The Aryne Sommelet–Hauser rearrangement

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Supporting Information

1. General Information

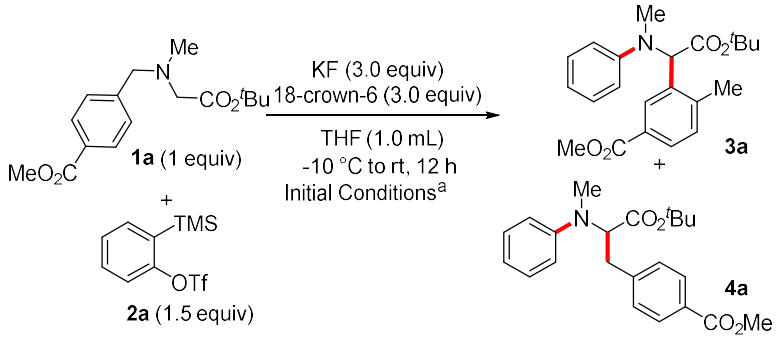
Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. 28 °C Corresponds to the room temperature (rt) of the lab when the experiments were carried out. THF was freshly purified by distillation over Na-benzophenone and was transferred under argon. 18-Crown-6 was recrystallized from dry CH_3CN and KF was dried by heating at 110 °C for 12 h and left to cool under argon and stored in argon filled glove-box. The 2(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** and the other symmetric and unsymmetric aryne precursors were synthesized following literature procedure.[1] All the tertiary amines **1** used were prepared following literature procedure.[2]

Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254}. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. Ether-EtOAc solvent system.

All compounds were fully characterized. ^1H and ^{13}C NMR spectra were recorded on Bruker Ultrashield spectrometer in $CDCl_3$ as solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). Infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer, ν-max in cm^{-1}. HRMS (ESI) data were recorded on a Waters Xevo G2-XS Q-TOF instrument.

[1](a) Y. Sato, T. Tamura, A. Kinbara and M. Morib, *Adv. Synth. Catal.,* 2007, **349**, 647. (b) D. Peña, A. Cobas, D. Pérez and E. Guitián, *Synthesis,* 2002, 1454.
[2]S. H. Lim, J. Yi, G. M. Moon, C. S. Ra, K. Nahm, D. W. Cho, K. Kim, T. G. Hyung, U. C. Yoon, G. Y. Lee, S. Kim, J. Kim and P. S. Mariano, *J. Org. Chem.* 2014, **79**, 6946.

2. General Procedure for the Optimization of the Reaction Conditions

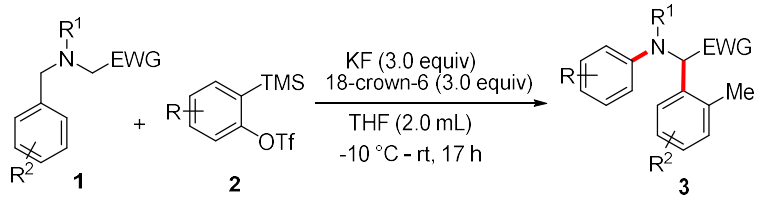


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the KF (87 mg, 1.5 mmol) and 18-crown-6 (396 mg, 1.5 mmol) in a glove box. The mixture was dissolved in THF (1.0 mL) under argon atmosphere. The benzylamine **1a** (0.50 mmol) was added outside the glove box under argon atmosphere and the temperature of the mixture was maintained at -10 °C (using salt and ice). To the stirring solution, aryne precursor **2a** (0.75 mmol) was added. It was allowed to warm to rt and stirred for 12 h. After 12 h, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography silica gel to afford the corresponding Sommelet-Hauser rearrangement product **3a** and Stevens rearrangement product **4a**.

entry	Variation of initial conditions	yield of **3a** (%)[b]	yield of **4a** (%)[b]
1	None	65	18
2	2.0 equiv of **2a**	61	<5
3[c]	CsF instead of KF and 18-crown-6	32	30
4	TBAF instead of KF and 18-crown-6	33	29
5	TBAT instead of KF and 18-crown-6	<5	33
6	-40 °C to rt instead of -10 °C to rt	65	15
7	-20 °C to rt instead of -10 °C to rt	64	18
8	0 ° to rt instead of -10 °C to rt	58	19
9	*-10 °C for 5h, warmed to rt, 12 h*	*70*	*7*
10	rt instead of -10 °C to rt.	35	38

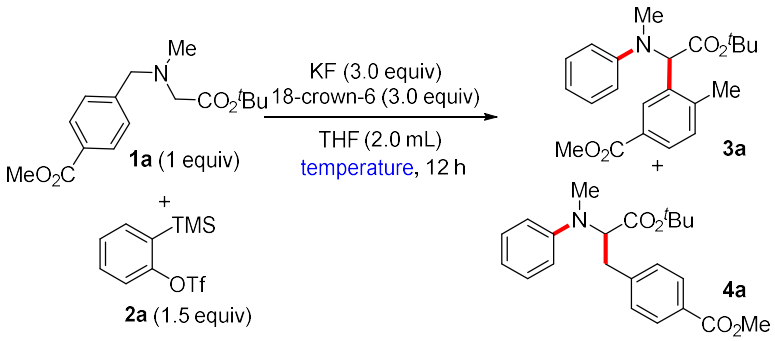
[a] Initial conditions: **1a** (0.25 mmol), **2a** (0.375 mmol), fluoride source (3.0 equiv), 18-crown-6 (3.0 equiv), THF (1.0 mL) [b] Yields of isolated products are given. [c] The reaction performed using CH_3CN as the solvent. 28 °C corresponds to the room temperature.

3. General Procedure for the Aryne Sommelet-Hauser Rearrangement



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the KF (87 mg, 1.5 mmol) and 18-crown-6 (396 mg, 1.5 mmol) in a glove box. The mixture was dissolved in THF (2.0 mL) under argon atmosphere. The benzylamine **1** (0.50 mmol) was added outside the glove box under argon atmosphere and the temperature of the mixture was maintained at -10 °C. To the stirring solution, aryne precursor **2** (0.75 mmol) was added. Then the reaction mixture was allowed to react at -10 °C for 5 h. It was then allowed to warm to rt and stirred for 12 h. After 12 h, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 97/03) on silica gel to afford the corresponding α–amino acid derivatives **3** in moderate to good yields.

4. General Procedure for the Temperature-Selectivity Study[a]



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the KF (87 mg, 1.5 mmol) and 18-crown-6 (396 mg, 1.5 mmol) in a glove box. The mixture was dissolved in THF (2.0 mL) under argon atmosphere. The methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.50 mmol) was added outside the glove box under argon. To the stirring solution, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a**

(0.223 g, 182 µL, 0.75mmol) was added. Then the reaction mixture is allowed to react at the temperature as mentioned in the table below for 12 h. After 12 h, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography silica gel to afford the corresponding Sommelet-Hauser rearrangement product **3a** and Stevens rearrangement product **4a**. A graph is plotted with the results obtained (See Figure 1.).

entry	Temperature	yield of **3a** (%)[b]	yield of **4a** (%)[b]
1	-40 °C	68	6
2	-20 °C	65	7
3	0 °C	55	20
4	20 °C	40	35
5	40 °C	34	38
6	60 °C	5	60

[a] Standard conditions: **1a** (0.50 mmol), **2a** (0.75 mmol), KF (1.5 mmol), 18-crown-6 (1.5 mmol), THF (2.0 mL) [b] Yields of isolated products are given.

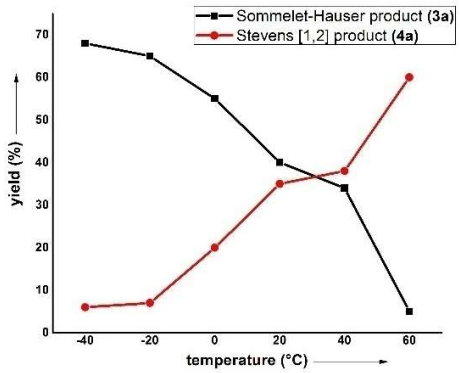
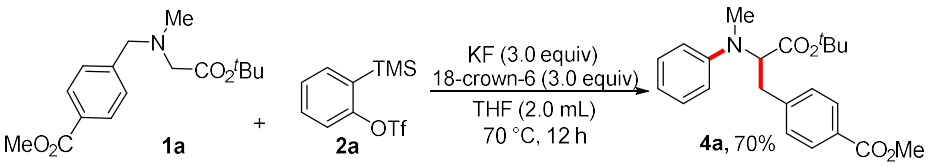


Figure 1. Variation of selectivity with temperature

5. Procedure for the Aryne [1,2] Stevens Rearrangement



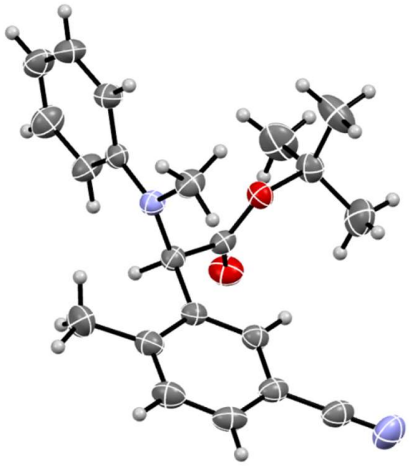
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in a glove box. The mixture was dissolved in THF (2.0 mL) under argon atmosphere. Methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.50 mmol) was added outside the glove box under argon atmosphere. To the stirring solution, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182µL, 0.75mmol) was added. Then, the reaction mixture was allowed to react at 70 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 97/03) on silica gel to afford the methyl 4-(3-(*tert*-butoxy)-2-(methyl(phenyl)amino)-3-oxopropyl)benzoate **4a** as a yellow sticky oil (0.129 g, 70% yield).

6. X-ray Data of 3j

Single crystal of **3j** (recrystallized from CH_2Cl_2 at 25 °C) was mounted and the diffraction data was collected at 296 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka radiation (71.073 pm). The structure was solved by direct methods using the SHELX-97[3] and refined by full-matrix least-squares on F2. Empirical absorption corrections were applied with SADABS.[4] All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:

[3]G. M. SHELXL-2013 Sheldrick, University of Göttingen: Göttingen, Germany, **2014**.
[4]G. M. Sheldrick, SADABS, University of Göttingen, Göttingen, Germany, **1999**.

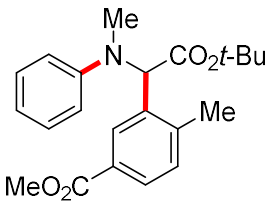
CCDC	CCDC 1866857
Identification code	**3j**
Empirical formula	$C_{21}H_{24}N_2O_2$
Formula weight	336.42
Temperature/K	296(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.1707(14)
b/Å	11.2534(18)
c/Å	19.035(3)
α/°	90
β/°	98.717(5)
γ/°	90
Volume/Å^3	1941.7(5)
Z	4
ρ_{calc}g/cm^3	1.151
μ/mm^{-1}	0.074
F(000)	720.0
Crystal size/mm^3	0.25 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.77 to 55.174
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-24 \leq l \leq 24$
Reflections collected	60101
Independent reflections	4473 [R_{int} = 0.0383, R_{sigma} = 0.0186]
Data/restraints/parameters	4473/0/231
Goodness-of-fit on F^2	1.360
Final R indexes [I>=2σ (I)]	R_1 = 0.0590, wR_2 = 0.1847
Final R indexes [all data]	R_1 = 0.0852, wR_2 = 0.1998
Largest diff. peak/hole / e Å^{-3}	0.19/-0.13



Ortep Diagram of **3j** (thermal ellipsoids are shown with 30% probability).

7. Synthesis and Characterization of α-Aryl Amino Acid Derivatives

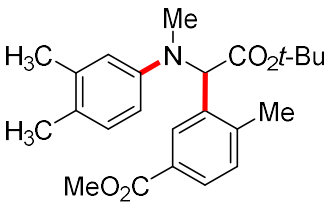
Methyl 3-(2-(*tert*-butoxy)-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3a)



Following the general procedure, treatment of methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182 µL, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(2-(*tert*-butoxy)-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate **3a** as a colourless sticky liquid (0.129 g, 70% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90-7.88 (m, 2H), 7.23 (m, 3H), 6.79-6.72 (m, 3H), 5.43 (s, 1H), 3.85 (s, 3H), 2.65 (s, 3H), 2.18 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.63, 166.89, 149.66, 144.15, 135.45, 131.08, 129.56, 129.46, 129.41, 128.12, 117.70, 112.68, 82.44, 63.96, 52.18, 33.78, 28.15, 19.45. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{22}H_{28}NO_4$: 370.2013, found: 370.2018. **FTIR (cm^{-1})** 2926, 2561, 1723, 1638, 1601, 1502, 1368, 1279, 1215, 1110, 846.

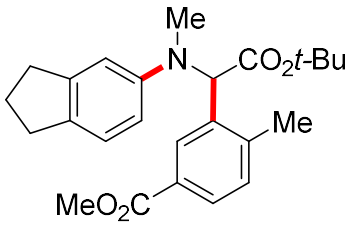
Methyl 3-(2-(*tert*-butoxy)-1-((3,4-dimethylphenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate (3b)



Following the general procedure, treatment of methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.5 mmol) and 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2b** (0.245 g, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10 °C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(2-(*tert*-butoxy)-1-((3,4-dimethylphenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate **3b** as a light yellow solid (0.148 g, 74% yield).

***R*f** (Pet. ether /EtOAc = 95/05): 0.23; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.97-7.94 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.66 (s, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 5.44 (s, 1H), 3.91 (s, 3H), 2.70 (s, 3H), 2.26 (s, 6H), 2.20 (s, 3H), 1.52 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 171.85, 166.95, 147.96, 144.23, 137.36, 135.65, 131.03, 130.46, 129.57, 129.39, 128.06, 125.66, 114.45, 110.22, 82.27, 64.00, 52.16, 33.93, 28.17, 20.55, 19.48, 18.76. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{32}NO_4$: 398.2326, found: 398.2332. **FTIR (cm^{-1})** 2925, 2859, 1727, 1613, 1571, 1510, 1447, 1368, 1276, 1101, 953, 843.

Methyl 3-(2-(*tert*-butoxy)-1-((2,3-dihydro-1*H*-inden-5-yl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate (3c)

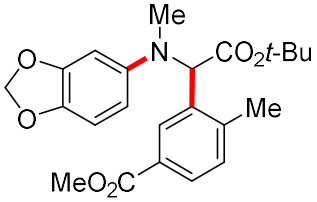


Following the general procedure, treatment of methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.5 mmol) and 6-(trimethylsilyl)-2,3-dihydro-1*H*-inden-5-yl trifluoromethanesulfonate **2c** (0.254 g, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(2-(*tert*-butoxy)-1-((2,3-dihydro-1*H*-inden-5-yl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate **3c** as a colourless sticky liquid (0.143 g, 70% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.59; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.96 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.73 (s, 1H), 6.64 (dd, *J* = 8.3, 2.2

Hz, 1H), 5.44 (s, 1H), 3.90 (s, 3H), 2.91-2.82 (m, 4H), 2.70 (s, 3H), 2.26 (s, 3H), 2.06 (p, J = 7.4 Hz, 2H), 1.51 (s, 9H). **^{13}C NMR (125 MHz, CDCl$_3$)**δ 171.88, 166.98, 148.70, 145.64, 144.24, 135.74, 133.41, 131.05, 129.55, 129.39, 128.07, 124.88, 111.03, 109.13, 82.32, 64.34, 52.19, 34.26, 33.52, 32.04, 28.20, 25.80, 19.54. **HRMS (ESI)** calculated [M+H] $^+$ for $C_{25}H_{32}NO_4$: 410.2326, found: 410.2331. **FTIR (cm^{-1})** 2977, 2361, 1727, 1606, 1439, 1367, 1217, 1193, 1153, 1111, 1005.

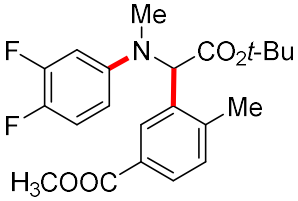
Methyl 3-(1-(benzo[*d*][1,3]dioxol-5-yl(methyl)amino)-2-(*tert*-butoxy)-2-oxoethyl)-4-methylbenzoate (3d)



Following the general procedure, treatment of methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.5 mmol) and 6-(trimethylsilyl)benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate **2d** (0.257 g, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(1-(benzo[d][1,3]dioxol-5yl(methyl)amino)-2-(*tert*-butoxy)-2-oxoethyl)-4-methylbenzoate **3d** as a yelliw sticky liquid (0.149 g, 72% yield).

***R*$_f$** (Pet. ether/EtOAc = 95/05): 0.38; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.96-7.91 (m, 2H), 7.28 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 6.48 (s, 1H), 6.25 (d, J = 8.4 Hz, 1H), 5.88 (s, 2H), 5.33 (s, 1H), 3.89 (s, 3H), 2.65 (s, 3H), 2.26 (s, 3H), 1.49 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 171.60, 166.91, 148.63, 145.97, 144.06, 139.94, 135.49, 131.08, 129.55, 129.43, 128.11, 108.63, 105.32, 100.85, 96.40, 82.41, 65.02, 52.18, 34.76, 28.16, 19.47. **HRMS (ESI)** calculated [M+H] $^+$ for $C_{23}H_{28}NO_6$: 414.1911, found: 414.1917. **FTIR (cm^{-1})** 2924, 2361, 1722, 1637, 1499, 1441, 1368, 1279, 1220, 1151, 1111, 979, 938.

Methyl 3-(2-(*tert*-butoxy)-1-((3,4-difluorophenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate(3e)

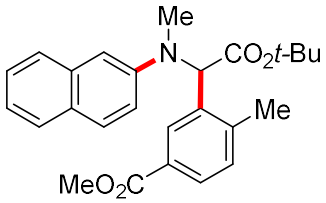


Following the general procedure, treatment of methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.5 mmol) and 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethane

sulfonate **2e** (0.251 g, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10 °C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(2-(*tert*-butoxy)-1-((3,4-difluorophenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate **3e** as a light yellow solid (0.075 g, 37% yield).

***R*f** (Pet. ether /EtOAc = 95/05): 0.26; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.96-7.93 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.09-7.02 (m, 1H), 6.62-6.58 (m, 1H), 6.49-6.46 (m, 1H), 5.35 (s, 1H), 3.90 (s, 3H), 2.65 (s, 3H), 2.24 (s, 3H), 1.50 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 171.12, 166.80, 150.93 (dd, *J* = 244.6, 13.2 Hz), 146.89 (d, *J* = 6.8 Hz), 143.96, 143.27 (dd, *J* = 237.7, 12.9 Hz), 134.86, 131.22, 129.67 (d, *J* = 9.2 Hz), 128.31, 117.59 (d, *J* = 17.7 Hz), 107.83 (dd, *J* = 5.1, 2.9 Hz), 101.92 (d, *J* = 21.4 Hz), 82.87, 64.37, 34.19, 52.24, 28.15, 19.37. **HRMS (ESI)** calculated [M+H] $^+$ for $C_{22}H_{26}F_2NO_4$: 406.1824, found: 4061826. **FTIR (cm^{-1})** 3066, 2953, 2927, 1727, 1602, 1520, 1440, 1370, 1254, 1214, 1154, 1096, 922, 838.

Methyl 3-(2-(*tert*-butoxy)-1-(methyl(naphthalen-2-yl)amino)-2-oxoethyl)-4-methylbenzoate (3f)



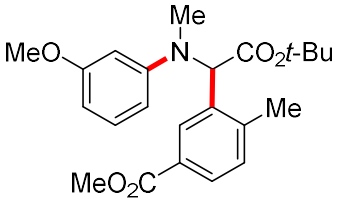
Following the general procedure, treatment of methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.5 mmol) and 1-(trimethylsilyl)naphthalen-2-yl trifluoromethane sulfonate **2f** (0.261 g, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(2-(*tert*-butoxy)-1-(methyl(naphthalen-2-yl)amino)-2-oxoethyl)-4-methylbenzoate **3f** as a brown solid (0.138 g, 66% yield).

Following the general procedure, using 3-(trimethylsilyl)naphthalen-2-yl trifluoromethane sulfonate **2g** (0.261 g, 0.75 mmol) as the aryne precursor, the product methyl 3-(2-(*tert*-butoxy)-1-(methyl(naphthalen-2-yl)amino)-2-oxoethyl)-4-methylbenzoate **3f** as a brown solid (0.130 g, 62% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.59; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.01 (s, 1H), 7.95 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.75 (d, *J* = 9.1 Hz, 1H), 7.69 (dd, *J* = 12.6, 8.2 Hz, 2H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.24-7.21 (m, 2H), 7.05 (d, *J* = 2.4 Hz, 1H), 5.62 (s, 1H), 3.89 (s,

3H), 2.82 (s, 3H), 2.23 (s, 3H), 1.51 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.60, 166.87, 147.57, 144.17, 135.33, 135.05, 131.14, 129.59, 129.53, 129.18, 128.17, 127.54, 127.42, 126.48, 126.45, 122.54, 115.80, 107.03, 82.54, 64.23, 52.18, 34.10, 28.16, 19.46. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{26}H_{30}NO_4$: 420.2169, found: 420.2175. **FTIR (cm^{-1})** 2925, 1926, 1724, 1606, 1438, 1367, 1218, 1153, 1110, 922.

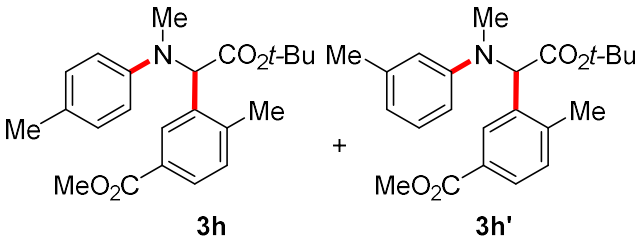
Methyl 3-(2-(*tert*-butoxy)-1-((3-methoxyphenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate (3g)



Following the general procedure, treatment of methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.5 mmol) and 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2h** (0.246 g, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10 °C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(2-(*tert*-butoxy)-1-((3-methoxyphenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate **3g** as alight yellow oil (0.075g, 38% yield).

***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.20; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95-7.93 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.21-7.17 (m, 1H), 6.46-6.44 (m, 1H), 6.38-6.36 (m, 2H), 5.45 (s, 1H), 3.90 (s, 3H), 3.81 (s, 3H), 2.69 (s, 3H), 2.23 (s, 3H), 1.51 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.58, 166.91, 160.96, 151.10, 144.19, 135.41, 131.11, 130.13, 129.57, 129.51, 128.16, 105.68, 102.48, 99.44, 82.49, 64.00, 55.27, 52.20, 33.90, 28.19, 19.47. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{30}NO_5$: 400.2118, found: 400.2125. **FTIR (cm^{-1})** 3658, 2926, 2583, 1724, 1608, 1579, 1498, 1368, 1301, 1255, 1252, 1105, 997, 837.

Methyl 3-(2-(*tert*-butoxy)-1-(methyl(p-tolyl)amino)-2-oxoethyl)-4-methylbenzoate (3h) and Methyl 3-(2-(*tert*-butoxy)-1-(methyl(m-tolyl)amino)-2-oxoethyl)-4-methylbenzoate (3h')

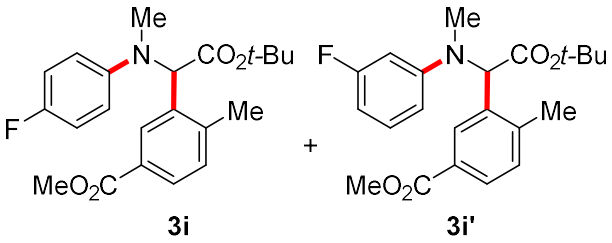


Following the general procedure, treatment of methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.5 mmol) and 4-methyl-2-

(trimethylsilyl)phenyl trifluoromethanesulfonate **2i** (0.235 g, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol)and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded inseparable mixture of methyl 3-(2-(*tert*-butoxy)-1-(methyl(*p*-tolyl)amino)-2-oxoethyl)-4-methylbenzoate **3h** and methyl 3-(2-(*tert*-butoxy)-1-(methyl(*m*-tolyl)amino)-2-oxoethyl)-4-methylbenzoate **3h'** as a yellow sticky liquid (0.113 g, 59% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.57; **^{1}H NMR (400 MHz, $CDCl_3$, major isomer)** δ 7.94-7.98 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.65-6.62 (m, 2H), 5.48 (s, 1H), 3.91 (s, 3H), 2.71 (s, 3H), 2.35 (s, 3H), 2.25 (s, 3H), 1.52 (s, 9H). **^{1}H NMR (400 MHz, $CDCl_3$, minor isomer))** δ 7.94-7.98 (m, 2H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.77 (d, *J* = 7.2 Hz, 1H), 6.65-6.62 (m, 2H), 5.46 (s, 1H), 3.91 (s, 3H), 2.71 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H), 1.52 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$, major isomer)** δ 171.72, 166.89, 149.77, 144.17, 135.52, 129.93, 129.57, 129.23, 128.13, 128.09, 113.55, 112.89, 82.35, 64.00, 52.14, 33.85, 28.16, 22.07, 19.44. **^{13}C NMR (100 MHz, $CDCl_3$, minor isomer (representative peaks))** δ 171.69, 166.91, 147.58, 139.03, 135.61, 118.69, 109.90, 82.31, 64.15, 52.14, 33.92, 20.37. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{30}NO_4$: 384.2169, found: 384.2175. **FTIR (cm^{-1})** 2952, 2103, 1724, 1608, 1438, 1279, 1217, 1153, 1110, 1009, 921.

Methyl 3-(2-(*tert*-butoxy)-1-((4-fluorophenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate (3i) and Methyl 3-(2-(*tert*-butoxy)-1-((3-fluorophenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate(3i')

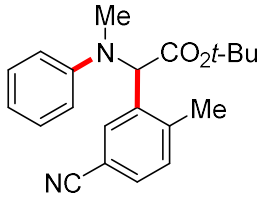


Following the general procedure, treatment of methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.5 mmol) and 5-fluoro-2-(trimethylsilyl)phenyl trifluoromethane sulfonate **2j** (0.237 g, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded inseparable mixture of methyl 3-(2-(*tert*-butoxy)-1-((4-fluorophenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate

3i and methyl 3-(2-(*tert*-butoxy)-1-((3-fluorophenyl)(methyl)amino) -2-oxoethyl)-4-methylbenzoate **3i'** as a yellow sticky liquid (0.077 g, 40% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.44; **^{1}H NMR (400 MHz, $CDCl_3$, major isomer)** δ 7.90-7.88 (m, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 8.8Hz, 2H), 6.73-6.71 (m, 2H), 5.34 (s, 1H), 3.84 (s, 3H), 2.62 (s, 3H), 2.20 (s, 3H), 1.43 (s, 9H). **^{1}H NMR (400 MHz, $CDCl_3$, minor isomer)** δ 7.90-7.88 (m, 2H),7.24 (d, *J* = 7.5 Hz, 1H), 7.18-7.12 (m, 1H), 6.53 (d, *J* =8.4 Hz, 1H),6.47-6.41 (m, 2H), 5.38 (s, 1H),3.84 (s, 3H), 2.62 (s, 3H), 2.17 (s, 3H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$, major isomer)** δ 171.48, 166.88, 156.08 (d, *J* = 235.2 Hz), 146.37, 144.03, 135.32, 131.12, 129.60, 129.51, 128.18, 115.77 (d, *J* = 22.1 Hz), 114.09 (d, *J* = 7.4 Hz), 82.53, 64.70, 52.18, 34.37, 28.14, 19.42. **^{13}C NMR (100 MHz, $CDCl_3$, minor isomer (representative peaks))** δ 171.21, 166.81, 164.76 (d, *J* = 242.2 Hz), 151.39 (d, *J* = 10.5 Hz), 134.96, 131.18, 130.48 (d, *J* = 10.2 Hz), 129.65, 128.26, 108.11 (d, *J* = 2.2 Hz), 104.20 (d, *J* = 21.2 Hz), 99.78 (d, *J* = 26.1 Hz), 82.76, 63.94, 52.20, 33.88, 28.14, 19.37. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{22}H_{27}FNO_4$: 388.1919, found: 388.1924. **FTIR (cm^{-1})** 2926, 2361, 1725, 1606, 1438, 1367, 1278, 1218, 1110, 843.

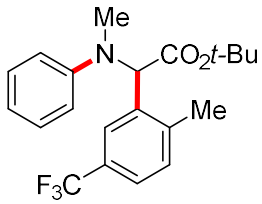
***tert*-Butyl 2-(5-cyano-2-methylphenyl)-2-(methyl(phenyl)amino)acetate (3j)**



Following the general procedure, treatment of *tert*-butyl *N*-(4-cyanobenzyl)-*N*-methylglycinate **1j** (0.130 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10 °C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 97/03) of the crude reaction mixture using silica gel afforded *tert*-butyl 2-(5-cyano-2-methylphenyl)-2-(methyl(phenyl)amino)acetate **3j** as a colourless sticky liquid (0.101 g, 60% yield).

***R*f** (Pet. ether /EtOAc = 95/05): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56-7.54 (m, 2H), 7.34-7.26 (m, 3H), 6.83-6.80 (m, 3H), 5.45 (s, 1H), 2.74 (s, 3H), 2.28 (s, 3H), 1.47 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.66, 149.40, 144.23, 136.71, 131.85, 131.80, 131.54, 129.41, 118.88, 118.23, 113.04, 110.09, 82.85, 64.00, 34.19, 28.10, 19.64. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{21}H_{25}N_2O_2$: 337.1911, found: 337.1919. **FTIR (cm^{-1})** 3431, 3064, 2977, 2929, 2229, 1733, 1599, 1501, 1367, 1290, 1214, 1154, 1109, 994, 832.

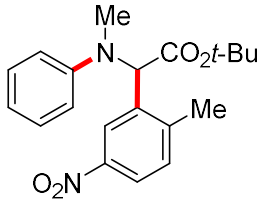
***tert*-Butyl 2-(methyl(phenyl)amino)-2-(2-methyl-5-(trifluoromethyl)phenyl)acetate (3k)**



Following the general procedure, treatment of *tert*-butyl *N*-methyl-*N*-(4-(trifluoromethyl)benzyl)glycinate **1k** (0. 152 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182µL, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 98/02) of the crude reaction mixture using silica gel afforded *tert*-butyl 2-(methyl(phenyl)amino)-2-(2-methyl-5-(trifluoromethyl)phenyl)acetate **3k** as a yellow sticky liquid (0.113 g, 61% yield).

***R*f** (Pet. ether/EtOAc = 97/03): 0.55; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54-7.52 (m, 2H), 7.35-7.27 (m, 3H), 6.85-6.80 (m, 3H), 5.48 (s, 1H), 2.72 (s, 3H), 2.25 (s, 3H), 1.48 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.34, 149.68, 142.79, 135.99, 131.38, 129.48, 128.59 (q, *J* = 32 Hz), 125.13, 124.32 (q, *J* = 272 Hz), 118.02, 112.95, 82.64, 64.05, 33.98, 28.15, 19.30. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{21}H_{25}F_3NO_2$: 380.1832, found: 380.1837. **FTIR (cm^{-1})** 2933, 2361, 1729, 1599, 1501, 1368, 1327, 1290, 1212, 1160, 1071, 987, 914.

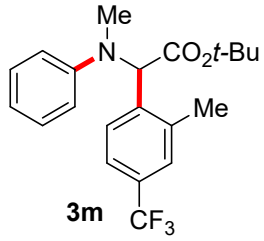
***tert*-Butyl 2-(methyl(phenyl)amino)-2-(2-methyl-5-nitrophenyl)acetate (3l)**



Following the general procedure, treatment of *tert*-butyl *N*-methyl-*N*-(4-nitrobenzyl)glycinate **1l** (0.140 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10 °C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl *tert*-butyl 2-(methyl(phenyl)amino)-2-(2-methyl-5-nitrophenyl)acetate **3l** as a colourless sticky liquid (0.090 g, 51% yield).

***R*f** (Pet. ether /EtOAc = 95/05): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19-7.18 (m, 1H), 8.15-8.13 (m, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.32-7.28 (m, 2H), 6.86-6.81 (m, 3H), 5.50 (s, 1H), 2.77 (s, 3H), 2.32 (s, 3H), 1.52 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.66, 149.46, 146.49, 146.39, 136.97, 131.76, 129.48, 123.28, 123.22, 118.29, 113.06, 83.04, 64.16, 34.21, 28.14, 19.56. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{20}H_{25}N_2O_4$: 357.1809, found: 357.1810. **FTIR (cm^{-1})** 3093, 2976, 2930, 2821, 1734, 1598, 1522, 1454, 1345, 1287, 1212, 1154, 991, 837.

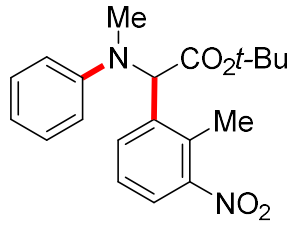
***tert*-Butyl 2-(methyl(phenyl)amino)-2-(2-methyl-4-(trifluoromethyl)phenyl)acetate (3m)**



Following the general procedure, treatment of *tert*-butyl *N*-methyl-*N*-(3-(trifluoromethyl)benzyl)glycinate **1m** (0.152 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182µL, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 98/02) of the crude reaction mixture using silica gel afforded *tert*-butyl 2-(methyl(phenyl)amino)-2-(2-methyl-4-(trifluoromethyl)phenyl)acetate **3m** as a yellow solid (0.104 g, 55% yield).

***R*f** (Pet. ether/EtOAc = 97/03): 0.55; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.50-7.48 (m, 2H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.30-7.26 (m, 2H), 6.84-6.79 (m, 3H), 5.48 (s, 1H), 2.72 (s, 3H), 2.26 (s, 3H), 1.47 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 171.19, 149.49, 139.29, 138.85, 129.31, 129.17, 128.75, 128.56, 128.44, δ 127.54 (q, *J* = 3.6 Hz), 122.84 (q, *J* = 4.0 Hz), 121.25, 120.44, 117.87, 112.79, 82.39, 63.91, 33.93, 28.03, 19.16. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{21}H_{25}F_3NO_2$: 380.1832, found: 380.1837. **FTIR (cm^{-1})** 2931, 2361, 1734, 1640, 1600, 1502, 1452, 1415, 1368, 1331, 1286, 1215, 1160, 993.

***tert*-Butyl 2-(methyl(phenyl)amino)-2-(2-methyl-3-nitrophenyl)acetate (3n)**

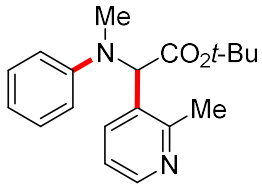


Following the general procedure, treatment of *tert*-butyl *N*-methyl-*N*-(2-nitrobenzyl)glycinate **1n** (0.140 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182µL, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 95/05) of the crude reaction mixture using silica gel afforded *tert*-butyl 2-(methyl(phenyl)amino)-2-(2-methyl-3-nitrophenyl)acetate **3n** as a colourless sticky liquid (0.100 g, 56% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.29; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.29 (t, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 3H), 5.51 (s, 1H), 2.77 (s, 3H), 2.30 (s, 3H), 1.47 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 170.95, 151.94, 149.33, 137.98, 132.57, 132.05, 129.51, 126.58, 123.85, 118.34, 113.06, 82.81,

64.28, 34.21, 28.15, 14.45. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{20}H_{25}N_2O_4$: 357.1809, found: 357.1814. **FTIR (cm^{-1})** 2924, 2361, 1721, 1599, 1499, 1439, 1262, 1220, 1127, 1003, 951.

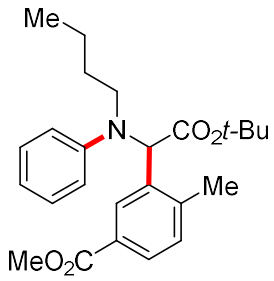
***tert*-Butyl 2-(methyl(phenyl)amino)-2-(2-methylpyridin-3-yl)acetate (3o)**



Following the general procedure, treatment of *tert*-butyl *N*-methyl-*N*-(pyridin-2-ylmethyl)glycinate **1o** (118 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10 °C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 97/03) of the crude reaction mixture using silica gel afforded *tert*-butyl 2-(methyl(phenyl)amino)-2-(2-methylpyridin-3-yl)acetate **3o** as a colourless sticky liquid (0.042 g, 27% yield).

***R*f** (Pet. ether /EtOAc = 95/05): 0.27; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48-8.47 (m, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.28-7.24 (m, 2H), 7.19-7.16 (m, 1H), 6.82-6.77 (m, 3H), 5.45 (s, 1H), 2.73 (s, 3H), 2.44 (s, 3H), 1.44 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.86, 158.67, 149.55, 148.21, 136.13, 130.87, 129.44, 121.31, 118.20, 113.12, 82.66, 63.92, 34.25, 28.15, 22.01. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{19}H_{25}N_2O_2$: 313.1911, found: 313.1913. **FTIR (cm^{-1})** 3060, 2975, 2926, 2853, 2820, 1733, 1598, 1502, 1443, 1367, 1285, 1153, 946, 840.

Methyl 3-(2-(*tert*-butoxy)-1-(butyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3p)

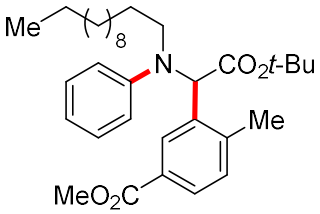


Following the general procedure, treatment of methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(butyl)amino)methyl)benzoate **1p** (0.168 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182µL, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(2-(*tert*-butoxy)-1-(butyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate **3p** as a colourless sticky liquid (0.123 g, 60% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.58; **^{1}H NMR (400 MHz, $CDCl_3$)** 7.95 (d, *J* = 7.8 Hz, 1H), 7.29-7.24 (m, 4H), 6.80-6.76 (m, 3H), 5.44 (s, 1H), 3.91 (s, 3H), 3.27-3.19 (m, 1H), 3.14- 3.07 (m,

1H), 2.31 (s, 3H), 1.49 (s, 9H), 1.07-0.94 (m, 2H), 0.90-0.84 (m, 2H), 0.67 (t, J = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.70, 166.94, 149.06, 144.48, 135.63, 130.84, 129.82, 129.55, 129.42, 128.12, 117.65, 113.09, 82.38, 63.60, 52.21, 47.94, 30.49, 28.17, 20.04, 19.48, 13.75. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{34}NO_4$: 412.2482, found: 412.2488. **FTIR (cm^{-1})** 2978, 2361, 1725, 1615, 1512, 1438, 1274, 1228, 1154, 1108, 1005, 893.

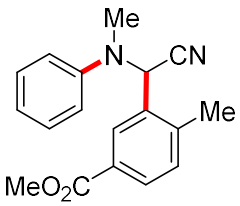
Methyl 3-(2-(*tert*-butoxy)-1-(dodecyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3q)



Following the general procedure, treatment of methyl methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(dodecyl)amino)methyl)benzoate **1q** (0.239 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10 °C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(2-(*tert*-butoxy)-1-(dodecyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate **3q** as a colourless oil (0.150 g, 54% yield).

***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.40;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99-7.94 (m, 2H), 7.29-7.24 (m, 3H), 6.80-6.76 (m, 3H), 5.44 (s, 1H), 3.91 (s, 3H), 3.27-3.19 (m, 1H), 3.14-3.06 (m, 1H), 2.31 (s, 3H), 1.49 (s, 9H), 1.33-0.87 (m, 23H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.69, 166.90, 149.05, 144.49, 135.64, 130.82, 129.83, 129.55, 129.42, 128.12, 117.60, 112.99, 82.37, 63.49, 52.19, 48.24, 32.06, 29.76, 29.65, 29.59, 29.48, 29.15, 28.25, 28.16, 26.82, 22.83, 19.49, 14.26. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{33}H_{50}NO_4$: 524.3734, found: 524.3741. **FTIR (cm^{-1})** 3579, 2925, 2852, 1725, 1599, 1502, 1437, 1367, 1277, 1150, 1223, 1017, 951, 844.

Methyl 3-(cyano(methyl(phenyl)amino)methyl)-4-methylbenzoate (3r)

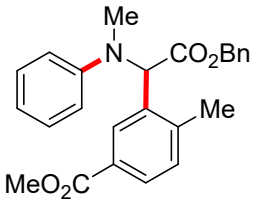


Following the general procedure, treatment of methyl 4-(((cyanomethyl)(methyl)amino)methyl)benzoate **1r** (0.109 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182µL, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using

silica gel afforded methyl 3-(cyano(methyl(phenyl)amino)methyl)-4-methylbenzoate **3r** as a yellow sticky liquid (0.103 g, 70% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.50; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.34 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.38-7.33 (m, 3H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 1H), 5.86 (s, 1H), 3.94 (s, 3H), 2.69 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.44, 148.77, 142.75, 131.69, 131.64, 130.73, 129.64, 129.62, 128.60, 121.43, 116.61, 116.04, 56.34, 52.32, 34.38, 19.37. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{18}H_{18}N_2O_2Na$: 317.1260, found: 317.1266. **FTIR (cm^{-1})** 2924, 2361, 1721, 1600, 1499, 1439, 1262, 1127, 1032, 952.

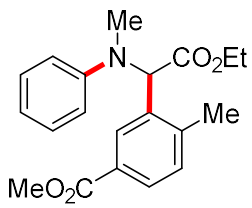
Methyl 3-(2-(benzyloxy)-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3s)



Following the general procedure, treatment of methyl 4-(((2-(benzyloxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1s** (0.098 g, 0.3 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.134 g, 109 µL, 0.45 mmol) in the presence of KF (0.052 g, 0.9 mmol) and 18-crown-6 (0.238 g, 0.9 mmol) in THF (1.2 mL) at -10 °C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(2-(benzyloxy)-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate **3s** as a light yellow oil (0.037g, 30% yield).

***R*f** (Pet. ether /EtOAc = 95/05): 0.23; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.83 (s, 1H), 7.31-7.26 (m, 8H), 6.85-6.80 (m, 3H), 5.70 (s, 1H), 5.28 (s, 2H), 3.89 (s, 3H), 2.73 (s, 3H), 2.25 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 172.12, 166.81, 149.52, 144.01, 135.52, 134.75, 131.24, 129.83, 129.53, 129.45, 128.68, 128.59, 128.46, 128.32, 118.17, 113.05, 67.17, 63.56, 52.24, 33.82, 19.52. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{26}NO_4$: 404.1856, found: 404.1860. **FTIR (cm^{-1})** 3062, 3033, 2954, 2926, 2855, 1724, 1600, 1501, 1442, 1370, 1278, 1171, 1110, 997.

Methyl 3-(2-ethoxy-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3t)

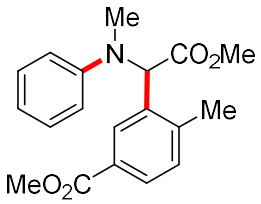


Following the general procedure, treatment of methyl methyl 4-(((2-ethoxy-2-oxoethyl)(methyl)amino)methyl)benzoate **1t** (0.133 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182µL, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-

crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(2-ethoxy-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate **3t** as a colourless sticky liquid (0.082 g, 48% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.57; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.87 (s, 1H), 7.31-7.26 (m, 3H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 5.63 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 2.74 (s, 3H), 2.26 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.18, 166.82, 149.52, 144.02, 135.00, 131.17, 129.67, 129.47, 129.42, 128.24, 117.99, 112.86, 63.39, 61.39, 52.20, 33.74, 19.49, 14.34. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{20}H_{24}NO_4$: 342.1700, found: 342.1705. **FTIR (cm^{-1})** 2924, 2105, 1722, 1641, 1502, 1439, 1368, 1278, 1219, 1187, 1026.

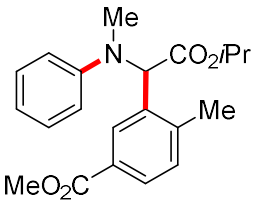
Methyl 3-(2-methoxy-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3u)



Following the general procedure, treatment of methyl 4-(((2-methoxy-2-oxoethyl)(methyl)amino)methyl)benzoate **1u** (0.126 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182µL, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(2-methoxy-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate **3u** as a yellow sticky liquid (0.072 g, 44% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.57; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.80 (s, 1H), 7.28-7.22 (m, 3H), 6.83-6.76 (m, 3H), 5.65 (s, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 2.71 (s, 3H), 2.23 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.67, 166.77, 149.46, 143.94, 134.87, 131.19, 129.73, 129.49, 129.32, 128.30, 118.09, 112.88, 63.36, 52.29, 52.20, 33.70, 19.48. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{19}H_{22}NO_4$: 328.1543, found: 328.1549. **FTIR (cm^{-1})** 2951, 1721, 1600, 1500, 1437, 1235, 1196, 1033, 1006, 953.

Methyl 3-(2-isopropoxy-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3v)

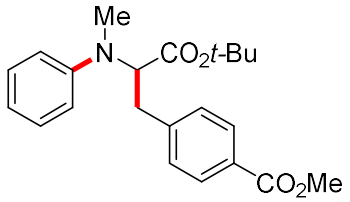


Following the general procedure, treatment of methyl 4-(((2-isopropoxy-2-oxoethyl)(methyl)amino)methyl)benzoate **1v** (0.140 g, 0.5 mmol) and 2-

(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182µL, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl methyl 3-(2-isopropoxy-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate **3v** as a yellow sticky liquid (0.142 g, 65% Sommelet-Hauser product and 15% [1,2]Stevens product).

***R*f** (Pet. ether/EtOAc = 95/05): 0.53; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.91 (s, 1H), 7.29 (m, 3H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 5.60 (s, 1H), 5.22 (m, 1H), 3.90 (s, 3H), 2.74 (s, 3H), 2.26 (s, 3H), 1.33 (d, *J* = 6.3 Hz, 3H), 1.24 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.70, 166.81, 149.59, 144.07, 135.08, 131.14, 129.59, 129.51, 129.43, 128.18, 117.91, 112.85, 69.11, 63.50, 52.17, 33.79, 22.03, 21.71, 19.47. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{21}H_{26}NO_4$: 356.1856, found: 356.1859. **FTIR (cm^{-1})** 2982, 2946, 1724, 1599, 1503, 1277, 1192, 1103, 962, 833.

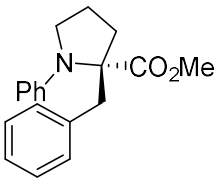
Methyl 4-(3-(*tert*-butoxy)-2-(methyl(phenyl)amino)-3-oxopropyl)benzoate (4a)



Following the procedure, treatment of methyl 4-(((2-(*tert*-butoxy)-2-oxoethyl)(methyl)amino)methyl)benzoate **1a** (0.147 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182µL, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at 70°C for 12h, followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 4-(3-(*tert*-butoxy)-2-(methyl(phenyl)amino)-3-oxopropyl)benzoate **4a** as a colourless sticky liquid (0.129 g, 70% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.51; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.19 (t, *J* = 8.4 Hz, 2H), 6.76-6.72 (m, 3H), 4.49 (dd, *J* = 8.2, 7.0 Hz, 1H), 3.89 (s, 3H), 3.33 (dd, *J* = 14.1, 6.8 Hz, 1H), 3.12 (dd, *J* = 14.1, 8.4 Hz, 1H), 2.90 (s, 3H), 1.36 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.97, 167.16, 150.02, 143.90, 129.82, 129.28, 129.12, 128.53, 118.00, 114.04, 81.78, 64.63, 52.14, 35.76, 33.79, 28.12. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{22}H_{28}NO_4$: 370.2013, found: 370.2018. **FTIR (cm^{-1})** 2926, 2360, 1722, 1643, 1503, 1279, 1219, 1153, 1108, 1025, 845.

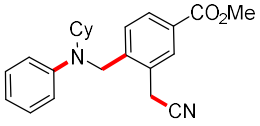
Methyl (*S*)-2-benzyl-1-phenylpyrrolidine-2-carboxylate (4w)



The treatment of methyl benzyl-*L*-prolinate **1w** (0.055 g, 0.25 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.112 g, 91 µL, 0.375mmol) in the presence of CsF (0.114 g, 0.75 mmol) in DME (1.0 mL) at -20°C for 6h, followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl (*S*)-2-benzyl-1-phenylpyrrolidine-2-carboxylate **4w** as a yellow sticky liquid (0.036 g, 49% yield).

***R*f** (Pet. ether/EtOAc = 95/05): 0.51; 87% ee, $[\alpha]_D^{25}$ = +39.21 (c 0.1, $CHCl_3$). **HPLC** (Chiralcel OD-H, 99 : 1 (hexane:IPA), 0.8 mL/min) Major: 11.9 min, Minor: 9.9 min. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32- 7.28 (m, 2H), 7.24-7.21 (m, 3H), 7.04-7.02 (m, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 3.82 (d, *J* = 14.1 Hz, 1H), 3.72 (s, 3H), 3.38 (q, *J* = 7.4 Hz, 1H), 3.25-3.19 (m, 2H), 2.29-2.16 (m, 2H), 1.82 – 1.76 (m, 1H), 1.14-1.04 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.48, 145.85, 137.26, 130.98, 129.37, 128.03, 126.55, 116.45, 112.96, 69.26, 52.56, 50.69, 37.71, 37.65, 22.54. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{19}H_{22}NO_2$: 296.1645, found: 296.1644. **FTIR (cm^{-1})** 2924, 1762, 1672, 1516, 1452, 1146, 1077, 1049, 906.

Methyl 3-(cyanomethyl)-4-((cyclohexyl(phenyl)amino)methyl)benzoate (5)



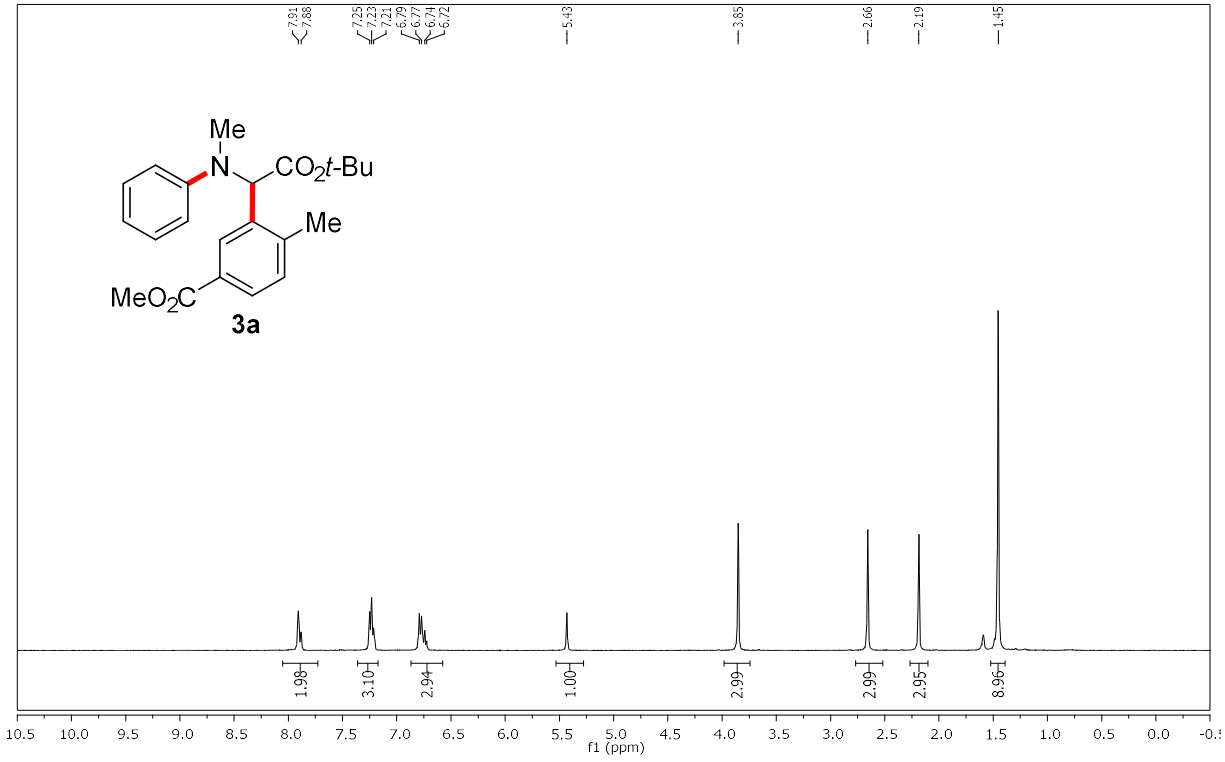
Following the general procedure, treatment of methyl 4-(((cyanomethyl)(cyclohexyl)amino)methyl)benzoate **1x** (0.143 g, 0.5 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.223 g, 182µL, 0.75mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at -10°C for 5 h, then warming to rt for 12 h followed by flash column chromatography (Pet. ether/EtOAc = 97/03) of the crude reaction mixture using silica gel afforded methyl 3-(cyanomethyl)-4-((cyclohexyl(phenyl) amino)methyl)benzoate **5** as a yellow sticky liquid (0.073 g, 40% yield).

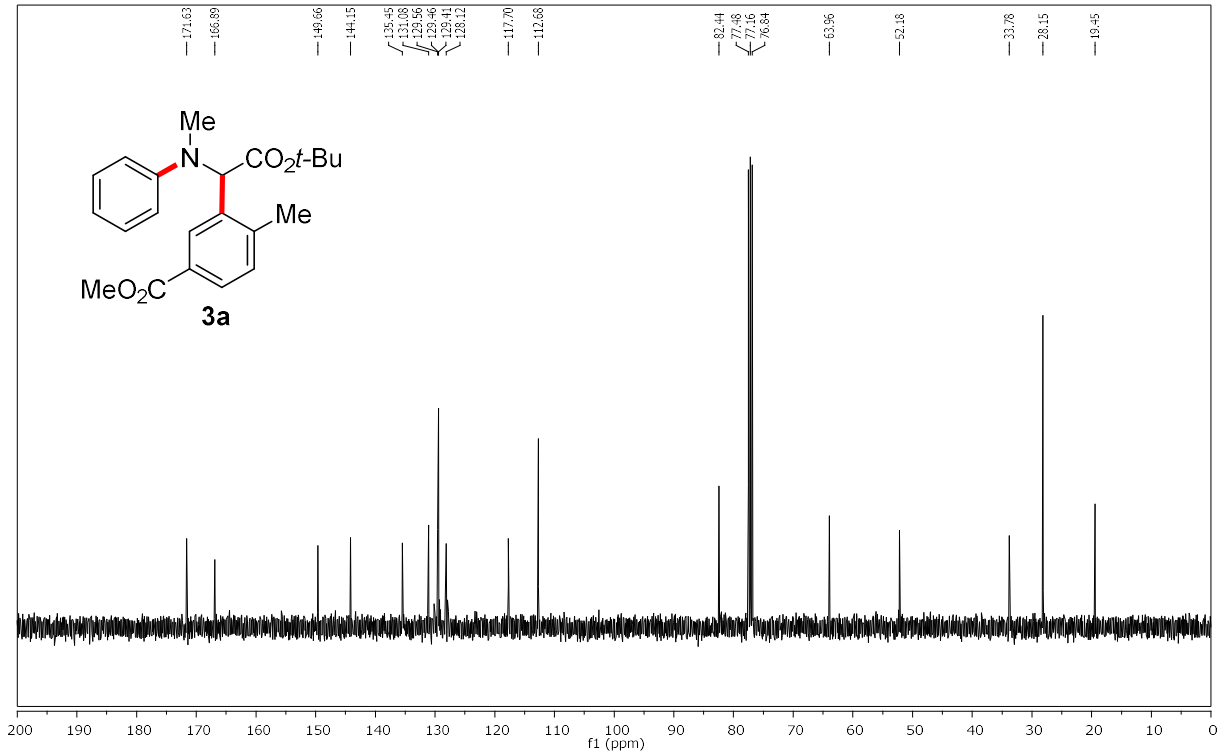
***R*f** (Pet. ether/EtOAc = 95/05): 0.44; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (s, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 2H), 4.45 (s, 2H), 3.91 (s, 3H), 3.84 (s, 2H), 3.77-3.72 (m, 1H), 1.92 (d, *J* = 10.4 Hz, 2H), 1.82 (d, *J* = 11.8 Hz, 2H), 1.68 (d, *J* = 13.2 Hz, 1H), 1.40-1.31 (m, 4H), 1.17-1.11 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.49, 148.71, 143.72, 130.53, 129.90, 129.55, 129.40, 128.47, 127.34, 117.83, 116.90, 114.15, 57.99, 52.38, 47.87, 30.46, 26.18, 25.88, 21.34. **HRMS (ESI)**

calculated $[M+H]^+$ for $C_{23}H_{27}N_2O_2$: 363.2067, found: 363.2073. **FTIR (cm^{-1})** 2925, 2348, 1722, 1635, 1499, 1440, 1368, 1279, 1223, 1152, 1113, 1039, 976, 939.

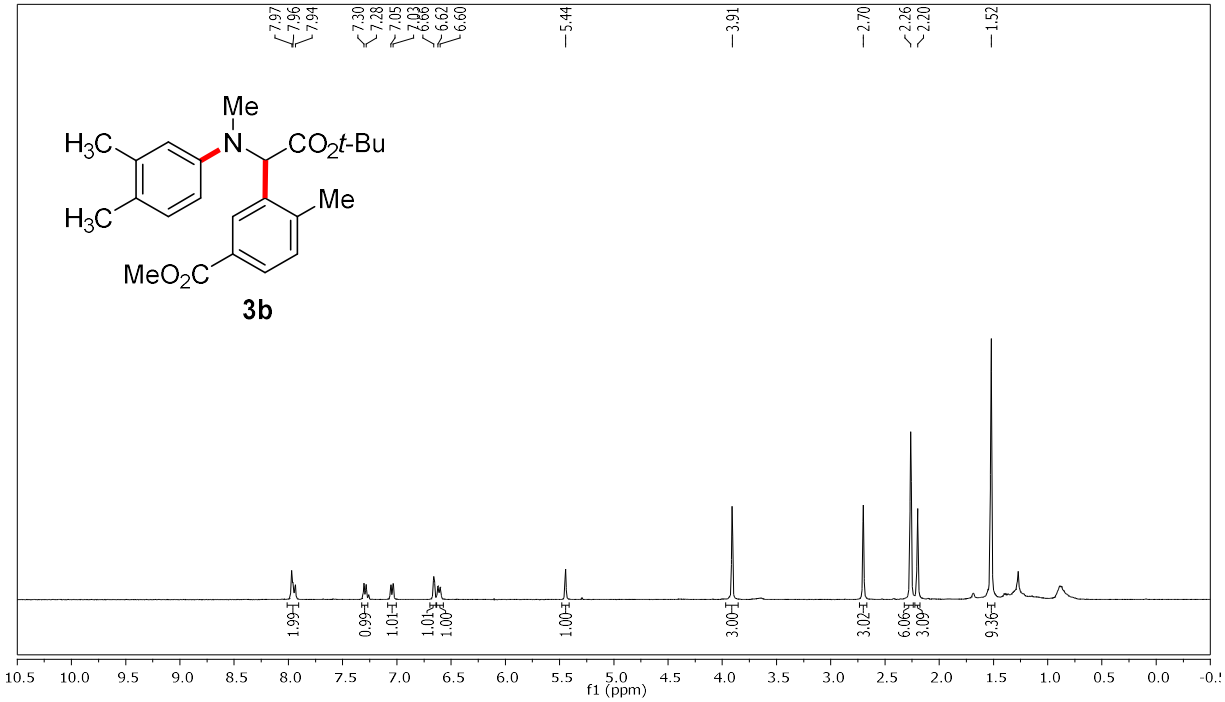
8. ^{1}H and ^{13}C NMR Spectra of α-Aryl Amino Acid Derivatives

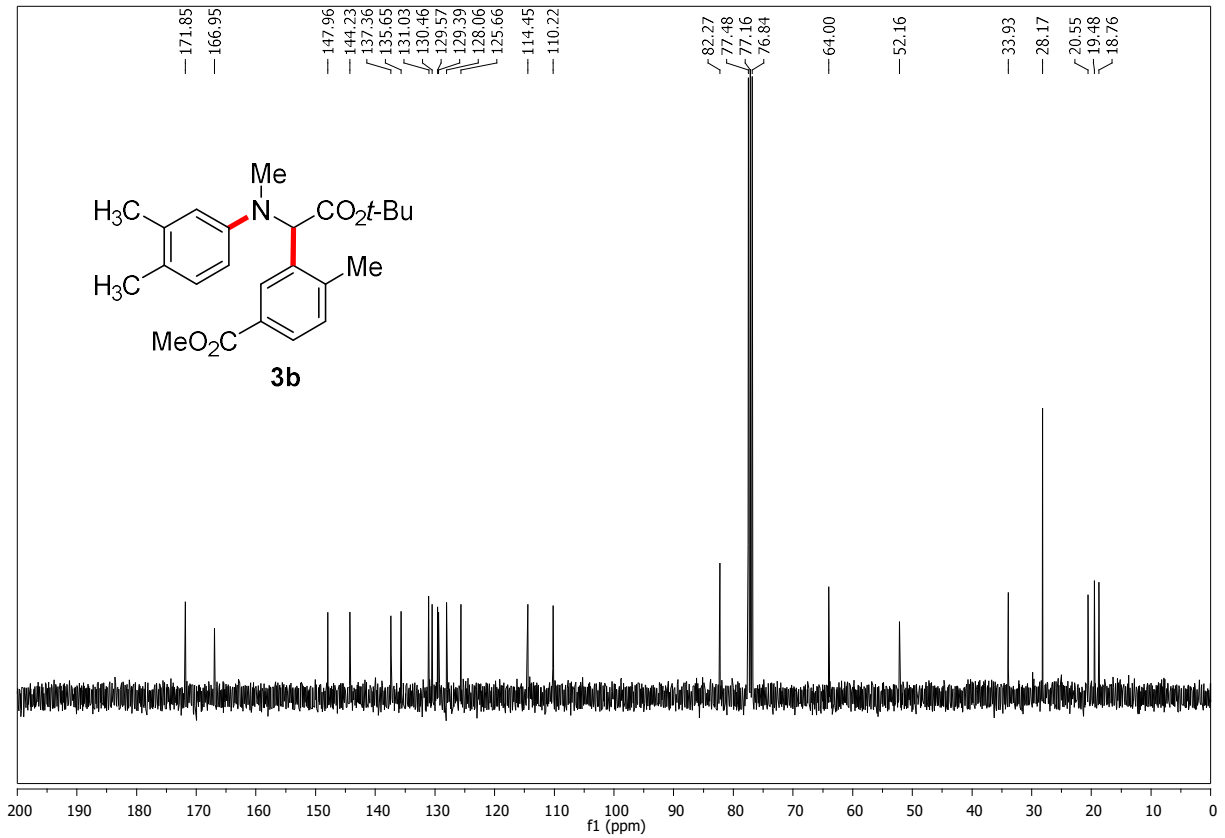
Methyl 3-(2-(*tert*-butoxy)-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3a)



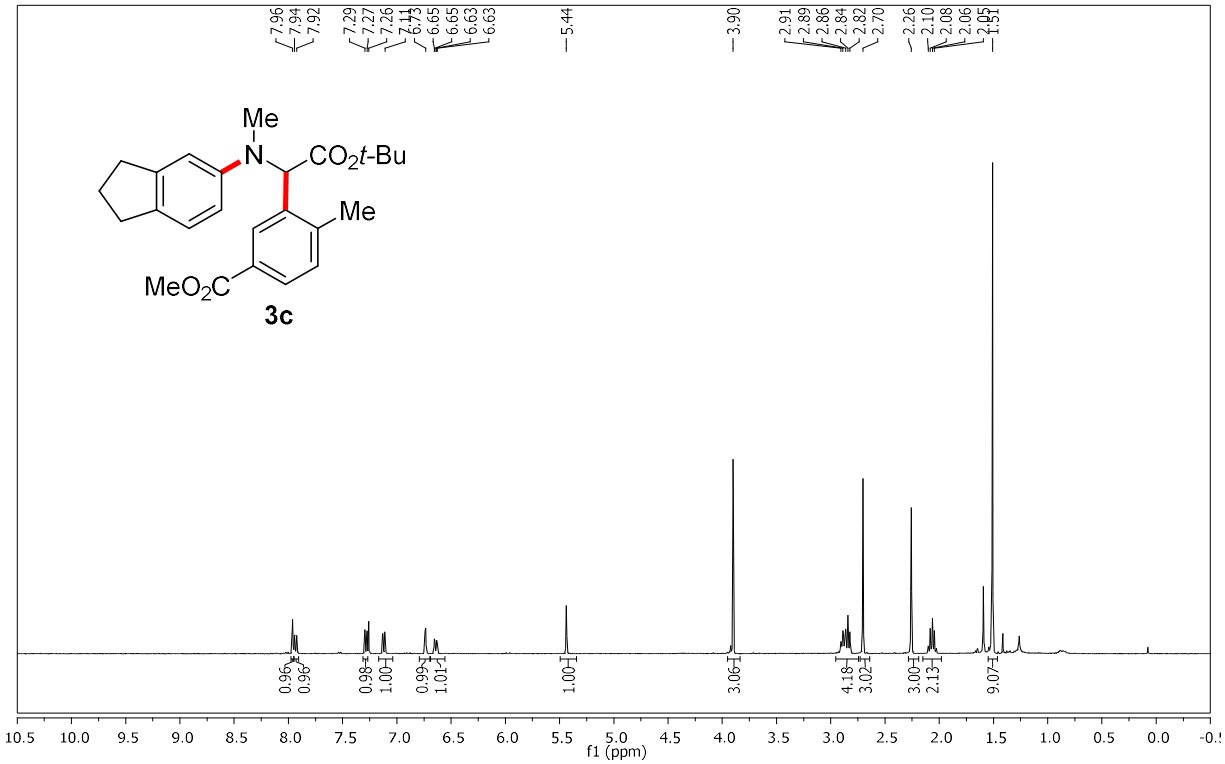


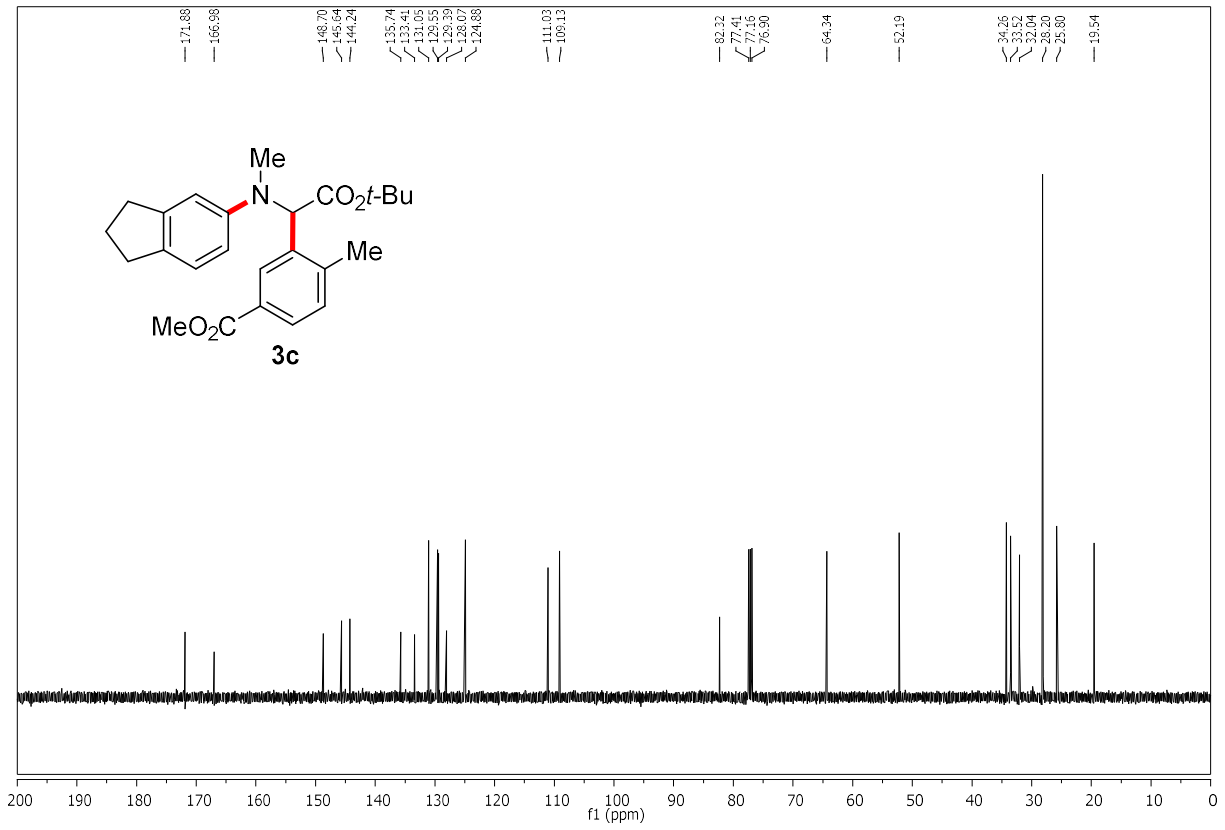
Methyl 3-(2-(*tert*-butoxy)-1-((3,4-dimethylphenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate(3b)



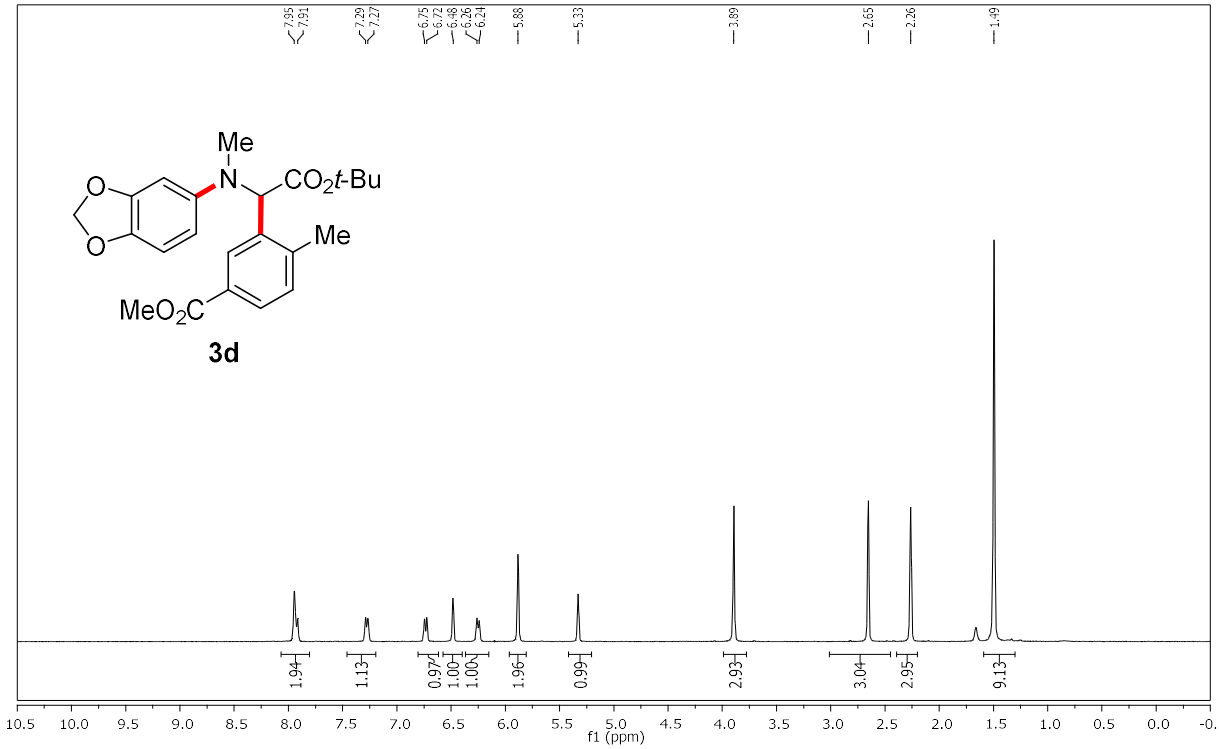


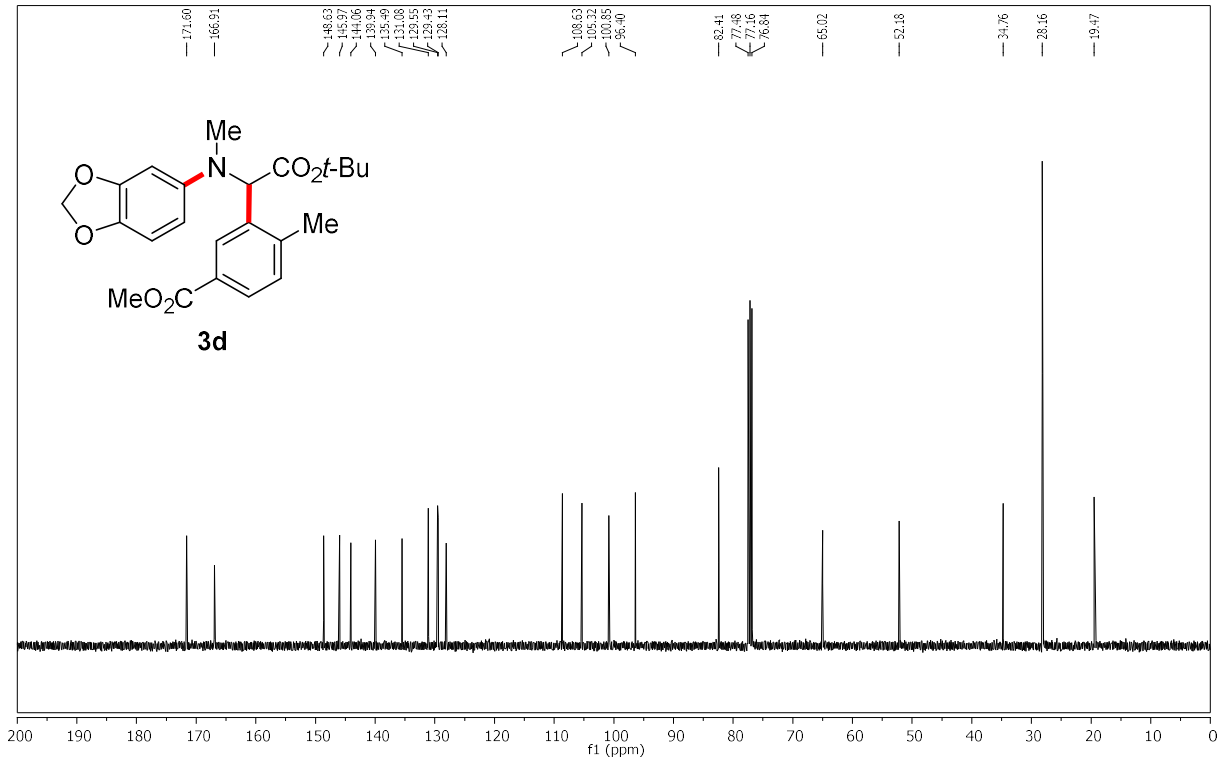
Methyl 3-(2-(*tert*-butoxy)-1-((2,3-dihydro-1*H*-inden-5-yl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate (3c)



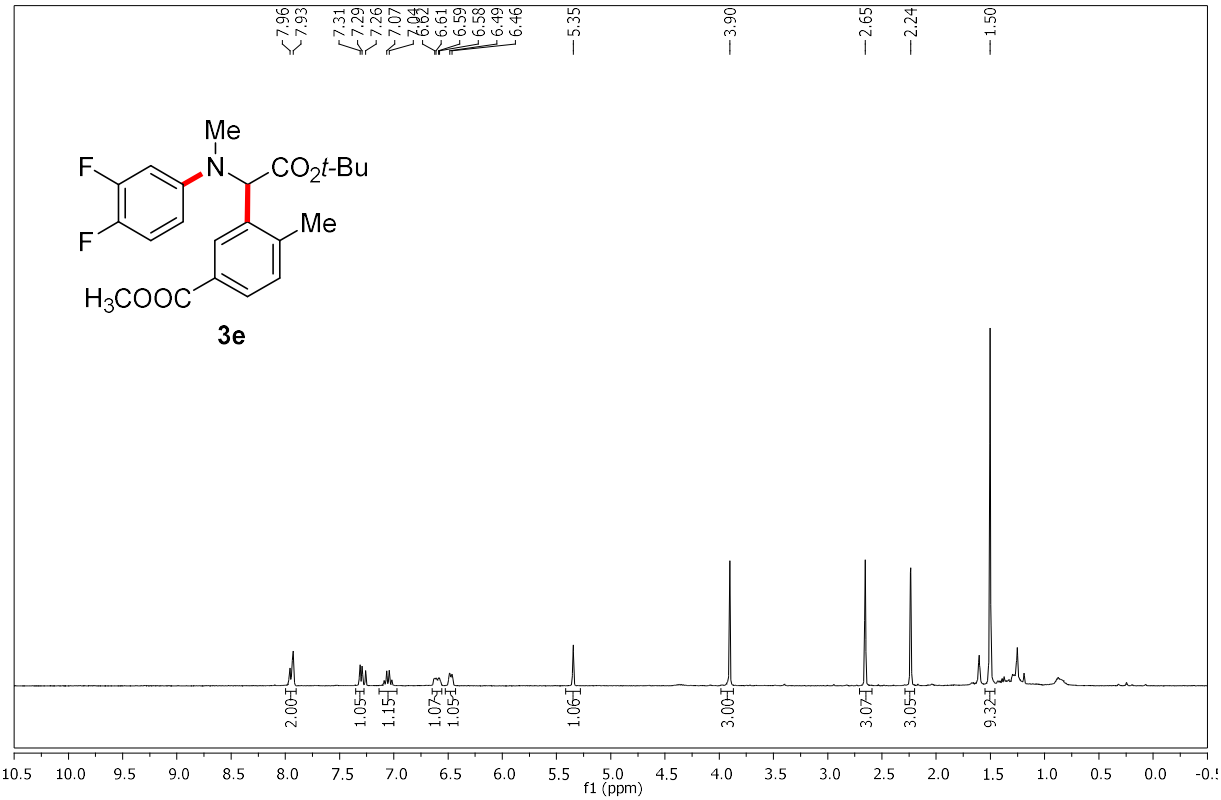


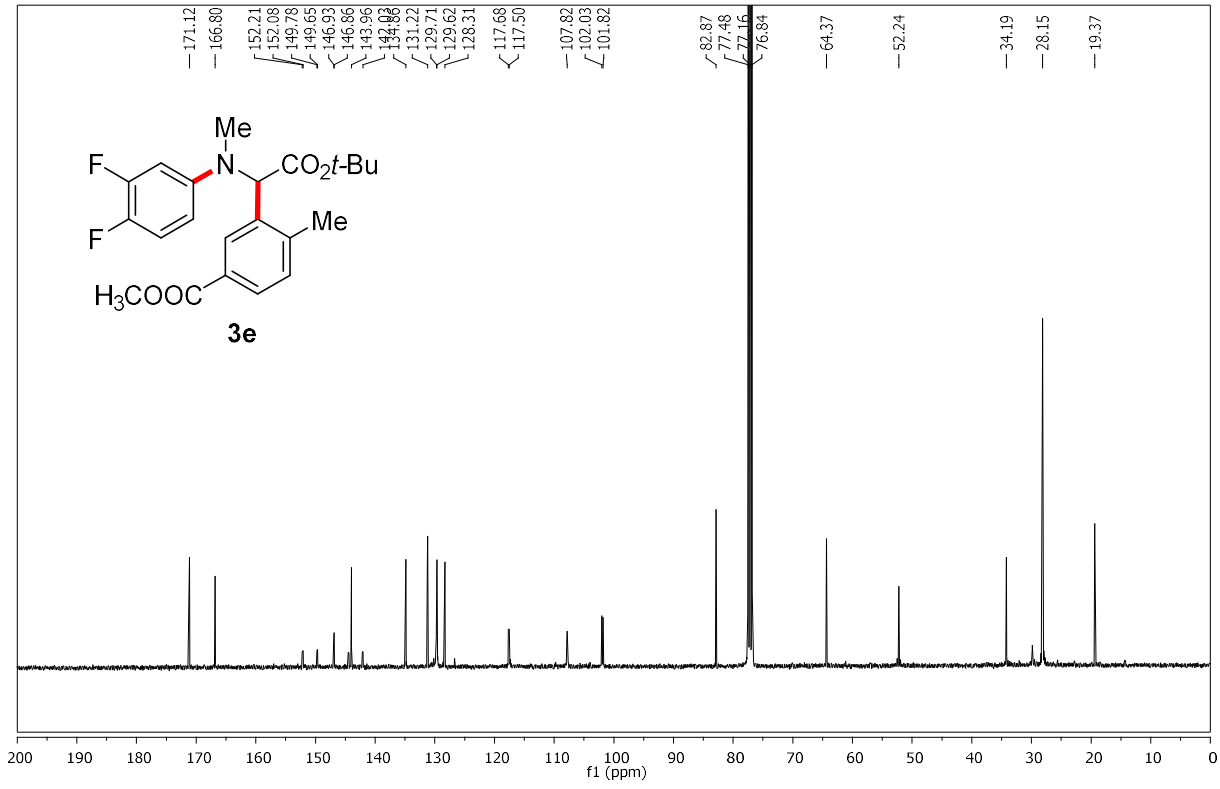
Methyl 3-(1-(benzo[*d*][1,3]dioxol-5-yl(methyl)amino)-2-(*tert*-butoxy)-2-oxoethyl)-4-methylbenzoate (3d)



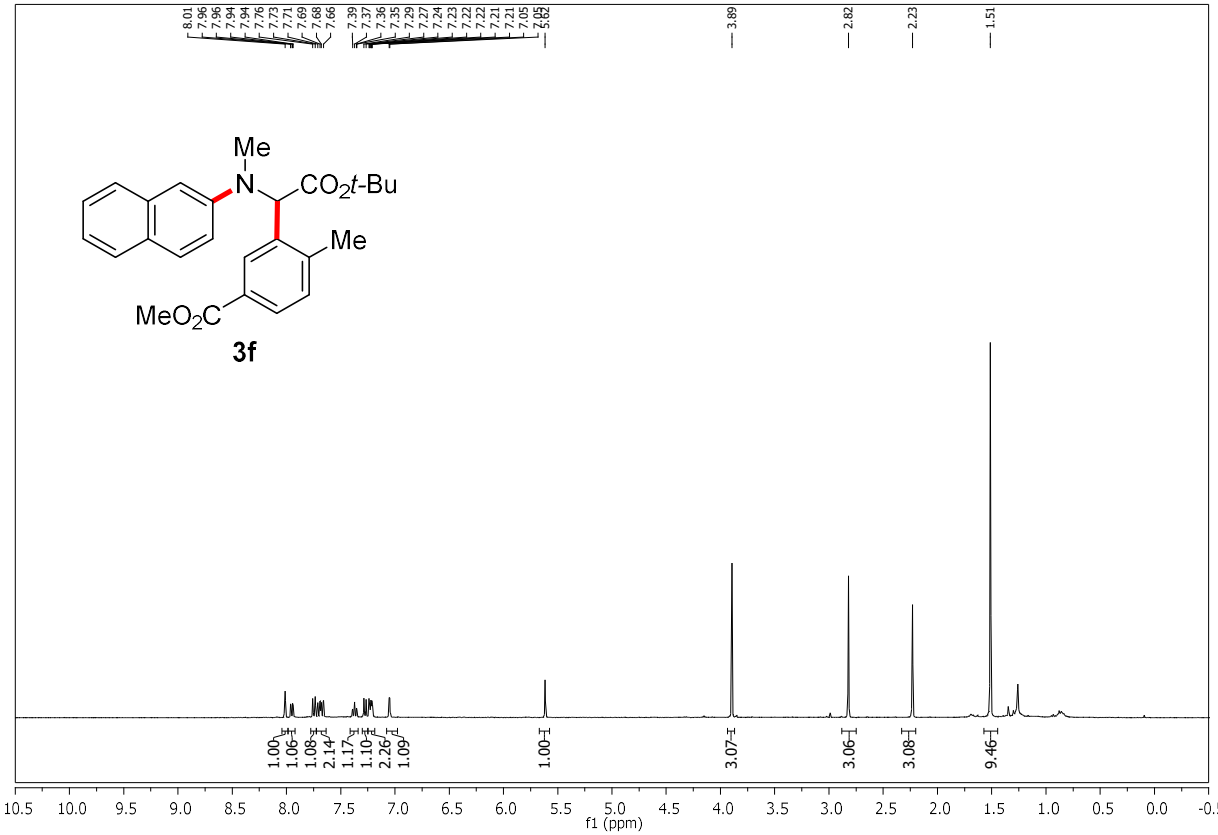


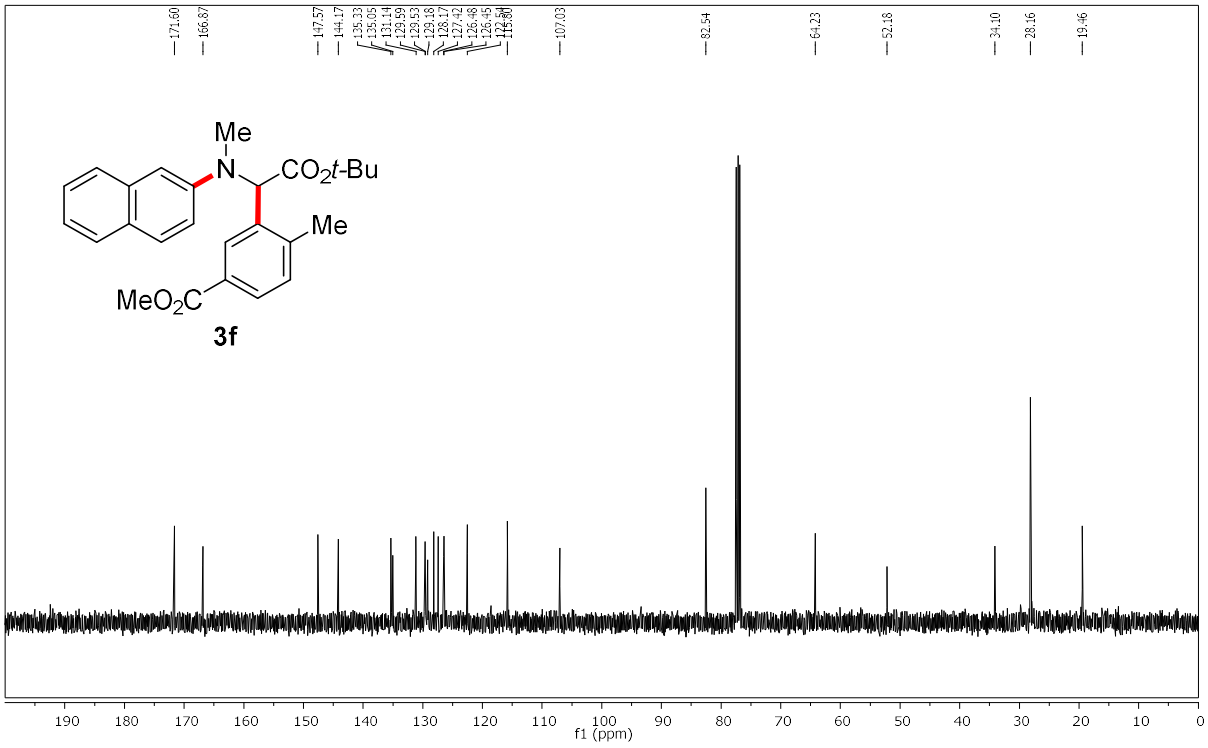
Methyl 3-(2-(*tert*-butoxy)-1-((3,4-difluorophenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate (3e)



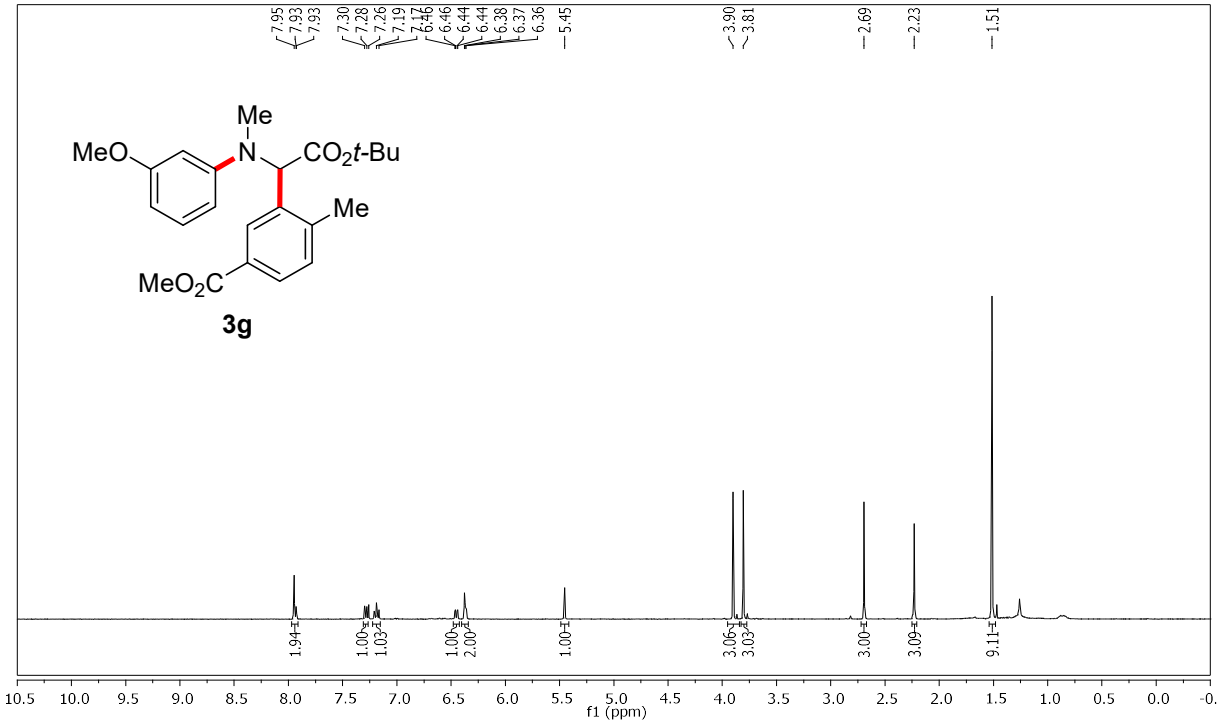


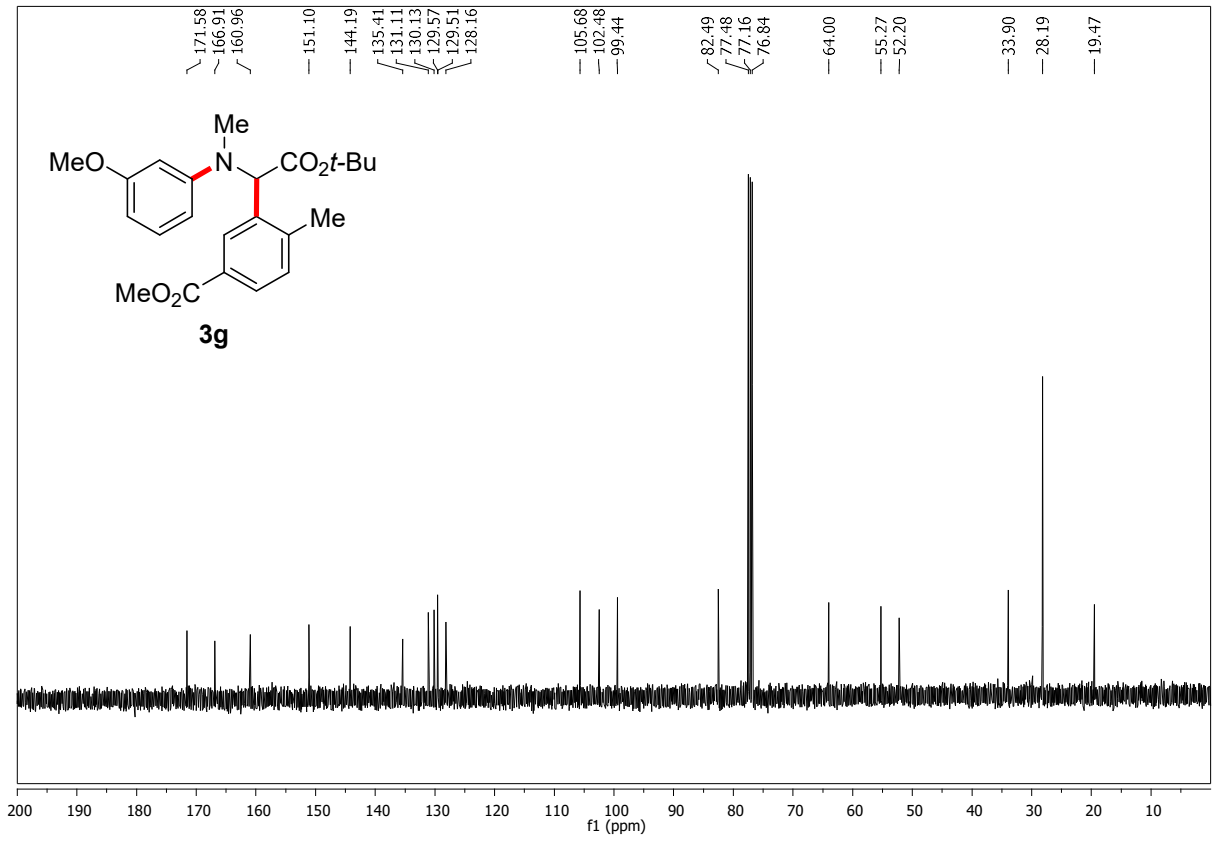
Methyl 3-(2-(*tert*-butoxy)-1-(methyl(naphthalen-2-yl)amino)-2-oxoethyl)-4-methylbenzoate (3f)



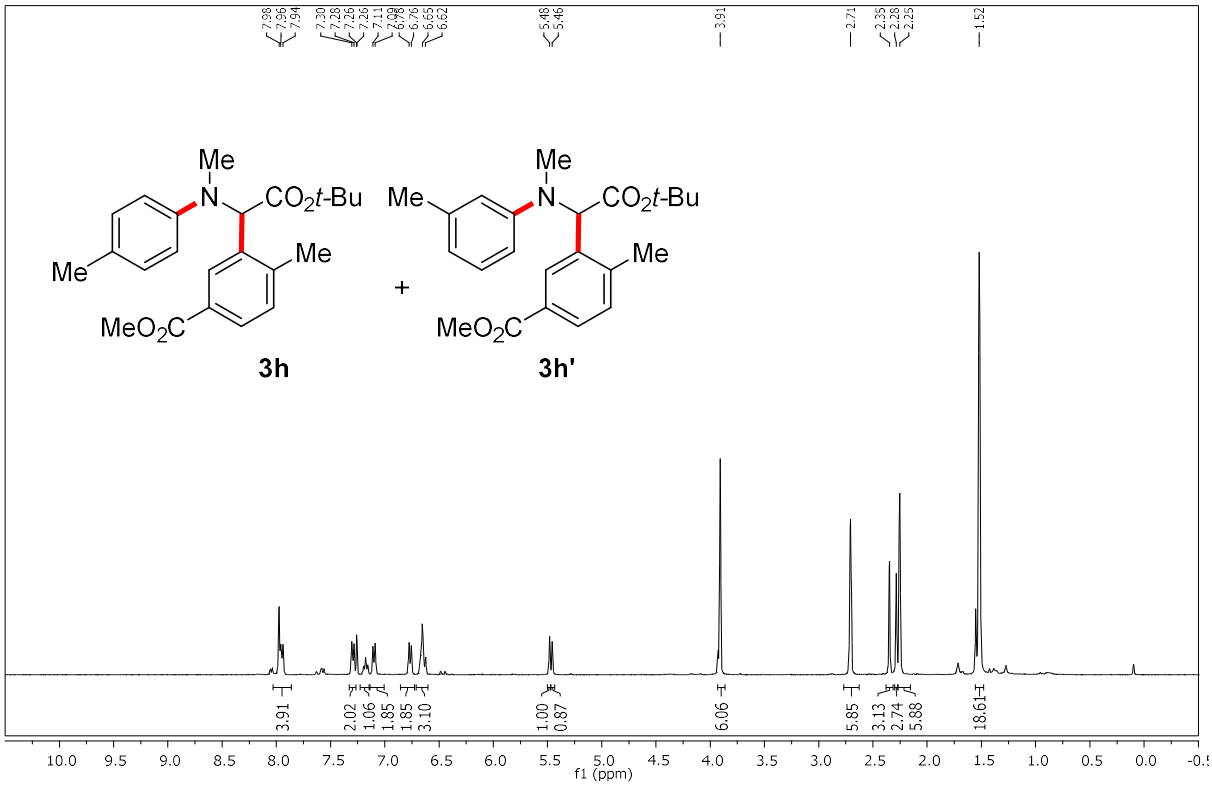


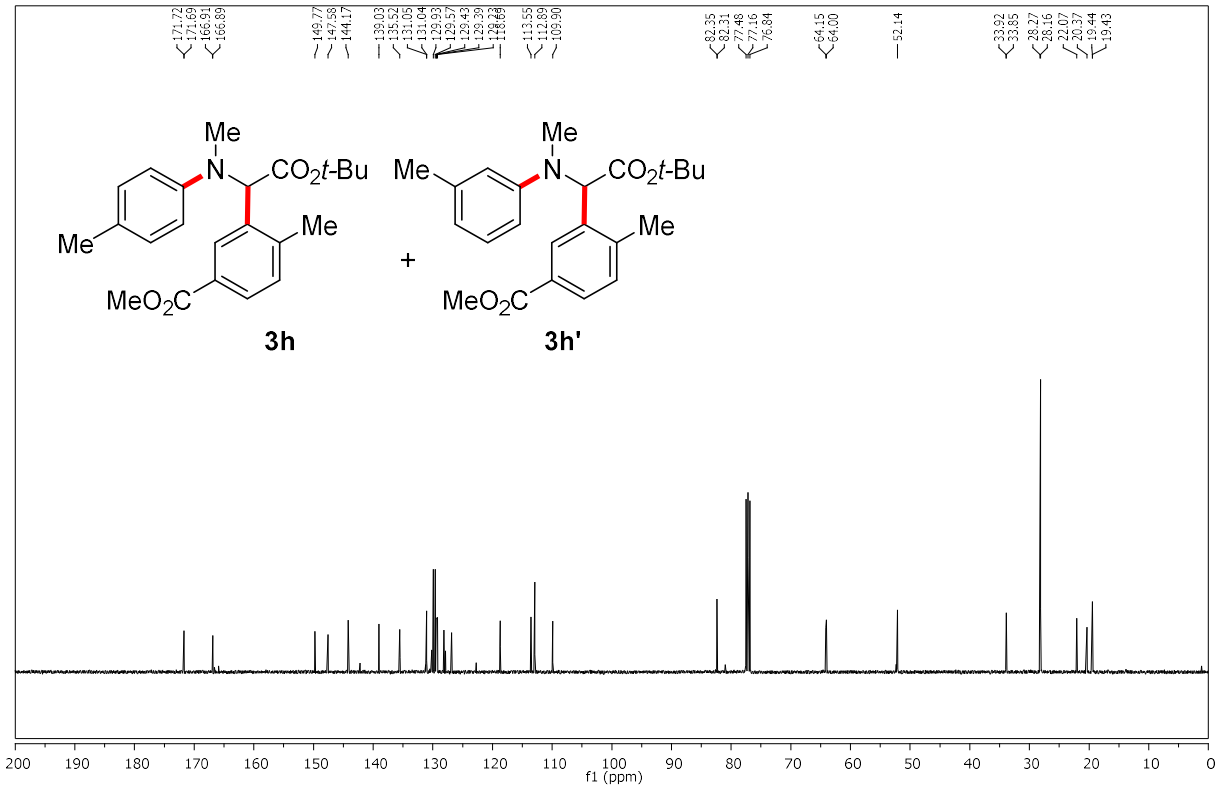
Methyl 3-(2-(*tert*-butoxy)-1-((3-methoxyphenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate (3g)



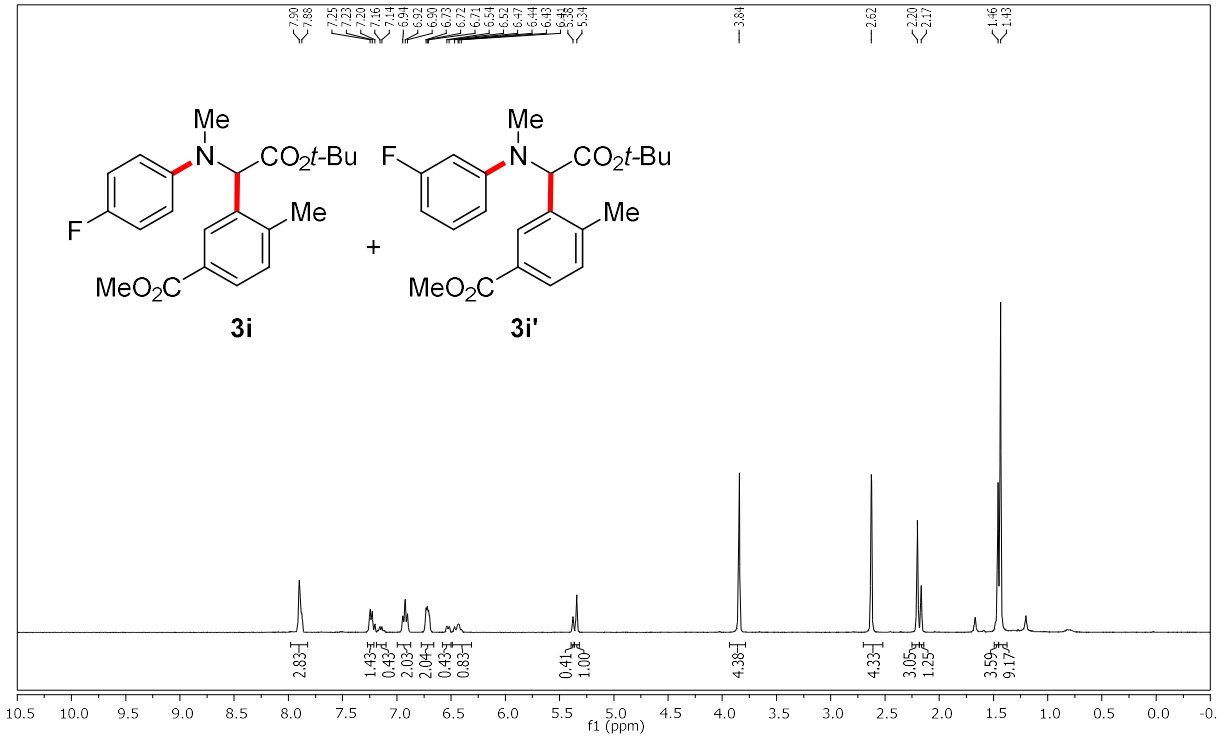


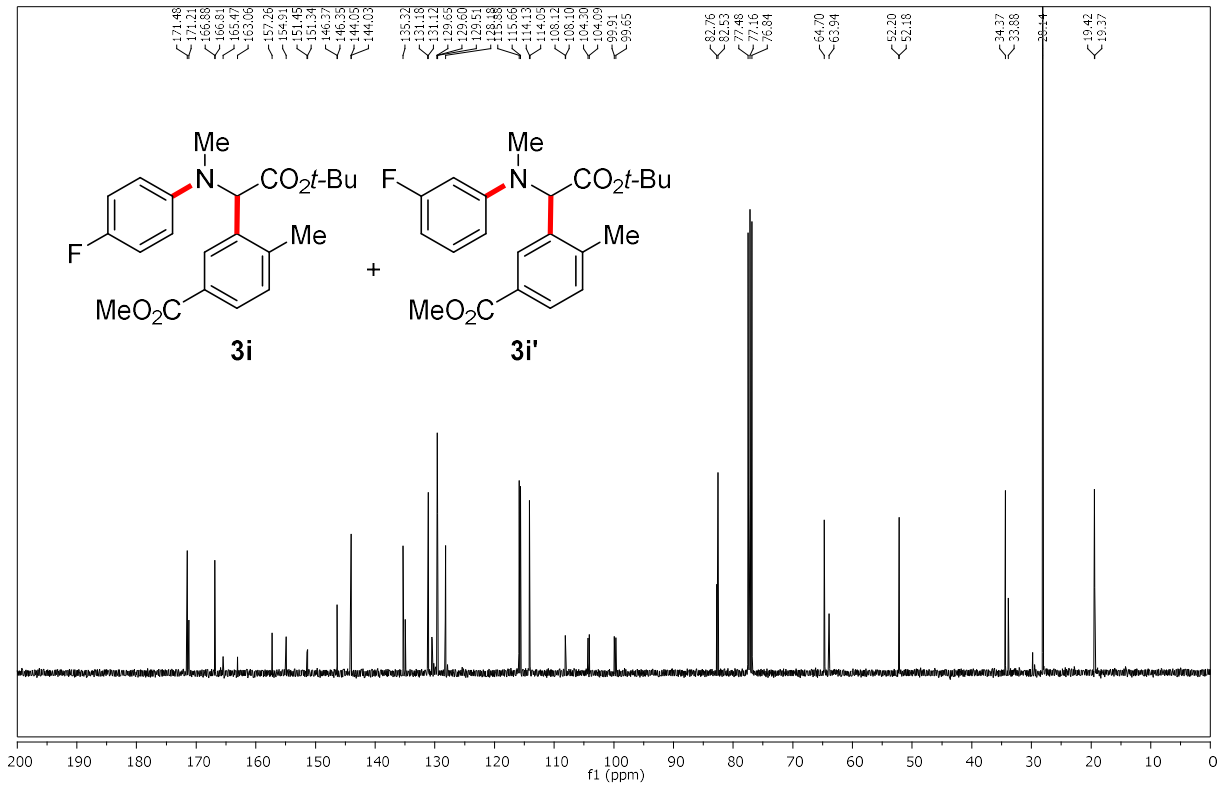
Methyl 3-(2-(*tert*-butoxy)-1-(methyl(*p*-tolyl)amino)-2-oxoethyl)-4-methylbenzoate (3h) and Methyl 3-(2-(*tert*-butoxy)-1-(methyl(*m*-tolyl)amino)-2-oxoethyl)-4-methylbenzoate (3h')



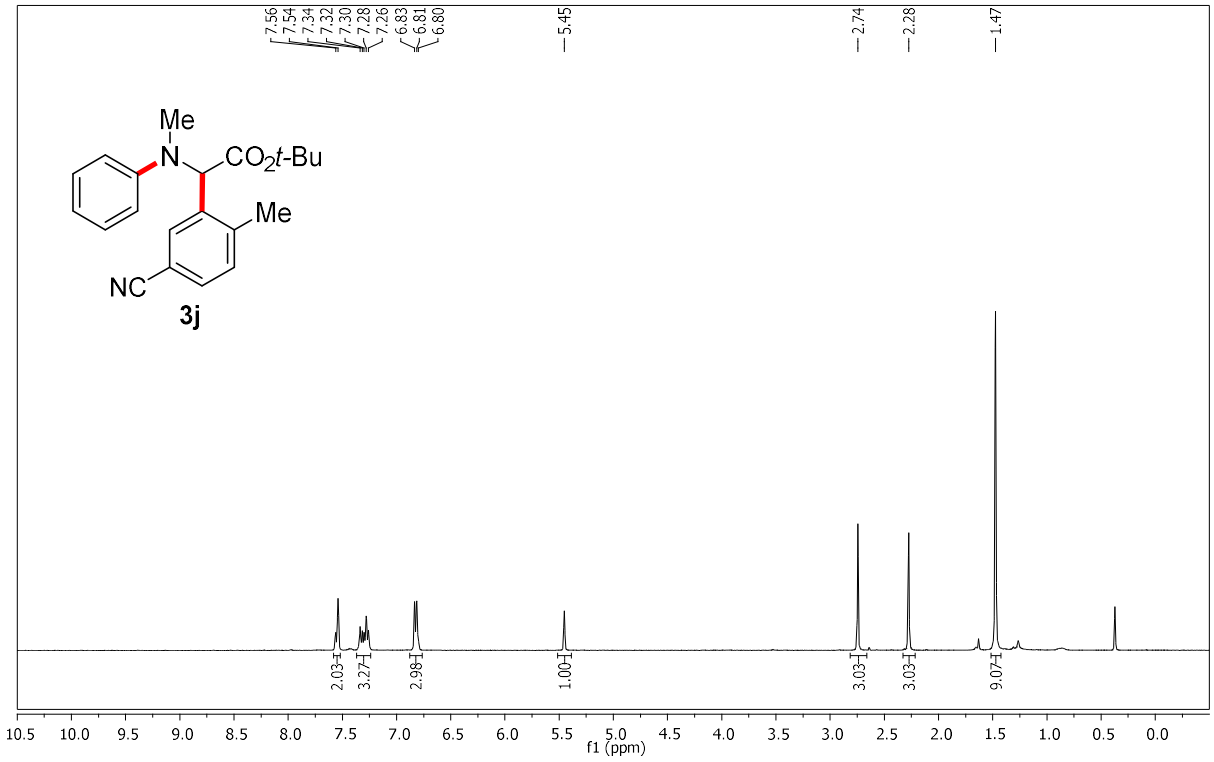


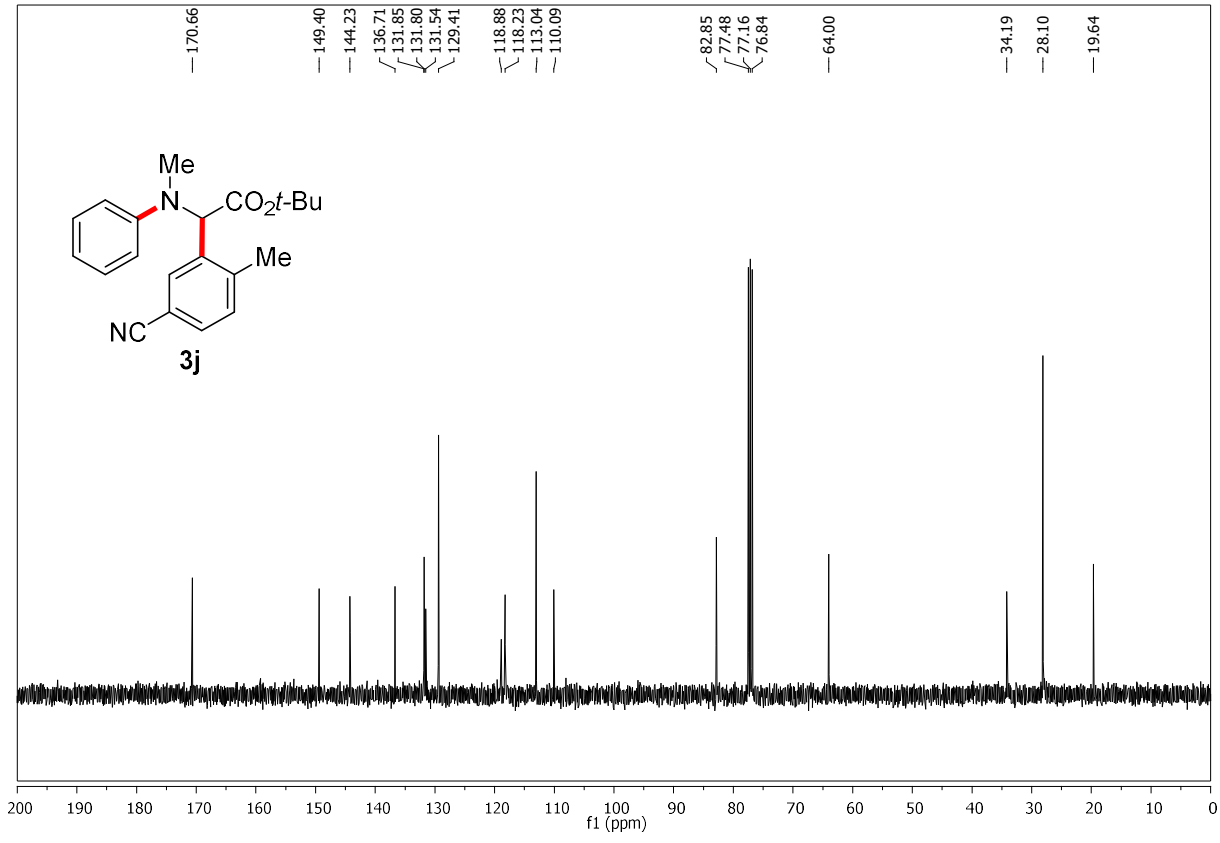
Methyl 3-(2-(*tert*-butoxy)-1-((4-fluorophenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate (3i) and Methyl 3-(2-(*tert*-butoxy)-1-((3-fluorophenyl)(methyl)amino)-2-oxoethyl)-4-methylbenzoate(3i')



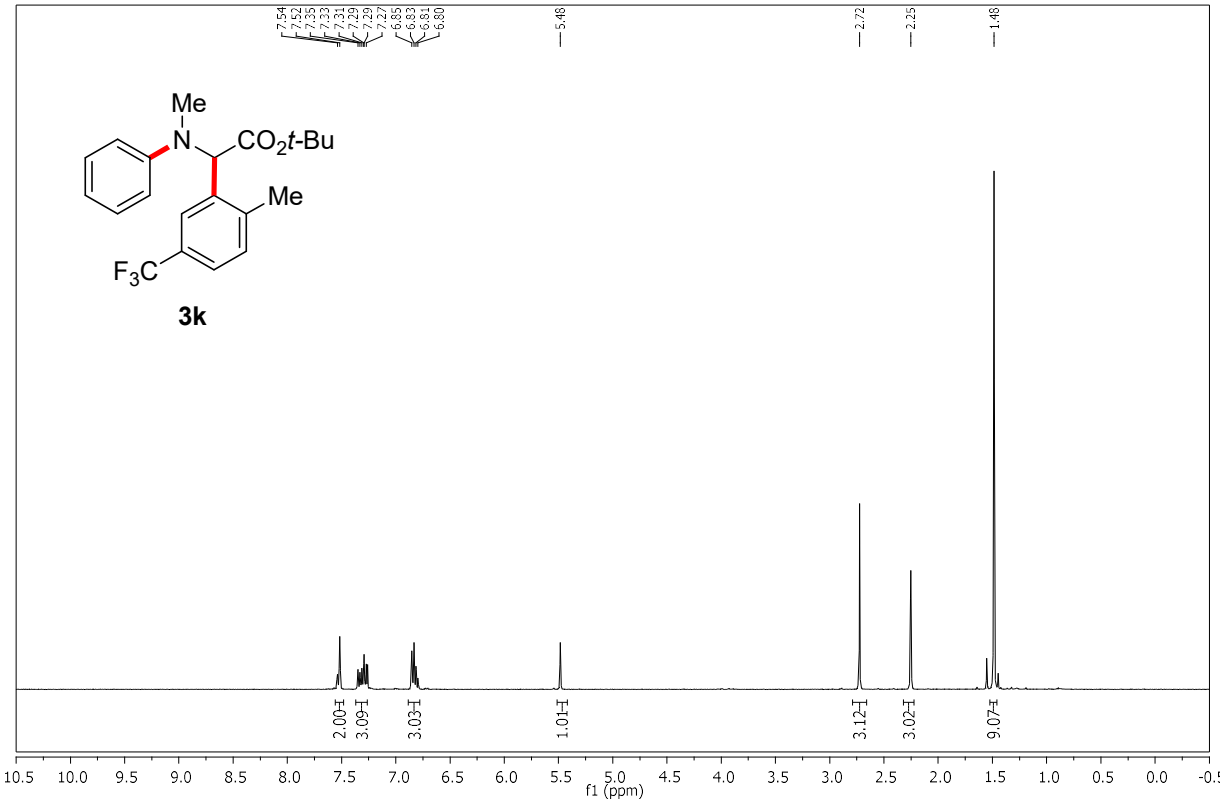


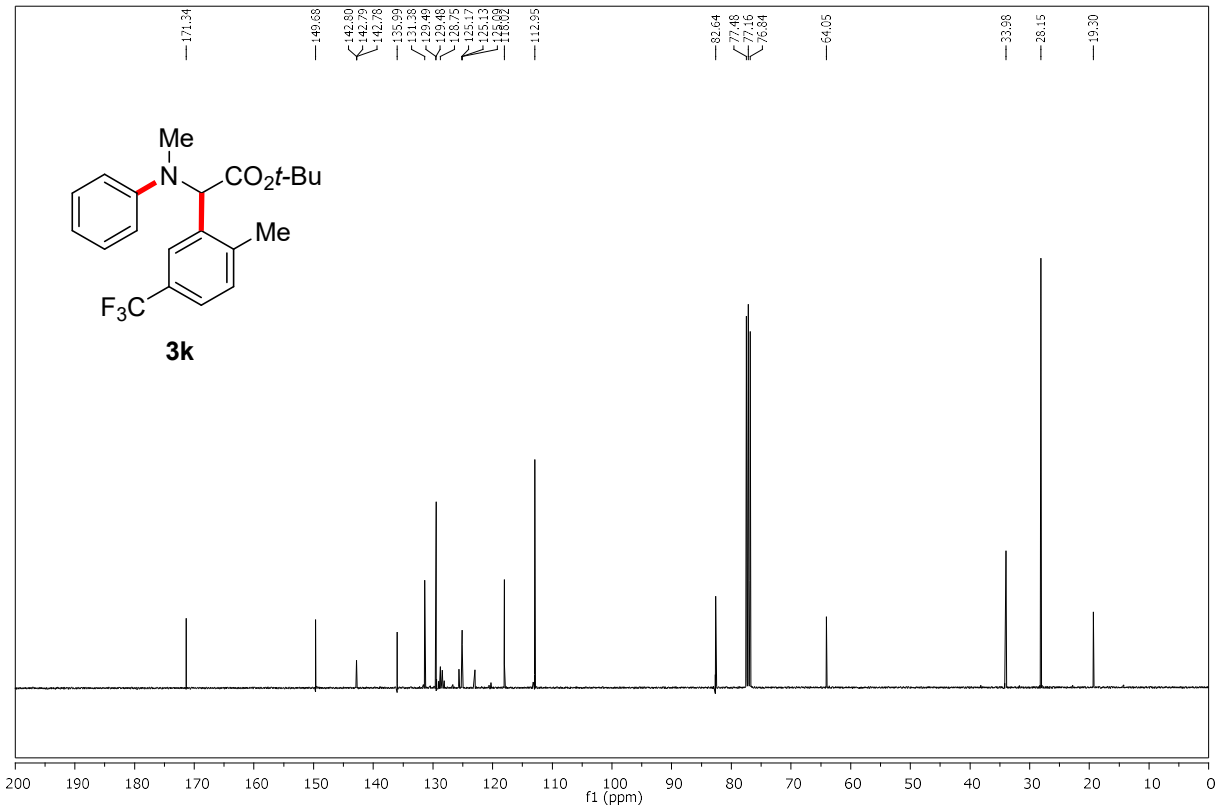
***tert*-Butyl 2-(5-cyano-2-methylphenyl)-2-(methyl(phenyl)amino)acetate (3j)**



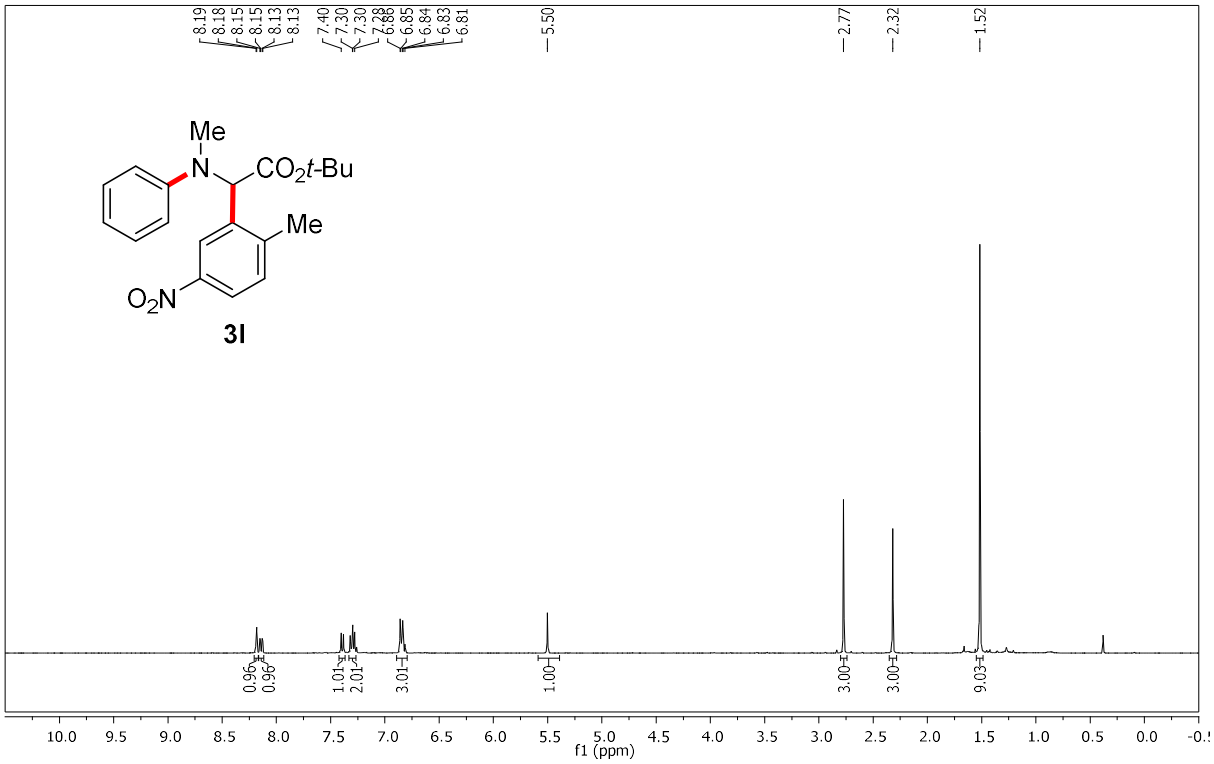


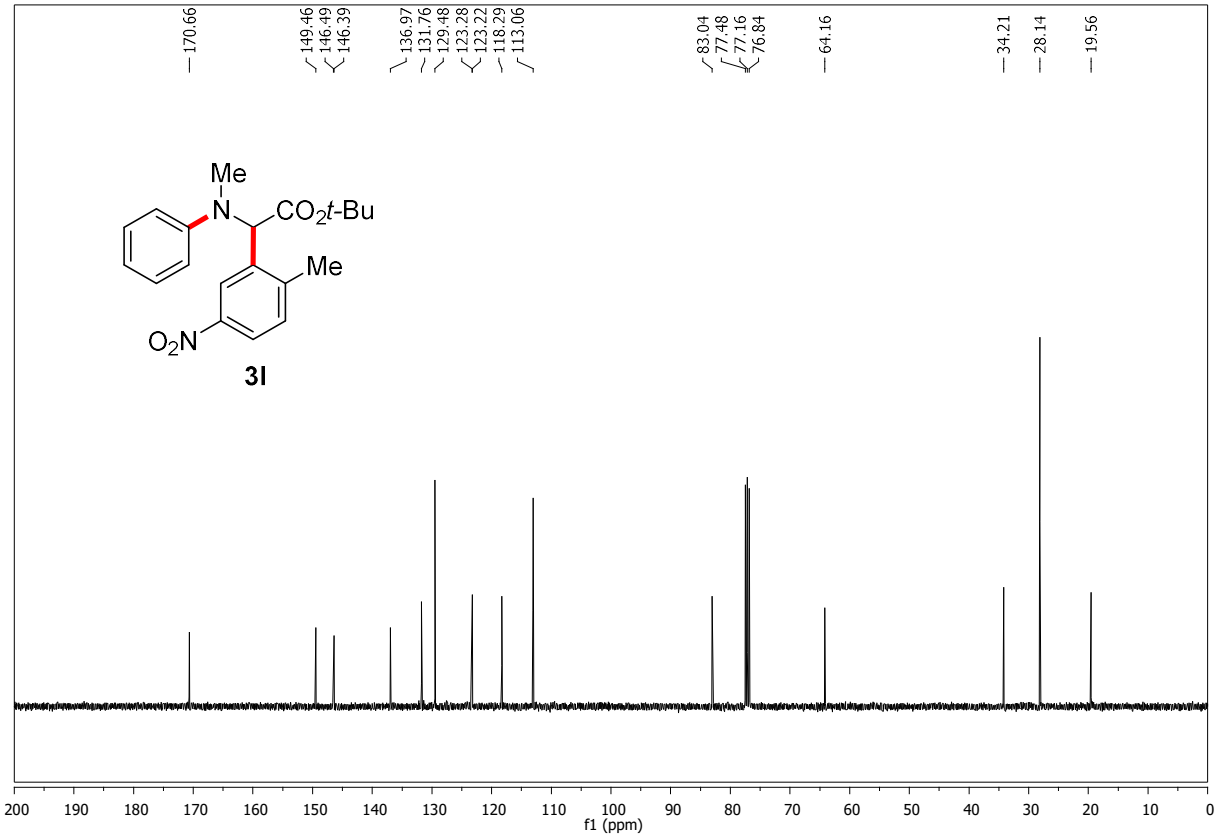
***tert*-Butyl 2-(methyl(phenyl)amino)-2-(2-methyl-5-(trifluoromethyl)phenyl)acetate (3k)**



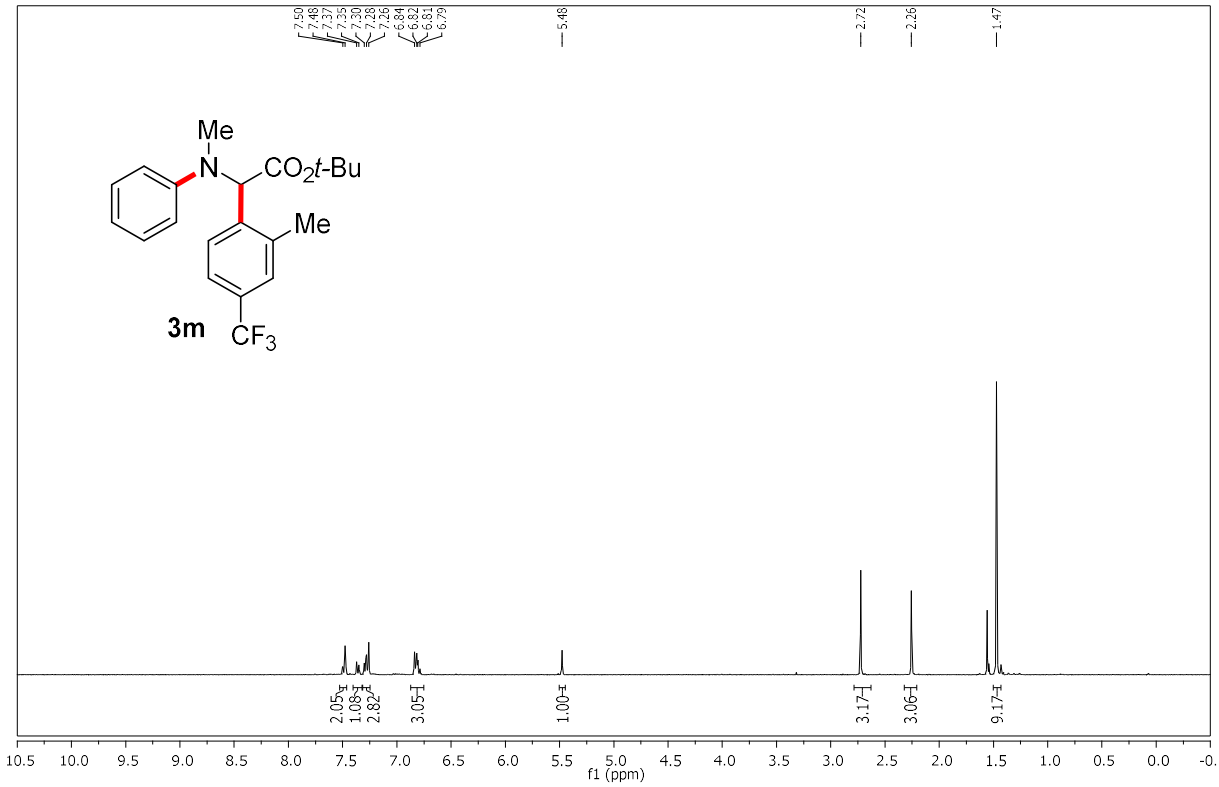


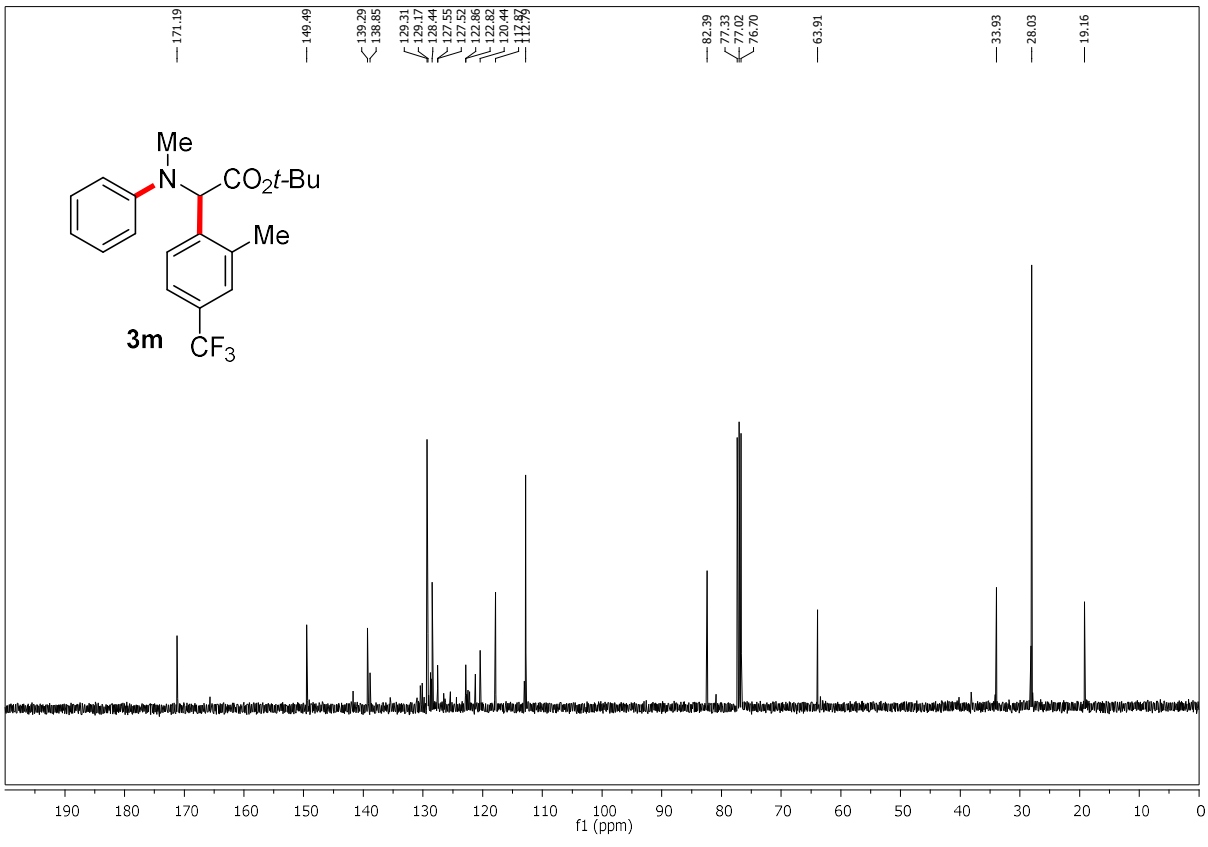
***tert*-Butyl 2-(methyl(phenyl)amino)-2-(2-methyl-5-nitrophenyl)acetate (3l)**



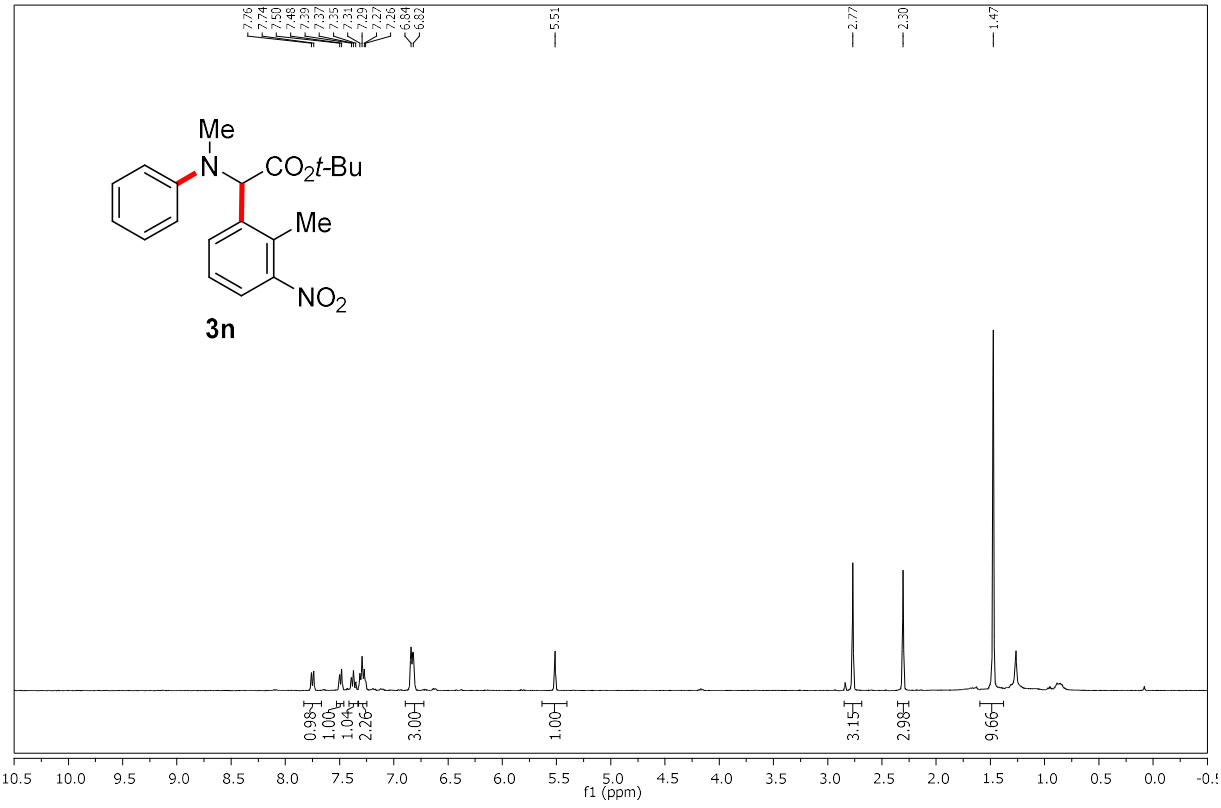


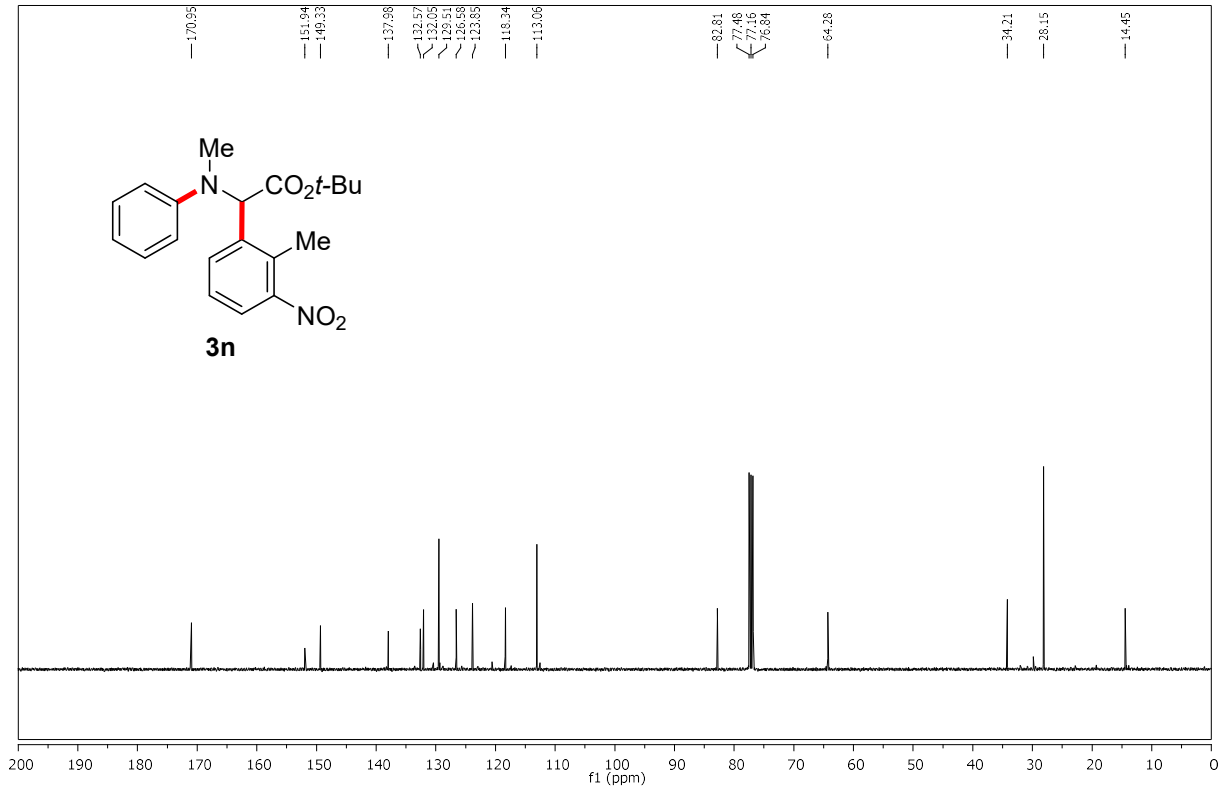
***tert*-Butyl 2-(methyl(phenyl)amino)-2-(2-methyl-4-(trifluoromethyl)phenyl)acetate (3m)**



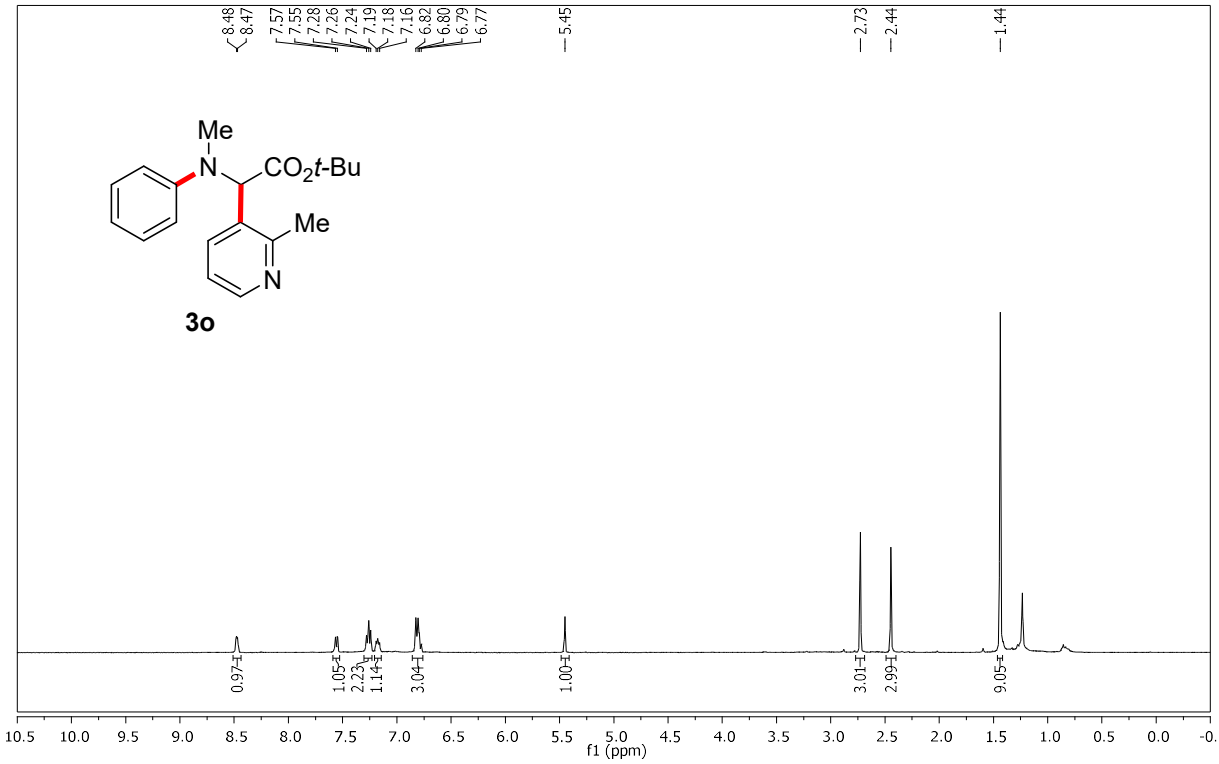


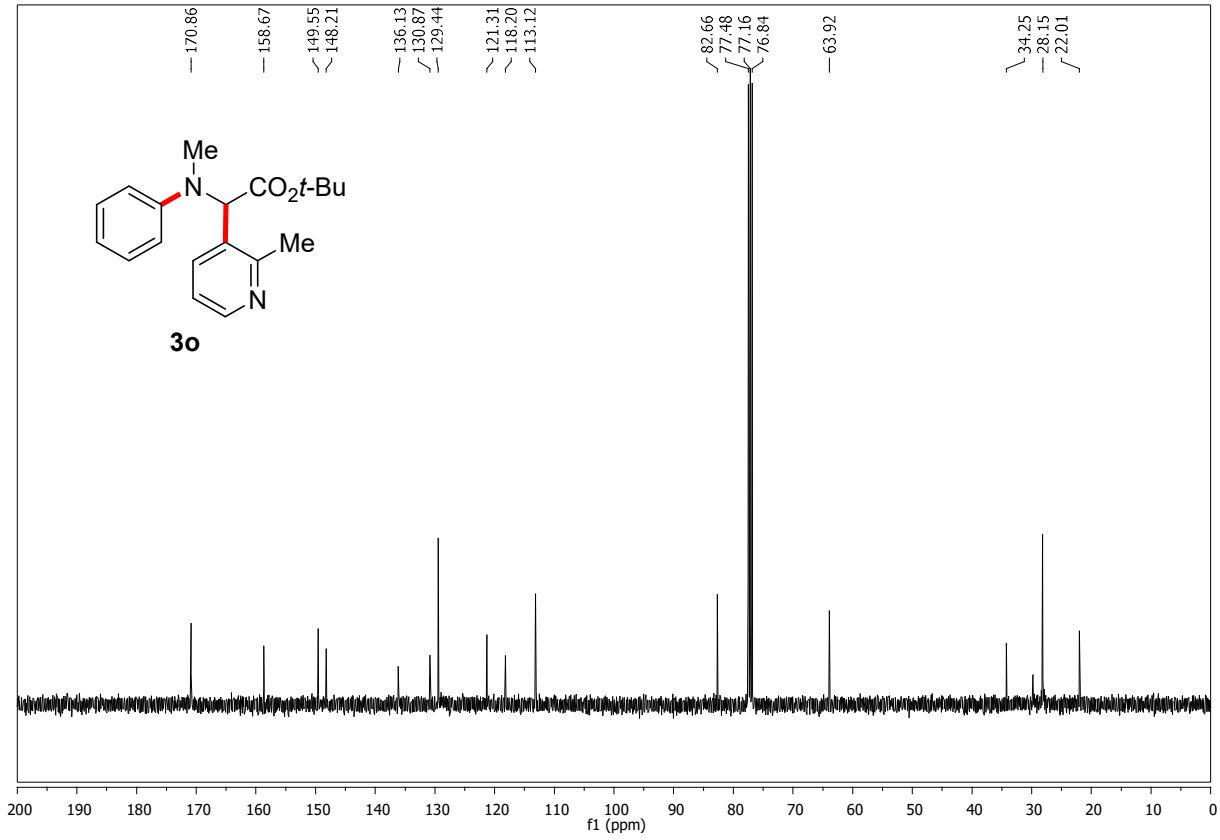
***tert*-Butyl 2-(methyl(phenyl)amino)-2-(2-methyl-3-nitrophenyl)acetate (3n)**



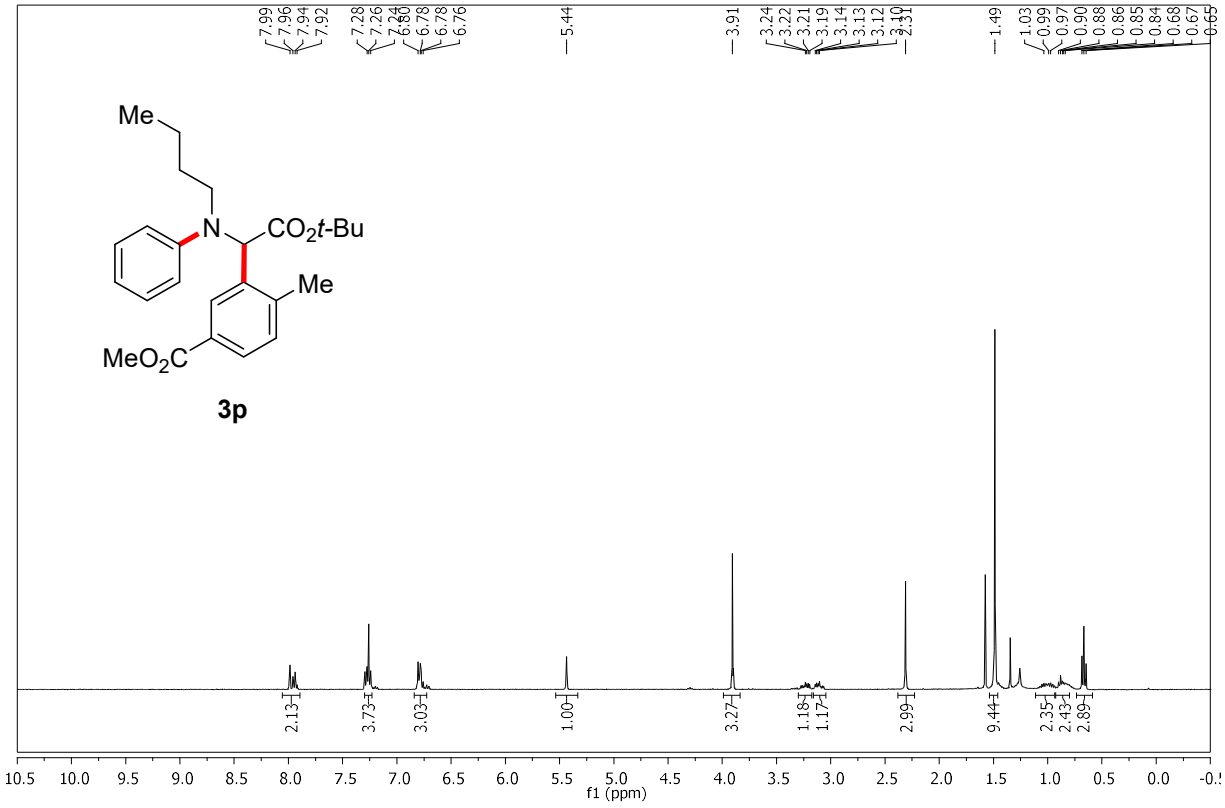


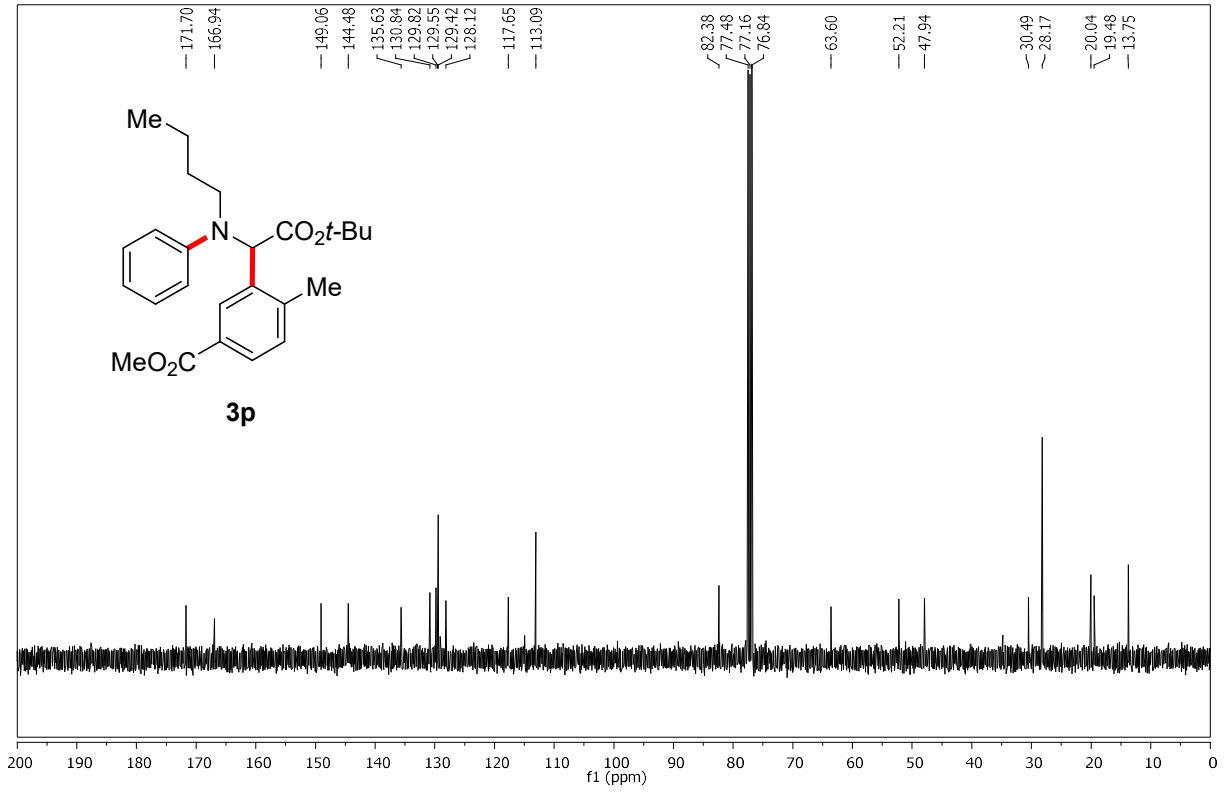
***tert*-Butyl 2-(methyl(phenyl)amino)-2-(2-methylpyridin-3-yl)acetate (3o)**



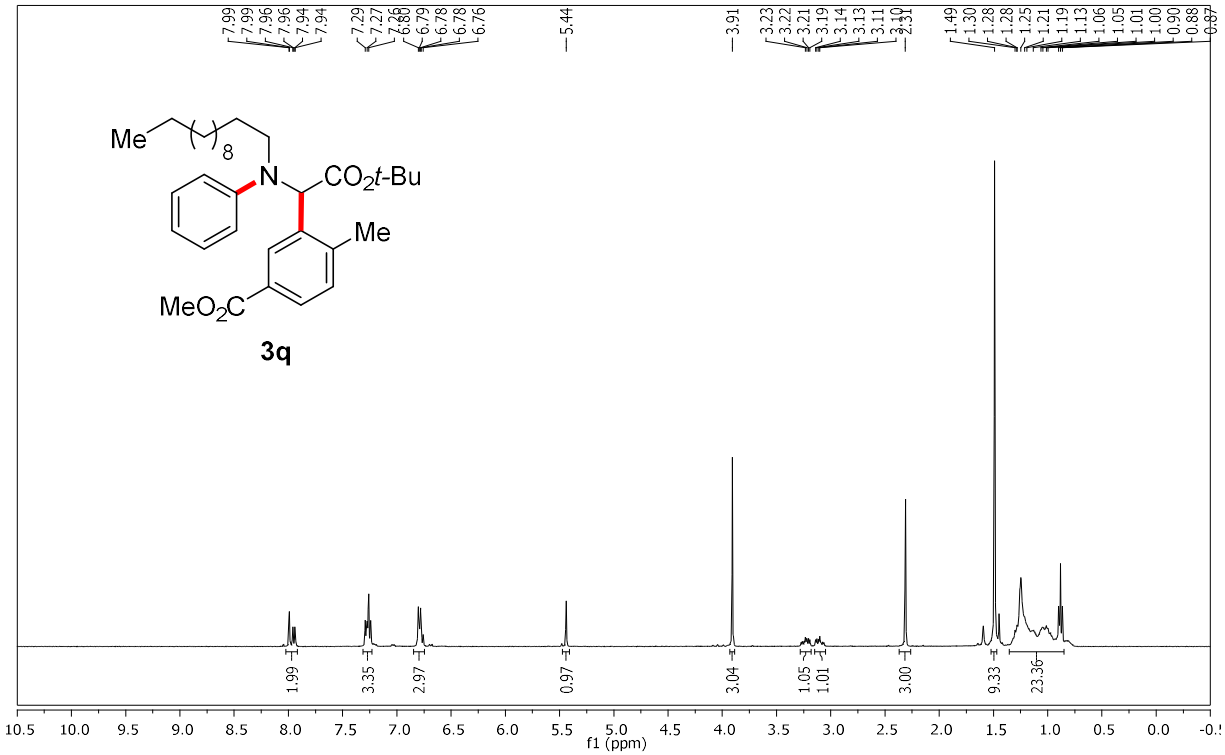


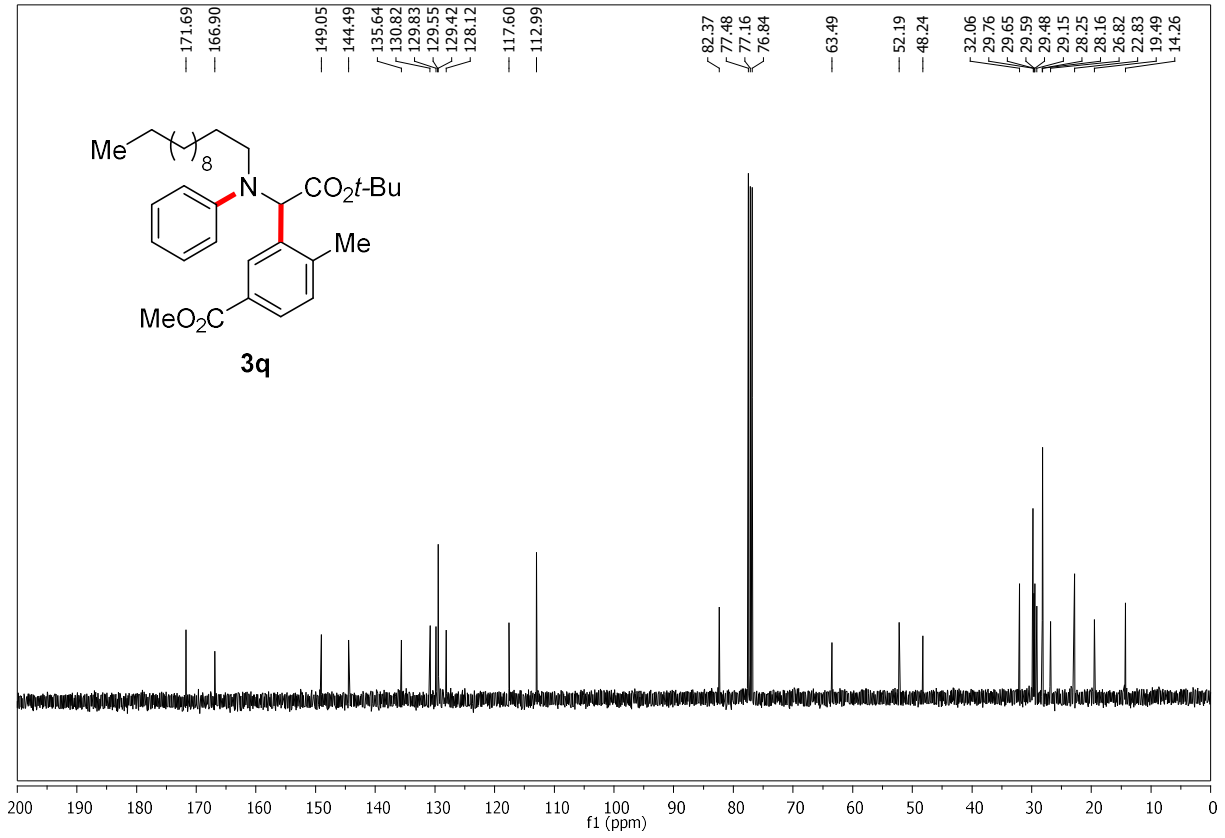
Methyl 3-(2-(*tert*-butoxy)-1-(butyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3p)



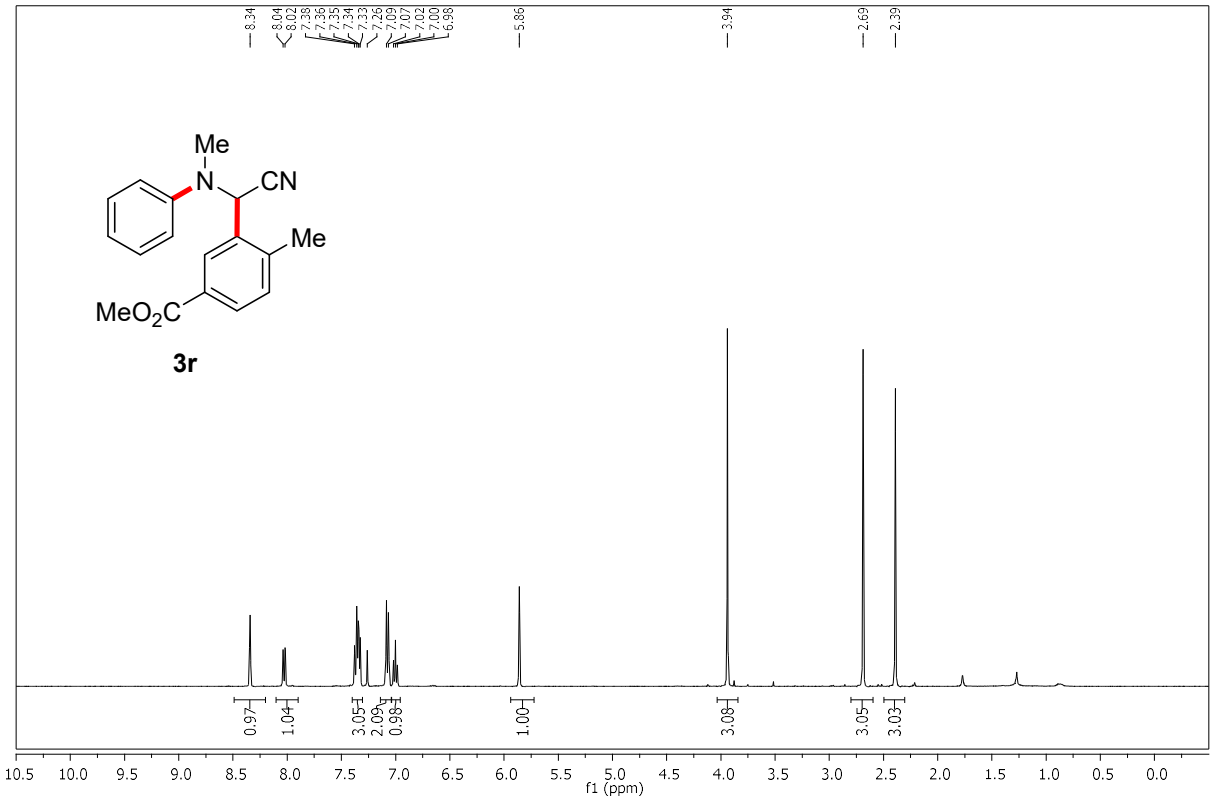


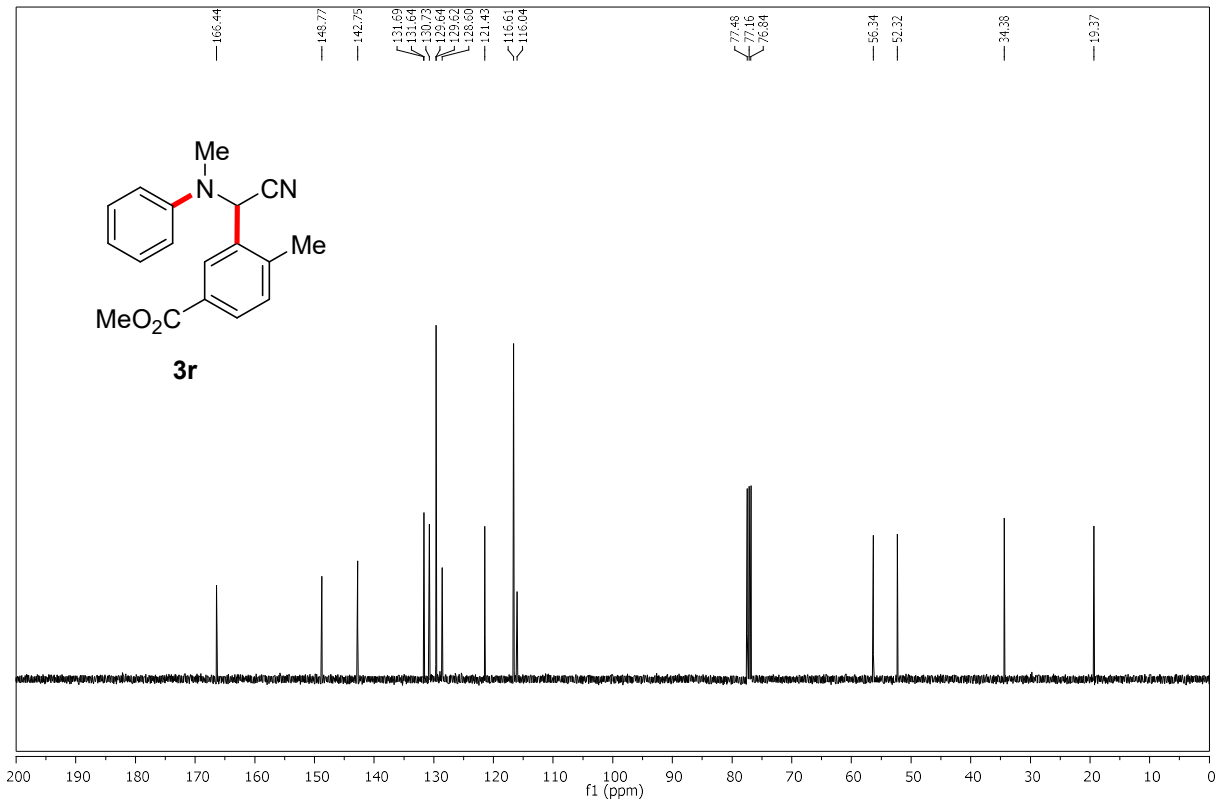
Methyl 3-(2-(*tert*-butoxy)-1-(dodecyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3q)



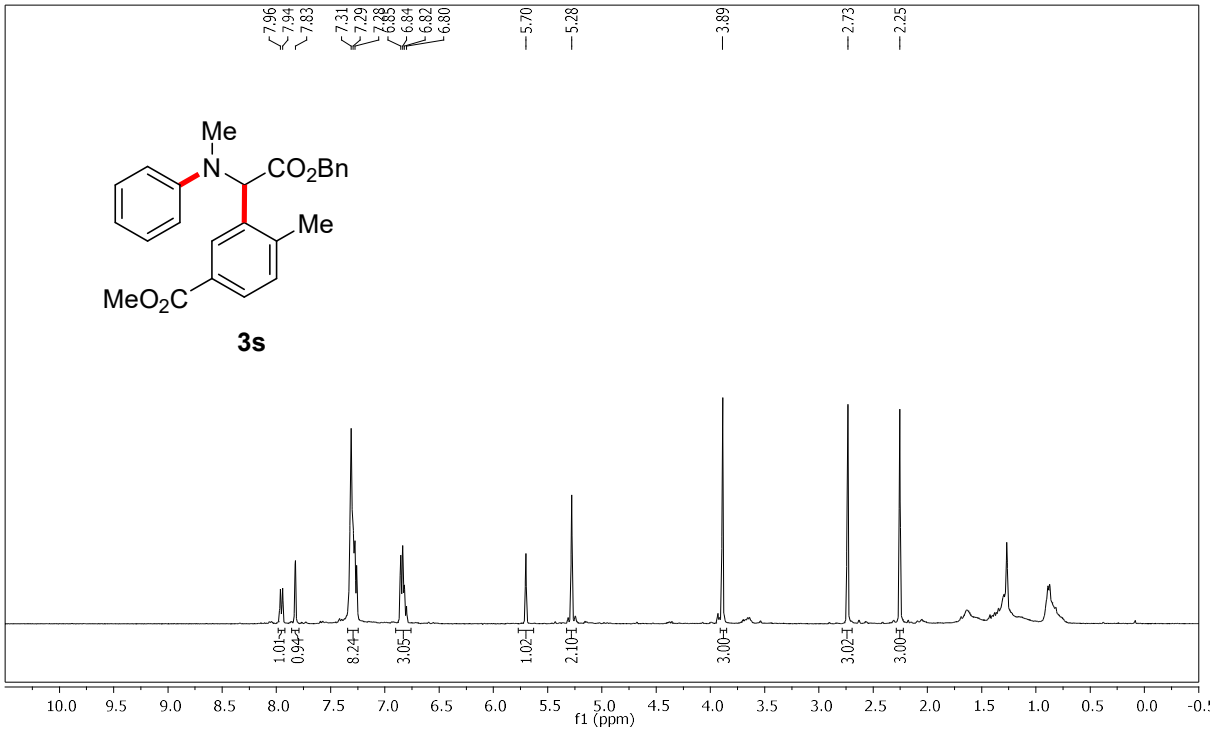


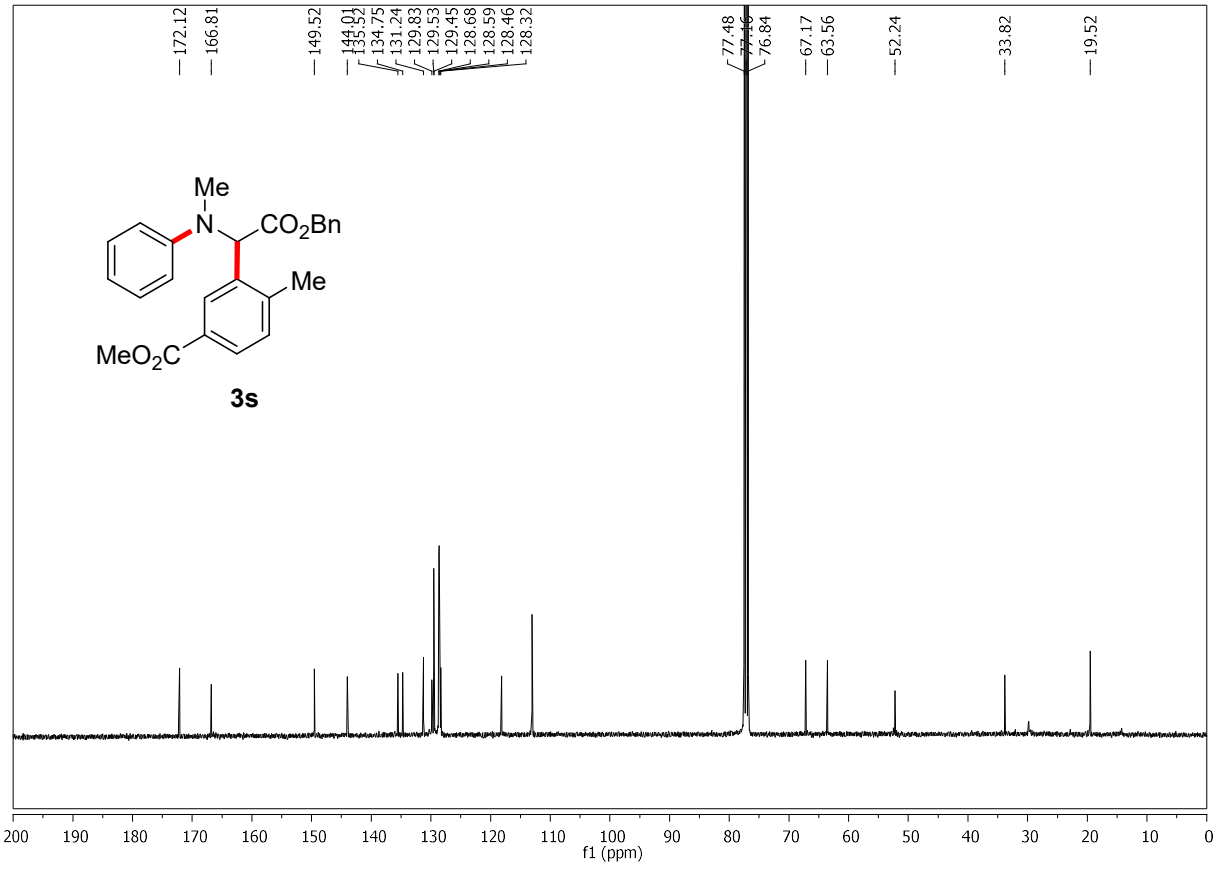
Methyl 3-(cyano(methyl(phenyl)amino)methyl)-4-methylbenzoate (3r)



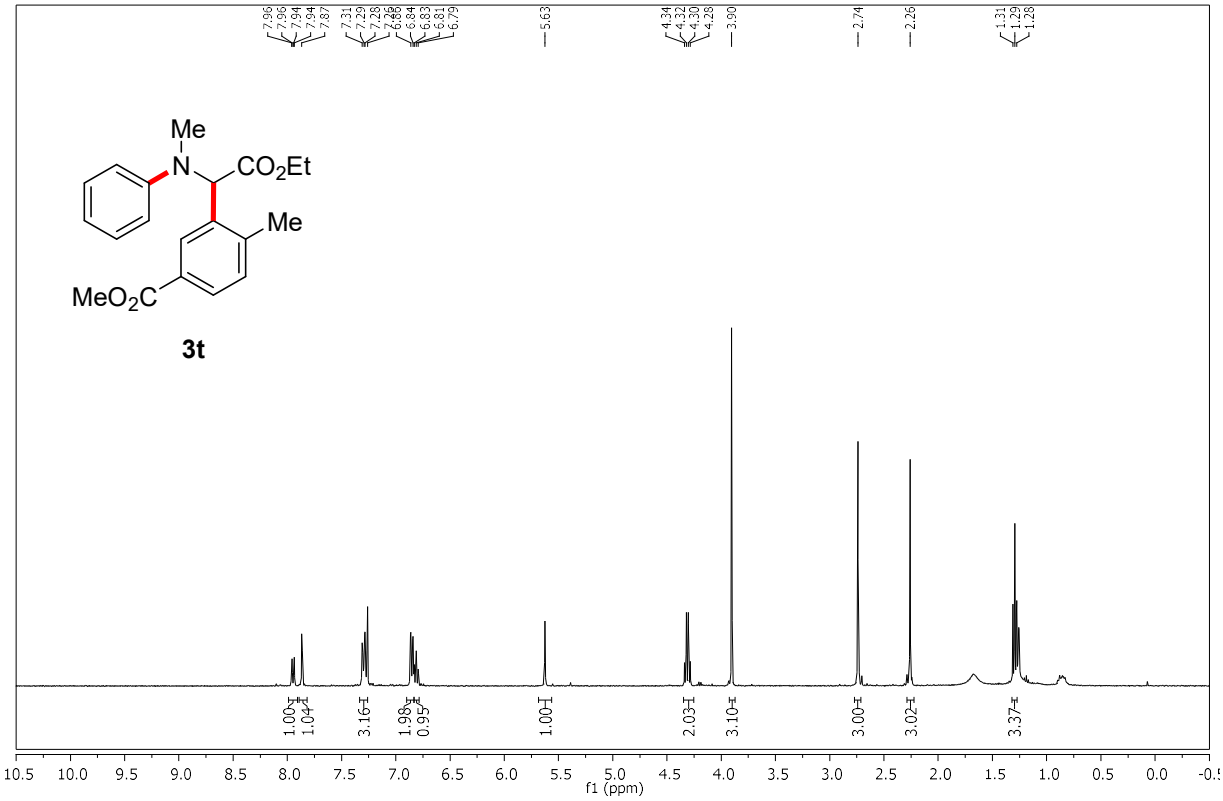


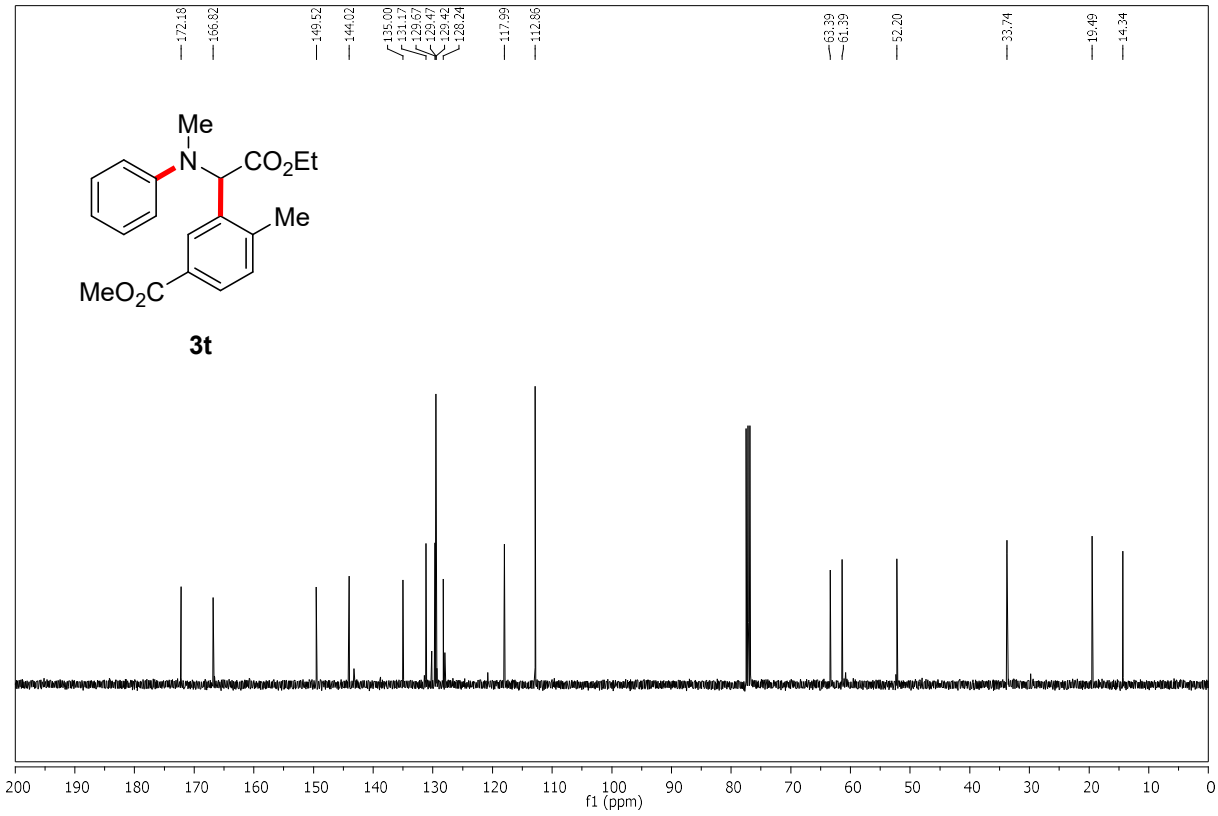
Methyl 3-(2-(benzyloxy)-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3s)



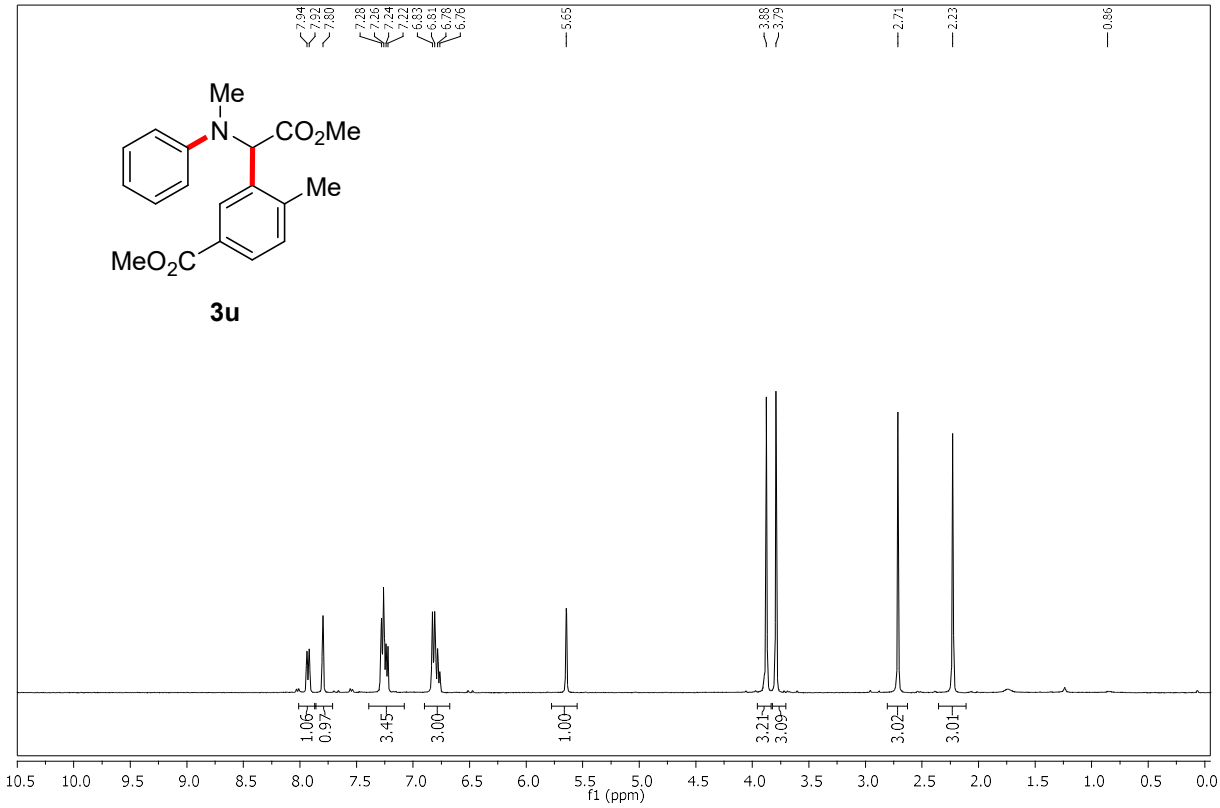


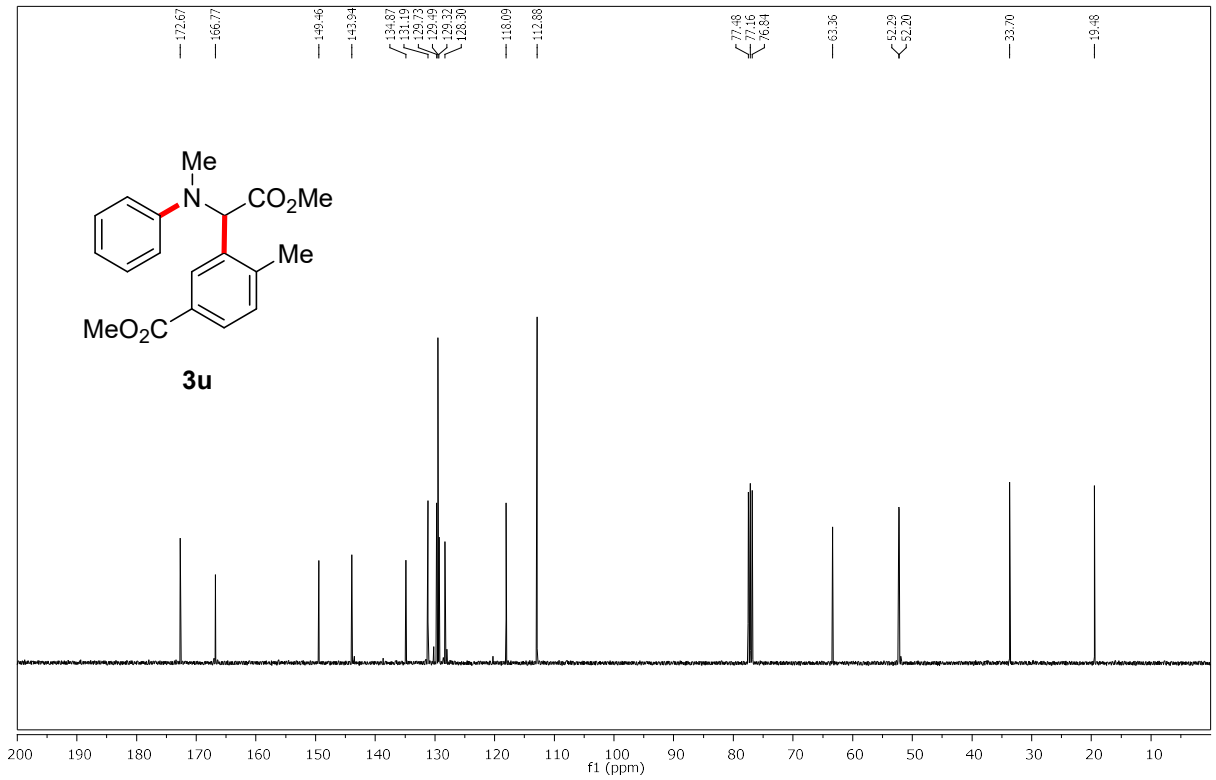
Methyl 3-(2-ethoxy-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3t)



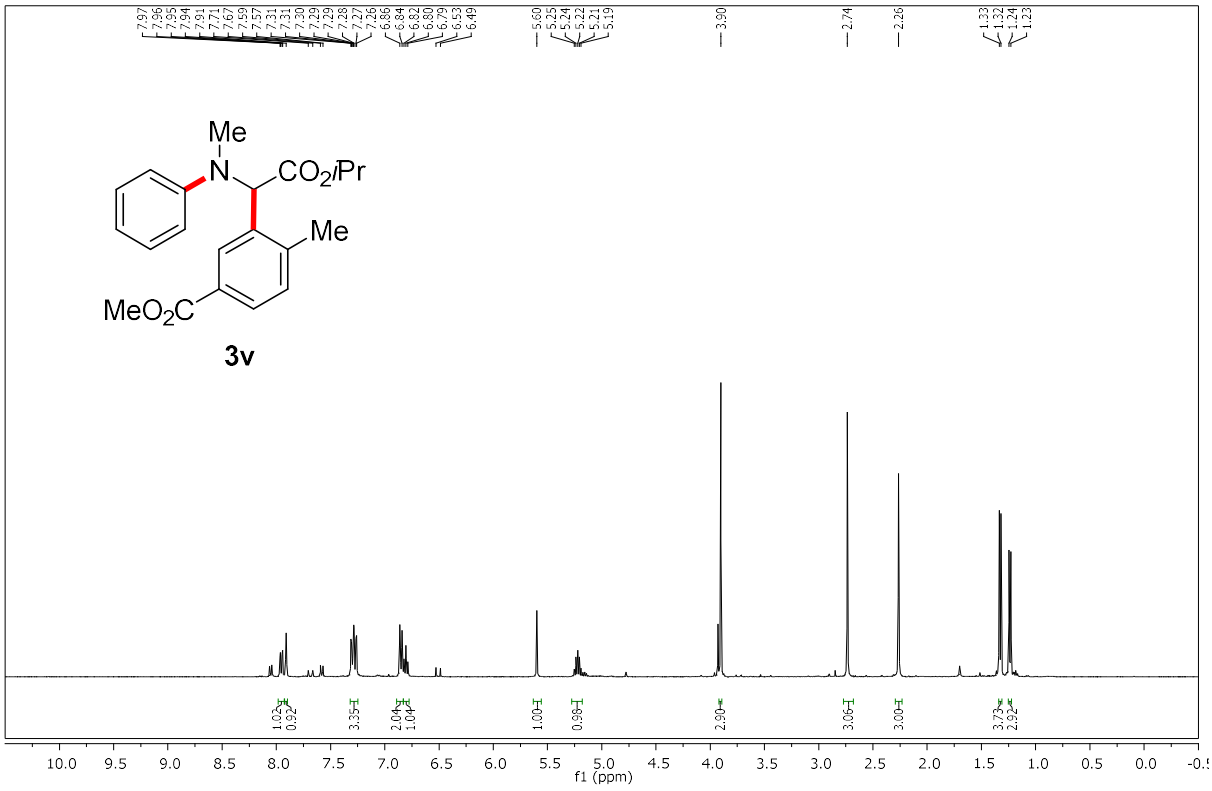


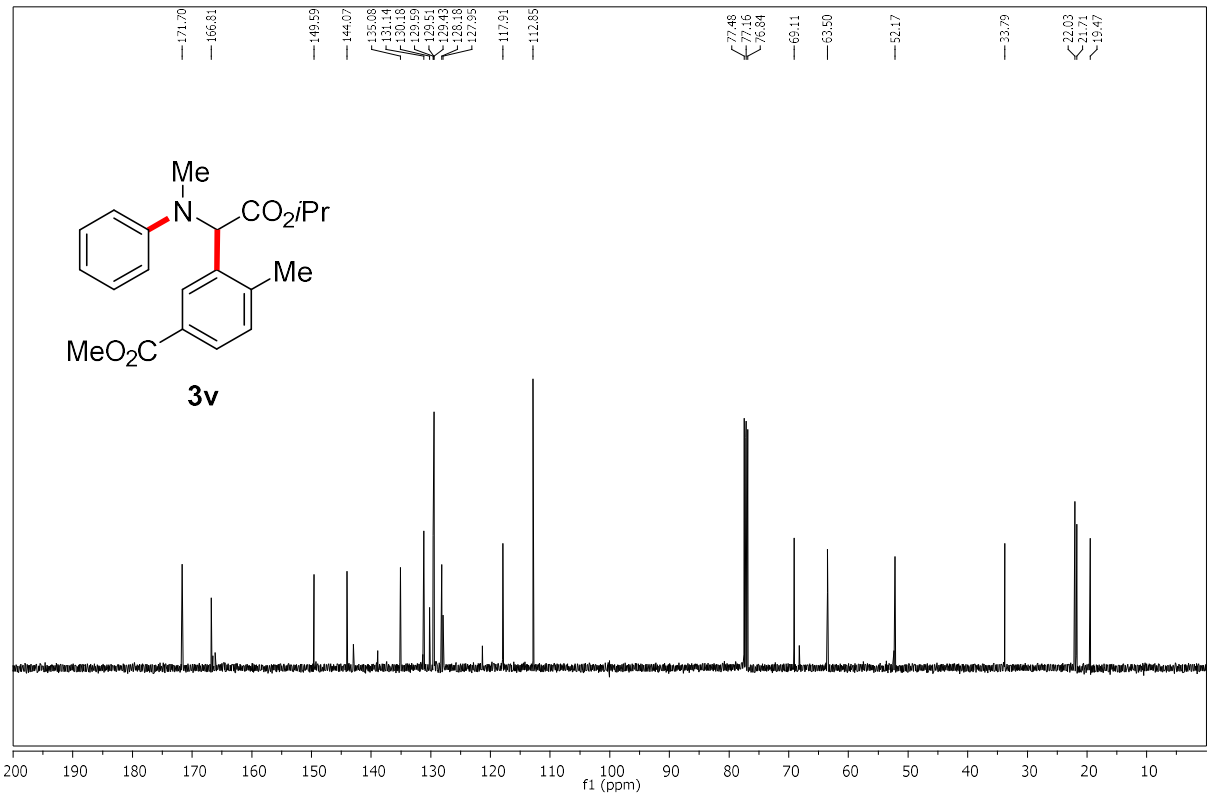
Methyl 3-(2-methoxy-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3u)



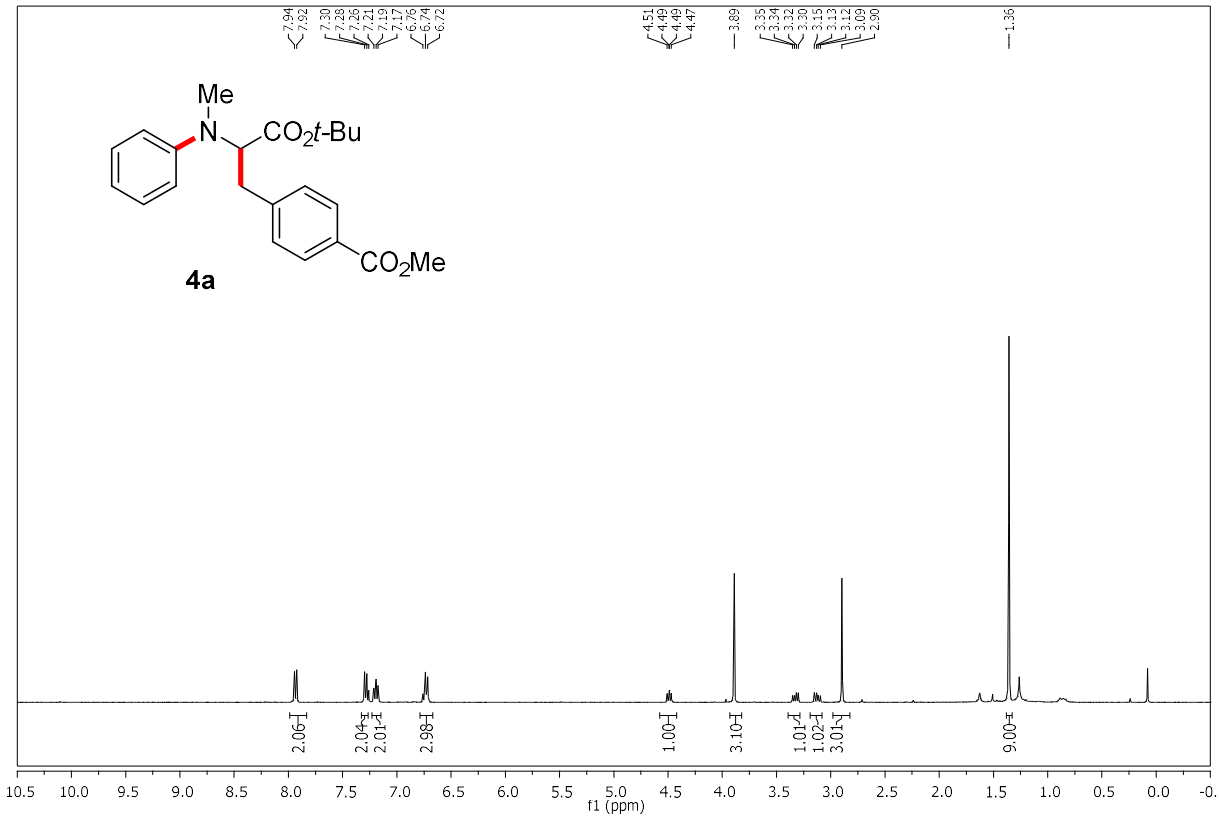


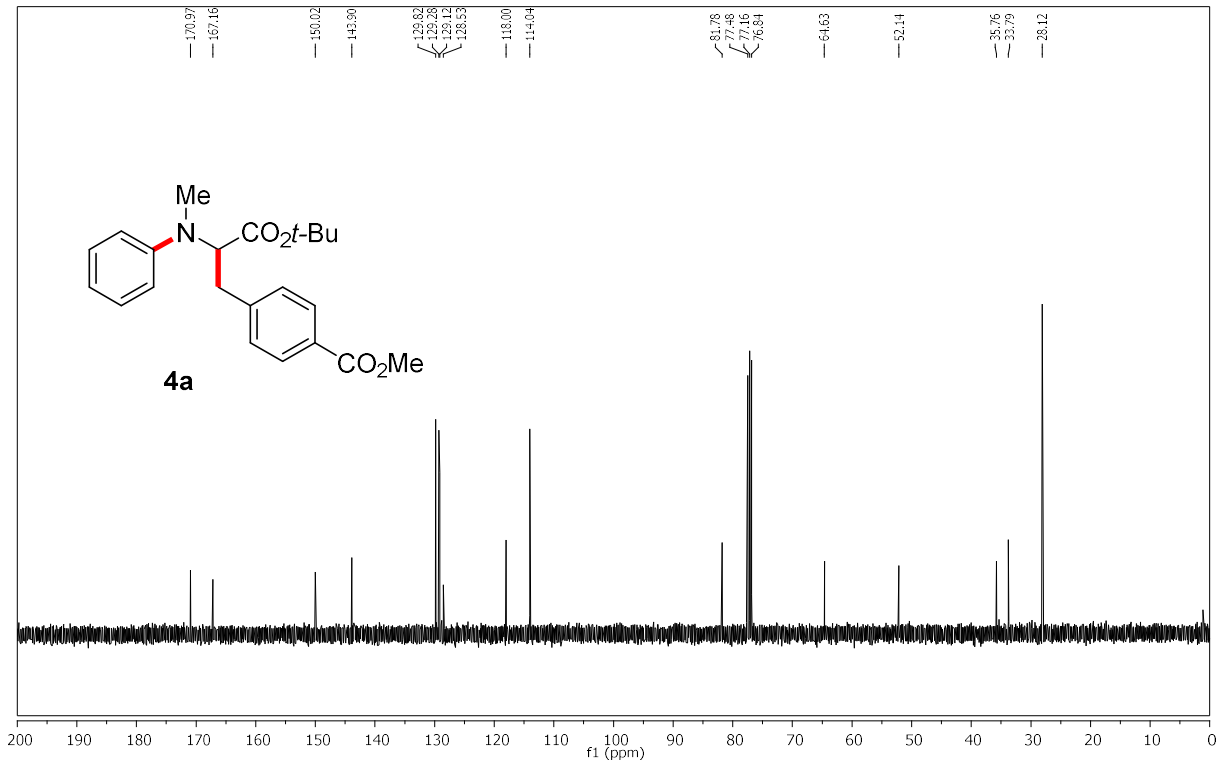
Methyl 3-(2-isopropoxy-1-(methyl(phenyl)amino)-2-oxoethyl)-4-methylbenzoate (3v)



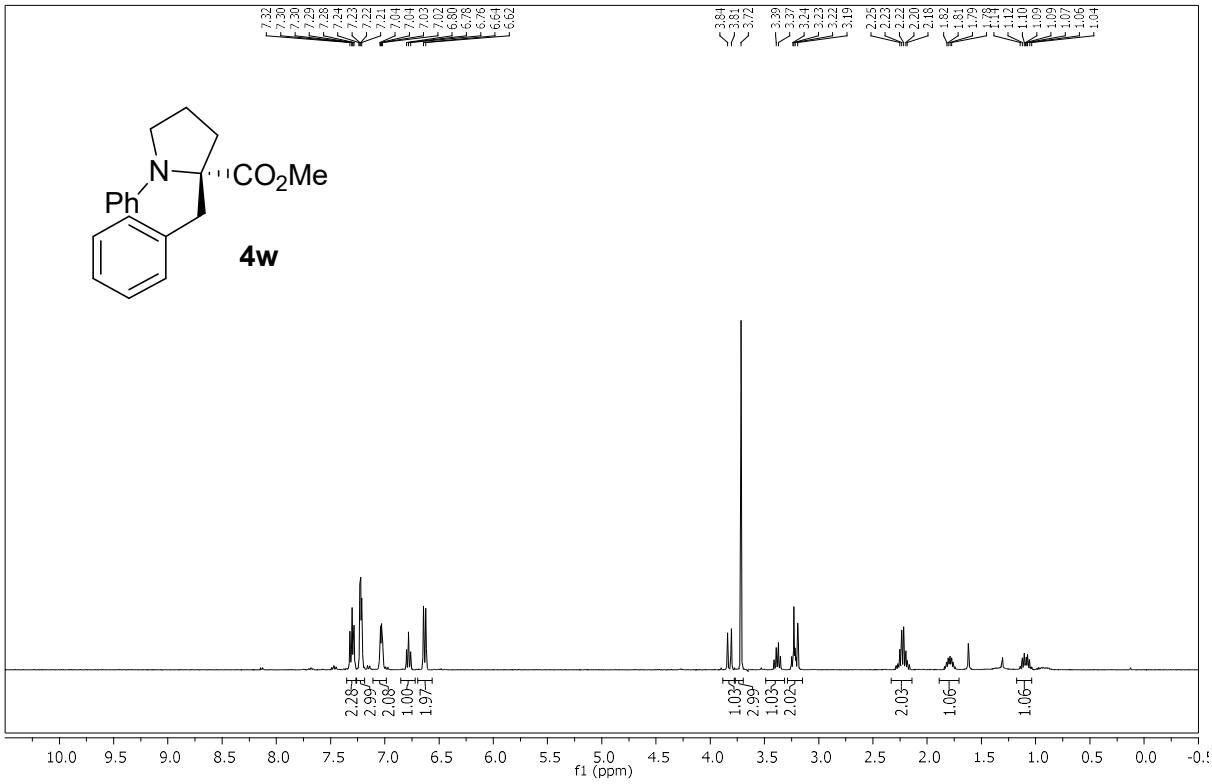


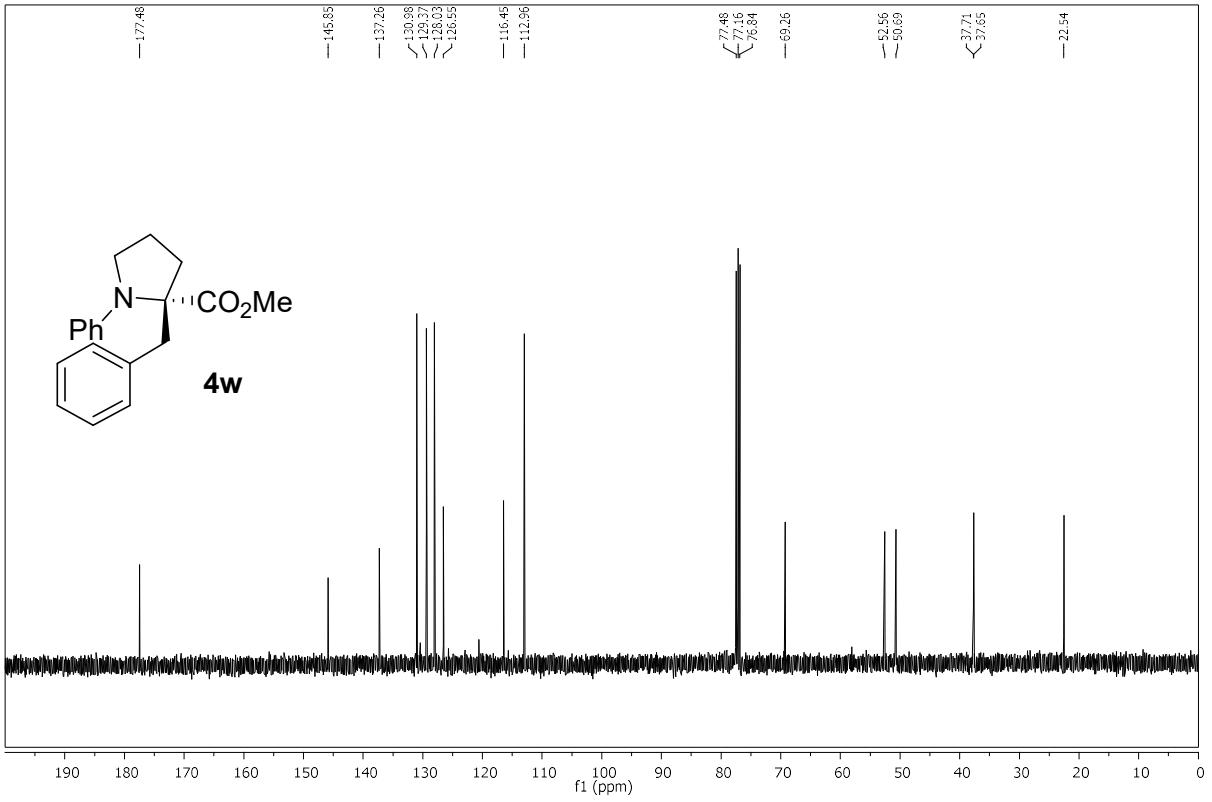
Methyl 4-(3-(*tert*-butoxy)-2-(methyl(phenyl)amino)-3-oxopropyl)benzoate (4a)



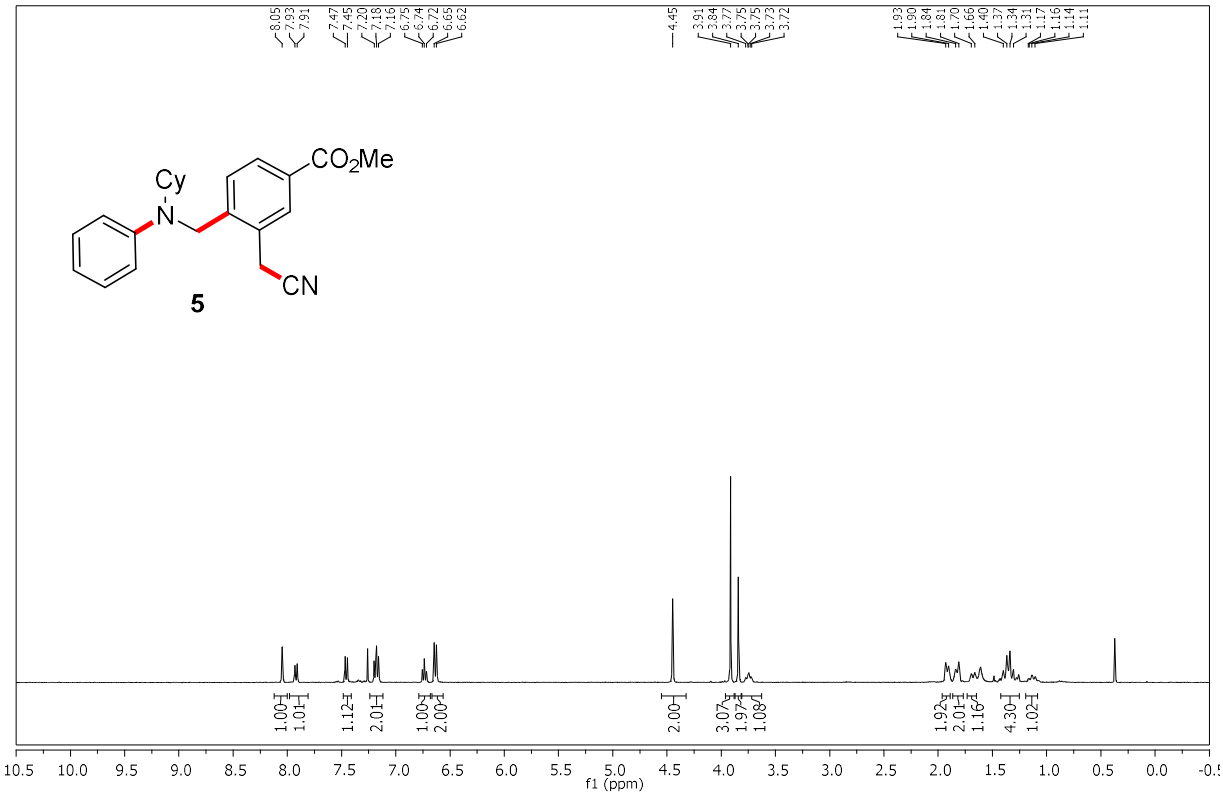


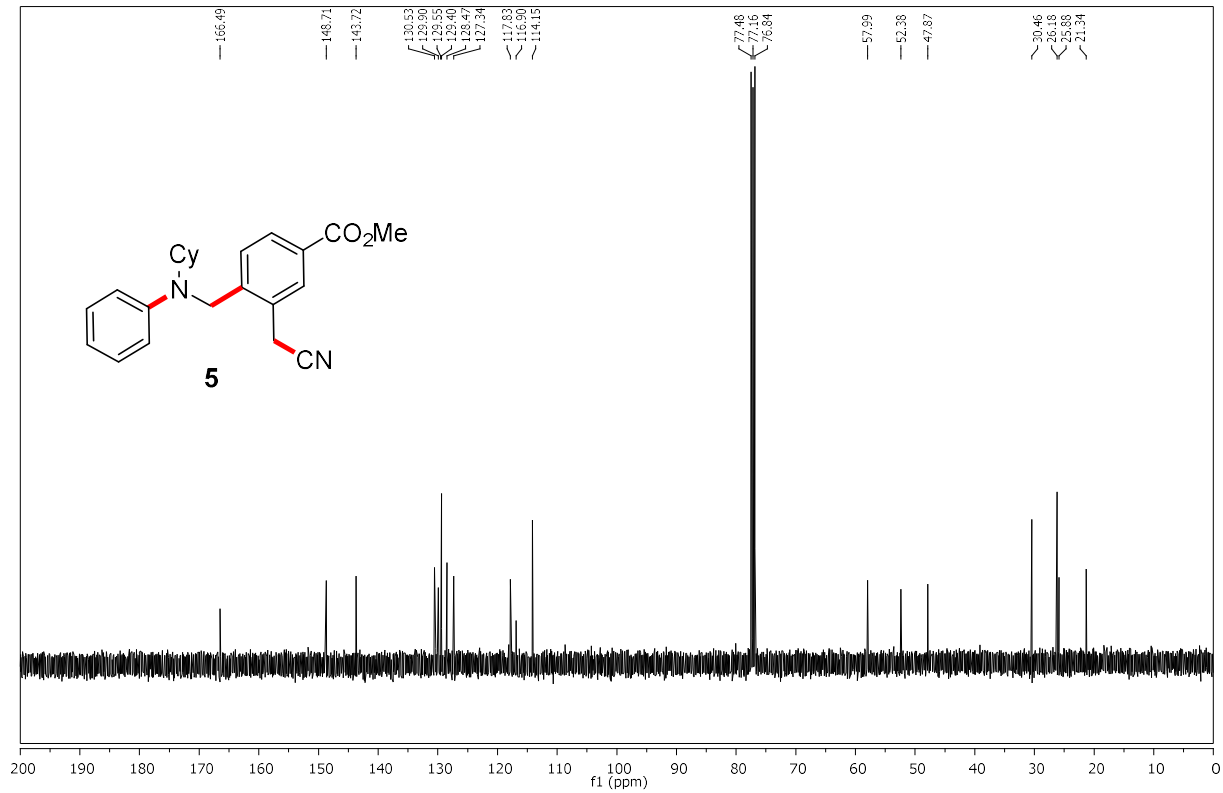
Methyl (*S*)-2-benzyl-1-phenylpyrrolidine-2-carboxylate (4w)





Methyl 3-(cyanomethyl)-4-((cyclohexyl(phenyl)amino)methyl)benzoate (5)

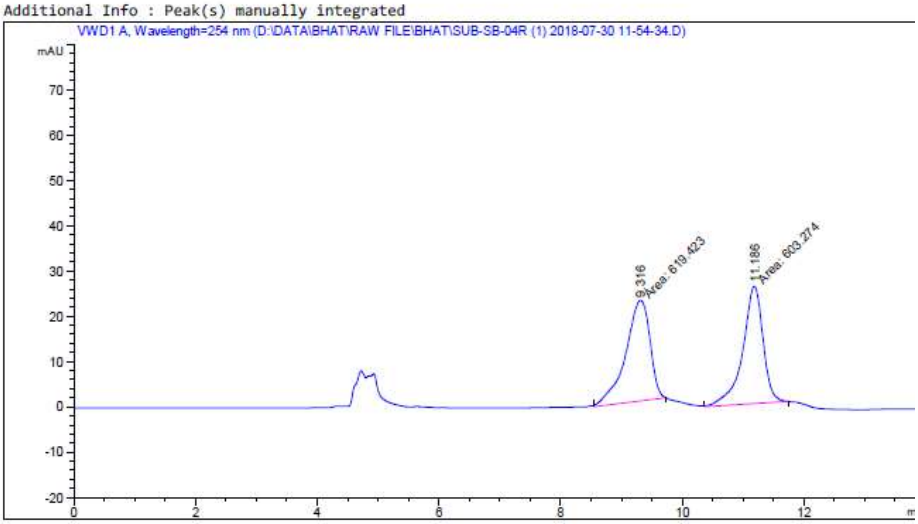




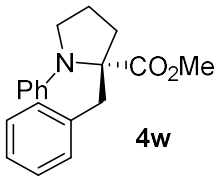
HPLC data of Chiral Proline Derivative 4w

Sample Info : ChiralpakCEL OD-H, 1% IPA-Hexane, 7.0 ml/min, 254nm

Additional Info : Peak(s) manually integrated



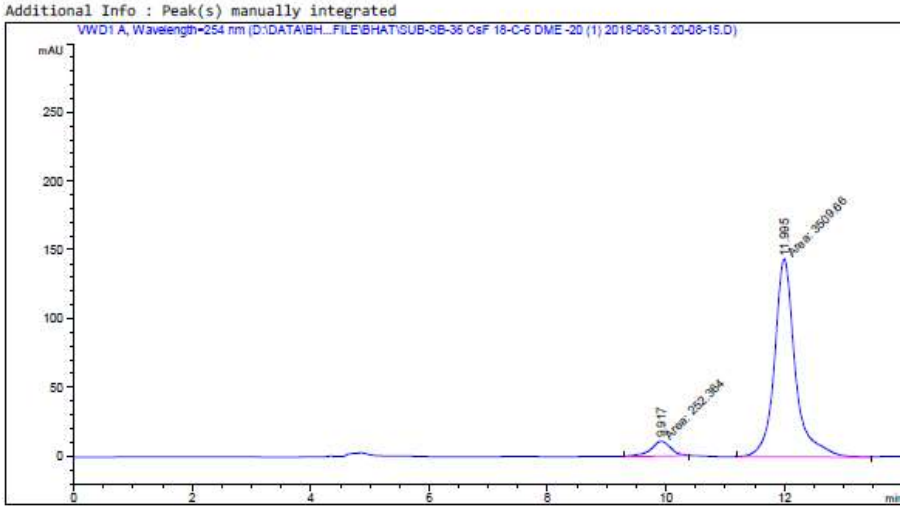
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.316	MM	0.4652	619.42291	22.19272	50.6604
2	11.186	MM	0.3873	603.27448	25.96322	49.3396
Totals :				1222.69739	48.15593	



4w

Sample Info : CHIRALCEL OD-H 1% ipa-Hexane, 0.70 ml/min, 254nm

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.917	MM	0.3925	252.36441	10.71515	6.7082
2	11.995	MM	0.4072	3509.65503	143.64973	93.2918
Totals :				3762.01944	154.36489	