

Supporting Information

for

Magnetic MoS₂ as an efficient heterogeneous photocatalyst for α -methoxymethylation and aminomethylation of aromatic ketones

Ya-Meng Wang^a, Wen-Jing Li,^a Miao-Miao Wang^a, Mo Zhang^{b,*}, Zhan-Hui Zhang^{a,*}

^a*Hebei Key Laboratory of Organic Functional Molecules, National Experimental Chemistry Teaching Center, College of Chemistry and Materials Science, Hebei Normal University, Shijiazhuang 050024, P. R. China*

^b*School of Pharmacy, Key Laboratory of Innovative Drug Development and Evaluation, Hebei Medical University, Shijiazhuang 050017, P. R. China*

Table of Contents

1. Spectra data of all products	S2-S9
2. Copies of NMR spectra for all products	S10-38
3. HPLC-MS chromatograms of intermediates A , B , C and D	S39-42

* Corresponding author.

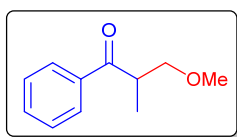
E-mail address: 3120185650@bit.edu.cn (M. Zhang)

* Corresponding author.

E-mail address: zhanhui@hebtu.edu.cn (Z.-H. Zhang)

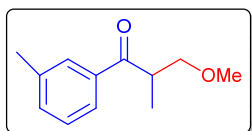
Spectra data of all products

3-Methoxy-2-methyl-1-phenylpropan-1-one (3a)



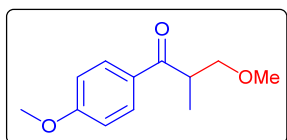
Colorless oil; IR (KBr): 2925, 1682, 1595, 1448, 1219, 1111, 793, 706, 647, 508 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.97 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 3.81 – 3.73 (m, 2H), 3.47 – 3.44 (m, 1H), 3.32 (s, 3H), 1.20 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 202.8, 136.7, 133.1, 128.6, 128.4, 75.0, 59.1, 41.3, 14.9 ppm.

3-Methoxy-2-methyl-1-(*m*-tolyl)propan-1-one (3b)



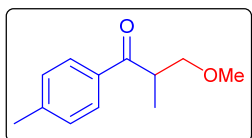
Colorless oil; IR (KBr): 2973, 1676, 1611, 1452, 1233, 1104, 762, 522 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.76 – 7.74 (m, 2H), 7.35 – 7.26 (m, 2H), 3.79 – 3.70 (m, 2H), 3.46 – 3.39 (m, 1H), 3.29 (s, 3H), 2.38 (s, 3H), 1.18 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 202.9, 138.4, 136.7, 133.8, 128.9, 128.5, 125.6, 75.0, 59.1, 41.2, 21.4, 14.9 ppm.

3-Methoxy-1-(4-methoxyphenyl)-2-methylpropan-1-one (3c)



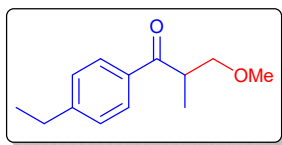
Colorless oil; IR (KBr): 2963, 2928, 1672, 1603, 1509, 1258, 1172, 1110, 964, 842, 758, 607, 516 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.97 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), 3.73 – 3.60 (m, 2H), 3.53 – 3.50 (m, 1H), 3.30 (s, 3H), 1.81 – 1.70 (m, 1H), 1.66 – 1.55 (m, 1H), 0.88 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 201.5, 167.0, 164.5, 134.2, 134.2, 131.1, 131.0, 115.8, 115.6, 73.9, 59.1, 48.1, 22.9, 11.8 ppm.

3-Methoxy-2-methyl-1-(*p*-tolyl)propan-1-one (3d)



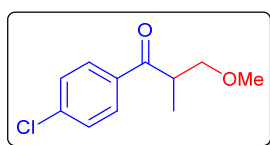
Colorless oil; IR (KBr): 2926, 1687, 1607, 1456, 1407, 1226, 1282, 1110, 973, 829, 747, 599, 478 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.86 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 3.77 – 3.70 (m, 2H), 3.45 – 3.39 (m, 1H), 3.29 (s, 3H), 2.37 (s, 3H), 1.17 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 202.3, 143.8, 134.1, 129.4, 129.3, 129.2, 128.6, 128.5, 75.0, 59.1, 41.1, 21.6, 14.9 ppm.

1-(4-Ethylphenyl)-3-methoxy-2-methylpropan-1-one (3e)



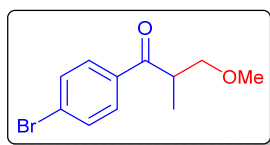
Colorless oil; IR (KBr): 2972, 1689, 1576, 1403, 1233, 1107, 964, 855, 762, 584, 453 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.90 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 3.80 – 3.72 (m, 2H), 3.48 – 3.43 (m, 1H), 3.32 (s, 3H), 2.73 – 2.67 (m, 2H), 1.25 (t, J = 7.6 Hz, 3H), 1.20 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 202.4, 150.0, 134.3, 128.7, 128.2, 75.1, 59.1, 41.1, 29.0, 15.2, 15.0 ppm.

1-(4-Chlorophenyl)-3-methoxy-2-methylpropan-1-one (3f)



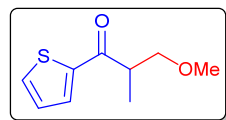
Colorless oil; IR (KBr): 2925, 1682, 1589, 1457, 1440, 1218, 1093, 977, 841, 748, 489 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.90 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 3.74 – 3.69 (m, 2H), 3.47 – 3.41 (m, 1H), 3.30 (s, 2H), 1.17 (d, J = 6.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 201.6, 139.5, 135.1, 129.9, 128.9, 75.0, 59.1, 41.3, 14.7 ppm.

1-(4-Bromophenyl)-3-methoxy-2-methylpropan-1-one (3g)



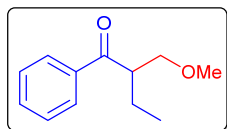
Colorless oil; IR (KBr): 2974, 2926, 1690, 1584, 1456, 1397, 1215, 1070, 978, 838, 751, 684, 519, 471 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.83 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 3.74 – 3.69 (m, 2H), 3.47 – 3.42 (m, 1H), 3.30 (s, 3H), 1.18 (d, J = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 201.9, 135.4, 132.1, 132.0, 123.0, 128.3, 75.0, 59.2, 41.3, 14.7 ppm.

3-Methoxy-2-methyl-1-(thiophen-2-yl)propan-1-one (3h)



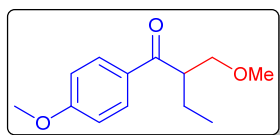
Colorless oil; IR (KBr): 2976, 2929, 1663, 1518, 1415, 1235, 1109, 925, 847, 725, 458 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.76 – 7.73 (m, 1H), 7.63 (dd, J = 4.8, 0.8 Hz, 1H), 7.12 (dd, J = 4.0, 0.4 Hz, 1H), 3.72 (dd, J = 7.6, 1.2 Hz, 1H), 3.63 – 3.55 (m, 1H), 3.42 (dd, J = 4.8, 3.2 Hz, 1H), 3.30 (s, 3H), 1.21 (d, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 195.4, 144.2, 134.0, 132.2, 128.2, 74.9, 59.1, 43.0, 15.0 ppm.

2-(Methoxymethyl)-1-phenylbutan-1-one (3i)



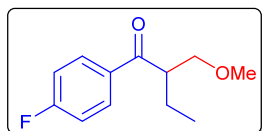
Pale yellow oil; IR (KBr): 2963, 2926, 1694, 1596, 1447, 1216, 1110, 963, 704, 655, 457 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.97 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 3.74 – 3.65 (m, 2H), 3.51 (dd, J = 4.0, 3.6 Hz, 1H), 3.29 (s, 3H), 1.81-1.72 (m, 1H), 1.65 – 1.55 (m, 1H), 0.89 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 203.0, 137.7, 133.0, 128.6, 128.3, 73.8, 59.1, 48.1, 22.9, 11.7 ppm.

2-(Methoxymethyl)-1-(4-methoxyphenyl)butan-1-one (3j)



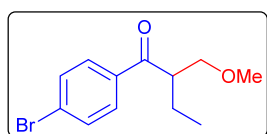
Colorless oil; IR (KBr): 2963, 2928, 1672, 1603, 1509, 1258, 1172, 1110, 964, 842, 758, 607, 516 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.97 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), 3.73 – 3.60 (m, 2H), 3.53 – 3.50 (m, 1H), 3.30 (s, 3H), 1.81 – 1.70 (m, 1H), 1.66 – 1.55 (m, 1H), 0.88 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 201.5, 167.0, 164.5, 134.2, 134.2, 131.1, 131.0, 115.8, 115.6, 73.9, 59.1, 48.1, 22.9, 11.8 ppm.

1-(4-Fluorophenyl)-2-(methoxymethyl)butan-1-one (3k)



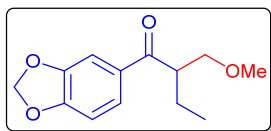
Colorless oil; IR (KBr): 2925, 1681, 1598, 1507, 1457, 1216, 1110, 965, 847, 755, 496, 444 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 8.00 (dd, J = 5.6, 3.2 Hz, 2H), 7.13 (t, J = 8.8 Hz, 2H), 3.72 – 3.60 (m, 2H), 3.52 – 3.49 (m, 1H), 3.28 (s, 3H), 1.81 – 1.70 (m, 1H), 1.64 – 1.53 (m, 1H), 0.88 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 201.5, 165.76 (d, $J_{\text{C-F}}$ = 253.2 Hz), 134.2 (d, $J_{\text{C-F}}$ = 2.9 Hz), 131.0 (d, $J_{\text{C-F}}$ = 9.2 Hz), 115.7 (d, $J_{\text{C-F}}$ = 21.7 Hz), 73.9, 59.1, 48.1, 22.9, 11.8 ppm.

1-(4-Bromophenyl)-2-(methoxymethyl)butan-1-one (3l)



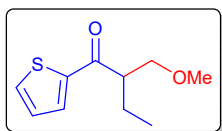
Colorless oil; IR (KBr): 2927, 2876, 1692, 1584, 1459, 1397, 1213, 1136, 1069, 1008, 963, 838, 746, 685, 458 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.83 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 3.70 – 3.58 (m, 2H), 3.50 (dd, J = 4.8, 3.6 Hz, 1H), 3.27 (s, 3H), 1.80-1.69 (m, 1H), 1.62 – 1.52 (m, 1H), 0.87 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 202.1, 136.5, 131.9, 129.9, 128.2, 73.9, 59.1, 48.2, 22.8, 11.8 ppm.

1-(Benzo[d][1,3]dioxol-5-yl)-2-(methoxymethyl)butan-1-one (3m)



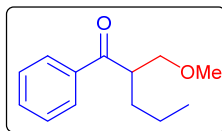
Colorless oil; IR (KBr): 2964, 2926, 1669, 1558, 1498, 1244, 1097, 1037, 932, 804, 749, 577 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.58 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.03 (s, 2H), 3.68 (t, J = 8.4 Hz, 1H), 3.61 – 3.55 (m, 1H), 3.48 (dd, J = 5.2, 3.6 Hz, 1H), 3.28 (s, 3H), 1.77 – 1.69 (m, 1H), 1.60 – 1.54 (m, 1H), 0.87 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 201.0, 151.8, 148.2, 132.6, 124.7, 108.2, 107.9, 101.9, 74.1, 59.1, 47.9, 23.1, 11.8 ppm.

2-(Methoxymethyl)-1-(thiophen-2-yl)butan-1-one (3n)



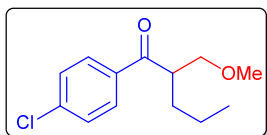
Colorless oil; IR (KBr): 2963, 2926, 1658, 1416, 1110, 850, 723, 458 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.76 (d, J = 3.6 Hz, 1H), 7.64 (d, J = 5.2 Hz, 1H), 7.13 (t, J = 4.4 Hz, 1H), 3.74 – 3.67 (m, 1H), 3.51 – 3.44 (m, 2H), 3.30 (s, 3H), 1.82 – 1.71 (m, 1H), 1.67 – 1.56 (m, 1H), 0.91 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 195.5, 145.4, 134.1, 132.2, 128.2, 73.9, 59.1, 50.2, 23.1, 11.9 ppm.

2-(Methoxymethyl)-1-phenylpentan-1-one (3o)



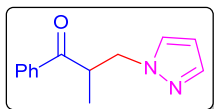
Colorless oil; IR (KBr): 2958, 2929, 1682, 1596, 1447, 1381, 1212, 1109, 951, 708, 687 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.97 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 3.80 – 3.69 (m, 2H), 3.50 (dd, J = 4.8, 3.6 Hz, 1H), 3.28 (s, 3H), 1.75 – 1.66 (m, 1H), 1.55 – 1.47 (m, 1H), 1.34 – 1.25 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 203.2, 137.7, 133.0, 128.6, 128.3, 74.3, 59.1, 46.6, 32.0, 20.7, 14.3 ppm.

1-(4-Chlorophenyl)-2-(methoxymethyl)pentan-1-one (3p)



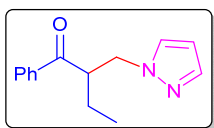
Colorless oil; IR (KBr): 2958, 2927, 1682, 1589, 1457, 1400, 1210, 1092, 950, 840, 754, 530 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.91 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 3.71 – 3.65 (m, 2H), 3.50 (t, J = 9.6 Hz, 1H), 3.27 (s, 1H), 1.73 – 1.64 (m, 1H), 1.53 – 1.44 (m, 1H), 1.32 – 1.22 (m, 2H), 0.86 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 202.1, 139.4, 136.1, 129.8, 128.9, 74.3, 59.1, 46.6, 31.9, 20.7, 14.2 ppm.

2-Methyl-1-phenyl-3-(1H-pyrazol-1-yl)propan-1-one (5a)



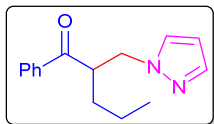
Colorless oil; IR (KBr): 2932, 1681, 1595, 1515, 1447, 1233, 1213, 1090, 977, 750, 701, 617 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.91 – 7.89 (m, 2H), 7.56 – 7.52 (m, 1H), 7.48 (d, J = 1.6 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.38 (d, J = 2.0 Hz, 1H), 4.63 – 4.57 (m, 1H), 4.27 – 4.18 (m, 2H), 1.20 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 202.2, 139.7, 135.8, 133.4, 130.6, 128.7, 128.4, 105.1, 54.0, 41.9, 16.1 ppm.

2-((1H-Pyrazol-1-yl)methyl)-1-phenylbutan-1-one (5b)



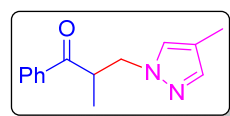
Colorless oil; IR (KBr): 2964, 2929, 1678, 1596, 1447, 1396, 1214, 1090, 751, 699, 617 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.86 (d, J = 7.6 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.35 (s, 1H), 6.10 (s, 1H), 4.57 (dd, J = 8.8, 4.8 Hz, 1H), 4.34 – 4.32 (m, 1H), 4.23 – 4.16 (m, 1H), 1.83 – 1.72 (m, 1H), 1.67 – 1.57 (m, 1H), 0.89 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 202.5, 139.8, 136.9, 133.4, 130.8, 128.7, 128.3, 105.3, 52.6, 48.3, 24.0, 11.2 ppm.

2-((1H-Pyrazol-1-yl)methyl)-1-phenylpentan-1-one (5c)



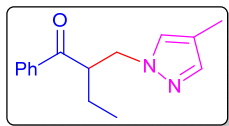
Colorless oil; IR (KBr): 2958, 2932, 1679, 1595, 1447, 1396, 1210, 1089, 965, 749, 701, 617, 511 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.82 (d, J = 7.6 Hz, 2H), 7.51 – 7.35 (m, 4H), 7.29 (s, 1H), 6.06 (s, 1H), 4.55 – 4.50 (m, 1H), 4.28 – 4.16 (m, 2H), 1.74 – 1.65 (m, 1H), 1.53 – 1.44 (m, 1H), 1.33 – 1.26 (m, 2H), 0.83 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 202.7, 139.7, 137.0, 133.3, 130.4, 128.6, 128.2, 105.1, 53.2, 47.0, 33.1, 20.2, 14.2 ppm.

2-Methyl-3-(4-methyl-1H-pyrazol-1-yl)-1-phenylpropan-1-one (5d)



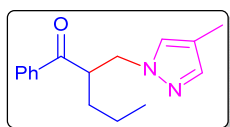
Colorless oil; IR (KBr): 2963, 2928, 1677, 1452, 1381, 1227, 1057, 962, 745, 607 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.92 – 7.89 (m, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.27 (s, 1H), 7.15 (s, 1H), 4.51 (dd, J = 7.2, 6.0 Hz, 1H), 4.21 – 4.10 (m, 2H), 1.99 (s, 3H), 1.19 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 202.3, 140.0, 135.9, 133.4, 129.4, 128.7, 128.4, 115.6, 53.9, 41.9, 16.1, 8.8 ppm.

2-((4-Methyl-1H-pyrazol-1-yl)methyl)-1-phenylbutan-1-one (5e)



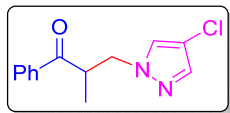
Colorless oil; IR (KBr): 2965, 2932, 1678, 1447, 1385, 1223, 1160, 990, 700, 612, 507 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.88 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.27 (d, J = 5.6 Hz, 1H), 7.11 (s, 1H), 4.49 (dd, J = 8.4, 4.8 Hz, 1H), 4.24 – 4.11 (m, 2H), 1.96 (s, 3H), 1.76 (m, 1H), 1.60 (m, 1H), 0.90 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ = 202.6, 134.0, 136.9, 133.3, 129.3, 128.7, 128.3, 115.6, 52.5, 48.3, 23.9, 11.2, 8.8 ppm.

2-((4-Methyl-1H-pyrazol-1-yl)methyl)-1-phenylpentan-1-one (5f)



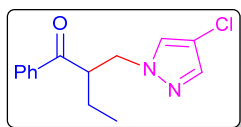
Colorless oil; IR (KBr): 2958, 2929, 1679, 1447, 1379, 1240, 1211, 989, 703, 612, 496 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.86 – 7.84 (m, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.24 (s, 1H), 7.08 (s, 1H), 4.50 – 4.44 (m, 1H), 4.22 – 4.17 (m, 2H), 1.94 (s, 3H), 1.75 – 1.66 (m, 1H), 1.54 – 1.45 (m, 1H), 1.35 – 1.28 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 202.8, 134.0, 137.0, 133.3, 129.3, 128.6, 128.3, 115.6, 53.0, 47.0, 33.1, 20.2, 14.2, 8.8 ppm.

3-(4-Chloro-1H-pyrazol-1-yl)-2-methyl-1-phenylpropan-1-one (5g)



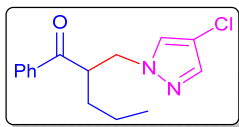
Colorless oil; IR (KBr): 2971, 1701, 1603, 1452, 1356, 989, 821, 733, 703, 593 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.92 – 7.88 (m, 2H), 7.57 – 7.53 (m, 1H), 7.45 – 7.41 (m, 2H), 7.38 (d, J = 6.8 Hz, 2H), 4.58 – 4.50 (m, 1H), 4.21 – 4.10 (m, 1H), 1.20 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 201.6, 138.1, 135.6, 133.6, 128.8, 128.6, 128.4, 109.5, 54.5, 41.7, 16.1 ppm.

2-((4-Chloro-1H-pyrazol-1-yl)methyl)-1-phenylbutan-1-one (5h)



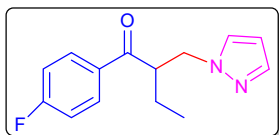
Colorless oil; IR (KBr): 2965, 1679, 1595, 1447, 1384, 1221, 970, 839, 741, 698, 611, 596 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.88 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 4.8 Hz, 1H), 4.53 (m, 1H), 4.22 (dd, J = 8.4, 5.2 Hz, 1H), 4.15 – 4.08 (m, 1H), 1.77 (m, 1H), 1.61 (m, 1H), 0.91 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 201.9, 138.1, 136.6, 133.5, 128.8, 128.5, 128.3, 109.8, 53.0, 48.0, 24.0, 11.2 ppm.

2-((4-Chloro-1*H*-pyrazol-1-yl)methyl)-1-phenylpentan-1-one (5i)



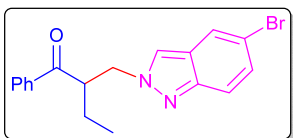
Colorless oil; IR (KBr): 2959, 2872, 1680, 1595, 1447, 1238, 970, 743, 700, 611, 507 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.87 – 7.85 (m, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 8.0 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 4.52 (dd, J = 8.8, 4.4 Hz, 1H), 4.23 – 4.13 (m, 2H), 1.75 – 1.66 (m, 1H), 1.55 – 1.46 (m, 1H), 1.37 – 1.29 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 202.1, 138.1, 136.7, 133.5, 128.8, 128.5, 128.3, 109.5, 53.5, 46.7, 33.1, 20.2, 14.2 ppm.

2-((1*H*-Pyrazol-1-yl)methyl)-1-(4-fluorophenyl)butan-1-one (5j)



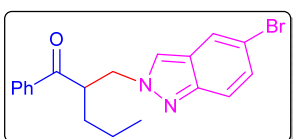
Colorless oil; IR (KBr): 2963, 2923, 1657, 1584, 1452, 1406, 1273, 945, 765, 700, 604 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.90 (dd, J = 5.6, 2.8 Hz, 2H), 7.52 (s, 1H), 7.37 (s, 1H), 7.07 (t, J = 8.8 Hz, 2H), 6.13 (s, 1H), 4.57 (dd, J = 9.2, 4.4 Hz, 1H), 4.41 (d, J = 9.6 Hz, 1H), 4.23 (s, 1H), 1.82 – 1.73 (m, 1H), 1.69 – 1.60 (m, 1H), 0.90 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 201.0, 166.0 (d, $J_{\text{C-F}}$ = 254.1 Hz), 139.9, 133.3 (d, $J_{\text{C-F}}$ = 2.6 Hz), 131.2 (d, $J_{\text{C-F}}$ = 28.9 Hz), 131.0, 115.8 (d, $J_{\text{C-F}}$ = 21.7 Hz), 105.44, 52.72, 48.13, 24.09, 11.14 ppm.

2-((5-Bromo-2*H*-indazol-2-yl)methyl)-1-phenylbutan-1-one (5k)



Colorless oil; IR (KBr): 2964, 2931, 1678, 1484, 1446, 1237, 1217, 1002, 793, 700, 573, 423 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.92 (s, 1H), 7.82 (d, J = 7.6 Hz, 2H), 7.75 (s, 1H), 7.51 – 7.35 (m, 5H), 4.85 – 4.79 (m, 1H), 4.52 – 4.48 (m, 1H), 4.35 – 4.29 (m, 1H), 1.89 – 1.78 (m, 1H), 1.72 – 1.62 (m, 1H), 0.92 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 202.4, 138.7, 136.7, 133.4, 133.0, 129.9, 128.6, 128.2, 124.9, 123.3, 113.9, 111.1, 49.6, 47.9, 24.1, 11.3 ppm.

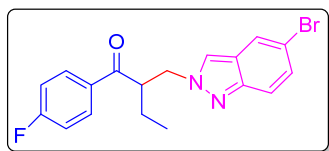
2-((5-Bromo-2*H*-indazol-2-yl)methyl)-1-phenylpentan-1-one (5l)



Colorless oil; IR (KBr): 2958, 2930, 1678, 1484, 1446, 1229, 1002, 873, 785, 705, 573, 496 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.87 (s, 1H), 7.81 – 7.79 (m, 2H), 7.74 (d, J = 1.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.43 – 7.34 (m, 4H), 4.82 – 4.77 (m, 1H), 4.45 – 4.40

(m, 1H), 4.37 – 4.30 (m, 1H), 1.82 – 1.73 (m, 1H), 1.61 – 1.52 (m, 1H), 1.37 – 1.30 (m, 1H), 0.86 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 202.6, 138.6, 136.8, 133.3, 132.8, 129.6, 128.6, 128.2, 125.1, 123.2, 113.7, 111.0, 50.0, 46.5, 33.2, 20.3, 14.2$ ppm.

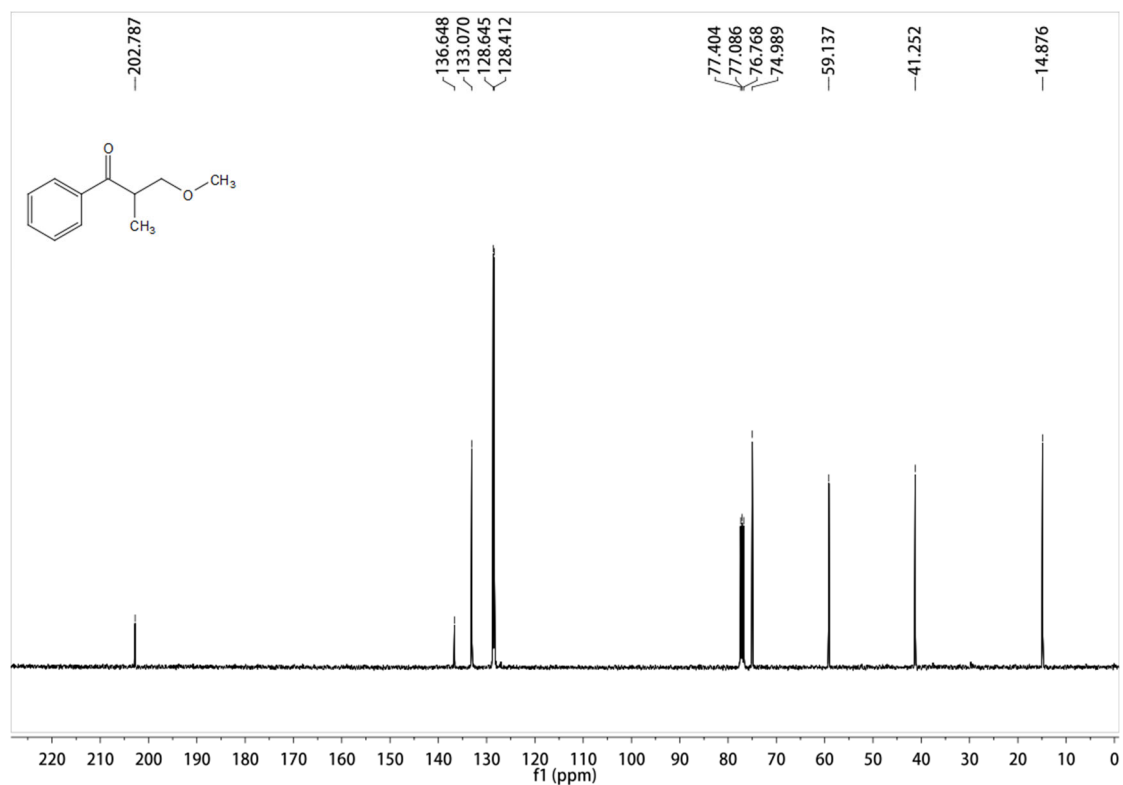
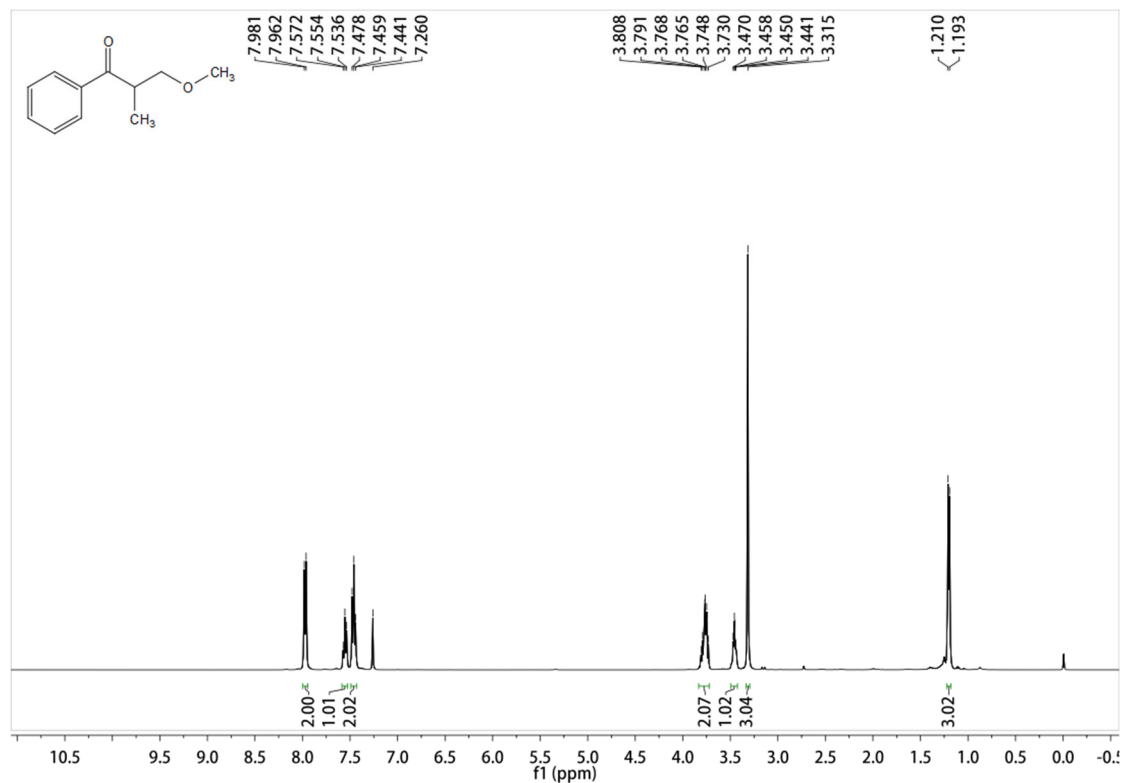
2-((5-Bromo-2*H*-indazol-2-yl)methyl)-1-(4-fluorophenyl)butan-1-one (5m)



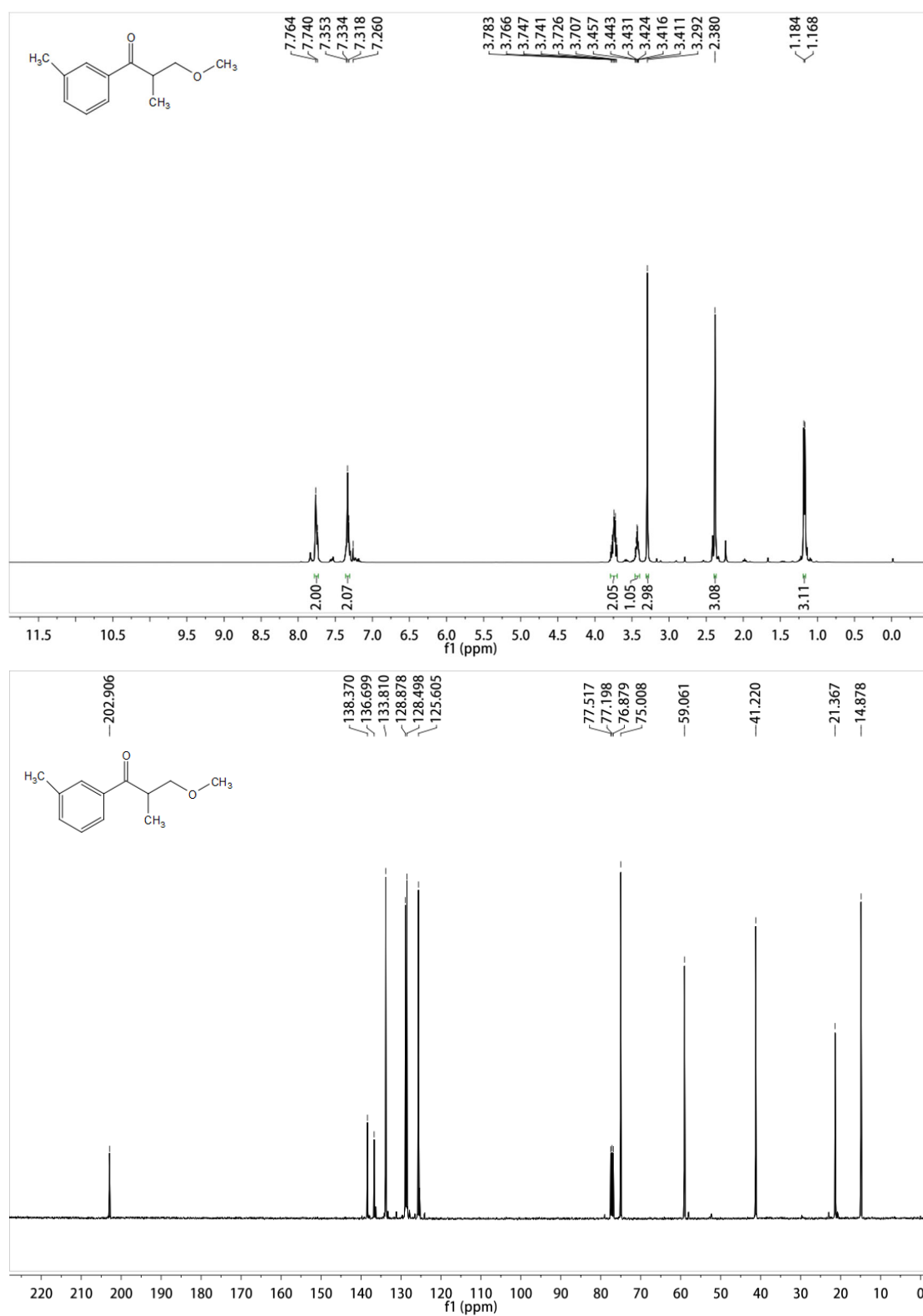
Colorless oil; IR (KBr): 2976, 1703, 1467, 1398, 1254, 989, 865, 693, 564, 501 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.88 - 7.80$ (m, 3H), 7.75 (d, $J = 1.2$ Hz, 1H), 7.43 – 7.35 (m, 2H), 7.02 (t, $J = 8.4$ Hz, 2H), 4.77 (dd, $J = 8.6, 5.2$ Hz, 1H), 4.43 (dd, $J = 5.6, 8.0$ Hz, 1H), 4.28 – 4.18 (m, 1H), 1.88 – 1.77 (m, 1H), 1.71 – 1.59 (m, 1H), 0.92 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) $\delta = 200.9, 165.9$ (d, $J_{\text{C-F}} = 254.1$ Hz), 138.64, 133.2 (d, $J_{\text{C-F}} = 2.7$ Hz), 132.9, 130.9 (d, $J_{\text{C-F}} = 9.3$ Hz), 129.61, 125.06, 123.27, 115.7 (d, $J_{\text{C-F}} = 21.7$ Hz), 113.74, 110.88, 49.64, 47.83, 24.12, 11.37 ppm.

Copies of NMR spectra for products

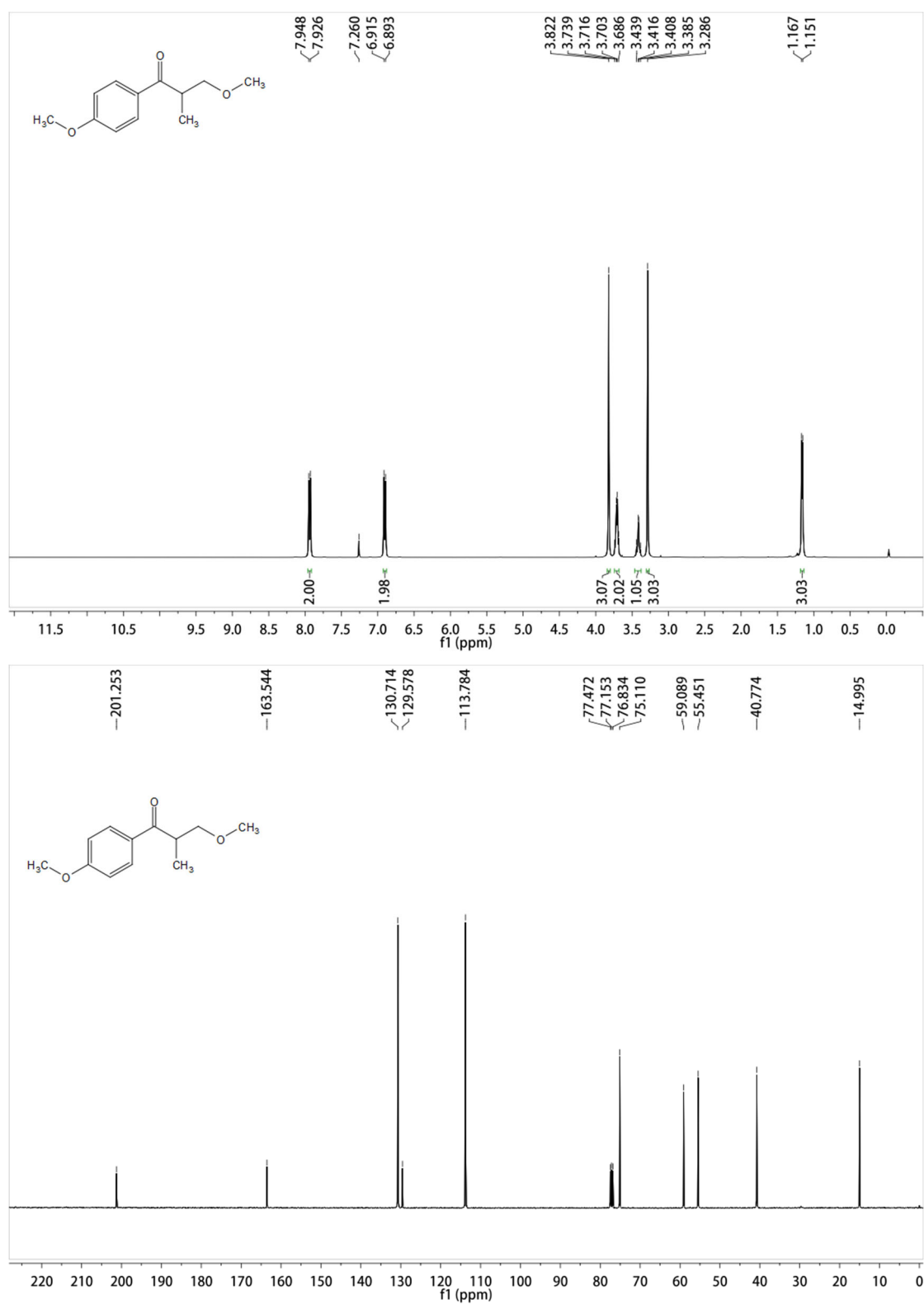
^1H NMR and ^{13}C NMR of compound **3a**



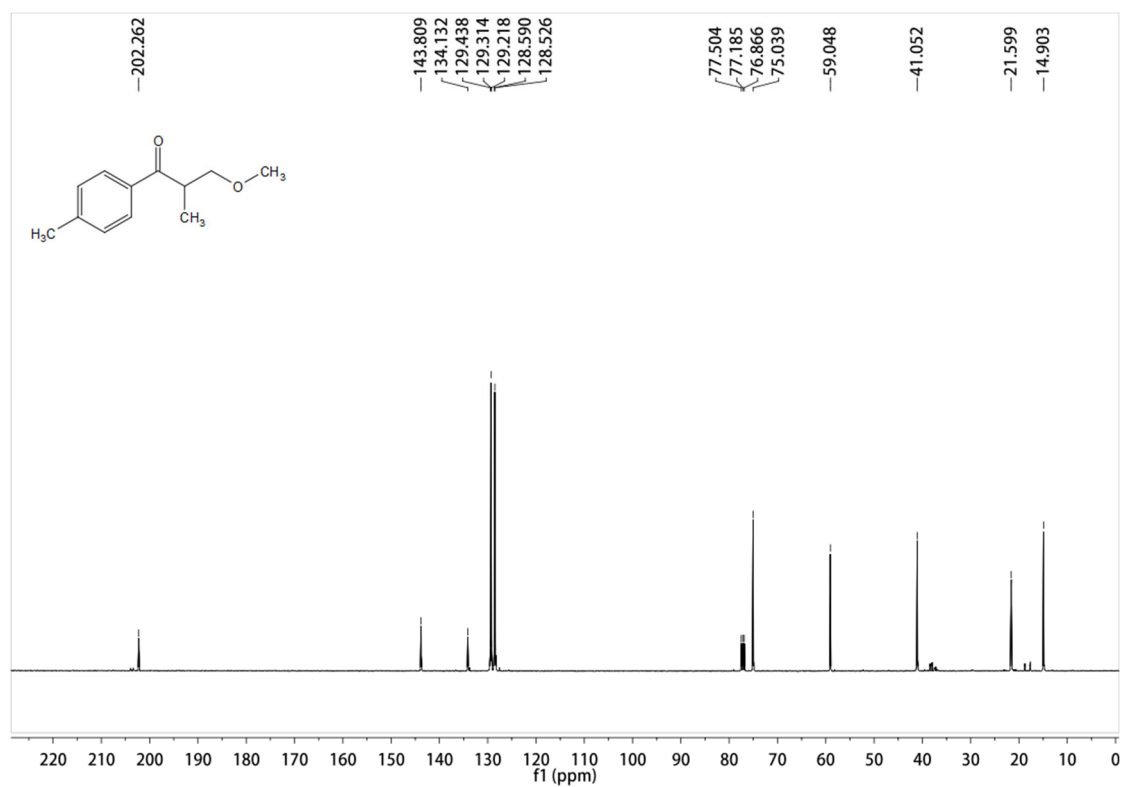
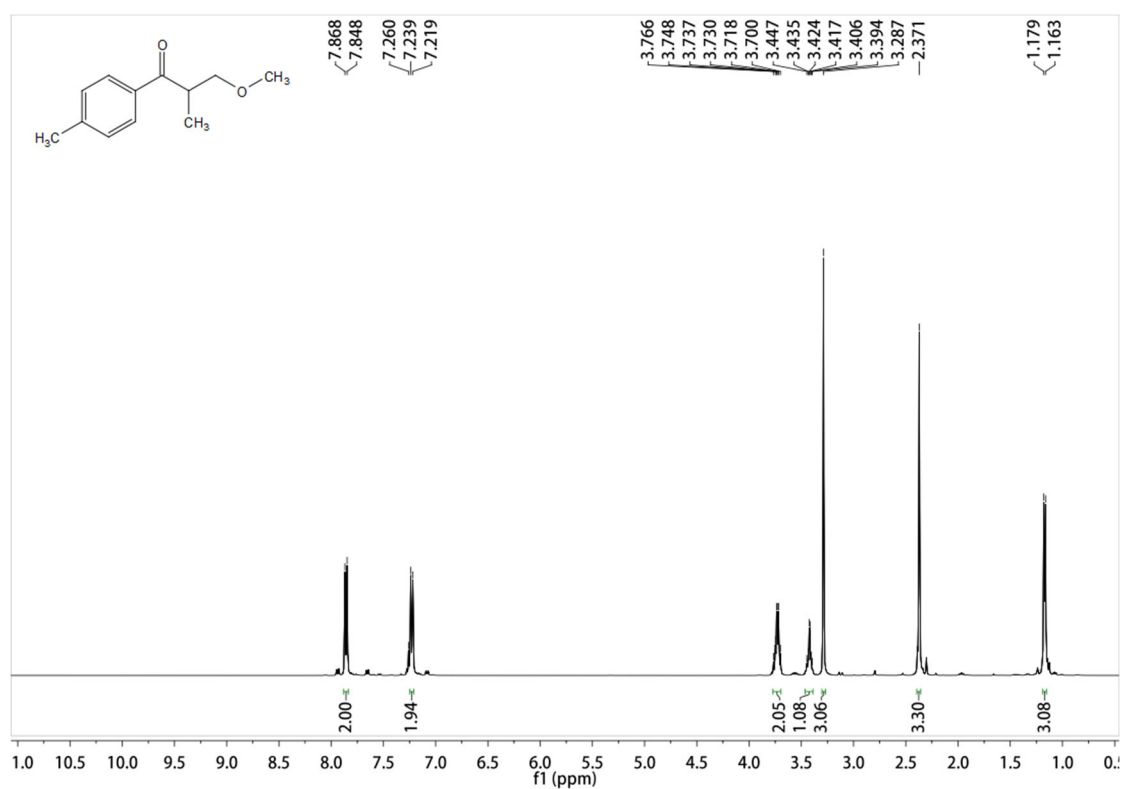
^1H NMR and ^{13}C NMR of compound **3b**



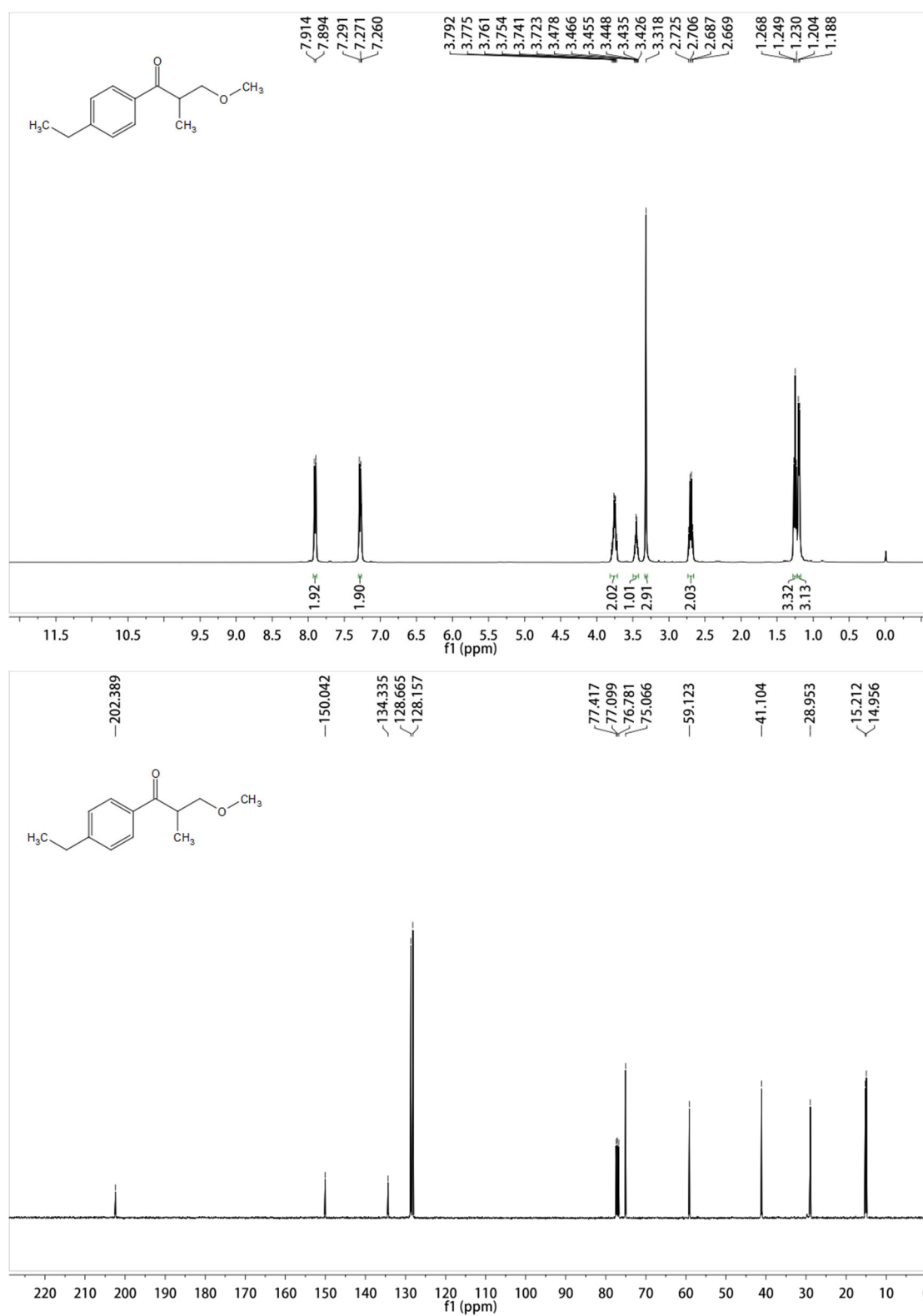
^1H NMR and ^{13}C NMR of compound **3c**



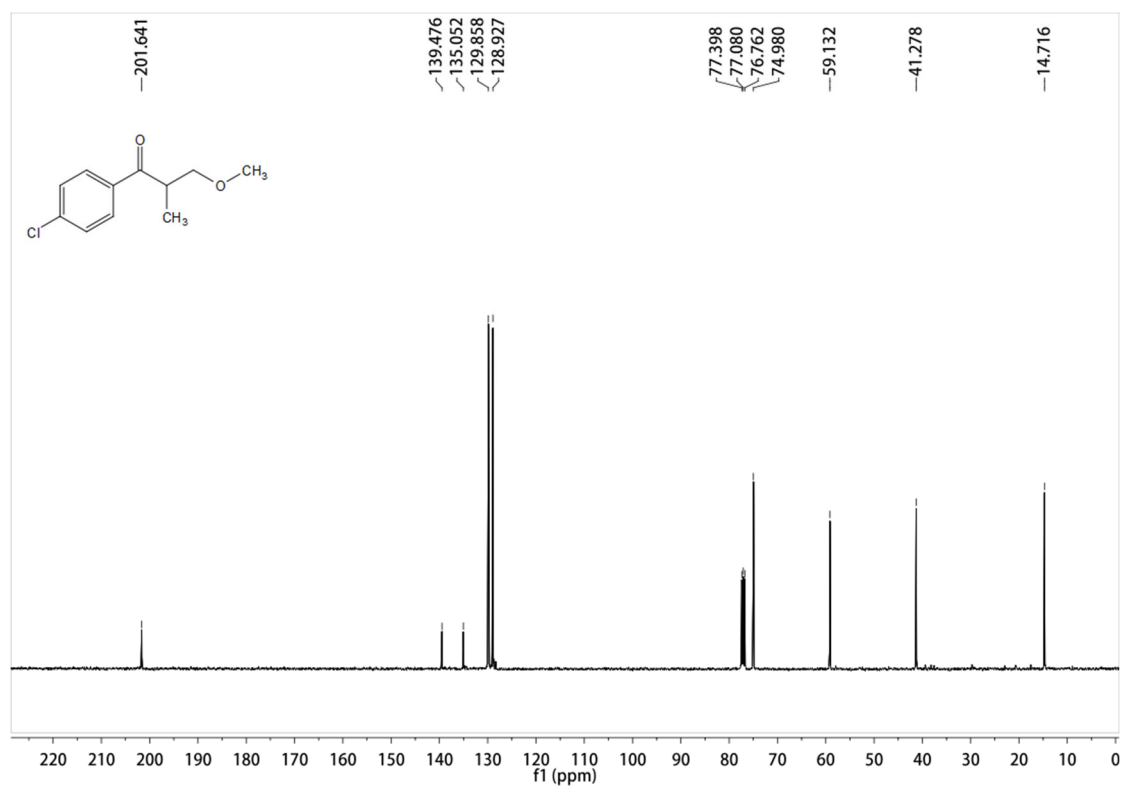
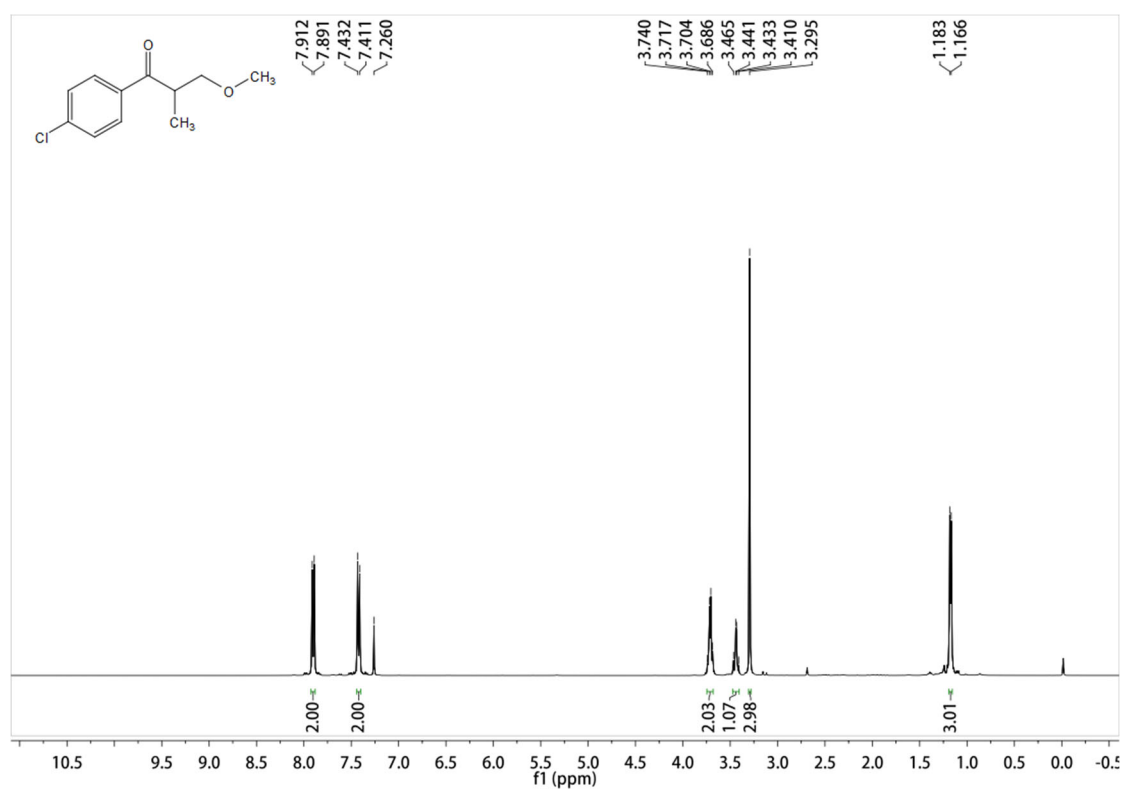
^1H NMR and ^{13}C NMR of compound **3d**



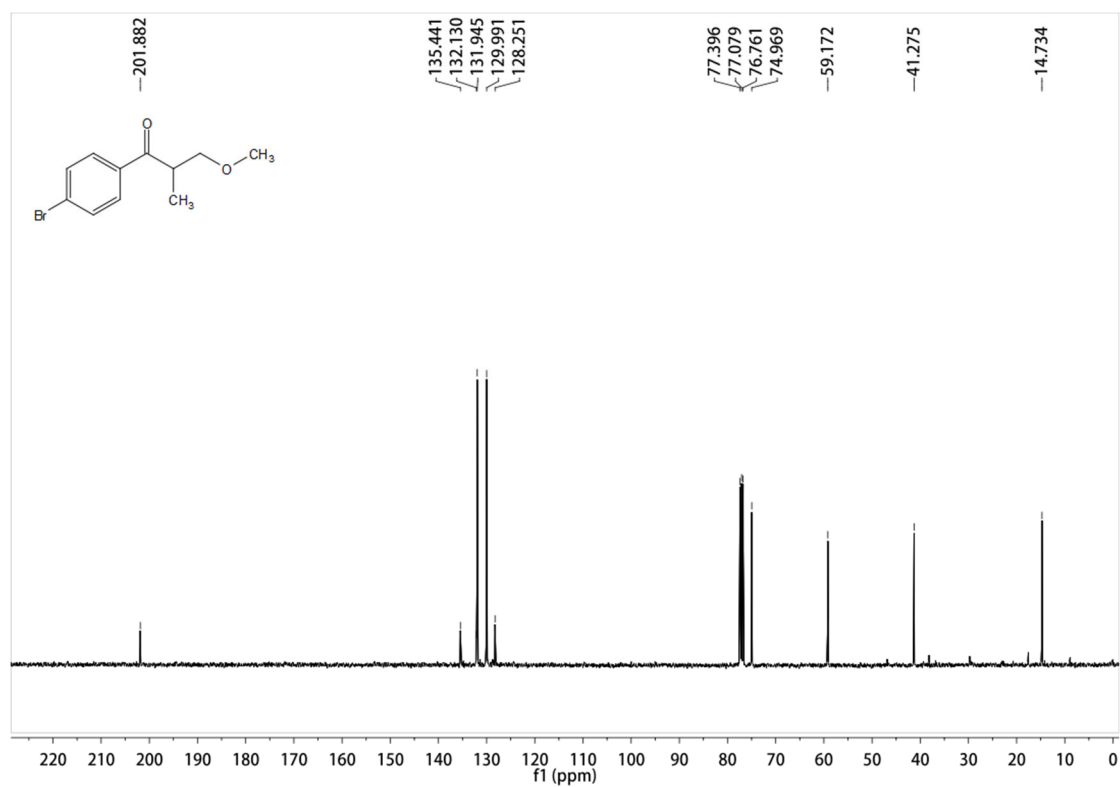
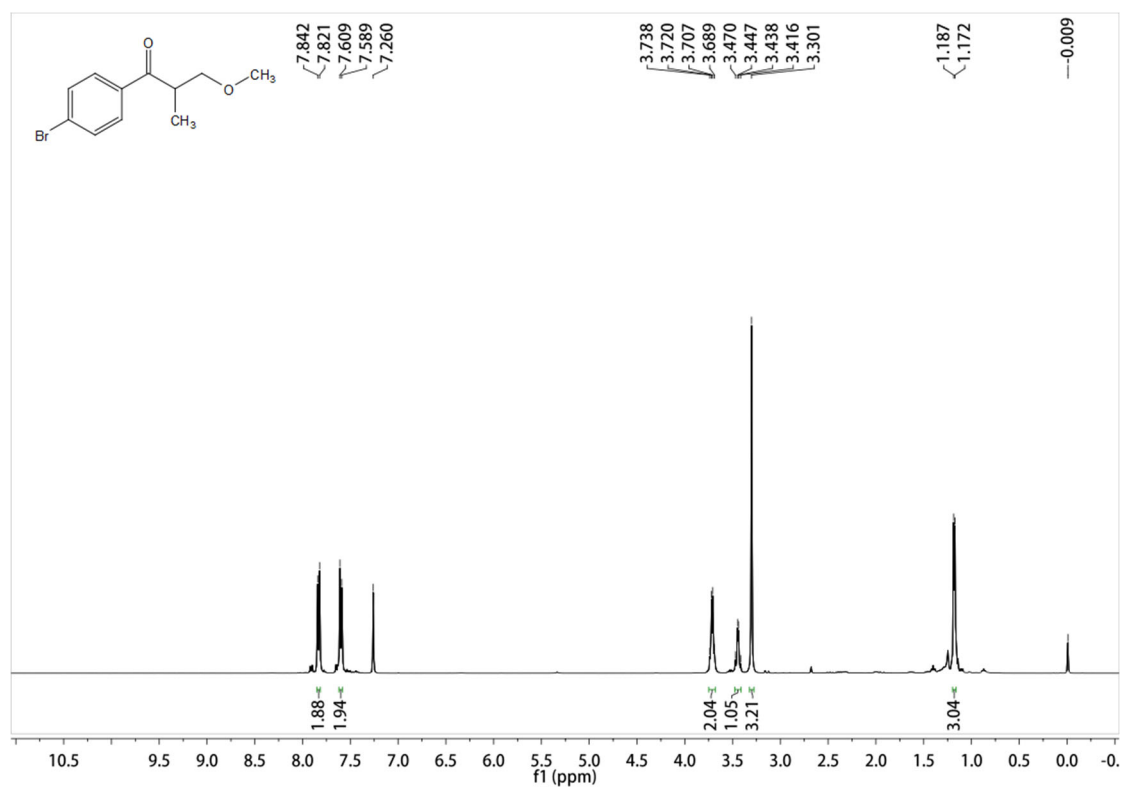
^1H NMR and ^{13}C NMR of compound **3e**



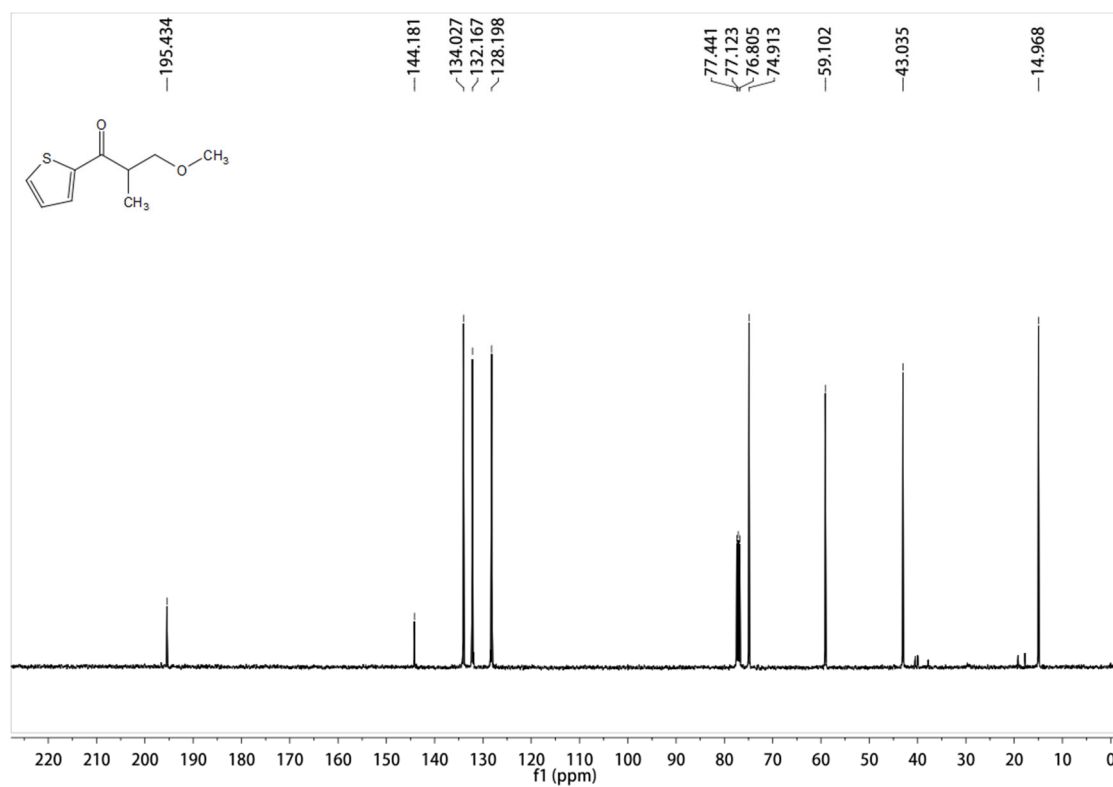
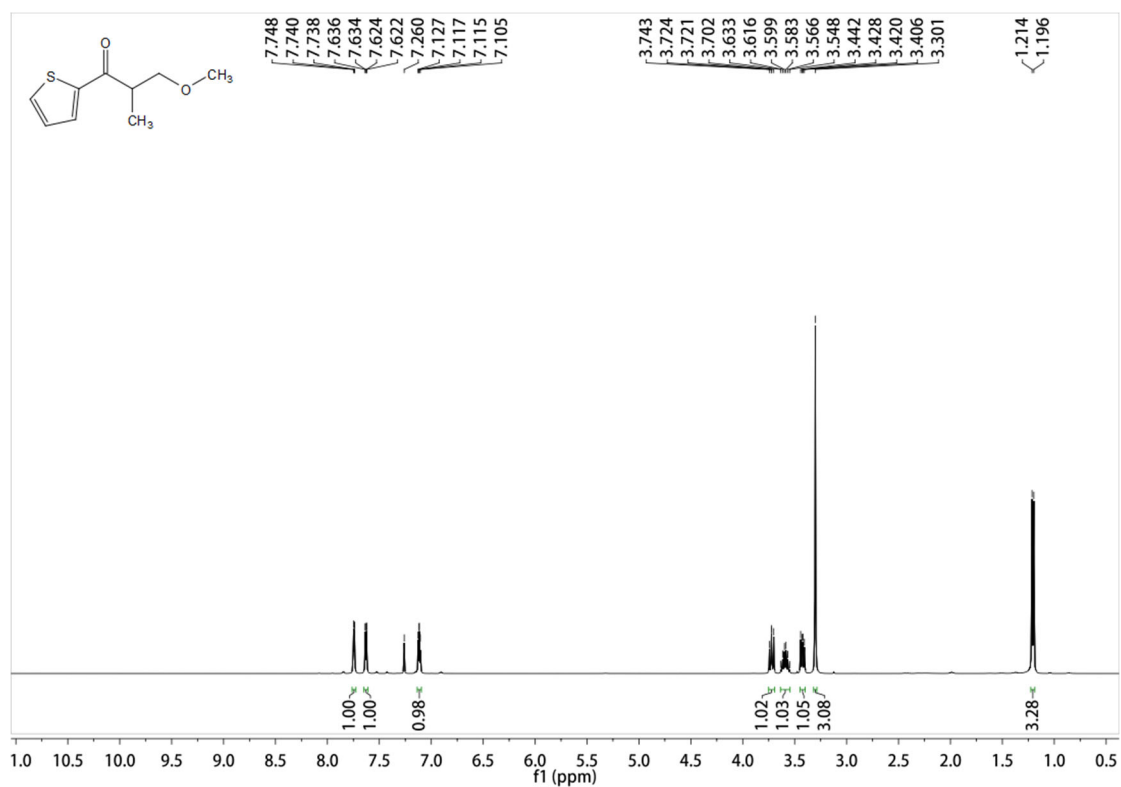
^1H NMR and ^{13}C NMR of compound **3f**



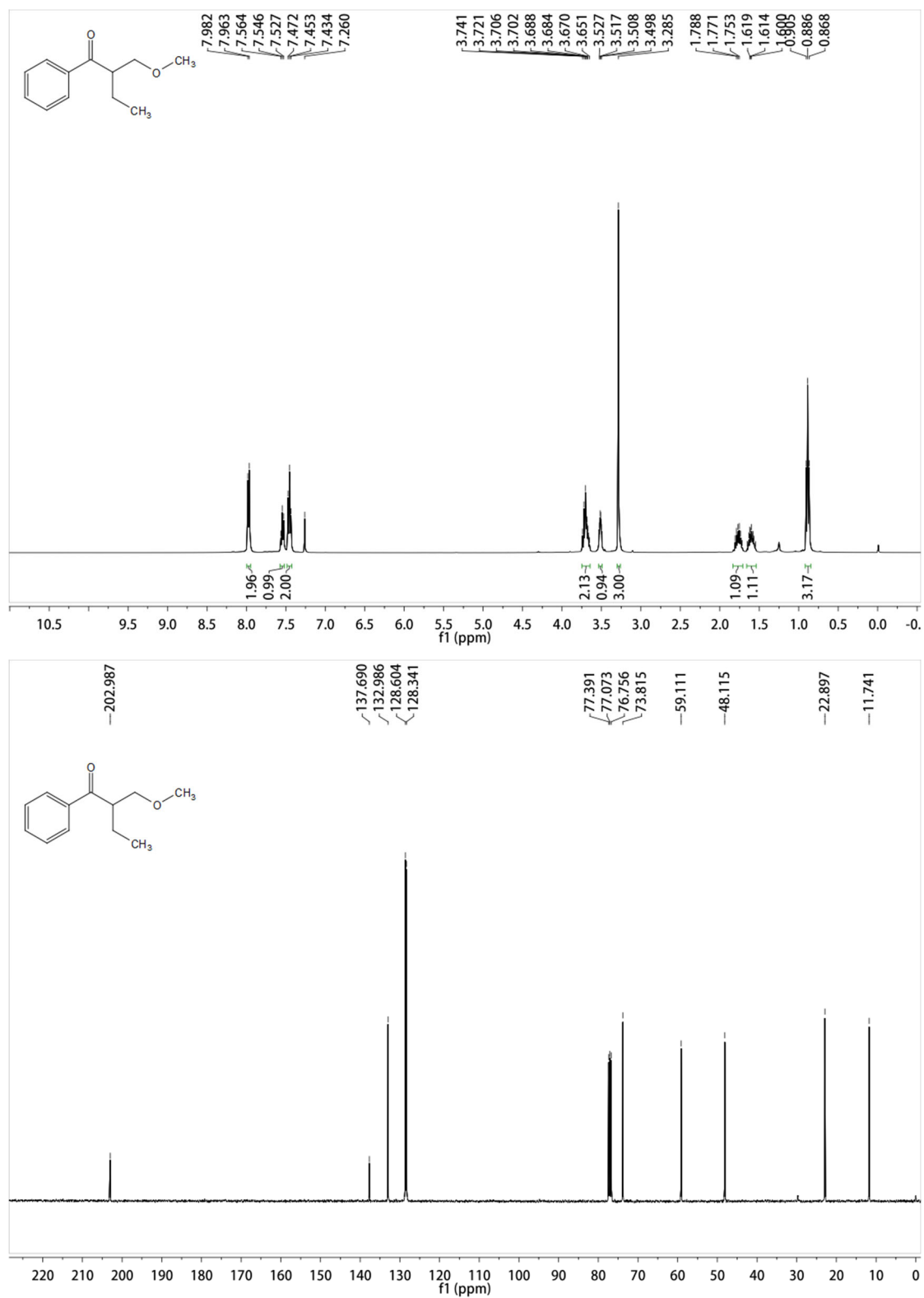
^1H NMR and ^{13}C NMR of compound **3g**



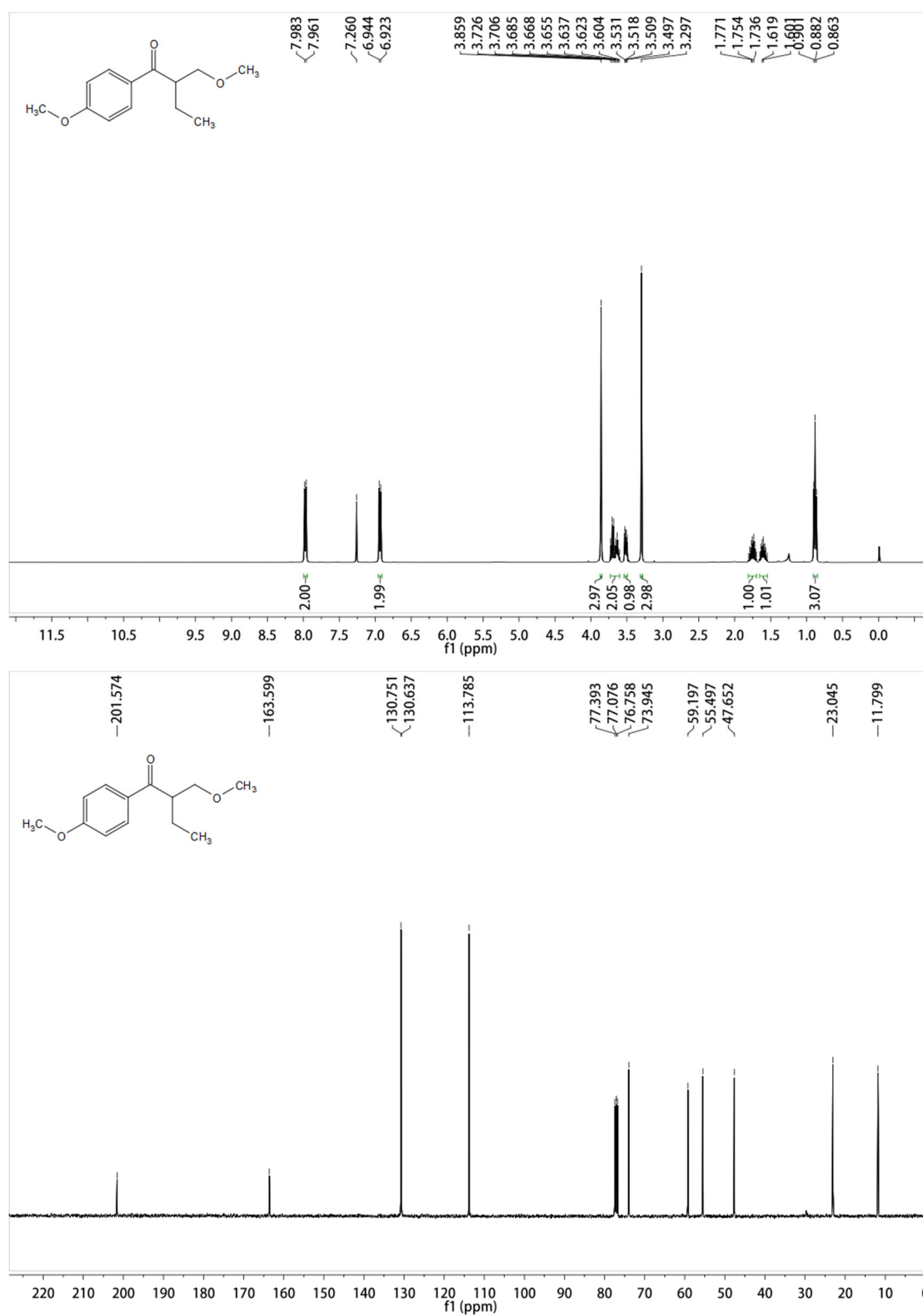
^1H NMR and ^{13}C NMR of compound **3h**



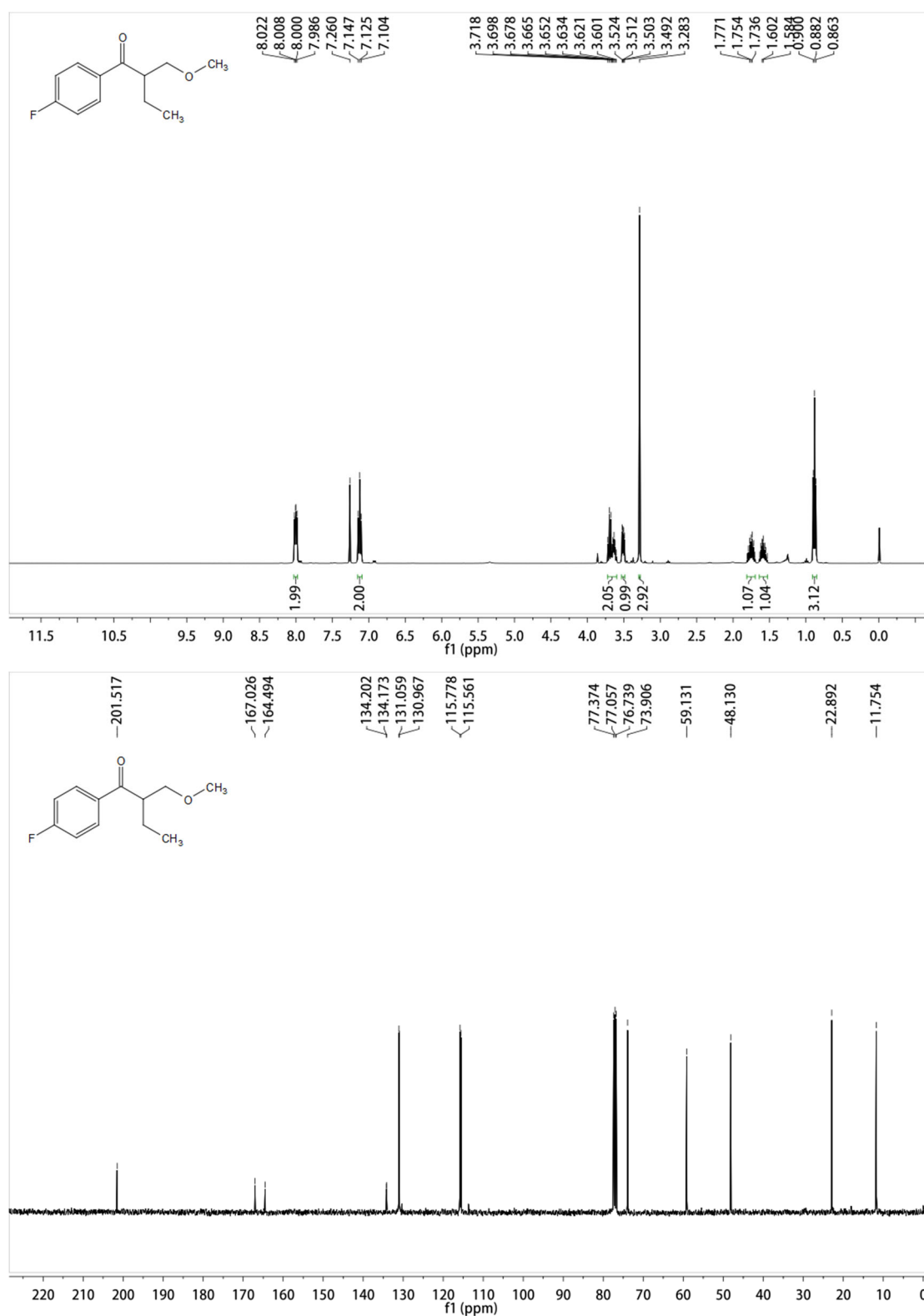
^1H NMR and ^{13}C NMR of compound **3i**



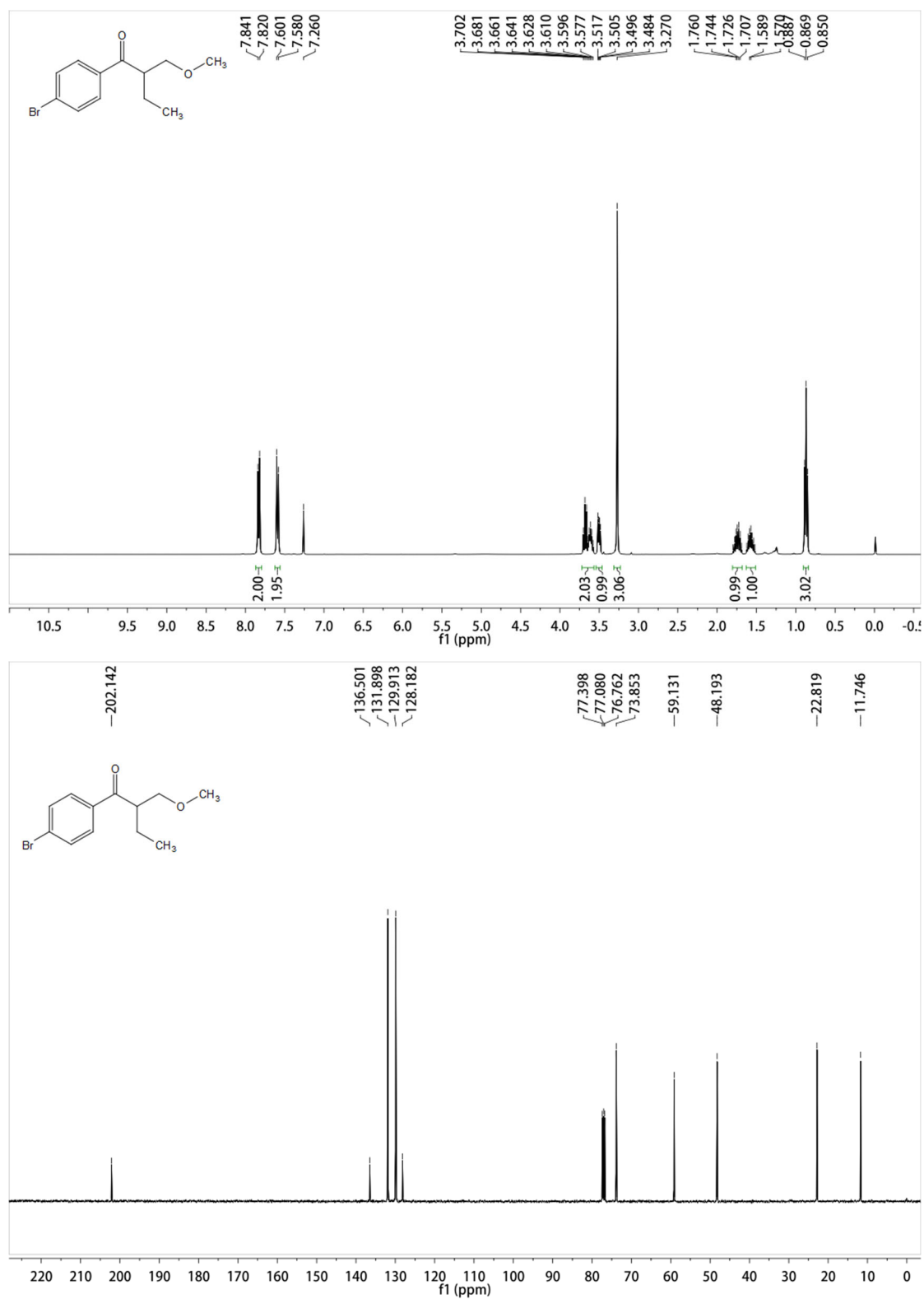
^1H NMR and ^{13}C NMR of compound **3j**



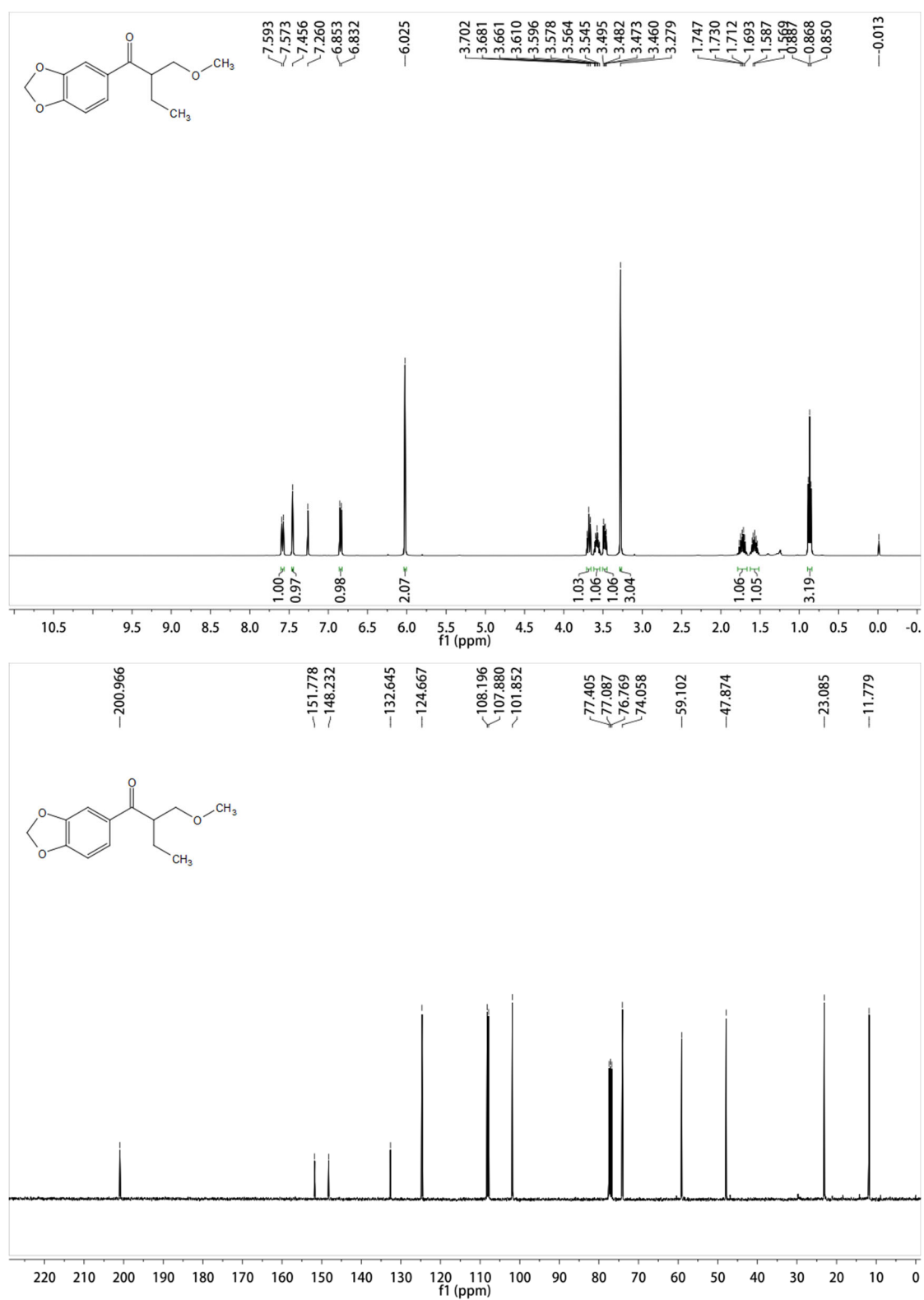
^1H NMR and ^{13}C NMR of compound **3k**



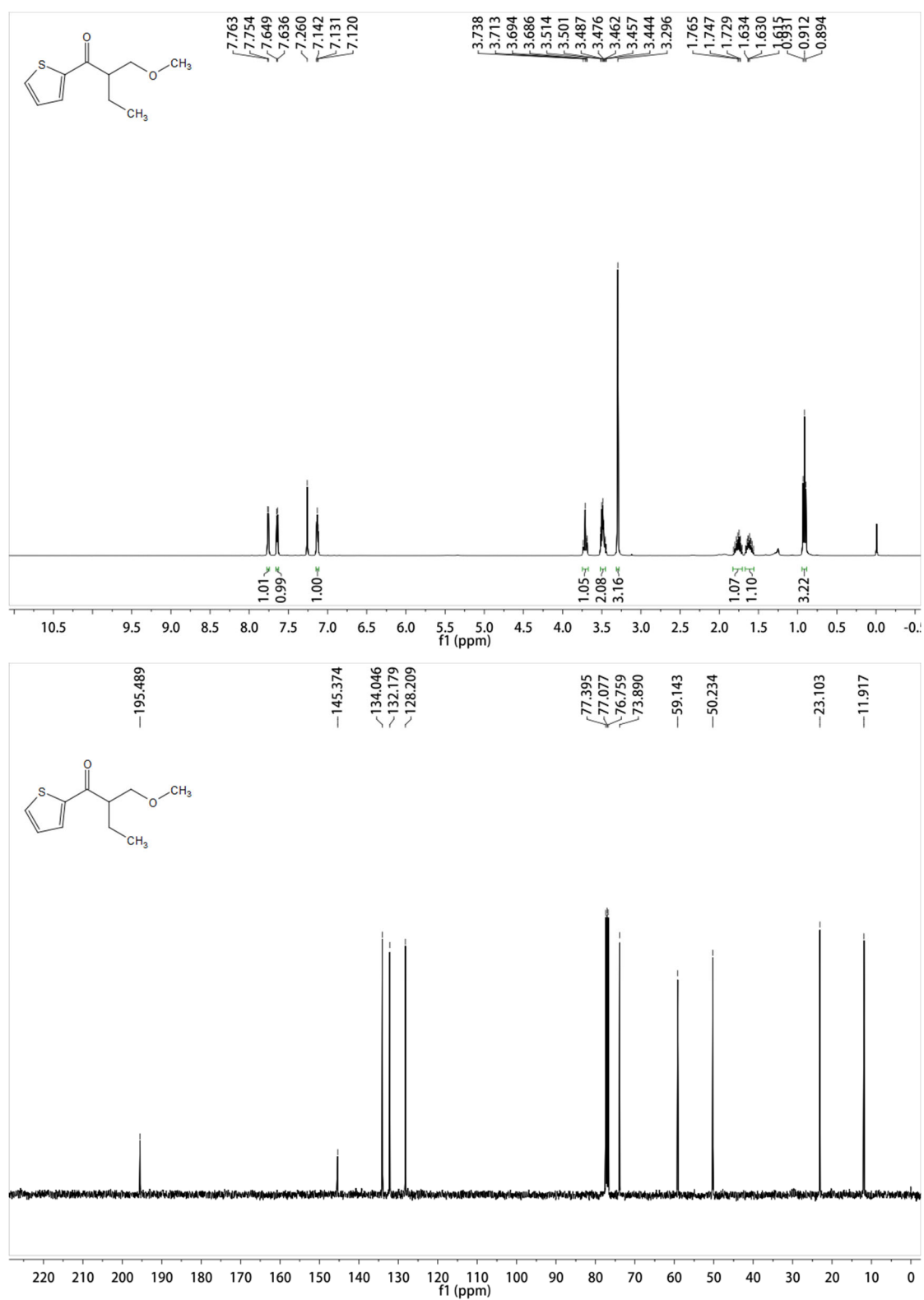
^1H NMR and ^{13}C NMR of compound **31**



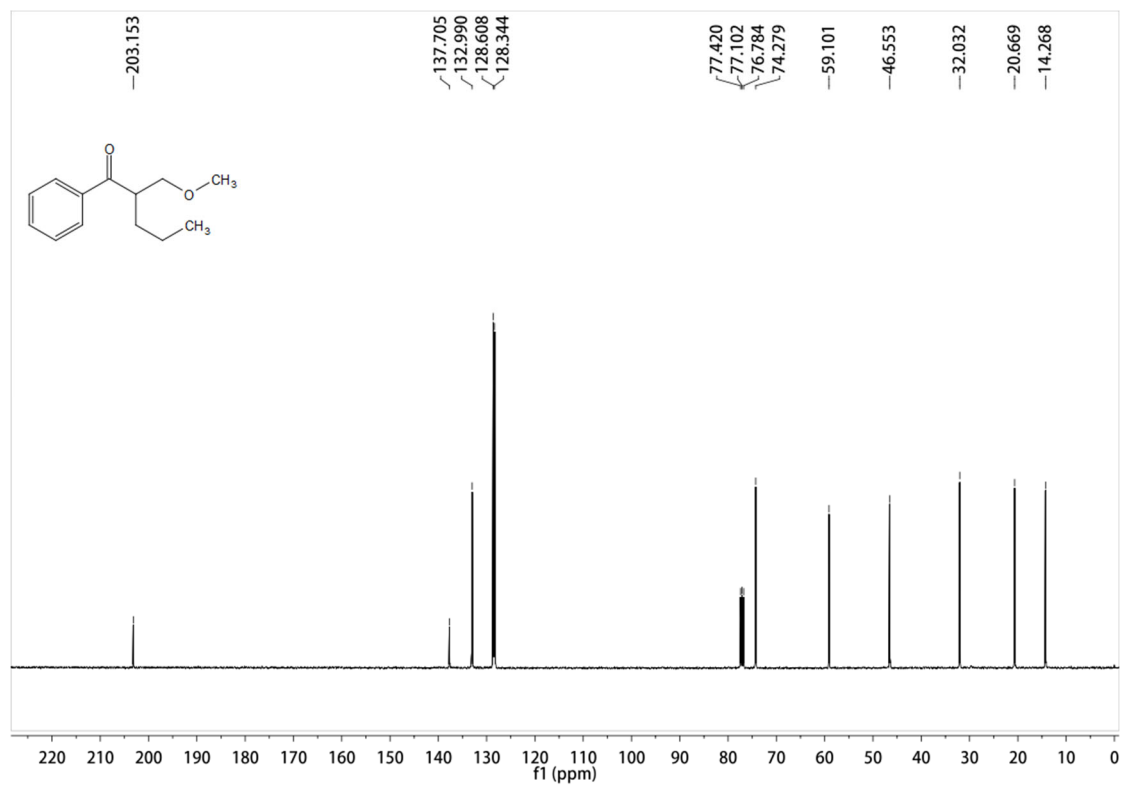
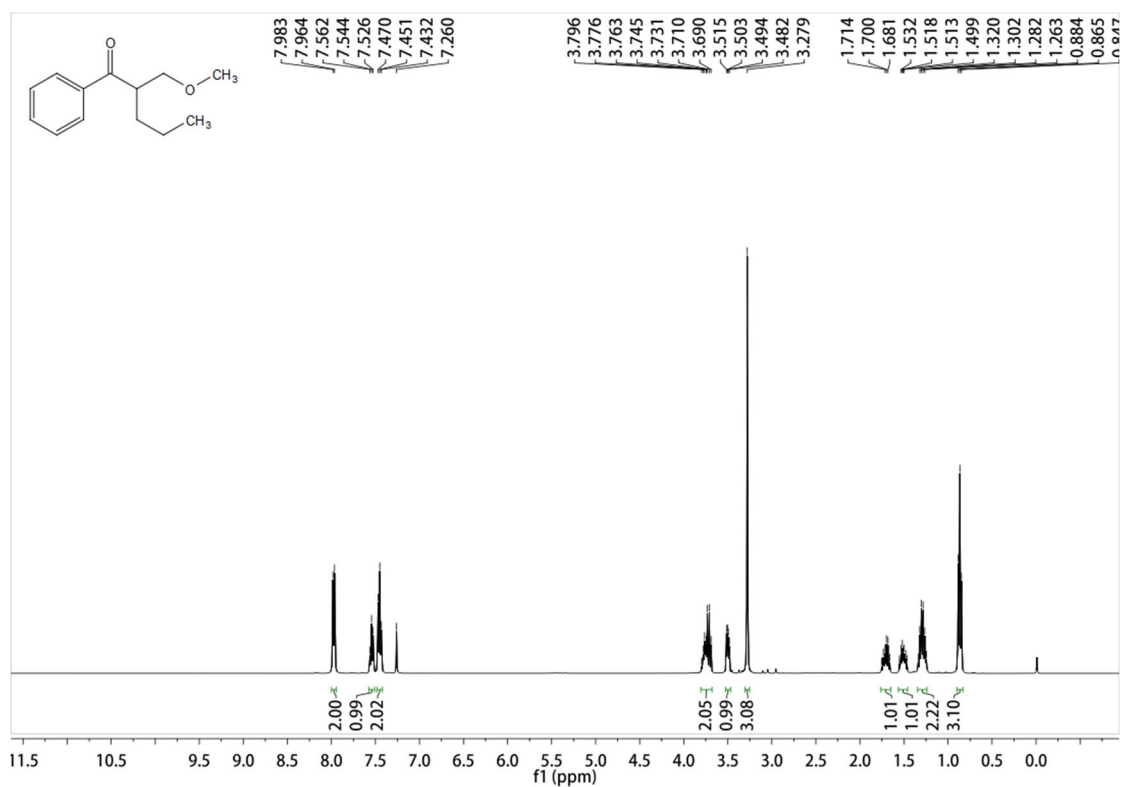
^1H NMR and ^{13}C NMR of compound **3m**



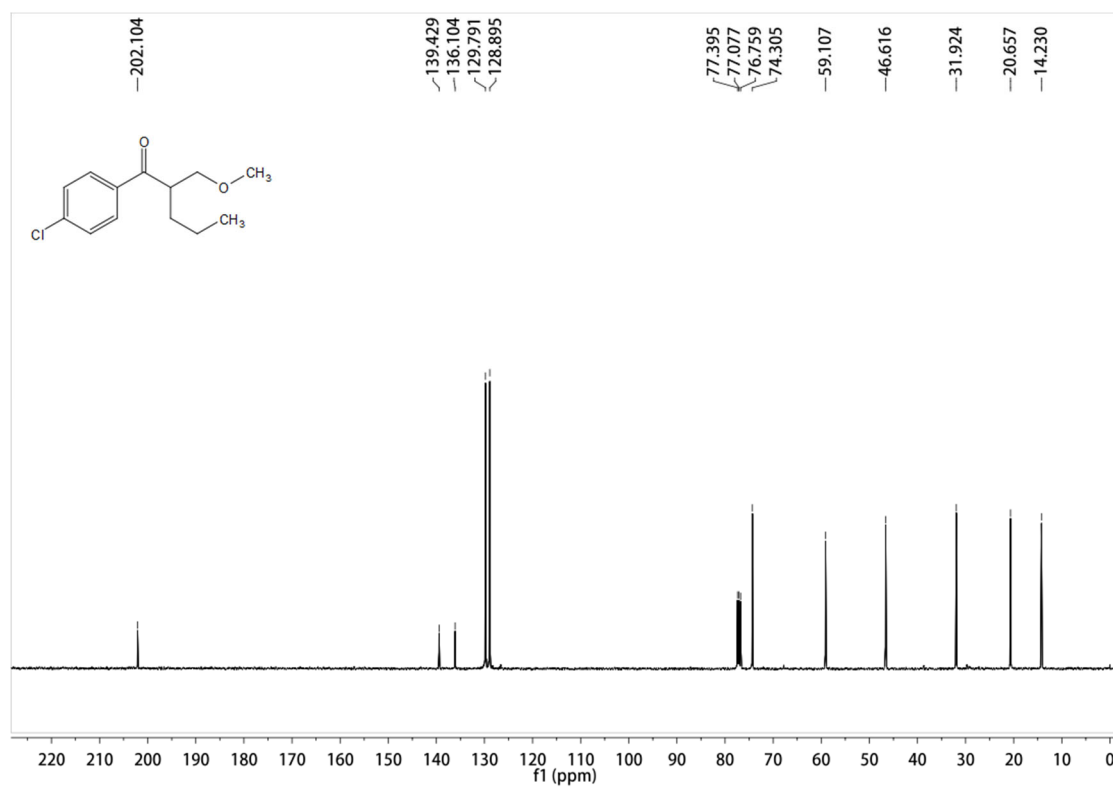
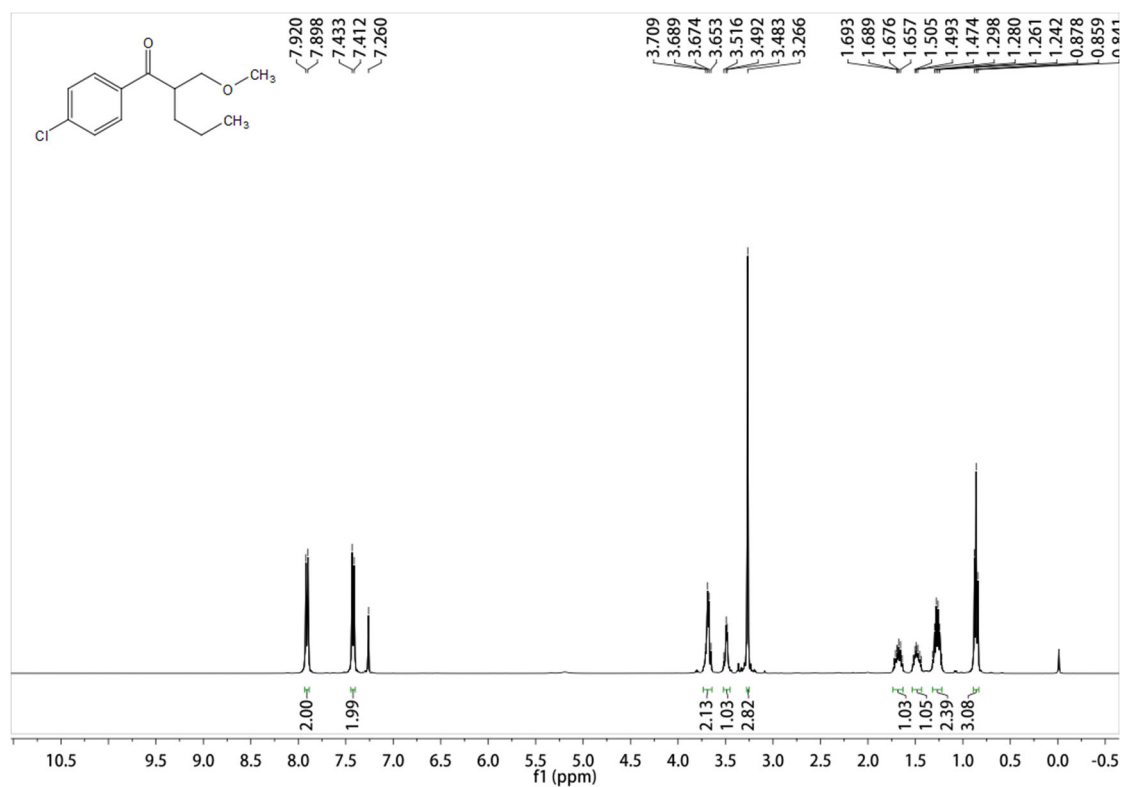
^1H NMR and ^{13}C NMR of compound **3n**



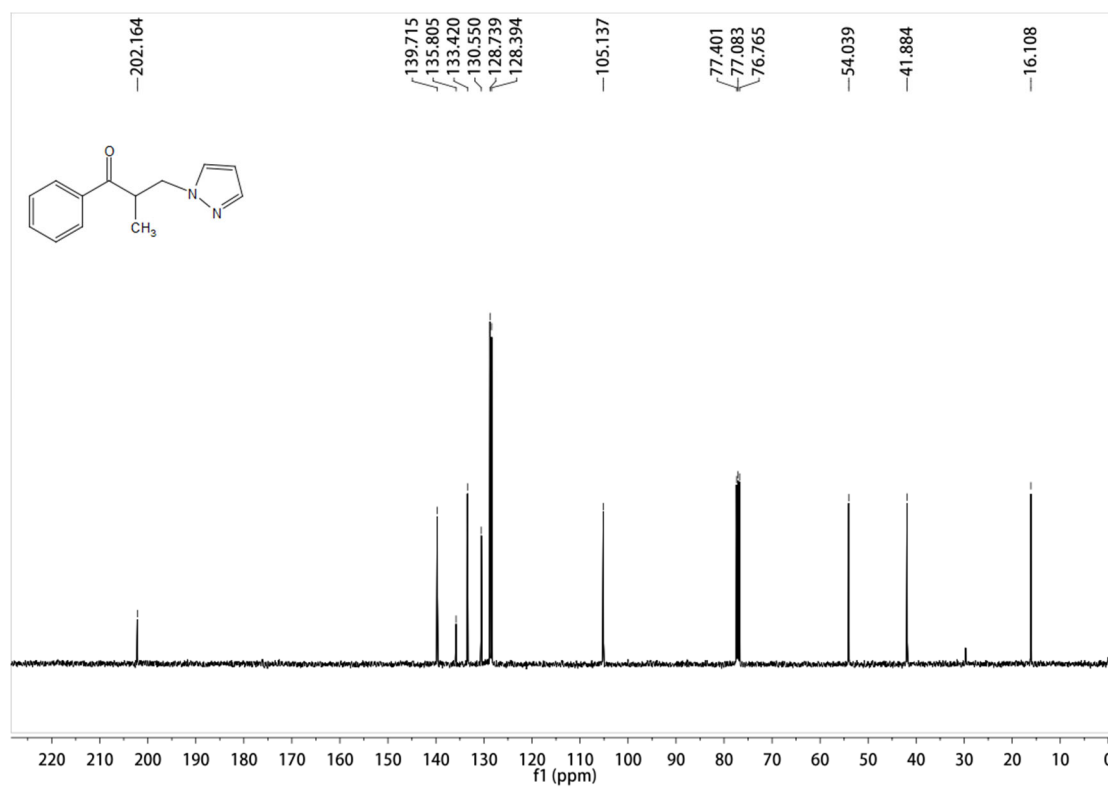
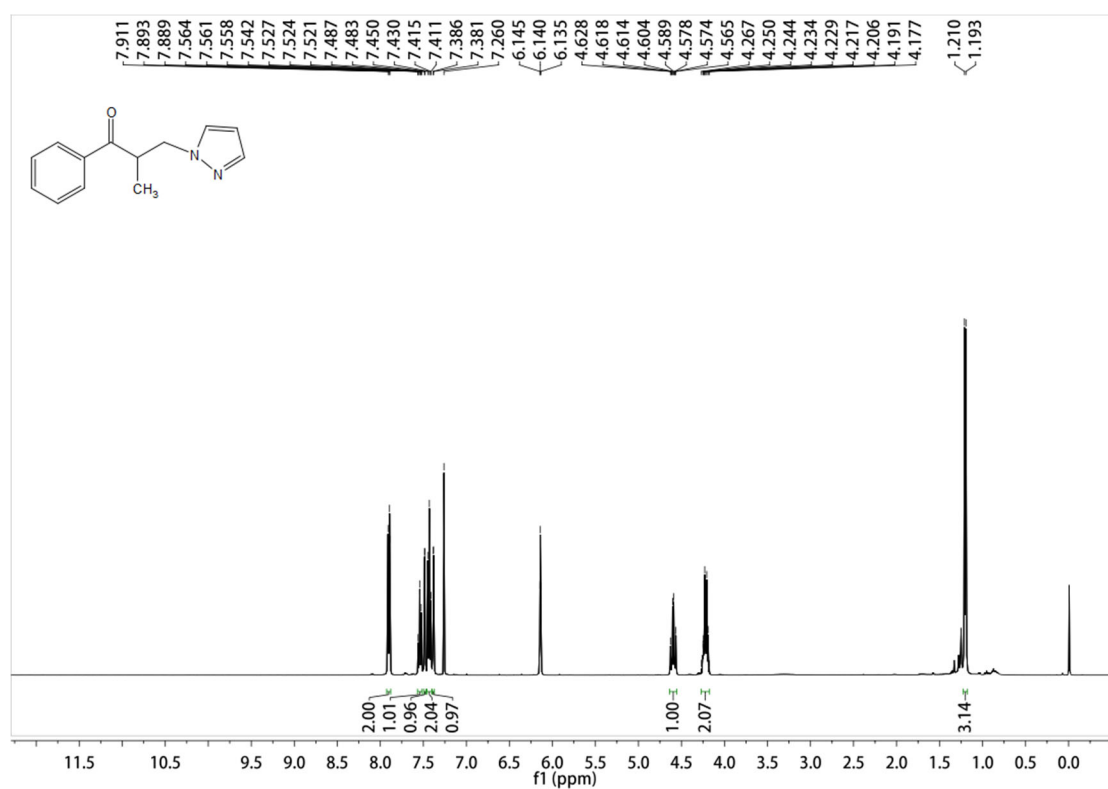
^1H NMR and ^{13}C NMR of compound **30**



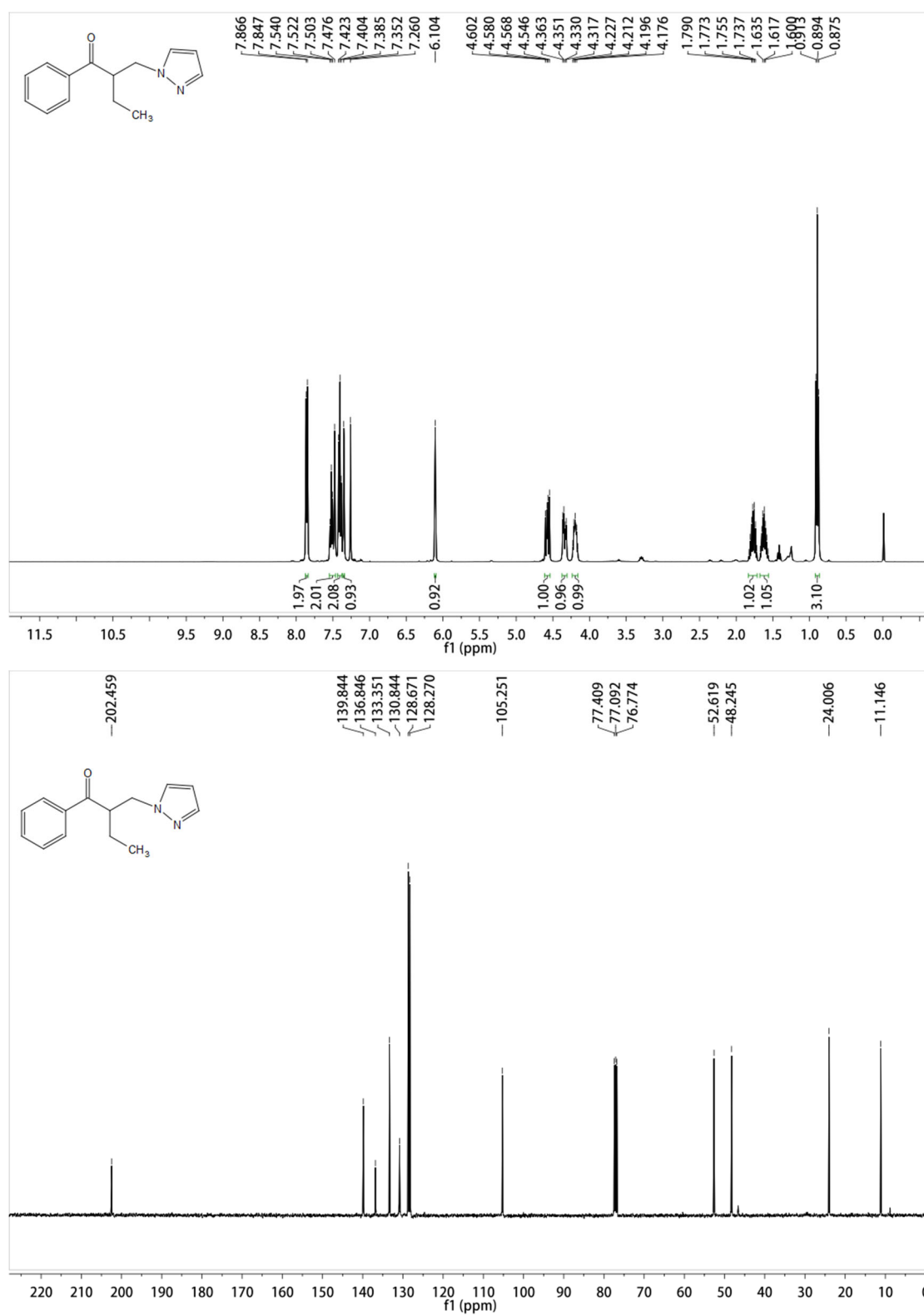
^1H NMR and ^{13}C NMR of compound **3p**



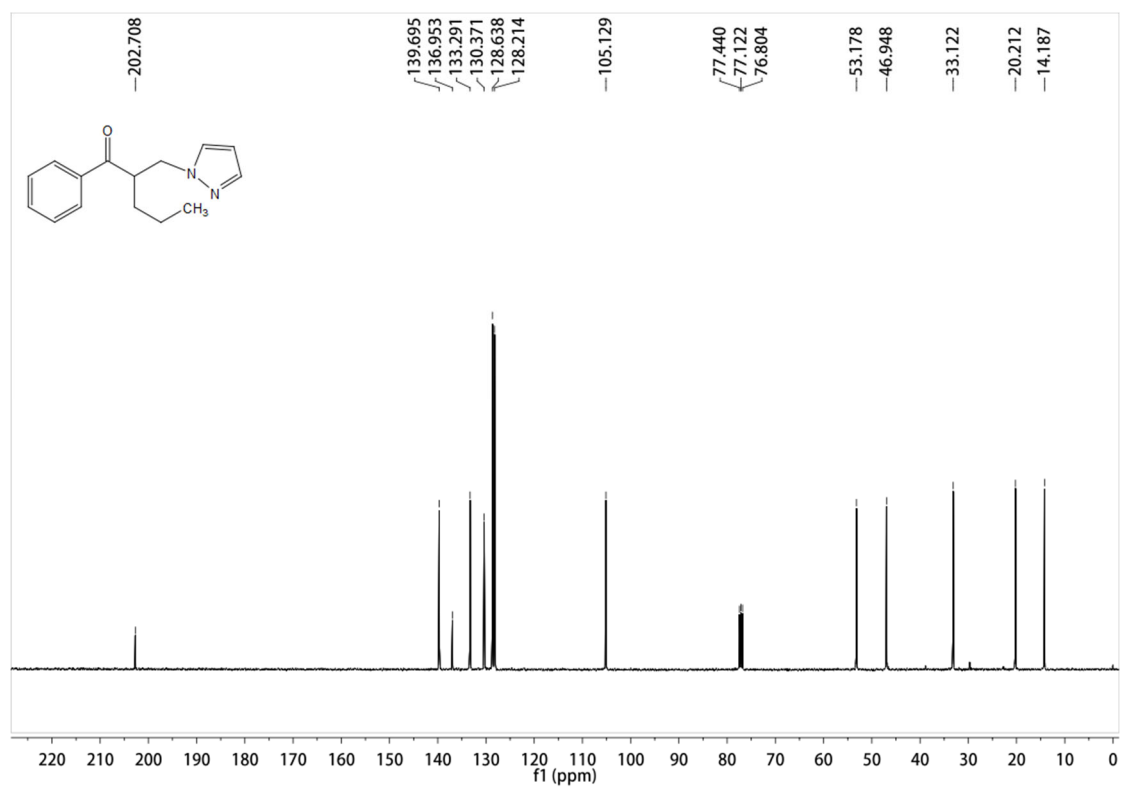
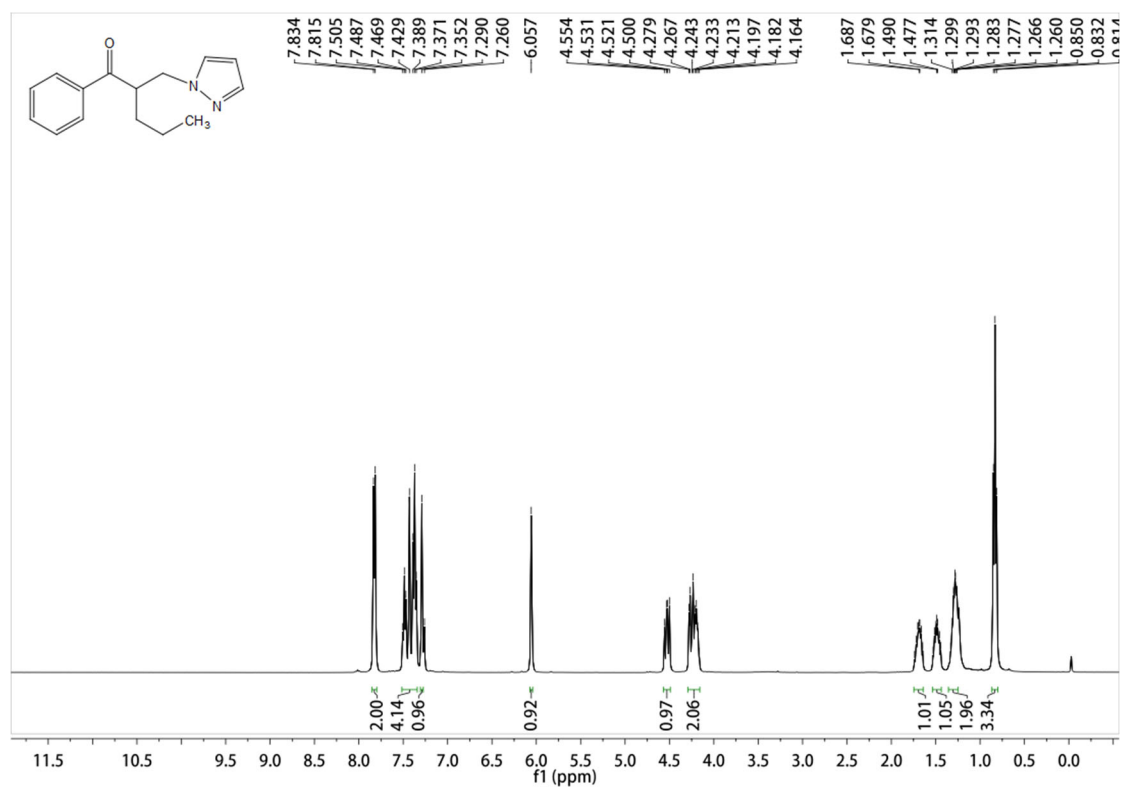
^1H NMR and ^{13}C NMR of compound **5a**



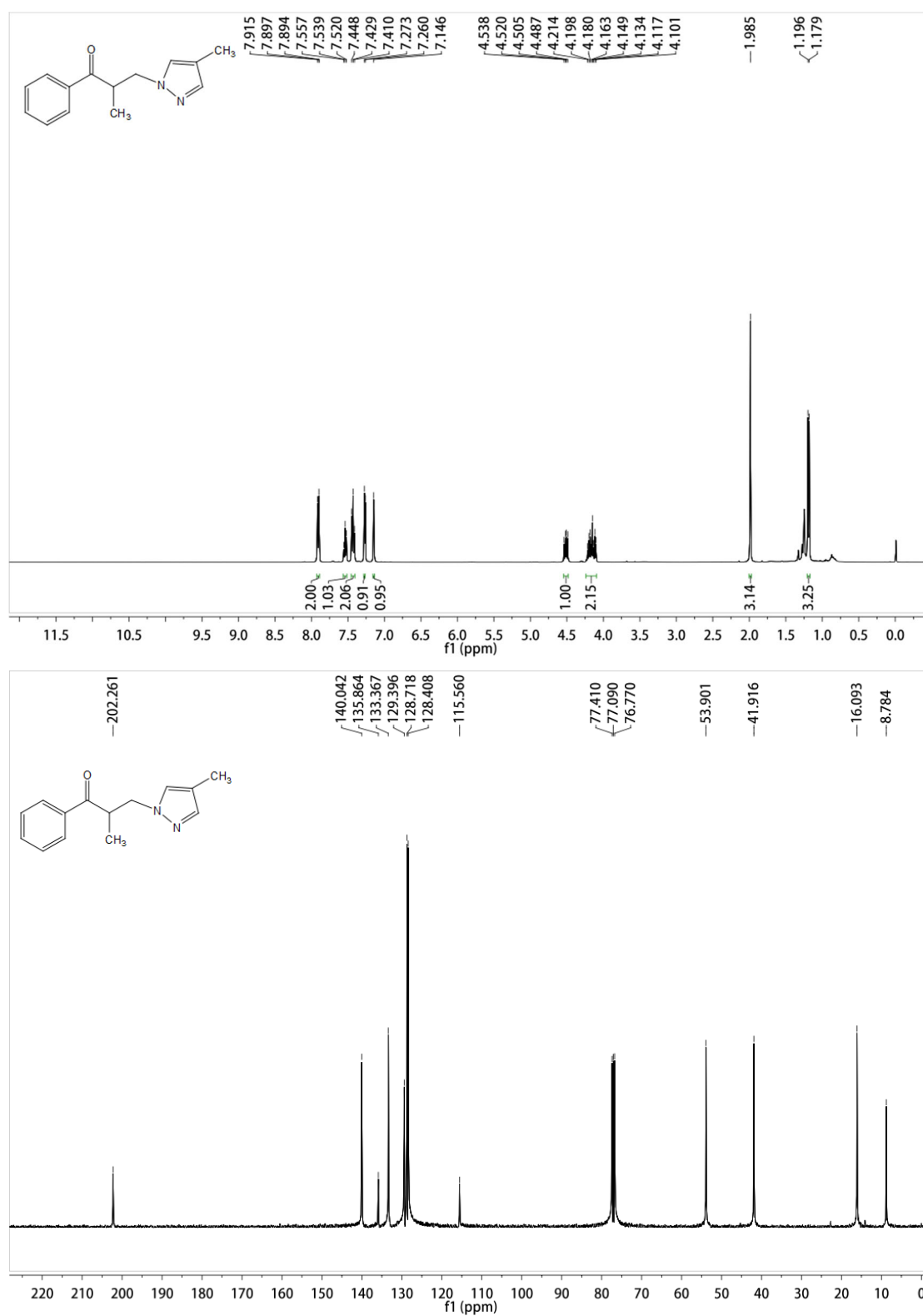
^1H NMR and ^{13}C NMR of compound **5b**



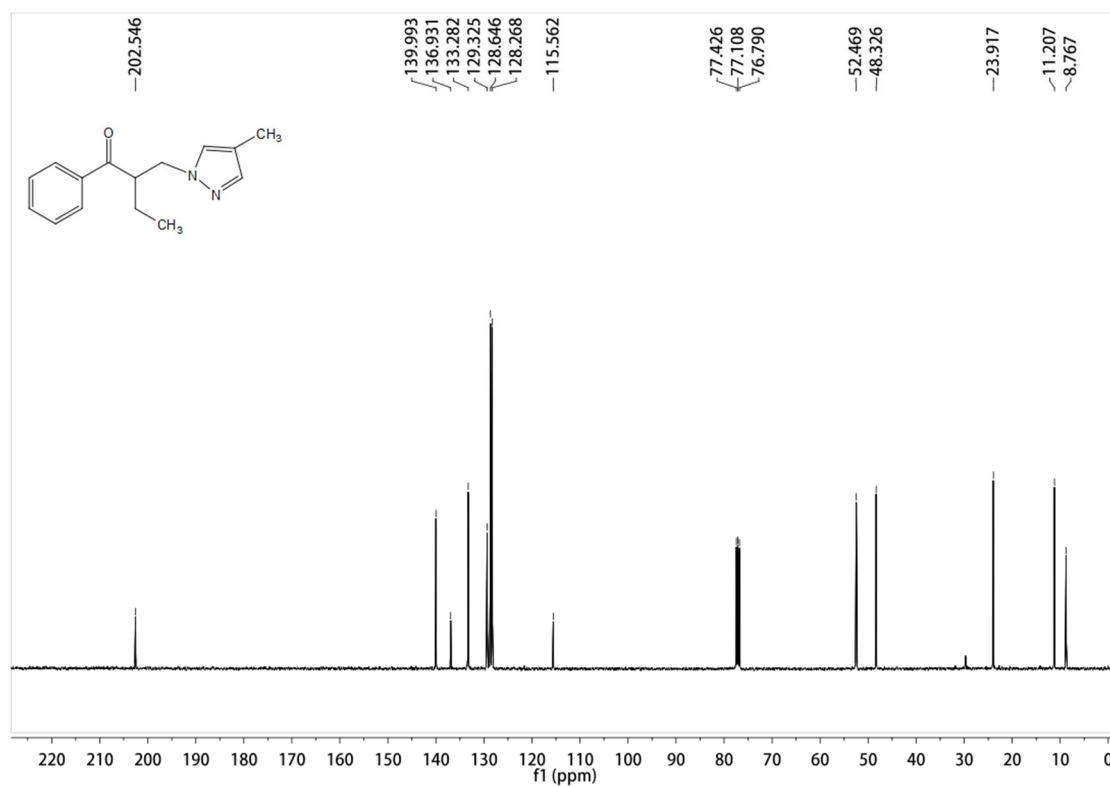
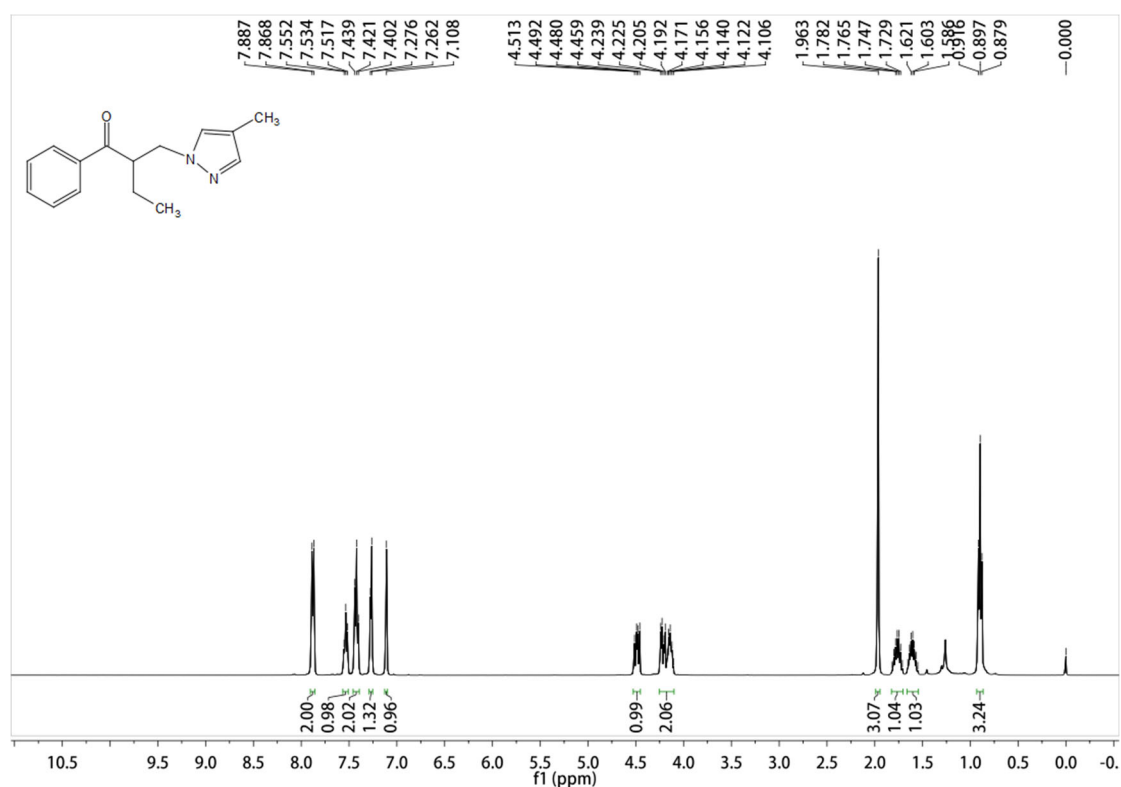
^1H NMR and ^{13}C NMR of compound **5c**



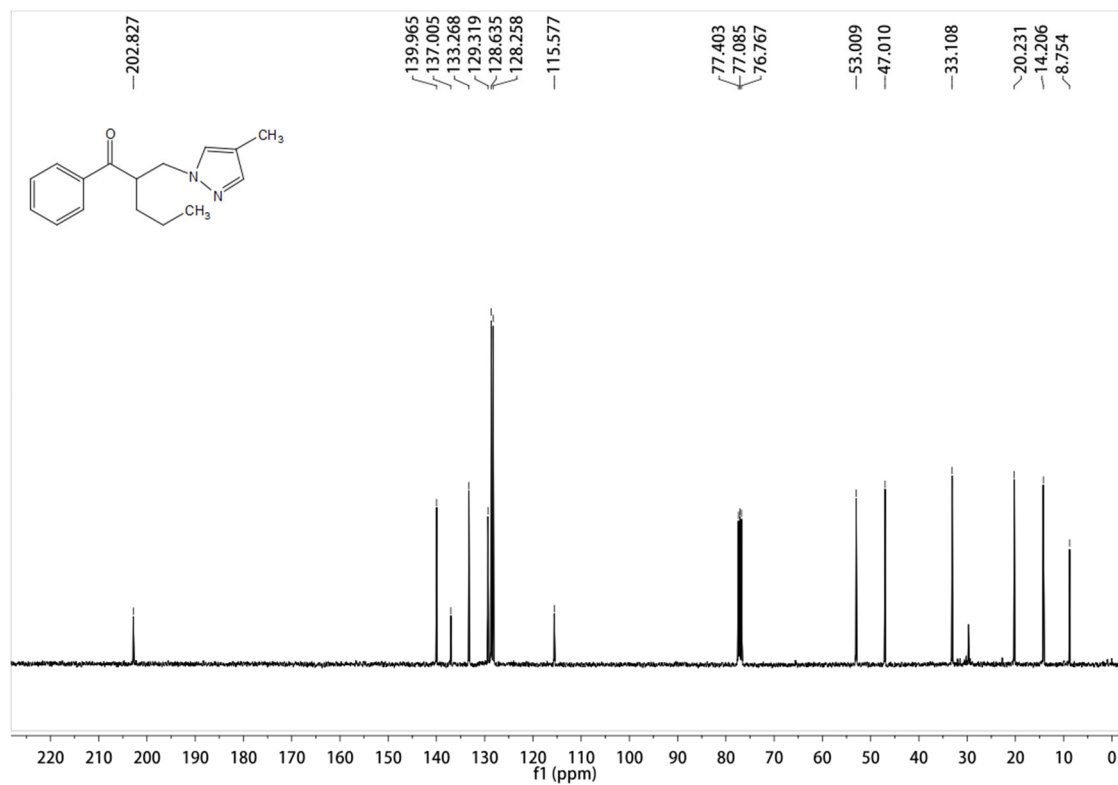
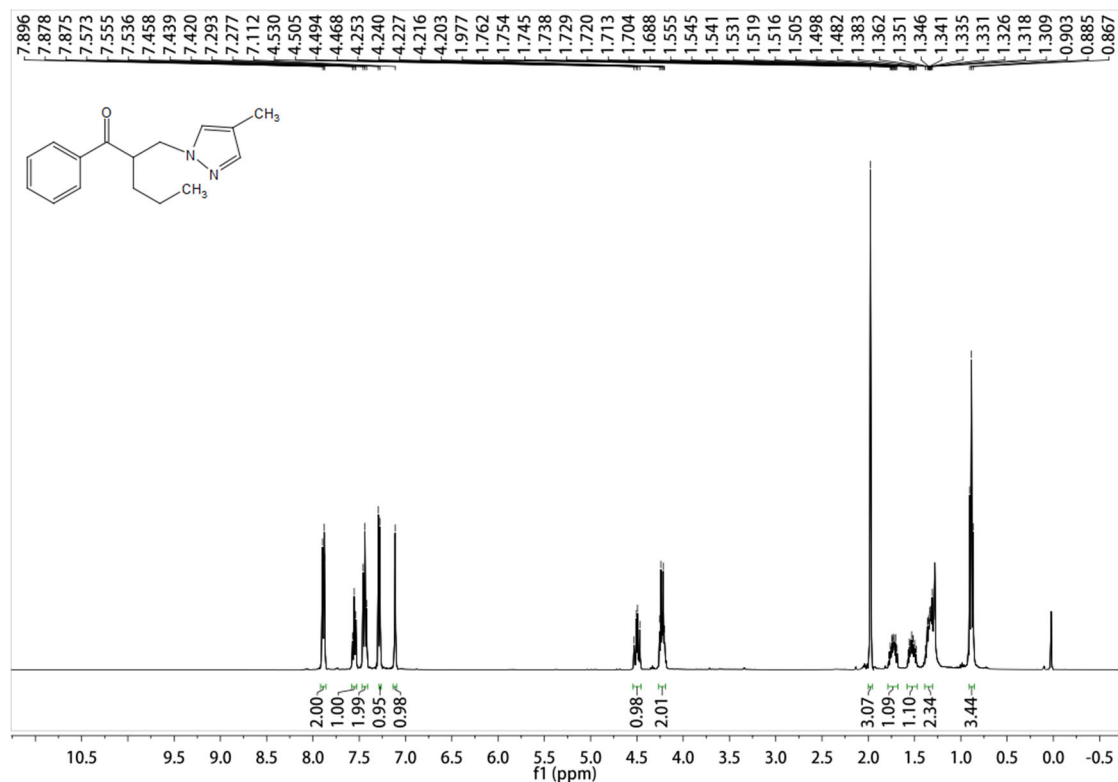
^1H NMR and ^{13}C NMR of compound **5d**



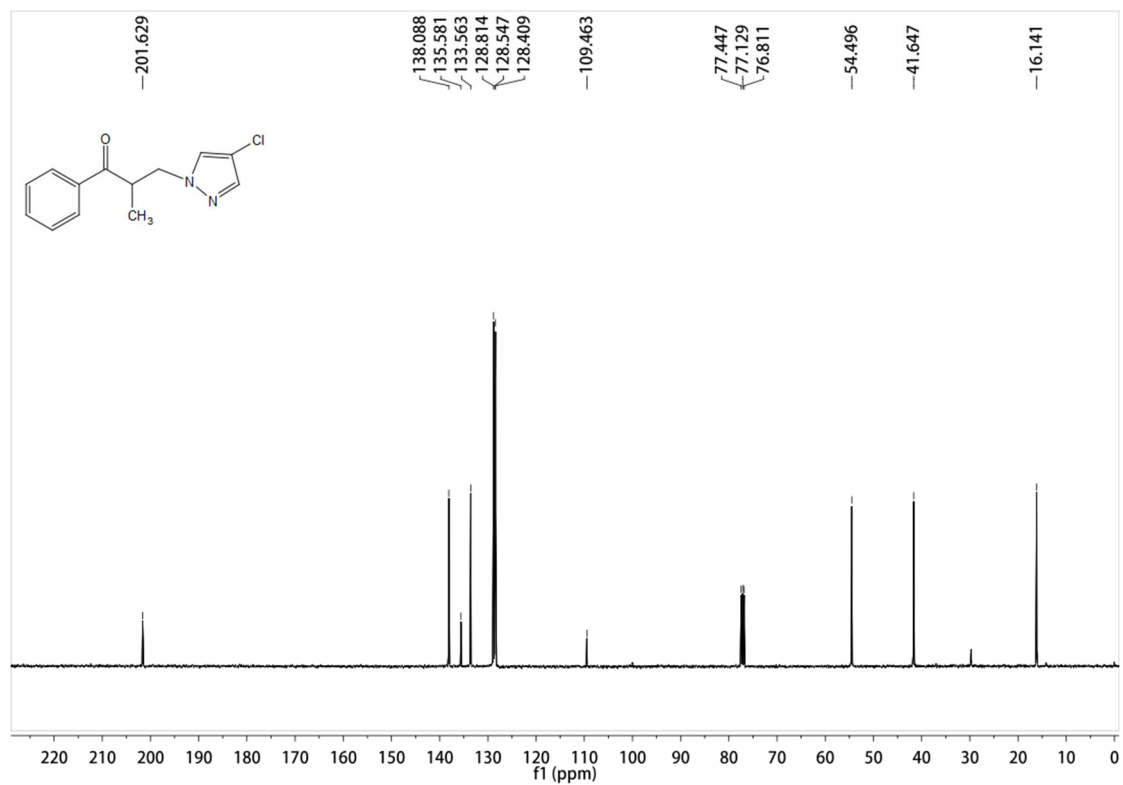
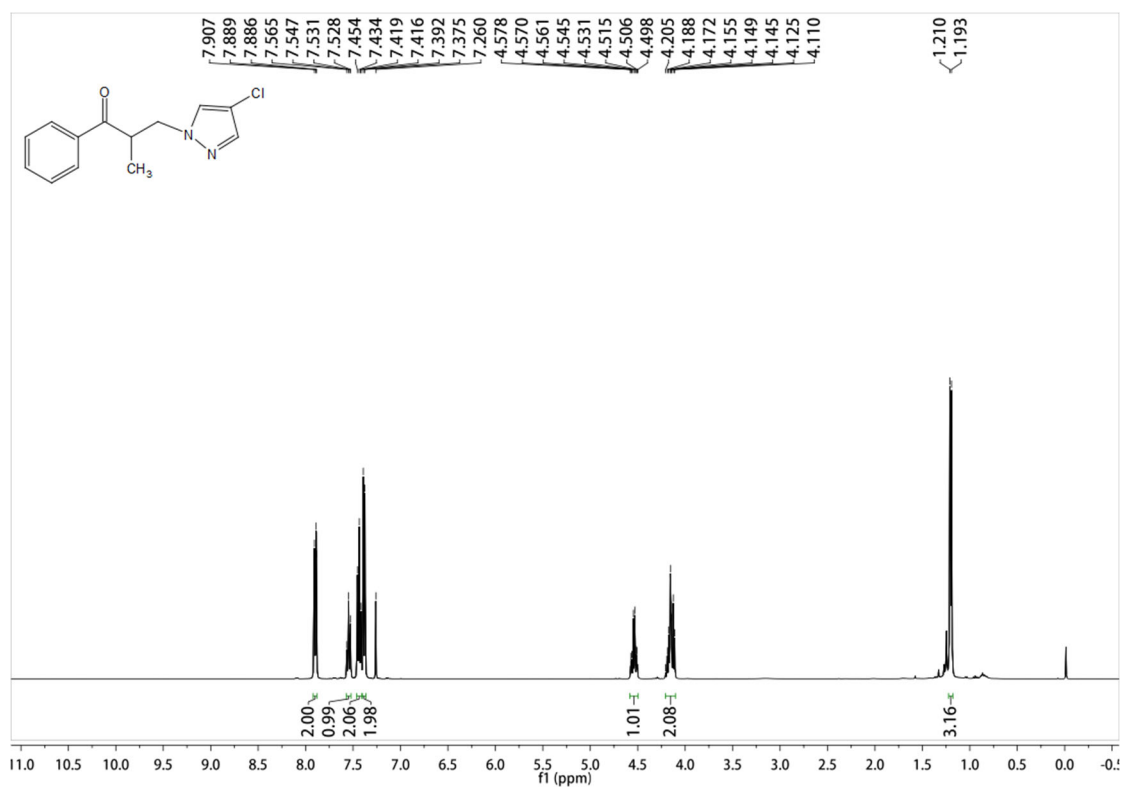
^1H NMR and ^{13}C NMR of compound **5e**



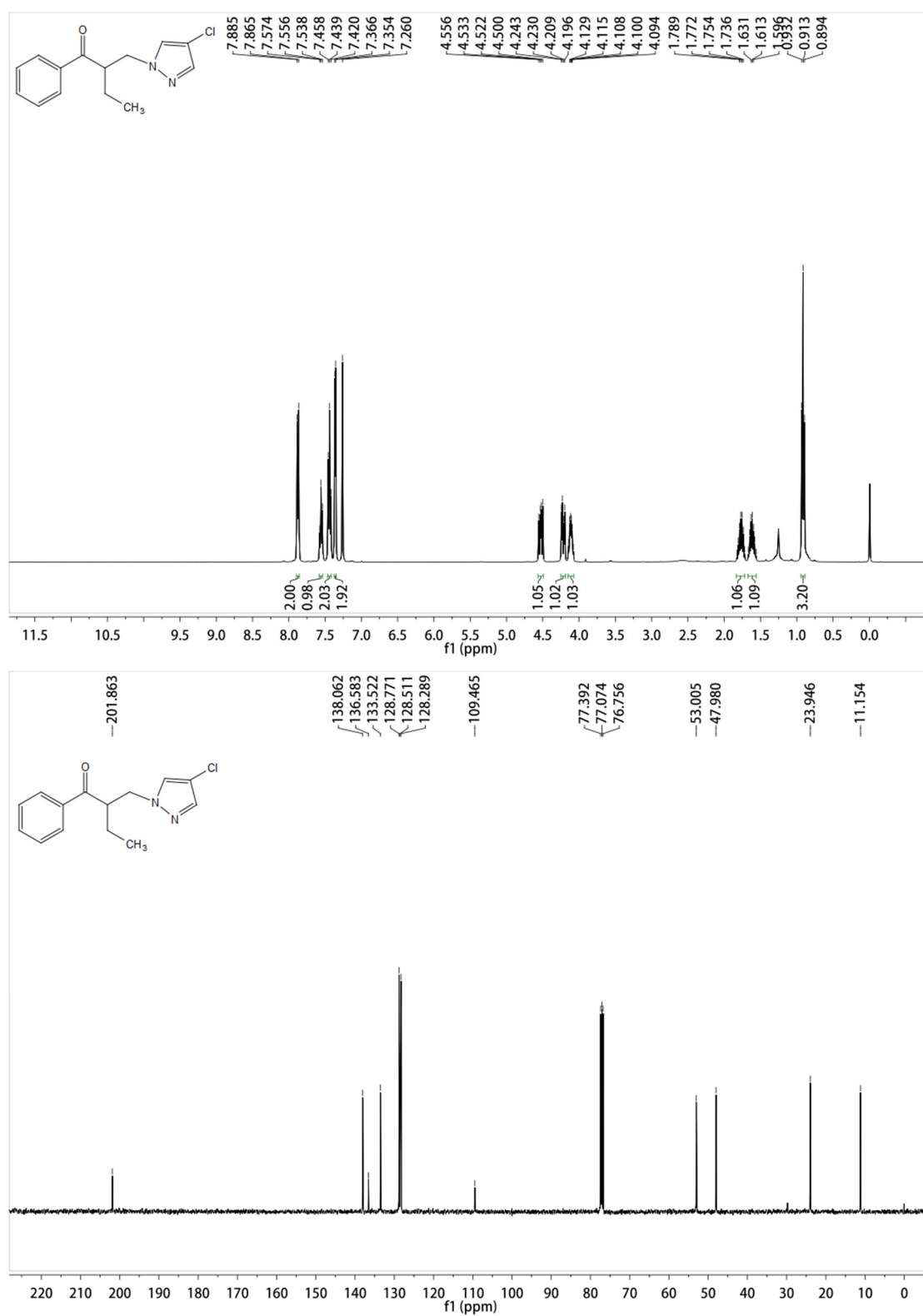
^1H NMR and ^{13}C NMR of compound **5f**



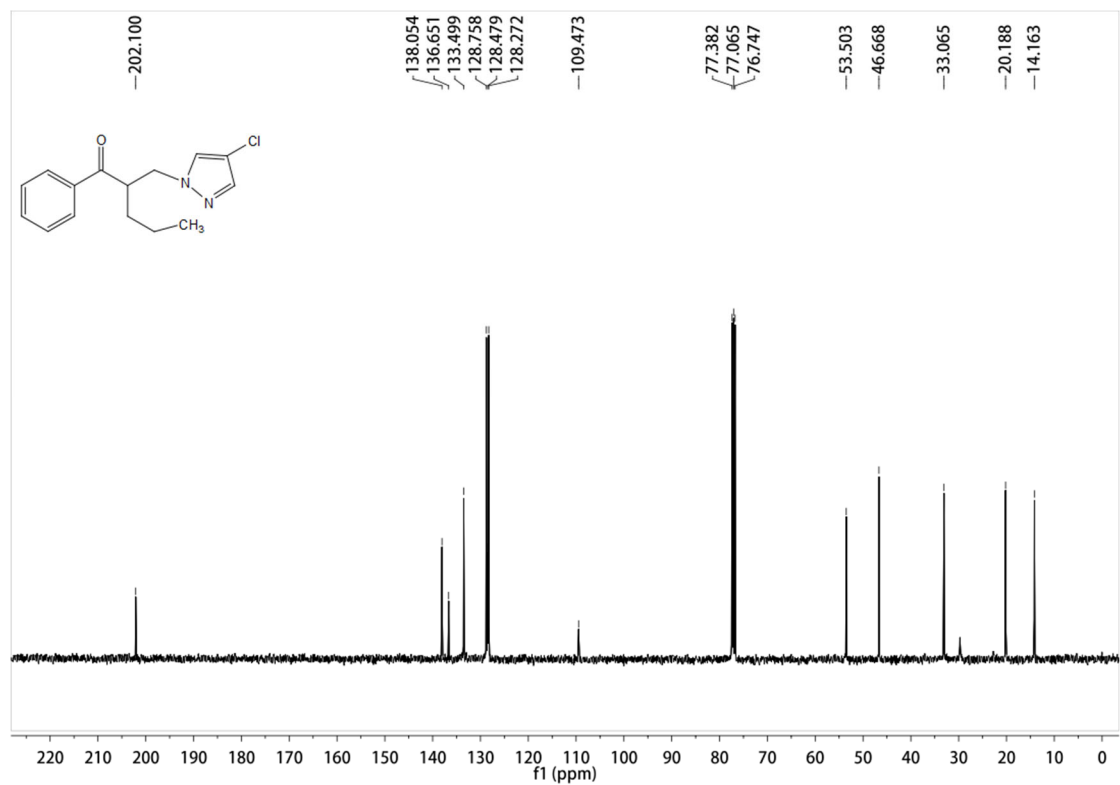
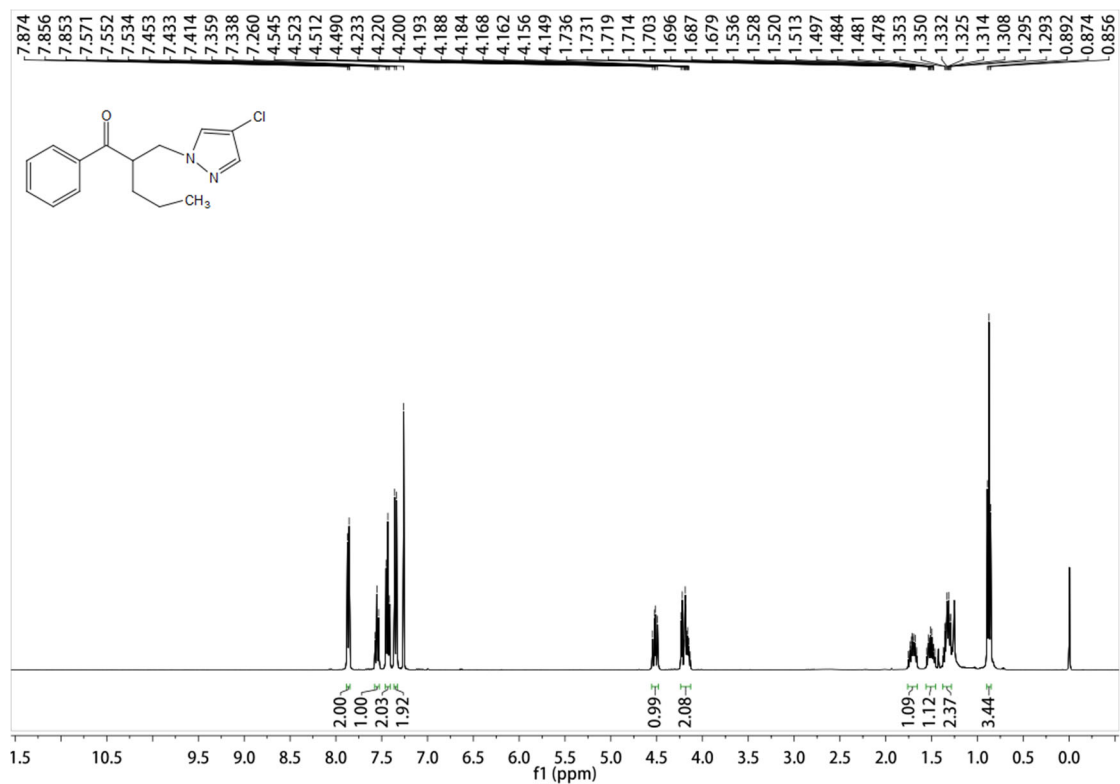
^1H NMR and ^{13}C NMR of compound **5g**



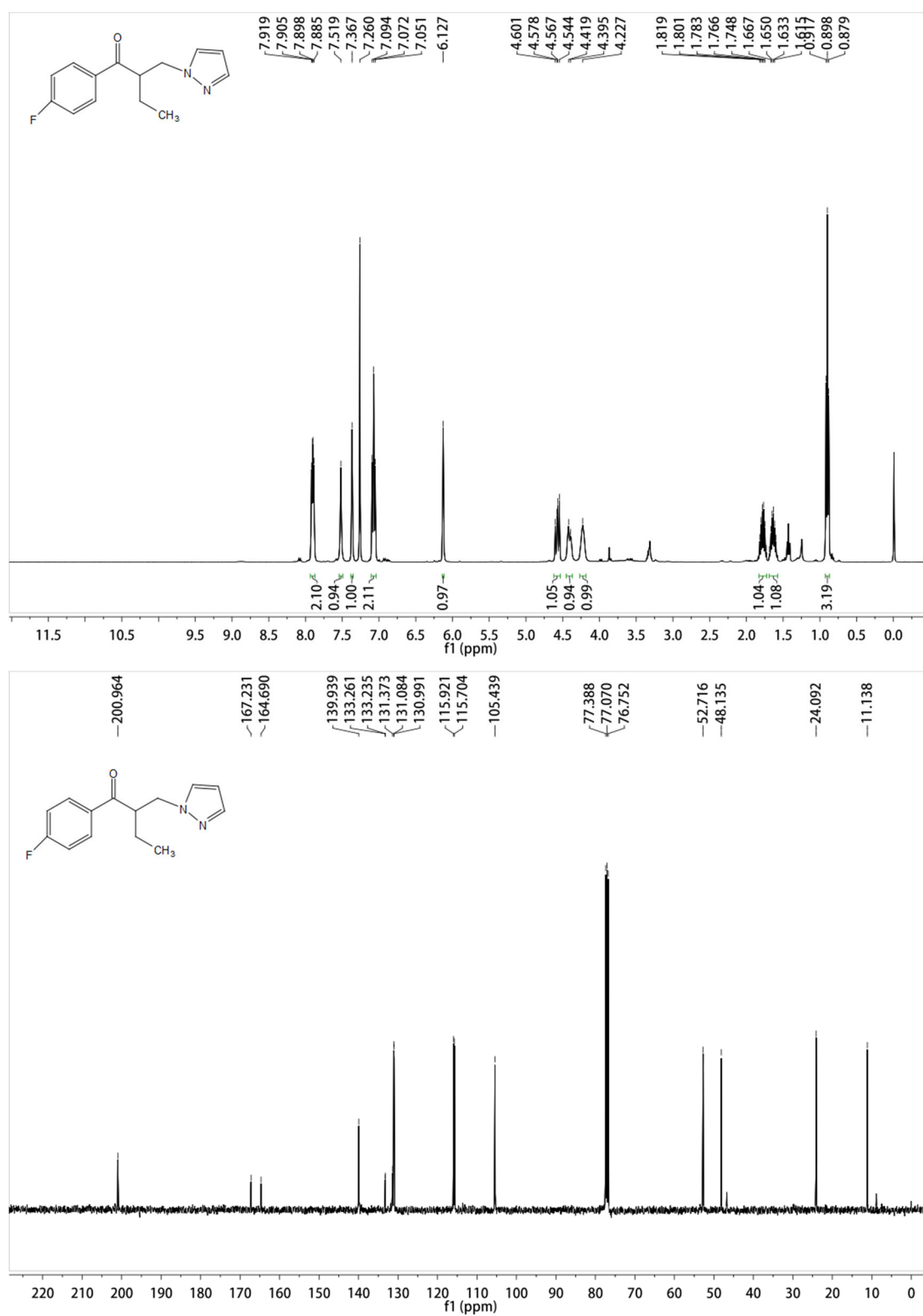
^1H NMR and ^{13}C NMR of compound **5h**



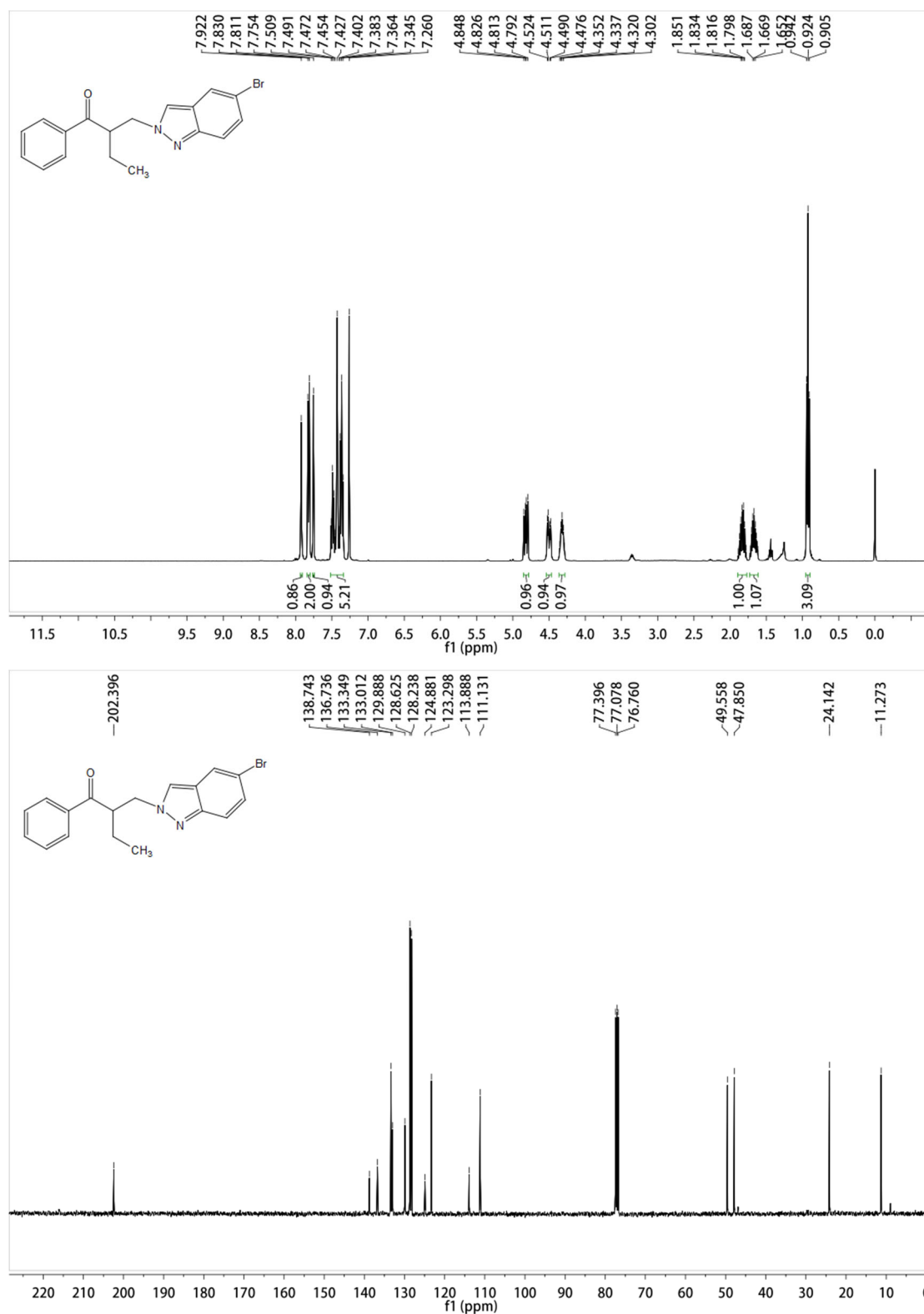
^1H NMR and ^{13}C NMR of compound **5i**



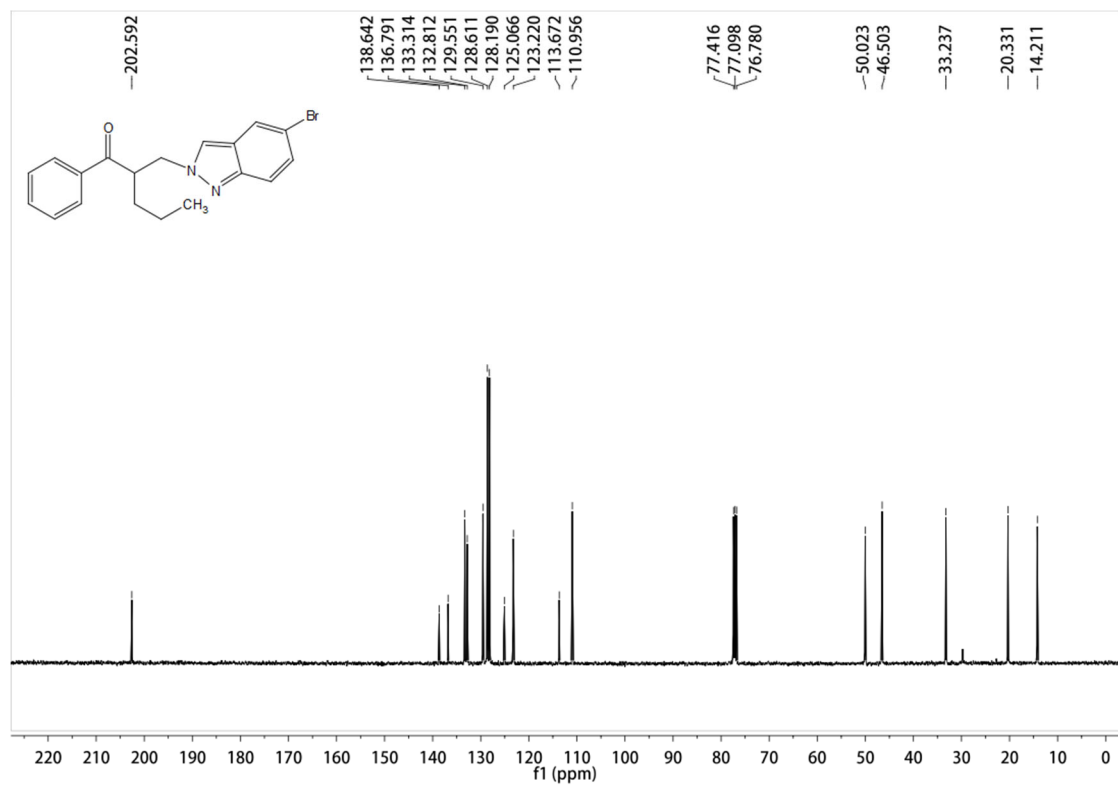
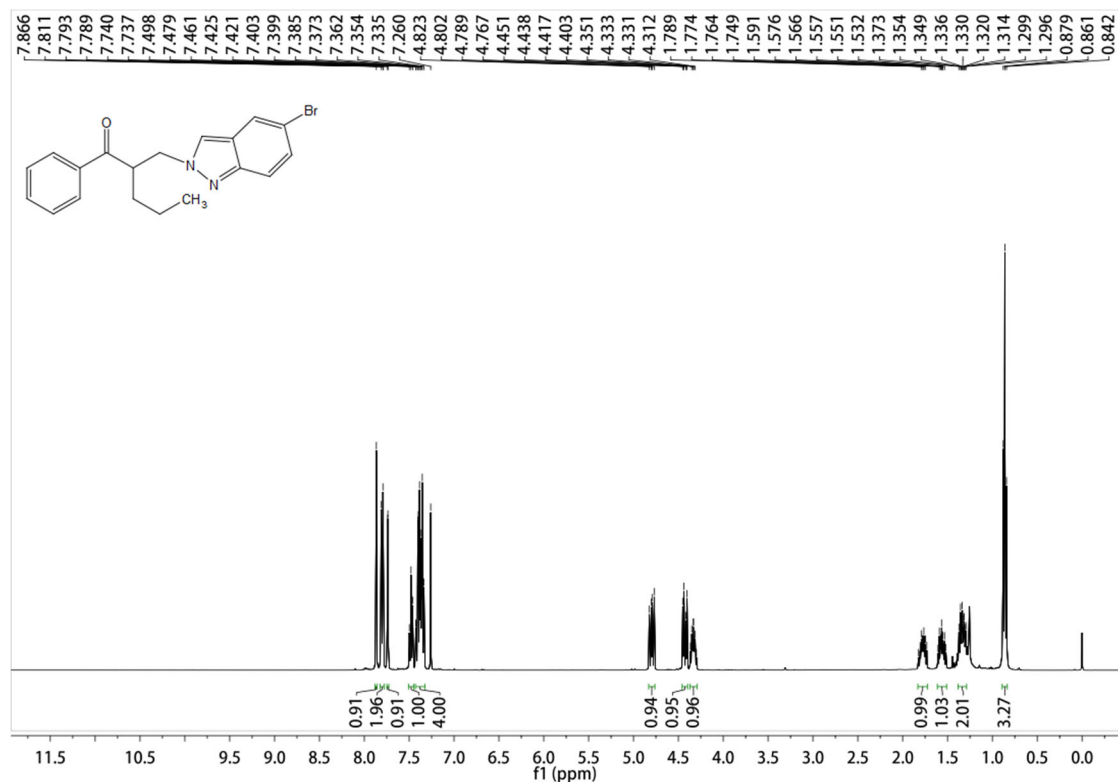
^1H NMR and ^{13}C NMR of compound **5j**



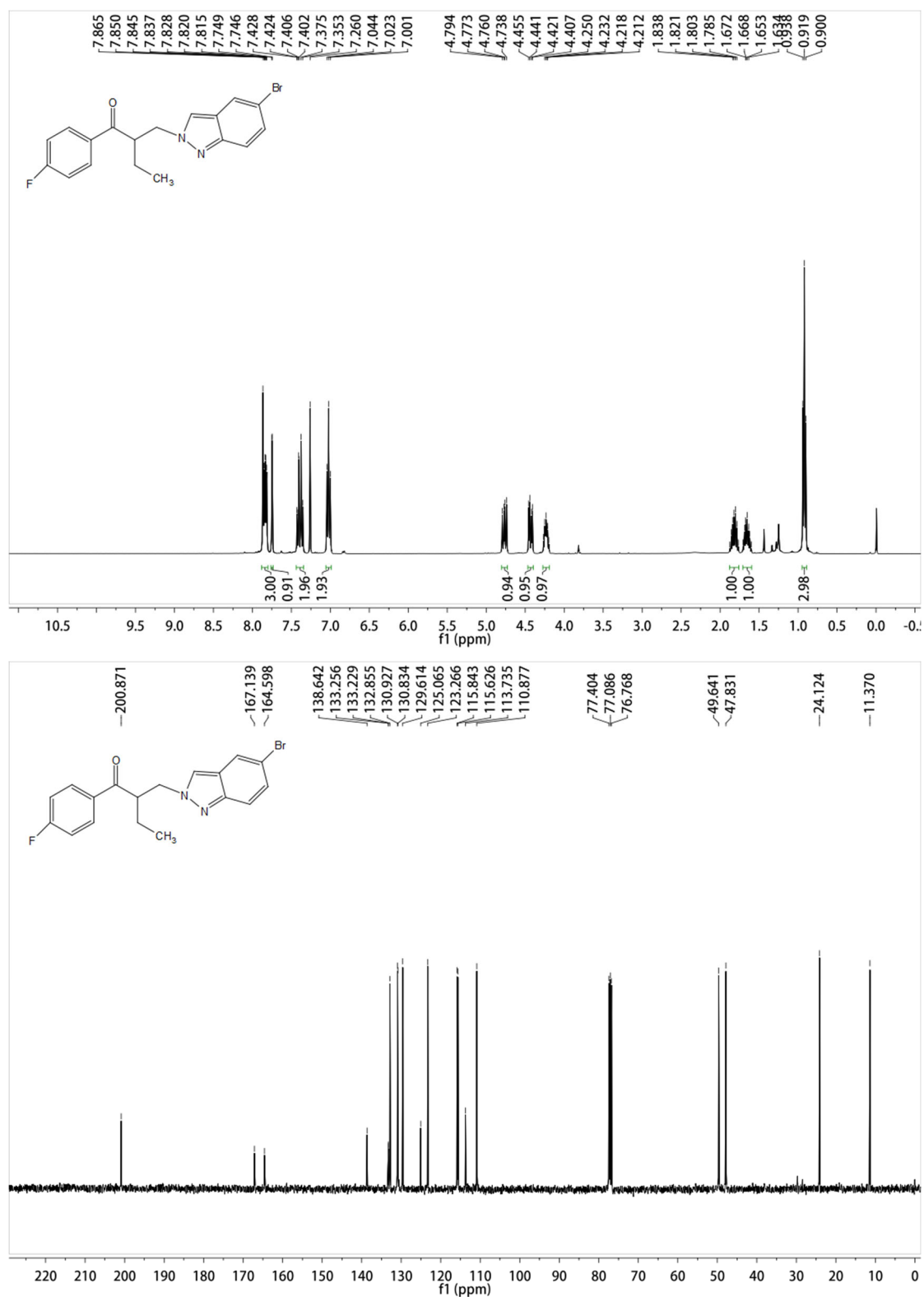
^1H NMR and ^{13}C NMR of compound **5k**



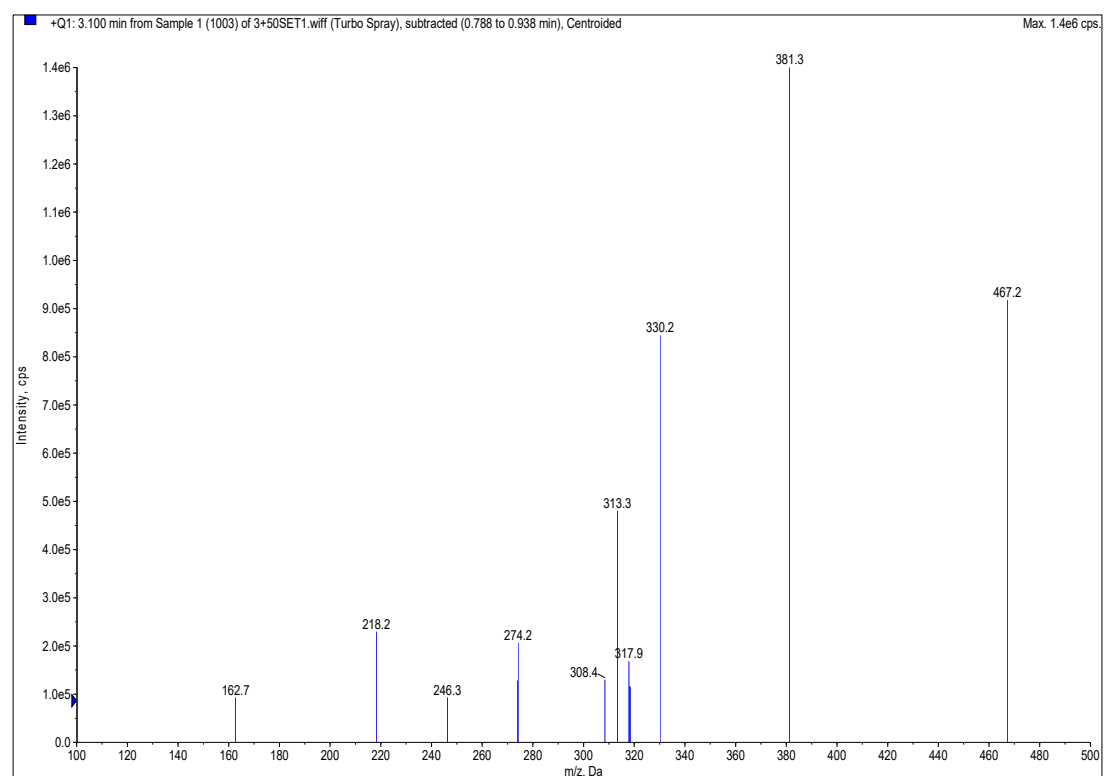
^1H NMR and ^{13}C NMR of compound **5l**



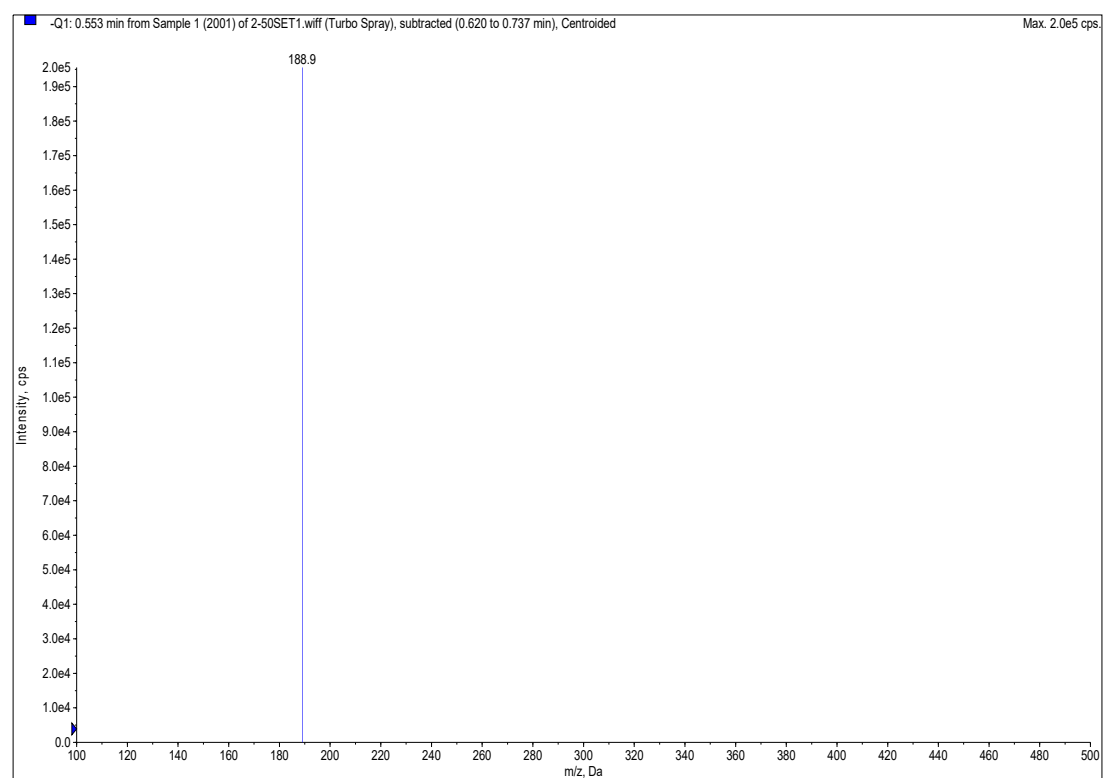
^1H NMR and ^{13}C NMR of compound **5m**



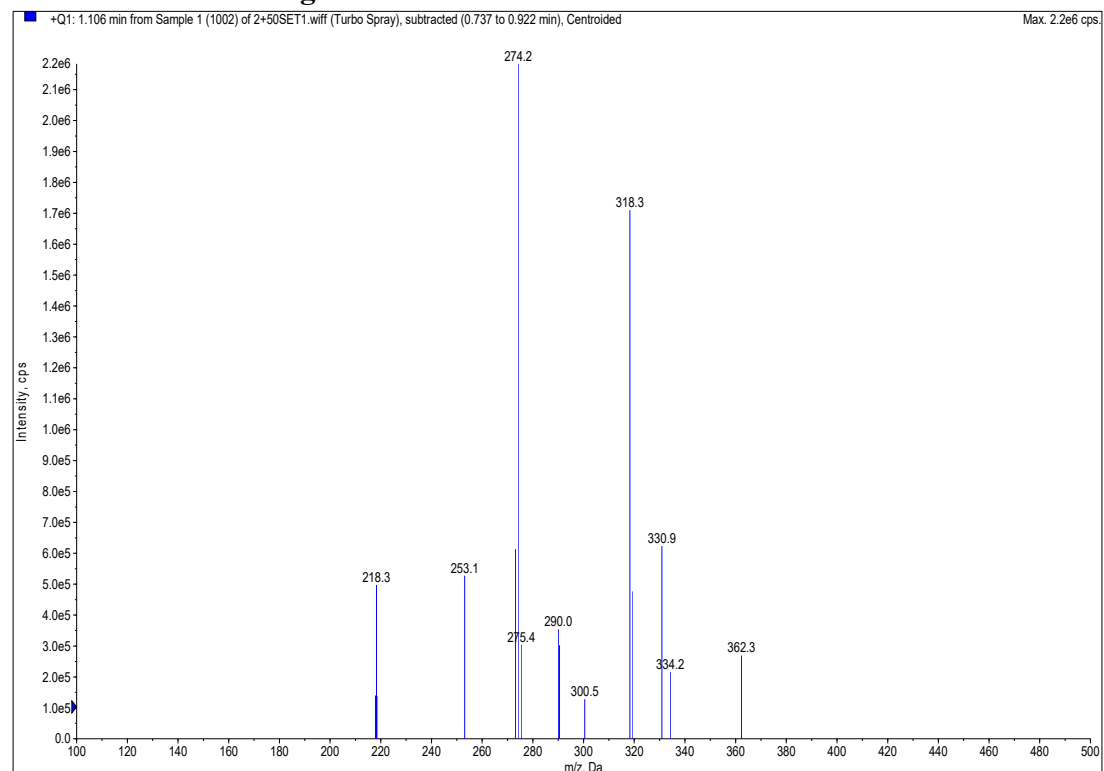
HPLC-MS chromatograms of intermediates A



HPLC-MS chromatograms of intermediates B



HPLC-MS chromatograms of intermediates C



HPLC-MS chromatograms of intermediates D

