Electronic Supplementary Information

Copper-Catalyzed Oxidative Esterification of Unactivated C(sp^3)−H Bonds with Carboxylic Acids via Cross Dehydrogenative Coupling

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Context

General methods.

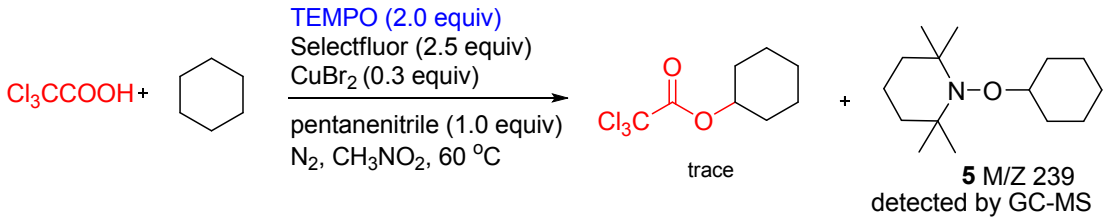
Solvents were dried according to standard procedures. All purchased chemicals were used as received without further purification. All reactions were monitored by TLC with silica gel-coated plates. IR spectra (KBr) were recorded on a FT-IR spectrophotometer. ^{1}H (400 MHz) NMR and ^{13}C (101 MHz) NMR spectra were recorded on a Varian spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standards. Mass spectra were measured with a HRMS-APCI instrument or a low-resolution MS instrument using ESI or EI ionization.

General procedure:C(sp^3)−H esterification of alkanes.

A flame-dried flask was charged with carboxylic acid (1.0 mmol, 1.0 equiv), adamantane (3.0 equiv) or other alkanes (10.0 equiv), F-TEDA-BF_4 (2.5 equiv), $CuBr_2$ (30 mol %), and pentanenitrile (1.0 equiv) and placed under an nitrogen atmosphere. CH_3NO_2 (10 mL) was then added and the resulting mixture became a light blue solution after being stirred for 15 min. The reaction was allowed to stir at 60 °C for 4 h. The mixture was extracted with dichloromethane (3 x 10 mL). The organic solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate 40/1) to afford the corresponding product.

Investigation of the mechanism.

The present esterification could be inhibited by TEMPO (2.0 equiv). In order to inspect whether the hydrocarbons are captured by TEMPO. We design the experiment to investigate the mechanism (Scheme 1).



Scheme 1 Investigation of the Mechanism

In this reaction almost no esterificaton product was detected. The compound **5** was detected as the major product by GC-MS analysis (Figure 1). According to the postulated mechanism, we infer that the hydrocarbon R−H is oxidized to R• by A, then R• is captured by TEMPO. So R• is failed to oxidized to the corresponding carbocation R+ by a copper(III) species, lead to no esterificaton product was obtained (Scheme 2).

Investigation of mechanism by GC-MS analysis.

3.05 min MS (EI) *m/z* (relative intensity) 82 ($[M-1]^+$, 25), 55 (25), 54 (100), 43 (55), 41 (60);
4.32 min MS (EI) *m/z* (relative intensity) 117 ($[M-1]^+$, 100), 82 (50), 59 (90), 35 (2);
5.78 min MS (EI) *m/z* (relative intensity) 156 ($[M]^+$, 100), 142 (78), 141 (55), 69 (75);
7.53 min MS (EI) *m/z* (relative intensity) 216 (18), 201 (100), 140 (40), 83 (85);
8.00 min MS (EI) *m/z* (relative intensity) 239 ($[M]^+$, 5), 157 (8), 143 (10), 142 (100), 83 (3).

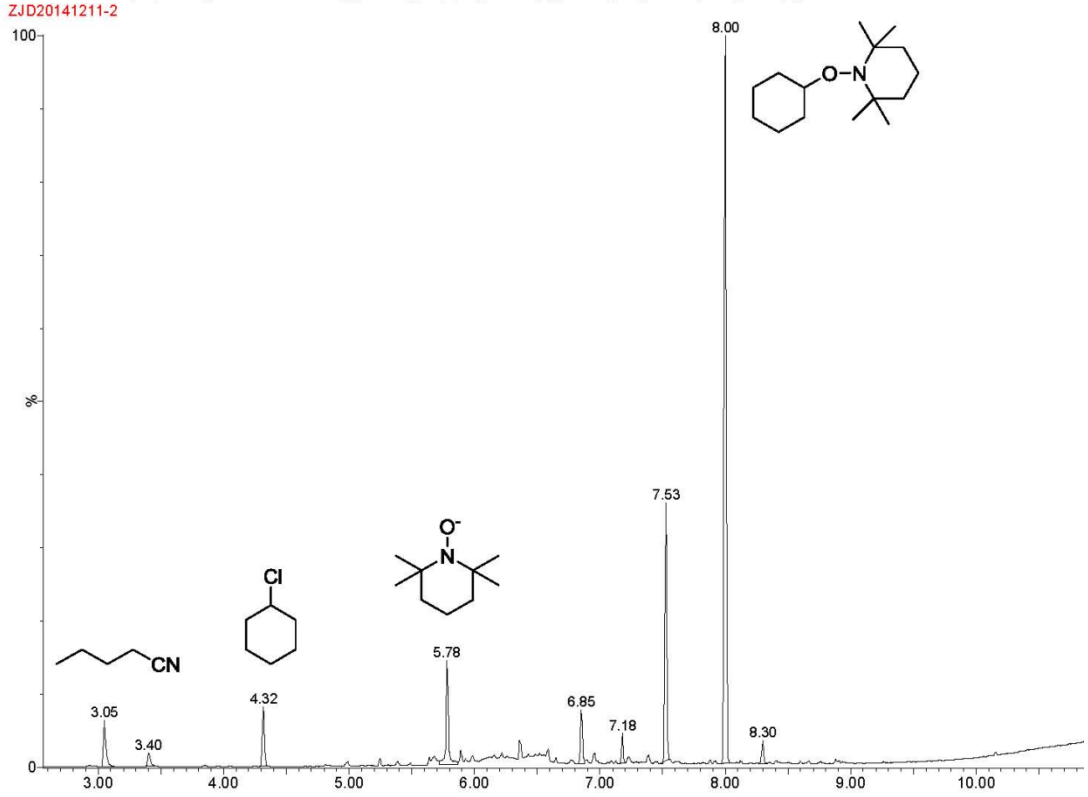
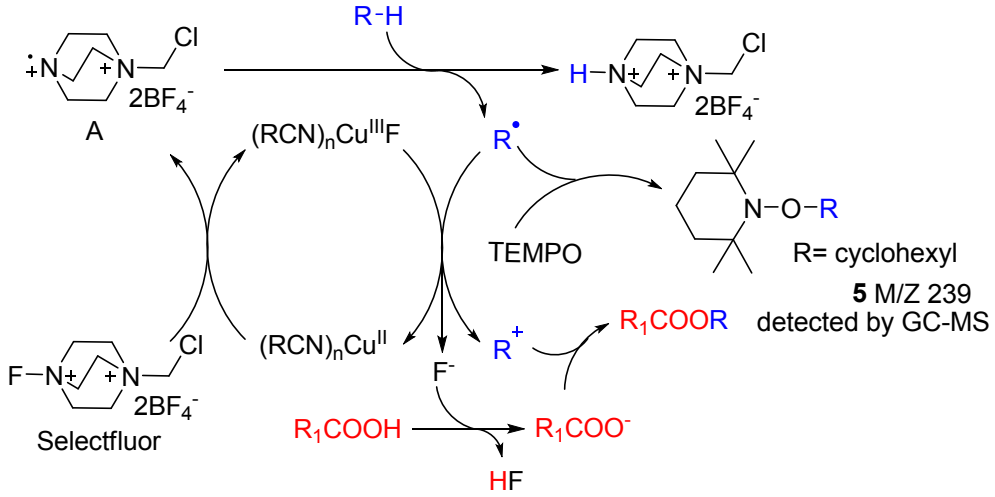


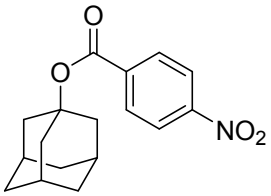
Figure 1 GC-MS Analysis



Scheme 2 Postulated Mechanism

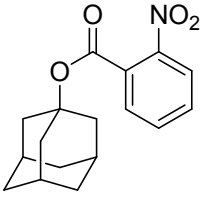
Characterization of the products.

1-Adamantanol 4-nitrobenzoate (3a)



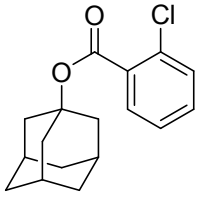
216.7 mg, 72% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2915, 2891, 2853, 1716, 1524, 1346, 1321, 1280, 1105, 1055, 843, 718; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.7 Hz, 2H), 8.12 (d, J = 8.7 Hz, 2H), 2.30 − 2.22 (m, 9H), 1.76 − 1.67 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 150.7, 138.0, 130.4 (2C), 124.0 (2C), 82.9, 41.9 (3C), 36.6 (3C), 31.5 (3C); MS (ESI$^+$) *m/z* 324.4 $[M+Na]^+$.

1-Adamantanol 2-nitrobenzoate (3b)



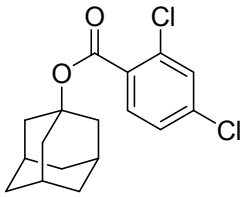
210.7 mg, 70% yield (Light yellow solid); IR (DTGS KBr, v/cm^{-1}) 2917, 2853, 1718, 1539, 1362, 1321, 1283, 1142, 1074, 1049, 847, 780, 741, 723; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 7.9, 1.2 Hz, 1H), 7.71 (dd, J = 7.5, 1.5 Hz, 1H), 7.65 − 7.55 (m, 2H), 2.26 − 2.14 (m, 9H), 1.75 − 1.65 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 148.2, 132.4, 131.0, 129.8, 128.7, 123.4, 83.8, 41.0 (3C), 36.1 (3C), 31.0 (3C); HRMS: $C_{17}H_{19}NNaO_4$ $[M+Na]^+$; calculated: 324.1206, found: 324.1215.

1-Adamantanol 2-chlorobenzoate (3c)



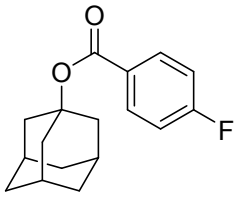
217.5 mg, 75% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2919, 2852, 1721, 1591, 1436, 1323, 1277, 1255, 1138, 1048, 851, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.6, 1.7 Hz, 1H), 7.40 − 7.31 (m, 2H), 7.28 − 7.23 (m, 1H), 2.30 − 2.19 (m, 9H), 1.75 − 1.65 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 132.9, 132.2, 131.5, 130.8, 130.6, 126.3, 82.5, 41.5 (3C), 36.3 (3C), 31.1 (3C); MS (EI) *m/z* (relative intensity) 290 ($[M]^+$, 9), 139 (24), 135 (29), 134 (100), 111 (11), 92 (22), 78 (11).

1-Adamantanol 2,4-dichlorobenzoate (3d)



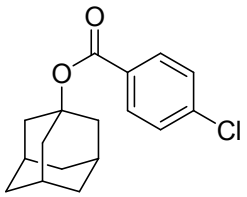
233.2 mg, 72% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2910, 2854, 1721, 1583, 1470, 1376, 1319, 1282, 1245, 1101, 1054, 857, 767; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 2.0 Hz, 1H), 7.24 (dd, J = 8.4, 2.0 Hz, 1H), 2.30 − 2.19 (m, 9H), 1.75 − 1.65 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 137.3, 134.1, 131.9, 130.6, 130.4, 126.7, 82.9, 41.5 (3C), 36.3 (3C), 31.1 (3C); MS (EI) *m/z* (relative intensity) 324 ($[M]^+$, 4), 173 (20), 135 (42), 134 (100), 133 (61), 92 (45), 79 (19); HRMS: $C_{17}H_{18}Cl_2NaO_2$ $[M+Na]^+$; calculated: 347.0576, found: 347.0577.

1-Adamantanol 4-fluorobenzoate (3e)



213.7 mg, 78% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2911, 2851, 1710, 1605, 1507, 1456, 1312, 1278, 1117, 1053, 852, 766; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 − 7.95 (m, 2H), 7.05 (t, J = 8.7 Hz, 2H), 2.28 − 2.19 (m, 9H), 1.77 − 1.66 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2 (d, $J_{C\text{-}F}$ = 253.1 Hz), 164.2, 131.7 (d, $J_{C\text{-}F}$ = 9.1 Hz, 2C), 128.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.8 Hz, 2C), 81.2, 41.5 (3C), 36.3 (3C), 31.0 (3C); MS (EI) *m/z* (relative intensity) 274 ($[M]^+$, 7), 135 (19), 134 (100), 123 (55), 95 (26), 92 (55).

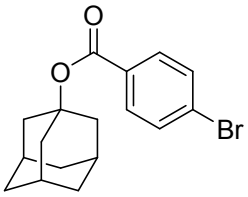
1-Adamantanol 4-chlorobenzoate (3f)



211.7 mg, 73% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2918, 2851, 2359,

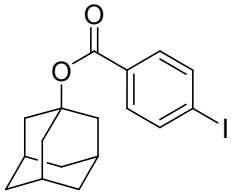
1712, 1593, 1445, 1321, 1273, 1120, 1053, 852, 762; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 2.27 − 2.20 (m, 9H), 1.75 − 1.66 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 138.5, 130.7 (2C), 130.6, 128.3 (2C), 81.5, 41.6 (3C), 36.4 (3C), 31.1 (3C); MS (EI) *m/z* (relative intensity) 290 ([M]$^+$, 7), 135 (37), 134 (100), 133 (70), 111 (16), 92 (51), 78 (20).

1-Adamantanol 4-bromobenzoate (3g)



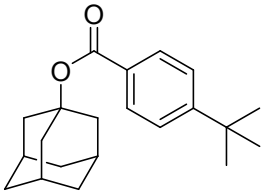
190.4 mg, 57% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2917, 2850, 1711, 1590, 1455, 1322, 1273, 1120, 1051, 1010, 851, 759; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 2.26 − 2.20 (m, 9H), 1.75 − 1.66 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 131.0 (2C), 130.7, 130.5 (2C), 126.9, 81.5, 41.7 (3C), 36.6 (3C), 31.3 (3C); MS (EI) *m/z* (relative intensity) 334 ([M]$^+$, 5), 185 (22), 135 (37), 134 (100), 93 (17), 92 (54), 79 (19); HRMS: $C_{17}H_{19}BrNaO_2$ [M+Na]$^+$; calculated: 357.0461, found: 357.0449.

1-Adamantanol 4-iodobenzoate (3h)



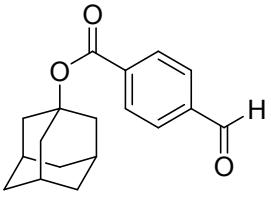
152.8 mg, 40% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2914, 2848, 1708, 1585, 1455, 1322, 1274, 1118, 1050, 1006, 852, 757; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 2.25 − 2.20 (m, 9H), 1.75 − 1.67 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 137.0 (2C), 131.3, 130.5 (2C), 99.6, 81.5, 41.8 (3C), 36.3 (3C), 31.4 (3C); MS (EI) *m/z* (relative intensity) 382 ([M]$^+$, 13), 230 (21), 135 (34), 134 (100), 93 (20), 92 (47), 79 (17); HRMS: $C_{17}H_{19}INaO_2$ [M+Na]$^+$; calculated: 405.0322, found: 405.0305.

1-Adamantanol 4-tert-butylbenzoate (3i)



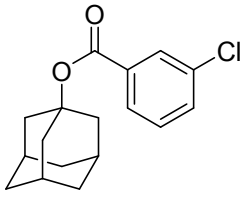
202.8 mg, 65% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2957, 2914, 2850, 1704, 1609, 1456, 1407, 1320, 1276, 1190, 1126, 1056, 857, 777, 708; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 2.27 − 2.18 (m, 9H), 1.75 − 1.65 (m, 6H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 155.4, 129.1, 128.9 (2C), 124.7 (2C), 80.7, 41.8 (3C), 36.7 (3C), 35.3, 31.5 (3C), 31.4 (3C); MS (EI) *m/z* (relative intensity) 312 ([M]$^+$, 7), 255 (18), 161 (41), 135 (35), 134 (100), 92 (40), 79 (13); HRMS: $C_{21}H_{28}NaO_2$ [M+Na]$^+$; calculated: 335.1982, found: 335.1971.

1-Adamantanol 4-formylbenzoate (3j)



193.12 mg, 68% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2917, 2893, 2854, 1702, 1576, 1458, 1386, 1321, 1274, 1201, 1119, 1053, 830, 757, 685; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 2.30 − 2.20 (m, 9H), 1.76 − 1.67 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 164.1, 138.8, 137.1, 129.9 (2C), 129.2 (2C), 82.1, 41.6 (3C), 36.3 (3C), 31.1 (3C); MS (EI) *m/z* (relative intensity) 284 ([M]$^+$, 6), 239 (17), 135 (29), 134 (100), 133 (68), 92 (38), 91 (65), 78 (19); HRMS: $C_{18}H_{20}NaO_3$ [M+Na]$^+$; calculated: 307.1305, found: 307.1292.

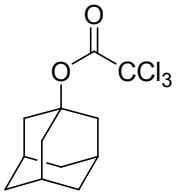
1-Adamantanol 3-chlorobenzoate (3k)



188.5 mg, 65% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2909, 1724, 1633, 1574, 1384, 1356, 1284, 1260, 1083, 1054, 741; ^{1}H NMR (400 MHz, $CDCl_3$)

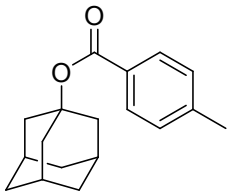
δ 7.92 (t, *J* = 2.0 Hz, 1H), 7.88 − 7.82 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.48 − 7.45 (m, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 2.26 − 2.20 (m, 9H), 1.73 − 1.66 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 134.1, 133.7, 132.2, 129.4, 129.3, 127.4, 81.7, 41.4 (3C), 36.3 (3C), 31.0 (3C); HRMS: $C_{17}H_{19}ClNaO_2$ $[M+Na]^+$; calculated: 313.0966, found: 313.0977.

1-Adamantanol 2,2,2-trichloroacetate (3l)



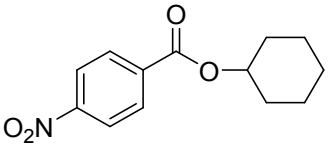
236.8 mg, 80% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2917, 2856, 1758, 1456, 1384, 1253, 1104, 1046, 968, 883, 825, 767, 679; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 − 2.18 (m, 9H), 1.72 − 1.68 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 91.0, 86.9, 40.7 (3C), 35.9 (3C), 31.1 (3C); HRMS: $C_{12}H_{15}Cl_3NaO_2$ $[M+Na]^+$; calculated: 319.0030, found: 319.0034.

1-Adamantanol 4-methylbenzoate (3m)



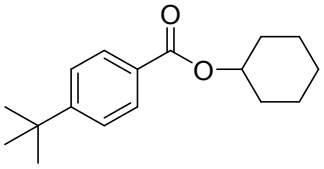
108.0 mg, 40% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2914, 2849, 1708, 1613, 1454, 1322, 1279, 1179, 1121, 1112, 1052, 757, 688; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H), 2.26 – 2.19 (m, 9H), 1.75 – 1.66 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 142.7, 129.3 (3C), 128.7 (2C), 80.7, 41.6 (3C), 36.4 (3C), 31.0 (3C), 21.7; HRMS: $C_{18}H_{22}NaO_2$ $[M+Na]^+$; calculated: 293.1512, found: 293.1505.

Cyclohexyl 4-nitrobenzoate (3o)



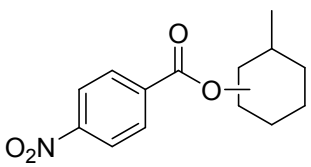
64.7 mg, 26% yield (Pale yellow solid); IR (DTGS KBr, v/cm^{-1}) 2939, 2861, 1721, 1608, 1529, 1349, 1280, 1116, 1013, 874, 835, 720; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.0 Hz, 2H), 8.19 (d, *J* = 9.0 Hz, 2H), 5.09 − 5.02 (m, 1H), 2.00 − 1.79 (m, 4H), 1.68 − 1.31 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 150.3, 136.4, 130.4 (2C), 123.3 (2C), 74.4, 31.7 (2C), 25.5, 23.8 (2C); MS (ESI) *m/z* 249.1 $[M]^+$.

Cyclohexyl 4-tert-butylbenzoate (3p)



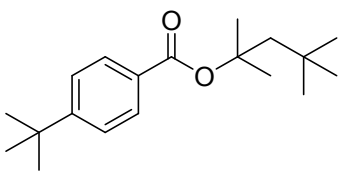
52.0 mg, 20% yield (White solid); IR (DTGS KBr, v/cm^{-1}) 2938, 2861, 1717, 1610, 1446, 1408, 1317, 1278, 1183, 1118,1016, 854, 775, 708; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 5.04 − 4.97(m, 1H), 1.94 − 1.76 (m, 4H), 1.62 − 1.38 (m, 6H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 156.0, 129.2 (2C), 128.1, 125.1 (2C), 72.7, 35.1, 31.7 (2C), 31.2 (3C), 25.6, 23.8 (2C); HRMS: $C_{17}H_{24}NaO_2$ $[M+Na]^+$; calculated: 283.1669, found: 283.1671.

Methylcyclohexyl 4-nitrobenzoate (3q)



73.6 mg, 28% yield (Light yellow oil); ^{1}H NMR (400 MHz, CDCl3) δ 8.29 – 8.23 (m, 2H), 8.22 − 8.15 (m, 2H), 5.39 − 5.25 (m, 0.37H), 5.02 – 4.91(m, 0.38H), 4.73 − 4.66 (m, 0.28H), 2.15 − 0.90 (m, 13H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.1, 80.3, 80.2, 75.1, 75.0, 72.3, 72.2; HRMS: $C_{14}H_{17}NNaO_4$ $[M+Na]^+$; calculated: 286.1050, found: 286.1049.

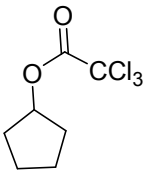
2,4,4-Trimethylpentan-2-yl 4-tert-butylbenzoate (3r)



49.3 mg, 17% yield (Light yellow oil); IR (DTGS KBr, v/cm^{-1}) 2959, 2915, 2871, 1714, 1610, 1574, 1538, 1463, 1384, 1367, 1286, 1247,

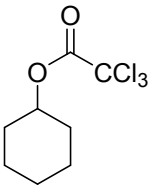
1204, 1185, 1113, 1016, 854, 775, 707; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 1.94 (s, 2H), 1.64 (s, 6H), 1.33 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 155.6, 129.2, 129.1 (2C), 125.0 (2C), 84.3, 52.4, 35.0, 31.6 (3C), 31.5, 31.2 (3C), 28.5 (2C); HRMS: $C_{19}H_{30}NaO_2$ $[M+Na]^+$; calculated: 313.2138, found: 313.2141.

Cyclopentyl 2,2,2-trichloroacetate (3t)



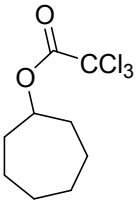
80.1 mg, 35% yield (Light yellow oil); IR (DTGS KBr, v/cm^{-1}) 2963, 2875, 1763, 1435, 1356, 1248, 1165, 1033, 983, 952, 865, 827, 681; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 − 5.31 (m, 1H), 1.95 − 1.87 (m, 4H), 1.82 − 1.76 (m, 2H), 1.71 − 1.65 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 90.2, 83.2, 32.4 (2C), 23.7 (2C); HRMS: $C_7H_9Cl_3NaO_2$ $[M+Na]^+$; calculated: 252.9566, found: 252.9571.

Cyclohexyl 2,2,2-trichloroacetate (3u)



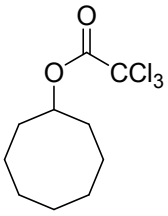
133.6 mg, 55% yield (Colorless oil); IR (DTGS KBr, v/cm^{-1}) 2940, 2862, 1762, 1450, 1251, 1119, 1032, 1006, 980, 906, 850, 749, 681; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 − 4.92 (m, 1H), 1.95 − 1.73 (m, 4H), 1.69 − 1.36 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 90.3, 78.4, 30.8 (2C), 25.2, 23.2 (2C); HRMS: $C_8H_{11}Cl_3NaO_2$ $[M+Na]^+$; calculated: 266.9717, found: 266.9718.

Cycloheptyl 2,2,2-trichloroacetate (3v)



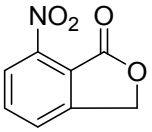
128.5 mg, 50% yield (Colorless oil); IR (DTGS KBr, v/cm^{-1}) 2930, 2861, 1760, 1573, 1537, 1462, 1248, 976, 889, 826, 681; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 − 5.06 (m, 1H), 2.02 − 1.94 (m, 2H), 1.90 − 1.80 (m, 2H), 1.77 − 1.68 (m, 2H), 1.64 − 1.44 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 90.4, 81.2, 33.1 (2C), 28.2 (2C), 22.7 (2C); HRMS: $C_9H_{13}Cl_3NaO_2$ $[M+Na]^+$; calculated: 280.9873, found: 280.9878.

Cyclooctyl 2,2,2-trichloroacetate (3w)



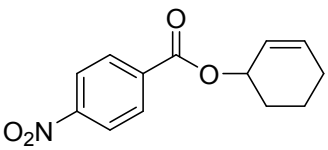
204 mg, 75% yield (Light yellow oil); IR (DTGS KBr, v/cm^{-1}) 2927, 2858, 1759, 1471, 1448, 1249, 1111, 1045, 976, 826, 681; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 − 5.05 (m, 1H), 1.94 − 1.88 (m, 4H), 1.80 − 1.50 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 90.4, 81.6, 30.9 (2C), 27.1 (2C), 25.3, 22.7 (2C); HRMS: $C_{10}H_{15}Cl_3NaO_2$ $[M+Na]^+$; calculated: 295.0030, found: 295.0027.

7-Nitroisobenzofuran-1(3H)-one (3x)



125.3 mg, 70% yield (Light yellow solid); IR (DTGS KBr, v/cm^{-1}) 3093, 1769, 1757, 1623, 1538, 1524, 1450, 1364, 1348, 1257, 1074, 1058, 1006, 788, 736; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.1 Hz, 1H), 8.27 (d, *J* = 7.5 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 5.76 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 142.8, 141.5, 131.4, 130.4, 129.0, 128.4, 70.3; MS (EI) *m/z* (relative intensity) 179 ($[M]^+$, 15), 161 (64), 149 (75), 131 (77), 117 (74), 103 (83), 75 (100).

Cyclohex-2-enyl 4-nitrobenzoate (3y)

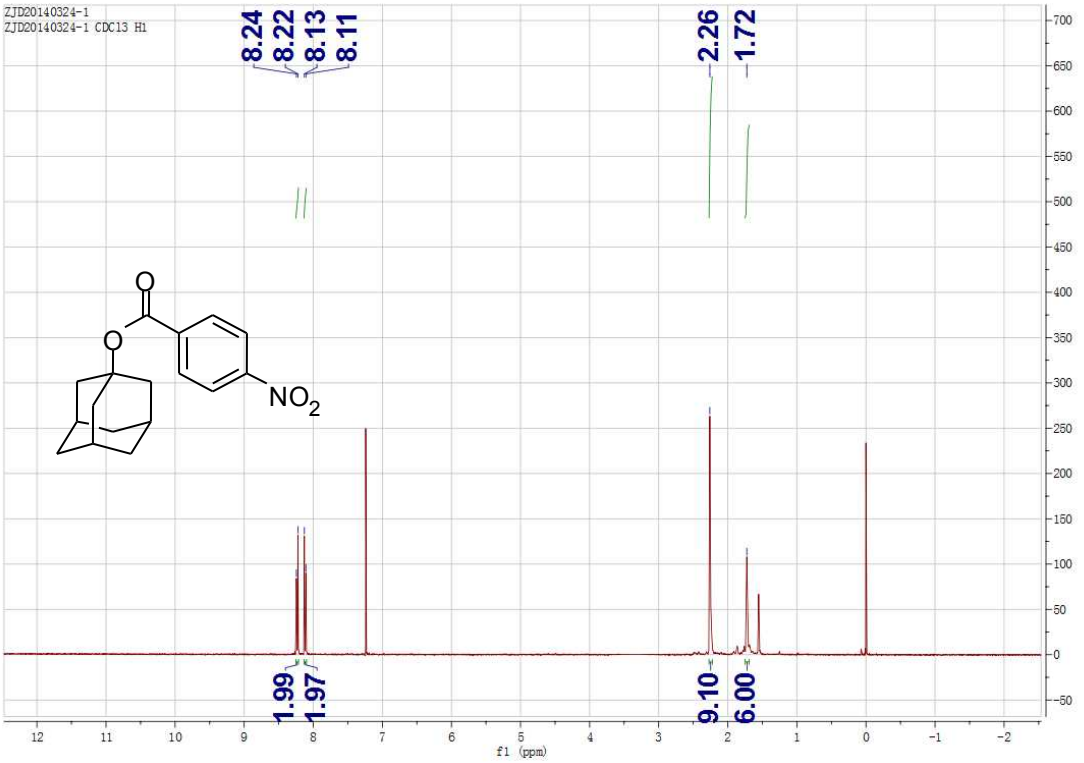


93.8 mg, 38% yield (Light yellow solid); IR (DTGS KBr, cm^{-1}): ν 3119, 3037, 2949, 2850, 1711, 1606, 1524, 1353, 1282, 1120, 907, 718; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 8.19 (d, *J* = 8.9 Hz,

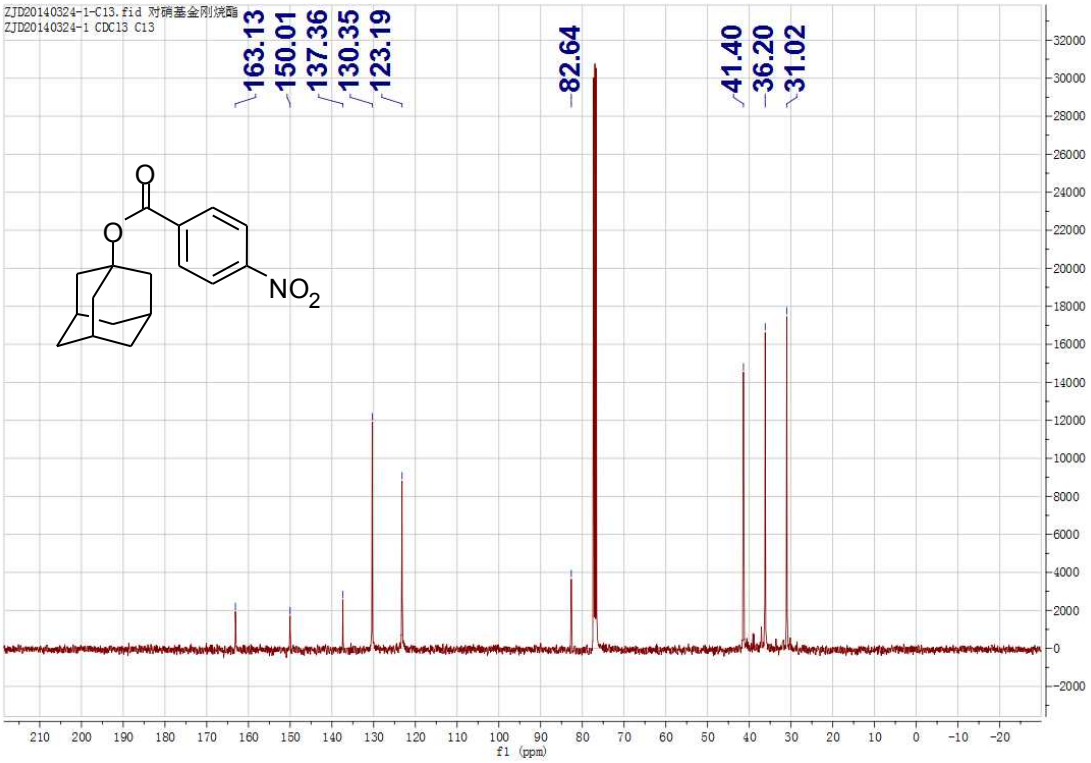
2H), 6.06 − 6.01 (m, 1H), 5.85 − 5.79 (m, 1H), 5.55 − 5.50 (m, 1H), 2.16 − 1.75 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 150.0, 135.8, 133.1, 130.2 (2C), 124.6, 123.0 (2C), 69.5, 28.1, 24.7, 18.6; MS (ESI) *m/z* 247.1 $[M]^+$.

NMR spectra for the products

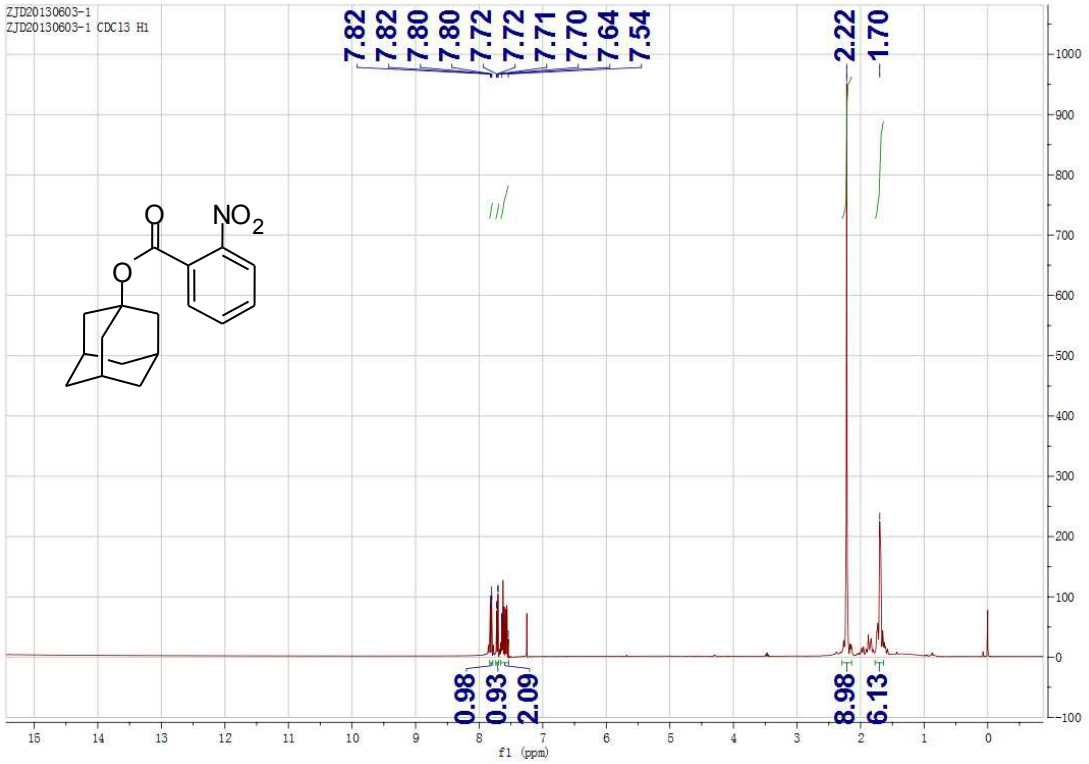
^{1}H NMR (400 MHz, $CDCl_3$) for1-Adamantanol 4-nitrobenzoate (3a)



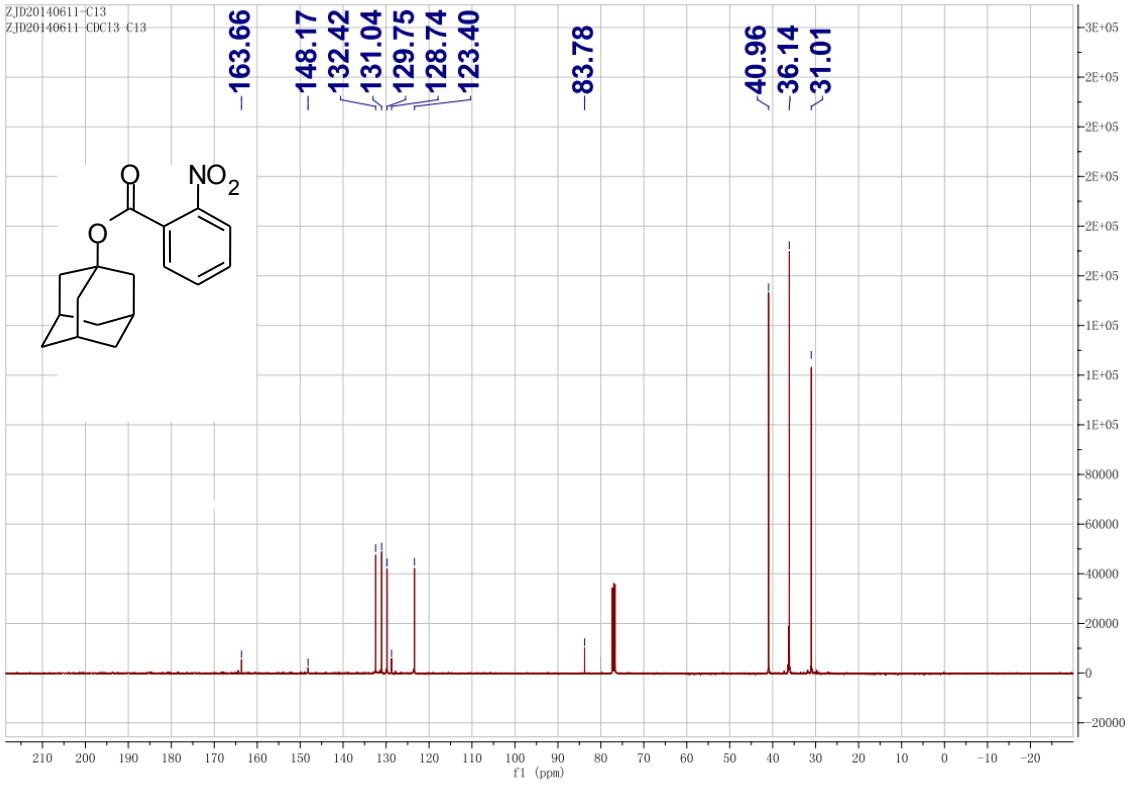
^{13}C NMR (101 MHz, $CDCl_3$) for1-Adamantanol 4-nitrobenzoate (3a)



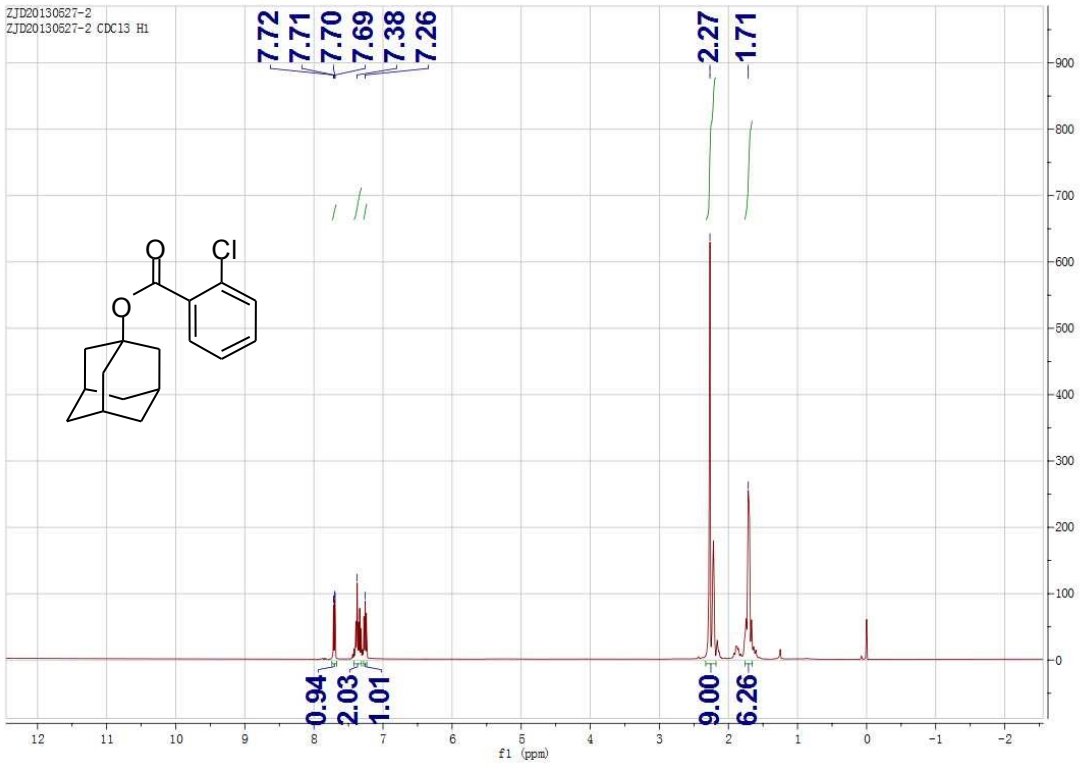
^{1}H NMR (400 MHz, $CDCl_3$) for1-Adamantanol 2-nitrobenzoate (3b)



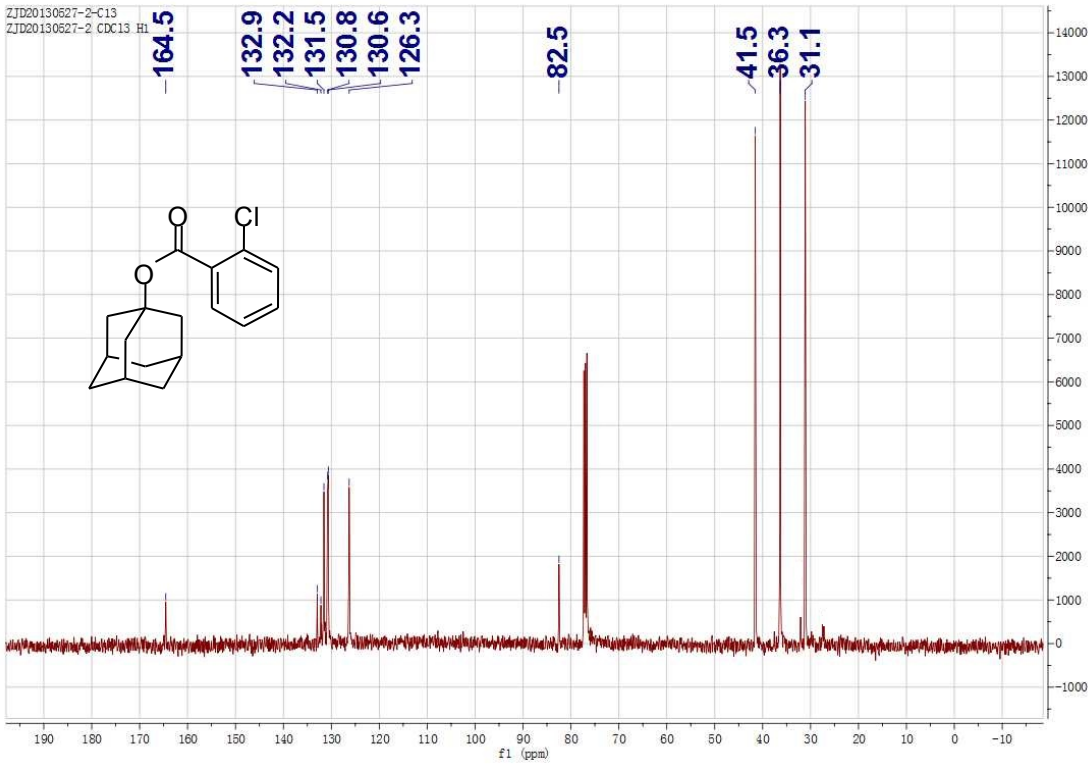
^{13}C NMR (101 MHz, $CDCl_3$) for1-Adamantanol 2-nitrobenzoate (3b)



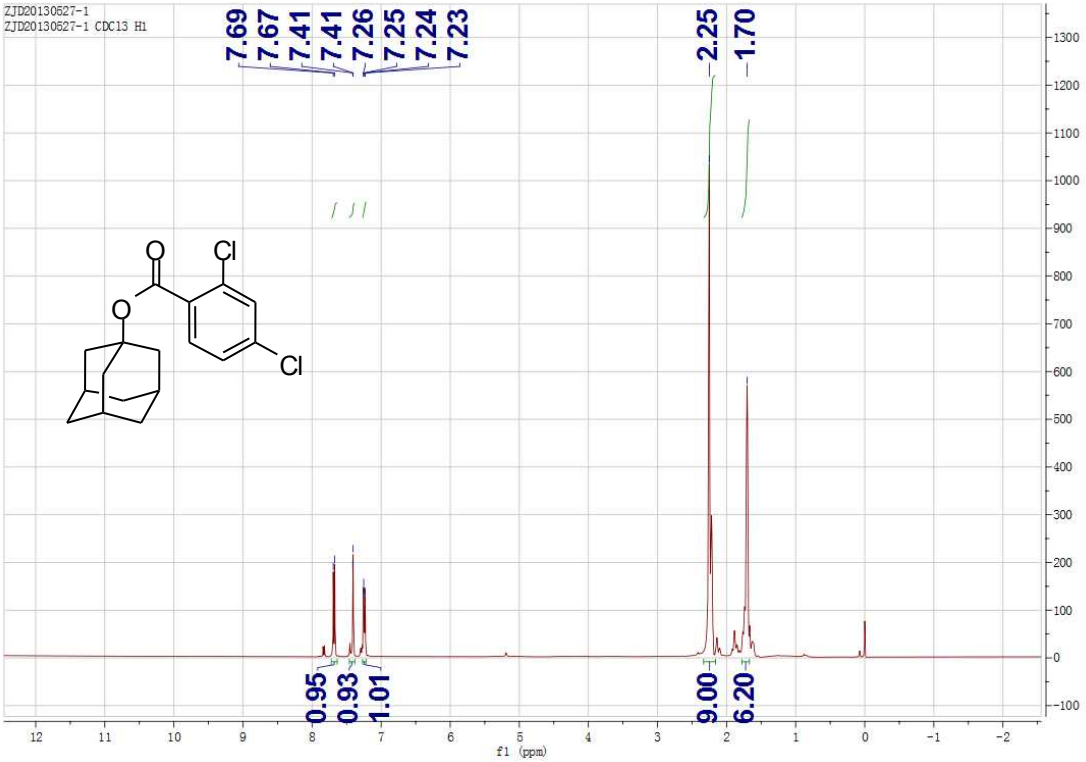
^{1}H NMR (400 MHz, $CDCl_3$) for 1-Adamantanol 2-chlorobenzoate (3c)



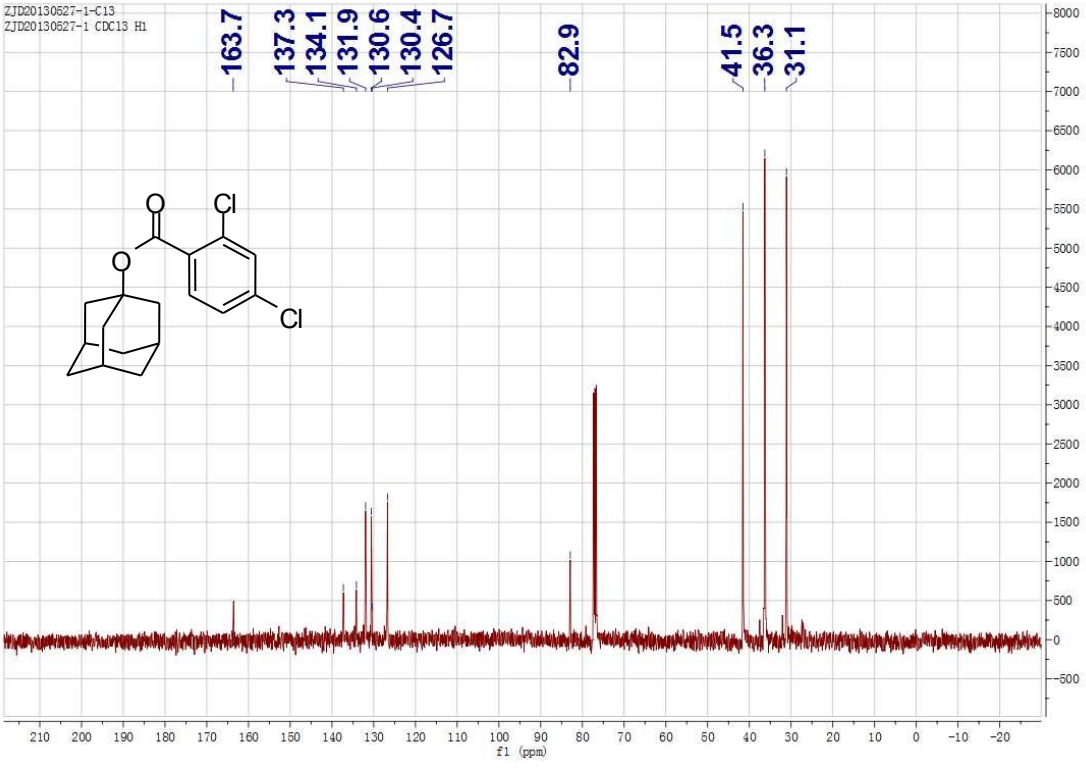
^{13}C NMR (101 MHz, $CDCl_3$) for 1-Adamantanol 2-chlorobenzoate (3c)



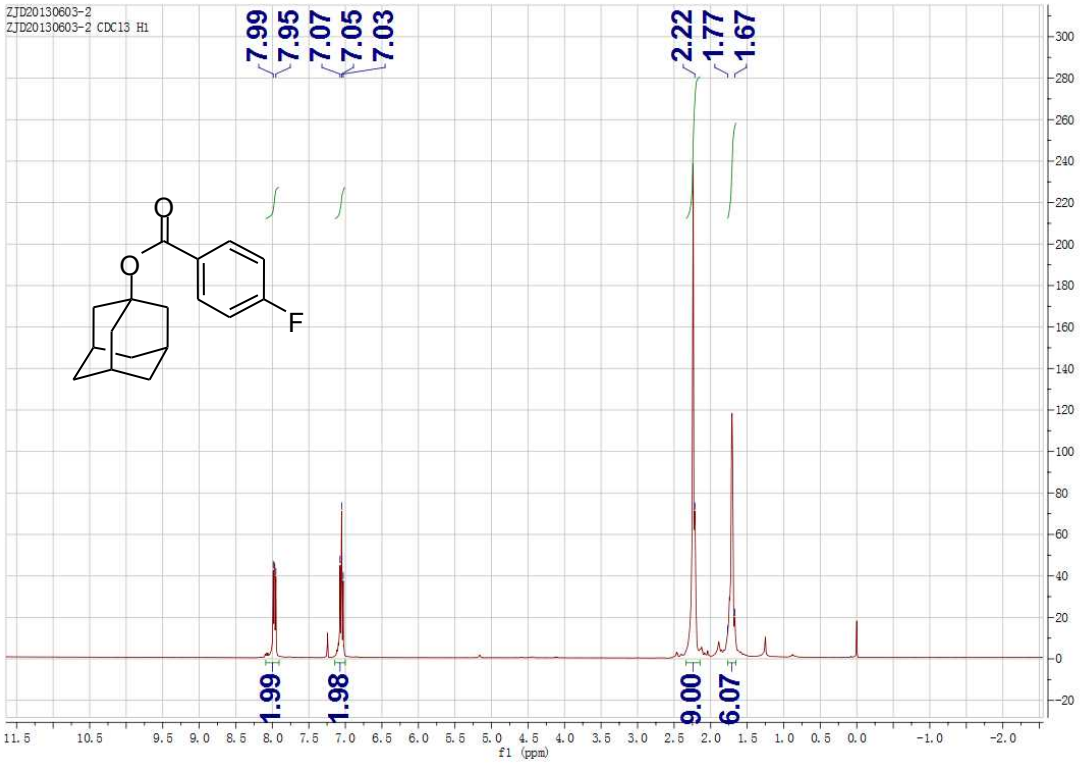
^{1}H NMR (400 MHz, $CDCl_3$) for 1-Adamantanol 2,4-dichlorobenzoate (3d)



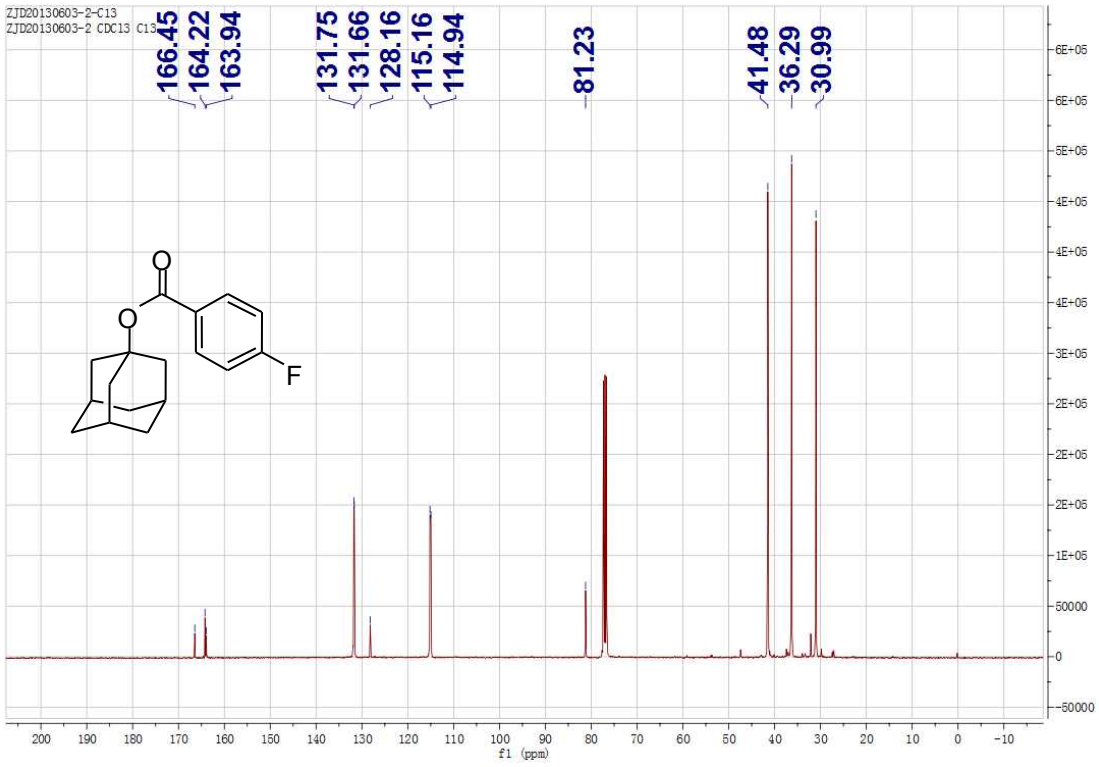
^{13}C NMR (101 MHz, $CDCl_3$) for 1-Adamantanol 2,4-dichlorobenzoate (3d)



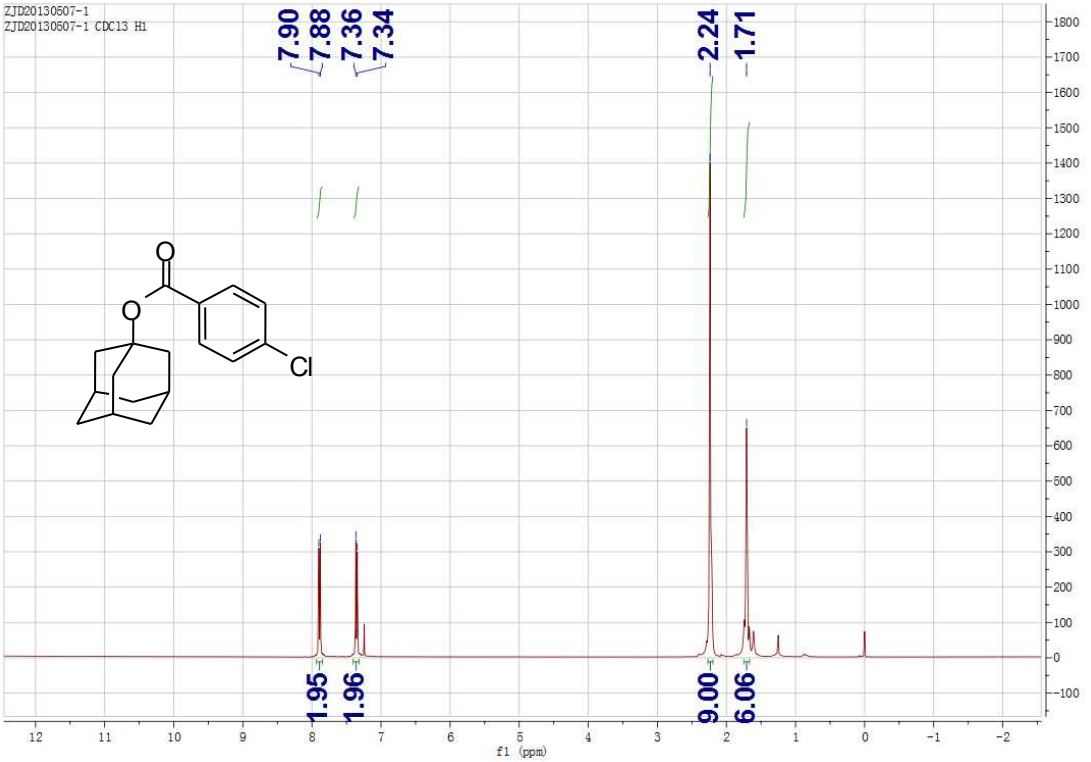
^{1}H NMR (400 MHz, $CDCl_3$) for Adamantanol 4-fluorobenzoate (3e)



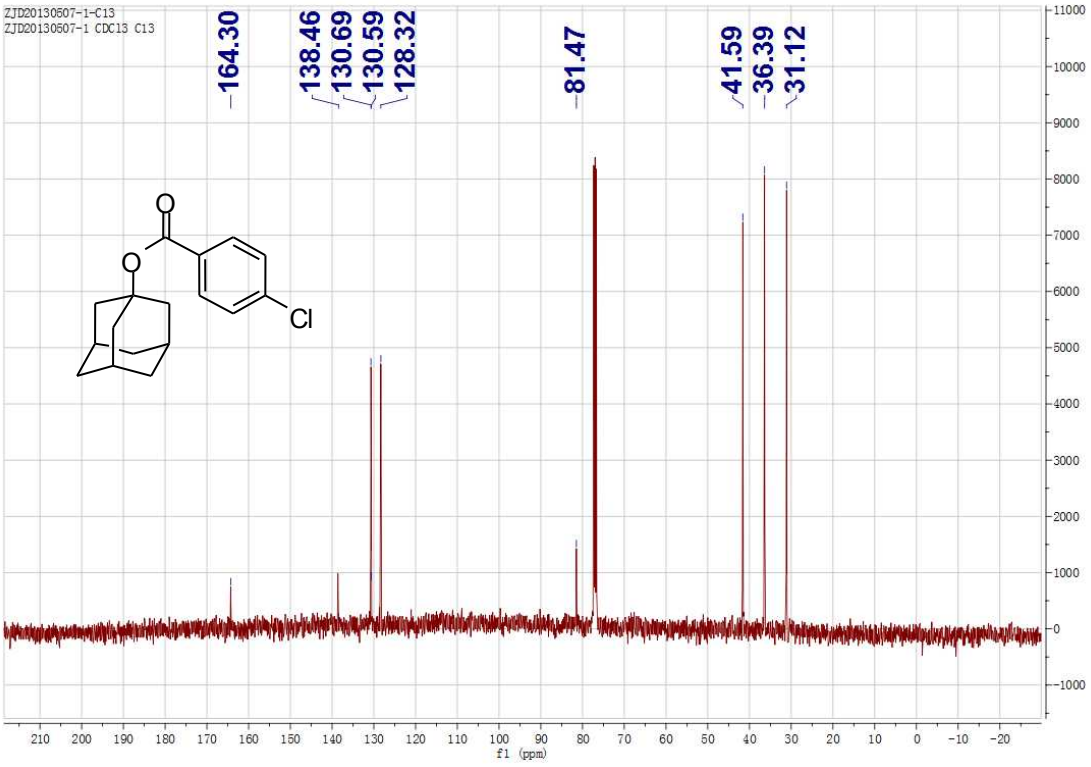
^{13}C NMR (101 MHz, $CDCl_3$) for Adamantanol 4-fluorobenzoate (3e)



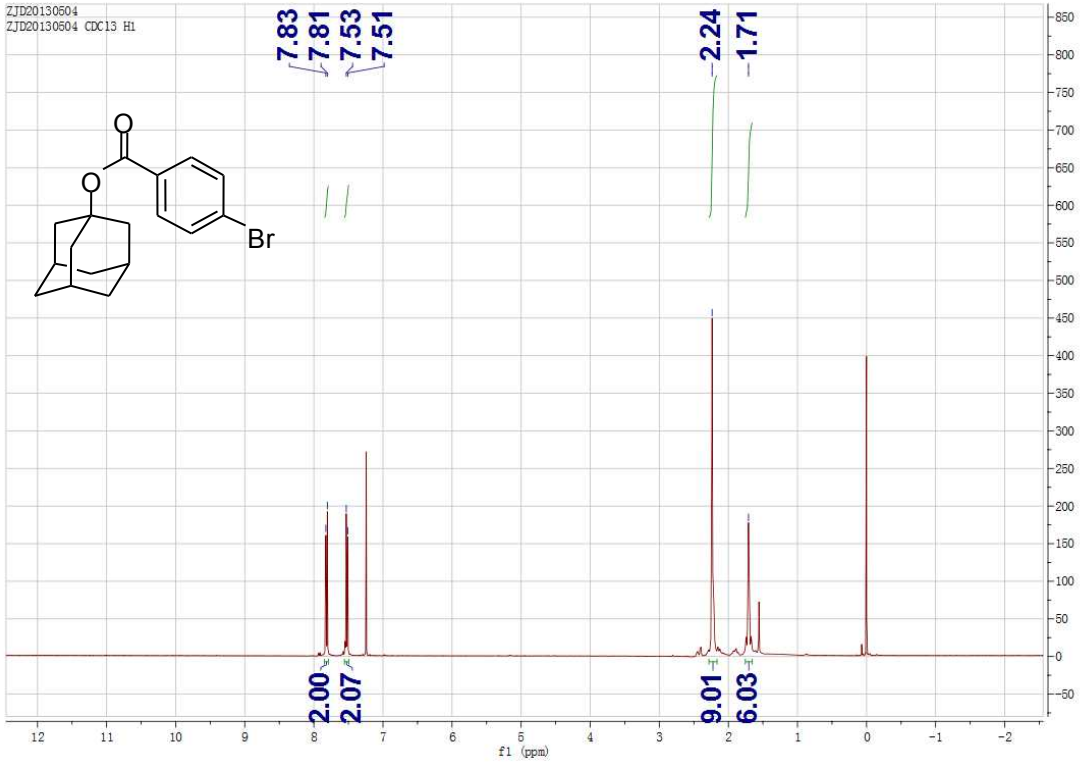
^{1}H NMR (400 MHz, $CDCl_3$) for 1-Adamantanol 4-chlorobenzoate (3f)



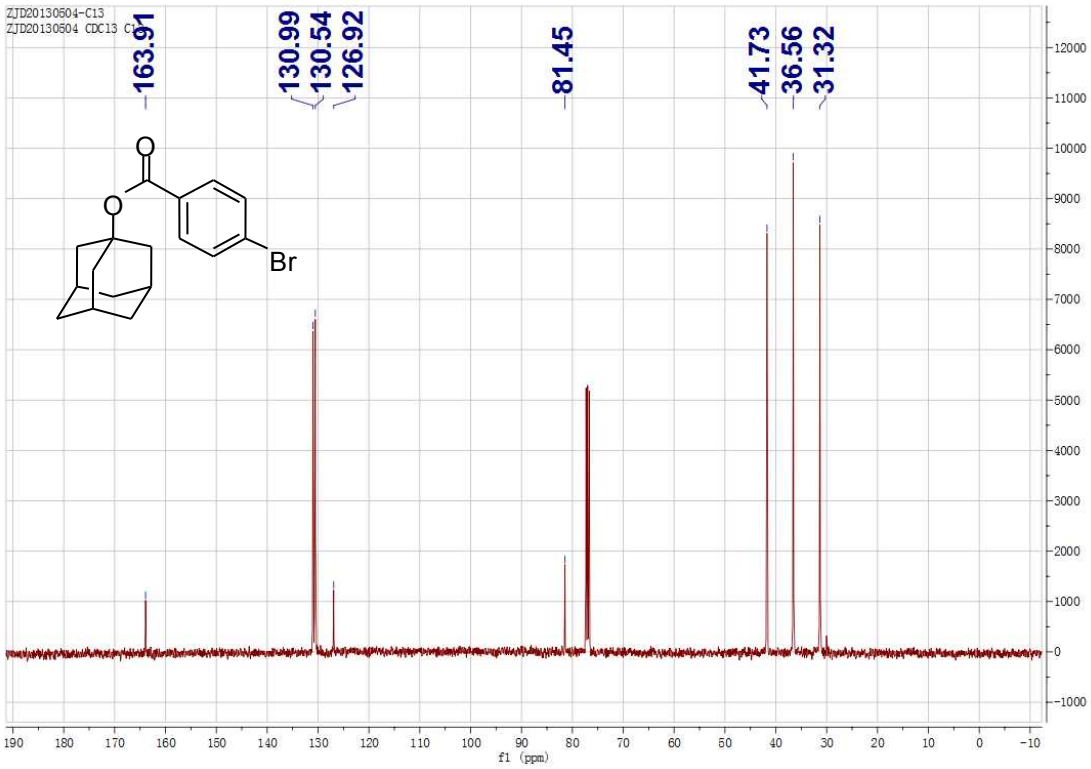
^{13}C NMR (101 MHz, $CDCl_3$) for 1-Adamantanol 4-chlorobenzoate (3f)



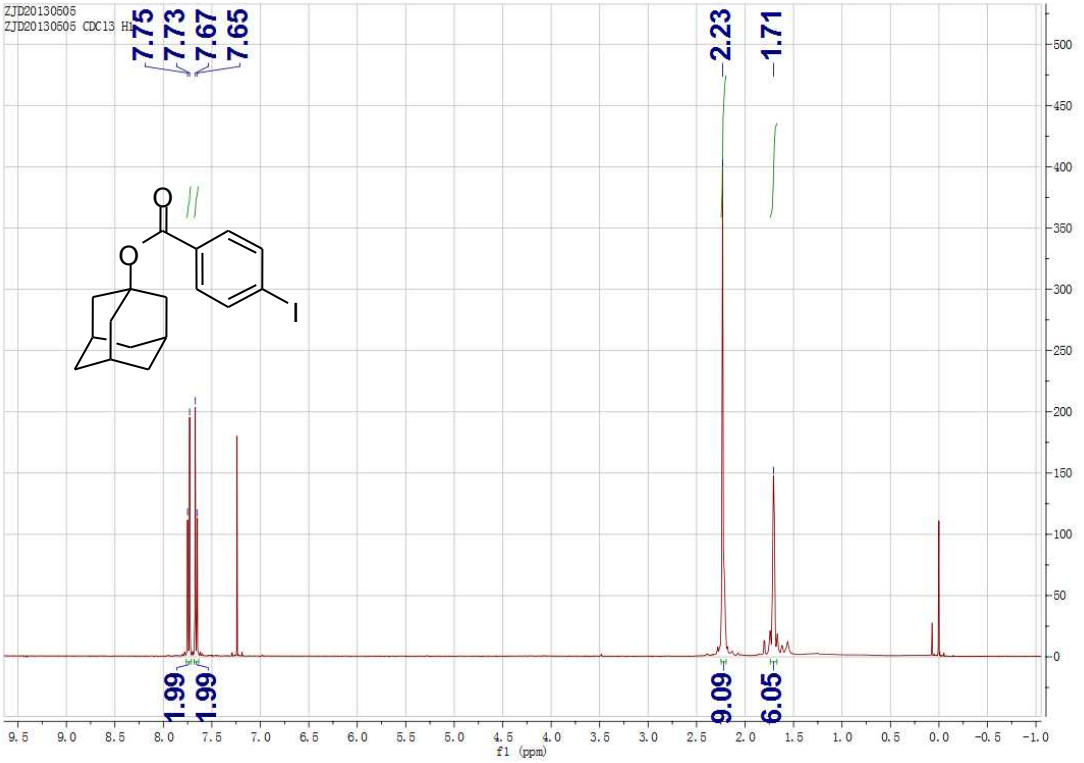
^{1}H NMR (400 MHz, $CDCl_3$) for 1-Adamantanol 4-bromobenzoate (3g)



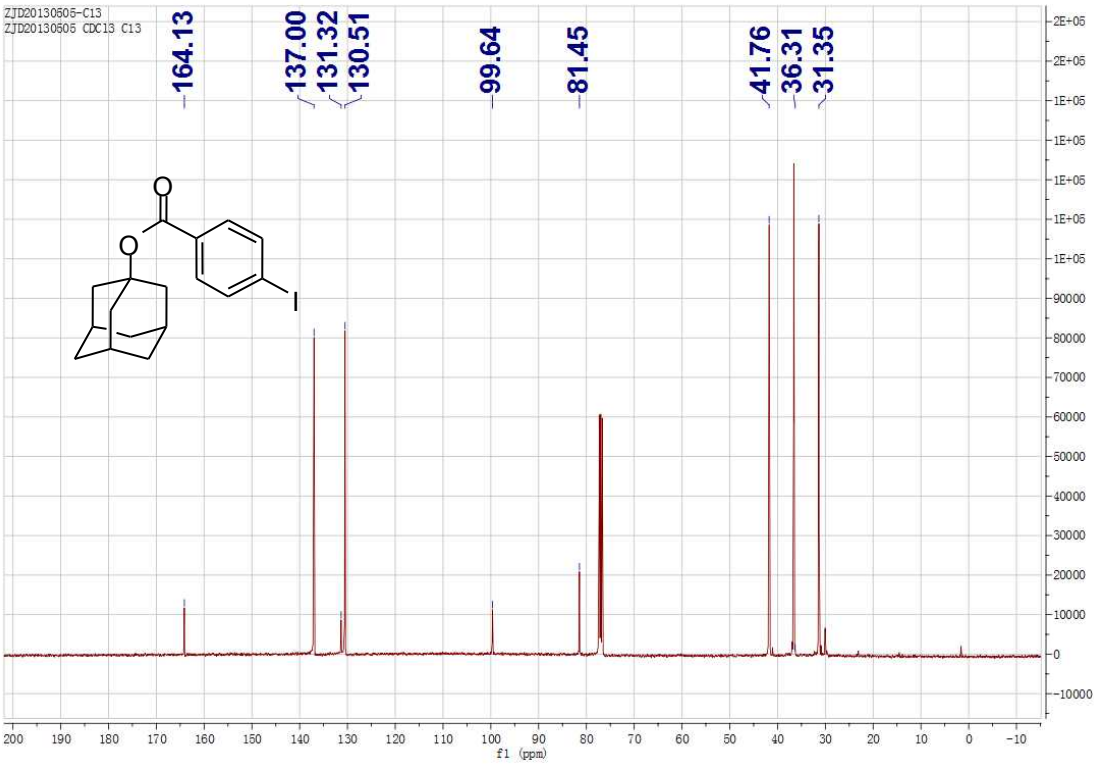
^{13}C NMR (101 MHz, $CDCl_3$) for 1-Adamantanol 4-bromobenzoate (3g)



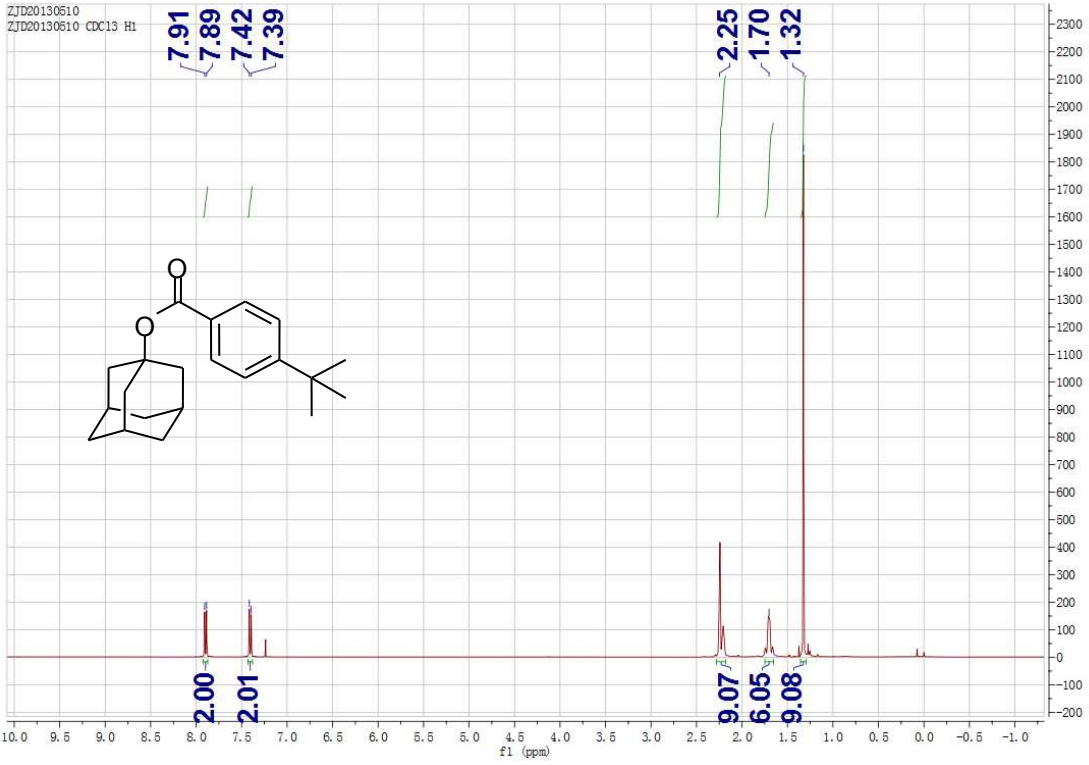
^{1}H NMR (400 MHz, $CDCl_3$) for 1-Adamantanol 4-iodobenzoate (3h)



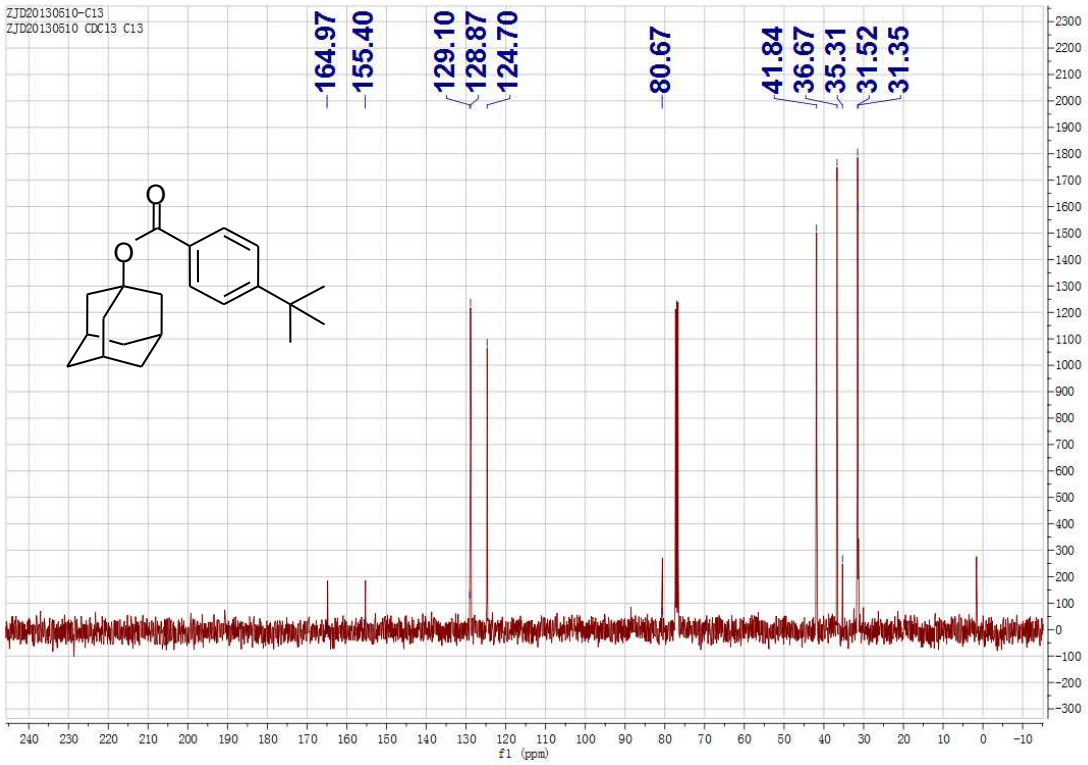
^{13}C NMR (101 MHz, $CDCl_3$) for 1-Adamantanol 4-iodobenzoate (3h)



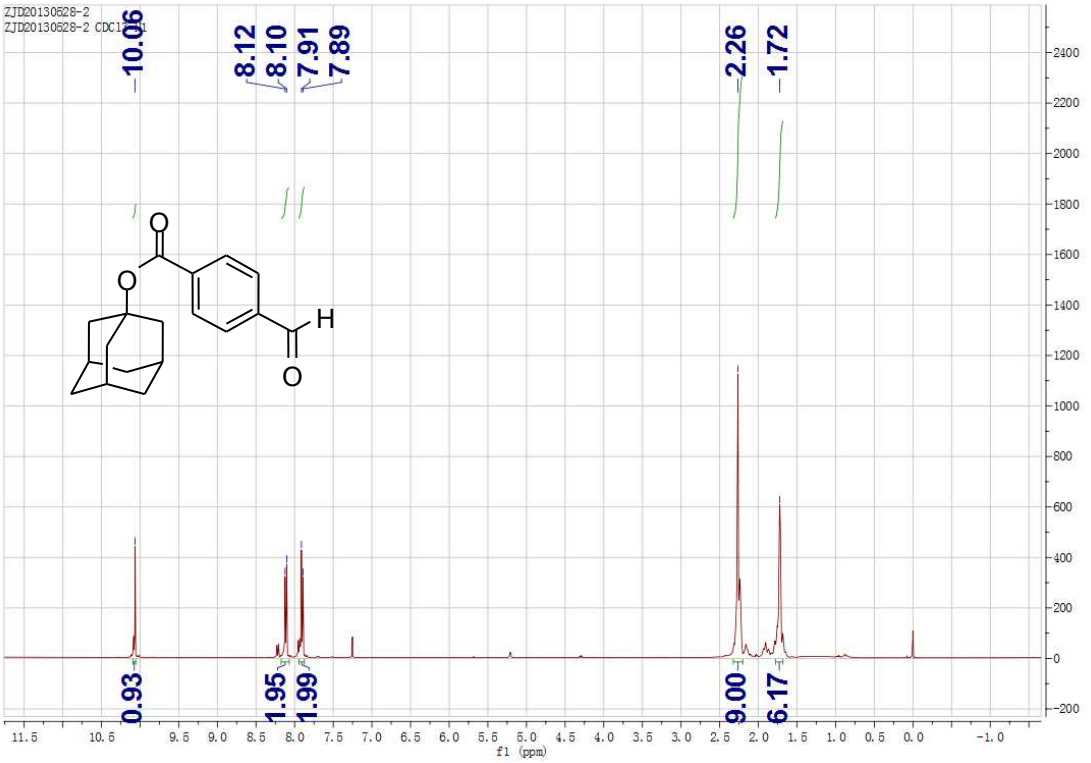
^{1}H NMR (400 MHz, $CDCl_3$) for 1-Adamantanol 4-tert-butylbenzoate (3i)



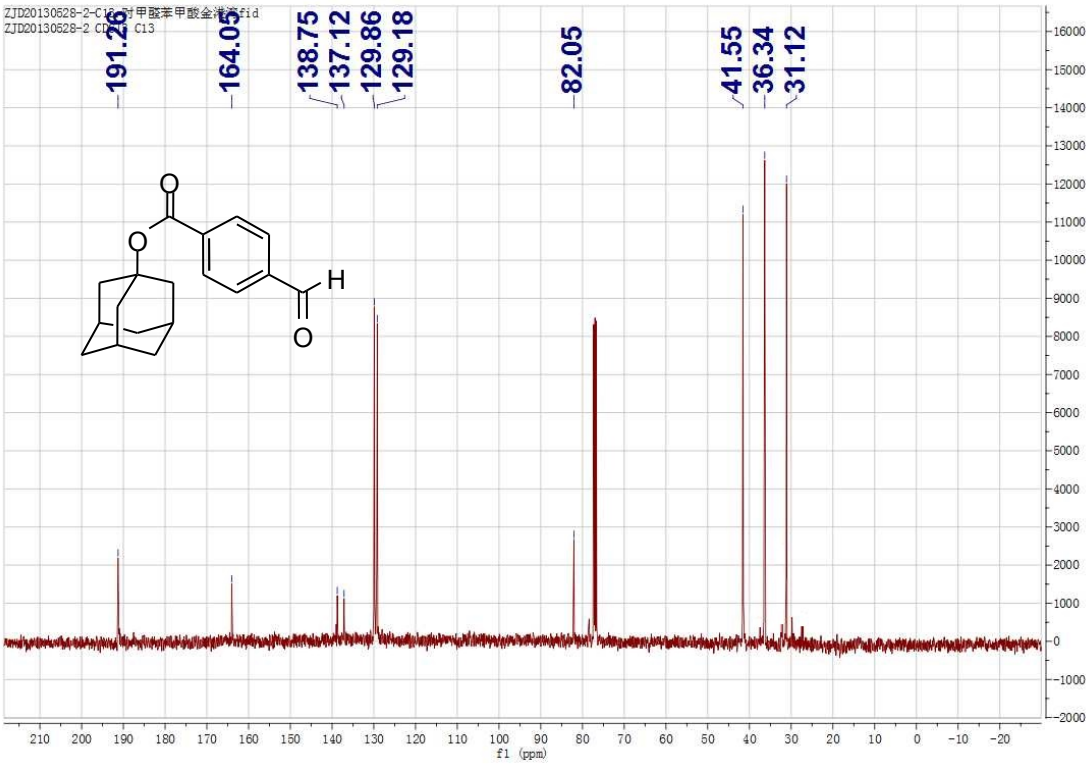
^{13}C NMR (101 MHz, $CDCl_3$) for 1-Adamantanol 4-tert-butylbenzoate (3i)



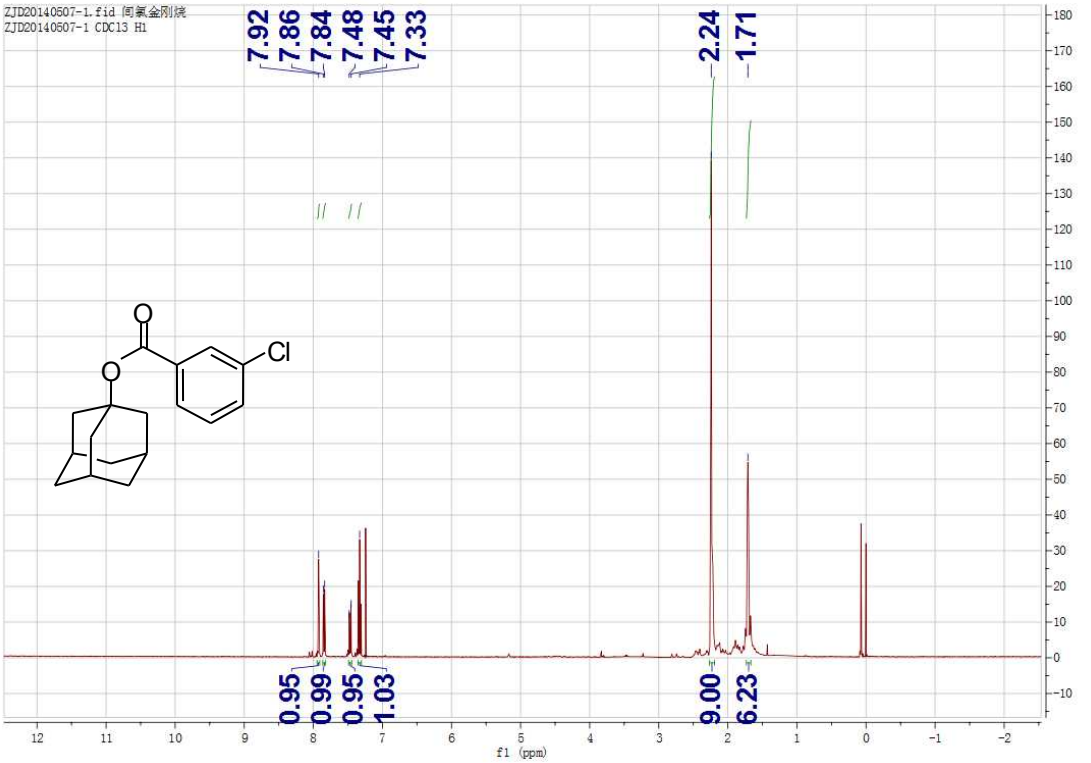
^{1}H NMR (400 MHz, $CDCl_3$) for 1-Adamantanol 4-formylbenzoate (3j)



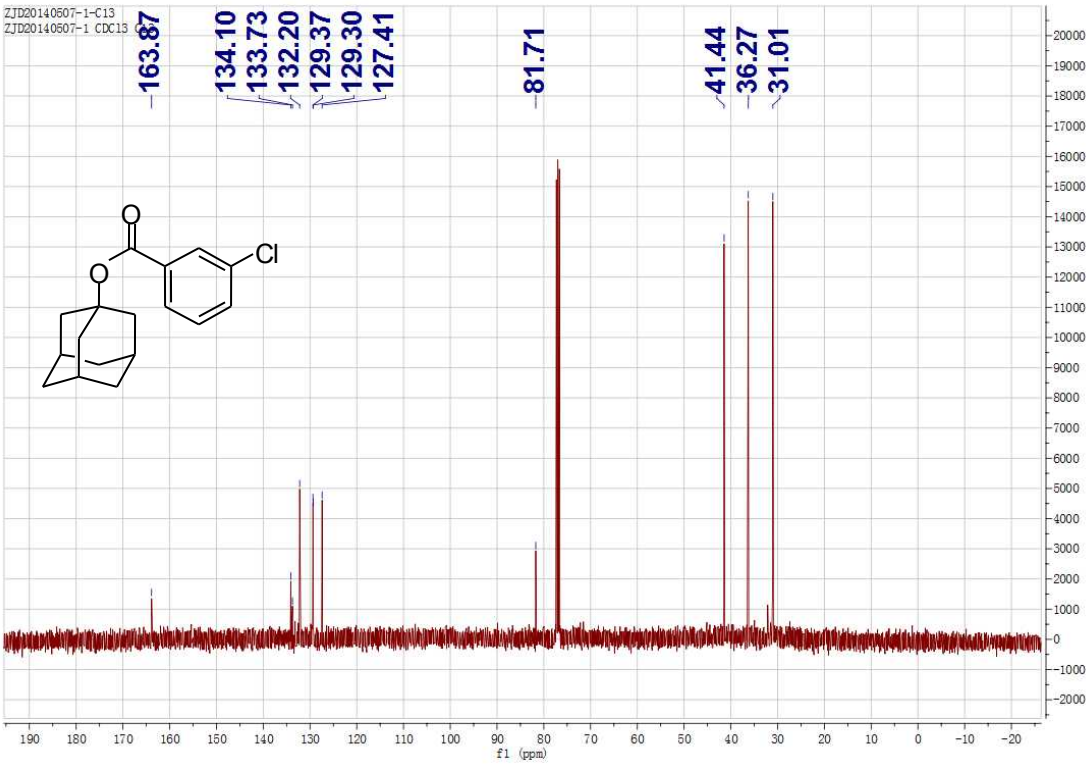
^{13}C NMR (101 MHz, $CDCl_3$) for 1-Adamantanol 4-formylbenzoate (3j)



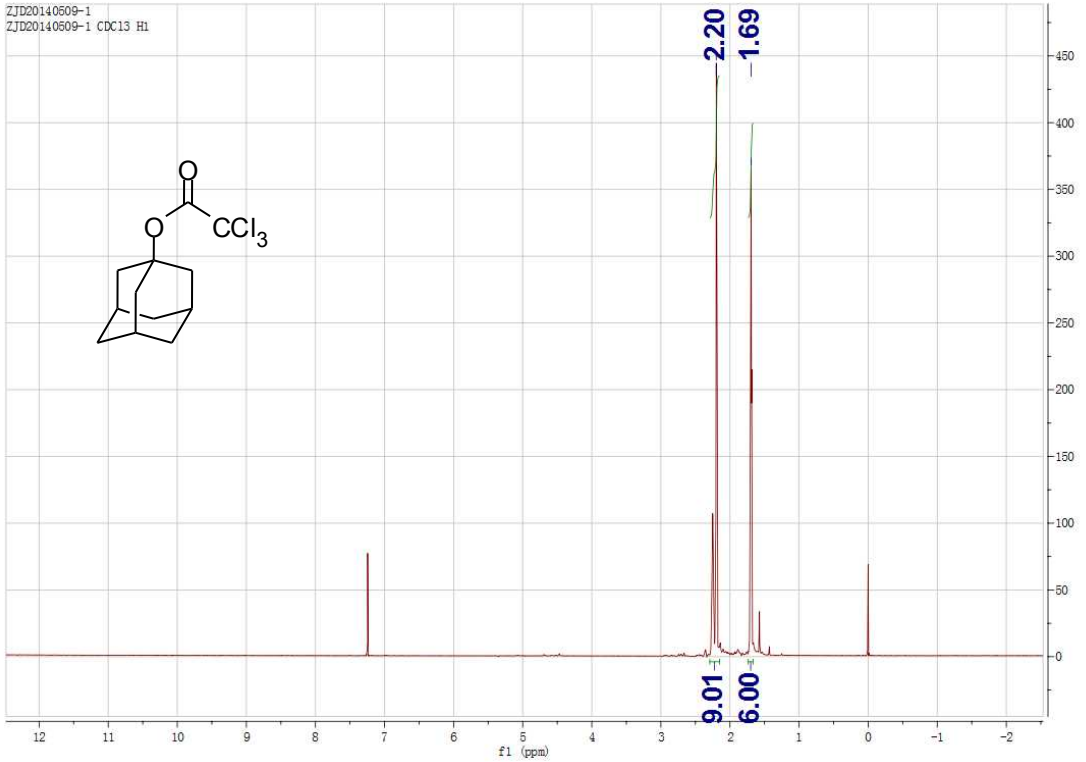
^{1}H NMR (400 MHz, $CDCl_3$) for 1-Adamantanol 3-chlorobenzoate (3k)



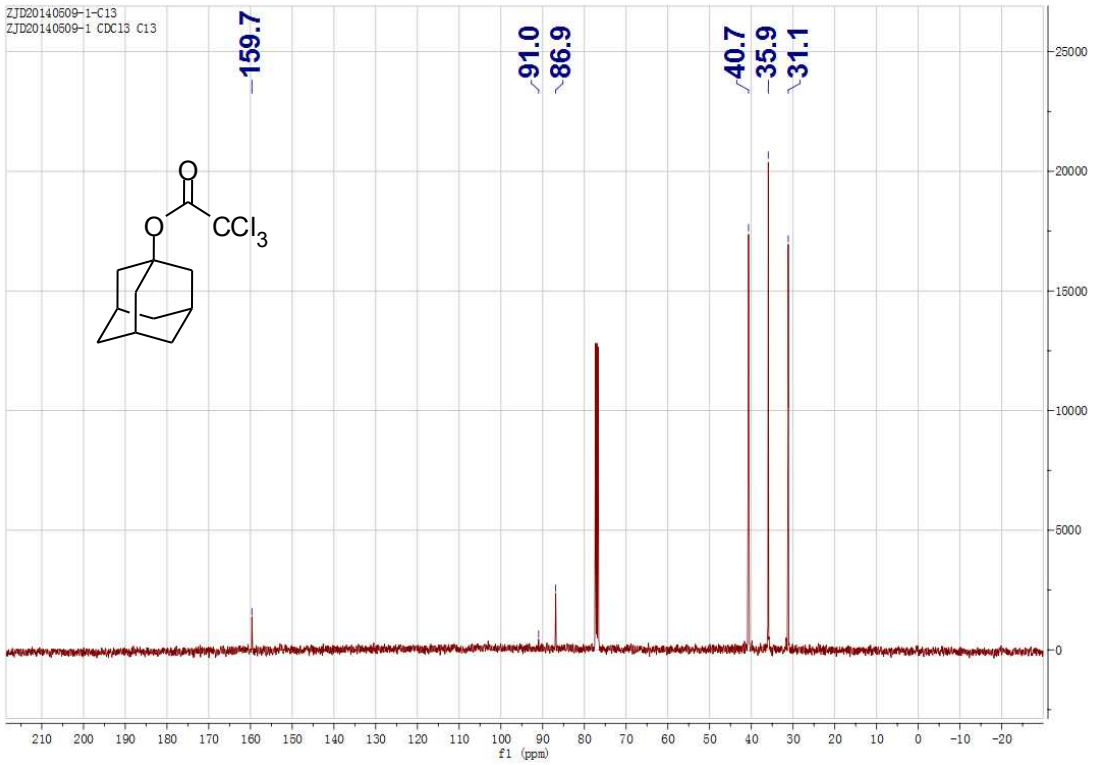
^{13}C NMR (101 MHz, $CDCl_3$) for 1-Adamantanol 3-chlorobenzoate (3k)



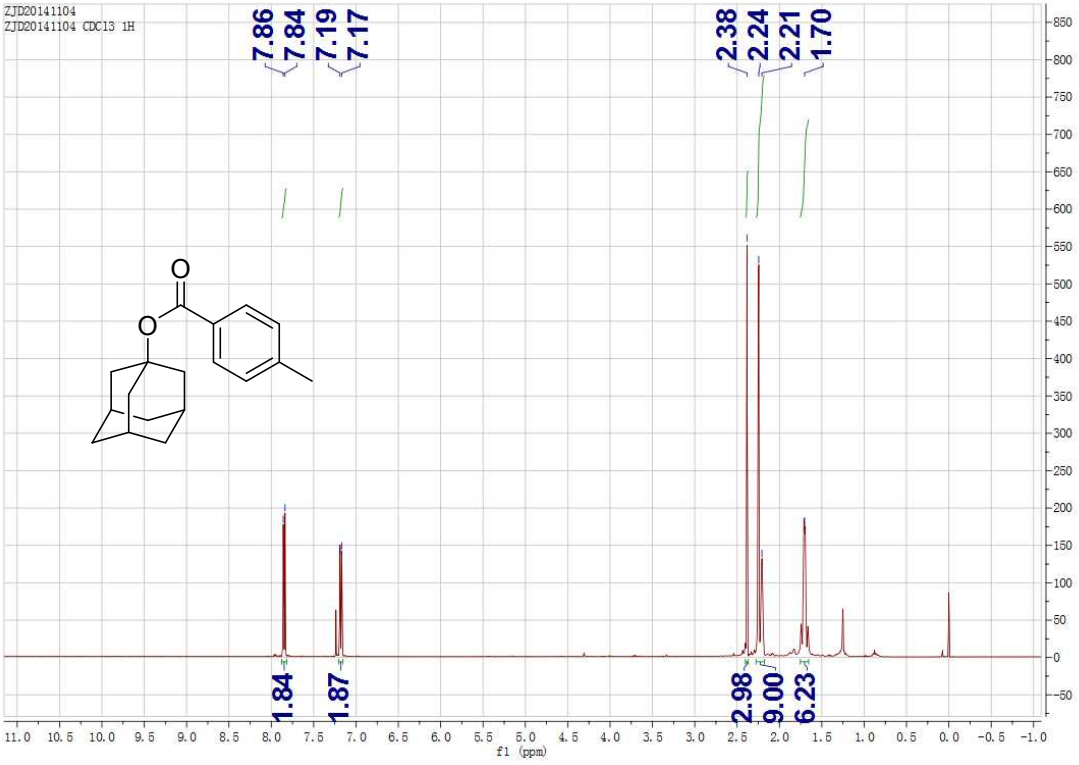
^{1}H NMR (400 MHz, $CDCl_3$) for Adamantanol 2,2,2-trichloroacetate (3l)



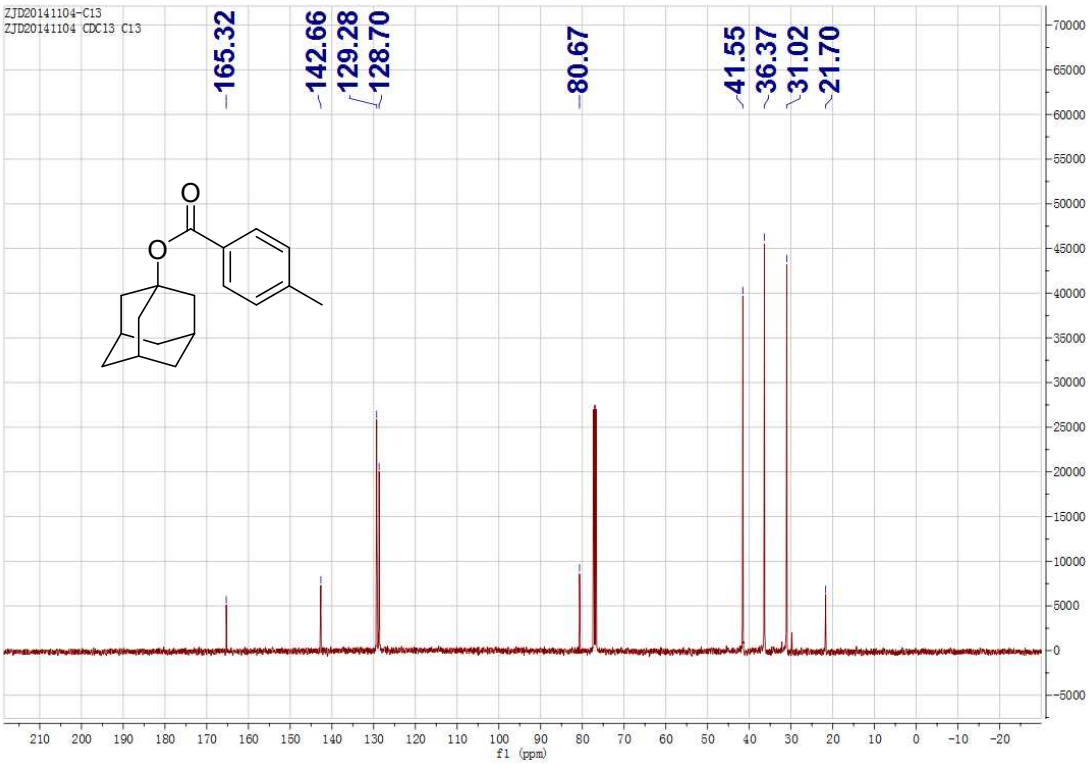
^{13}C NMR (101 MHz, $CDCl_3$) for Adamantanol 2,2,2-trichloroacetate (3l)



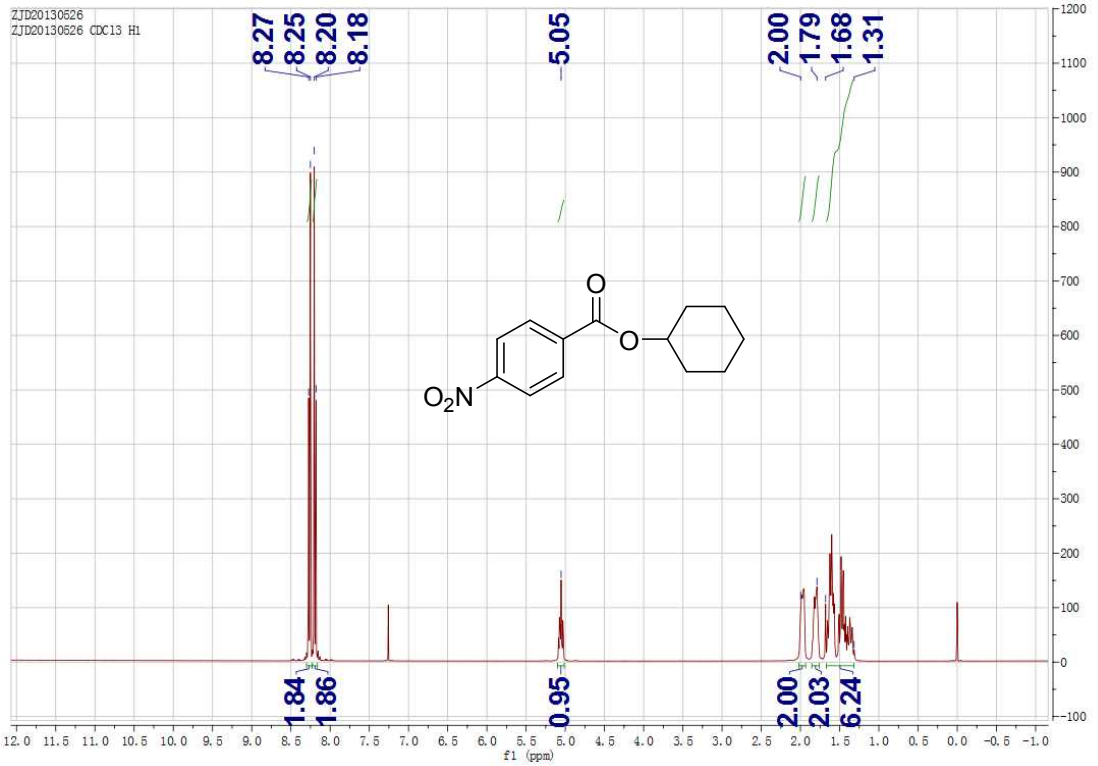
^{1}H NMR (400 MHz, $CDCl_3$) for Adamantanol 4-methylbenzoate (3m)



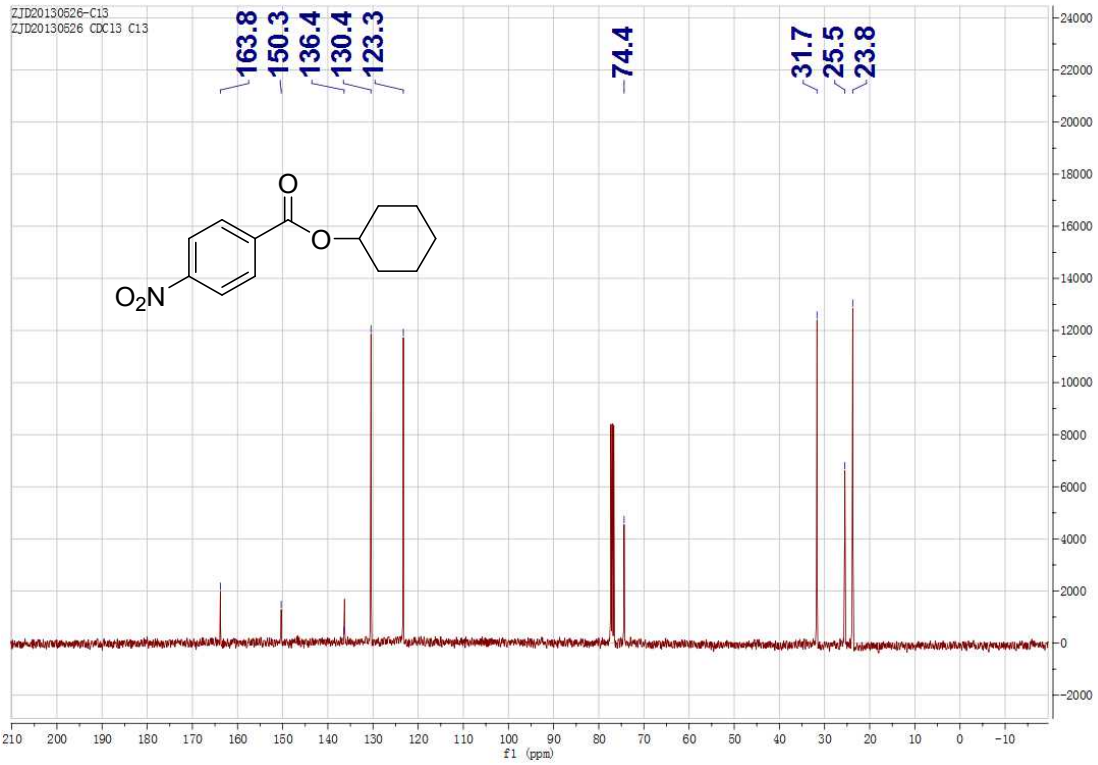
^{13}C NMR (400 MHz, $CDCl_3$) for Adamantanol 4-methylbenzoate (3m)



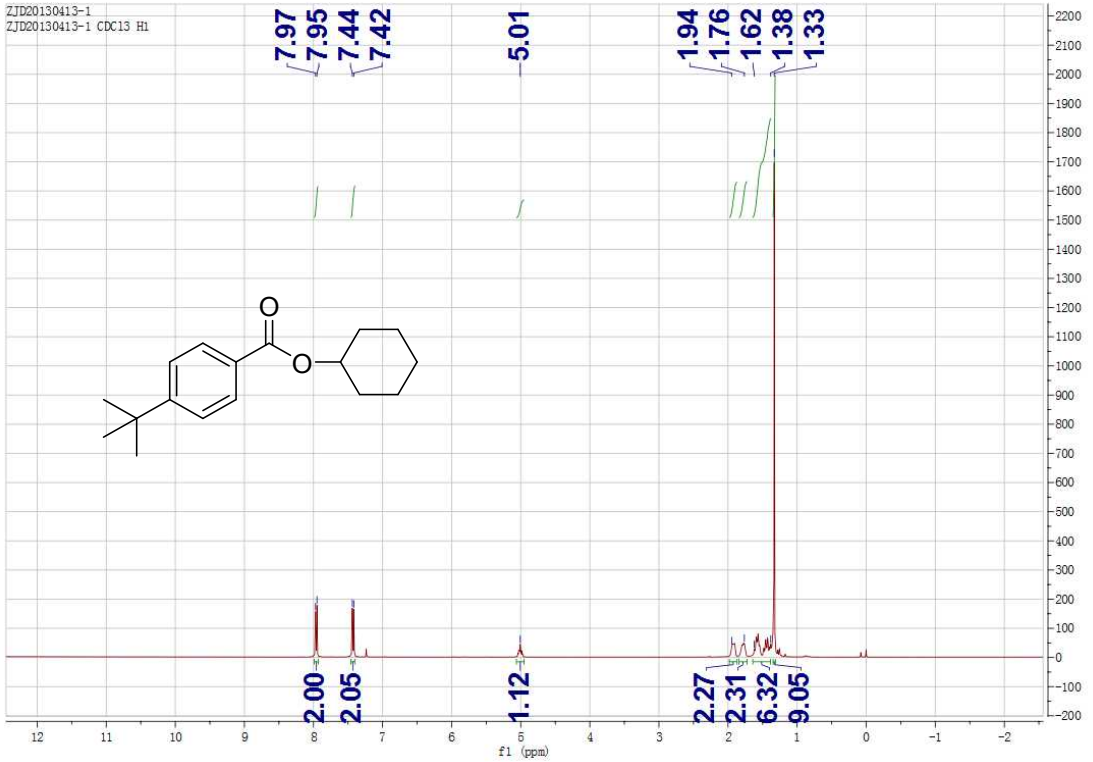
^{1}H NMR (400 MHz, $CDCl_3$) for Cyclohexyl 4-nitrobenzoate (3o)



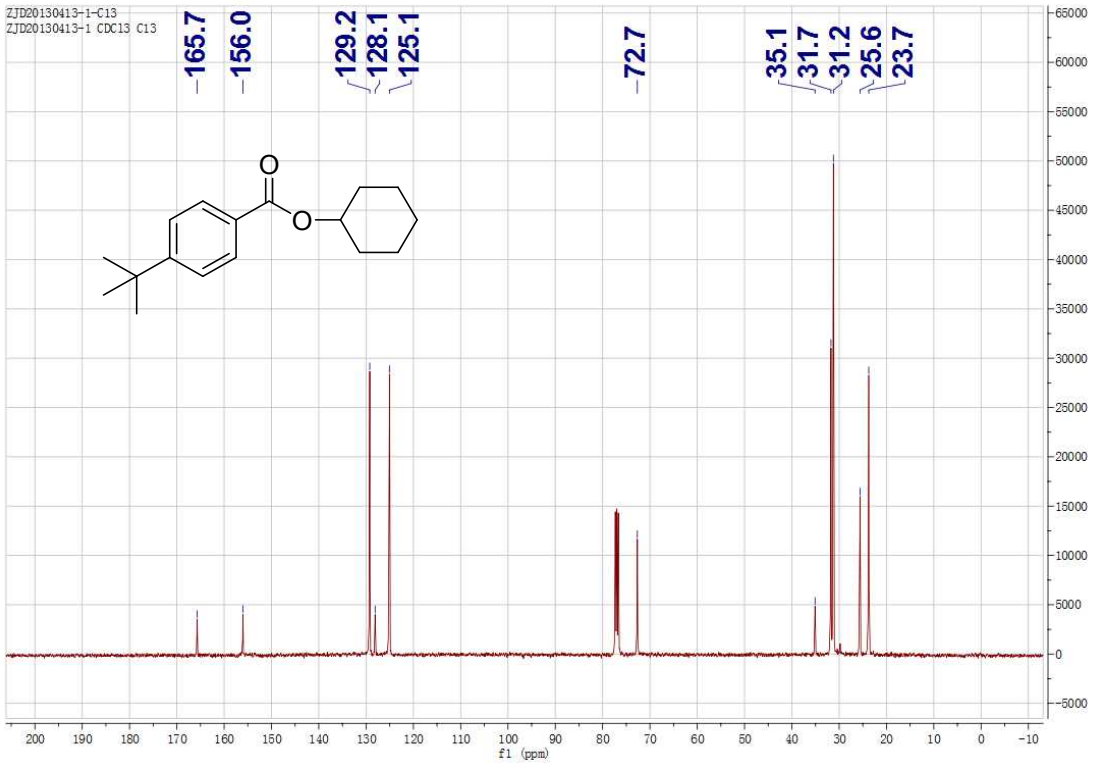
^{13}C NMR (400 MHz, $CDCl_3$) for Cyclohexyl 4-nitrobenzoate (3o)



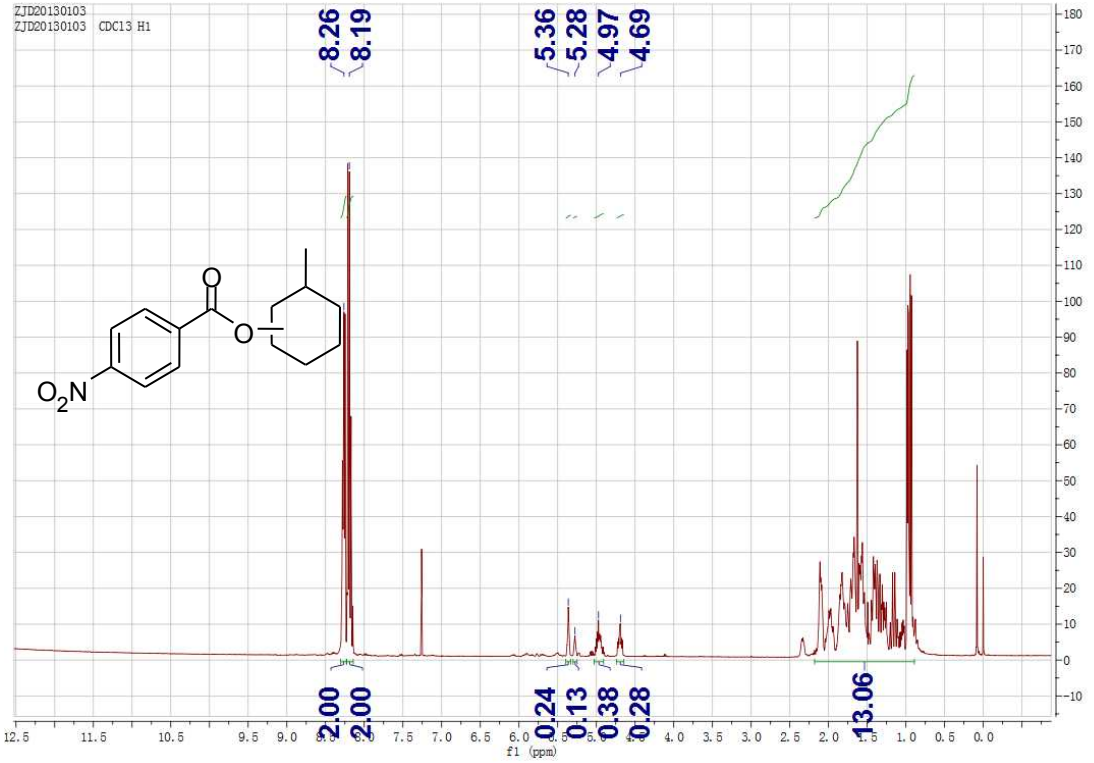
^{1}H NMR (400 MHz, $CDCl_3$) for Cyclohexyl 4-tert-butylbenzoate (3p)



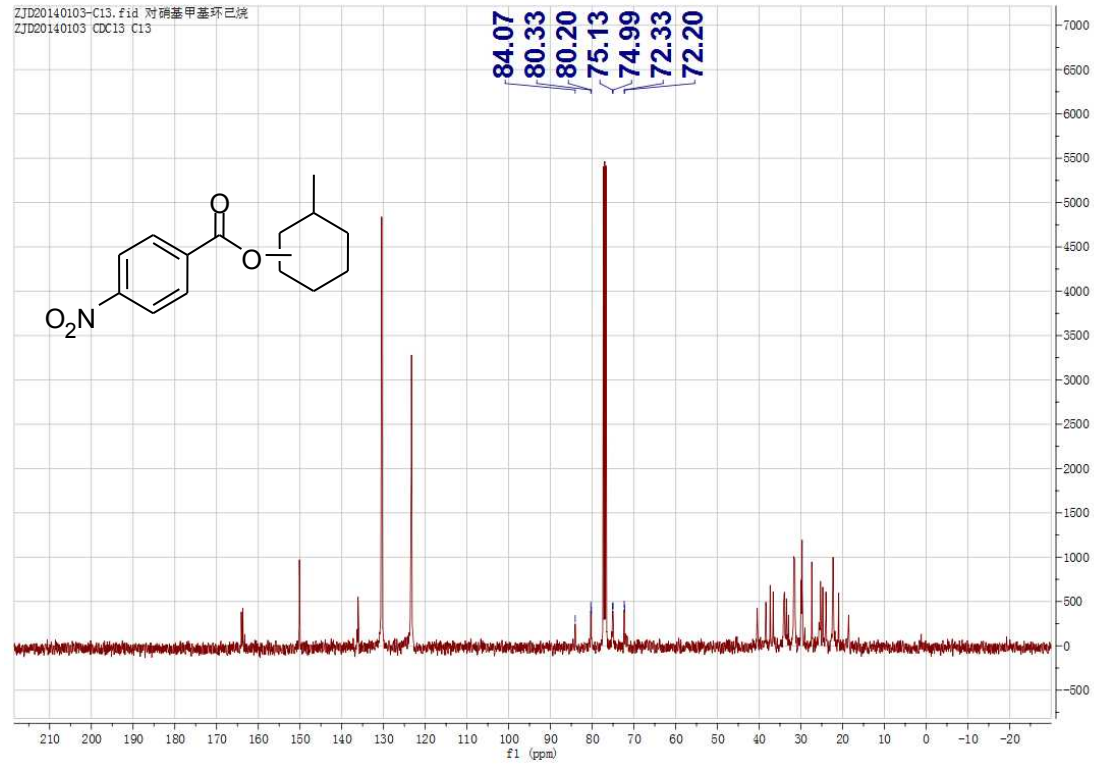
^{13}C NMR (400 MHz, $CDCl_3$) for Cyclohexyl 4-tert-butylbenzoate (3p)



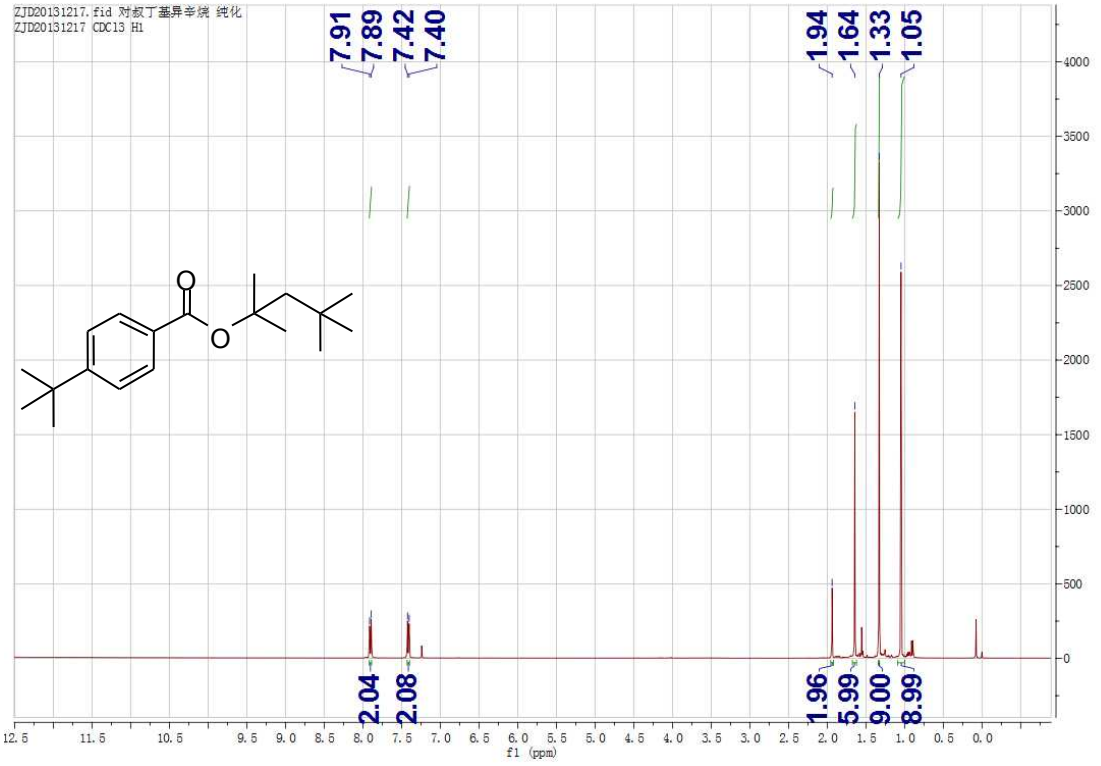
^{1}H NMR (400 MHz, $CDCl_3$) for methylcyclohexyl 4-nitrobenzoate (3q)



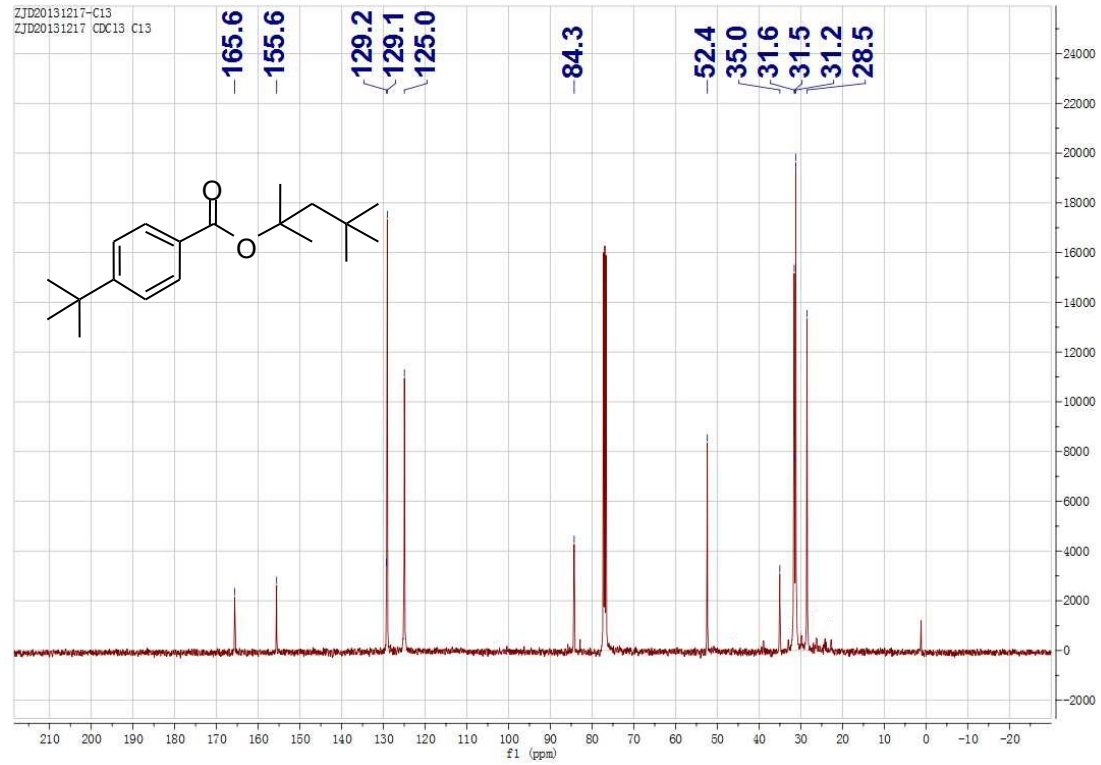
^{13}C NMR (101 MHz, $CDCl_3$) for methylcyclohexyl 4-nitrobenzoate (3q)



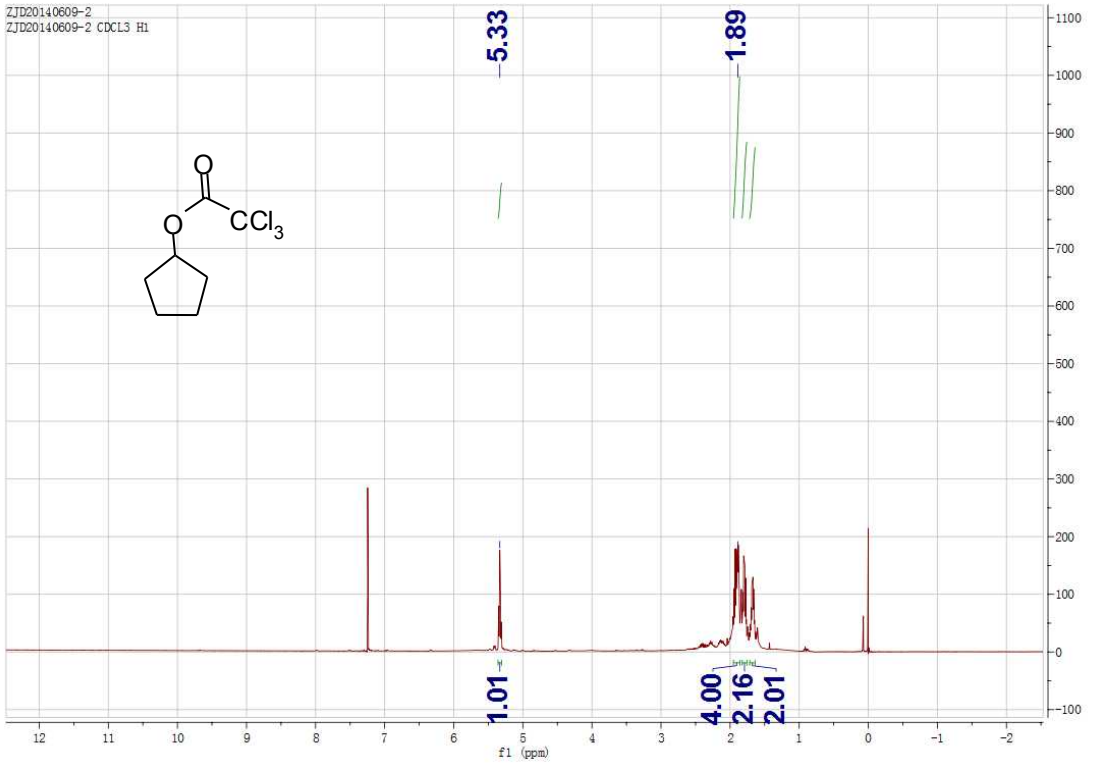
^{1}H NMR (400 MHz, $CDCl_3$) for 2,4,4-trimethylpentan-2-yl 4-tert-butylbenzoate (3r)



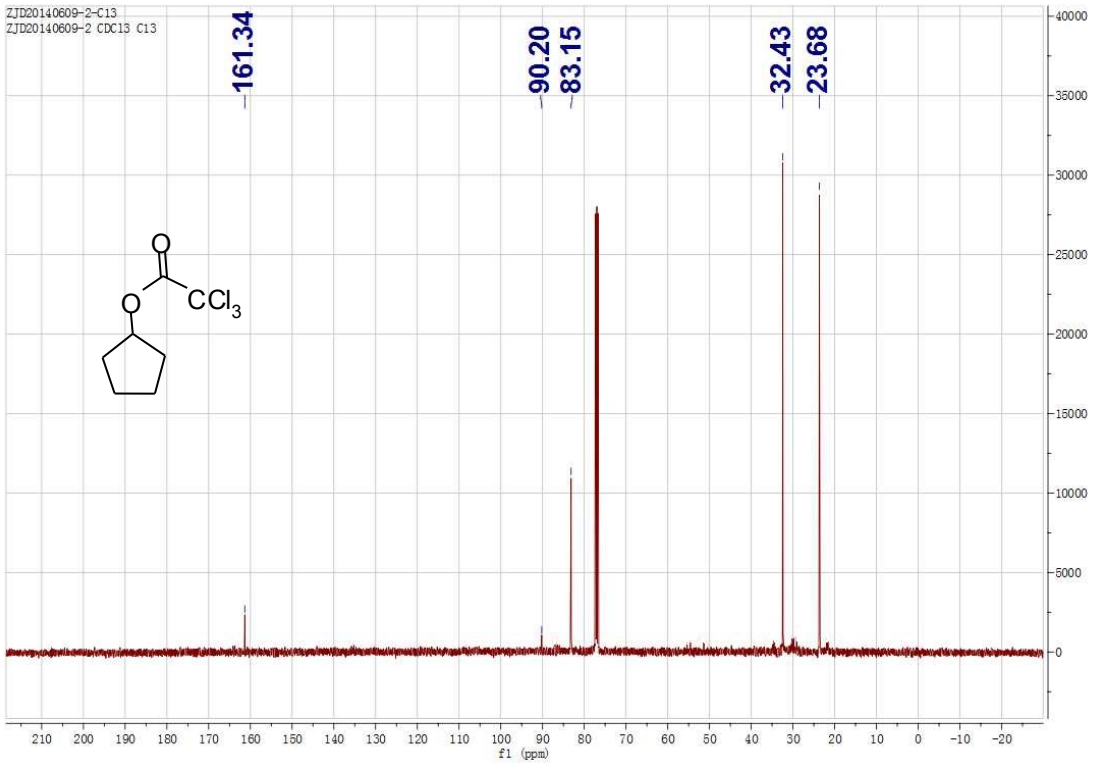
^{13}C NMR (101 MHz, $CDCl_3$) for 2,4,4-trimethylpentan-2-yl 4-tert-butylbenzoate (3r)



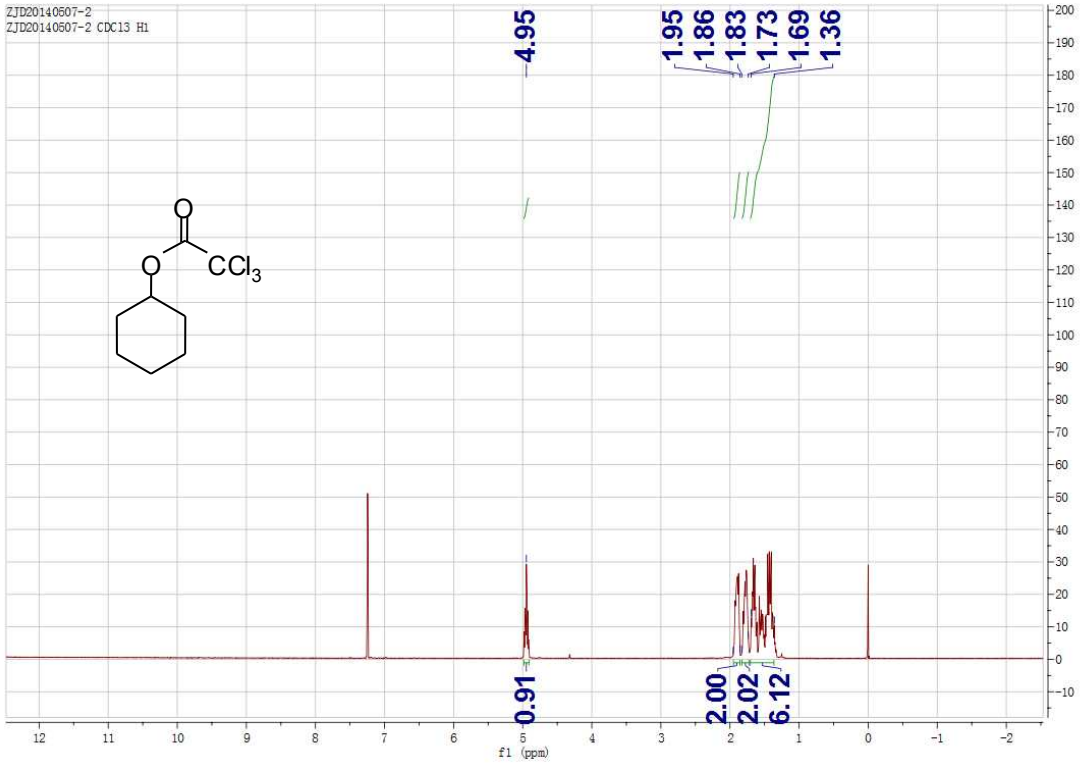
^{1}H NMR (400 MHz, $CDCl_3$) for cyclopentyl 2,2,2-trichloroacetate (3t)



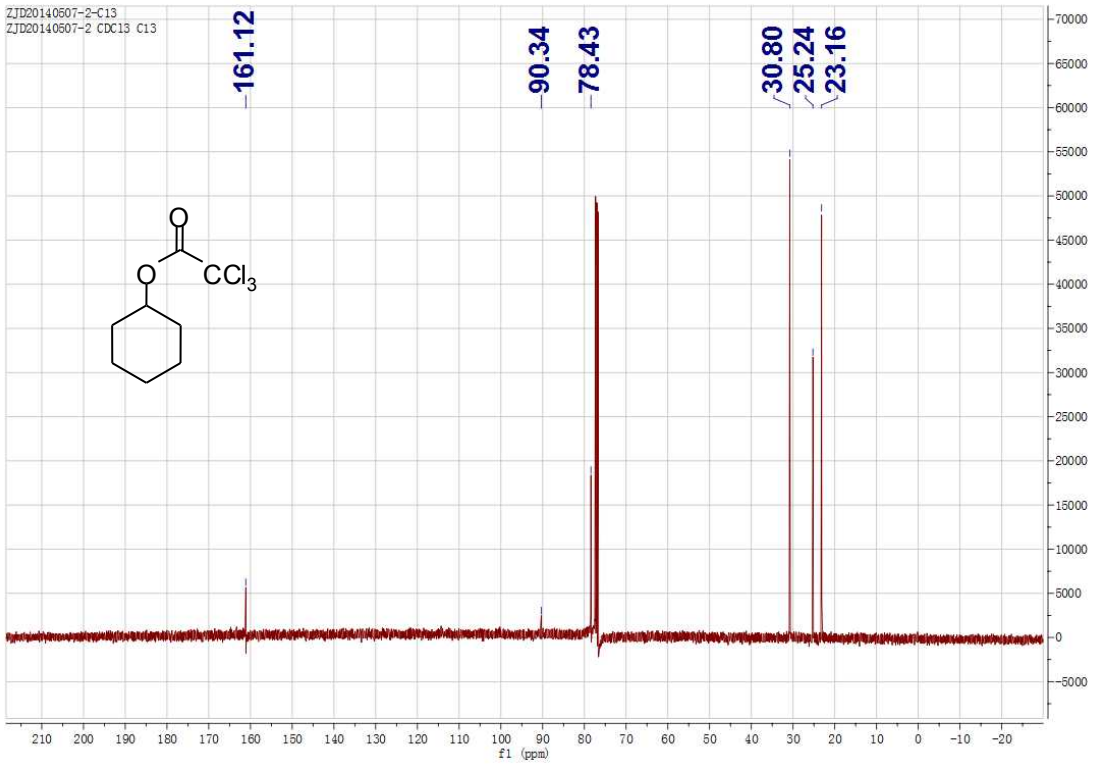
^{13}C NMR (101 MHz, $CDCl_3$) for cyclopentyl 2,2,2-trichloroacetate (3t)



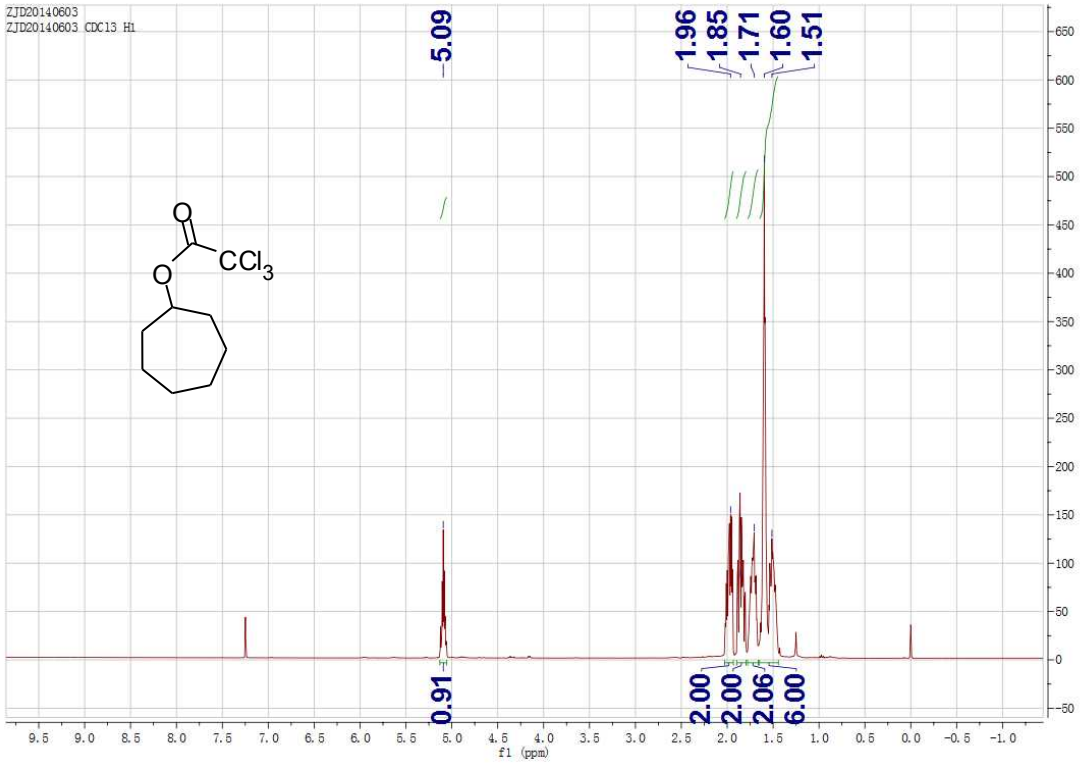
^{1}H NMR (400 MHz, $CDCl_3$) for cyclohexyl 2,2,2-trichloroacetate (3u)



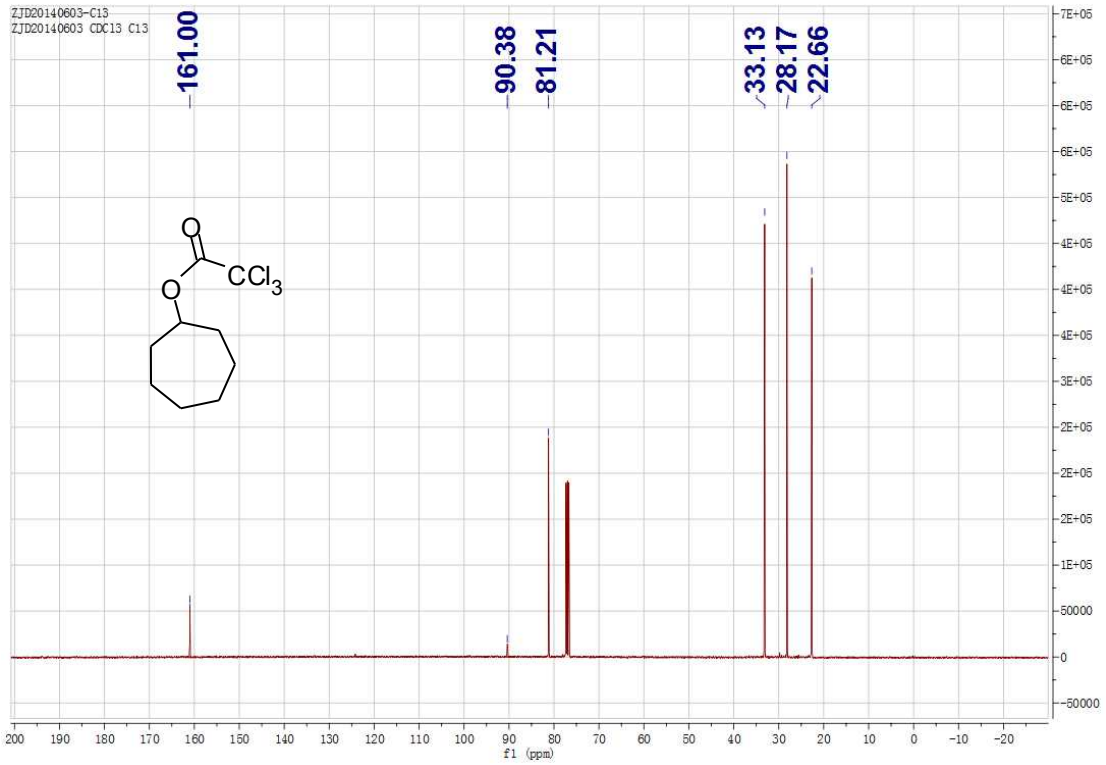
^{13}C NMR (101 MHz, $CDCl_3$) for cyclohexyl 2,2,2-trichloroacetate (3u)



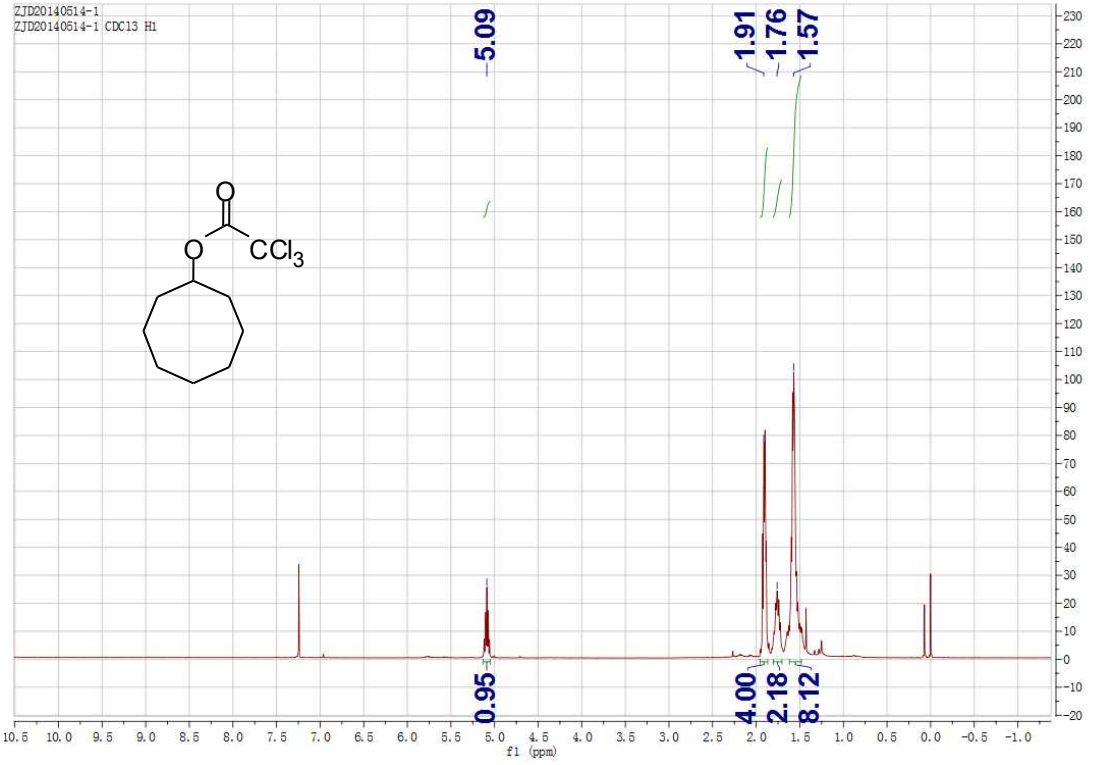
^{1}H NMR (400 MHz, $CDCl_3$) for cycloheptyl 2,2,2-trichloroacetate (3v)



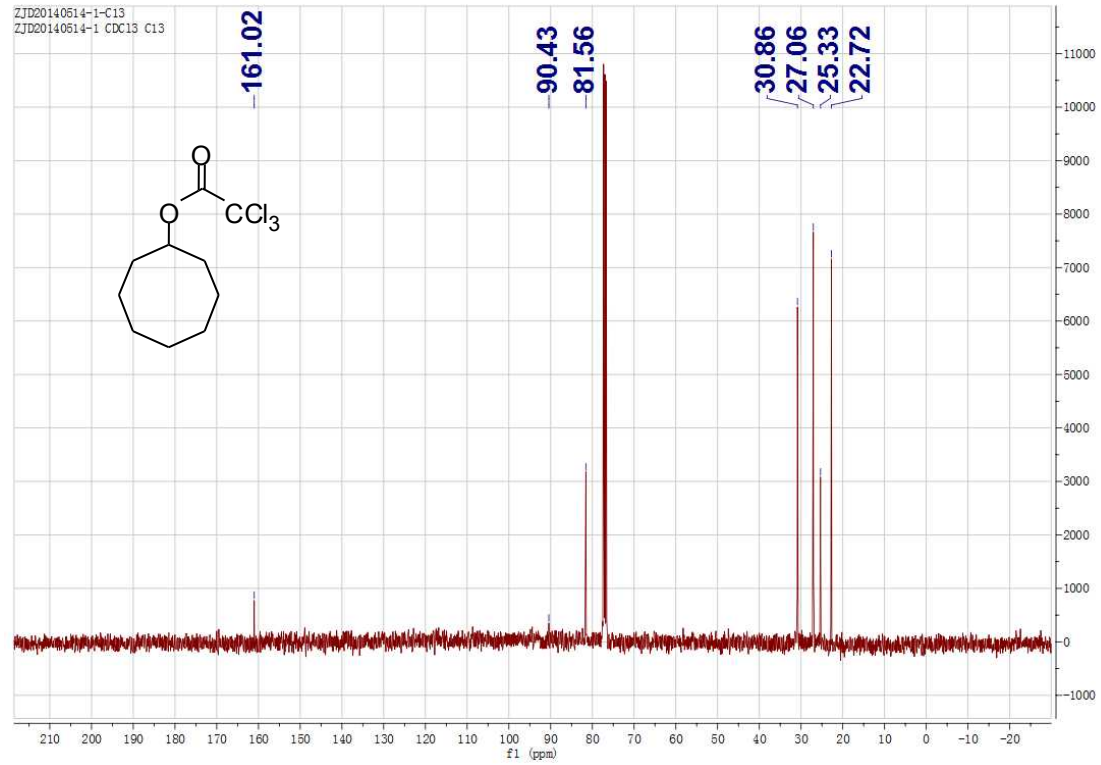
^{13}C NMR (101 MHz, $CDCl_3$) for cycloheptyl 2,2,2-trichloroacetate (3v)



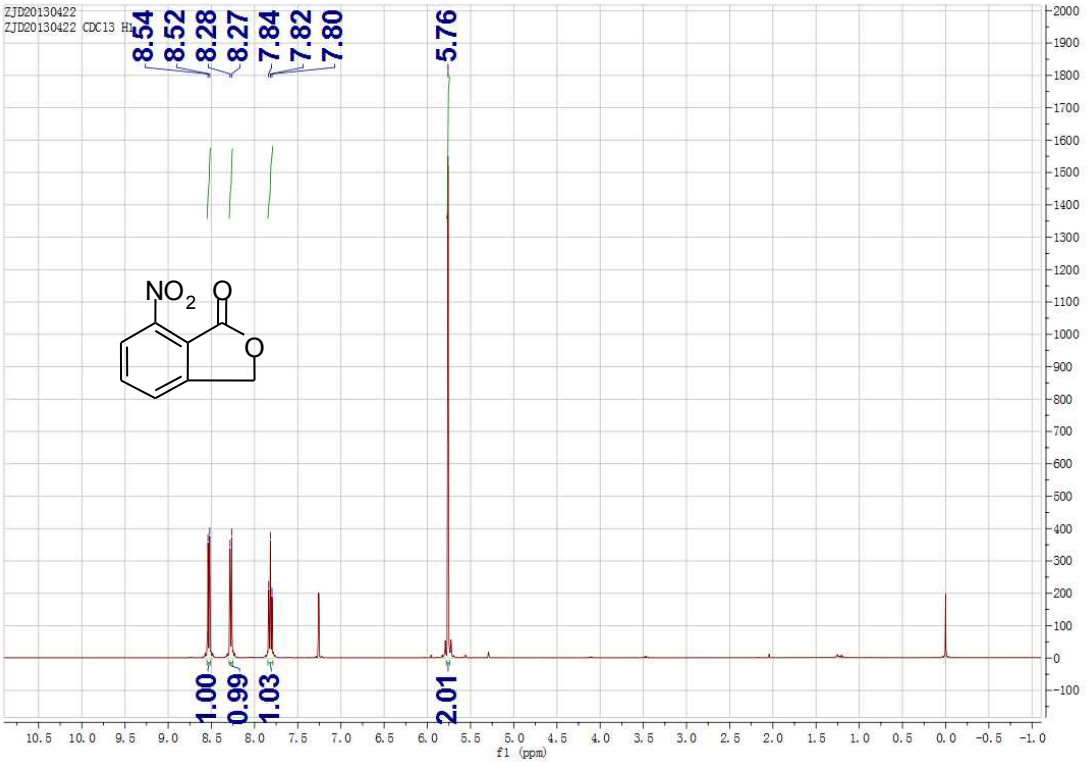
^{1}H NMR (400 MHz, $CDCl_3$) for cyclooctyl 2,2,2-trichloroacetate (3w)



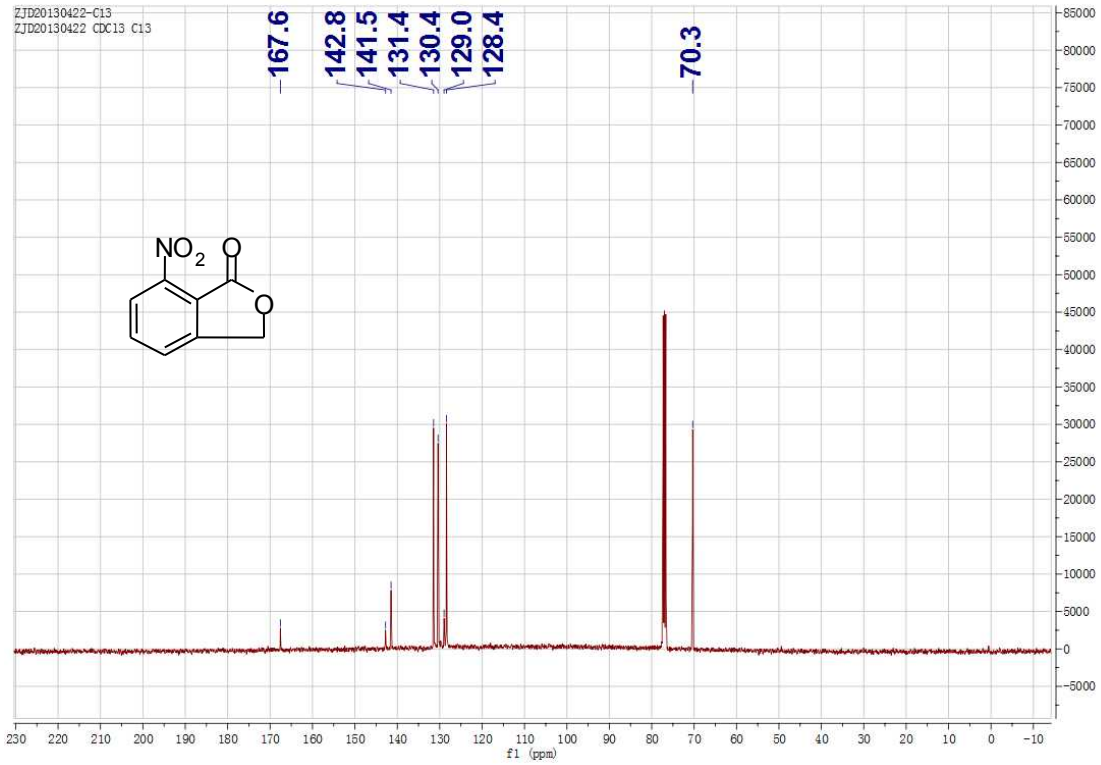
^{13}C NMR (101 MHz, $CDCl_3$) for cyclooctyl 2,2,2-trichloroacetate (3w)



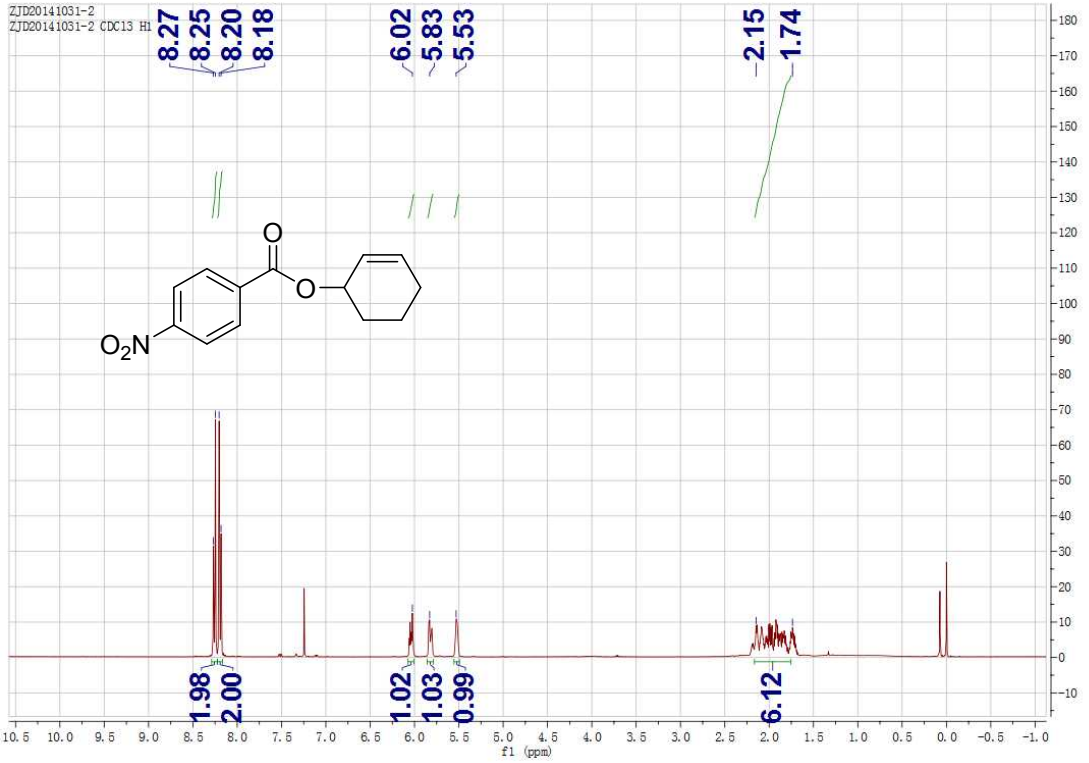
^{1}H NMR (400 MHz, $CDCl_3$) for 7-nitroisobenzofuran-1(3H)-one (3x)



^{13}C NMR (101 MHz, $CDCl_3$) for 7-nitroisobenzofuran-1(3H)-one (3x)



^{1}H NMR (400 MHz, $CDCl_3$) for Cyclohex-2-enyl 4-nitrobenzoate (3y)



^{13}C NMR (400 MHz, $CDCl_3$) for Cyclohex-2-enyl 4-nitrobenzoate (3y)