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Infrared spectroscopic detection of ketene formation from carbene and CO source: amide synthesis

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Supporting Information

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1. General Information. Unless and otherwise specified all the reactions were carried out with oven dried glassware under nitrogen atmosphere. All the solvents were distilled prior to use by using standard procedures. Dichloromethane was distilled from the CaH_2 and used. Amines were procured from Aldrich chemicals and used as received without any further purification. All the diazo compounds were prepared by following the standard literature procedures, characterized and confirmed by the spectral data.[21] TLC was performed on pre-coated silica gel 60 F254 on aluminum plates and UV light (254 nm). Column chromatography was performed on silica gel 100−200 mesh size. ^1H and ^{13}C NMR spectra were recorded on 400 MHz (^1H) and 100 MHz (^{13}C), Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references for ^1H NMR and ^{13}C NMR. HR-MS was recorded on UHD Q-TOF mass spectrometer. CCDC1948319 (for **3h**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

2. General procedure for amine addition into ketene generated from diazo compounds (A). An oven dried 20 mL Schlenk flask was charged with amine (1 mmol) and $[Co_2(CO)_8]$ (0.5 equiv.), then 5 mL of dichloromethane was added to the reaction mixture. Then a dichloromethane solution of diazo compound (1.1 mmol) was added dropwise to the reaction mixture and the reaction mixture was stirred at room temperature for 14 h. The completion of the reaction was monitored by TLC using appropriate mixture of hexane and ethyl acetate as an eluent. After completion of reaction, the reaction mixture was extracted with 15 mL (5 mL × 3) of diethyl ether. Then diethyl ether was evaporated under reduced pressure and the crude residue was purified using column chromatography on silica gel using hexane/ethyl acetate.

Crystallographic information

Empirical formula	$C_{24}H_{35}NO_3$
Formula weight	257.03
Temperature/K	298 K
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.2702(8)
b/Å	20.6229(13)
c/Å	10.9839(10)
α/°	90
β/°	105.215(8)
γ/°	90
Volume/Å^3	2244.9(3)
Z	6
ρ_{calc}g/cm^3	1.1407
μ/mm^{-1}	0.074
F(000)	840.4
Crystal size/mm^3	0.8 0.2 0.16
Reflections collected	12603
Independent reflections	5328
Parameters	254
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R1 = 0.0683
Final R indexes [all data]	wR2 = 0.2268
CCDC no.	1948319

X-ray data collection and refinement:

X-ray data collectionwas performed on an OXFORD XCALIBUR diffractometer, equipped with a CCD area detector, using graphite-monochromated Mo Ka(l¼0.71073Å) radiation.[1] All calculations were executed using SHELXS-97 and SHELXL-97 respectively using Olex 2-1.1 software package.[2] The structurewas solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against F2). All non-hydrogen atoms were refined anisotropically. The crystallographic figures have been generated using Ortep3 (v1.0.3) software package (50% probability thermal ellipsoids).These data can be obtainedfree of charge from The Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

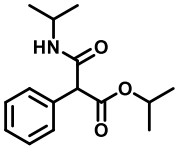
References:

[1] CrysAlisPro, Oxford Diffraction Ltd., Abingdon, U.K., 2010.

[2] G.M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Germany,1997.

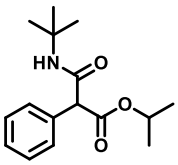
Experimental section

Isopropyl 3-(isopropylamino)-3-oxo-2-phenylpropanoate (3a).



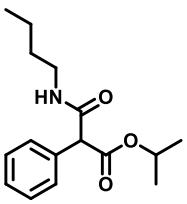
White solid in 80% yield (211 mg). Melting point: 96 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 5.2, 3.0 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.34 – 7.28 (m, 2H), 6.76 (t, J = 11.6 Hz, 1H), 5.04 (hept, J = 6.3 Hz, 1H), 4.43 (s, 1H), 4.07 (qt, J = 13.2, 6.6 Hz, 1H), 1.27 (d, J = 6.3 Hz, 3H), 1.16 (t, J = 6.6 Hz, 6H), 1.12 (d, J = 6.6 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.61, 166.48, 134.57, 129.05, 128.20, 77.48, 77.16, 76.84, 69.62, 58.82, 41.75, 22.59, 21.76, 21.52. IR (KBr) 3350, 3035, 2975, 2927, 2854, 1732, 1655, 1523, 1455, 1356, 1311, 1278, 1229, 1177, 1101, 1021, 972, 806, 742, 703, 605, 504 (cm^{-1}). HRMS (ESI-MS) calcd for $C_{15}H_{22}NO_3$m/z [M + H]$^{+}$:264.1600; found:264.1593.

Isopropyl 3-(tert-butylamino)-3-oxo-2-phenylpropanoate (3b).



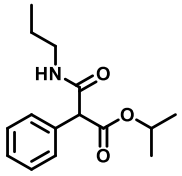
White solid in 75% yield (200 mg). Melting point: 135.8 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 5.0, 2.9 Hz, 1H), 7.37 (d, J = 1.3 Hz, 1H), 7.35 (d, J = 6.6 Hz, 1H), 7.34 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 6.73 (s, 1H, NH), 5.04 (hept, J = 6.3 Hz, 1H), 4.36 (s, 1H), 1.32 (s, 9H), 1.27 (d, J = 6.3 Hz, 3H), 1.17 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.75, 166.42, 134.83, 129.02, 128.15, 77.48, 77.16, 76.84, 69.54, 59.70, 51.52, 28.67, 21.78, 21.54; IR (KBr) 3307, 3076, 2980, 2935, 1739, 1648, 1553, 1456, 1362, 1226, 1178, 1105, 966, 809, 711, 582 (cm^{-1}); HRMS calcd for $C_{16}H_{24}NO_3$(ESI-MS) m/z [M + H]$^{+}$: 278.1756; found: 278.1755.

Isopropyl 3-(butylamino)-3-oxo-2-phenylpropanoate (3c).



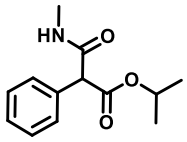
White solid in81% yield (225 mg).Melting point: 121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dt, J = 3.6, 2.1 Hz, 2H), 7.35 (s, 1H), 7.31 (ddd, J = 11.9, 8.2, 5.4 Hz, 2H), 6.90 (s, 1H, NH), 5.05 (hept, J = 6.3 Hz, 1H), 4.46 (s, 1H), 3.25 (qd, J= 7.0, 1.0 Hz, 2H), 1.51 – 1.43 (m, 2H), 1.32 (dd, J = 15.2, 7.6 Hz, 2H), 1.27 (d, J = 6.3 Hz, 3H), 1.16 (d, J = 6.3 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.59, 167.34, 134.55, 129.05 , 128.20, 77.48 , 77.16 , 76.84 , 69.62 , 58.86 , 39.54 , 31.48 , 21.75 , 21.51 , 20.09 , 13.79.IR (KBr) 3297, 3087, 2974, 2956, 2868, 1741, 1645, 1558, 1455, 1368, 1281, 1235, 1172, 1103, 984, 797, 702, 614 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{16}H_{24}NO_3$m/z $[M + H]^+$: 278.1756; found: 278.1760.

Isopropyl 3-oxo-2-phenyl-3-(propylamino)propanoate (3d).



White solid in 82% yield (216 mg).Melting point: 108°C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.34 (ddd, J = 7.5, 4.8, 1.8 Hz, 2H), 7.31 – 7.27 (m, 1H), 6.92 (s, 1H), 5.04 (hept, J = 6.3 Hz, 1H), 4.46 (s, 1H), 3.20 (dd, J = 13.4, 6.5 Hz, 2H), 1.49 (dt, J = 14.6, 7.3 Hz, 2H), 1.26 (d, J = 6.3 Hz, 3H), 1.16 (d, J = 6.3 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.52, 167.38, 134.50, 129.01, 128.18, 77.48, 77.16, 76.84, 69.58, 58.81, 41.42, 22.66, 21.72, 21.48, 11.34. IR (KBr) 3332, 3017, 2963, 2910, 2841, 1768, 1693, 1541, 1449, 1369, 1303, 1284, 1244, 1201, 1158, 1011, 985, 818, 740, 717, 622, 600, 534 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{15}H_{22}NO_3$, m/z $[M + H]^+$: 264.1600; found: 264.1594.

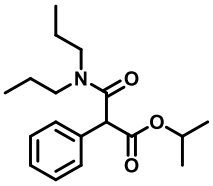
Isopropyl 3-(methylamino)-3-oxo-2-phenylpropanoate (3e).



White solid in 58% yield (137 mg).Melting point: 76 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.34 – 7.30 (m, 2H), 7.30 – 7.27 (m, 1H), 6.95 (s, 1H), 5.09 – 4.97 (m, 1H), 4.46 (s, 1H), 2.77 (dd, J = 4.8, 1.4 Hz, 3H), 1.25 (d, J = 6.3 Hz, 3H), 1.15 (d, J = 6.3 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.35, 168.11, 134.34, 128.97, 128.19, 77.48 , 77.16, 76.84, 69.55, 58.62, 26.52, 21.67, 21.44.IR (KBr) 3448, 3338, 1738, 1648, 1543, 1454, 1410, 1308, 1410,

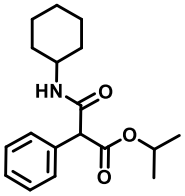
1279, 1182, 1106, 974, 718, 576 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{12}H_{16}NO_3$, m/z $[M + H]^+$: 236.1287; found: 236.1287.

Isopropyl 3-(dipropylamino)-3-oxo-2-phenylpropanoate (3f).



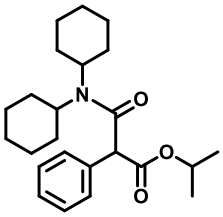
White solid in 77% yield (235 mg).Melting point: 98 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 1.8 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.25 – 7.22 (m, 1H), 7.23 – 7.17 (m, 1H), 5.03 – 4.91 (m, 1H), 4.69 (s, 1H), 3.32 – 3.15 (m, 2H), 3.13 – 3.01 (m, 2H), 1.57 – 1.35 (m, 4H), 1.16 (dd, J = 6.2, 2.8 Hz, 6H), 0.77 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.53, 167.57, 133.93, 129.35, 128.54, 127.83, 77.48, 77.16, 76.84, 69.13, 56.35, 47.82, 22.14, 21.75, 21.53, 20.61, 11.22. IR (KBr) 3299, 3070, 2985, 2926, 1734, 1654, 1591, 1553, 1474, 1370, 1342, 1314, 1239, 1186, 1038, 1008, 835, 811, 747, 697, 641, 504 (cm^{-1}). HRMS (ESI-MS) calcd for $C_{18}H_{28}NO_3$, m/z $[M + H]^+$: 306.2069; found: 306.2077.

Isopropyl 3-(cyclohexylamino)-3-oxo-2-phenylpropanoate (3g).



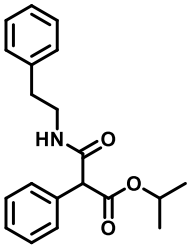
White solid in 82% yield (252 mg).Melting point: 84 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.6 Hz, 2H), 7.34 (s, 2H), 7.32 (s, 1H), 6.84 (s, 1H), 5.05 (dd, J = 12.6, 6.1 Hz, 1H), 4.44 (s, 1H), 3.78 (d, J = 9.3 Hz, 1H), 1.86 (t, J = 13.9 Hz, 2H), 1.74 (d, J = 14.1 Hz, 2H), 1.64 (s, 4H), 1.38 – 1.31 (m, 2H), 1.28 (d, J = 6.2 Hz, 3H), 1.17 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.58, 166.37, 153.56, 134.63, 133.55, 128.78, 128.19, 77.47, 77.16, 76.84, 69.56, 58.84, 48.27, 32.72, 25.13, 21.75. IR (KBr) 3420, 2933, 2854, 1741, 1645, 1540, 1452, 1373, 1165, 1110, 1031, 894, 579 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{18}H_{26}NO_3$,m/z $[M + H]^+$: 304.1913; found:304.1905.

Isopropyl 3-(dicyclohexylamino)-3-oxo-2-phenylpropanoate (3h).



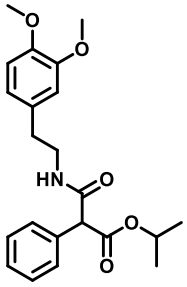
White solid in 85% yield (328 mg).Melting point: 98 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 7.32 (s, 2H), 7.31 – 7.26 (m, 1H), 5.04 (hept, *J* = 6.3 Hz, 1H), 4.73 (s, 1H), 3.40 (dd, *J* = 15.8, 7.4 Hz, 1H), 2.80 (s, 1H), 2.52 (s, 2H), 1.83 – 1.76 (m, 2H), 1.74 (s, 2H), 1.53 (dd, *J* = 19.0, 10.7 Hz, 4H), 1.47 – 1.30 (m, 2H), 1.23 (d, *J* = 6.3 Hz, 6H), 1.20 (d, *J* = 9.8 Hz, 4H), 1.13 – 0.92 (m, 2H), 0.92 – 0.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.78, 166.96, 134.57, 129.34, 128.58, 127.72, 77.48, 77.16, 76.84, 69.09, 58.68, 56.55, 29.80, 29.26, 26.65, 26.13, 25.85, 25.30, 21.83. IR (KBr) 3462, 2978, 2928, 2854, 1741, 1635, 1450, 1361, 1307, 1176, 1110, 992, 896, 714, 567 (cm^{-1}). HRMS (ESI-MS)$C_{24}H_{36}NO_3$,m/z $[M + H]^+$: calcd for 386.2695; found: 386.2704.

Isopropyl 3-oxo-3-(phenethylamino)-2-phenylpropanoate (3i).



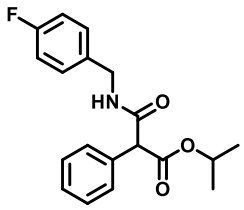
White solid in87% yield**(**283 mg).Melting point: 83°C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 5H), 7.30 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 7.13 – 7.10 (m, 2H), 6.83 (dd, *J* = 6.7, 2.2 Hz, 1H), 5.05 (hept, *J* = 6.3 Hz, 1H), 4.46 (s, 1H), 3.56 – 3.50 (m, 2H), 2.80 (t, *J* = 6.9 Hz, 2H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.31 (s), 167.44 (s), 138.80 (s), 134.26 (s), 129.09 (s), 128.88 (s), 128.68 (s), 128.25 (d, *J* = 3.3 *Hz*), 126.56, 77.48, 77.16, 76.84, 69.64, 58.94, 41.03, 35.51, 21.76, 21.53. IR (KBr) 3307, 3080, 3030, 2871, 1730, 1653, 1521, 1461, 1356, 1279, 1226, 1108, 1087, 1008, 904, 806, 741, 697, 536, 538, 497 (cm^{-1}). HRMS (ESI-MS)calcd for $C_{20}H_{24}NO_3$,m/z $[M + H]^+$: 326.1756; found: 326.1768.

Isopropyl 3-((3,4-dimethoxyphenethyl)amino)-3-oxo-2-phenylpropanoate (3j).



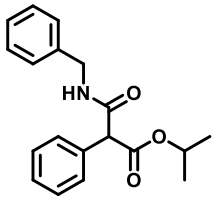
White solid in84% yield(324 mg). Melting point: 78.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 4H), 6.88 (s, 1H), 6.76 – 6.72 (m, 1H), 6.67 – 6.61 (m, 2H), 5.01 (hept, J = 6.3 Hz, 1H), 4.43 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.48 (ddd, J = 12.5, 7.0, 2.3 Hz, 2H), 2.73 (t, J = 7.0 Hz, 2H), 1.24 (d, J = 6.3 Hz, 3H), 1.13 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.27, 167.38, 149.03, 147.68, 134.25, 131.26, 128.96, 128.15, 120.70, 111.97, 111.41, 77.48, 77.16, 76.84, 69.56, 58.80, 55.89, 41.03, 35.00, 21.66, 21.43. IR (KBr) 3313, 3056, 2984, 2936, 2838, 1733, 1652, 1523, 1455, 1235, 1190, 1147, 1102, 1027, 850, 808, 708 (cm^{-1}). HRMS (ESI-MS) calcd for $C_{22}H_{28}NO_5$,m/z $[M + H]^+$: 386.1967; found: 386.1972.

Isopropyl 3-((4-fluorobenzyl)amino)-3-oxo-2-phenylpropanoate (3k).



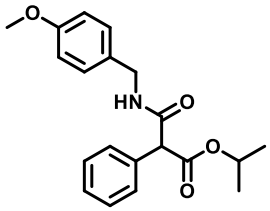
White solid in 85% yield (330 mg).Melting point: 108 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 6.9 Hz, 2H), 7.41 (d, J = 6.4 Hz, 1H), 7.39 (s, 2H), 7.35 (d, J = 6.5 Hz, 2H), 7.33 – 7.27 (m, 2H), 5.19 – 5.05 (m, 1H), 4.61 (s, 1H), 4.49 (d, J = 5.5 Hz, 2H), 1.33 (d, J = 6.0 Hz, 3H), 1.23 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.09, 167.47, 137.97, 134.20, 129.49, 129.10, 129.10, 128.00, 127.52, 127.43, 77.48, 77.16, 76.84, 69.59, 58.70, 43.55, 23.19, 20.52. IR (KBr) 3314, 3060, 2982, 2940, 1740, 1650, 1608, 1532, 1453, 1356, 1211, 1228, 1179, 1102, 1020, 973, 829, 750, 704, 581, 487 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{19}H_{21}FNO_3$,m/z $[M + H]^+$: 330.1505; found:330.1500.

Isopropyl 3-(benzylamino)-3-oxo-2-phenylpropanoate (3l).



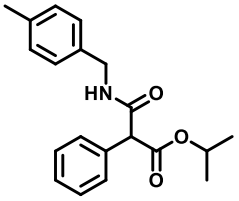
White solid in 92% yield(285 mg).Melting point: 107.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dt, J = 3.9, 2.2 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.33 (dd, J = 3.2, 1.7 Hz, 1H), 7.31 (dd, J = 4.2, 1.2 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.22 (dd, J = 5.2, 2.9 Hz, 2H), 5.06 (hept, J = 6.3 Hz, 1H), 4.54 (s, 1H), 4.46 (d, J = 5.8 Hz, 2H), 1.27 (d, J = 6.3 Hz, 3H), 1.17 (d, J = 6.3 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.42, 138.06, 134.36, 129.17, 128.80, 128.33, 127.62, 77.48, 77.16, 76.84, 69.80, 58.91, 43.77, 21.80, 21.54. IR (KBr) 3348, 3033, 2980, 2938, 1732, 1656, 1521, 1455, 1355, 1309, 1278, 1230, 1178, 1102, 1017, 973, 807, 742, 702, 605, 505, 422 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{19}H_{22}NO_3$, m/z $[M + H]^+$: 312.1600; found: 312.1602.

Isopropyl 3-((4-methoxybenzyl)amino)-3-oxo-2-phenylpropanoate (3m).



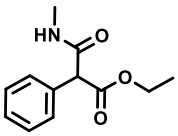
White solid in 82% yield (280 mg).Melting point: 79 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 1H), 7.39 (dq, J = 3.3, 2.2 Hz, 2H), 7.37 (dd, J = 3.4, 1.1 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.36 – 7.32 (m, 2H), 7.34 – 7.29 (m, 1H), 5.06 (dq, J = 12.5, 6.3 Hz, 1H), 4.60 (s, 1H), 3.75 (s, 3H), 1.26 (d, J = 6.3 Hz, 3H), 1.21 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.87, 167.68, 132.92, 129.86, 129.35, 128.70, 128.30, 128.07, 77.21, 76.84, 76.84, 69.62, 58.13, 52.83, 21.63.IR (KBr) 3348, 3033, 2980, 2938, 1732, 1656, 1521, 1455, 1355, 1309, 1278, 1230, 1178, 1102, 1017, 973, 807, 742, 702, 605, 505, 422 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{19}H_{22}NO_3$, m/z $[M + H]^+$: 312.1600; found: 312.1602.

Isopropyl 3-((4-methylbenzyl)amino)-3-oxo-2-phenylpropanoate (3n).



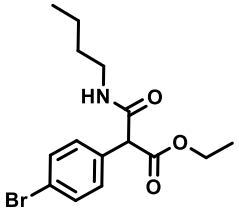
White solid in 88% yield(287 mg).Melting point: 79 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dt, J = 4.0, 2.2 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.50 – 7.45 (m, 2H), 7.48 – 7.44 (m, 1H), 7.46 – 7.40 (m, 1H), 7.34 – 7.27 (m, 1H), 5.21 (hept, J = 6.3 Hz, 1H), 4.70 (s, 1H), 4.54 (d, J = 5.7 Hz, 2H), 2.47 (s, 3H), 1.43 (d, J = 6.3 Hz, 3H), 1.33 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.01 – 170.10, 170.00, 168.68, 187.01 – 135.06, 152.30, 187.01, 129.32, 187.01, 128.96, 187.01, 128.46, 141.22, 187.01, 127.82, 219.37, 127.34, 113.96, 77.48, 77.16, 76.84, 69.48, 58.67, 43.28, 21.59, 21.38, 21.02. IR (KBr) 3351, 3024, 2994, 2905, 1741, 1662, 1533, 1441, 1325, 1313, 1262, 1209, 1182, 1102, 1007, 981, 800, 736, 698, 627, 514, 438 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{20}H_{24}NO_4$,m/z $[M + H]^+$: 342.1705; found:342.1711.

Ethyl 3-(methylamino)-3-oxo-2-phenylpropanoate (6a).



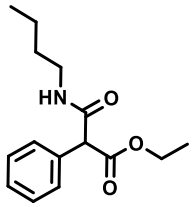
White solid in 59% yield (131 mg).Melting point: 75°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dt, J = 8.3, 2.2 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.14 – 7.10 (m, 1H), 6.84 – 6.74 (m, 1H), 4.51 (s, 1H), 4.17 (ddd, J = 7.4, 5.1, 4.7 Hz, 2H), 2.78 (dd, J = 4.8, 0.7 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.73, 168.00, 134.19, 128.99, 128.28, 127.78, 114.02, 77.48, 77.16, 76.84, 61.84, 58.50, 26.54, 13.98. IR (KBr) 3453, 3324, 1758, 1653, 1555, 1474, 1410, 1399, 1321, 1283, 1179, 1096, 981, 743, 601, 581 cm^{-1}. HRMS (ESI-MS) calcd for $C_{12}H_{16}NO_3$,m/z $[M + H]^+$: 222.1130; found:222.1125.

Ethyl 2-(4-bromophenyl)-3-(butylamino)-3-oxopropanoate (6b).



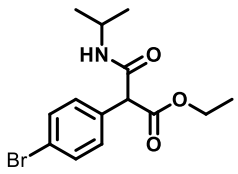
White solid in 88% yield(302 mg).Melting point: 72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 2H), 7.30 – 7.21 (m, 2H), 6.95 (s, 1H), 4.43 (s, 1H), 4.26 – 4.11 (m, 2H), 3.23 (dd, J = 13.4, 6.6 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.34 – 1.26 (m, 2H), 1.23 (dd, J = 7.4, 6.9 Hz, 3H), 0.89 (d, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.59, 166.67, 133.38, 132.12, 130.06, 122.46, 77.47, 77.16, 76.84, 62.11, 57.85, 39.62, 31.36, 20.06, 14.02, 13.74.IR (KBr) 3242, 3081, 2995, 2953, 2879, 1744, 1650, 1559, 1441, 1378, 1275, 1221, 1173, 1052, 982, 748, 690, 602, 596 (cm^{-1}).HRMS (ESI-MS)calcd for $C_{15}H_{21}BrNO_3$, m/z $[M + H]^+$: 342.0705; found:342.0699.

Ethyl 3-(butylamino)-3-oxo-2-phenylpropanoate (6c).



White solid in86% yield **(**227 mg).Melting point: 82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.30 (d, J = 2.3 Hz, 1H), 7.28 – 7.22 (m, 2H), 6.89 (s, 1H), 4.45 (s, 1H), 4.20 – 4.06 (m, 2H), 3.18 (td, J = 7.1, 5.8 Hz, 2H), 1.40 (dt, J= 12.4, 7.2 Hz, 2H), 1.25 (dd, J = 15.2, 7.6 Hz, 2H), 1.18 (t, J = 7.1 Hz, 3H), 0.82 (t, J = 7.3 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.83, 167.23, 134.32, 128.96, 128.22,77.48, 77.16, 76.85, 61.80, 58.56, 39.48, 31.36, 19.99, 13.97, 13.69.IR (KBr) 3237, 3074, 2981, 2961, 2884, 1753, 1662, 1571, 1461, 1382, 1267, 1241, 1192, 1092, 971, 771, 695, 596 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{15}H_{22}NO_3$,m/z $[M + H]^+$: 264.1600; found:264.1599.

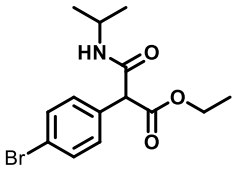
Ethyl 2-(4-bromophenyl)-3-(isopropylamino)-3-oxopropanoate (6d).



White solid in 71% yield (233 mg).Melting point:88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 6.76 (s, 1H), 4.40 (s, 1H), 4.24 – 4.13 (m, 2H), 4.04 (dd, J = 13.7, 6.9 Hz, 1H), 1.25 (d, J = 7.1 Hz, 3H), 1.13 (t, J = 6.4 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.56, 165.80, 133.39, 132.10, 130.05, 122.42, 77.48, 77.00, 62.09, 57.81, 41.86,

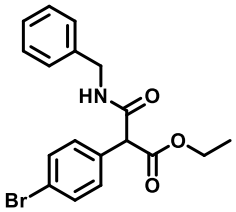
22.51, 14.02. IR (KBr) 3272, 3088, 2972, 2929, 2873, 1737, 1644, 1555, 1514, 1460, 1365, 1275, 1234, 1172, 1031, 757, 681, 507 (cm^{-1}). HRMS (ESI-MS)calcd for $C_{14}H_{19}BrNO_3$,m/z [M + H]$^+$: 328.0548; found:328.0551.

Ethyl 3-(isopropylamino)-3-oxo-2-(*p*-tolyl)propanoate (6e).



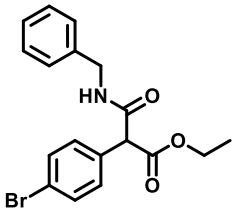
White solid in 68% yield(179 mg).`Melting point:98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.7 Hz, 2H), 6.70 (s, 1H), 4.45 (s, 1H), 4.25 – 4.14 (m, 2H), 4.12 – 4.02 (m, 1H), 2.34 (s, 3H), 1.26 (td, J = 7.1, 1.2 Hz, 3H), 1.14 (dd, J = 10.4, 6.6 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 174.33, 139.58, 128.63, 128.03, 127.19, 60.74, 51.92, 33.46, 29.87, 22.59, 14.26, 14.02.IR (KBr) 3373, 3041, 2974, 2917, 1744, 1695, 1544, 1463, 1430, 1372, 1309, 1230, 1180, 1077, 1025, 847, 740, 699, 606, 563, 502 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{14}H_{19}BrNO_3$,m/z [M + H]$^+$: 328.0548; found:328.0535.

Ethyl 3-(benzylamino)-2-(4-bromophenyl)-3-oxopropanoate (6f).



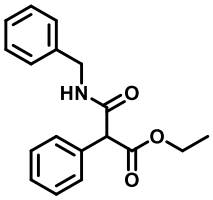
White solid in 94% yield (356 mg).Melting point: 84°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.33 (d, J = 4.8 Hz, 2H), 7.31 (d, J = 2.1 Hz, 2H), 7.27 (d, J = 4.4 Hz, 2H), 5.24 – 5.14 (m, 2H), 4.62 (s, 1H), 4.26 – 4.12 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.05, 131.27, 130.54, 128.02, 127.70, 76.85, 76.54, 76.22, 67.09, 61.60, 56.80, 13.44. IR (KBr) 3329, 3030, 2962, 2923, 2871, 1627, 1570, 1452, 1365, 1260, 1090, 1021, 866, 802, 751, 697, 589, 483 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{18}H_{19}BrNO_3$,m/z [M + H]$^+$: 376.0548; found:376.0546.

Methyl 3-(benzylamino)-3-oxo-2-phenylpropanoate (6g).



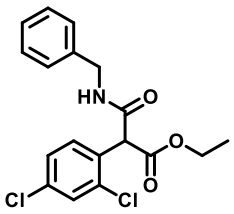
White solid in 90% yield(255 mg).Melting point: 78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.39 (s, 1H), 7.37 (d, J = 1.9 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.26 – 7.22 (m, 2H), 7.19 – 7.10 (m, 2H), 6.86 – 6.82 (m, 1H), 4.62 (s, 1H), 4.49 (d, J = 5.8 Hz, 2H), 3.78 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 171.22, 167.28, 133.96, 129.21, 128.78, 128.46, 127.87, 127.60, 114.05, 77.4, 77.16, 76.84, 58.45, 52.94, 43.76. IR (KBr) 3315, 3049, 3001, 2957, 2824, 1720, 1663, 1504, 1442, 1256, 1187, 1112, 1100, 1077, 987, 845, 804, 757 (cm^{-1}). HRMS (ESI-MS) calcd for $C_{17}H_{18}NO_3$, m/z $[M + H]^+$: 284.1287; found:284.1290.

Ethyl 3-(benzylamino)-3-oxo-2-phenylpropanoate (6h).



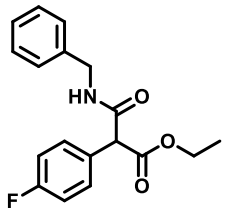
White solid in 91 % yield (271 mg).Melting point: 91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.47 – 7.43 (m, 2H), 7.42 – 7.38 (m, 2H), 7.38 – 7.36 (m, 1H), 7.34 (dd, *J* = 5.8, 1.5 Hz, 2H), 7.32 – 7.29 (m, 1H), 7.25 (d, *J* = 6.5 Hz, 2H), 4.61 (s, 1H), 4.49 (d, *J* = 5.8 Hz, 2H), 4.24 (qd, *J* = 10.8, 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.81, 167.39, 137.97, 134.17, 129.17, 128.77, 128.39, 127.59, 77.48, 77.16, 76.84, 62.03, 58.66, 43.75, 14.06. IR (KBr) 3386, 3030, 2983, 2937, 1723, 1672, 1527, 1453, 1428, 1366, 1310, 1227, 1178, 1078, 1021, 925, 808, 740, 699, 606, 563, 502, 473 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{18}H_{20}NO_3$,m/z $[M + H]^+$: 298.1443; found:298.1438.

Ethyl 3-(benzylamino)-2-(2,4-dichlorophenyl)-3-oxopropanoate (6i).



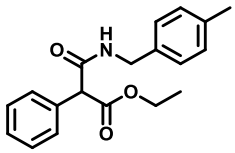
White solid in 88% yield(324 mg).Melting point: 86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 2.2 Hz, 1H), 7.33 (ddd, J = 7.3, 4.5, 1.6 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.25 (s, 1H), 6.86 (s, 1H), 4.97 (s, 1H), 4.48 (qd, J = 14.9, 5.8 Hz, 2H), 4.22 (qd, J = 7.1, 0.8 Hz, 2H), 1.58 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 131.52, 130.87, 129.66, 128.89, 127.93, 127.66, 77.48, 77.16, 76.84, 62.44, 54.70, 44.09, 14.09. IR (KBr) 3031, 2975, 2918, 2864, 1633, 1581, 1448, 1379, 1271, 1088, 1017, 859, 817, 756, 700, 588, 472 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{18}H_{18}Cl_2NO_3$, m/z $[M + H]^+$: 366.0664; found: 366.0667.

Ethyl 3-(benzylamino)-2-(4-fluorophenyl)-3-oxopropanoate (6j).



White solid in 88% yield(278 mg).Melting point: 108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 6.9 Hz, 2H), 7.40 (d, J = 7.3 Hz, 2H), 7.35 (d, J = 6.5 Hz, 2H), 7.32 (d, J = 6.3 Hz, 1H), 7.27 (d, J = 7.1 Hz, 2H), 5.18 – 5.05 (m, 1H), 4.61 (s, 1H), 4.49 (d, J = 5.5 Hz, 2H), 1.33 (d, J = 6.0 Hz, 3H), 1.23 (d, J = 6.0 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.09, 167.47, 137.97, 134.20, 129.49, 129.10, 129.10, 128.00, 127.43, 77.48, 77.16, 76.84, 69.59, 58.70, 43.55, 21.38. IR (KBr) 3389, 3031, 2981, 2936, 1730, 1658, 1518, 1454, 1428, 1365, 1310, 1280, 1231, 1180, 1106, 1079, 1013, 976, 914, 809, 743, 700, 606, 561, 505, 479, 421 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{18}H_{19}FNO_3$,m/z $[M + H]^+$: 316.1349; found:316.1345.

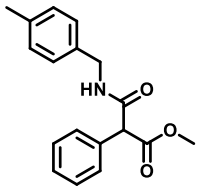
Ethyl 3-((4-methylbenzyl)amino)-3-oxo-2-phenylpropanoate (6k).



White solid in 89 % yield (277 mg).Melting point: 94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.31 – 7.27 (m, 2H), 7.16 (d, J = 4.5 Hz, 1H), 7.12 (s, 1H), 7.12 (s, 2H), 4.48 (s, 1H), 4.40 (dd, J = 5.7, 2.6 Hz, 2H), 4.19 (dddd, J = 17.9, 10.8, 7.1, 3.7 Hz, 2H), 2.33 (s, 3H), 1.25 (dd, J = 9.5, 4.8 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.50, 166.67, 133.20, 132.25, 130.13, 129.52, 127.75, 77.48, 77.16, 76.84, 62.26, 57.89, 43.66, 21.23, 14.07. IR (KBr) 3348,

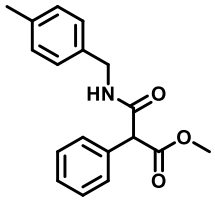
3033, 2980, 2938, 1732, 1656, 1521, 1455, 1355, 1309, 1578, 1230, 1178, 1102, 1017,973, 807, 742, 702, 605, 505, 422 cm-1. HRMS (ESI-MS) calcd for $C_{19}H_{22}NO_3$, m/z $[M + H]^+$: 312.1600; found: 312.1613.

Methyl 3-((4-methylbenzyl)amino)-3-oxo-2-phenylpropanoate (6l).



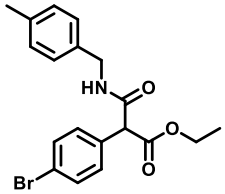
White solid in 81 % yield (241 mg).Melting point: 92 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 4H), 7.53 (dd, J = 8.0, 5.1 Hz, 4H), 7.49 – 7.47 (m, 2H), 7.34 – 7.30 (m, 4H), 7.28 (s, 4H), 7.01 – 6.93 (m, 1H), 4.74 (s, 2H), 4.55 (d, J = 5.7 Hz, 4H), 3.89 (s, 6H), 2.48 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.14, 167.17, 137.20, 134.84, 133.99, 129.40, 129.14, 128.43, 127.62, 114.05, 77.48, 77.16, 76.84, 58.46, 52.86, 43.52, 21.17. IR (KBr) 3300, 3023, 2991, 2945, 2837, 1731, 1641, 1510, 1439, 1251, 1178, 1137, 1114, 1077, 968, 839, 822, 743 (cm^{-1}). HRMS (ESI-MS) calcd for $C_{18}H_{20}NO_3$, m/z$[M + H]^+$: 298.1443; found:298.1447.

Ethyl 3-((4-methylbenzyl)amino)-3-oxo-2-(*p*-tolyl)propanoate (6m).



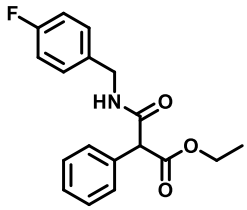
White solid in 89% yield (290 mg).Melting point: 83°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.31 (s, 2H), 7.30 (d, J = 2.9 Hz, 2H), 7.19 (s, 1H), 4.67 (s, 1H), 4.55 (dd, J = 5.7, 1.9 Hz, 2H), 4.34 (dd, J = 15.7, 7.2 Hz, 2H), 2.48 (s, 3H), 2.47 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.95, 167.52, 138.24, 137.22, 134.98, 131.17, 129.88, 129.51, 128.27, 127.98, 127.66, 77.48, 77.16, 76.84, 61.94, 58.39, 43.53, 21.21, 14.09. IR (KBr) 3386, 3030, 2983, 2937, 1723, 1672, 1527, 1453, 1428, 1366, 1310, 1227, 1178, 1078, 1021, 740, 699, 606, 563, 502 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{20}H_{24}NO_3$,m/z $[M + H]^+$: 326.1756; found: 326.1748.

Ethyl 2-(4-bromophenyl)-3-((4-methylbenzyl)amino)-3-oxopropanoate (6n).



White solid in 83% yield(325 mg).Melting point: 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.30 – 7.26 (m, 2H), 7.18 – 7.12 (m, 2H), 7.12 (s, 2H), 4.48 (s, 1H), 4.40 (dd, J = 5.7, 2.6 Hz, 2H), 4.19 (dd, J = 10.7, 7.1 Hz, 2H), 2.33 (s, 3H), 1.23 (d, J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.50, 166.67, 133.20, 132.25, 130.13, 129.52, 127.75, 77.48, 77.16, 76.84, 62.26, 57.89, 43.66, 21.23, 14.07. IR (KBr) 3456, 3283, 3064, 2978, 2924, 1739, 1646, 1544, 1488, 1448, 1366, 1327, 1268, 1232, 1178, 1073, 1019, 890, 805, 737, 600, 502 (cm^{-1}).HRMS (ESI-MS) calcd for $C_{19}H_{21}BrNO_3$, m/z $[M + H]^+$: 390.0705; found: 390.0683.

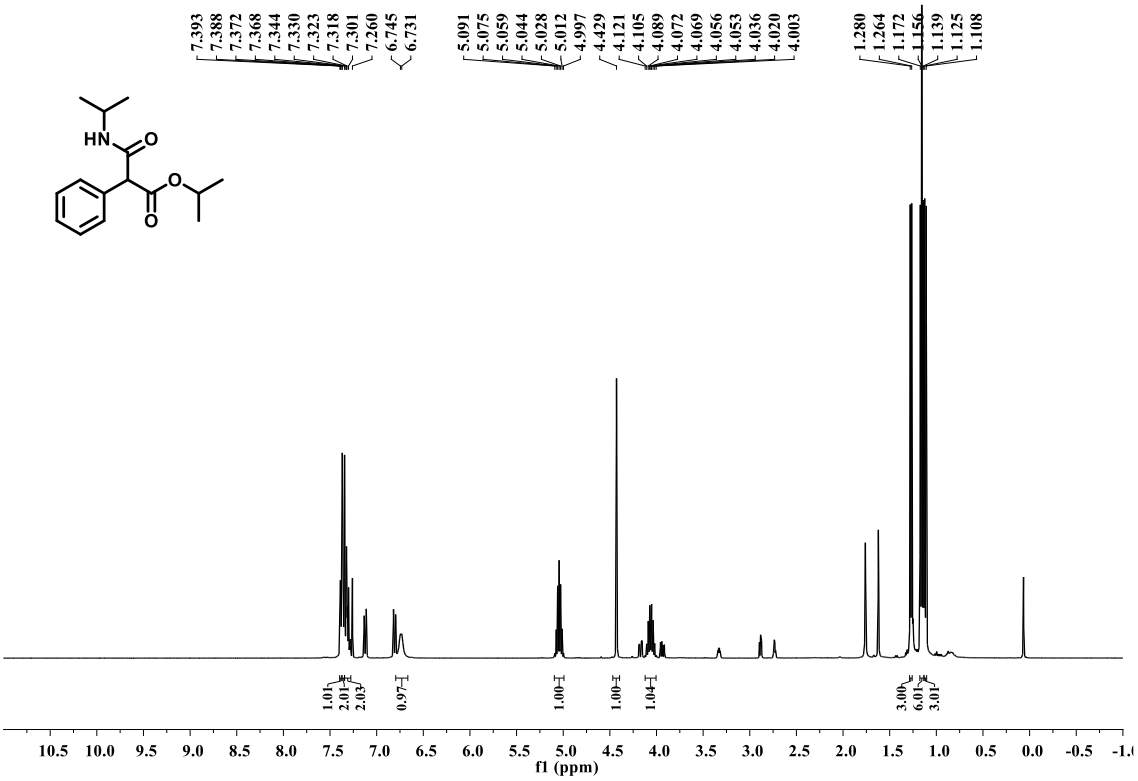
Ethyl 3-((4-fluorobenzyl)amino)-3-oxo-2-phenylpropanoate (6o).

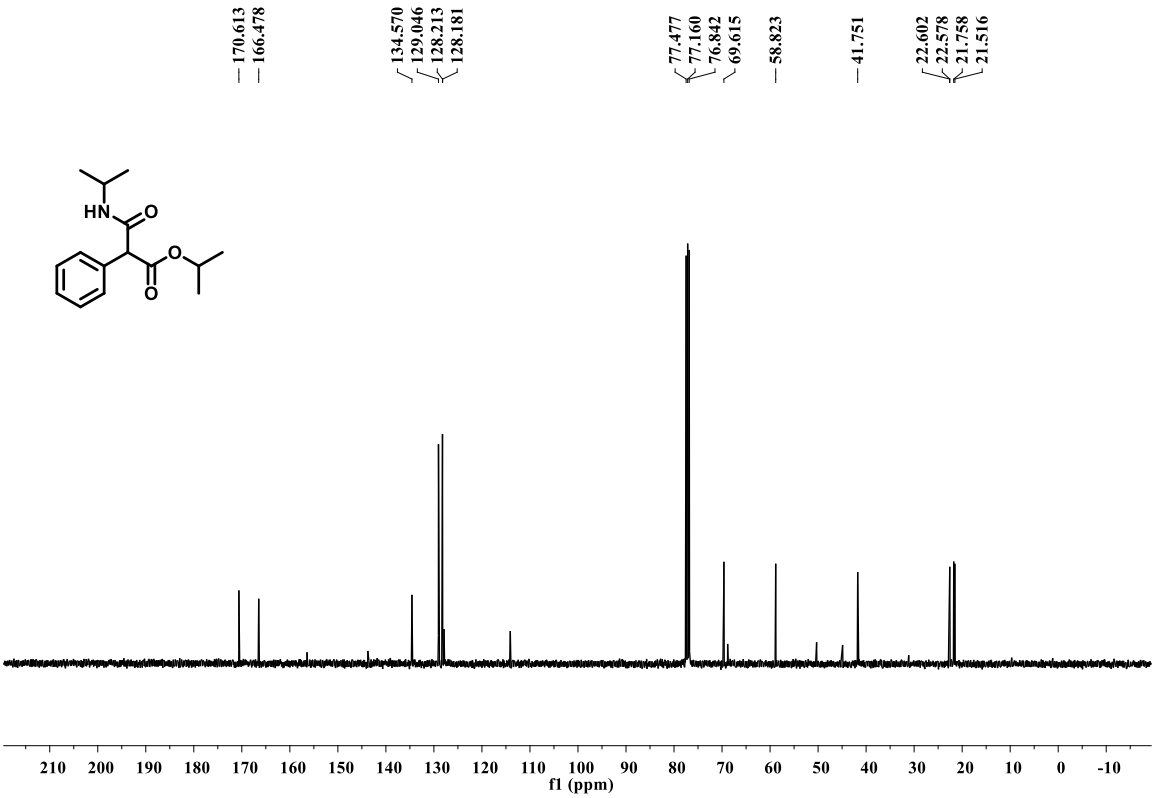


White solid in 81% yield (256 mg).Melting point: 66 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, J = 4.2, 2.1 Hz, 1H), 7.39 – 7.36 (m, 2H), 7.35 (dd, J = 4.8, 2.4 Hz, 2H), 7.18 (dd, J = 8.7, 5.4 Hz, 3H), 6.98 (t, J = 8.7 Hz, 2H), 4.56 (s, 1H), 4.42 (d, J = 5.8 Hz, 2H), 4.27 – 4.13 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.94, 167.43, 134.15, 129.55, 129.16, 128.50, 128.30, 115.75, 115.54, 77.48, 77.16, 76.84, 62.12, 58.61, 43.05, 14.08. IR (KBr) 3303, 3065, 2982, 2937, 1740, 1652, 1610, 1536, 1510, 1438, 1364, 1311, 1228, 1184, 1095, 1022, 827, 751, 701, 585, 491 (cm^{-1}). HRMS (ESI-MS) calcd for $C_{18}H_{19}FNO_3$,m/z $[M + H]^+$: 316.1349; found: 316.1358.

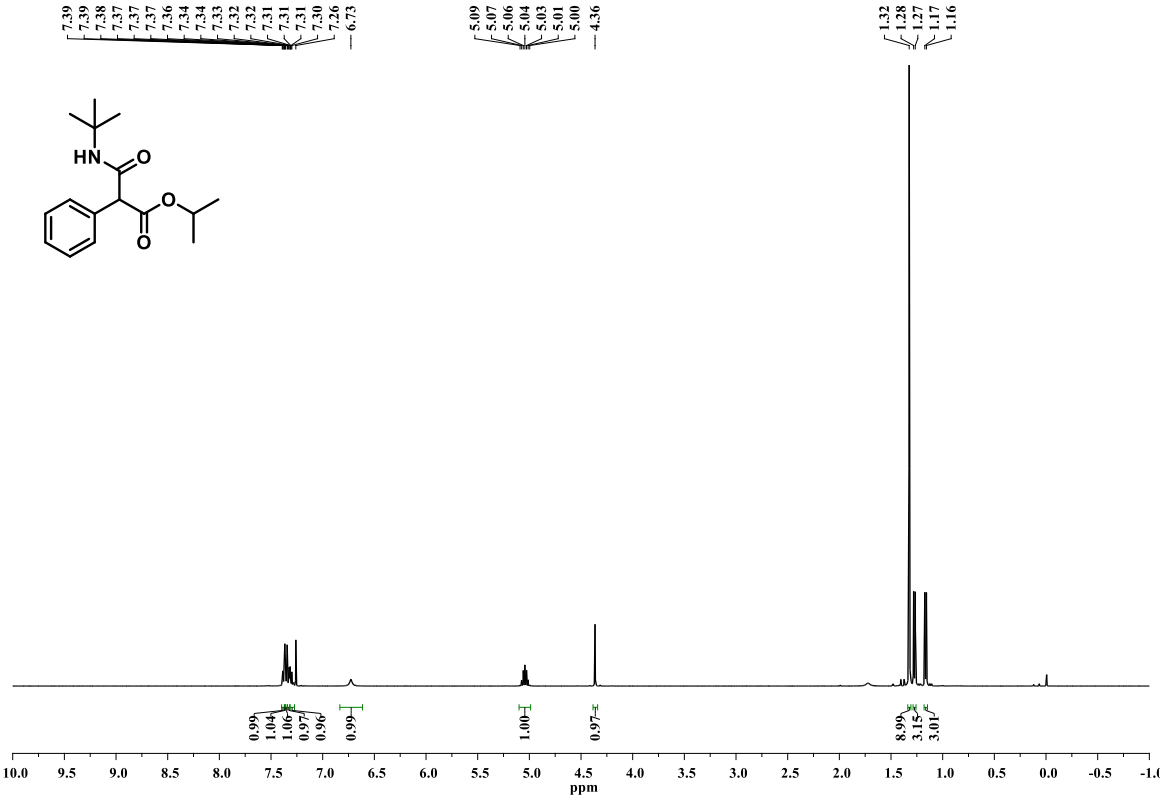
Analytical data

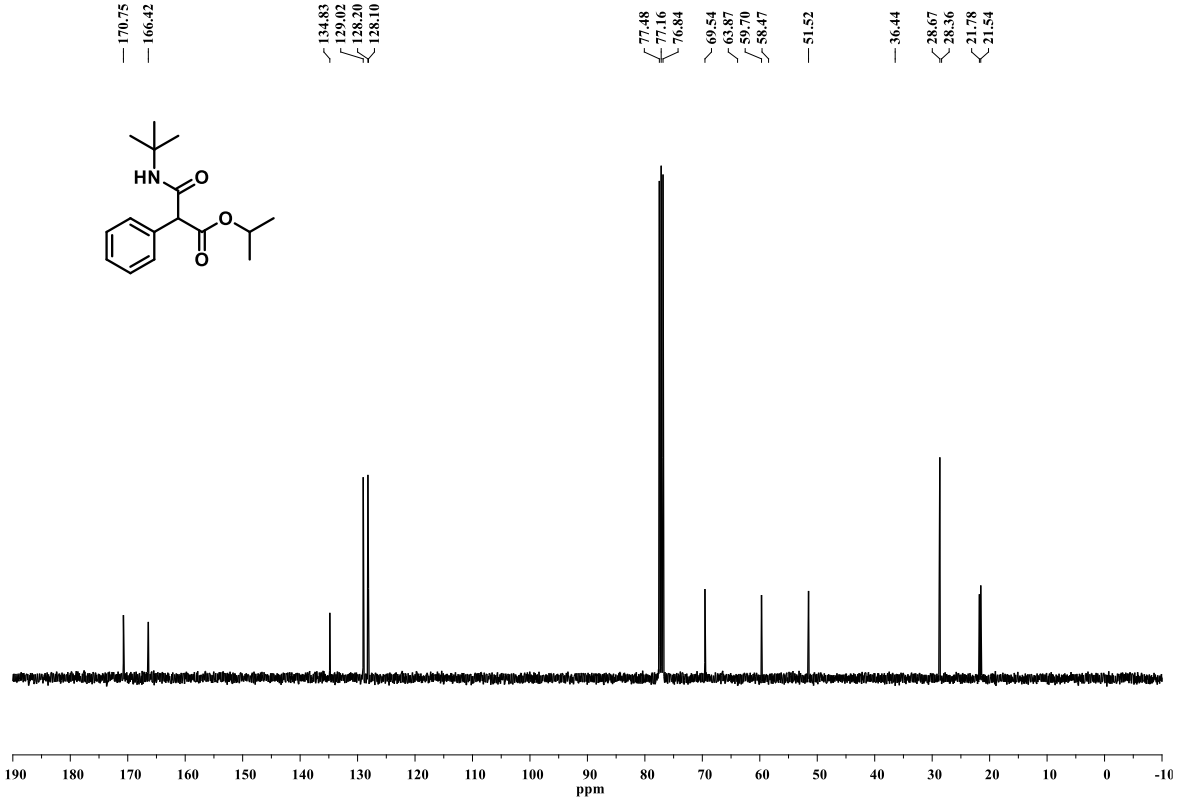
Isopropyl 3-(isopropylamino)-3-oxo-2-phenylpropanoate (3a)



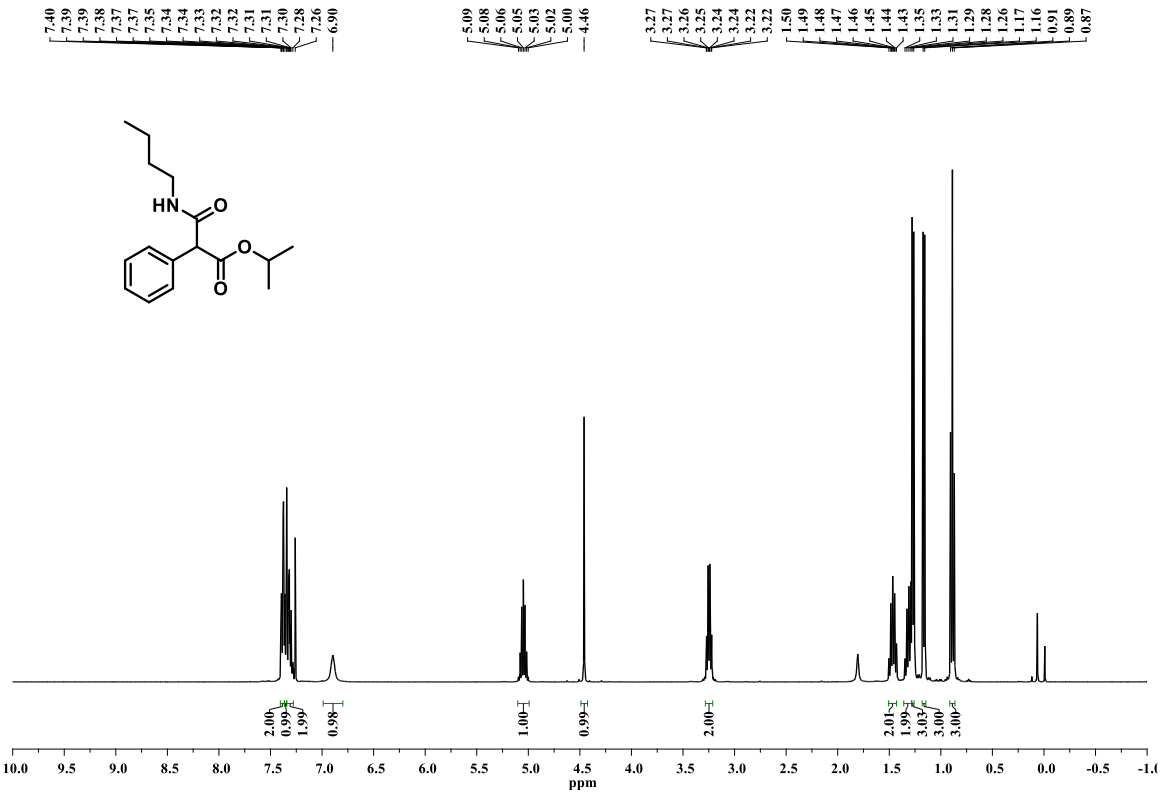


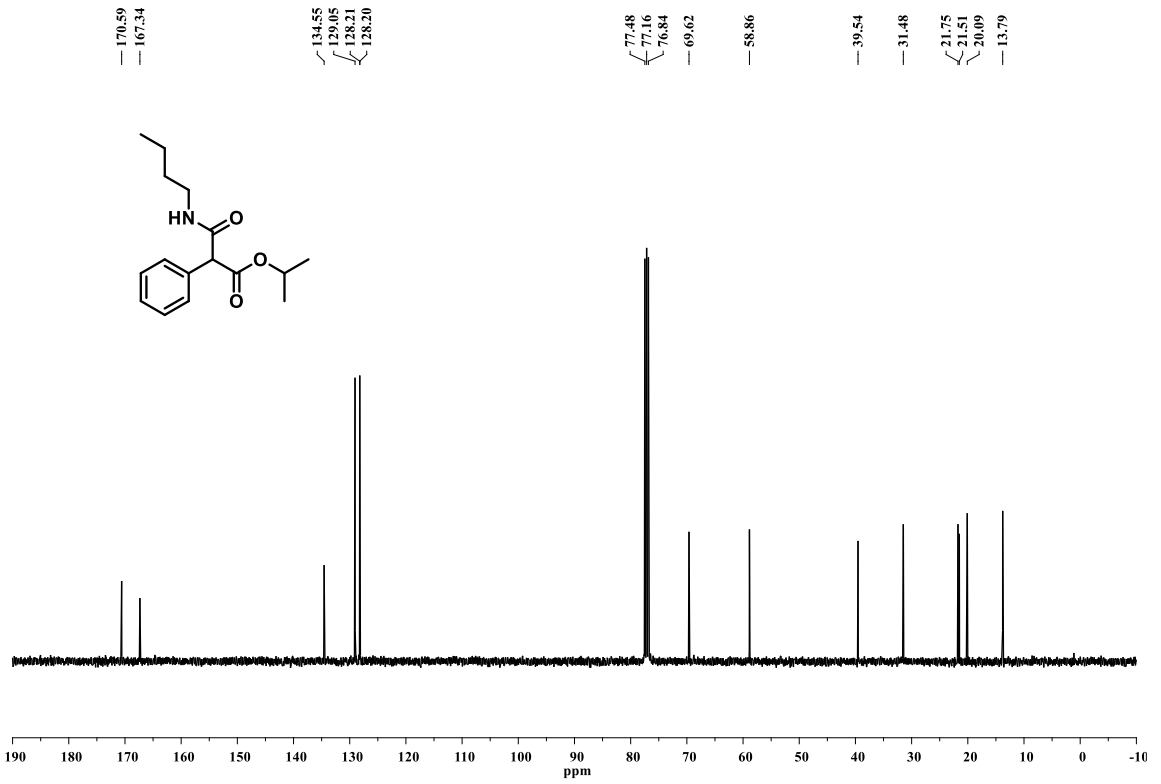
Isopropyl 3-(tert-butylamino)-3-oxo-2-phenylpropanoate (3b)



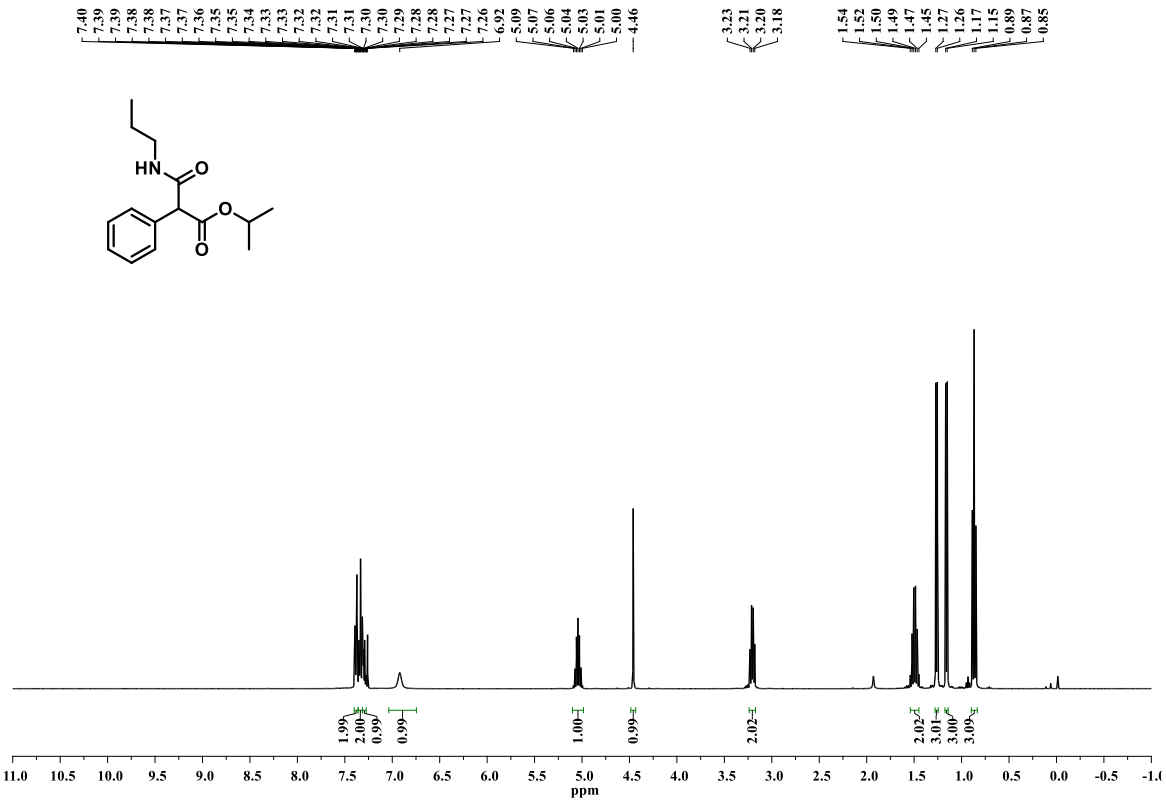


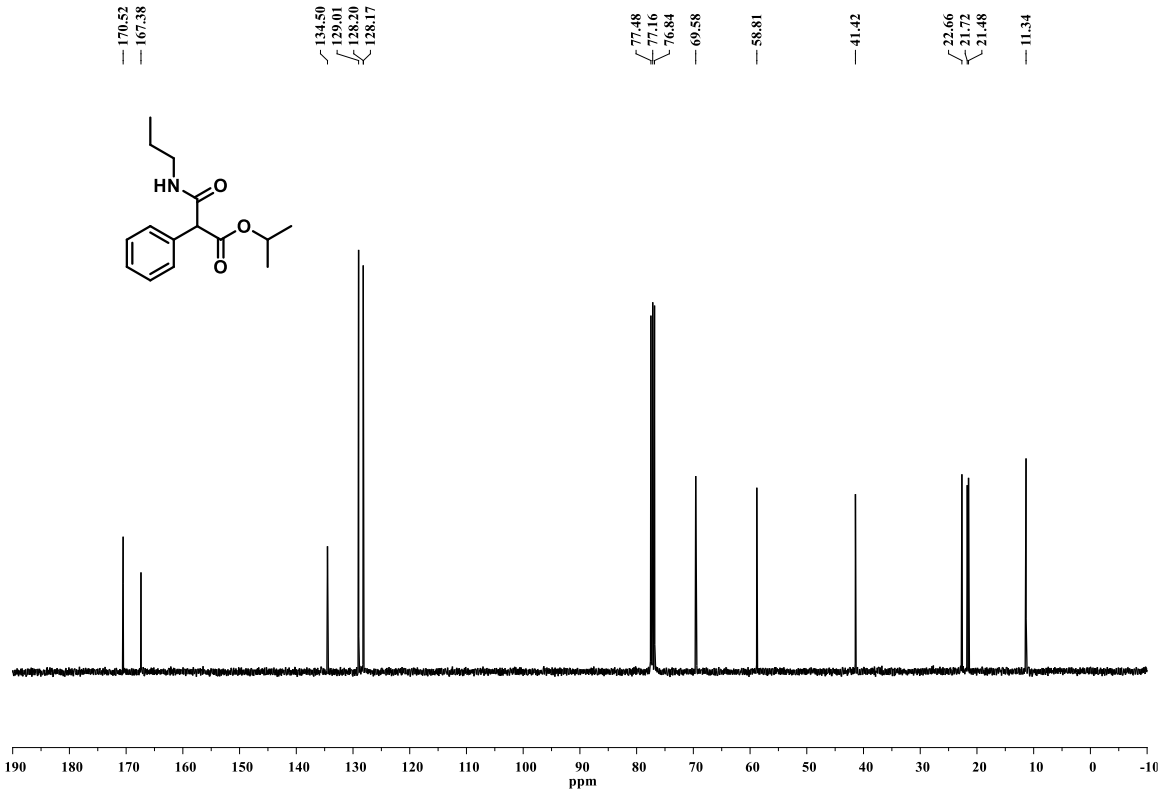
Isopropyl 3-(butylamino)-3-oxo-2-phenylpropanoate(3c)



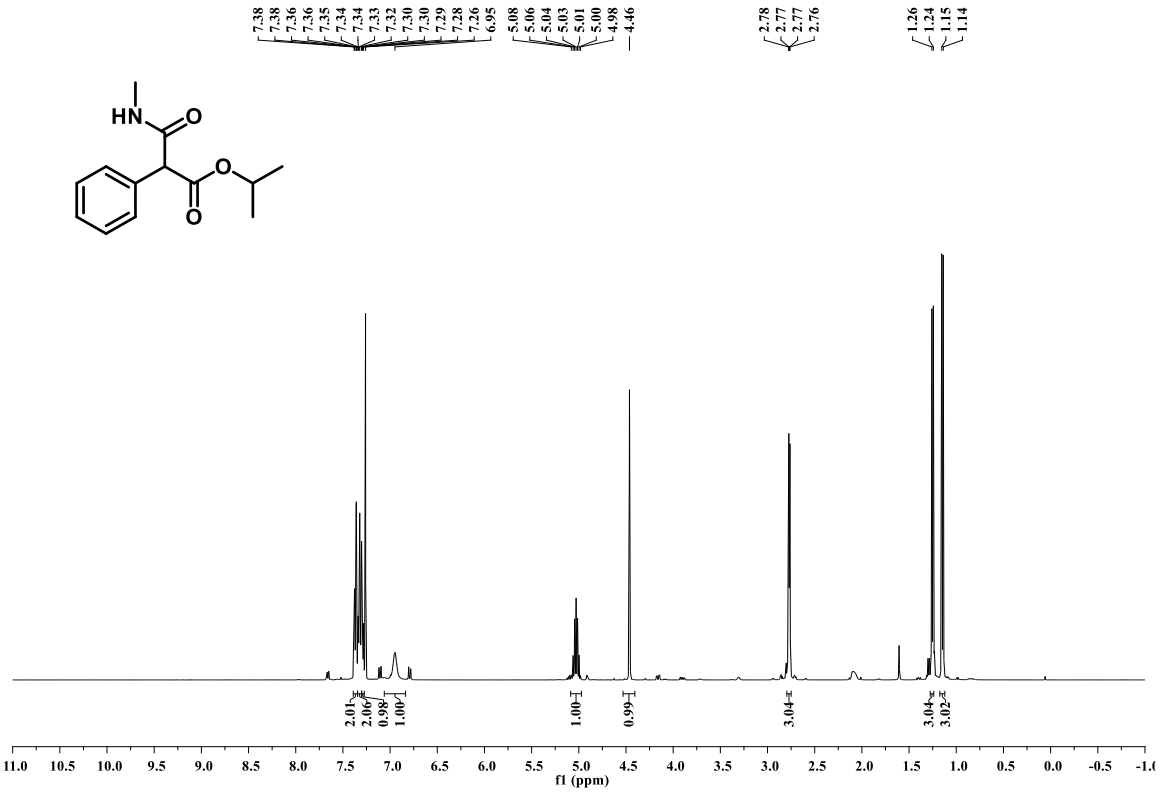


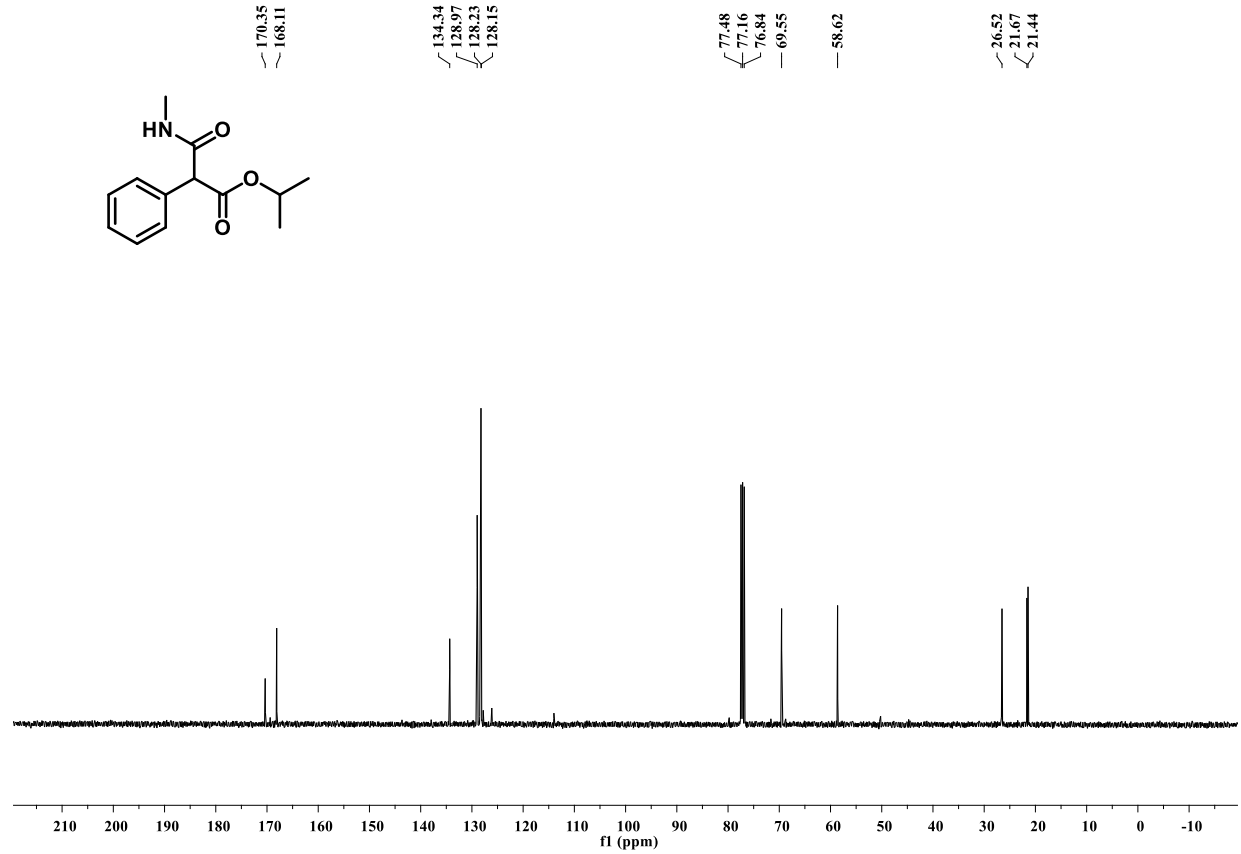
Isopropyl 3-oxo-2-phenyl-3-(propylamino)propanoate (3d)



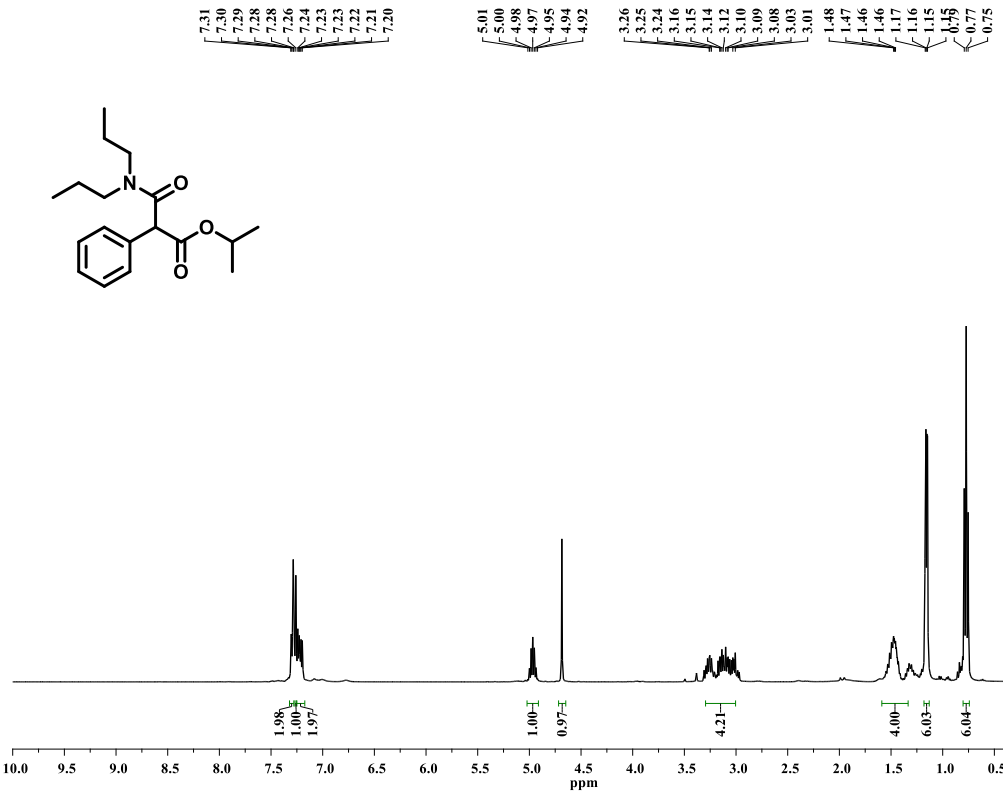


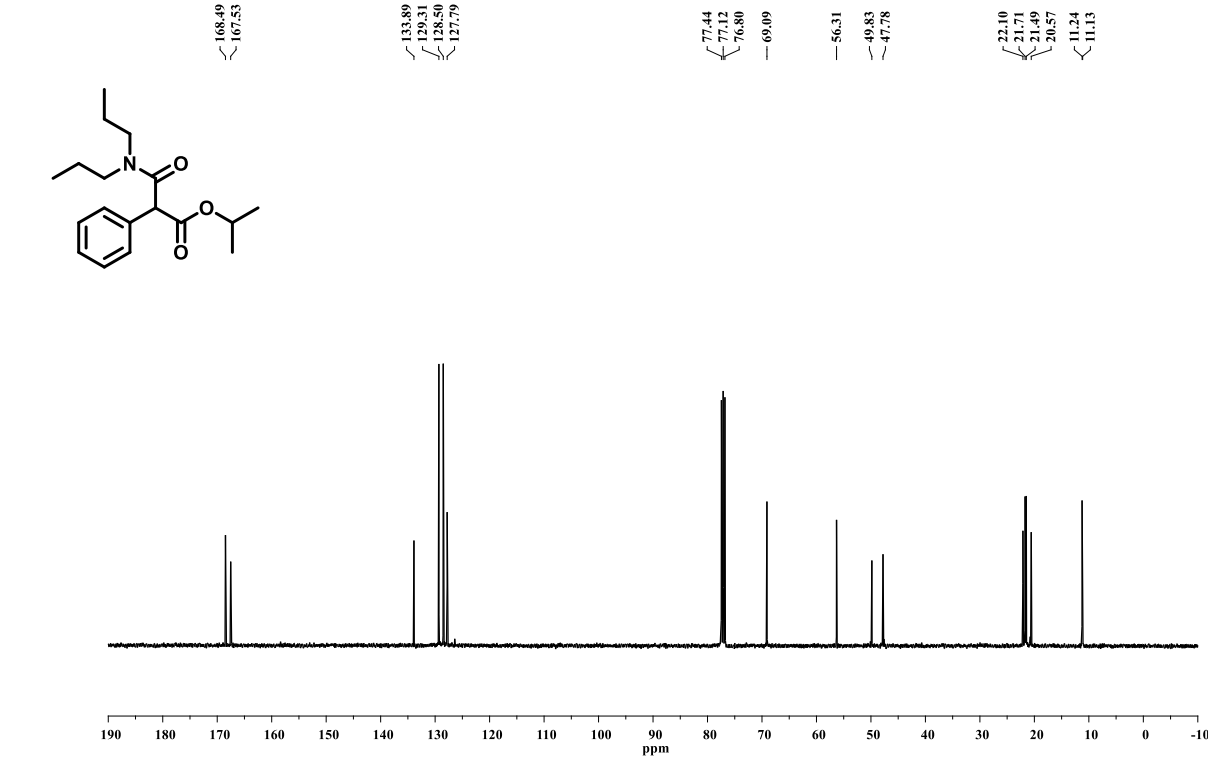
Isopropyl 3-(methylamino)-3-oxo-2-phenylpropanoate (3e)



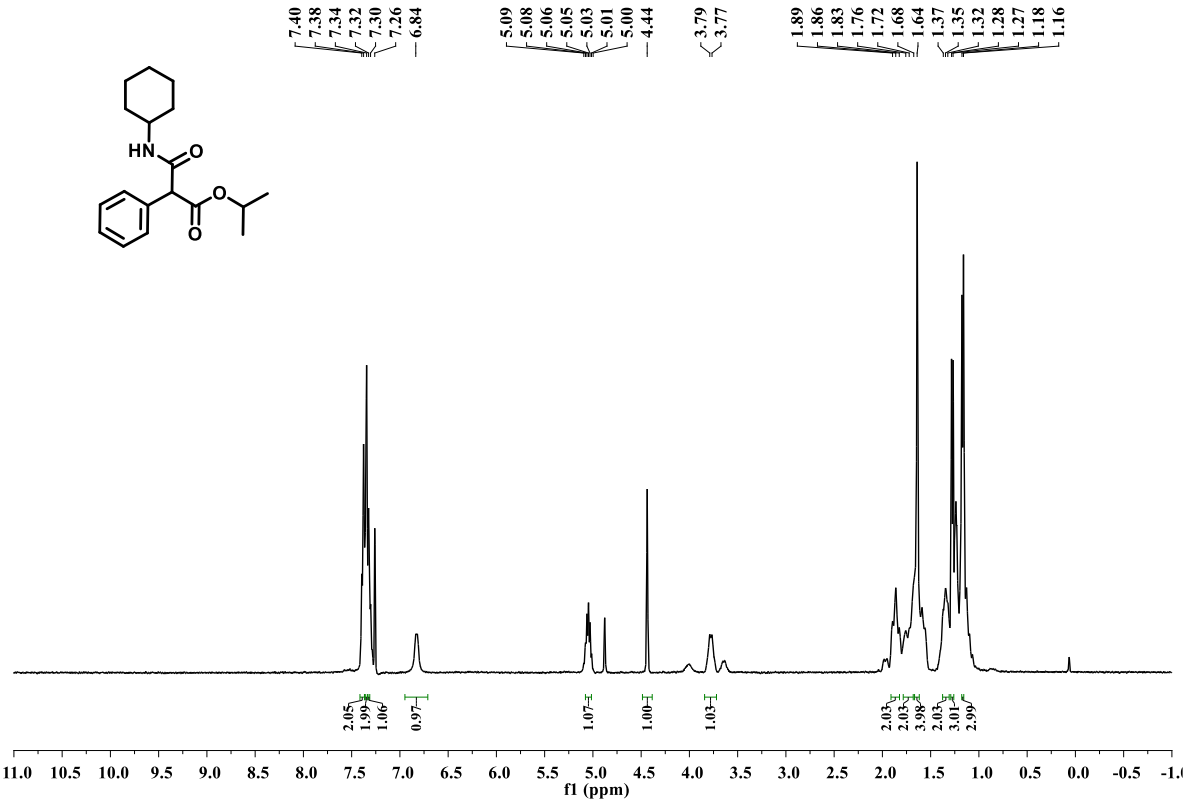


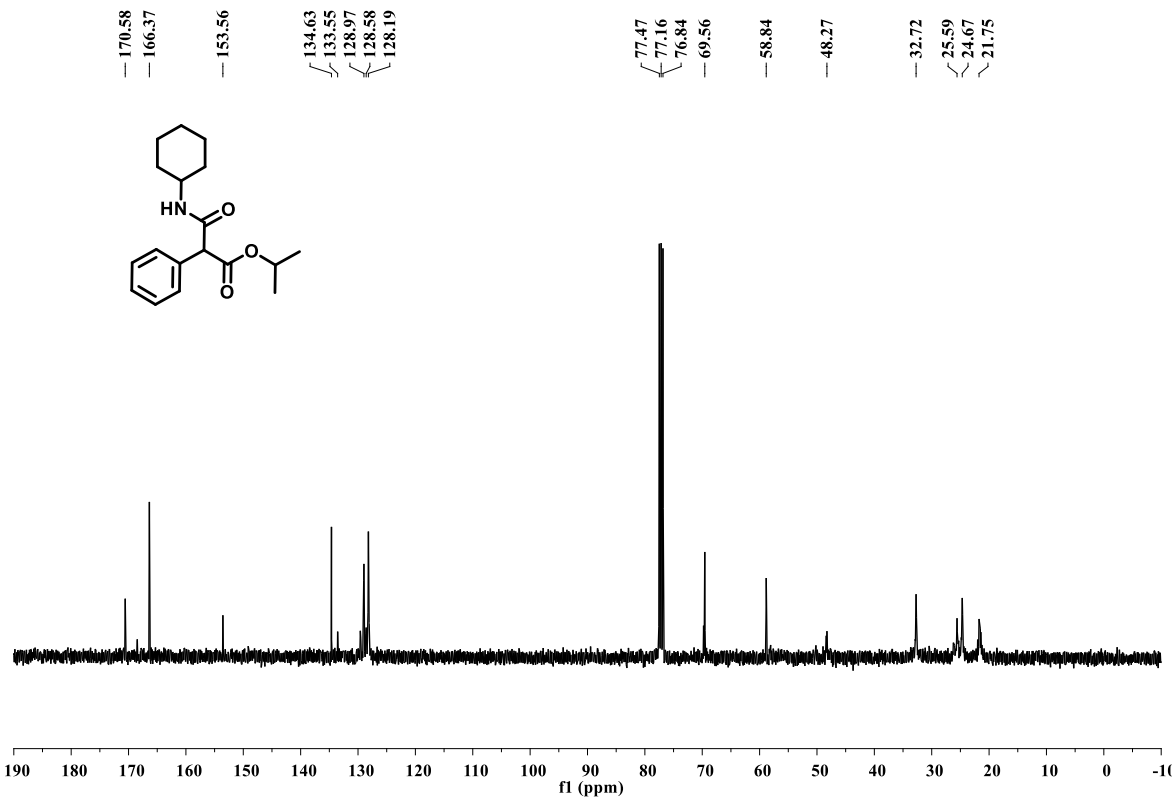
Isopropyl 3-(dipropylamino)-3-oxo-2-phenylpropanoate (3f)



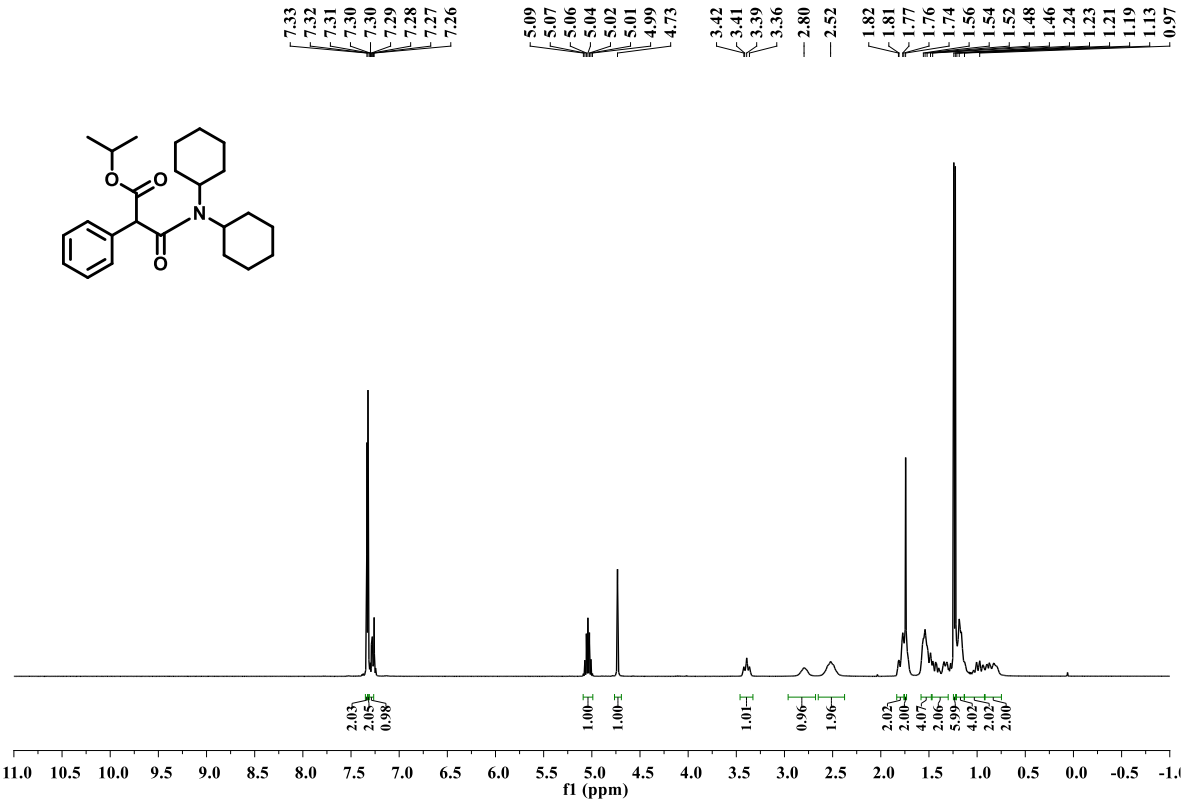


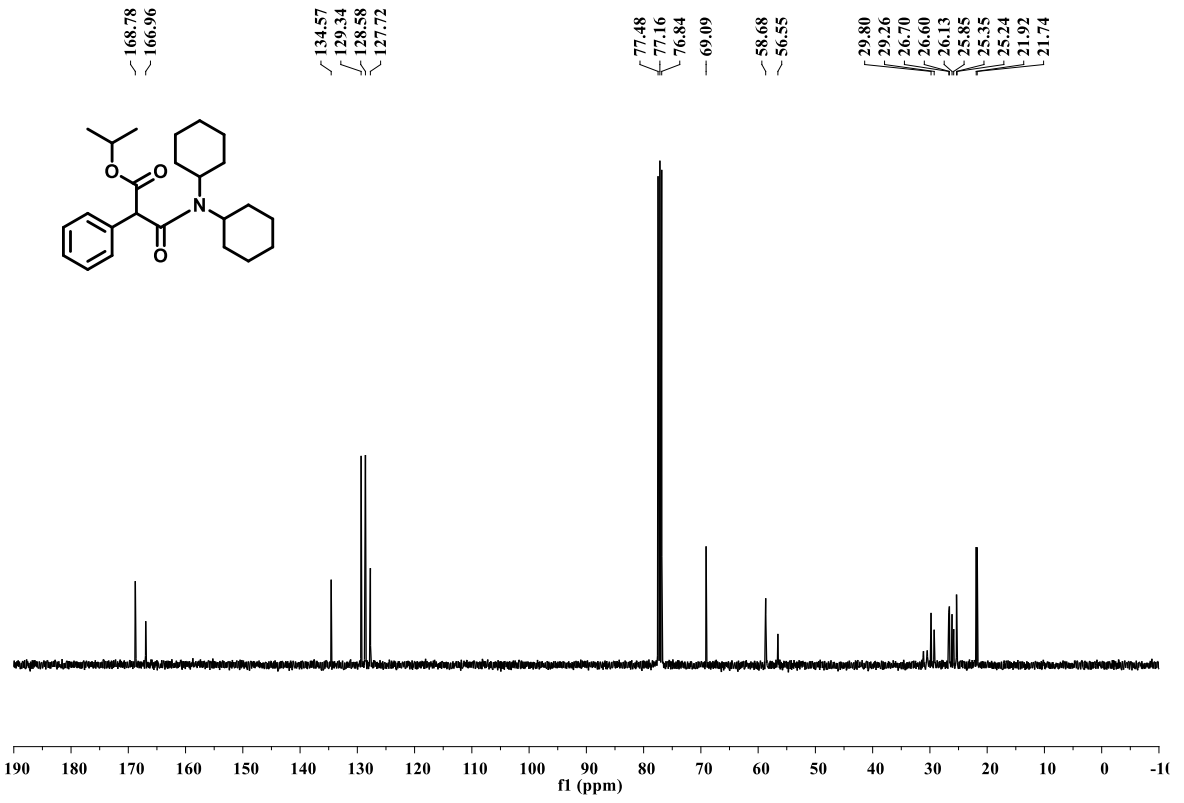
Isopropyl 3-(cyclohexylamino)-3-oxo-2-phenylpropanoate (3g)



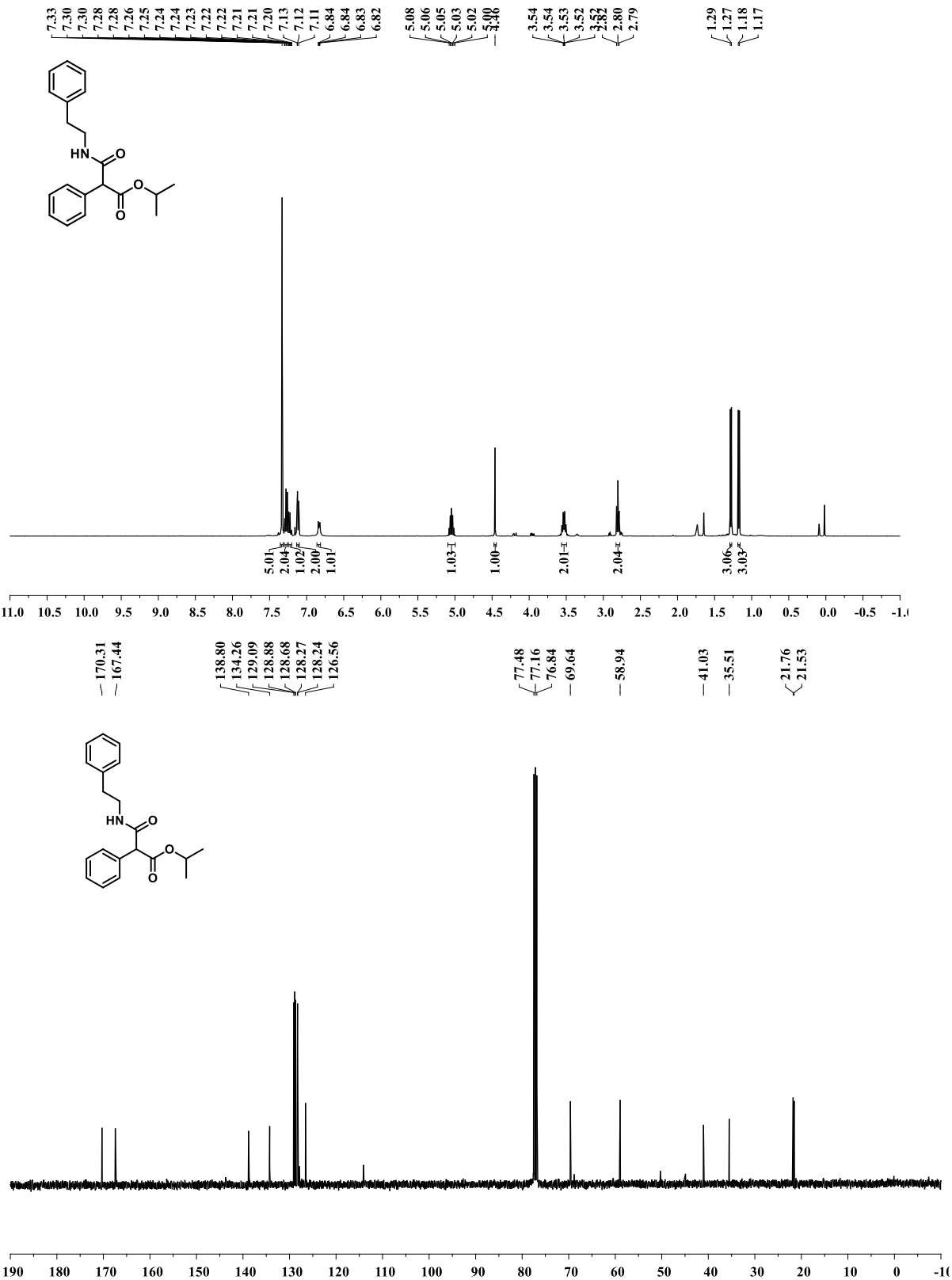


Isopropyl 3-(dicyclohexylamino)-3-oxo-2-phenylpropanoate (3h)

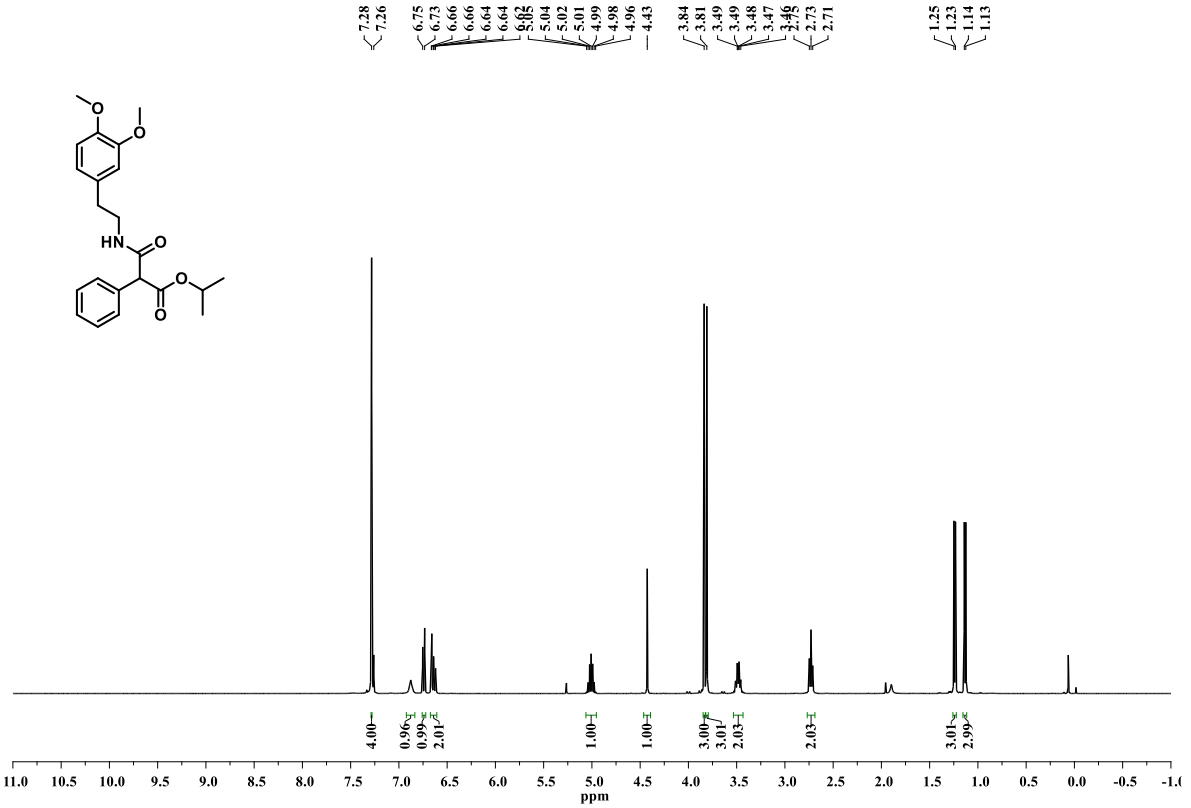


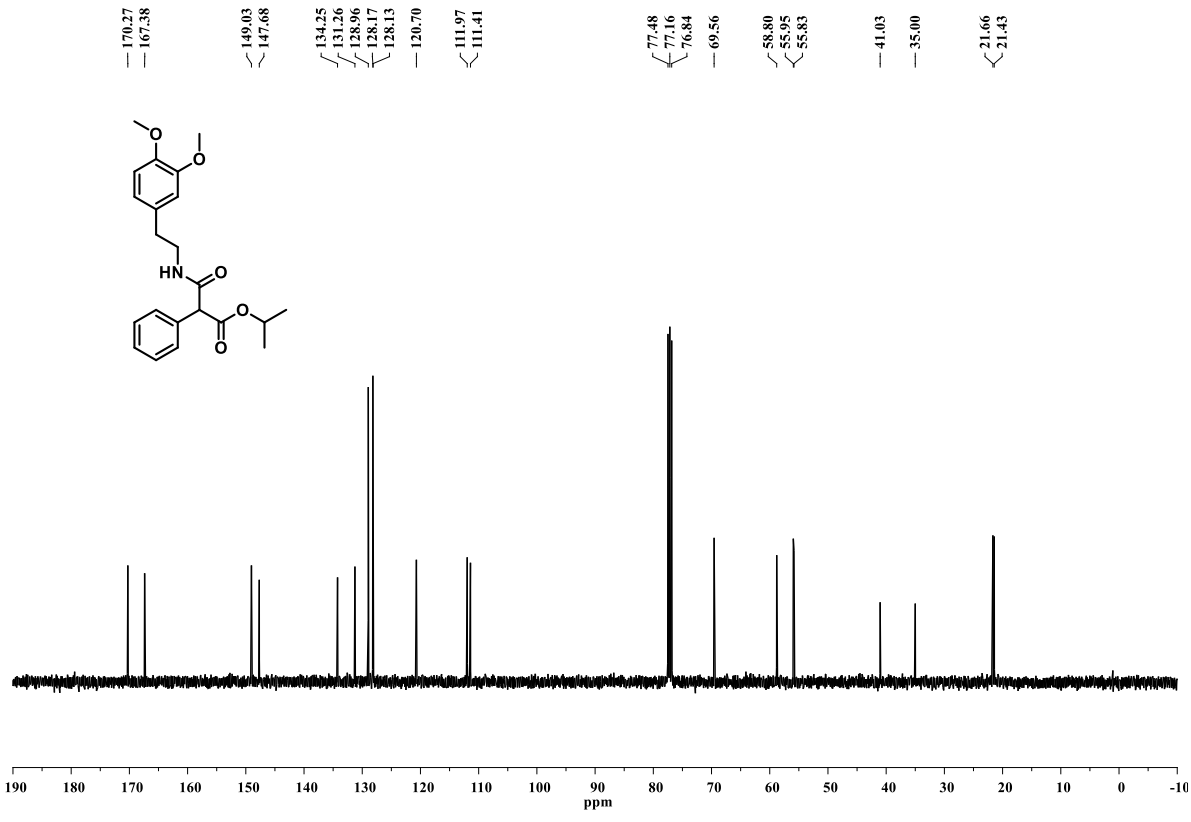


Isopropyl 3-oxo-3-(phenethylamino)-2-phenylpropanoate (3i)

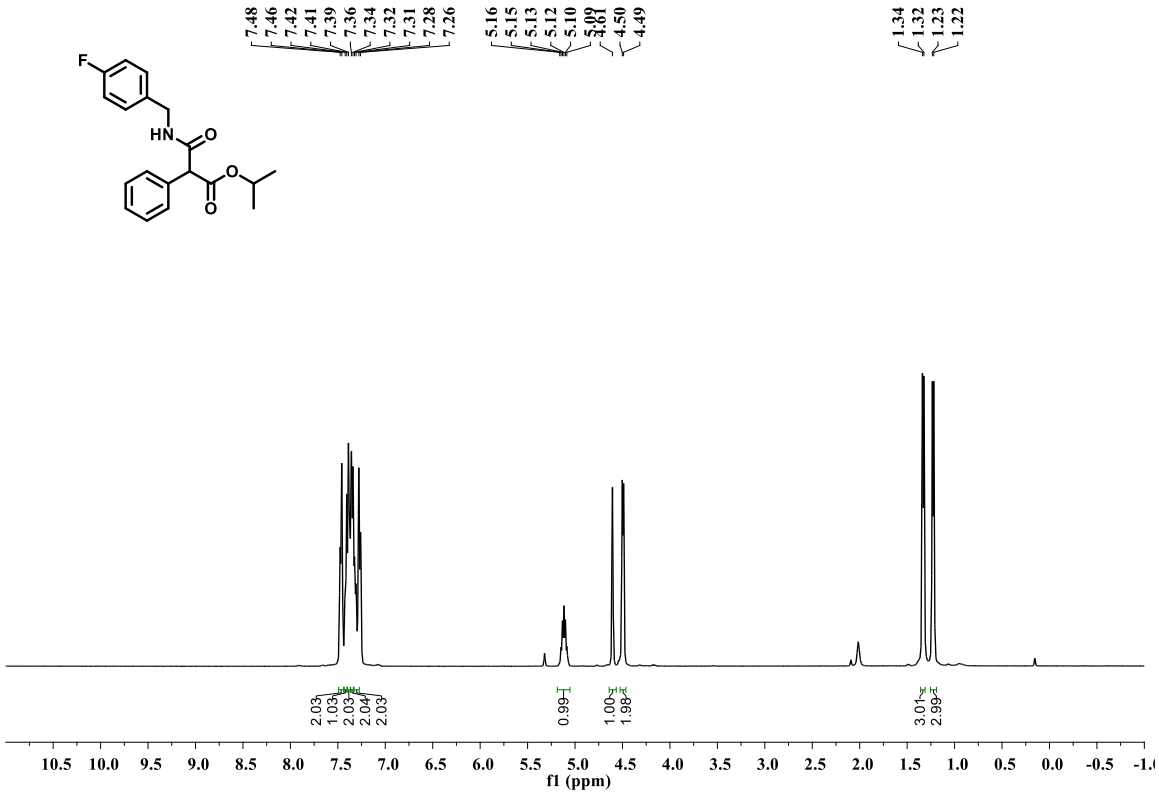


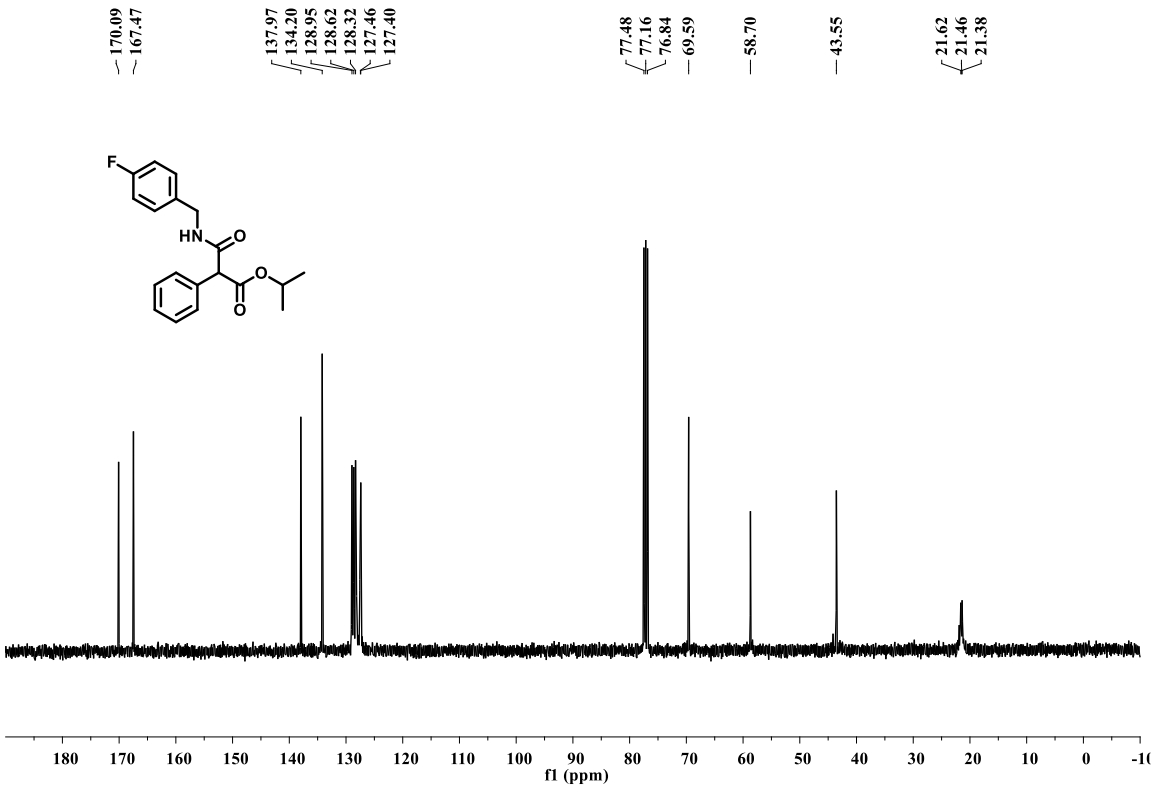
Isopropyl 3-((3,4-dimethoxyphenethyl)amino)-3-oxo-2-phenylpropanoate (3j)



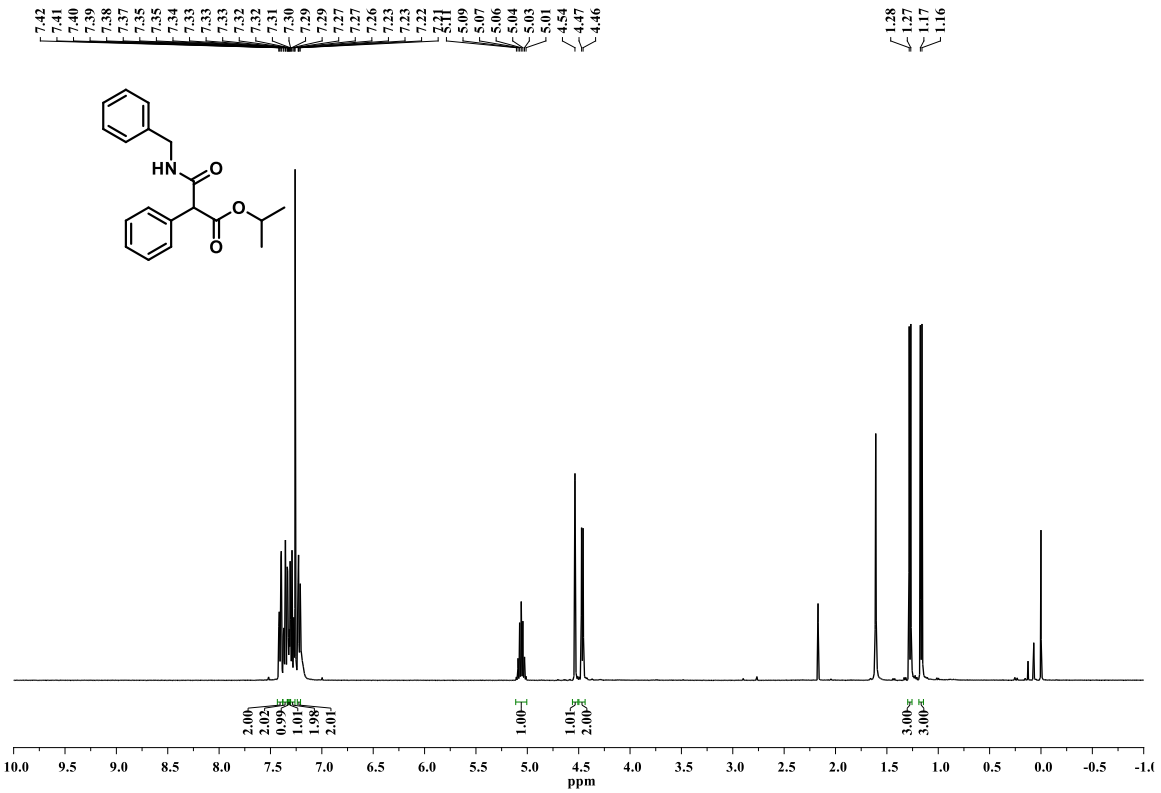


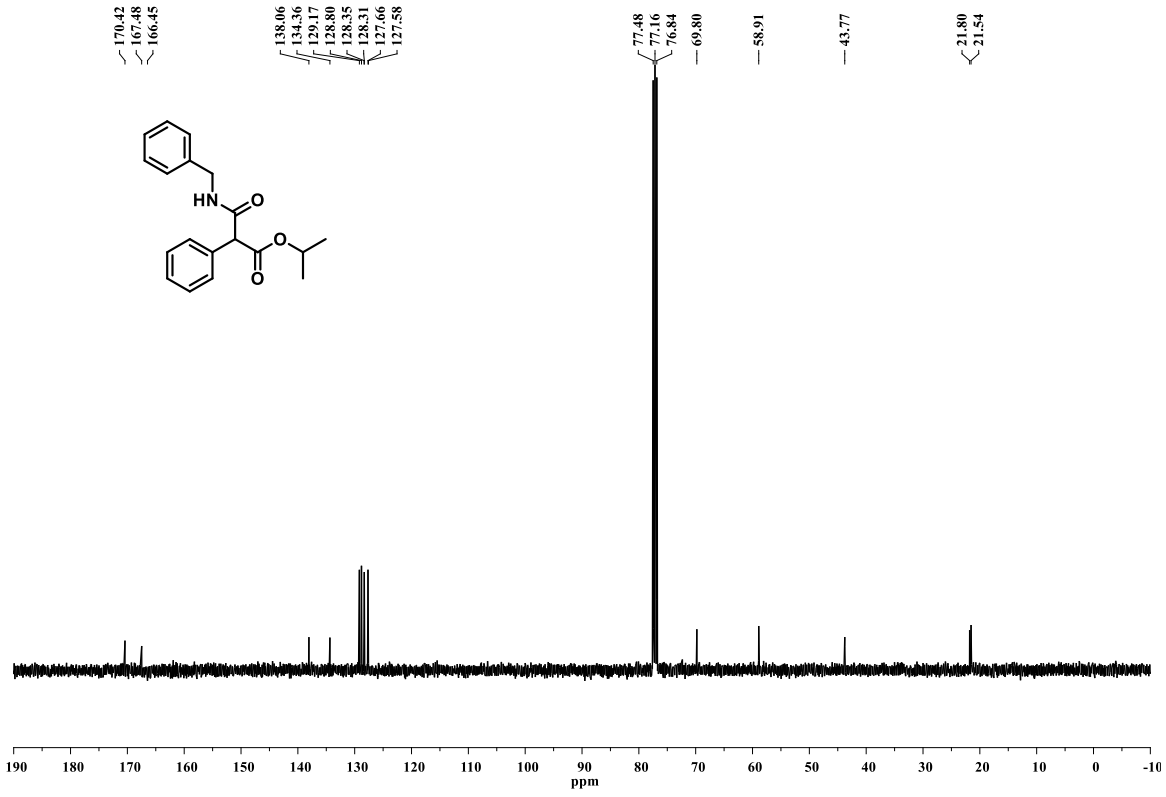
Isopropyl 3-((4-fluorobenzyl)amino)-3-oxo-2-phenylpropanoate (3k)



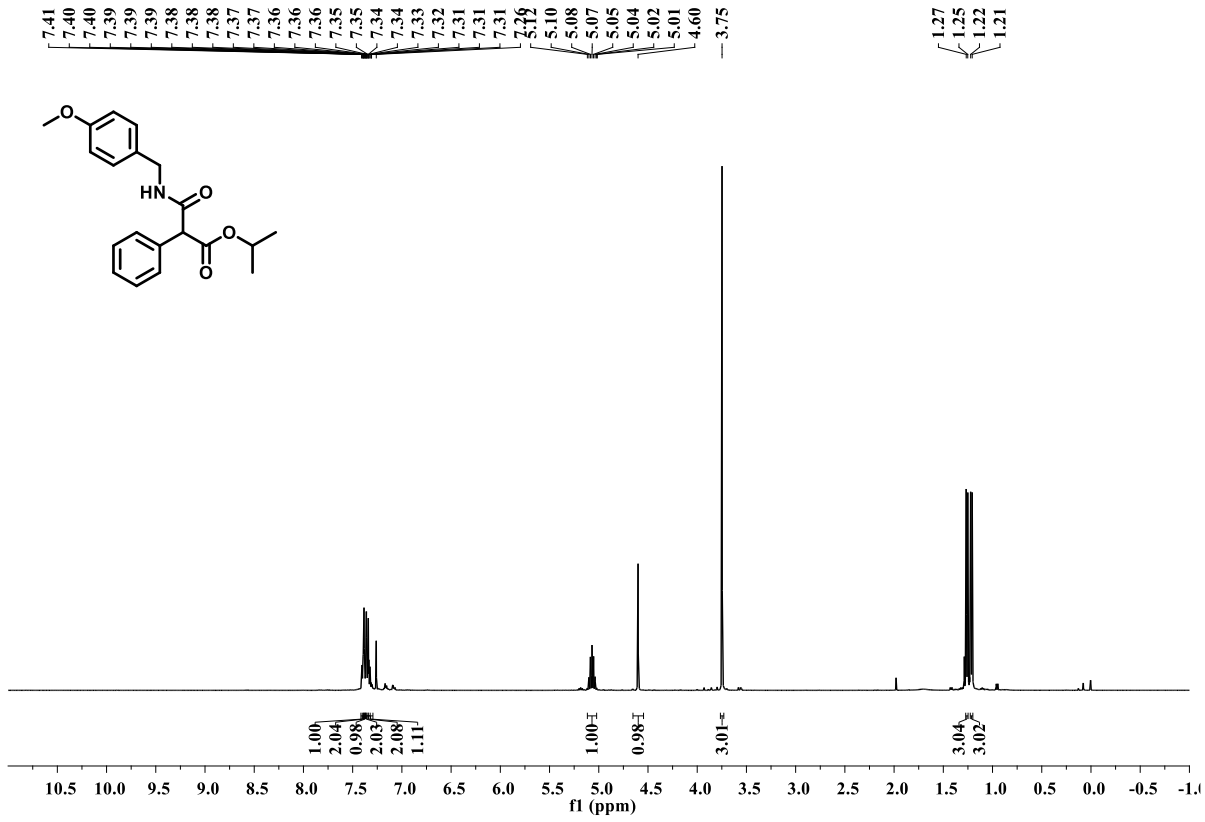


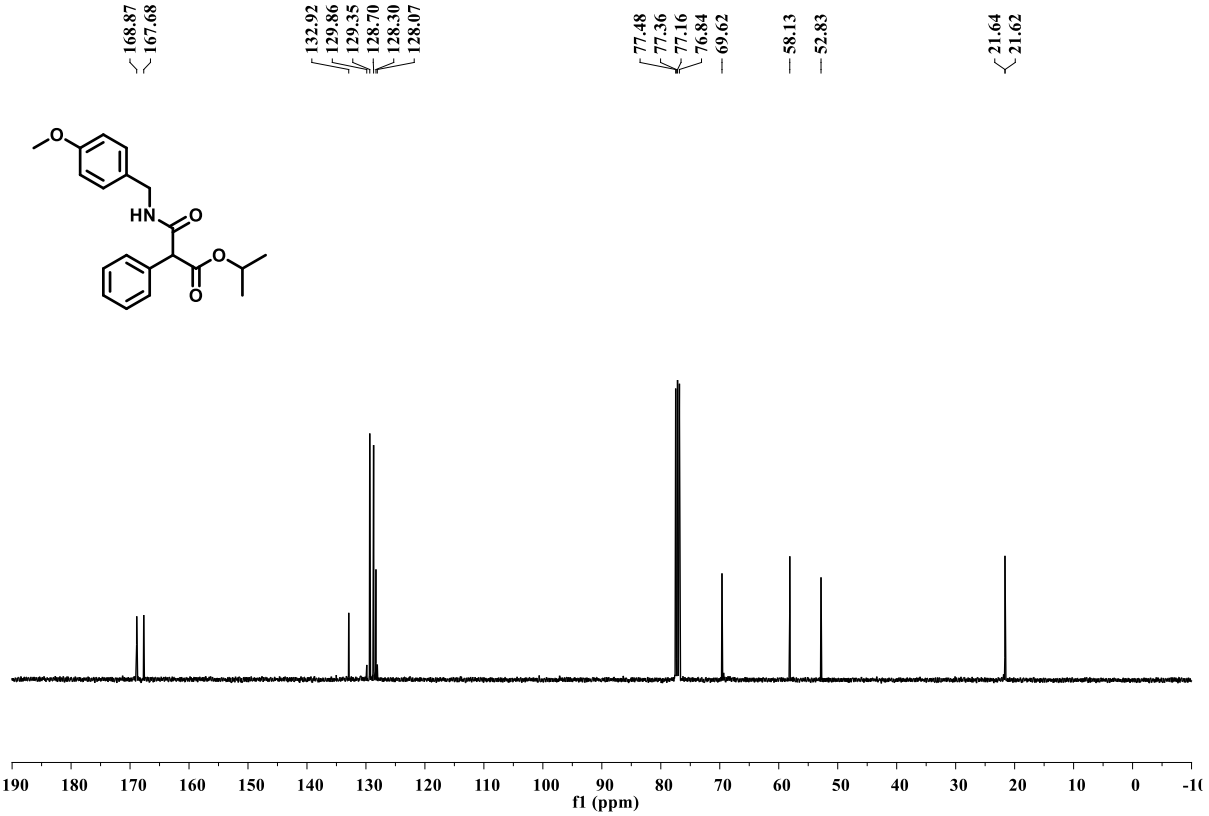
Isopropyl 3-(benzylamino)-3-oxo-2-phenylpropanoate (3l)



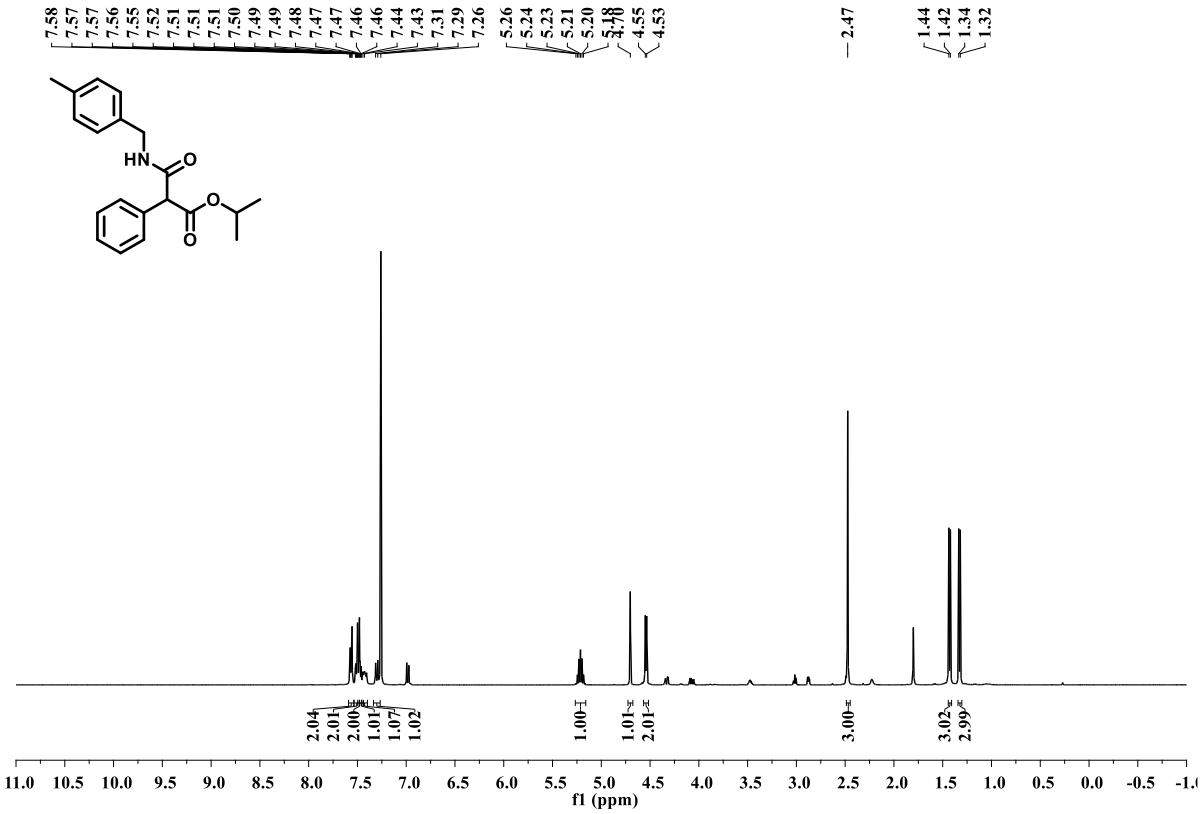


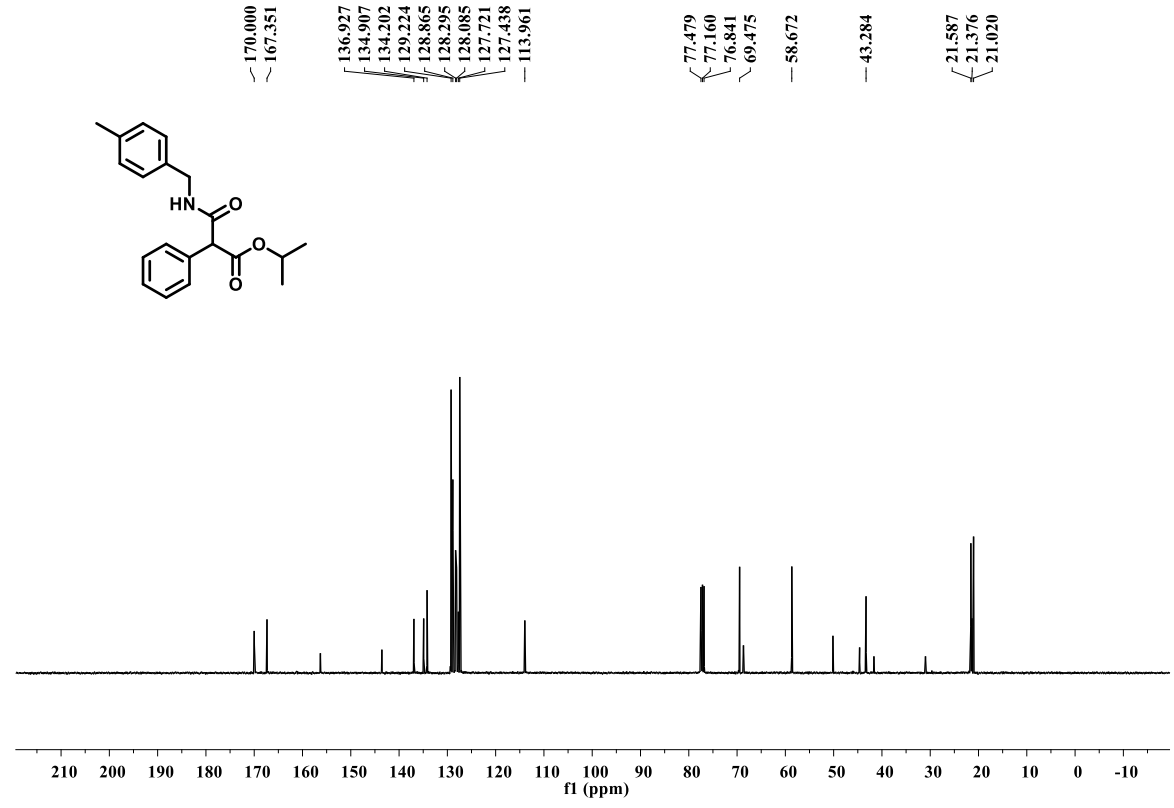
Isopropyl 3-((4-methoxybenzyl)amino)-3-oxo-2-phenylpropanoate (3m)



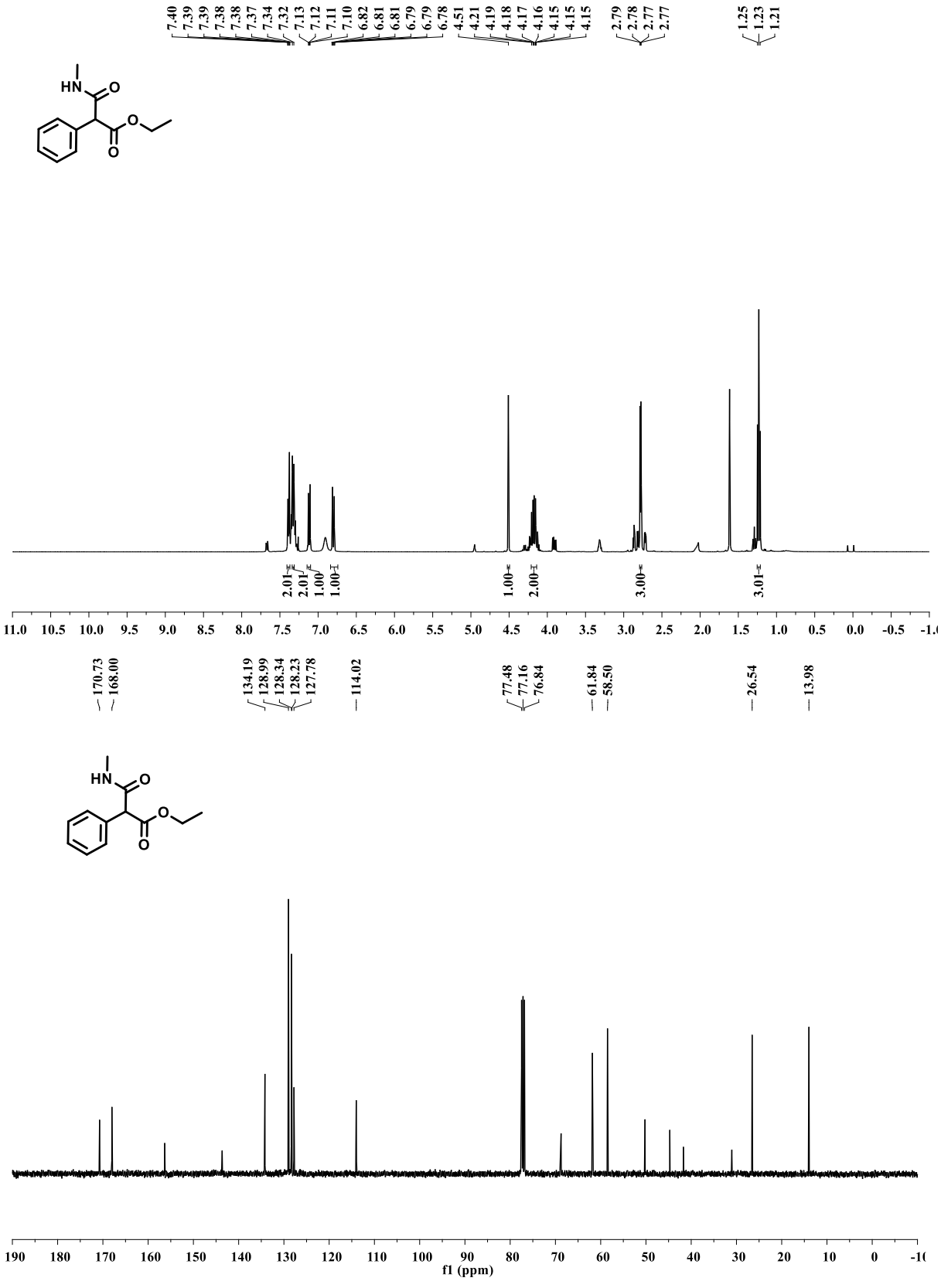


Isopropyl 3-((4-methylbenzyl)amino)-3-oxo-2-phenylpropanoate (3n)

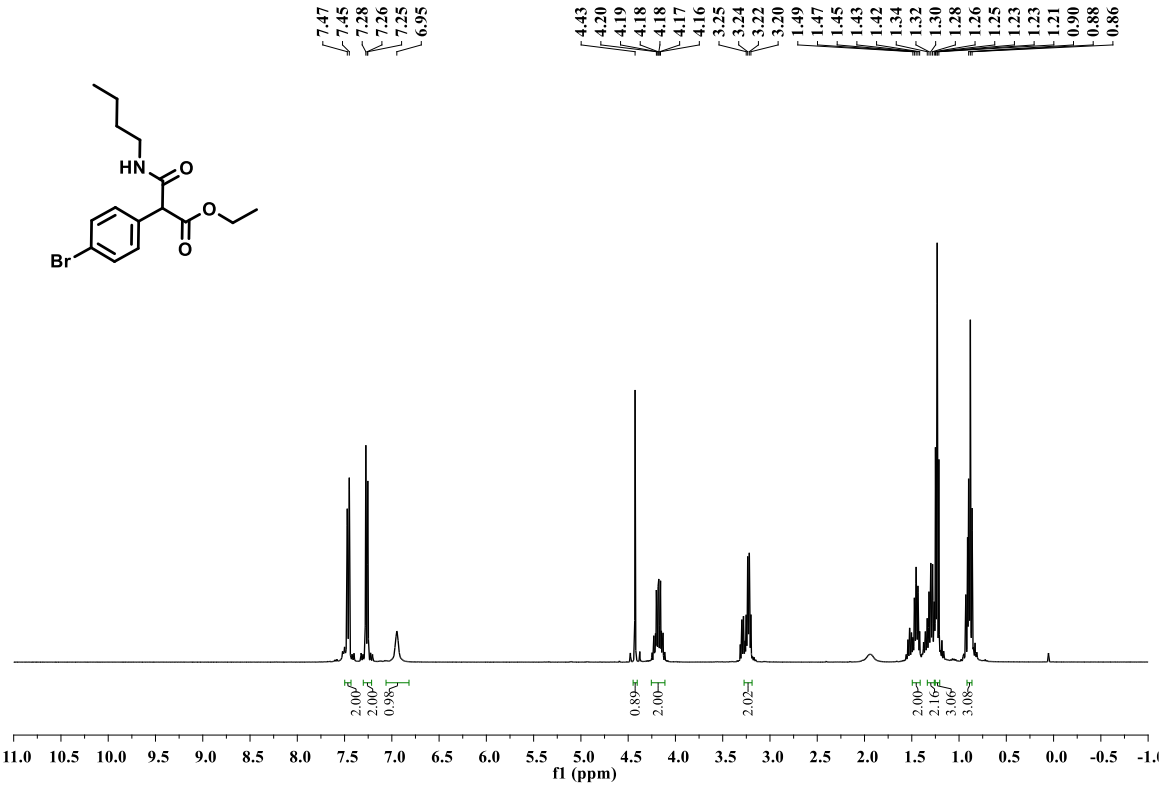


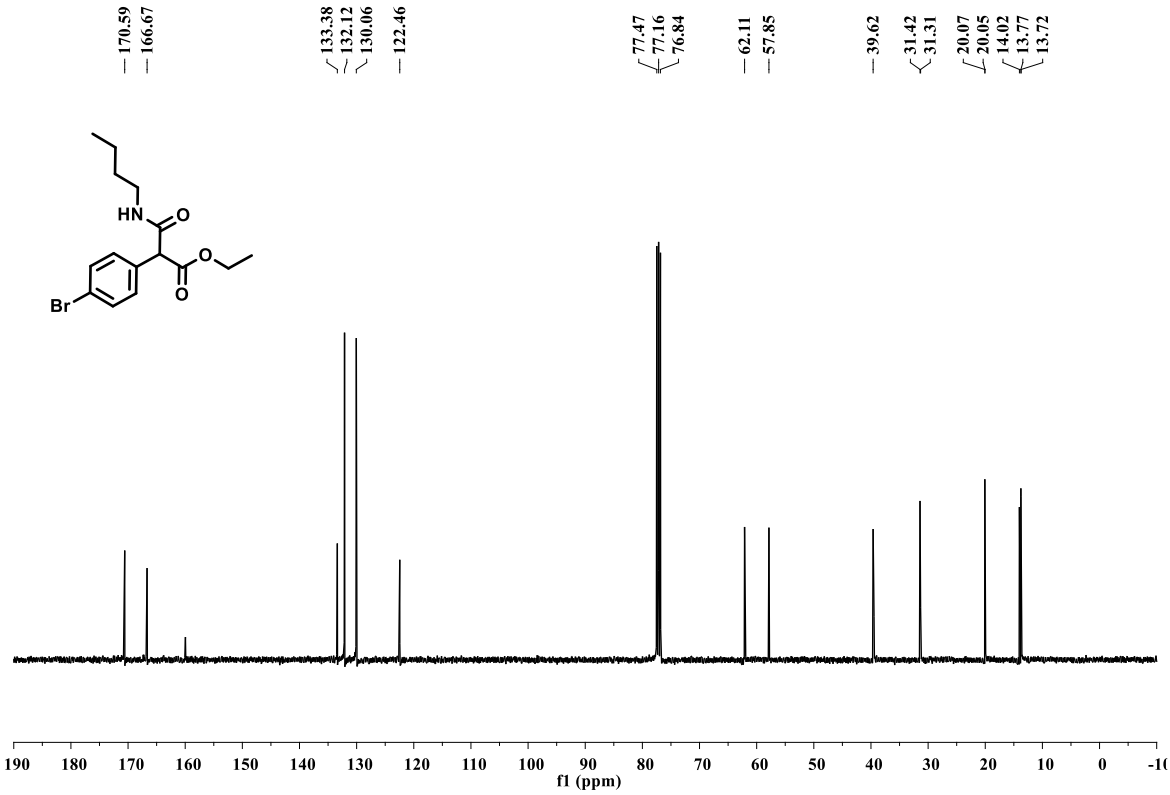


Ethyl 3-(methylamino)-3-oxo-2-phenylpropanoate (6a)

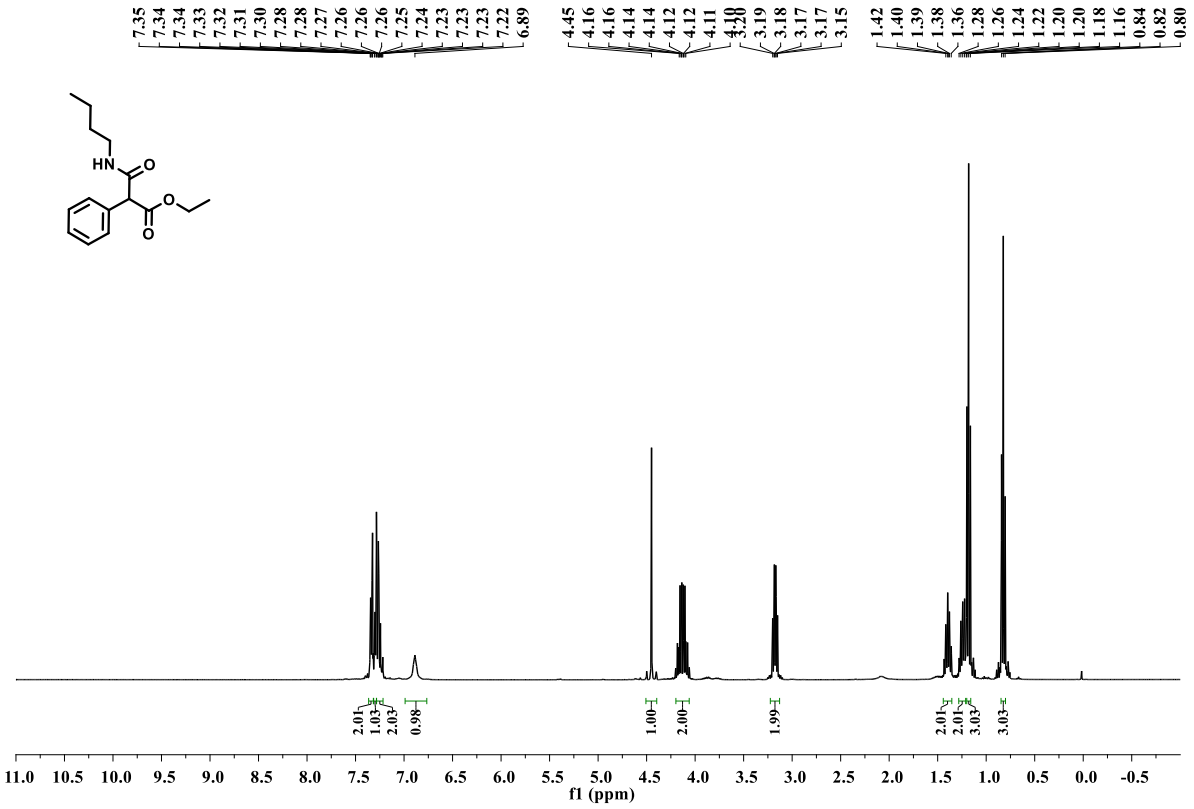


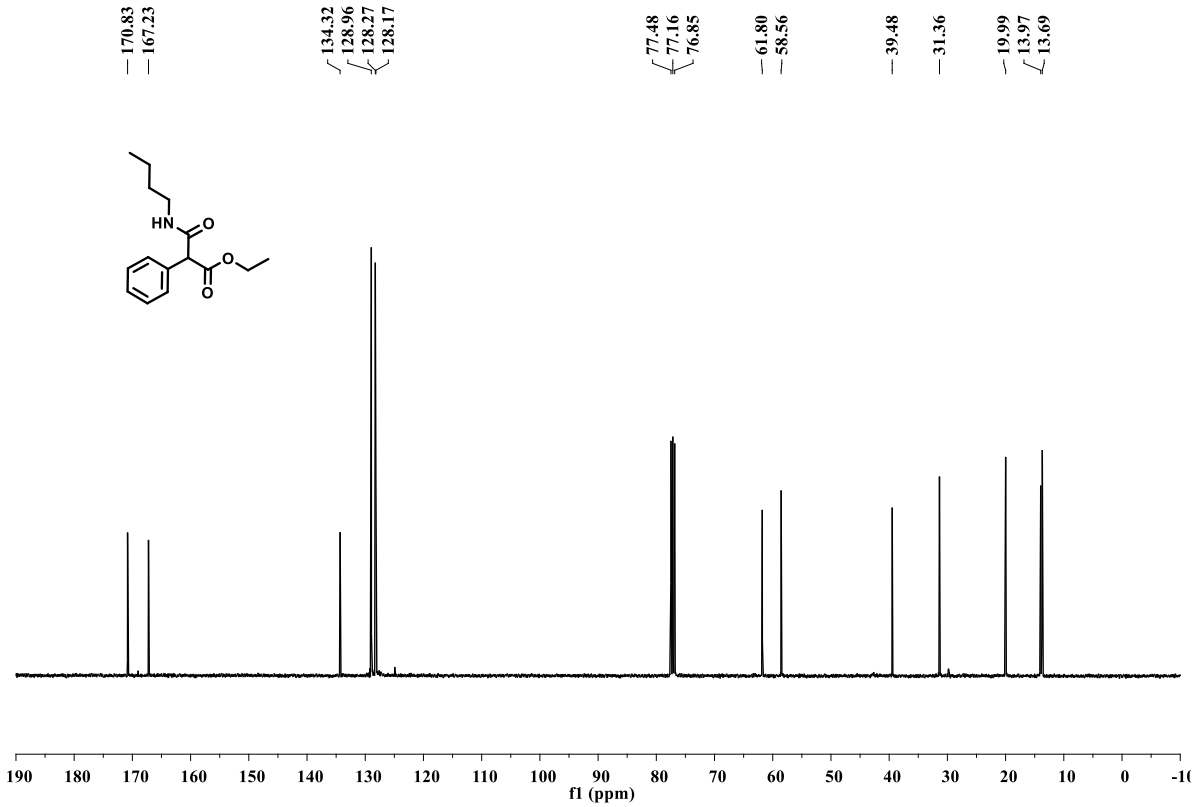
Ethyl 2-(4-bromophenyl)-3-(butylamino)-3-oxopropanoate (6b)



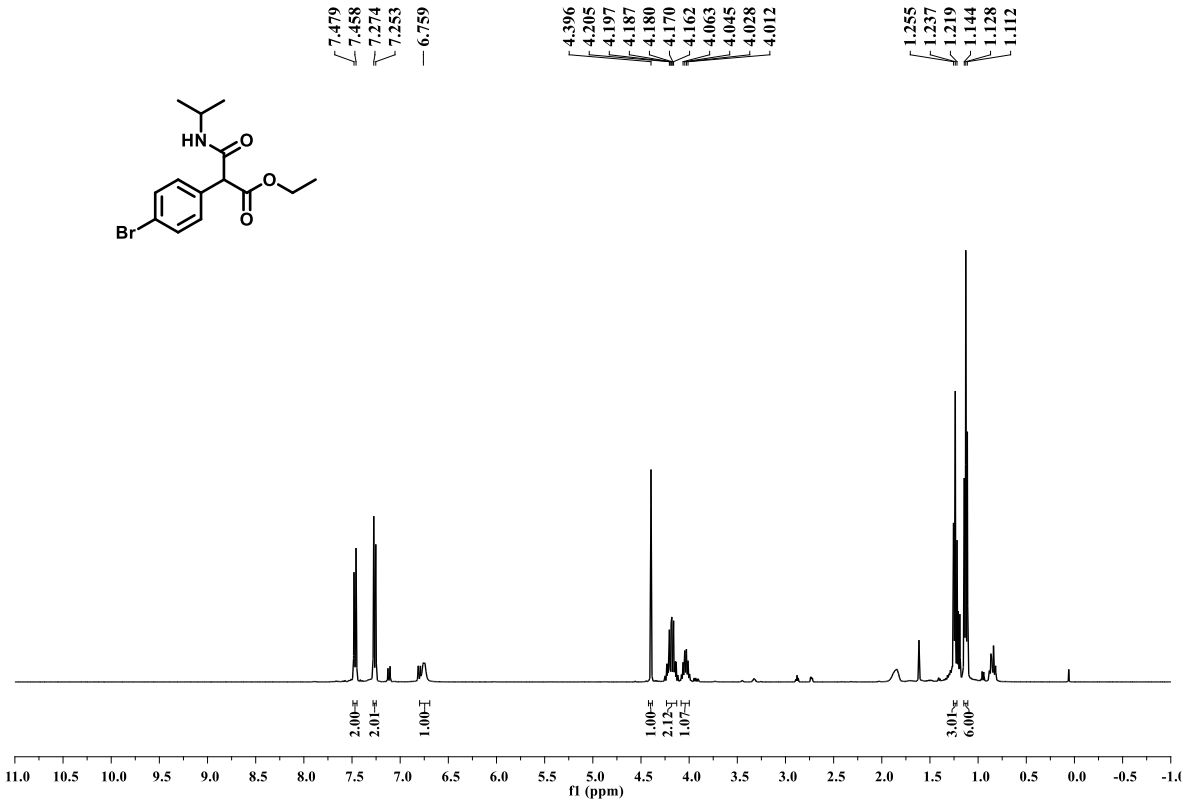


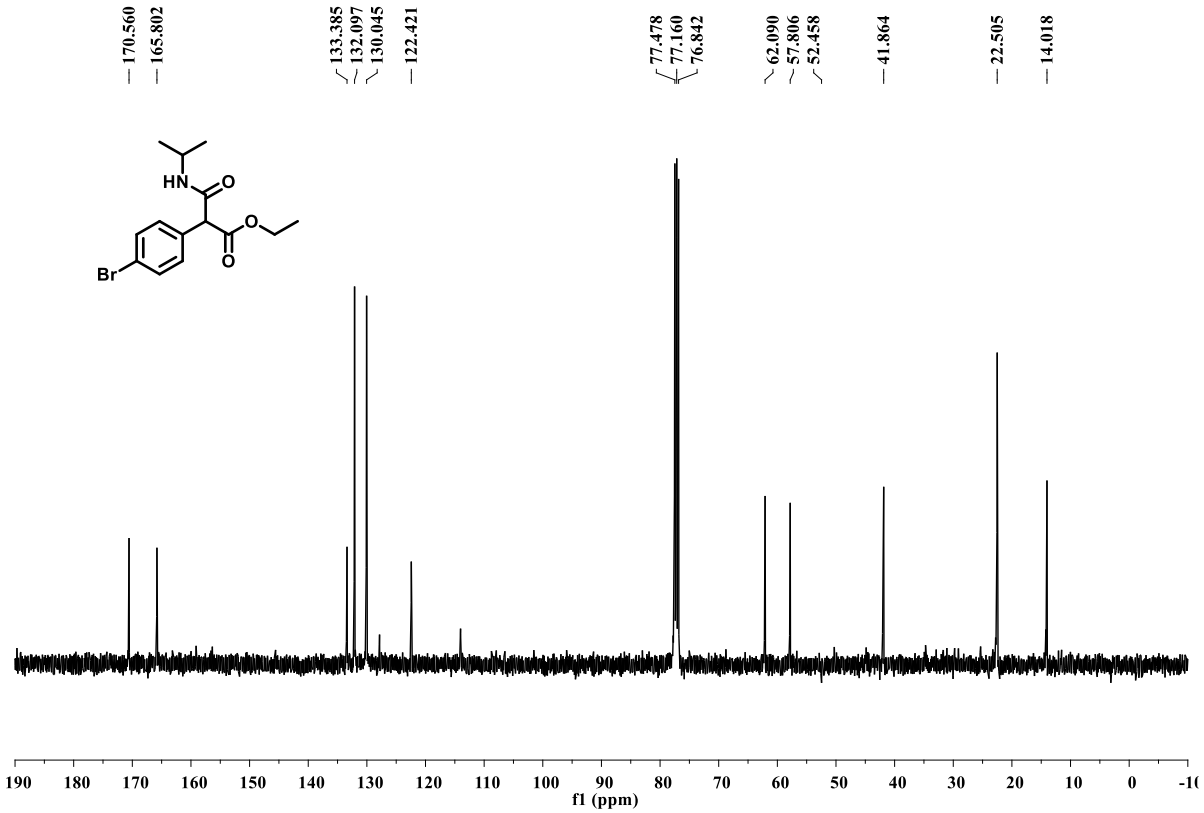
Ethyl 3-(butylamino)-3-oxo-2-phenylpropanoate (6c)



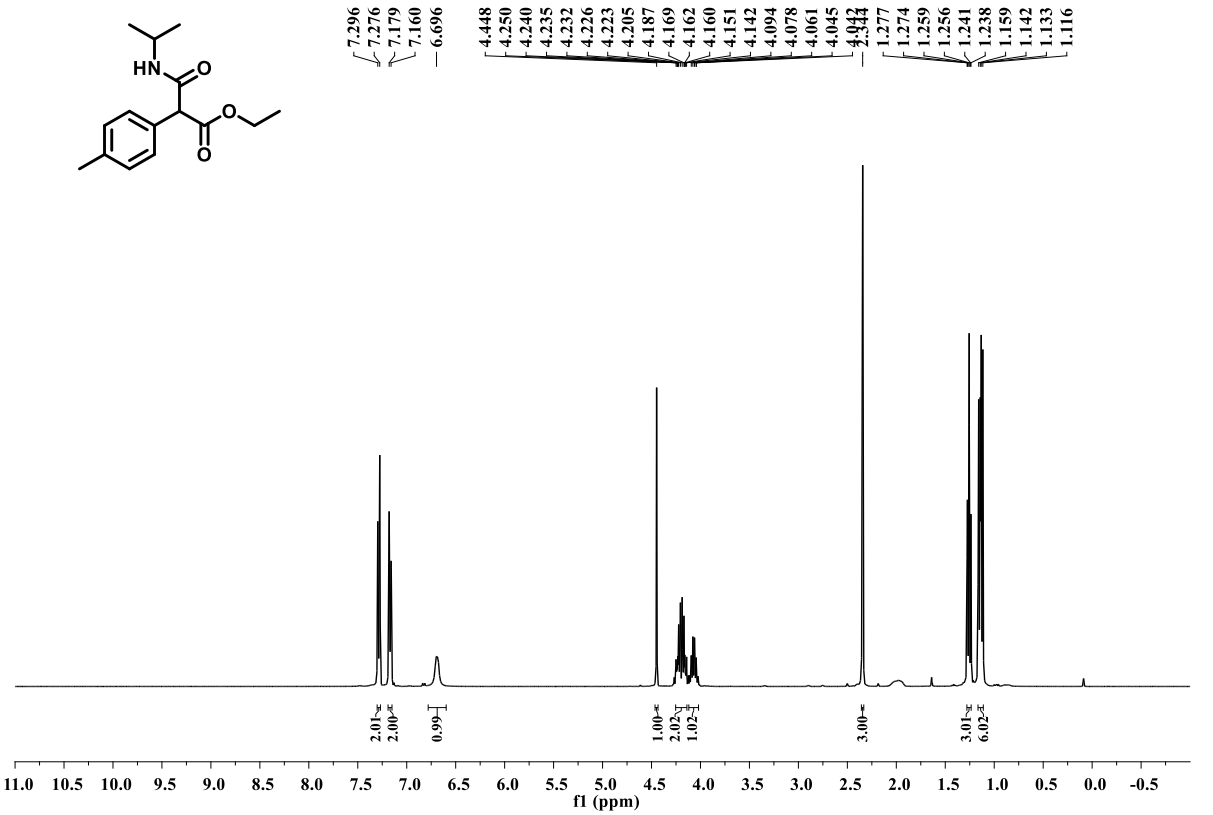


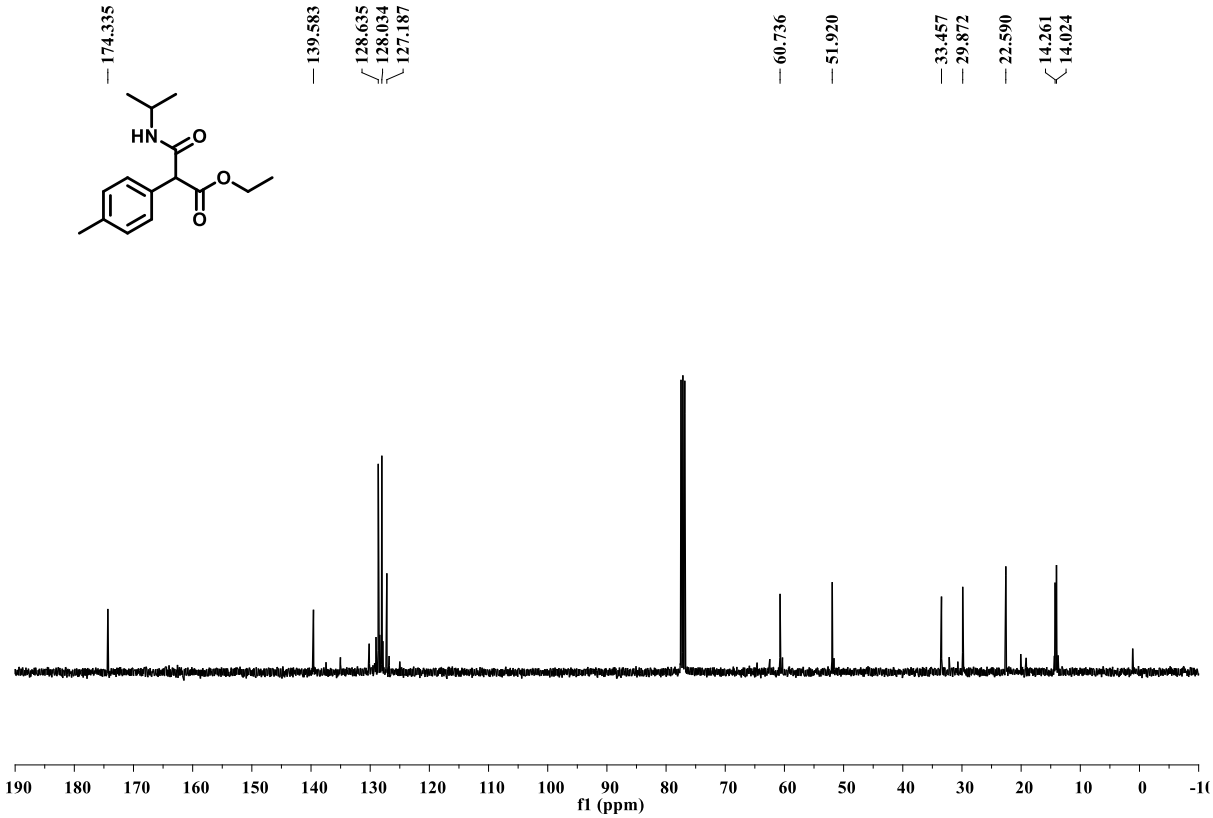
Ethyl 2-(4-bromophenyl)-3-(isopropylamino)-3-oxopropanoate (6d)



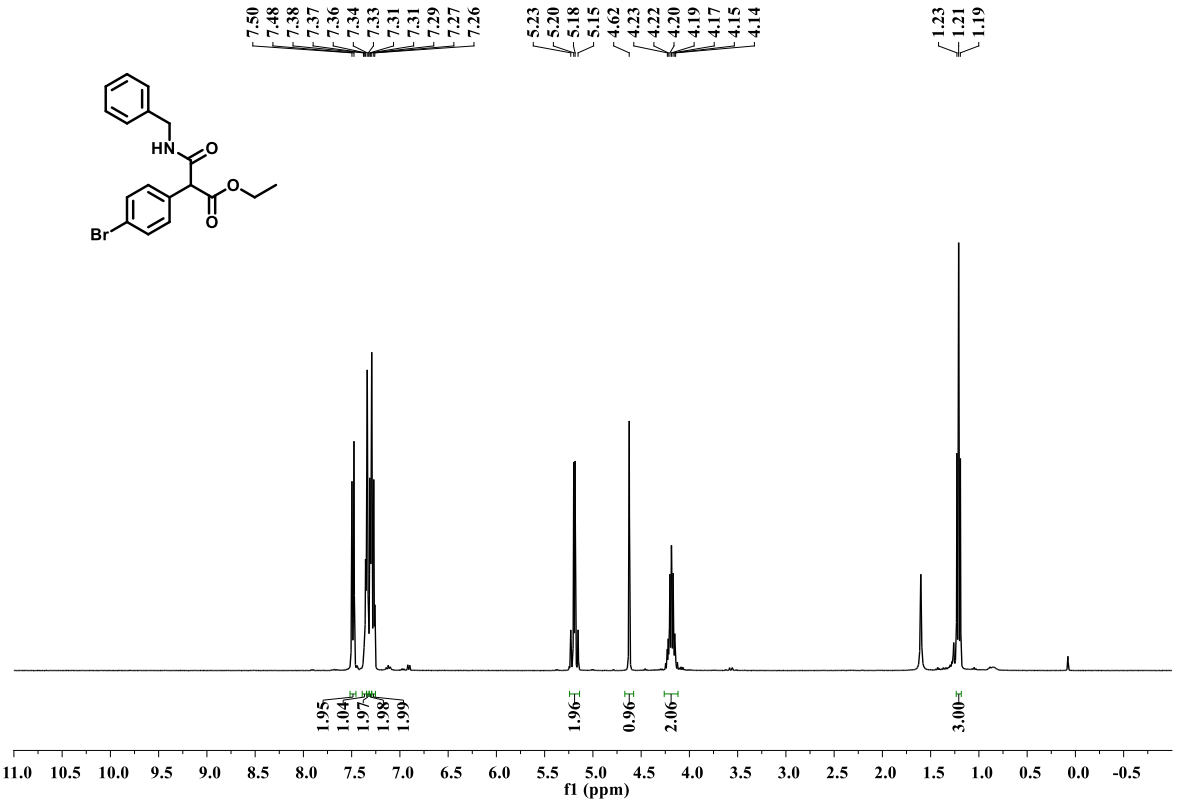


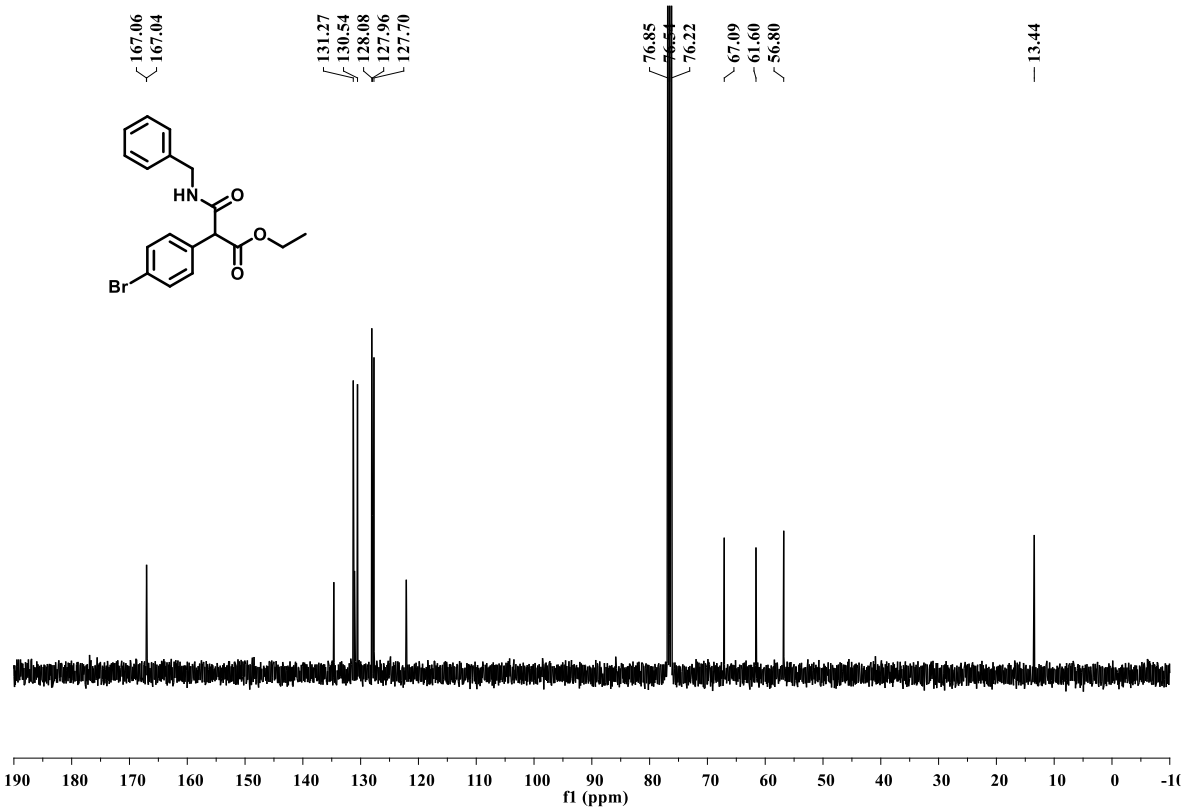
Ethyl 3-(isopropylamino)-3-oxo-2-(*p*-tolyl)propanoate (6e)



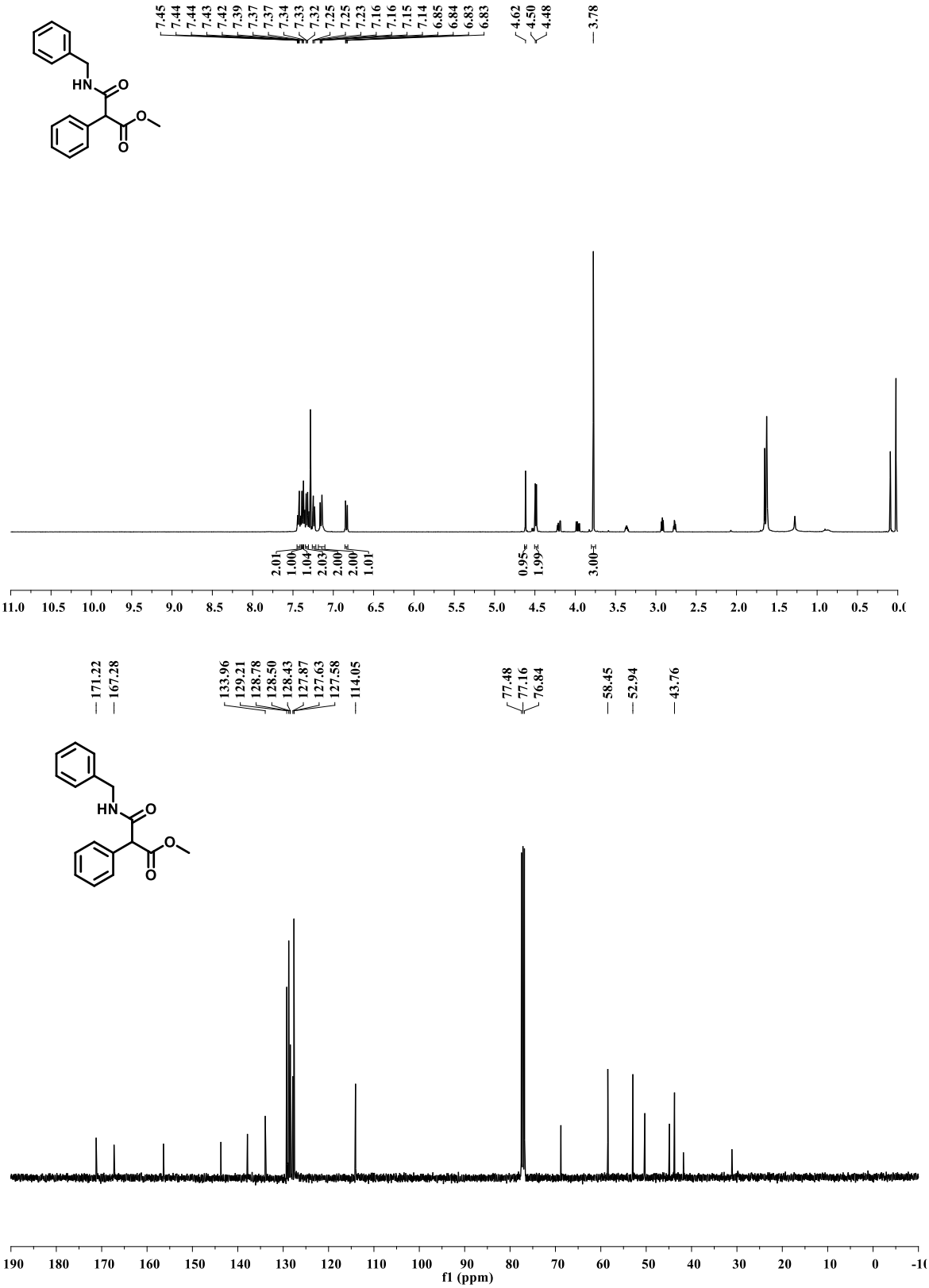


Ethyl 3-(benzylamino)-2-(4-bromophenyl)-3-oxopropanoate (6f)

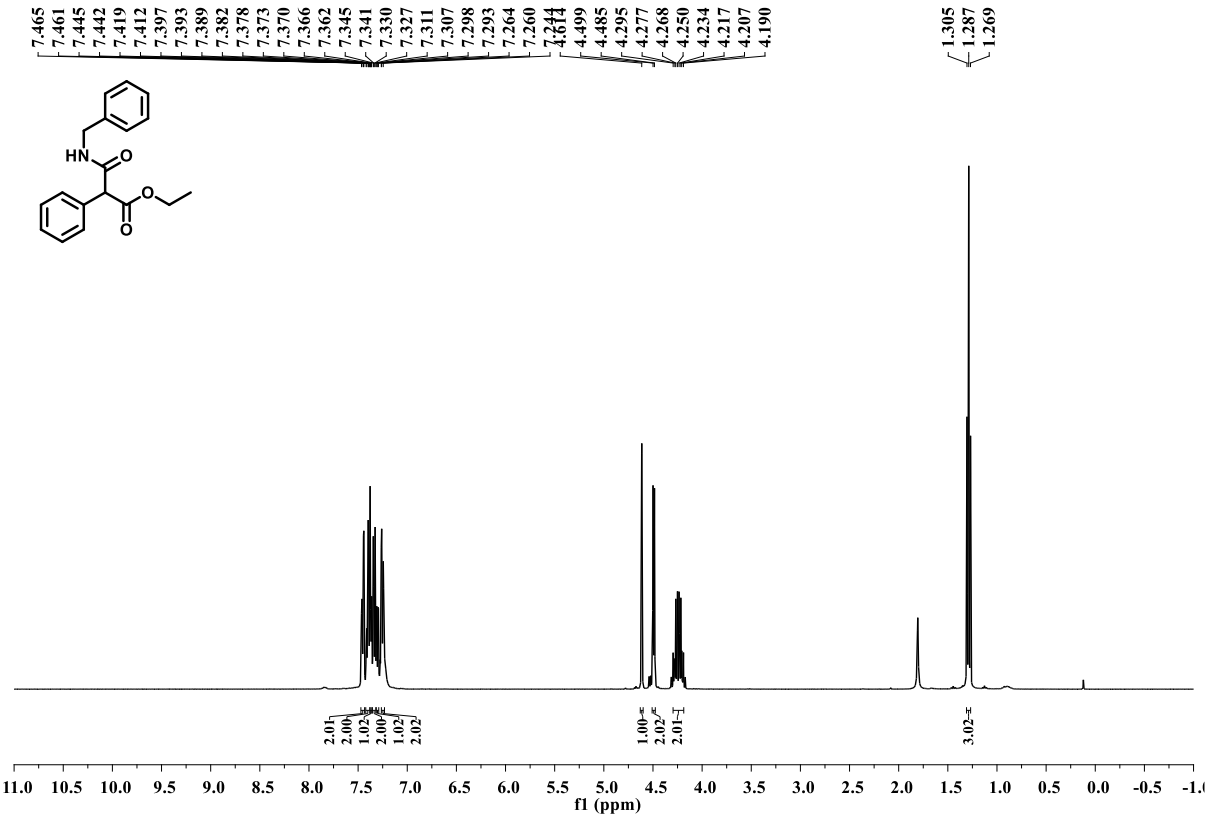


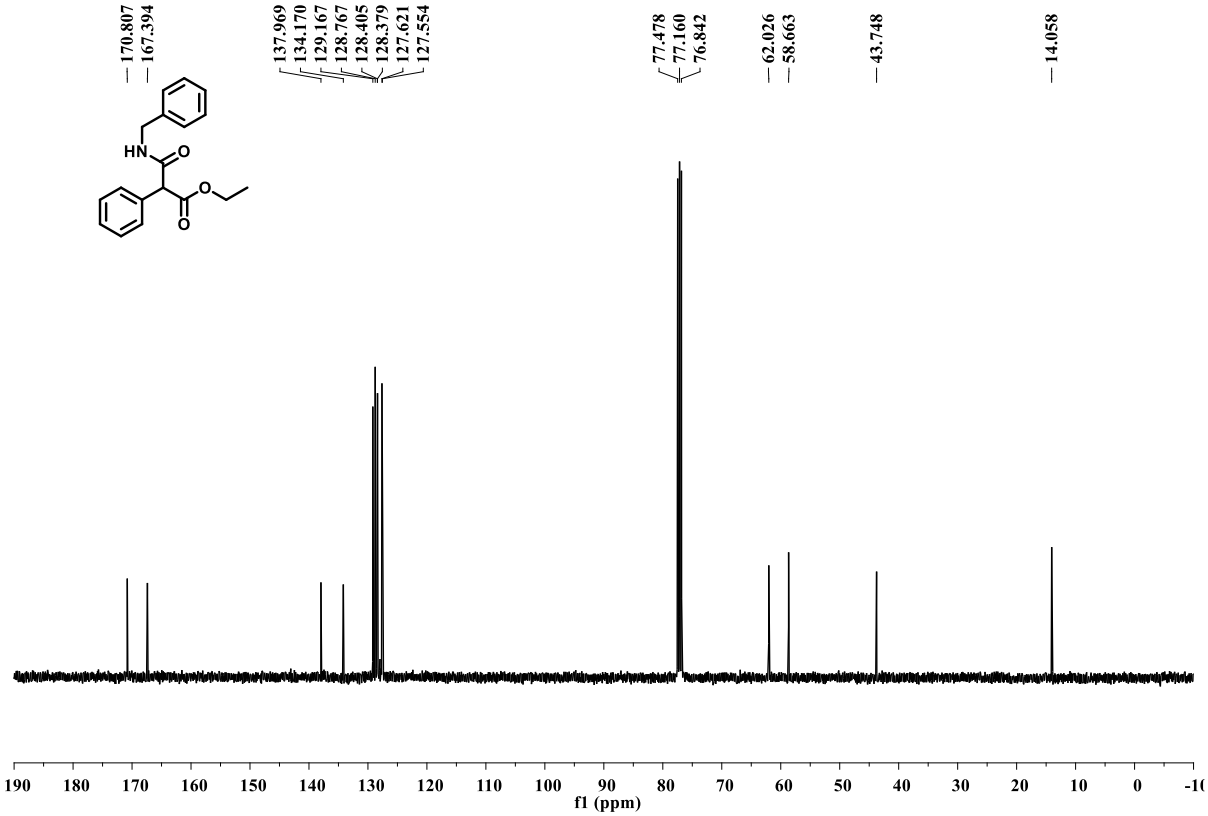


Methyl 3-(benzylamino)-3-oxo-2-phenylpropanoate (6g)



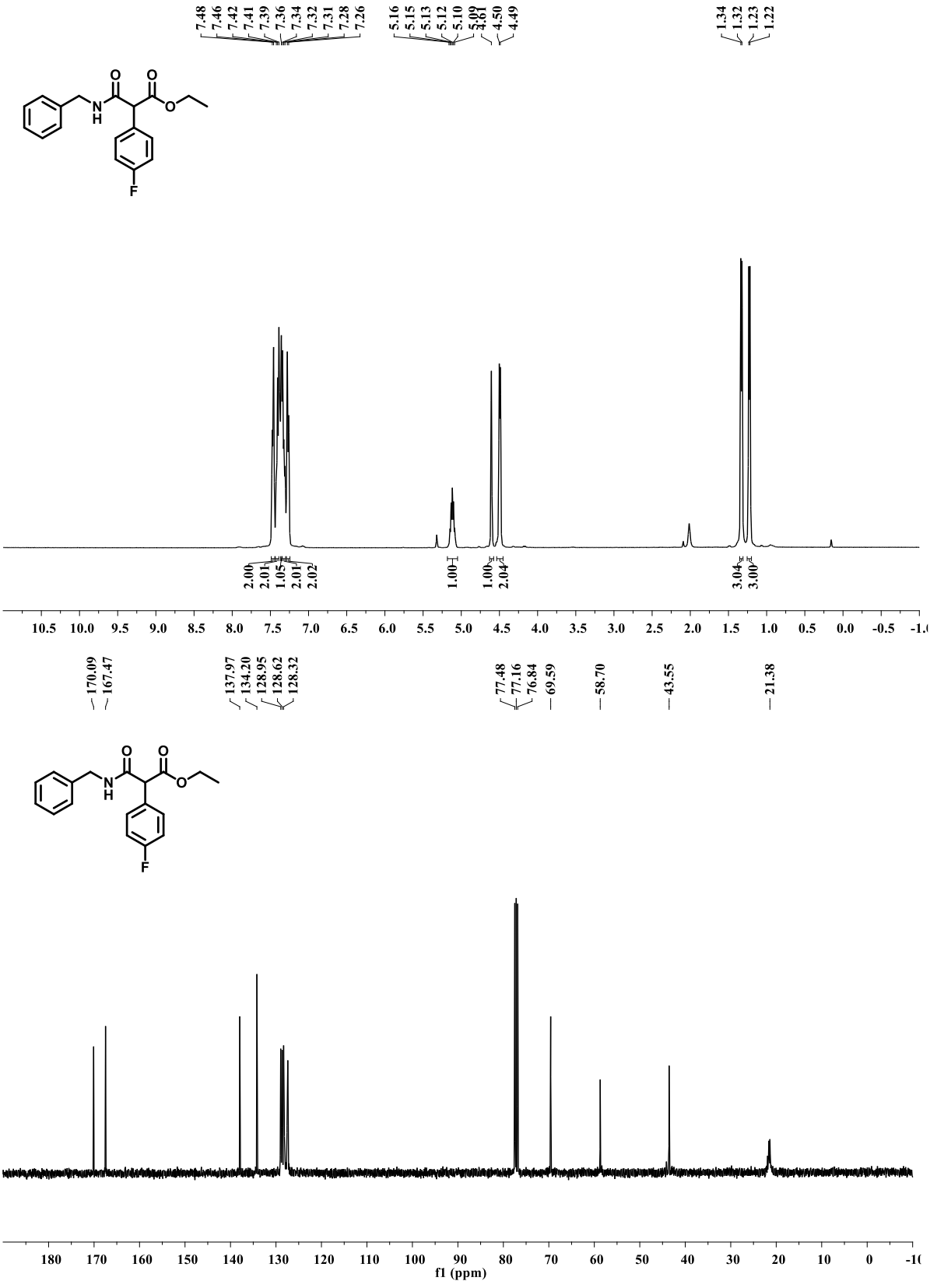
Ethyl 3-(benzylamino)-3-oxo-2-phenylpropanoate (6h)



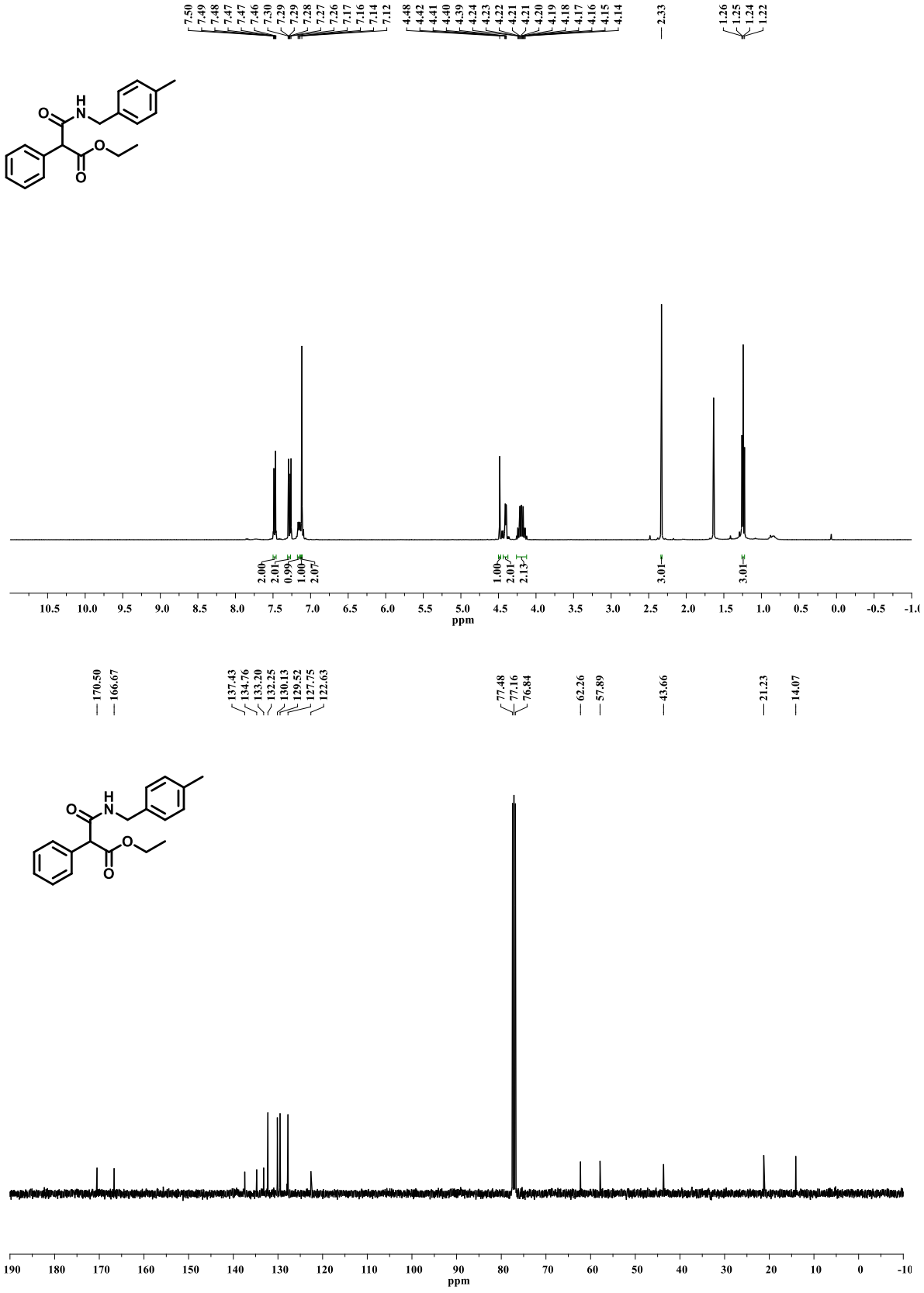


150 Ethyl 3-(benzylamino)-2-(2,4-dichlorophenyl)-3-oxopropanoate (6i)

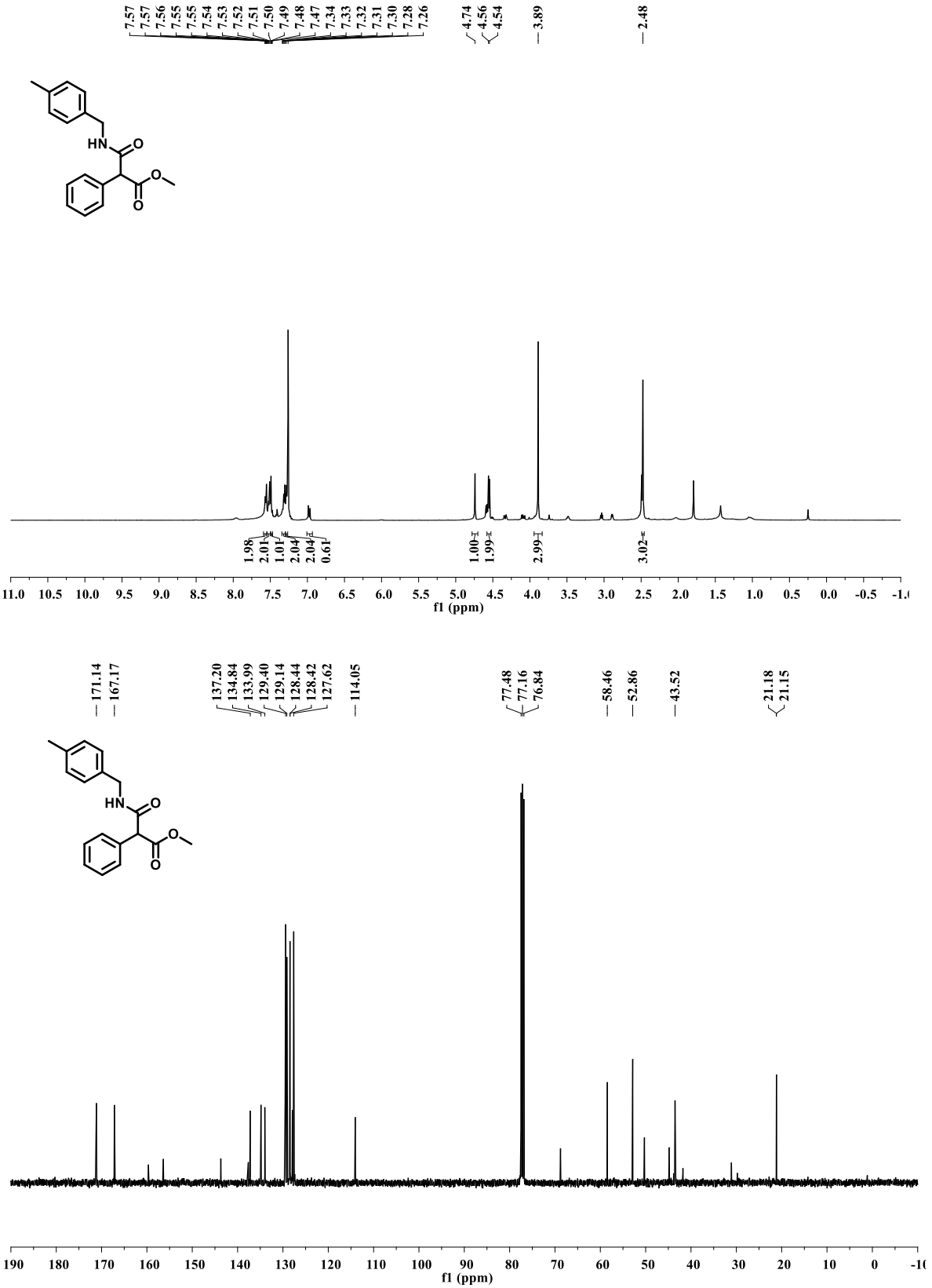
Ethyl 3-(benzylamino)-2-(4-fluorophenyl)-3-oxopropanoate (6j)



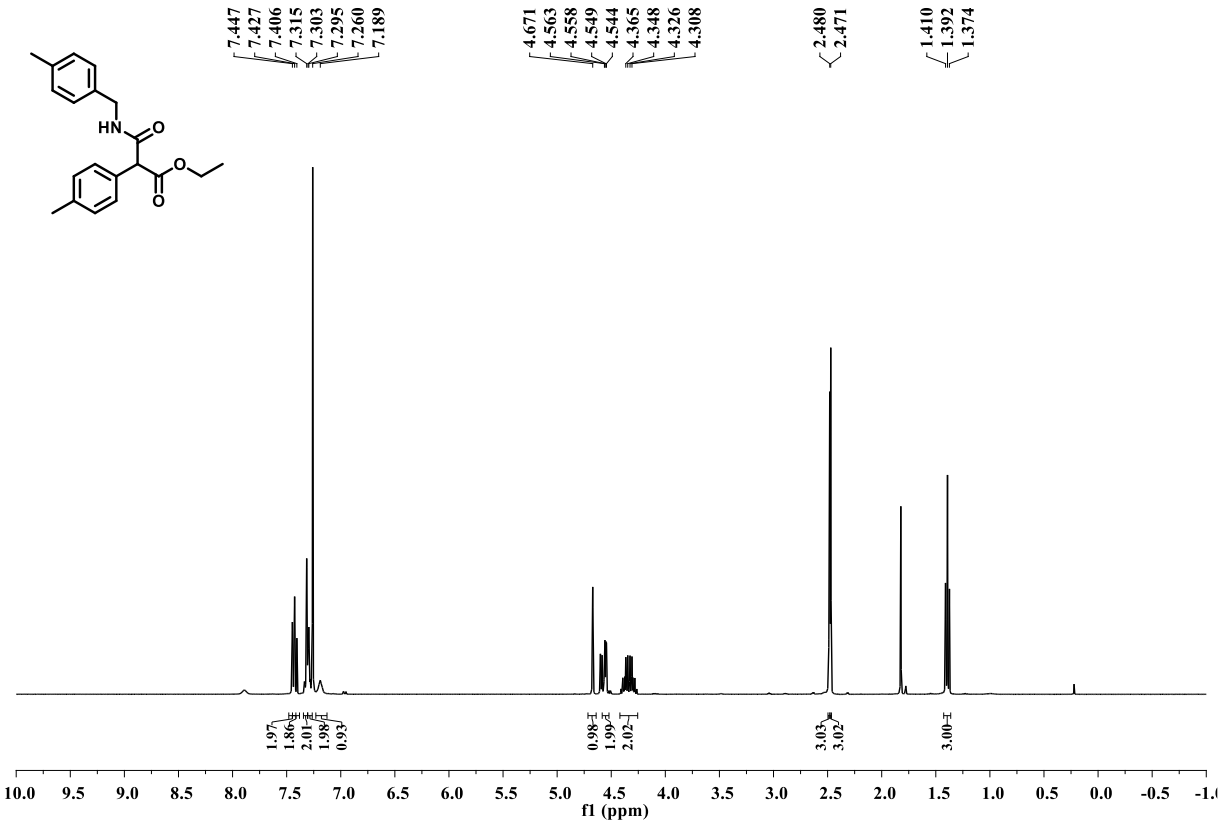
Ethyl 3-((4-methylbenzyl)amino)-3-oxo-2-phenylpropanoate (6k)

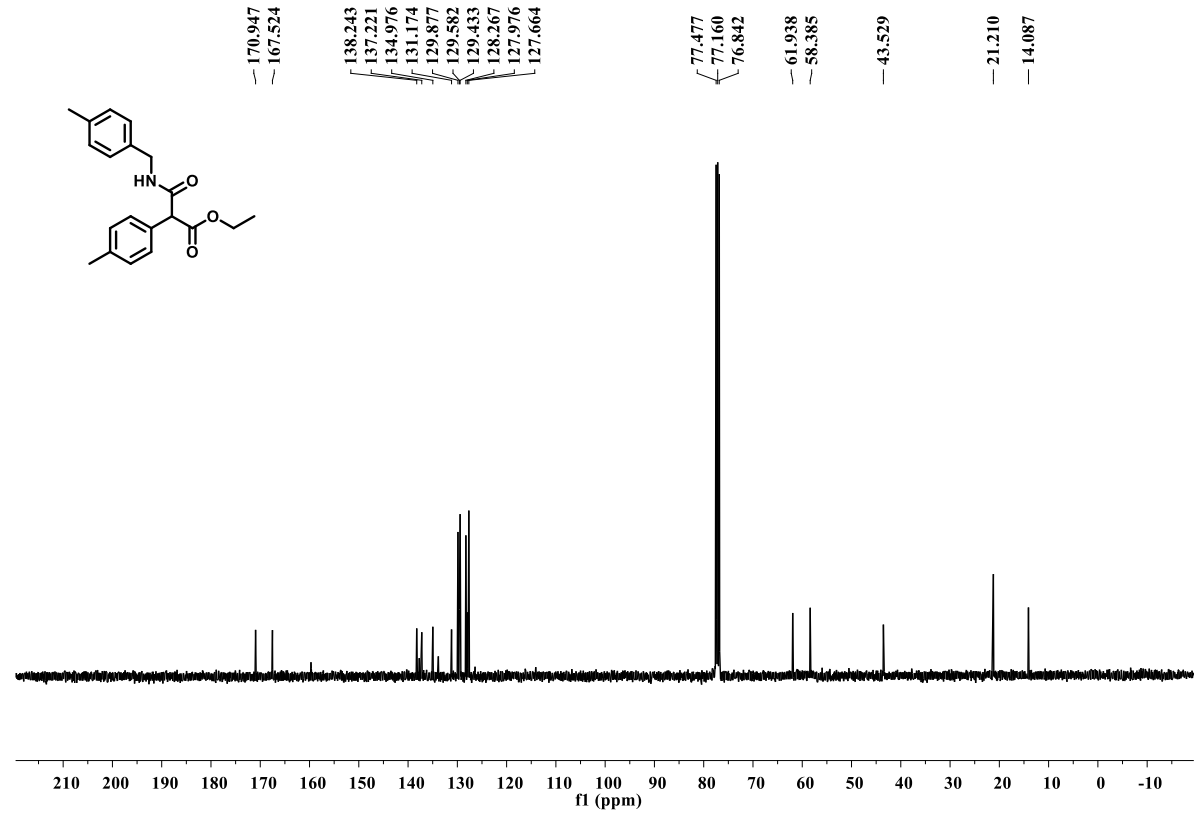


methyl 3-((4-methylbenzyl)amino)-3-oxo-2-phenylpropanoate (3l)

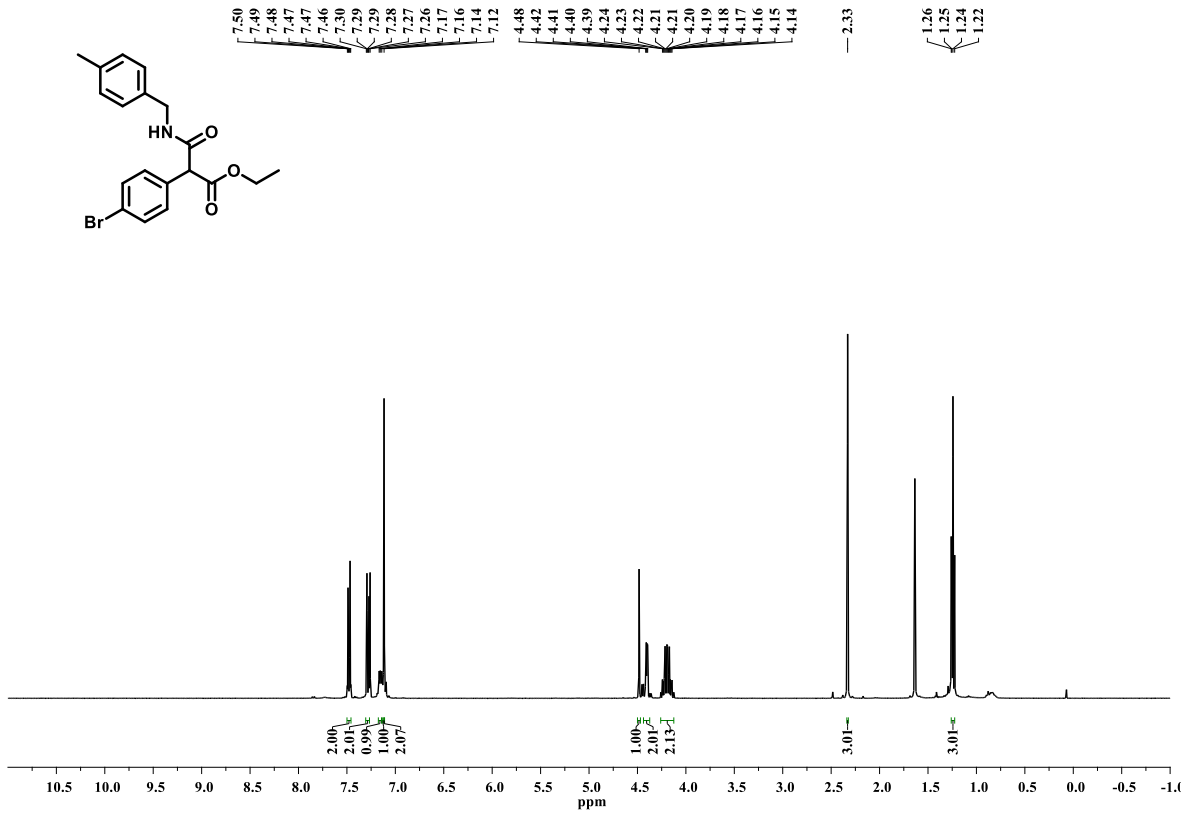


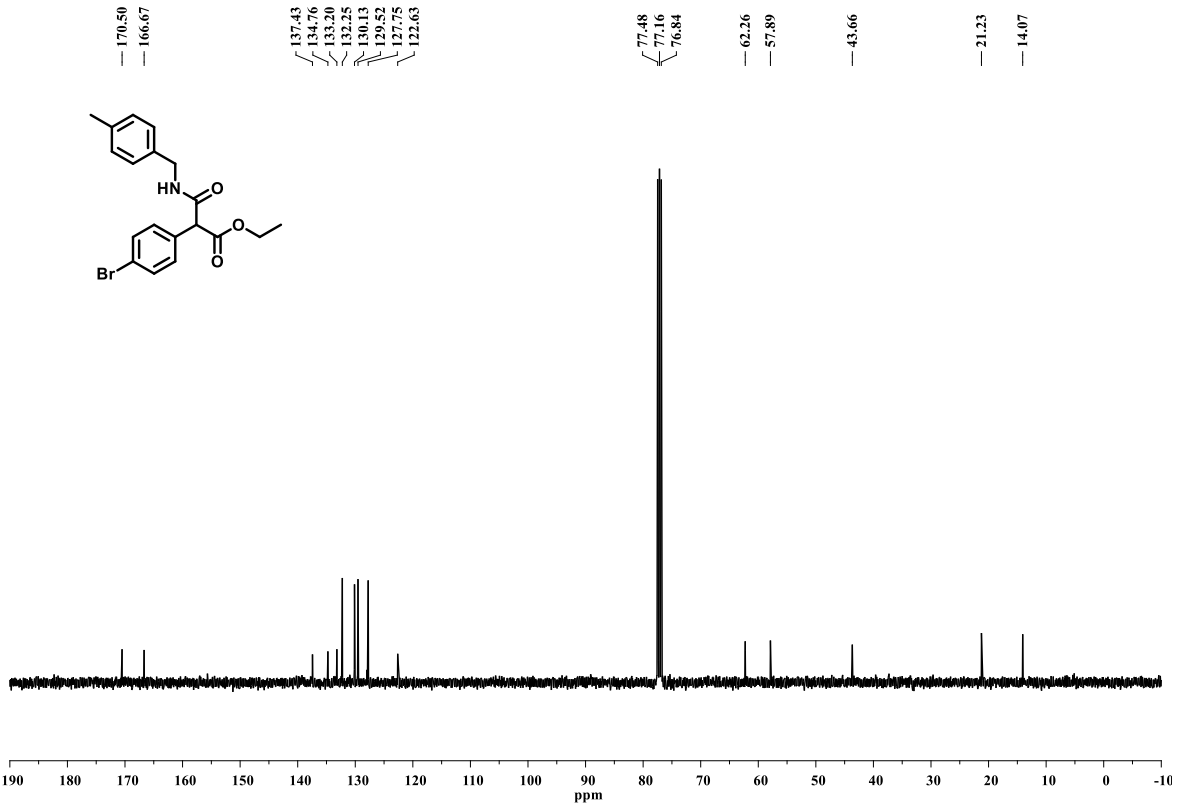
Ethyl 3-((4-methylbenzyl)amino)-3-oxo-2-(*p*-tolyl)propanoate (6m)



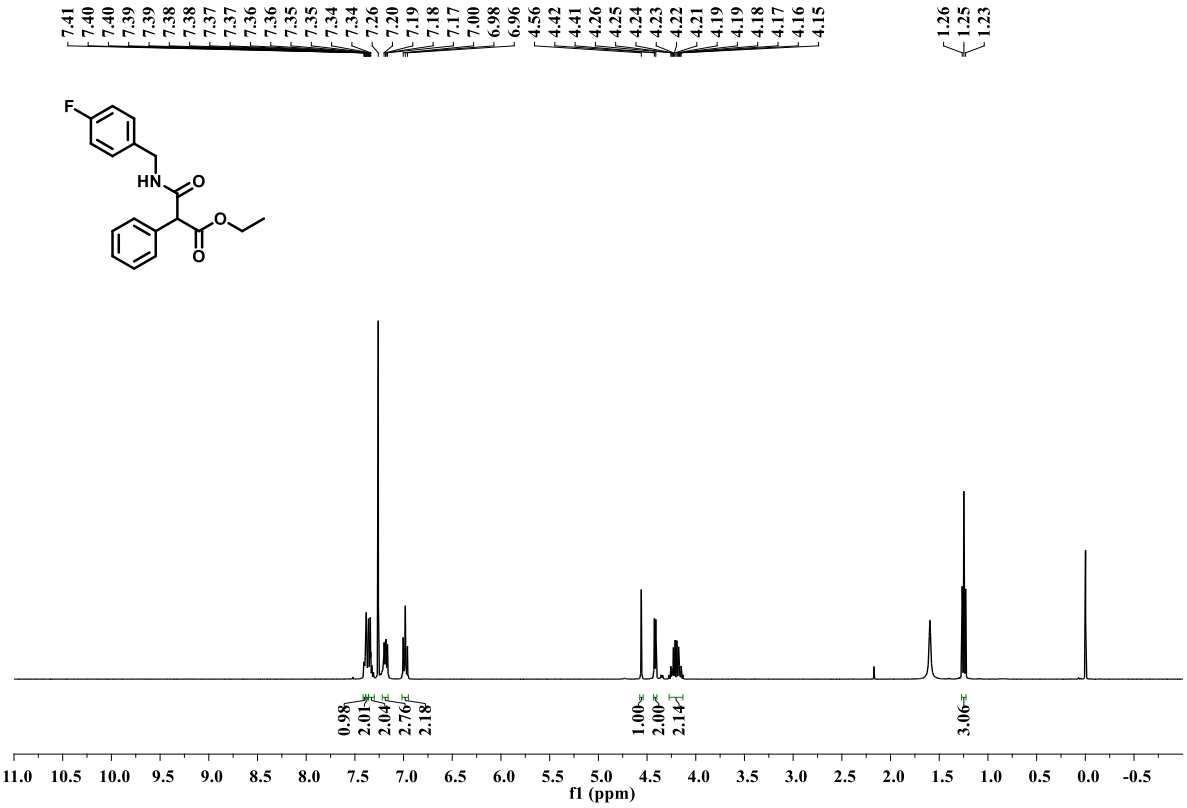


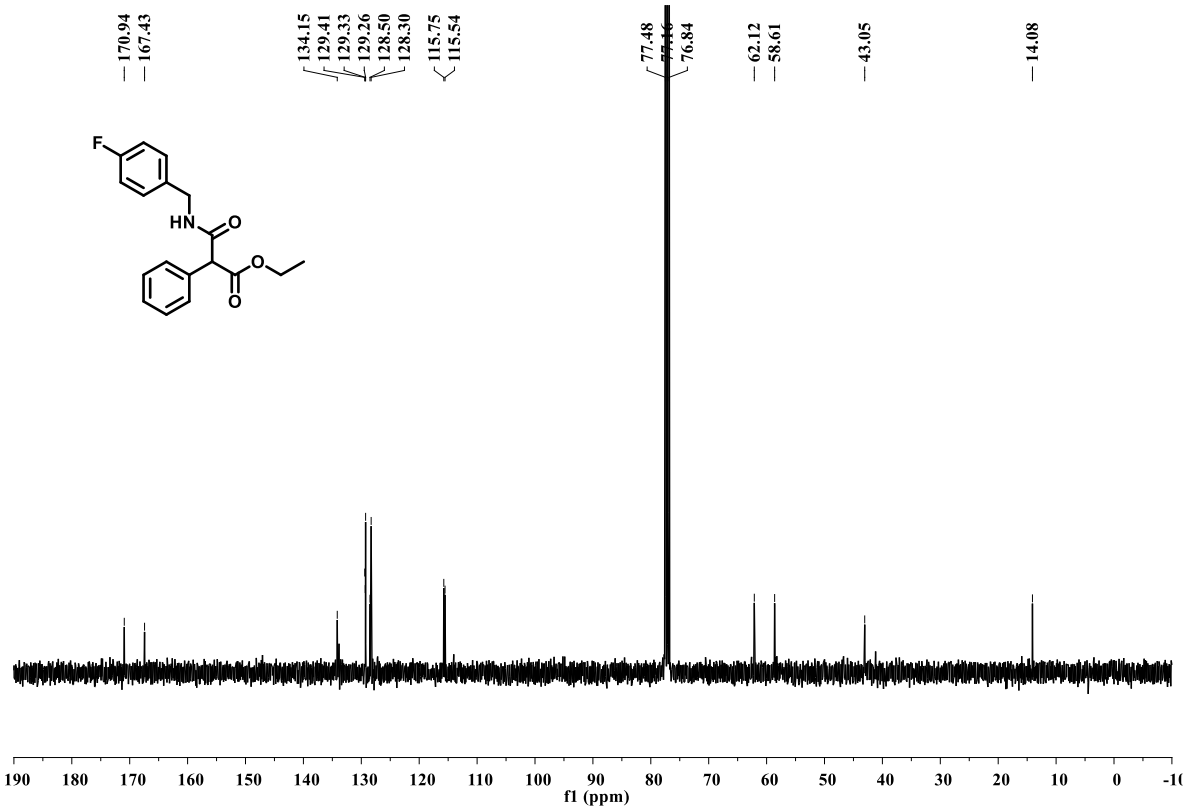
Ethyl 2-(4-bromophenyl)-3-((4-methylbenzyl)amino)-3-oxopropanoate (6n)





Ethyl 3-((4-fluorobenzyl)amino)-3-oxo-2-phenylpropanoate (6o)





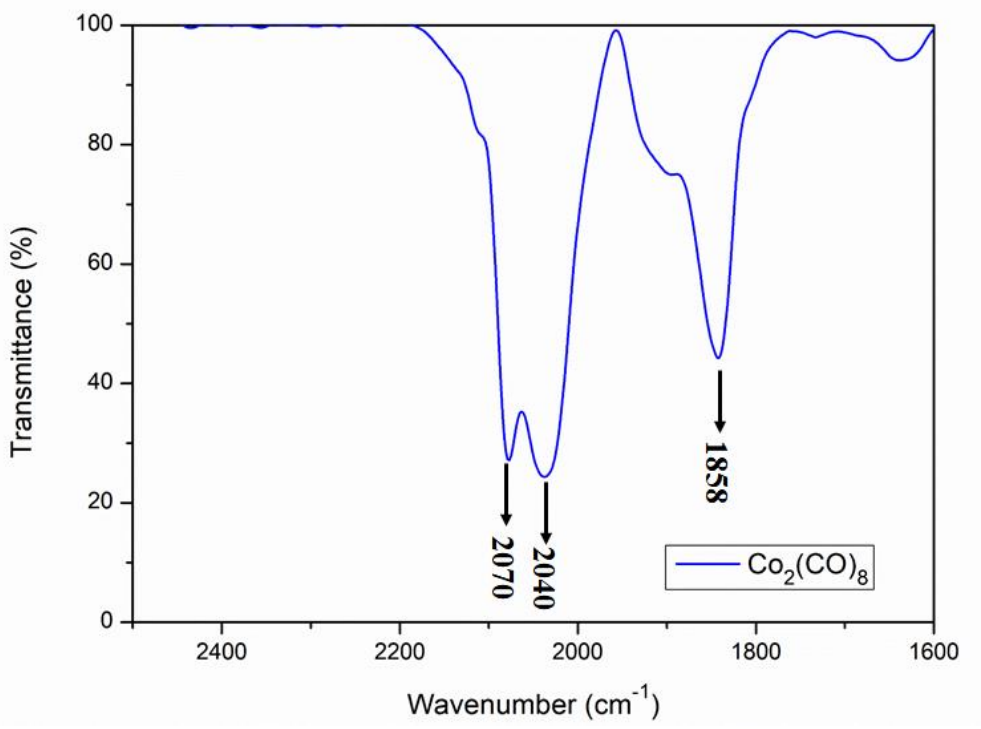


Figure S1: IR spectrum of [Co_2CO_8]

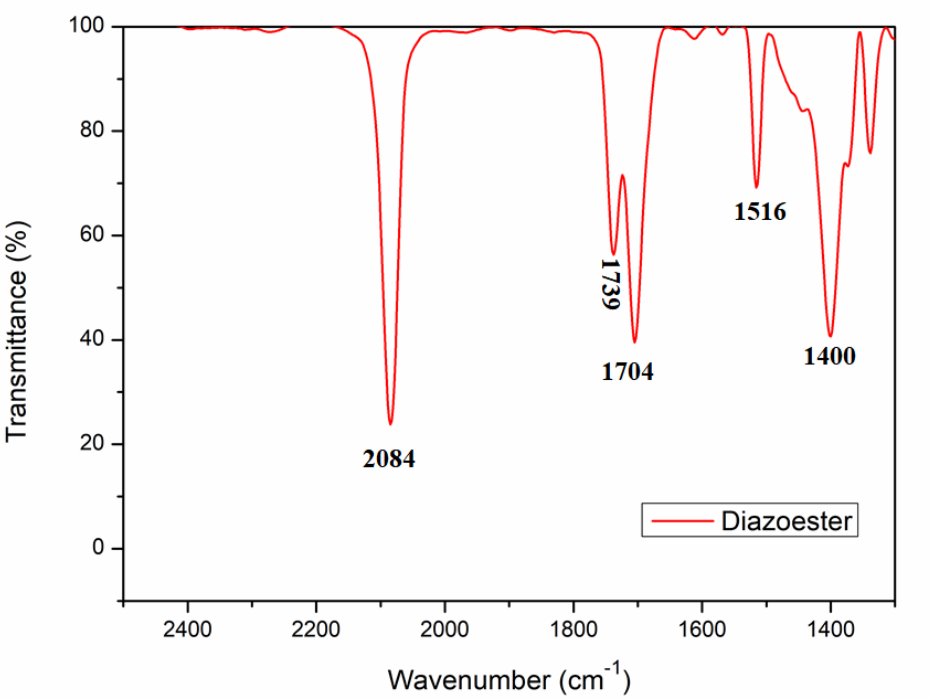


Figure S2: IR spectrum of ethyl-2-diazo-2-phenylacetate.