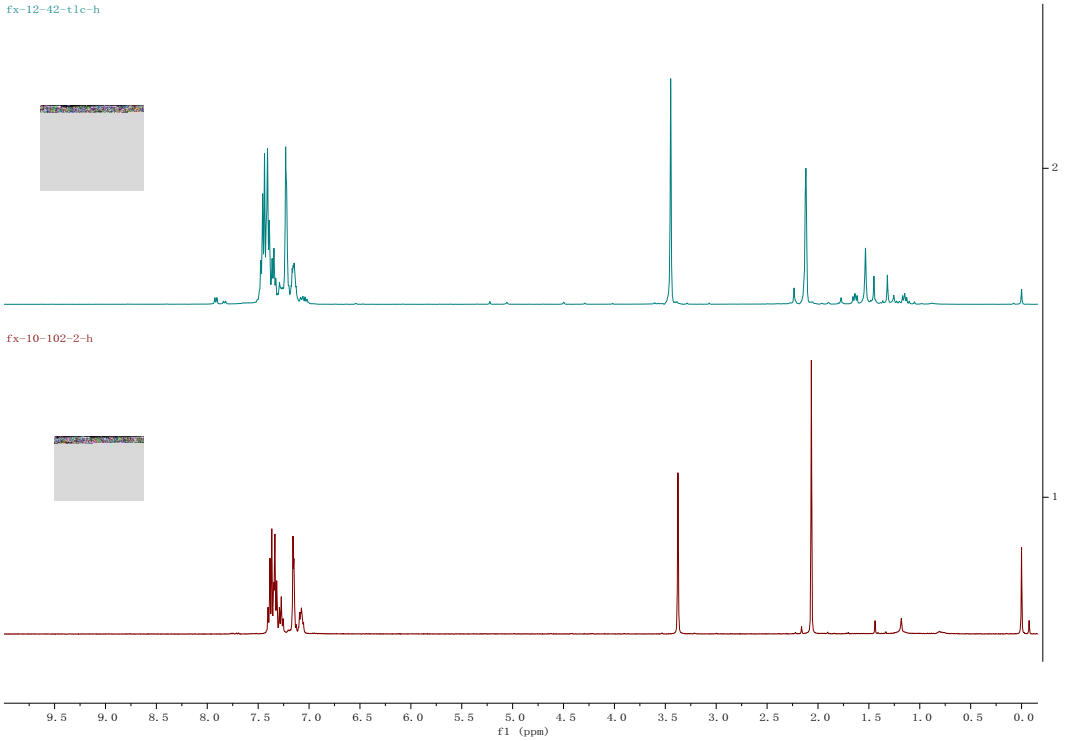

O
D
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

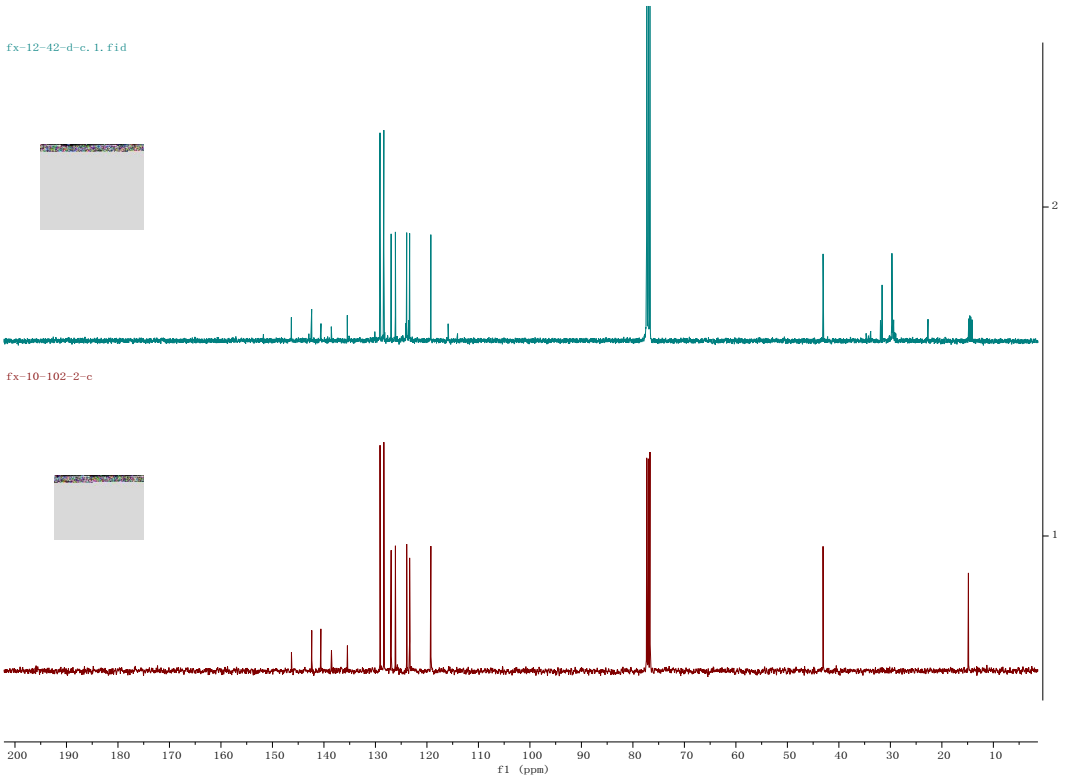




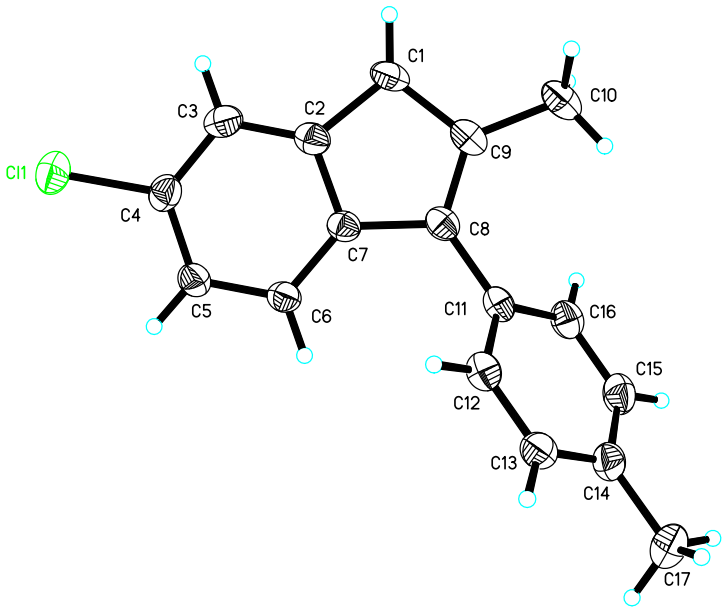
Compound 2a-*d*: A colorless oil (29.0 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.12 (s, 2H), 3.45 (s, 2H), 7.10 – 7.19 (m, 1H), 7.19 – 7.25 (m, 2H), 7.34 (dd, *J* = 7.2 Hz, 1H), 7.37 – 7.50 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 14.46 (d, *J* = 20.0 Hz), 43.07, 119.24, 123.36, 123.93, 126.12, 126.95, 128.37, 129.11, 135.46, 138.57, 140.57, 142.38, 146.32. HRMS (EI) Calcd. for $C_{16}H_{13}D$ requires (M^+): 207.1158, Found: 207.1160.


7.475
7.456
7.438
7.409
7.390
7.383
7.345
7.327
7.230
7.221
7.177
7.166
7.157
7.147
7.126
3.447
2.119
-0.000
H
D
Ph
4.84
1.14
2.14
1.13
2.00
1.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
146.32
142.38
140.57
138.57
135.46
129.11
128.37
126.95
126.12
124.06
123.68
123.50
123.36
119.24
115.88
43.07
14.77
14.58
14.38
14.15
H
D
Ph
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


fx-12-42-tlc-h
fx-10-102-2-h
2
1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


fx-12-42-d-c.1.fid
fx-10-102-2-c
2
1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

X-ray crystal data of compound **2k**



The crystal data of **2k** have been deposited in CCDC with number 1888696. Empirical Formula: $C_{17}H_{14}Cl$; Formula Weight: 253.73; Crystal Dimensions: 0.150 x 0.120 x 0.080 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 10.013(5)Å, b = 12.073(6)Å, c = 12.827(6)Å, α = 111.893(15)°, β = 107.027(17)°, γ = 93.776(19)°, V = 1348.7(12)$Å^3$; Space group: P -1; Z = 4; D_{calc} = 1.250 g/cm^3; F_{000} = 532; Final R indices [I>2sigma(I)] R1 = 0.0594, wR2 = 0.1447.

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[4] (a) M. V. Troutman, D. H. Appella and S. L. Buchwald, *J. Am. Chem. Soc.*, 1999, **121**, 4916; (b) M. Biosca, E. Salomó, P. de la Cruz-Sánchez, A. Riera, X. Verdaguer, O. Pàmies and M. Diéguez, *Org. Lett.*, 2019, **21**, 807.

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