Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Iron-Catalyzed C(sp^3)−H Functionalization of *N,N*-Dimethylanilines with Isocyanides

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1.-General Considerations

Reagents. Commercially available materials were used without further purification. Iron(II) acetate (anhydrous) was purchased from Strem Chemicals. *N,N*-Dimethylaniline, *tert*-butyl hydroperoxide solution (5.0-6.0 M in decane) and isocyanides were purchased from Sigma-Aldrich. Acetonitrile (99.9%) was purchased from Acros Organics. Most of the required *N,N*-dimethylanilines are known compounds and were synthesized following reported procedures.

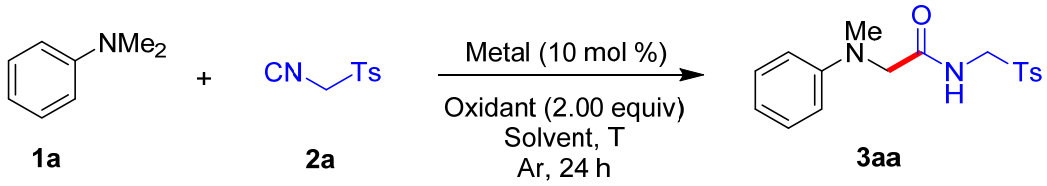
Analytical Methods. ^{1}H NMR and ^{13}C NMR spectra as well as IR, HRMS and melting points (where applicable) are included for all new compounds. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz at 20 ^{o}C. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for $CHCl_3$ (7.26 ppm), unless otherwise indicated. All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77 ppm), unless otherwise indicated, and were obtained with ^{1}H decoupling. Coupling constants, *J*, are reported in hertz. Melting points were measured using open glass capillaries in a Büchi SMP-20 apparatus. High resolution mass spectra (HRMS) were performed by SGIker and were acquired on a LC/Q-TOF mass spectrometer equipped with an electrospray source ESI Agilent Jet Stream. Infrared spectra were recorded on a Bruker Alpha P. Flash chromatography was performed with EM Science silica gel 60 (230-400 mesh). The yields reported in the manuscript correspond to isolated yields and represent an average of at least two independent runs.

2.-Optimization Details

2.1.-General Procedure: Ugi-type Coupling of 1a and 2a

A reaction tube containing a stirring bar was charged with commercially available **2a** (0.50 mmol, 98 mg), oxidant (1.00 mmol) (if solid), and metal source (10 mol %). The reaction tube was then evacuated and back-filled with dry argon (this sequence was repeated up to three times). Then, commercially available **1a** (0.50 mmol, 62 μL), oxidant (if liquid), and the corresponding solvent (2 mL) were added by syringe under argon atmosphere. The reaction tube was next warmed up to the corresponding temperature and stirred for 24 hours. The mixture was allowed to warm to room temperature, concentrated under reduced pressure and the corresponding product was purified by flash chromatography (hexanes/AcOEt 1/1). The purity of the corresponding product **3aa** was verified by ^{1}H NMR.

Table S1. Screening Process[a]

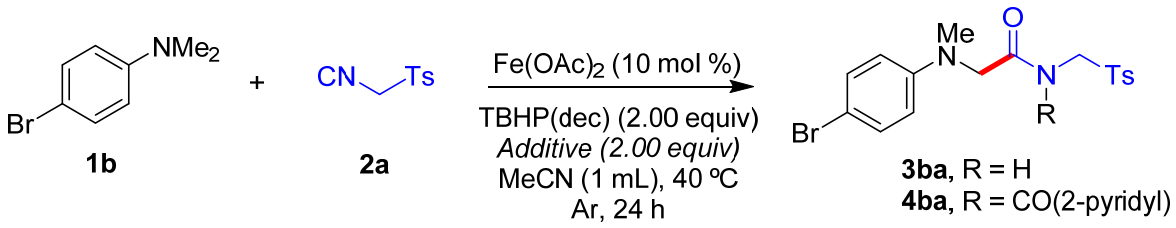


1a **2a** **3aa**

Entry	Metal	Oxidant	Solvent	T (° C)	Yield (%)[h]
1	none	TBHPdec	MeCN	40	traces
2	$Fe(OAc)_2$	none	MeCN	40	traces
3	$FeCl_2$	TBHPdec	MeCN	rt	26
4	$Fe(OAc)_2$	TBHPdec	MeCN	rt	44
5	$FeBr_2$	TBHPdec	MeCN	rt	35
6	$FeBr_3$	TBHPdec	MeCN	rt	traces
7	$Fe(OAc)_2$	TBHPdec	MeCN	60	0
8	$Fe(OAc)_2$	TBHPdec	MeCN	50	41
9	$Fe(OAc)_2$	TBHPdec	MeCN	40	64
10	$Fe(acac)_3$	TBHPdec	MeCN	40	46
11	CoF_3	TBHPdec	MeCN	40	34
12	CoF_2	TBHPdec	MeCN	40	30
13	$Co(acac)_2$	TBHPdec	MeCN	40	0
14	$Fe(OAc)_2$	TBHPaq	MeCN	40	23
15	$Fe(OAc)_2$	TBPB	MeCN	40	0
16	$Fe(OAc)_2$	DCP	MeCN	40	0
17	$Fe(OAc)_2$	DDQ	MeCN	40	0
18	$Fe(OAc)_2$	$(NH_4)_2S_2O_8$	MeCN	40	0
19	$Fe(OAc)_2$	H_2O_2	MeCN	40	23
20	$Fe(OAc)_2$	O_2 (1atm)	MeCN	40	29
21	$Fe(OAc)_2$	TBHPdec	DCM	40	51
22	$Fe(OAc)_2$	TBHPdec	$CHCl_3$	40	63
23	$Fe(OAc)_2$	TBHPdec	DCE	40	60
24[b]	**$Fe(OAc)_2$**	**TBHPdec**	**MeCN**	**40**	**81 (91)[c]**
25[b,d]	$Fe(OAc)_2$	TBHPdec	MeCN	40	74
26[b,e]	$Fe(OAc)_2$	TBHPdec	MeCN	40	75
27[b,f]	$Fe(OAc)_2$	TBHPdec	MeCN	40	71
28[b,g]	$Fe(OAc)_2$	TBHPdec	MeCN	40	74

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), metal (10 mol %), oxidant (2.00 equiv), solvent (2 mL), 24h. [b] **2a** (2.00 equiv). [c] 1.0 gram-scale of **2a**. [d] $Fe(OAc)_2$ (5 mol %). [e] under air. [f] **2a** (3.0 equiv).[g] TBHPdec = 1.00 equiv. [h] Isolated yield after column chromatography. TBHPaq = *tert*-butyl hydroperoxide (70 wt. % in H_2O), TBHPdec = *tert*-butyl hydroperoxide (5.0-6.0 M in decane), DTBP = di-*tert*-butyl peroxide, DCP = dicumyl peroxide.

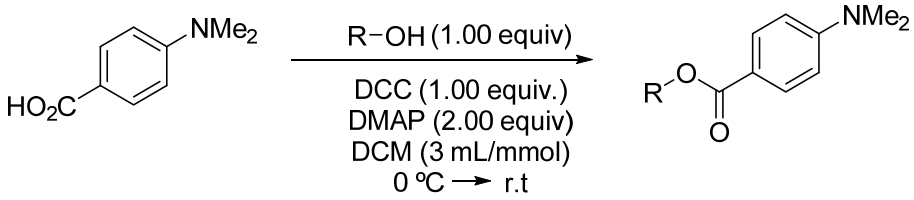
Table S2. Effect of Additives[a]



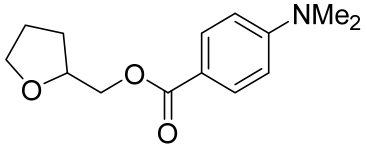
Entry	Additive	Yield (%)[b]
1	--	68 (**3ba**)
2	TFA	nd
3	AcOH	81 (**3ba**)
4	PivOH	59 (**3ba**)
5	$AdCO_2H$	81 (**3ba**)
6	$MesCO_2H$	44 (**3ba**)
7	$PhCO_2H$	42 (**3ba**)[c]
8	2-nitrobenzoic acid	nd
9	Nicotinic acid	55 (**3ba**)
10	2-Methylnicotinic acid	51 (**3ba**)
11	Picolinic acid	62 (**4ba**)

[a] Reaction conditions: **1b** (0.5 mmol), **2a** (0.25 mmol), $Fe(OAc)_2$ (10 mol %), TBHP(dec) (2.00 equiv), MeCN (1 mL) at 40 °C, 24h. [b] Isolated yield after column chromatography. [c] 21% yield of the benzoylated amide was obtained along with **3ba**. nd = not determined

3.-Synthesis of *N,N*-Dimethylanilines

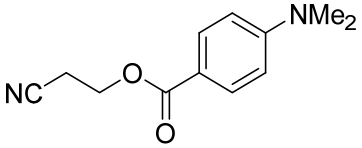


General Procedure: A reaction flask containing a stirring bar was charged with 4-(dimethylamino)benzoic acid (1.00 mmol, 1.00 equiv), the corresponding alcohol (1.00 mmol, 1.00 equiv), DCC (1.00 mmol, 1.00 equiv) and DMAP (2.00 mmol, 2.00 equiv) in DCM at 0 ºC. The resulting solution was stirred at room temperature for 24 hours. The mixture was then concentrated under reduced pressure and the corresponding product was purified by flash chromatography (hexane/AcOEt 7/3), unless otherwise indicated.



(1i)

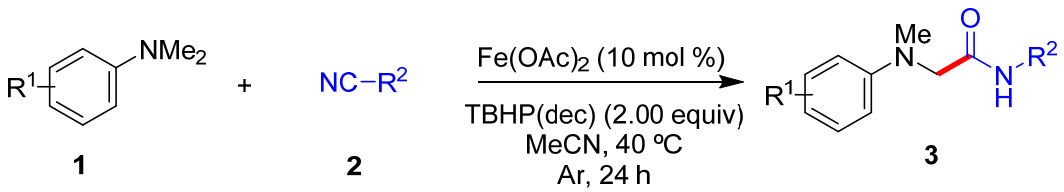
(Tetrahydrofuran-2-yl)methyl 4-(dimethylamino)benzoate (1i). Following the general procedure, using 4-(dimethylamino)benzoic acid (6.05 mmol, 1.00 g) and tetrahydrofurfuryl alcohol (6.05 mmol, 0.6 mL) provided 1.34 g (89 % yield) of **1i** as a white solid. Mp 52-53 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 9.0 Hz, 2H), 6.63 (d, J = 9.0 Hz, 2H), 4.33 (d, J = 7.2 Hz, 1H), 4.30 – 4.20 (m, 2H), 4.00 – 3.89 (m, 1H), 3.82 (q, J = 7.6 Hz, 1H), 3.02 (s, 6H), 2.12 – 2.02 (m, 1H), 2.02 – 1.83 (m, 2H), 1.83 – 1.66 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 153.5, 131.6, 116.9, 110.8, 77.0, 68.7, 66.4, 40.2, 28.3, 25.9. IR (neat, cm^{-1}): 1692, 1604, 1271, 1182. HRMS *calcd*.for ($C_{14}H_{19}NO_3$): 249.1365, *found* 249.1364.



(1j)

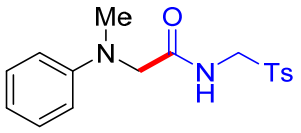
2-Cyanoethyl 4-(dimethylamino)benzoate (1j). Following the general procedure, using 4-(dimethylamino)benzoic acid (6.05 mmol, 1.00 g) and 3-hydroxypropionitrile (6.05 mmol, 0.41 mL) provided 987 mg (75 % yield) of **1j** as a white solid. Mp 109-110 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 9.0 Hz, 2H), 6.72 (d, J = 9.0 Hz, 2H), 4.51 (t, J = 6.3 Hz, 2H), 3.09 (s, 6H), 2.84 (t, J = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 153.5, 131.6, 117.1, 115.9, 110.9, 58.4, 40.2, 18.3. IR (neat, cm^{-1}): 2855, 2252, 1694, 1607, 1273, 1103, 765. HRMS *calcd*.for ($C_{12}H_{14}N_2O_2$): 218.1055, *found* 218.1053.

4.-Fe-Catalyzed C(sp^3)-H Functionalization of Anilines 1 with Isocyanides 2



1 **2** **3**

General Procedure: A reaction tube containing a stirring bar was charged with the corresponding *N,N*-dimethylaniline **1** (if solid) (1.00 mmol, 2.00 equiv), isocyanide **2** (if solid) (0.50 mmol, 1.00 equiv) and $Fe(OAc)_2$ (10 mol %). The reaction tube was then evacuated and back-filled with dry argon (this sequence was repeated up to three times). The corresponding *N,N*-dimethylaniline **1** (1.00 mmol, 2.00 equiv), and isocyanide **2** (0.50 mmol, 1.00 equiv) (if liquids), TBHP (5.0-6.0M in decane) (2.00 equiv), and MeCN (2.00 mL) were then added under argon atmosphere. The reaction tube was next warmed up to 40 ºC and stirred for 24 hours. The mixture was then allowed to warm to room temperature, concentrated under reduced pressure and the corresponding product was purified by flash chromatography (hexanes/AcOEt 1/1), unless otherwise indicated. The yields reported in the manuscript refer to isolated yields and represent an average of at least two independent runs.



(3aa)

2-[Methyl(phenyl)amino]-*N*-(tosylmethyl)acetamide (1a). Following the general procedure, using commercially available *N,N*-dimethylaniline (1.00 mmol, 126 µL) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 135 mg (81% yield) of **3aa** as a white solid. Mp 125-126 ºC (Lit.[1] 111-112 ºC). The spectroscopic data correspond to those previously reported in the literature.[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.66 (m, 2H), 7.46 (t, J = 7.0 Hz, 1H), 7.43 – 7.21 (m, 4H), 6.89 (t, J = 7.3 Hz, 1H), 6.74 – 6.61 (m, 2H), 4.68 (d, J = 6.9 Hz, 2H), 3.76 (s, 2H), 2.99 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 148.9, 145.4, 133.7, 129.8, 129.3, 128.7, 118.9, 113.2, 59.8, 58.3, 39.9, 21.7. *This reaction was also performed in a higher scale: the use of N,N-dimethylaniline (10.20 mmol, 1.29 mL) and p-toluenesulfonylmethyl isocyanide (5.12 mmol, 1.00 g) provided 1.54 g (91% yield) of* ***3aa*** *as a white solid.*

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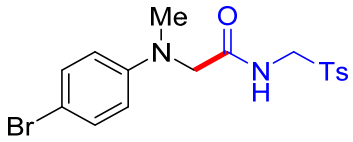
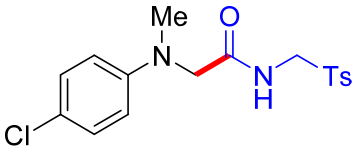
[1] Katritzky, A. R.; Mohapatra, P. P.; Singh, S.; Clemens, N.; Kirichenko, K. *J. Serb. Chem. Soc.* **2005**, *70*, 319.
[2] Yadav, A. K.; Yadav, L. D. S. *Chem. Commun.* **2016**, *52*, 10621.



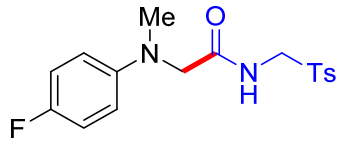
(**3ba**)

2-[(4-Bromophenyl)(methyl)amino]-*N*-(tosylmethyl)acetamide (3ba). Following the general procedure adding AcOH (2.0 equiv), using commercially available 4-bromo-*N,N*-dimethylaniline (1.00 mmol, 200 mg) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 167 mg (81% yield) of **3ba** as a white solid. Mp 163-164 ºC (Lit. 144-146 ºC). The spectroscopic data correspond to those previously reported in the literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.63 (m, 2H), 7.43 – 7.23 (m, 4H), 6.60 – 6.46 (m, 2H), 4.70 (d, J = 6.8 Hz, 2H), 3.76 (s, 2H), 2.99 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.8, 147.9, 145.6, 133.7, 132.1, 129.9, 128.7, 114.9, 111.3, 59.8, 58.2, 40.1, 21.8.



(**3ca**)

2-[(4-Chlorophenyl)(methyl)amino]-*N*-(tosylmethyl)acetamide (3ca). Following the general procedure adding AcOH (2.0 equiv), using 4-chloro-*N,N*-dimethyl-4aniline[4] (1.00 mmol, 155 mg) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 119 mg (65 % yield) of **3ca** as a white solid. Mp 177-178 ºC (Lit. 157-160 ºC). The spectroscopic data correspond to those previously reported in the literature.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.1 Hz, 3H), 7.32 (s, 1H), 7.22 (d, J = 9.0 Hz, 1H), 6.58 (d, J = 9.0 Hz, 2H), 4.70 (d, J = 6.8 Hz, 2H), 3.76 (s, 2H), 2.99 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 147.9, 145.9, 134.0, 130.3, 129.5, 129.2, 124.5, 114.9, 60.2, 58.7, 40.5, 22.1.

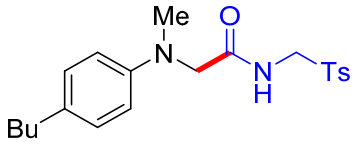


(**3da**)

2-[(4-Fluorophenyl)(methyl)amino]-*N*-(tosylmethyl)acetamide (3da). Following the general procedure adding AcOH (2.0 equiv), using 4-fluoro-*N,N*-dimethyl aniline[6] (1.00 mmol, 139 mg), *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 124 mg (75% yield) of **3da** as a white solid. Mp 160-161 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.44 (t, J = 6.3 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.00 (t, J = 8.7 Hz, 2H),

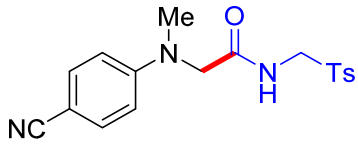
[3] Ye, X.; Xie, C.; Huang, R.; Liu, J. *Synlett* **2012**, *23*, 409.
[4] Kawade, R. K.; Huple, D. B.; Lin, R.-J.; Liu, R.-S. *Chem. Commun.* **2015**, *51*, 6625.
[5] Rueping, M.; Vila, C. *Org. Lett*. **2013**, *15*, 2092.
[6] Lewis, R.; Wisthoff, M. F.; Grissmerson, J.; Chain, W. J. *Org. Lett.* **2014**, *16*, 3832.

6.70 – 6.61 (m, 2H), 4.72 (d, J = 6.9 Hz, 2H), 3.73 (s, 2H), 2.97 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.2 (d, $J_{C\text{-}F}$ = 242.4 Hz), 145.9 (d, $J_{C\text{-}F}$ = 10.1 Hz), 134.1, 130.3, 129.1, 116.2 (d, $J_{C\text{-}F}$ = 20.2 Hz), 115.4 (d, $J_{C\text{-}F}$ = 10.1 Hz), 60.2, 59.5, 41.1, 22.1. IR (neat, cm^{-1}): 3318, 1690, 1508, 1136, 818, 579, 509. HRMS *calcd.*for ($C_{17}H_{19}FN_2O_3S$): 350.1100, *found* 350.1100.



(3ea)

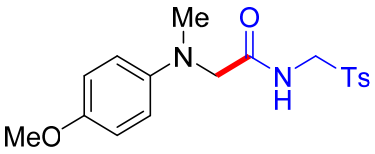
2-[(4-Butylphenyl)(methyl)amino]-*N*-(tosylmethyl)acetamide (3ea). Following the general procedure, using 4-butyl-*N,N*-dimethylaniline[7] (1.00 mmol, 177 mg) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 132 mg (68 % yield) of **3ea** as a brownish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.40 (t, J = 6.9 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 6.61 (d, J = 8.6 Hz, 2H), 4.68 (d, J = 6.9 Hz, 2H), 3.70 (s, 2H), 2.95 (s, 3H), 2.55 (t, J = 7.7 Hz, 2H), 2.46 (s, 3H), 1.65 – 1.51 (m, 2H), 1.43 – 1.30 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 147.2, 145.5, 133.9, 133.7, 129.9, 129.3, 128.9, 113.6, 60.0, 58.7, 40.2, 34.6, 33.9, 22.4, 21.8, 14.0. IR (neat, cm^{-1}): 3324, 1685, 1518, 1319, 110, 809. HRMS *calcd.* for ($C_{21}H_{28}N_2O_3S$): 388.1821, *found* 388.1815.



(3fa)

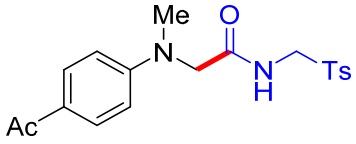
2-[(4-Cyanophenyl)(methyl)amino]-*N*-(tosylmethyl)acetamide (3fa). Following the general procedure, using commercially available 4-cyano-*N,N*-dimethylaniline (1.00 mmol, 146 mg) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 124 mg (70 % yield) of **3fa** as a pink solid. Mp 180-181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.9 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 6.6 Hz, 1H), 6.63 (d, J = 9.0 Hz, 2H), 4.68 (d, J = 6.8 Hz, 2H), 3.88 (s, 2H), 3.09 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 151.6, 146.0, 133.8, 130.2, 128.9, 128.8, 119.8, 112.7, 100.9, 60.0, 57.2, 39.9, 21.9. IR (neat, cm^{-1}): 3314, 2213, 1688, 1606, 1522, 1320, 1142, 818. HRMS *calcd.* for ($C_{18}H_{19}N_3O_3S$): 357.1147, *found* 357.1151.

[7] Heijnen, D.; Tosi, F.; Vila, C.; Stuart, M. C. A.; Elsinga, P. H.; W. Szymanski; Feringa, B. L. *Angew. Chem. Int. Ed*. **2017**, *56*, 3354.



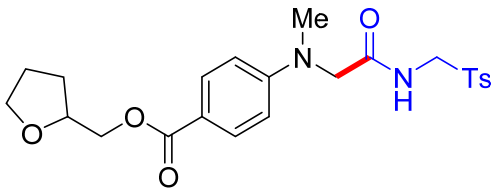
(3ga)

2-[(4-Methoxyphenyl)(methyl)amino]-*N*-(tosylmethyl)acetamide (3ga). Following the general procedure adding AcOH (2.0 equiv), using *N,N*-dimethyl-4-anisidine[8] (1.00 mmol, 151 mg), *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 110 mg (64% yield) of **3ga** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.56 (t, J = 6.4 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 9.1 Hz, 2H), 6.70 (d, J = 9.1 Hz, 2H), 4.72 (d, J = 6.9 Hz, 2H), 3.81 (s, 3H), 3.68 (s, 2H), 2.93 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 153.9, 145.8, 143.9, 134.2, 130.3, 129.1, 116.0, 115.2, 60.2, 59.9, 56.0, 41.4, 22.1. IR (neat, cm^{-1}): 3318, 2928, 1678, 1509, 1138, 813. HRMS *calcd*. for ($C_{18}H_{22}N_2O_4S$): 362.1300, *found* 362.1303.



(3ha)

2-((4-Acetylphenyl)(methyl)amino)-*N*-(tosylmethyl)acetamide (3ha). Following the general procedure at 70 ºC, using commercially available 1-[4-(dimethylamino)phenyl]ethan-1-one (1.00 mmol, 163 mg) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 105 mg (56 % yield) of **3ha** as a white solid. Mp 178-179 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 7.18 (t, J = 5.8 Hz, 1H), 6.64 (d, J = 8.7 Hz, 2H), 4.70 (d, J = 6.7 Hz, 2H), 3.91 (s, 2H), 3.11 (s, 3H), 2.55 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 169.5, 152.4, 146.2, 134.0, 130.9, 130.3, 129.1, 128.1, 112.1, 60.3, 57.5, 40.1, 26.5, 22.1. IR (neat, cm^{-1}): 3289, 3016, 1666, 1279, 1139, 816. HRMS *calcd*. for ($C_{19}H_{22}N_2O_4S$): 374.1300, *found* 374.1298.

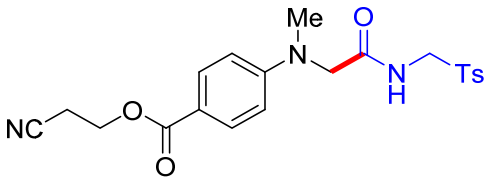


(3ia)

(Tetrahydrofuran-2-yl)methyl 4-(methyl(2-oxo-2-((tosylmethyl)amino)ethyl)amino) benzoate (3ia). Following the general procedure, using (tetrahydrofuran-2-yl)methyl 4-(dimethylamino)benzoate (**1i**) (1.00 mmol, 265 mg) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 160 mg (69% yield) of **3ia** as a white solid. Mp 155-156 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.9 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.0

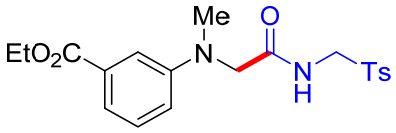
[8] Fava, E.; Millet, A.; Nakajima, M.; Loescher, S.; Rueping, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 1433.

Hz, 2H), 7.03 (t, J = 6.7 Hz, 1H), 6.63 (d, J = 8.9 Hz, 2H), 4.71 (d, J = 6.8 Hz, 2H), 4.39 (q, J = 6.5 Hz, 1H), 4.35 – 4.24 (m, 2H), 4.02 – 3.91 (m, 1H), 3.89 (s, 2H), 3.86 (d, J = 7.1 Hz, 1H), 3.10 (s, 3H), 2.49 (s, 3H), 2.10 (td, J = 13.1, 12.1, 5.7 Hz, 1H), 1.99 (dt, J = 14.8, 7.8 Hz, 2H), 1.76 (dp, J = 15.1, 7.0, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 166.7, 152.3, 146.1, 133.9, 131.9, 130.3, 129.11, 120.4, 112.2, 68.9, 66.9, 60.1, 57.8, 40.2, 28.5, 26.1, 22.1. IR (neat, cm^{-1}): 3294, 2926, 1691, 1281, 1139, 766. HRMS *calcd*. for ($C_{23}H_{28}N_2O_6S$): 460.1668, *found* 460.1665.



(3ja)

2-Cyanoethyl 4-[methyl(2-oxo-2-((tosylmethyl)amino)ethyl)amino]benzoate (3ja). Following the general procedure, using 4-(2-isocyanoethyl)-*N,N*-dimethylaniline (**1j**) (0.50 mmol, 218 mg) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 100 mg (70% yield) of **3ja** as a white solid. Mp 171-172 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.6 Hz, 2H), 7.75 (d, J = 7.9 Hz, 2H), 7.38 (d, J = 7.9 Hz, 2H), 6.98 (br s, 1H), 6.65 (d, J = 8.7 Hz, 2H), 4.72 (d, J = 6.7 Hz, 2H), 4.54 (t, J = 6.2 Hz, 2H), 3.91 (s, 2H), 3.13 (s, 3H), 2.86 (t, J = 6.2 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 166.1, 152.7, 146.1, 133.9, 132.1, 130.4, 129.1, 119.2, 117.3, 112.3, 60.1, 59.1, 57.7, 40.2, 22.1, 18.6. IR (neat, cm^{-1}): 3283, 2923, 2100, 1700, 1672, 1314, 1140, 765. HRMS *calcd*. for ($C_{21}H_{23}N_3O_5S$): 429.1358, *found* 429.1355.

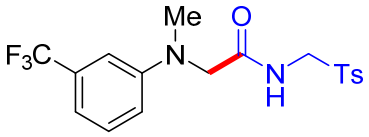


(3ka)

Ethyl 3-[methyl(2-oxo-2-((tosylmethyl)amino)ethyl)amino]benzoate (3ka). Following the general procedure, using *m*-ethyl *N,N*-dimethylaminobenzoate[9] (1.00 mmol, 193 mg) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 181 mg (90 % yield) of **3ka** as a white solid. Mp 135-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 7.7 Hz, 1H), 7.44 (s, 1H), 7.37 (d, J = 8.1 Hz, 2H), 7.32 – 7.27 (m, 1H), 6.89 – 6.80 (m, 1H), 4.71 (d, J = 6.9 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 3.83 (s, 2H), 3.05 (s, 3H), 2.48 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 166.8, 149.1, 145.6, 133.8, 131.7, 130.0, 129.4, 128.8, 120.0, 117.5, 114.0, 61.1, 60.0, 58.0, 39.9, 21.8,

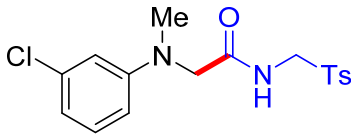
[9] Guyon, C.; Duclos, M.-C.; Métay, E.; Lemaire, M. *Tetrahedron Lett*. **2016**, *57*, 3002.

14.4. IR (neat, cm^{-1}): 3324, 2980, 2929, 1708, 1493, 1267, 1140, 752. HRMS *calcd.* for ($C_{20}H_{24}N_2O_5S$): 404.1406, *found* 404.1399.



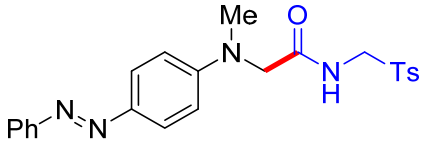
(3la)

2-[Methyl(3-(trifluoromethyl)phenyl)amino]-*N*-(tosylmethyl]acetamide (3la). Following the general procedure, using *N,N*-dimethyl-3-trifluoromethyl aniline[10] (1.00 mmol, 189 mg) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 156 mg (78 % yield) of **3la** as a white solid. Mp 148-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.44 – 7.31 (m, 3H), 7.13 (d, J = 7.5 Hz, 2H), 6.91 (s, 1H), 6.80 (dd, J = 8.4, 2.7 Hz, 1H), 4.69 (d, J = 6.9 Hz, 2H), 3.82 (s, 2H), 3.03 (s, 3H), 2.45 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 149.3, 145.8, 133.9, 131.9 (q, $J_{C\text{-}F}$ = 31.3 Hz), 130.1, 128.8, 116.4, 115.6 (q, $J_{C\text{-}F}$ = 4.0 Hz), 109.6 (q, $J_{C\text{-}F}$ = 4.0 Hz), 60.0, 58.1, 40.0, 21.9. IR (neat, cm^{-1}): 3319, 3055, 2927, 1685, 1611, 1507, 1319, 1142, 1119. HRMS *calcd.* for ($C_{18}H_{19}F_3N_2O_3S$): 400.1068, *found* 400.1067.



(3ma)

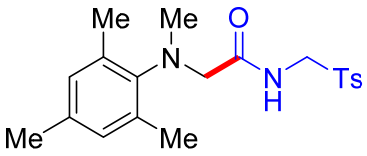
2-[(3-Chlorophenyl)(methyl)amino)-*N*-(tosylmethyl]acetamide (3ma). Following the general procedure, using commercially available 3-chloro-*N,N*-dimethylaniline (1.00 mmol, 156 mg) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 135 mg (74 % yield) of **3ma** as a white solid. Mp 148-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.23 – 7.11 (m, 2H), 6.86 (d, J = 7.8 Hz, 1H), 6.66 (t, J = 4 Hz, 1H), 6.54 (dd, J = 8.4, 2.5 Hz, 1H), 4.68 (d, J = 6.8 Hz, 2H), 3.76 (s, 2H), 2.99 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 150.1, 145.8, 135.5, 133.8, 130.5, 130.1, 128.9, 119.1, 113.3, 111.5, 60.0, 58.1, 40.0, 21.9. IR (neat, cm^{-1}): 3321, 3056, 2924, 1685, 1595, 1491, 1320, 1141, 1084. HRMS *calcd.* for ($C_{17}H_{19}ClN_2O_3S$): 366.0805, *found* 366.0802.



(3na)

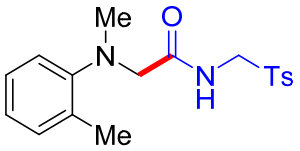
[10] Kirij, N. V.; Filatov, A. A.; Khrapach, G. Yu.; Yagupolskii, Y. L. *Chem. Commun.* **2017**, *53*, 2146.

(*E*)-2-[Methyl(4-(phenyldiazenyl)phenyl)amino)-*N*-(tosylmethyl]acetamide (3na). Following the general procedure adding AcOH (2.0 equiv.) at 70 °C, using commercially available 4-(phenylazo)-*N,N*-dimethylaniline (0.50 mmol, 113 mg), *p*-toluenesulnylmethyl isocyanide (0.25 mmol, 49 mg) provided 53 mg (49 % yield) of **3na** as a brownish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 4H), 7.72 (d, J = 8.3 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.46 – 7.40 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 4.0 Hz, 1H), 6.73 (d, J = 9.0 Hz, 2H), 4.71 (d, J = 6.8 Hz, 2H), 3.92 (s, 2H), 3.13 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 153.1, 151.2, 145.9, 145.5, 133.9, 130.4, 130.3, 129.3, 129.0, 125.2, 122.7, 112.9, 60.2, 57.9, 40.3, 22.1. IR (neat, cm^{-1}): 3340, 2923, 1685, 1599, 1513, 1319, 1140. HRMS *calcd.* for ($C_{23}H_{24}N_4O_3S$): 436.1569, *found* 436.1562.



(3oa)

2-[Mesityl(methyl)amino]-*N*-(tosylmethyl)acetamide (3oa). Following the general procedure adding AcOH (2.0 equiv), using *N,N*-dimethyl-2,4,6-trimethyl-aniline[11] (1.00 mmol, 163 mg) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 64 mg (34% yield) of **3oa** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (t, J = 6.7 Hz, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.89 (s, 2H), 4.80 (d, J = 6.9 Hz, 2H), 3.58 (s, 2H), 2.73 (s, 3H), 2.45 (s, 3H), 2.35 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 146.2, 145.8, 136.2, 135.9, 134.2, 130.6, 130.3, 129.0, 60.7, 60.2, 42.1, 22.0, 20.9, 19.8. IR (neat, cm^{-1}): 3287, 2925, 1679, 1124, 732. HRMS *calcd*. for ($C_{20}H_{26}N_2O_3S$): 374.1664, *found* 374.1660.

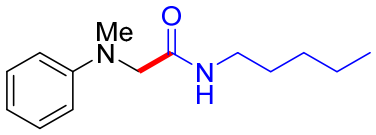


(3pa)

2-[Methyl(*o*-tolyl)amino]-*N*-(tosylmethyl)acetamide (3pa) Following the general procedure at 70 ºC, using commercially available *N,N*-dimethyl-*o*-toluidine (1.00 mmol, 140 µL), *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 72 mg (41% yield) of **3pa** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (t, J = 6.4 Hz, 1H), 7.70 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.24 (dd, J = 18.3, 7.6 Hz, 3H), 7.15 – 7.06 (m, 2H), 4.77 (d, J = 6.9 Hz, 2H), 3.51 (s, 2H), 2.70 (s, 3H), 2.45 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz,

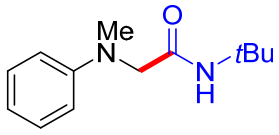
[11] Giumanini, A. G.; Chiavari, G.; Musiani, M. M.; Rossi, P. *Synthesis* **1980**, 743.

$CDCl_3$) δ 170.2, 150.9, 145.7, 134.3, 132.9, 131.9, 130.3, 128.9, 127.4, 125.1, 120.7, 60.6, 60.2, 44.0, 22.1, 18.8. IR (neat, cm^{-1}): 3359, 2947, 1687, 1490, 1140, 726. HRMS *calcd*. for ($C_{18}H_{22}N_2O_3S$): 346.1351, *found* 346.1349.



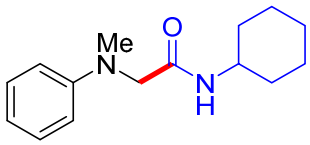
(3ab)

2-[Methyl(phenyl)amino]-*N*-pentylacetamide (3ab). Following the general procedure at 70 ºC using *N,N*-dimethylaniline (1.00 mmol, 126 µL) and pentyl isocyanide (0.50 mmol, 63 µL) provided 87 mg (71% yield) of **3ab** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (dd, J = 8.8, 7.2 Hz, 2H), 6.93 – 6.70 (m, 3H), 6.61 (s, 1H), 3.86 (s, 2H), 3.43 – 3.21 (m, 2H), 3.03 (s, 3H), 1.48 (p, J = 7.3 Hz, 2H), 1.41 – 1.17 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.1, 149.2, 129.3, 118.5, 113.0, 58.8, 39.7, 39.1, 29.2, 28.9, 22.2, 13.9. IR (neat, cm^{-1}): 3267, 1642, 1505. HRMS *calcd.* for ($C_{14}H_{22}N_2O$): 234.1732, *found* 234.1725.



(3ac)

***N*-(*tert*-Butyl)-2-[methyl(phenyl)amino]acetamide (3ac).** Following the general procedure, using *N,N*-dimethylaniline (1.00 mmol, 126 µL) and *tert*-butyl isocyanide (0.50 mmol, 56 µL) provided 49 mg (44% yield) of **3ac** as a white solid. Mp 112-113 ºC (Lit.[12] 95-97 ºC). The spectroscopic data correspond to those previously reported in the literature. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.22 (m, 2H), 6.95 – 6.84 (m, 1H), 6.84 – 6.70 (m, 2H), 6.42 (s, 1H), 3.75 (s, 2H), 3.01 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.5, 149.4, 129.2, 118.6, 113.3, 59.8, 50.9, 39.7, 28.6.

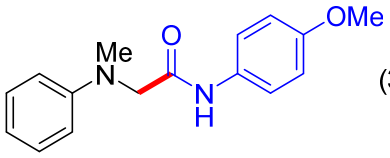


(3ad)

***N*-Cyclohexyl-2-[methyl(phenyl)amino]acetamide (3ad).** Following the general procedure at 70 ºC, using *N,N*-dimethylaniline (1.00 mmol, 126 µL) and cyclohexyl isocyanide (0.50 mmol, 62 µL) provided 59 mg (48% yield) of **3ad** as a white solid. Mp 77-

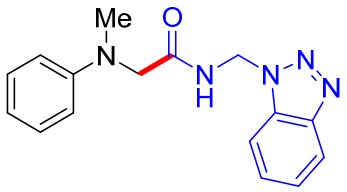
[12] Rueping, M.; Vila, C.; Bootwicha, T. *ACS Catal.* **2013**, *3*, 1676.

78 ºC (Lit.[5] 92-95 ºC). The spectroscopic data correspond to those previously reported in the literature. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.23 (m, 2H), 6.95 – 6.83 (m, 1H), 6.83 – 6.69 (m, 2H), 6.49 (d, J = 8.5 Hz, 1H), 3.86 – 3.84 (m, 3H), 3.01 (s, 3H), 1.88 (dq, J = 12.1, 3.8 Hz, 2H), 1.64 (ddt, J = 27.3, 12.7, 3.9 Hz, 3H), 1.48 – 1.24 (m, 2H), 1.24 – 0.99 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.2, 149.4, 129.2, 118.6, 113.2, 59.1, 47.7, 39.6, 32.9, 25.34 24.7.



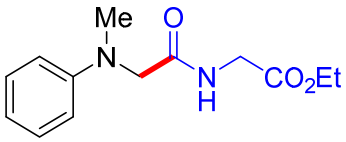
(3ae)

***N*-[4-(Methoxyphenyl)-2-(methyl(phenyl)amino]acetamide (3ae).** Following the general procedure at 70 ºC, using *N,N*-dimethylaniline (0.50 mmol, 126 µL) and 4-methoxyphenyl isocyanide (0.50 mmol, 67 mg) provided 73 mg (54% yield) of **3ae** as a yellow solid. Mp 99-100 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.45 (d, J = 9.0 Hz, 2H), 7.33 (dd, J = 8.8, 7.2 Hz, 3H), 6.99 – 6.78 (m, 4H), 3.98 (s, 2H), 3.81 (s, 3H), 3.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4, 156.6, 149.4, 130.3, 129.5, 121.7, 119.3, 114.1, 113.6, 59.9, 55.4, 40.0. IR (neat, cm^{-1}): 3292, 1683, 1382, 1192. HRMS *calcd.* for ($C_{16}H_{18}N_2O_2$): 270.1368, *found* 270.1360.



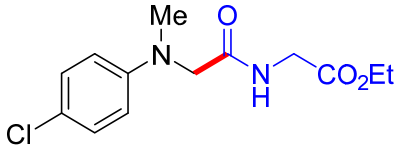
(3af)

***N*-[(1*H*-benzo[*d*][1,2,3]triazol-1-yl)methyl]-2-(methyl(phenyl)amino)acetamide (3af)**. Following the general procedure adding AcOH (2.0 equiv) at 70 ºC, using *N,N*-dimethylaniline (1.00 mmol, 126 µL) and 1-(isocyanomethyl)-1*H*-benzotriazole (0.50 mmol, 79 mg) and provided 80 mg (54 % yield) of **3af** as a yellow oil, which was found to be unstable. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.6 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.22 – 7.11 (m, 2H), 6.82 (t, J = 7.8 Hz, 1H), 6.63 (d, J = 8.1 Hz, 2H), 6.14 (d, J = 7.0 Hz, 2H), 3.91 (s, 2H), 2.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 148.8, 146.0, 132.3, 129.3, 128.0, 124.3, 119.7, 119.1, 113.2, 110.7, 58.6, 50.5, 40.1. IR (neat, cm^{-1}): 3245, 3000, 1680, 1502, 732. HRMS *calcd*. for ($C_{16}H_{17}N_5O$): 295.1433, *found* 295.1431.



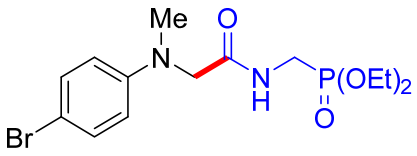
(3ag)

Ethyl *N*-methyl-*N*-phenylglycylglycinate (3ag). Following the general procedure adding AcOH (2.0 equiv) at 70 ºC, using *N,N*-dimethylaniline (1.00 mmol, 126 µL) and ethyl isocyanoacetate (0.50 mmol, 55 µL) provided 96 mg (77 % yield) of **3ag** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 2H), 7.08 (s, 1H), 6.87 (t, J = 7.3 Hz, NH), 6.81 (d, J = 8.0 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 4.08 (d, J = 5.7 Hz, 2H), 3.94 (s, 2H), 3.07 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 169.8, 149.7, 129.7, 119.1, 113.7, 61.8, 59.1, 41.3, 40.0, 14.4. IR (neat, cm^{-1}): 3282, 2980, 1741, 1670, 1188. HRMS *calcd*. for ($C_{13}H_{18}N_2O_3$): 250.1317, *found* 250.1307.



(3bg)

Ethyl *N*-(4-chlorophenyl)-*N*-methylglycylglycinate (3bg). Following the general procedure adding AcOH (2.0 equiv) at 70 ºC, using *N,N*-dimethyl-4-chloroaniline (1.00 mmol, 155 mg) and ethyl isocyanoacetate (0.50 mmol, 55 µL) provided 65 mg (47 % yield) of **3bg** as a yellow solid. Mp 77-78 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 9.0 Hz, 2H), 6.98 (br s, 1H), 6.71 (d, J = 9.0 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 4.08 (d, J = 5.6 Hz, 2H), 3.91 (s, 2H), 3.06 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 169.8, 148.2, 129.5, 124.2, 114.8, 61.9, 59.0, 41.3, 40.3, 14.4. IR (neat, cm^{-1}): 3270, 2981, 1733, 1650, 1496, 1204, 804. HRMS *calcd*. for ($C_{13}H_{17}ClN_2O_3$): 284.0928, *found* 284.0925.

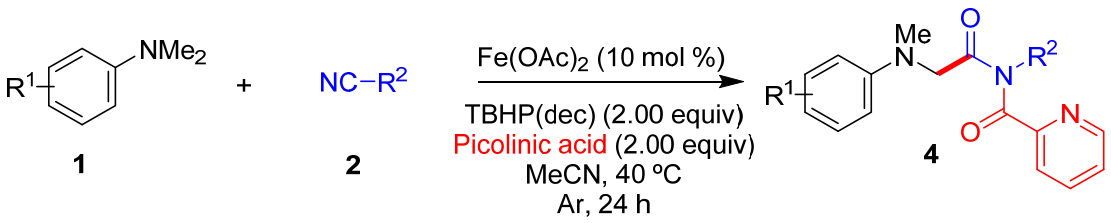


(3bh)

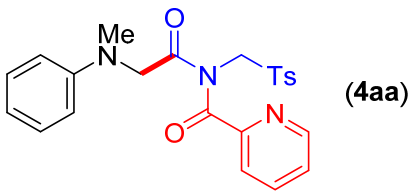
Diethyl [(2-((4-bromophenyl)(methyl)amino)acetamido)methyl]phosphonate (3bh). Following the general procedure adding AcOH (2.0 equiv) at 70 ºC, using commercially available 4-bromo-*N,N*-dimethylaniline (1.00 mmol, 200 mg) and diethyl isocyanomethylphosphonate (0.50 mmol, 80 µL) provided 158 mg (81 % yield) of **3bh** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 9.1 Hz, 2H), 6.74 (br s, 1H), 6.61 (d, J = 9.1 Hz, 2H), 4.08 (p, J = 7.2 Hz, 4H), 3.88 (s, 2H), 3.76 – 3.68 (m, 2H), 3.03 (s, 3H), 1.28 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8 (d, $J_{C\text{-}P}$ = 10.1Hz), 148.0, 132.0,

114.8, 111.0, 62.5 (d, $J_{C\text{-}P}$ = 8.08 Hz), 58.5, 40.0, 35.2, 33.6, 16.3(d, $J_{C\text{-}P}$ = 10.1 Hz). IR (neat, cm^{-1}): 3268, 2980, 1751, 1495, 1208, 10020. HRMS *calcd*. for ($C_{14}H_{22}BrN_2O_4P$): 392.0501, *found* 392.0493.

5.-Fe-Catalyzed Ugi-type Multicomponent Reaction with Picolinic Acid

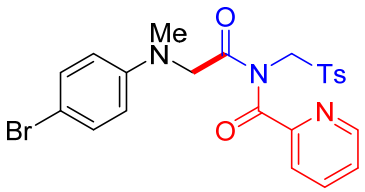


General Procedure: A reaction tube containing a stirring bar was charged with the corresponding *N,N*-dimethylaniline **1** (if solid) (1.00 mmol, 2.00 equiv), isocyanide **2** (if solid) (0.50 mmol, 1.00 equiv), picolinic acid (1.00 mmol, 2.00 equiv) and $Fe(OAc)_2$ (10 mol %). The reaction tube was then evacuated and back-filled with dry argon (this sequence was repeated up to three times). The corresponding *N,N*-dimethylaniline **1** (1.00 mmol, 2.00 equiv), and isocyanide **2** (0.50 mmol, 1.00 equiv) (if liquids), TBHP (5.0-6.0M in decane) (2.00 equiv), and MeCN (2.00 mL) were then added under argon atmosphere. The reaction tube was next warmed up to 40 ºC and stirred for 24 hours. The mixture was then allowed to warm to room temperature, concentrated under reduced pressure and the corresponding product was purified by flash chromatography (hexanes/AcOEt 1/1), unless otherwise indicated. The yields reported in the manuscript refer to isolated yields and represent an average of at least two independent runs.



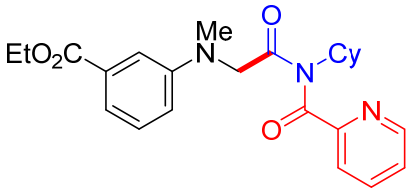
(4aa)

***N*-(*N*-methyl-*N*-phenylglycyl)-*N*-(tosylmethyl)picolinamide (4aa)**. Following the general procedure, using *N,N*-dimethylaniline (1.00 mmol, 126 µL) and *p*-toluenesulfonylmethyl isocyanide (0.50 mmol, 98 mg) provided 54 mg (49% yield) of **4aa** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 4.6 Hz, 1H), 8.04 (d, J = 7.9 Hz, 1H), 7.89 (t, J = 8.5 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.60 – 7.47 (m, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.17 (t, J = 8.0 Hz, 2H), 6.76 (t, J = 7.3 Hz, 1H), 6.51 (d, J = 8.2 Hz, 2H), 5.62 (s, 2H), 4.34 (s, 2H), 2.75 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 169.9, 150.9, 148.7, 148.5, 145.7, 137.9, 134.5, 130.2, 129.3, 127.4, 126.3, 118.3, 113.1, 64.5, 57.7, 39.5, 22.1. IR (neat, cm^{-1}): 3059, 2254, 1700, 1681, 1597, 1335, 1085, 689. HRMS *calcd.* for ($C_{23}H_{23}N_3O_4S$): 437.1409, *found* 437.1400.



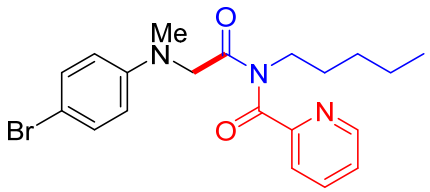
(4bb)

***N*-[*N*-(4-Bromophenyl)-*N*-methylglycyl]-*N*-(tosylmethyl)picolinamide (4bb).** Following the general procedure, using 4-bromo-*N,N*-dimethylaniline (0.50 mmol, 100 mg) and *p*-toluenesulfonylmethyl isocyanide (0.25 mmol, 49 mg) provided 82.4 mg (64% yield) of **4bb** as an orange solid. Mp 132-133 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (ddd, J = 4.8, 1.6, 0.9 Hz, 1H), 8.12 – 7.84 (m, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.52 (ddd, J = 7.6, 4.8, 1.3 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 9.0 Hz, 2H), 6.37 (d, J = 8.9 Hz, 2H), 5.62 (s, 2H), 4.37 (s, 2H), 2.75 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 170.0, 150.4, 148.1, 147.5, 145.5, 137.7, 134.1, 131.6, 129.8, 128.9, 127.1, 126.2, 114.1, 109.7, 63.9, 57.3, 39.2 21.7. IR (neat, cm^{-1}): 1701, 1591, 1085. HRMS *calcd.* for ($C_{23}H_{22}BrN_3O_4S$): 515.0514, *found* 515.0505.



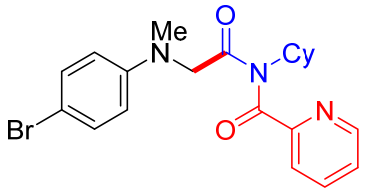
(4kd)

Ethyl 3-[(2-(*N*-cyclohexylpicolinamido)-2-oxoethyl)(methyl)amino] benzoate (4kd). Following the general procedure, using *m*-ethyl *N,N*-dimethylaminobenzoate[9] (0.50 mmol, 97 mg) and cyclohexyl isocyanide (0.25 mmol, 31 µL) provided 65 mg (61 % yield) of **4kd** as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 4.5 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.60 (td, J = 7.7, 1.8 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.33 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H), 7.07 (s, 1H), 6.64 (dd, J = 8.3, 2.8 Hz, 1H), 4.37 (q, J = 7.1 Hz, 3H), 3.96 (s, 2H), 2.66 (s, 3H), 1.92 (qd, J = 11.8, 3.2 Hz, 2H), 1.83 – 1.73 (m, 4H), 1.61 (d, J = 11.3 Hz, 1H), 1.40 (t, J = 7.1 Hz, 3H), 1.35 – 1.24 (m, 2H), 1.21 – 1.10 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 170.4, 166.6, 151.8, 148.4, 148.1, 136.8, 130.9, 128.8, 126.3, 123.7, 119.9, 117.5, 114.0, 60.8, 58.1, 58.0, 39.2, 30.4, 26.2, 25.2, 14.3. IR (cm^{-1}): 3377, 1718, 1602, 1507, 1274, 1114, 713. HRMS *calcd.* for ($C_{24}H_{29}N_3O_4$): 423.2158, *found* 423.2157.



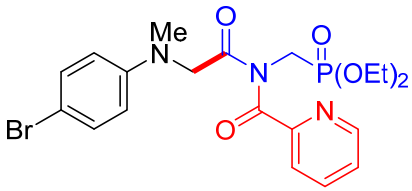
(**4bb**)

***N*-[*N*-(4-Bromophenyl)-*N*-methylglycyl]-*N*-pentylpicolinamide (4bb).** Following the general procedure, using 4-bromo-*N,N*-dimethylaniline (0.50 mmol, 100 mg) and pentyl isocyanide (0.25 mmol, 31 μL) provided 58.5 mg (56% yield) of **4bb** as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, J = 4.8 Hz, 1H), 7.97 – 7.70 (m, 2H), 7.46 (ddd, J = 6.8, 4.8, 2.0 Hz, 1H), 7.27 (d, J = 8.9 Hz, 2H), 6.49 (d, J = 9.0 Hz, 2H), 4.28 (s, 2H), 4.10 – 3.53 (m, 2H), 2.85 (s, 3H), 1.65 – 1.58 (m, 2H), 1.37 – 1.11 (m, 4H), 0.85 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.3, 171.5, 152.3, 148.4, 147.1, 137.3, 131.7, 126.3, 124.1, 114.5, 110.0, 58.3, 46.5, 39.6, 28.9, 28.7, 22.1, 13.9. IR (neat, cm^{-1}): 1685, 1495, 1092. HRMS *calcd.* for ($C_{20}H_{24}BrN_3O_2$): 417.1052, *found* 417.1050.



(**4bd**)

***N*-[*N*-(4-Bromophenyl)-*N*-methylglycyl]-*N*-cyclohexylpicolinamide (4bd).** Following the general procedure, using 4-bromo-*N,N*-dimethylaniline (0.50 mmol, 100 mg) and cyclohexyl isocyanide (0.25 mmol, 31 μL) provided 66 mg (61% yield) of **4bd** as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 – 8.49 (m, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.74 – 7.66 (m, 1H), 7.44 – 7.35 (m, 1H), 7.19 (d, J = 9.0 Hz, 2H), 6.32 (d, J = 9.0 Hz, 2H), 4.33 (ddd, J = 12.0, 8.5, 3.6 Hz, 1H), 3.87 (s, 2H), 2.59 (s, 3H), 2.03 – 1.69 (m, 6H), 1.69 – 1.54 (m, 1H), 1.44 – 0.99 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.8, 170.1, 151.5, 148.1, 146.9, 136.6, 131.2, 126.2, 126.1, 123.5, 114.8, 110.8, 57.8, 57.8, 39.2, 30.0, 25.9, 24.9. IR (neat, cm^{-1}): 1652, 1494, 1113. HRMS *calcd.* for ($C_{21}H_{24}BrN_3O_2$): 429.1052, *found* 429.1050.

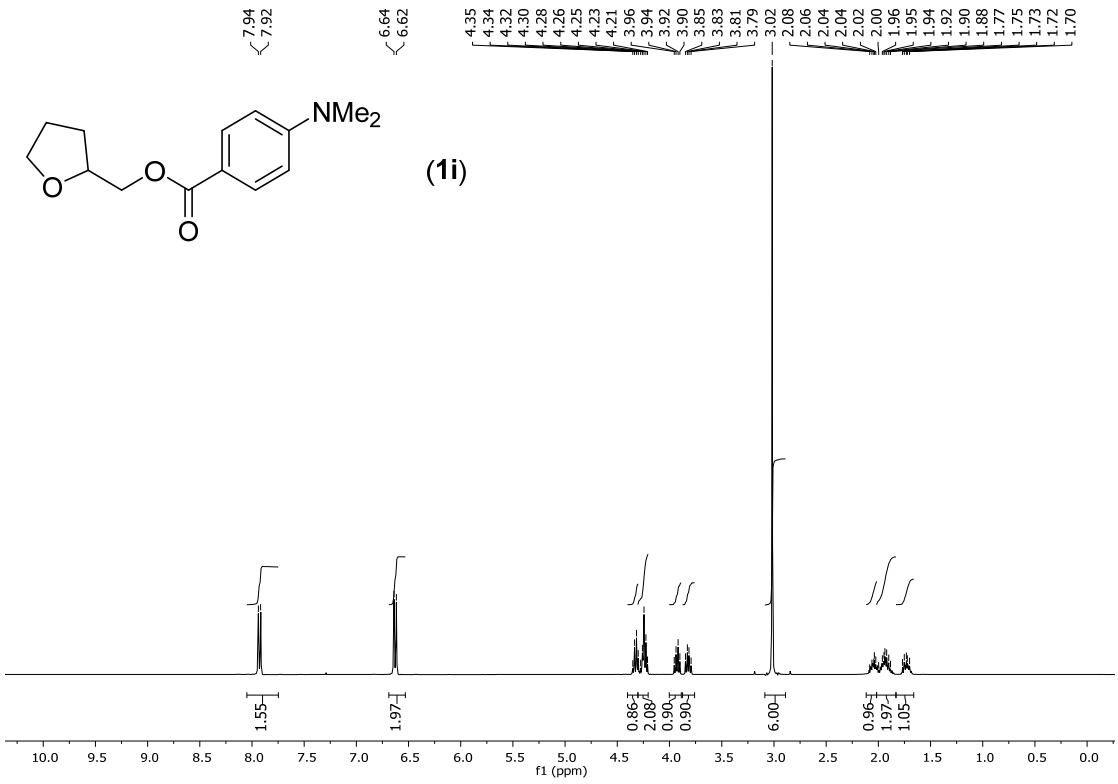


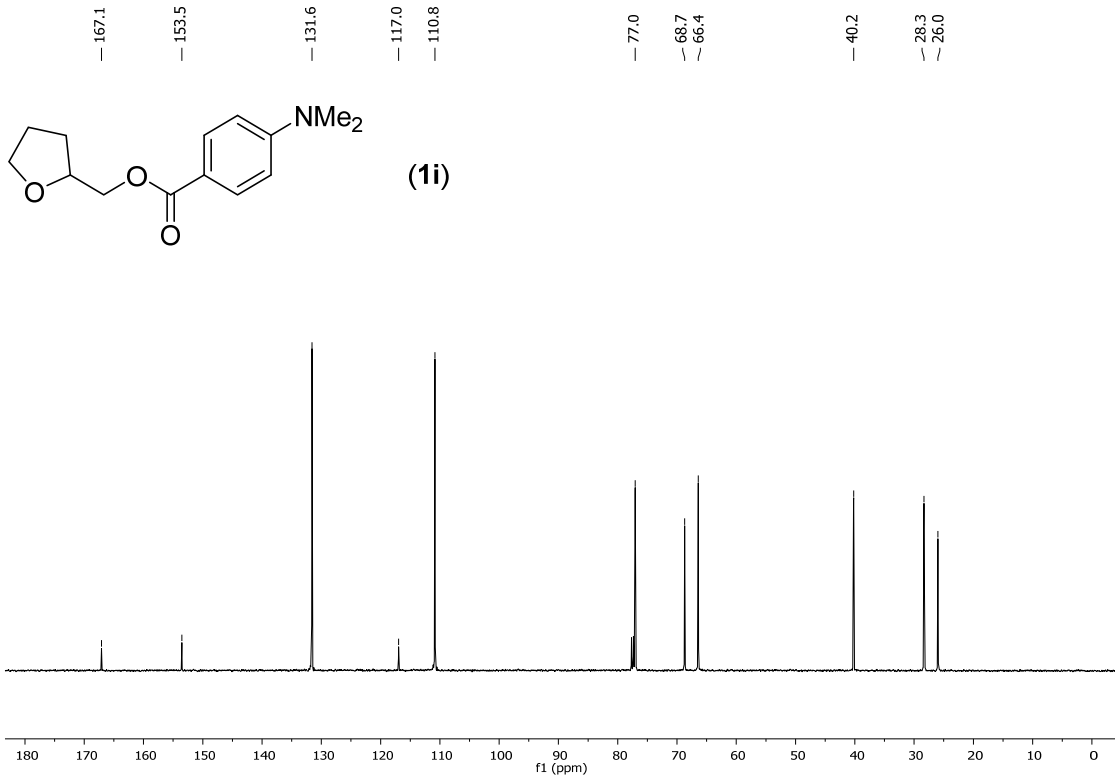
(**4bh**)

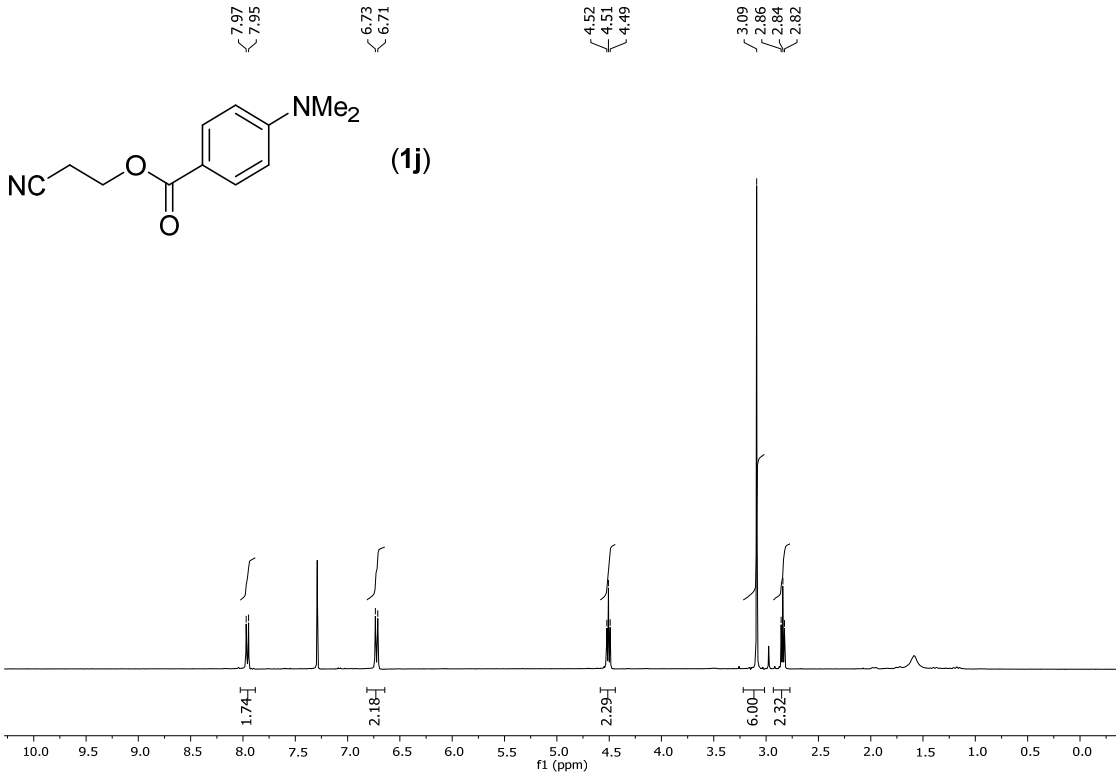
Diethyl [(*N*-(*N*-(4-bromophenyl)-*N*-methylglycyl)picolinamido)methyl]phosphonate (4bh). Following the general procedure, using 4-bromo-*N,N*-dimethylaniline (0.50 mmol,

100 mg) and diethyl isocyanomethylphosphonate (0.25 mmol, 40 μL) provided 78 mg (63% yield) of **4bh** as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (dt, J = 4.6, 1.4 Hz, 1H), 8.01 – 7.80 (m, 2H), 7.49 (d, J = 1.3 Hz, 1H), 7.27 (d, J = 9.0 Hz, 2H), 6.53 (d, J = 9.0 Hz, 2H), 4.58 (d, J = 10.8 Hz, 2H), 4.45 (s, 2H), 4.18 – 3.91 (m, 4H), 2.93 (s, 3H), 1.23 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.2, 170.4, 151.5, 148.1, 147.8, 137.4, 131.7, 126.6, 125.3, 114.2, 109.7, 62.5 (d, $J_{C\text{-}P}$ = 7.1 Hz), 58.0, 40.4 (d, $J_{C\text{-}P}$ = 156.0 Hz), 39.4, 16.2 (d, $J_{C\text{-}P}$ = 6.1 Hz). IR (neat, cm^{-1}): 1696, 1656, 1494, 1020, 728. HRMS *calcd.* for ($C_{20}H_{25}BrN_3O_5P$): 497.0715, *found* 497.0711.

6.- ^{1}H NMR and ^{13}C NMR Spectra



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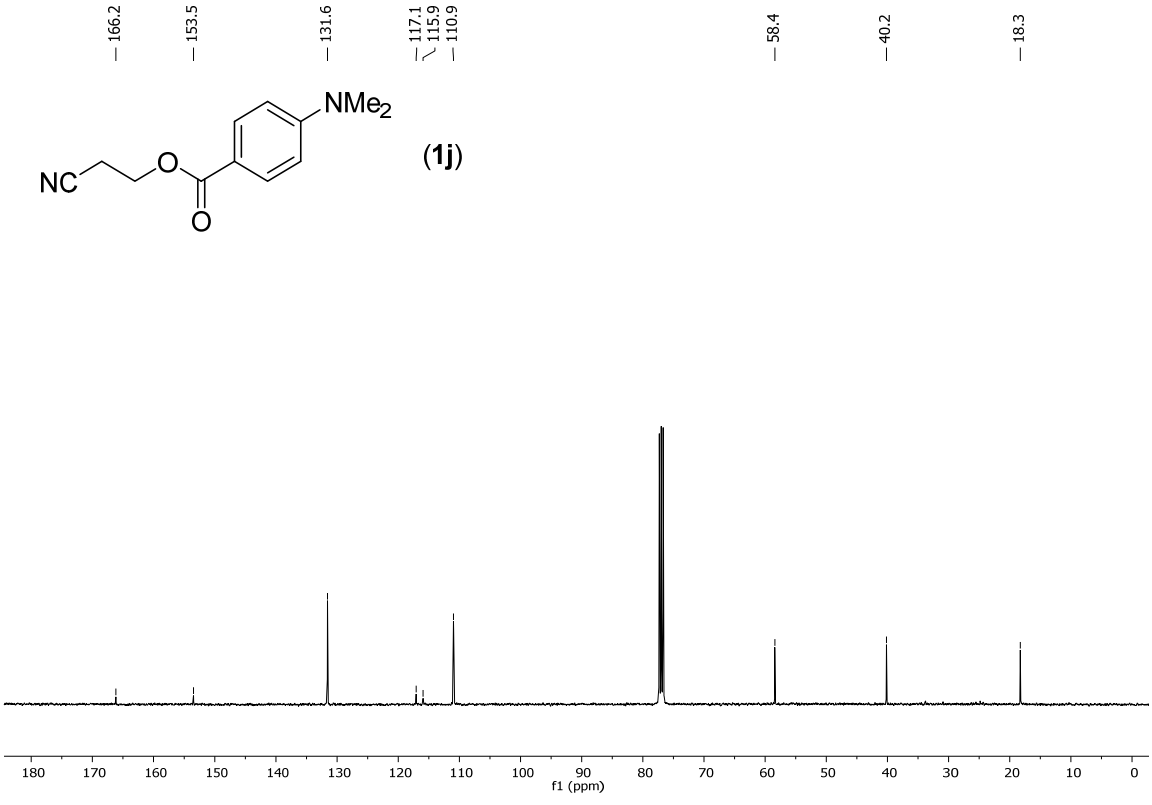
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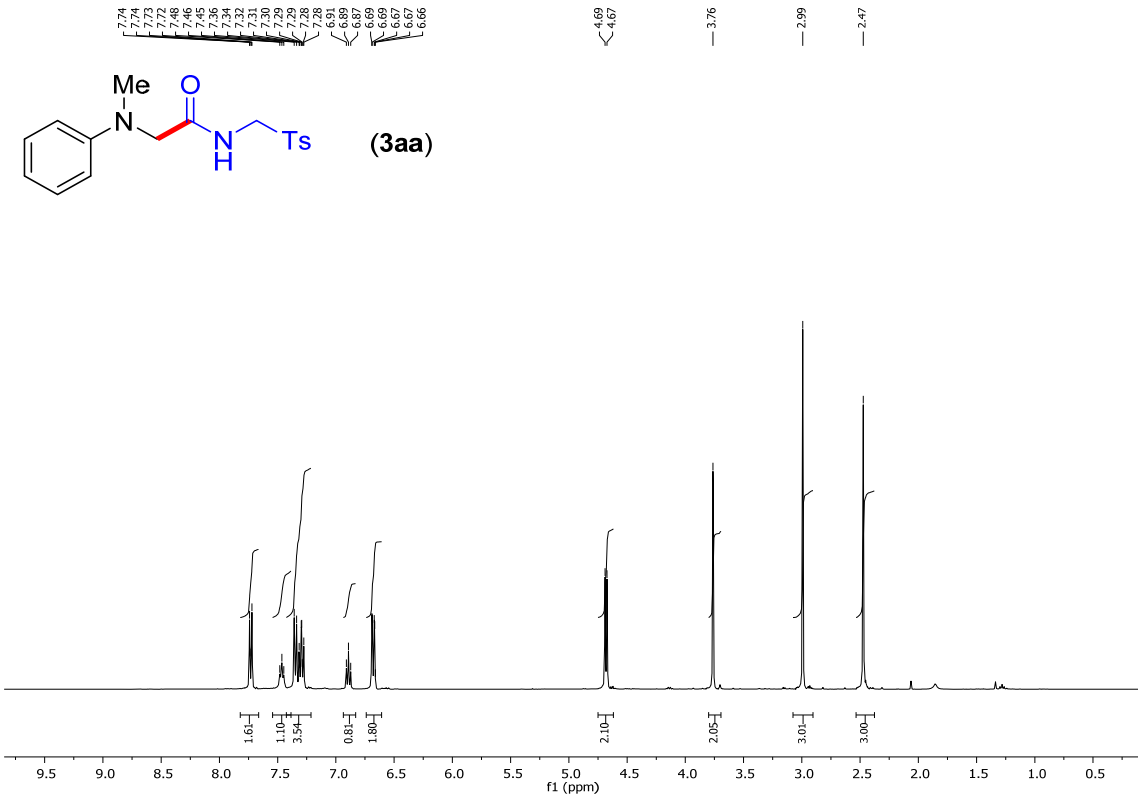
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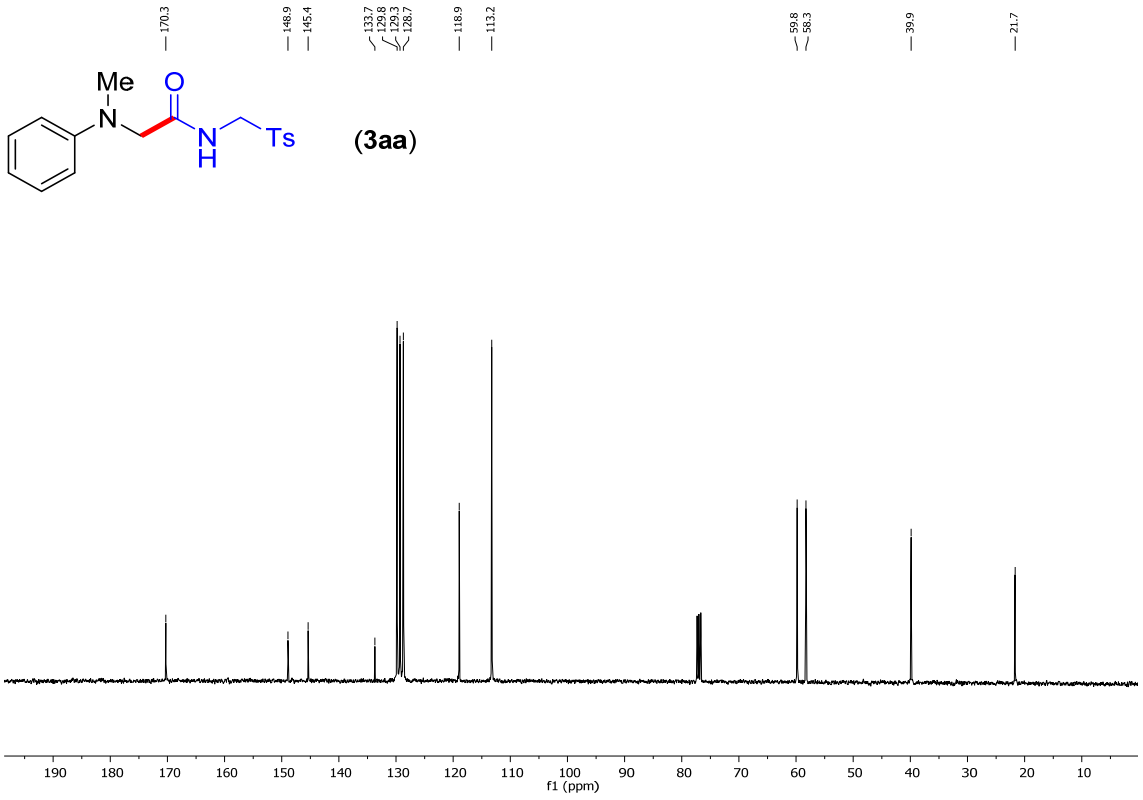
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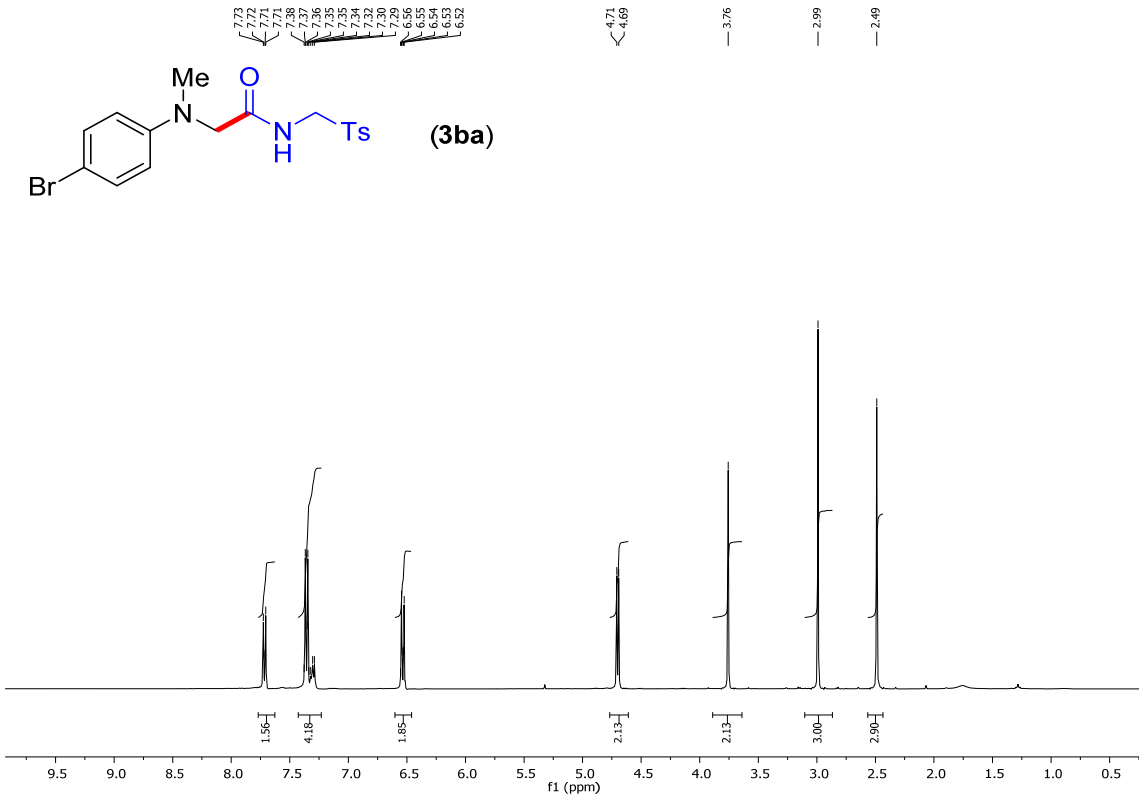
f1 (ppm)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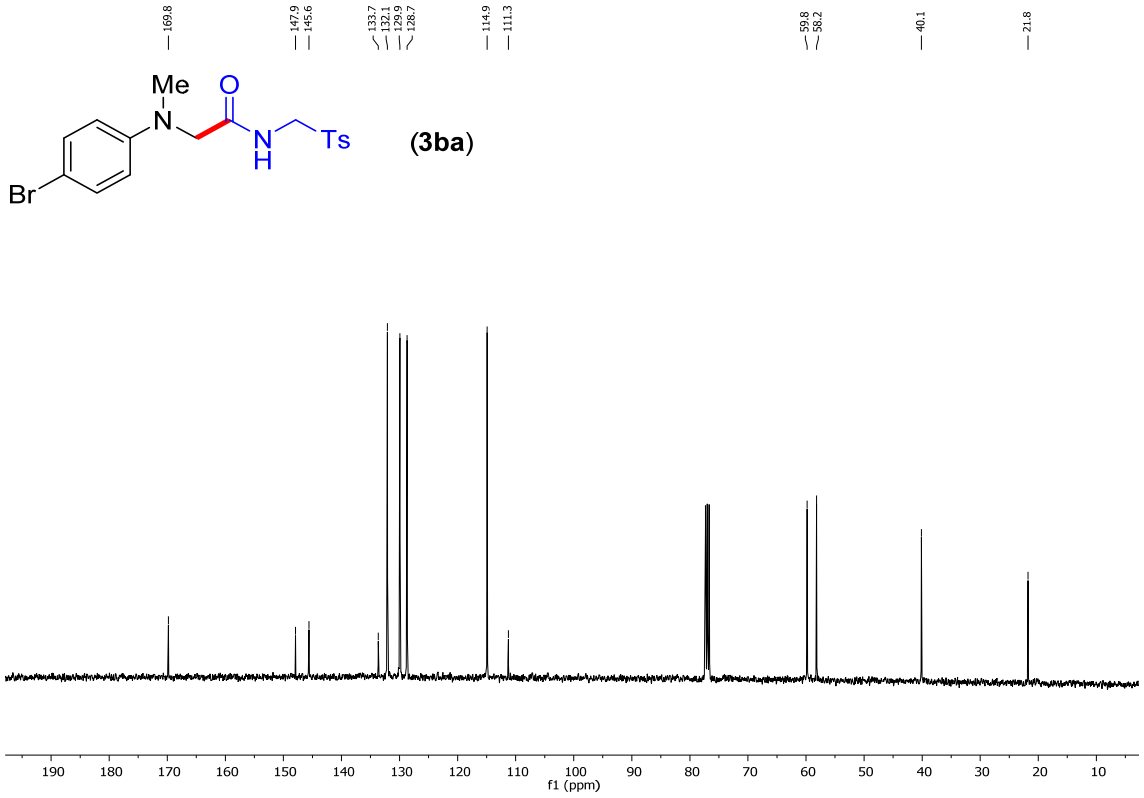
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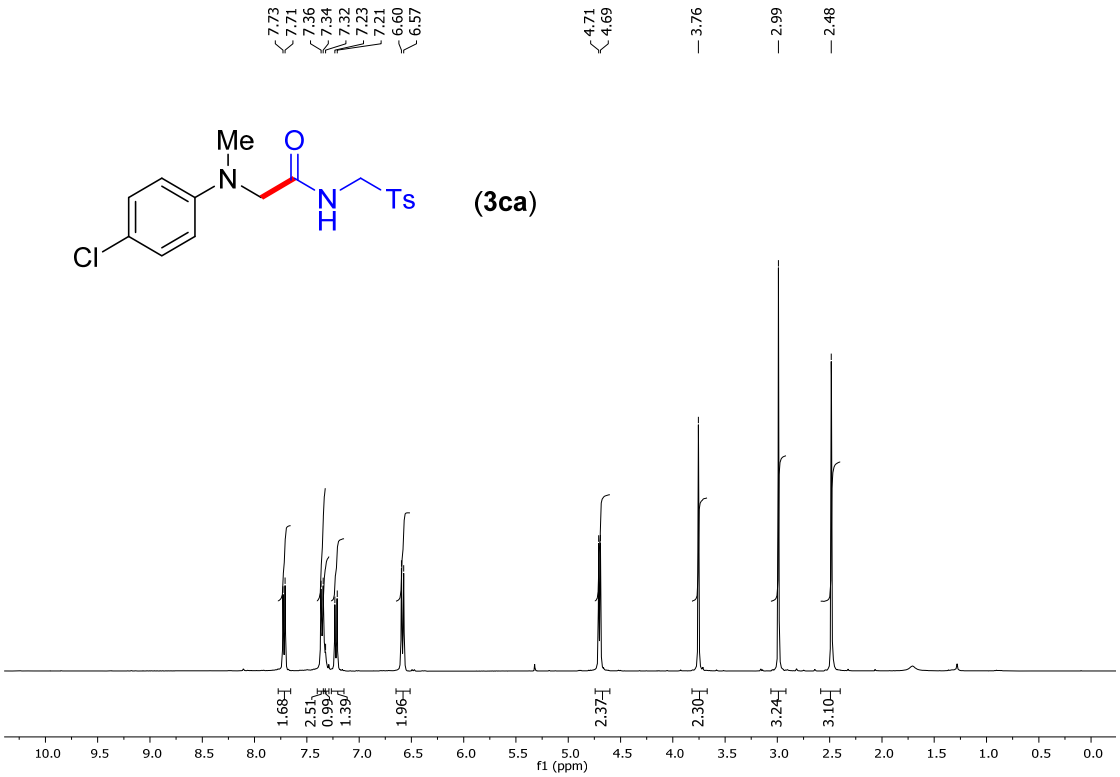
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2.30
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3.10
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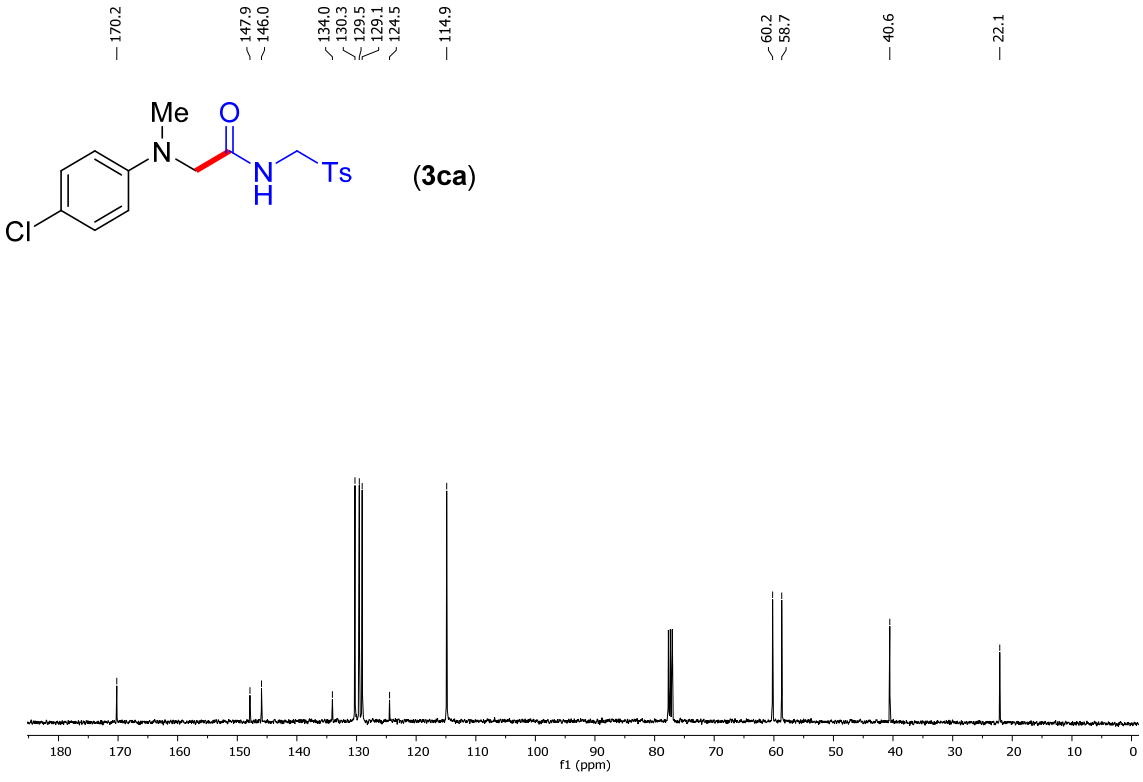
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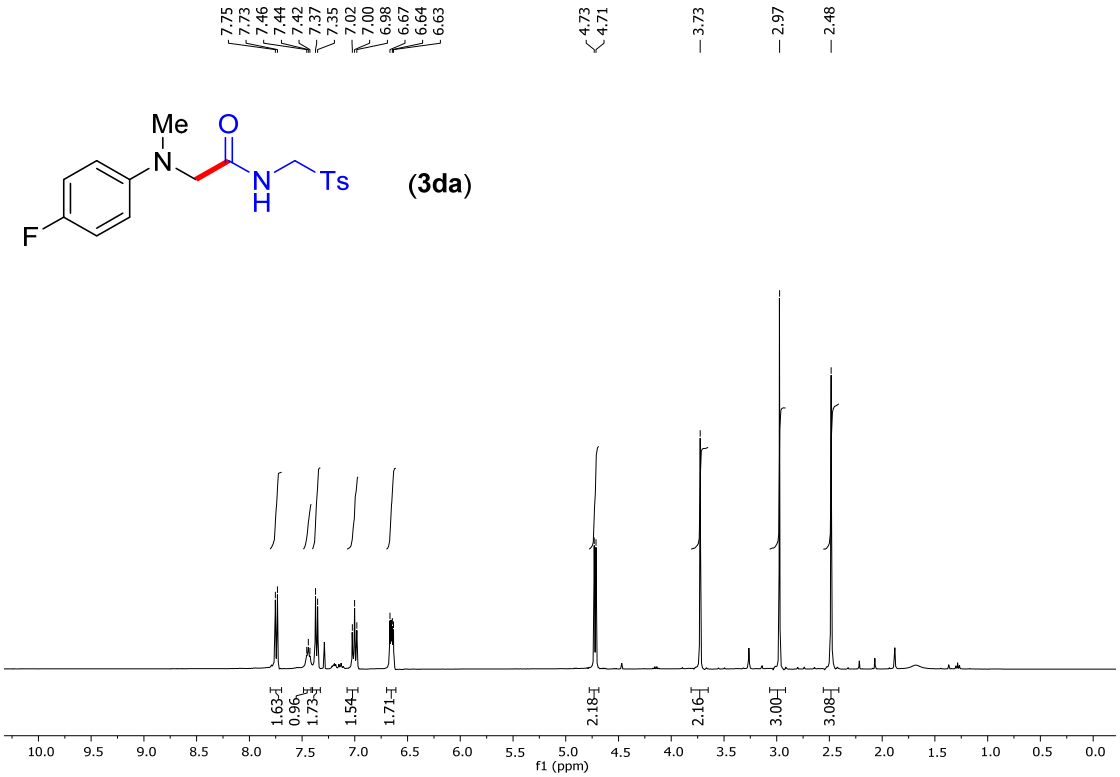
O
N
N
H
Ts
Cl
(3ca)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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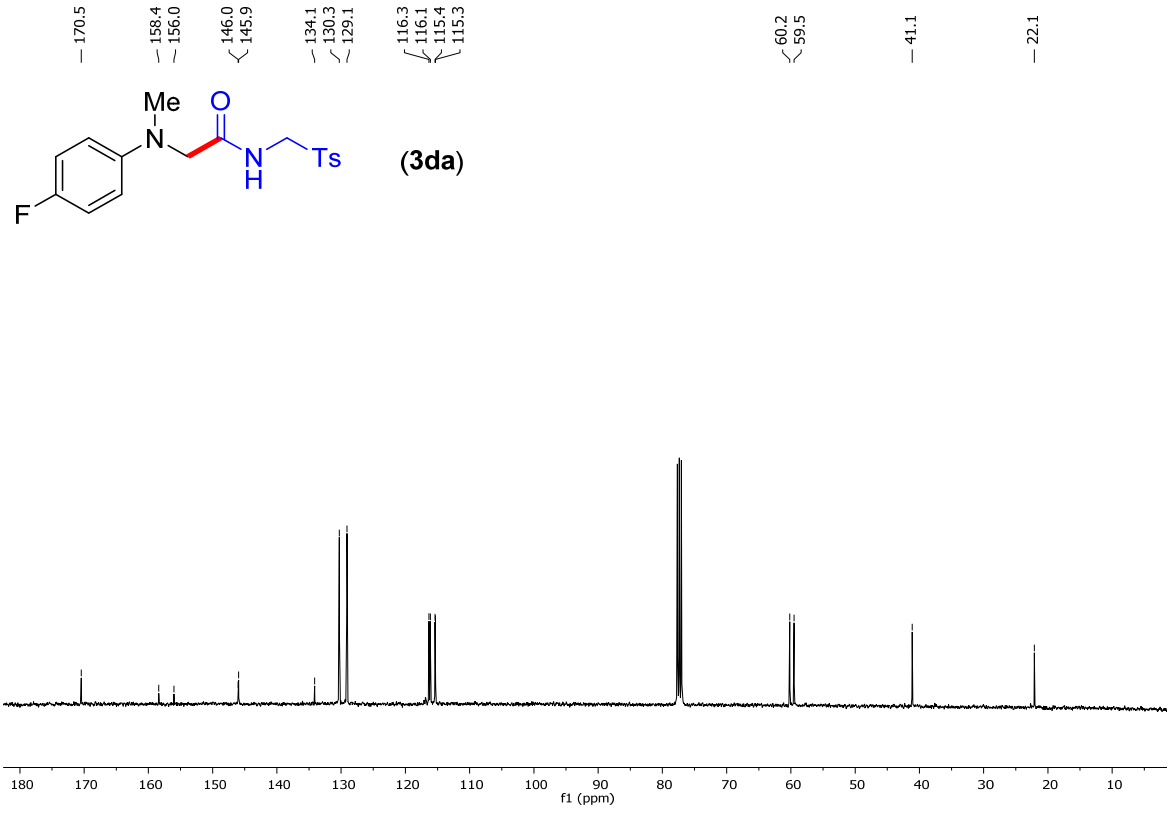
7.73
7.46
7.44
7.42
7.37
7.35
7.02
7.00
6.98
6.67
6.64
6.63
4.73
4.71
3.73
2.97
2.48
Me
O
N
N
H
Ts
F
(3da)
1.63
0.96
1.73
1.54
1.71
2.18
2.16
3.00
3.08
f1 (ppm)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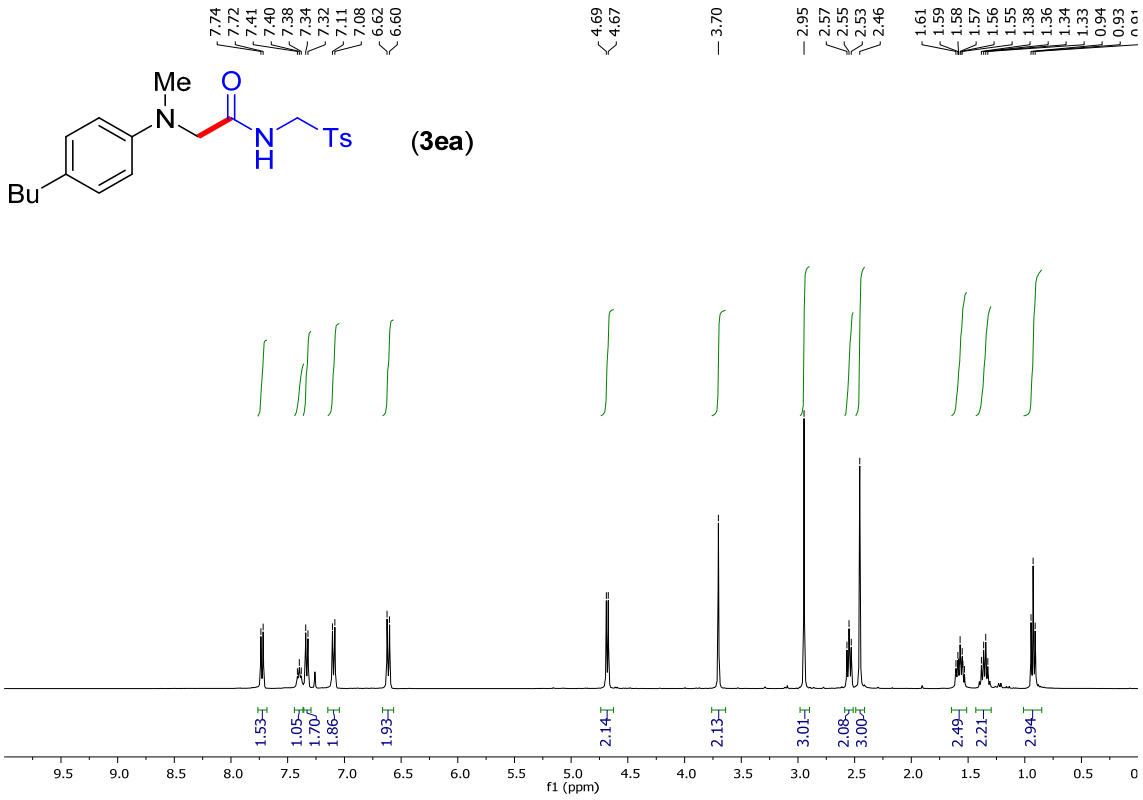
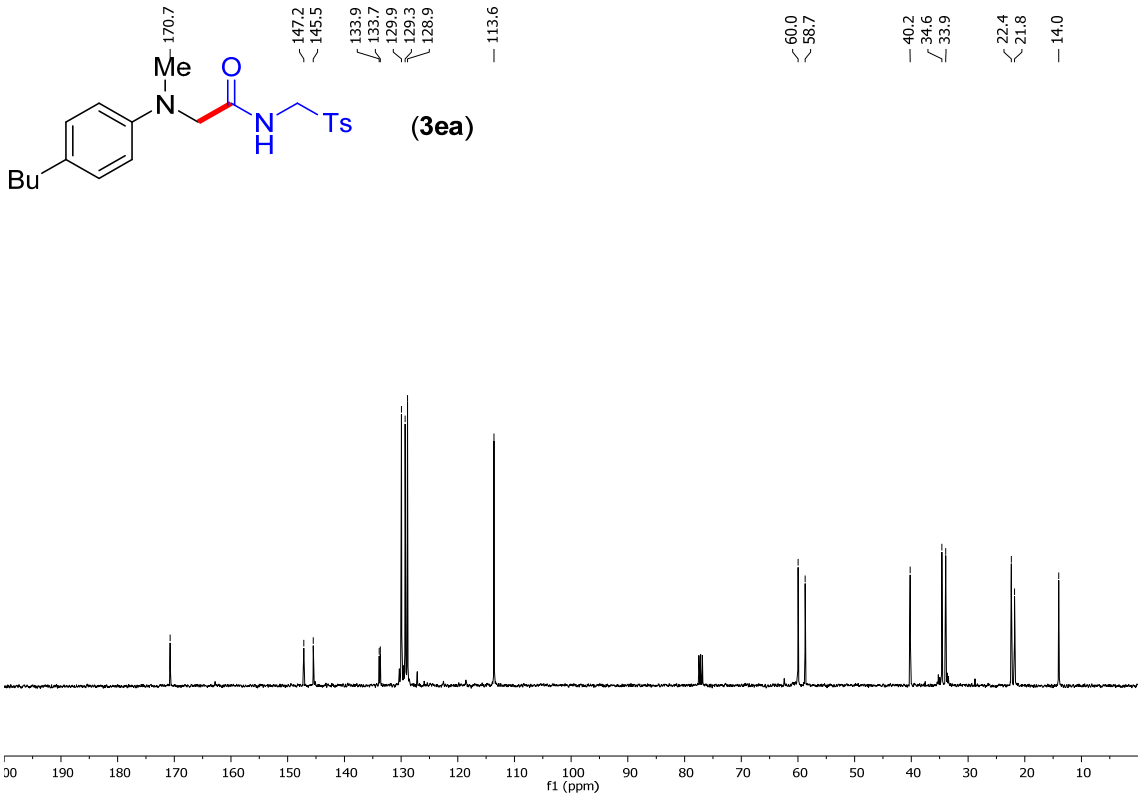
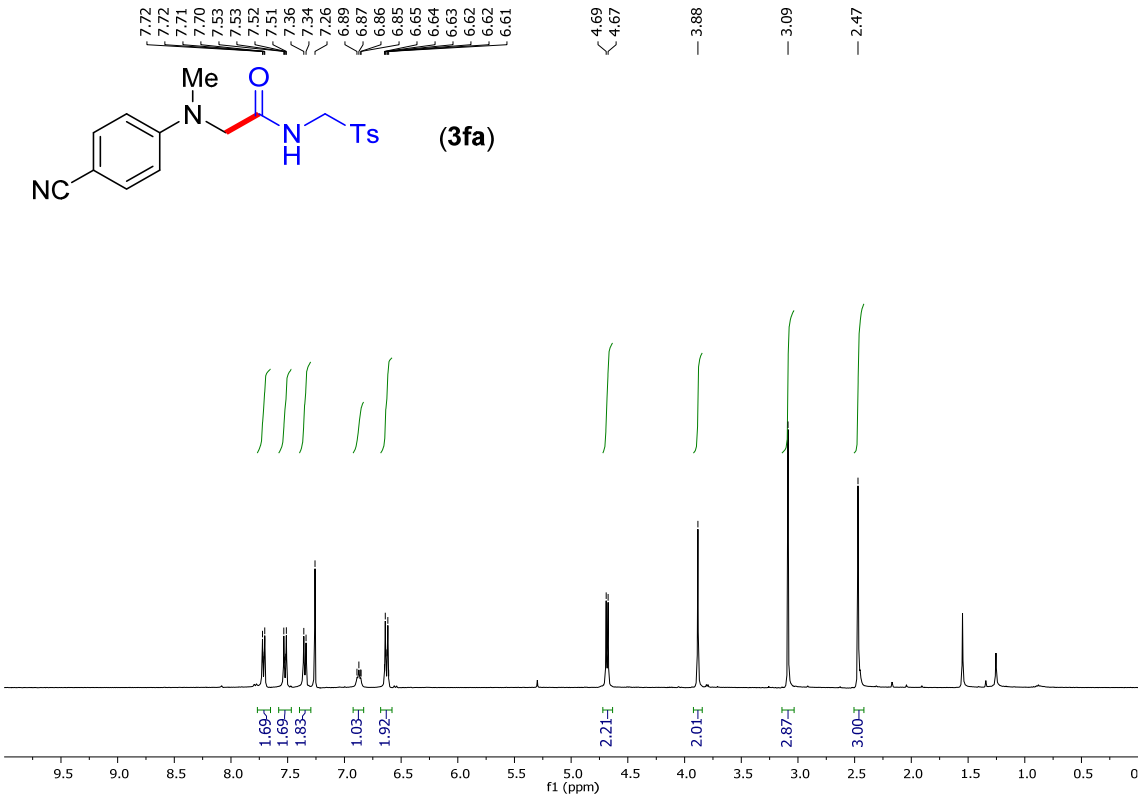
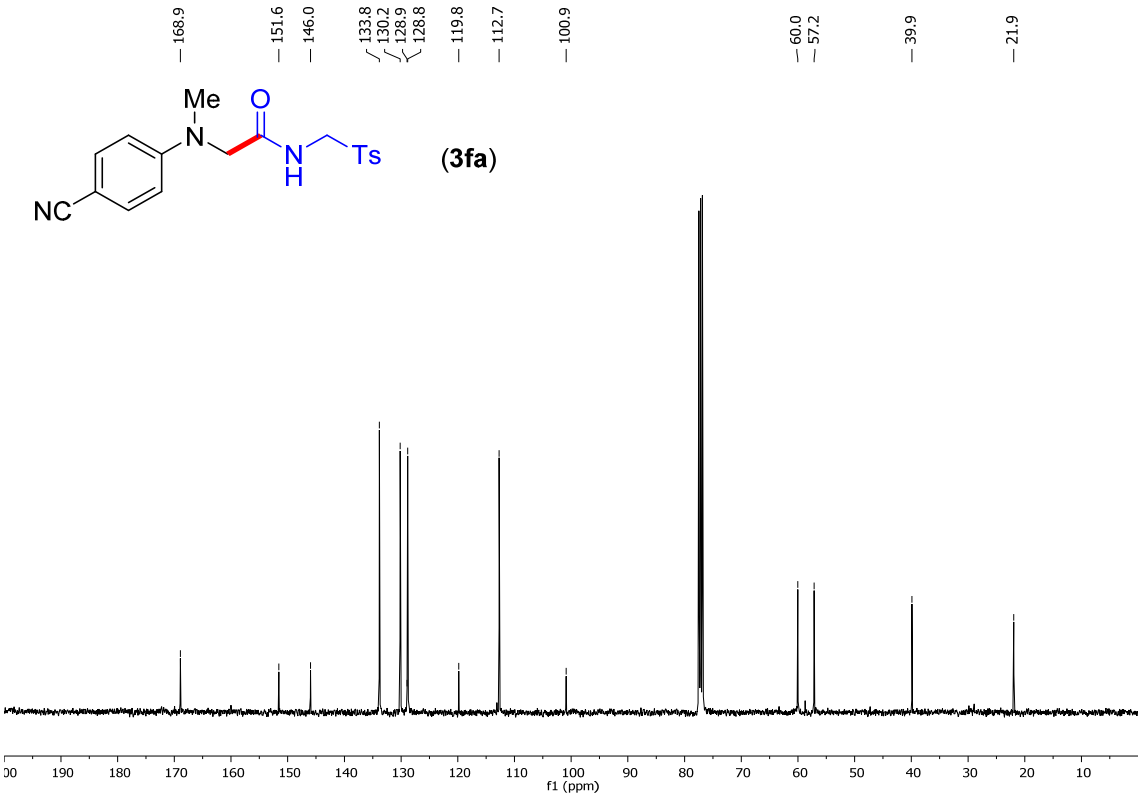
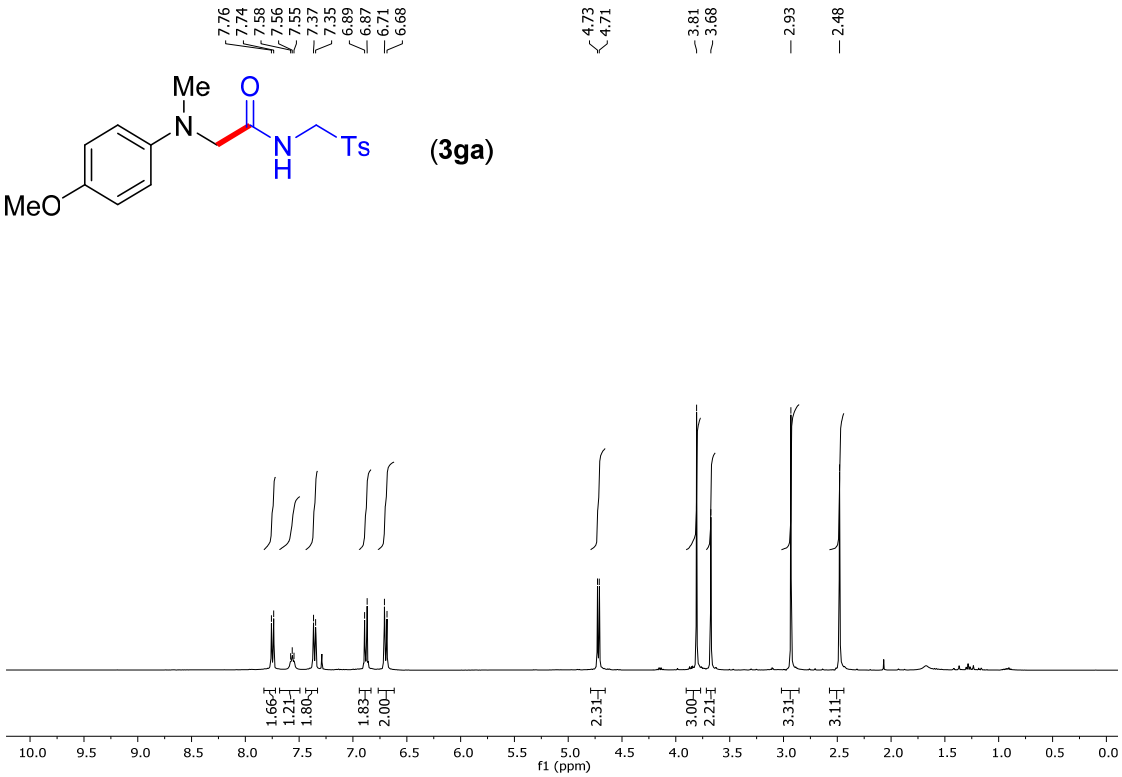
158.4
156.0
146.0
145.9
134.1
130.3
129.1
116.3
116.1
115.4
115.3
60.2
59.5
41.1
22.1
Me
O
N
N
H
Ts
F
(3da)
f1 (ppm)

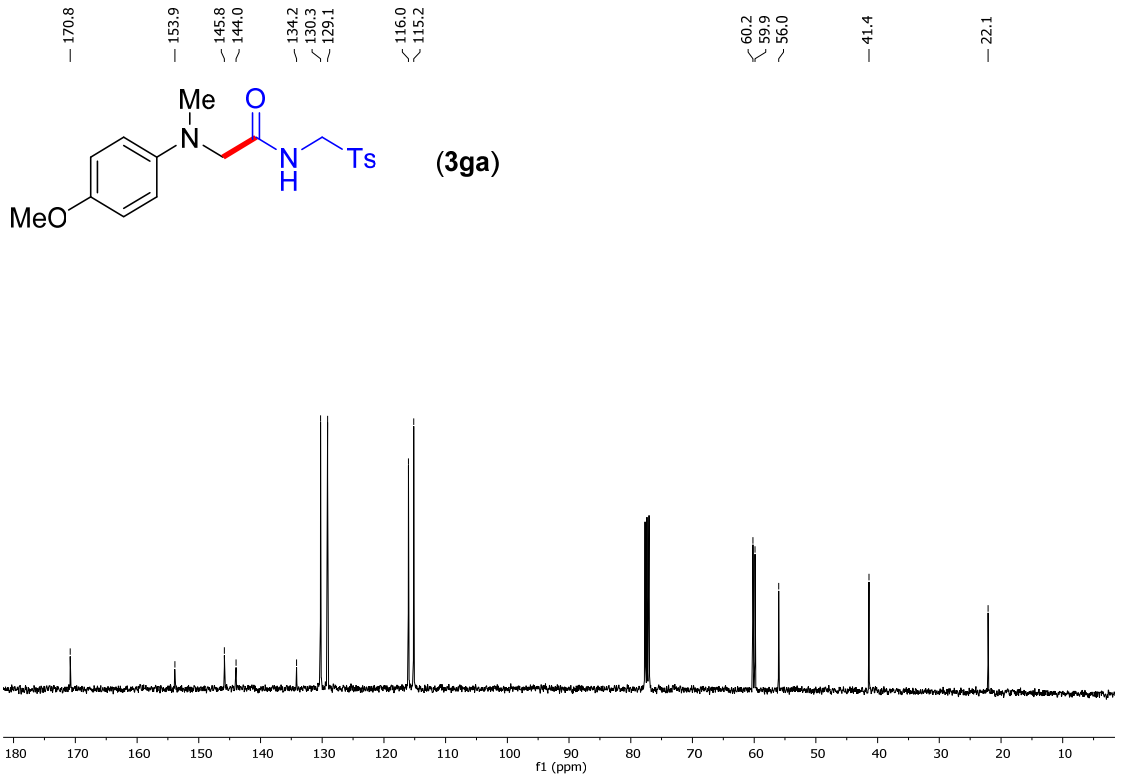

7.74
7.72
7.41
7.40
7.38
7.34
7.32
7.11
7.08
6.62
6.60
4.69
4.67
3.70
2.95
2.57
2.55
2.53
2.46
1.61
1.59
1.58
1.57
1.56
1.55
1.38
1.36
1.34
1.33
0.94
0.93
Me
O
N
N
H
Ts
Bu
(3ea)
1.53
1.05
1.70
1.86
1.93
2.14
2.13
3.01
2.08
3.00
2.49
2.21
2.94
f1 (ppm)

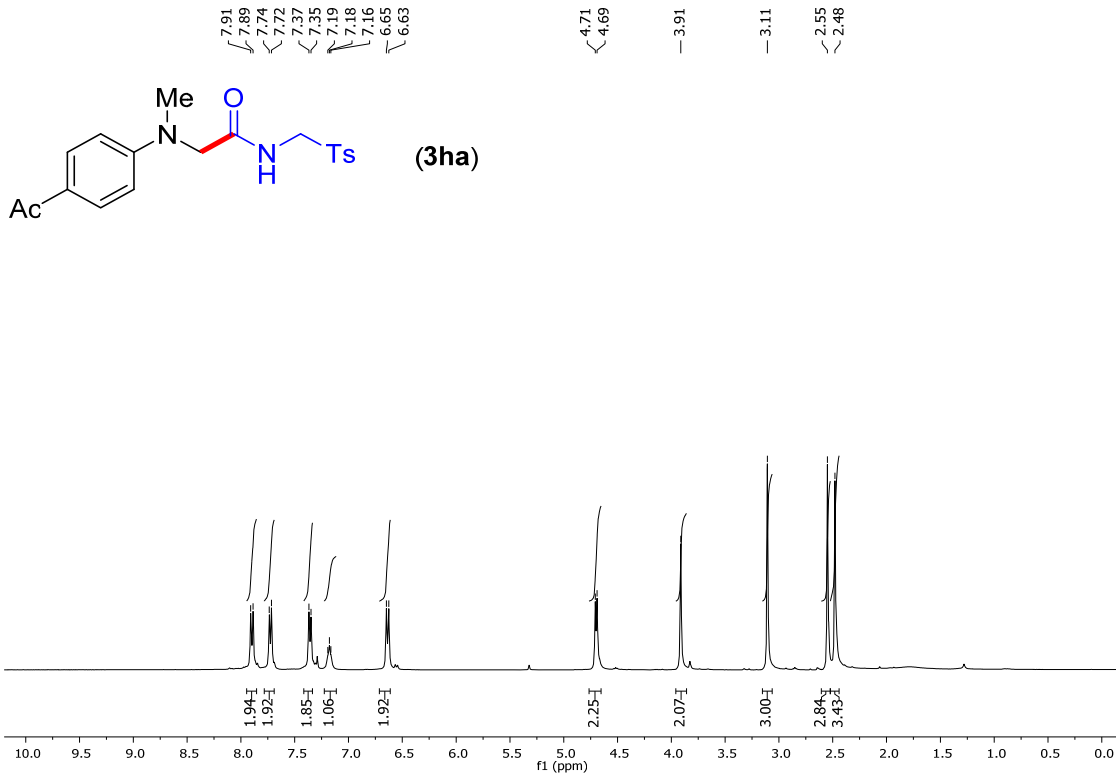

170.7
147.2
145.5
133.9
133.7
129.9
129.3
128.9
113.6
60.0
58.7
40.2
34.6
33.9
22.4
21.8
14.0
Me
O
N
N
H
Ts
Bu
(3ea)
f1 (ppm)

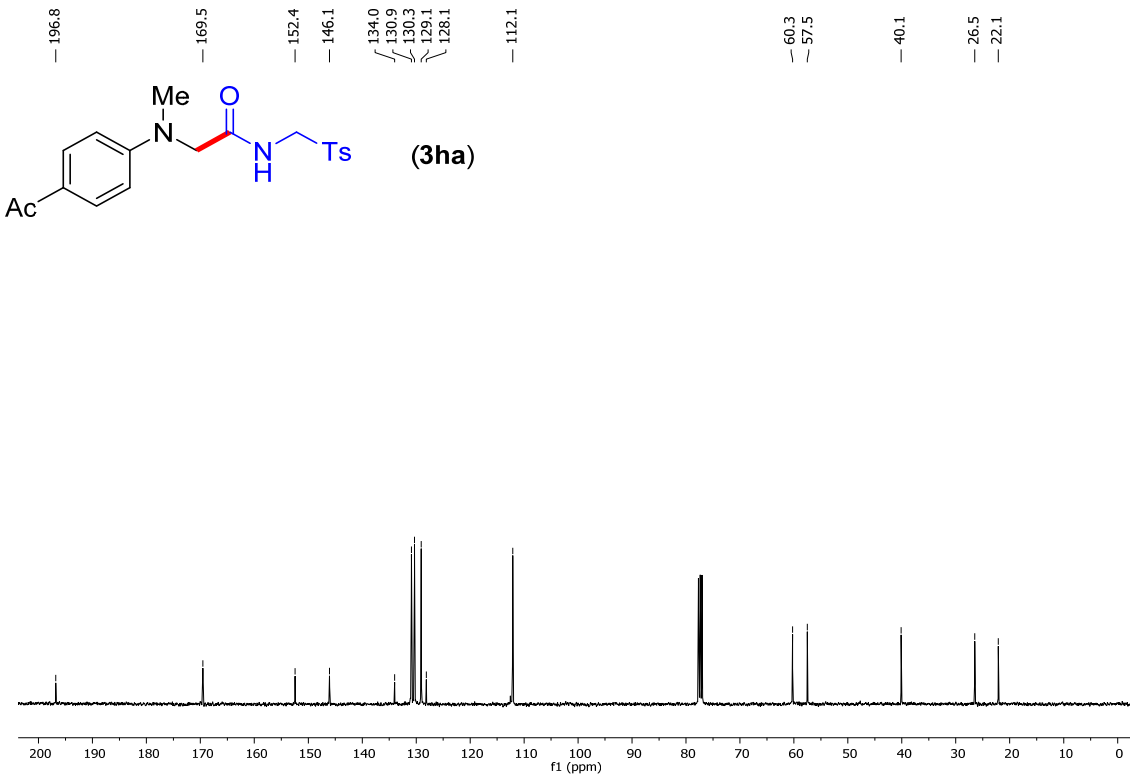

7.72
7.72
7.71
7.70
7.53
7.53
7.52
7.51
7.36
7.34
7.26
6.89
6.87
6.86
6.85
6.65
6.64
6.63
6.62
6.62
6.61
4.69
4.67
3.88
3.09
2.47
Me
O
N
N
H
Ts
NC
(3fa)
1.69
1.69
1.83
1.03
1.92
2.21
2.01
2.87
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

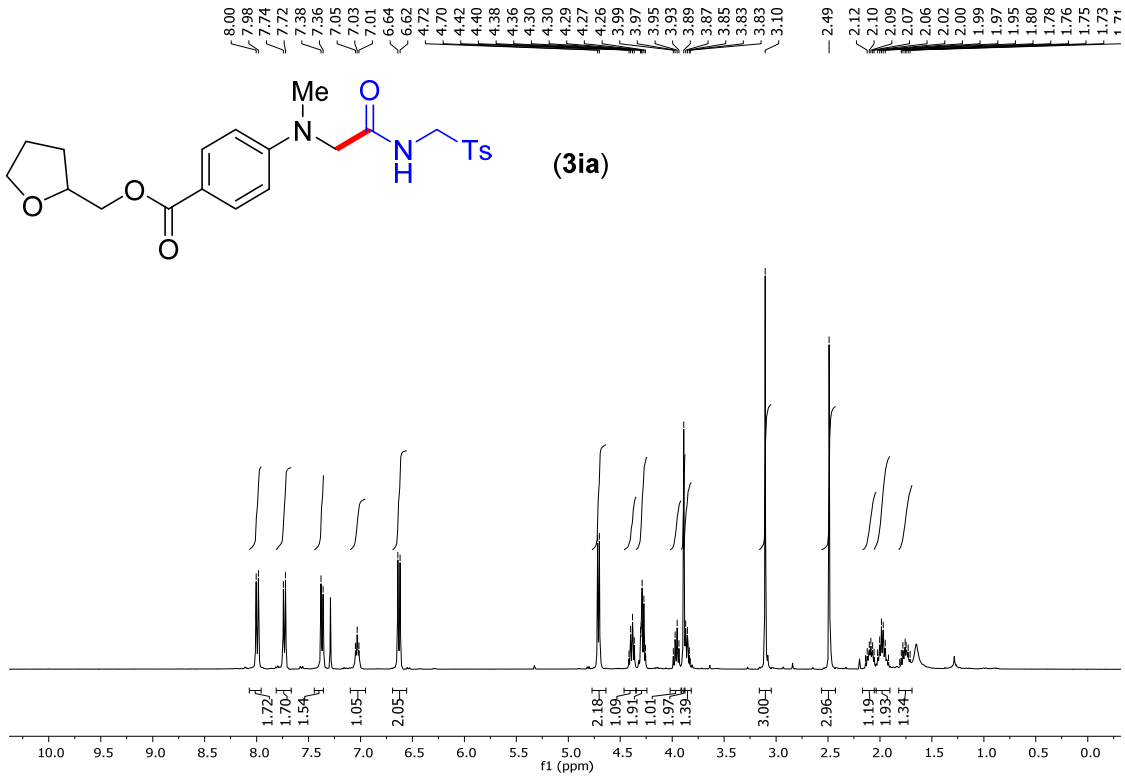

168.9
151.6
146.0
133.8
130.2
128.9
128.8
119.8
112.7
100.9
60.0
57.2
39.9
21.9
Me
O
N
N
H
Ts
NC
(3fa)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

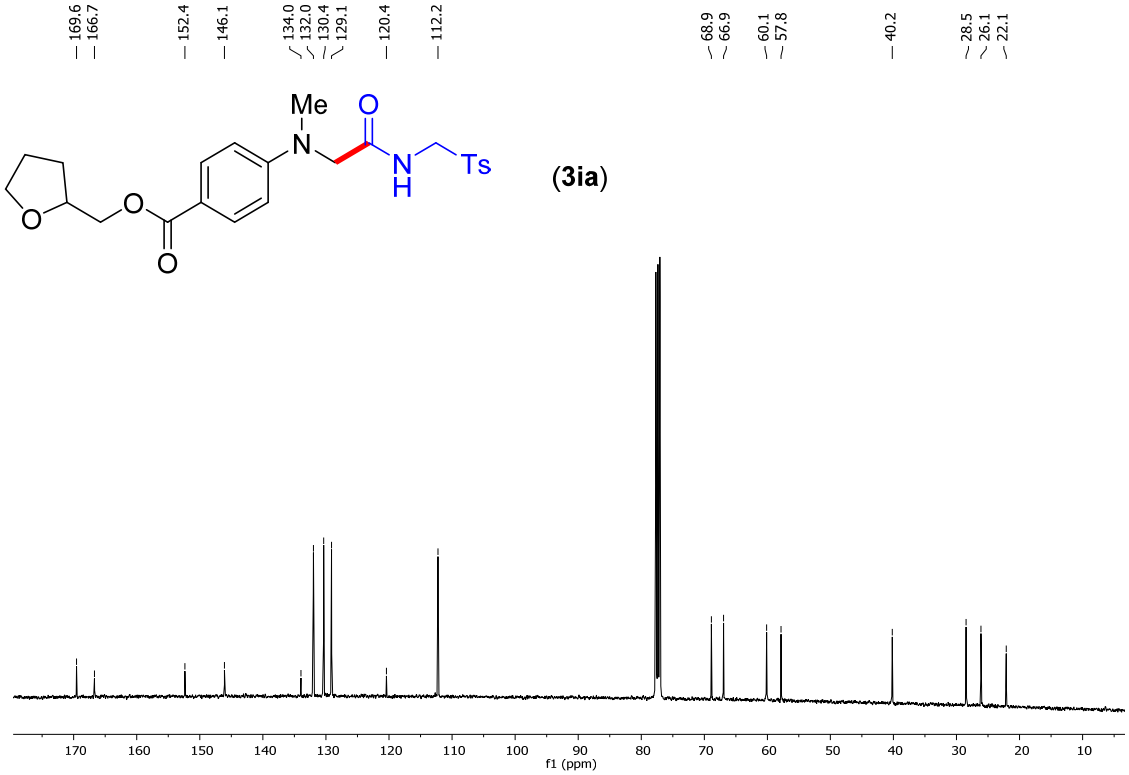

7.76
7.74
7.58
7.56
7.55
7.37
7.35
6.89
6.87
6.71
6.68
4.73
4.71
3.81
3.68
2.93
2.48
Me
O
N
N
H
Ts
MeO
(3ga)
1.66
1.21
1.80
1.83
2.00
2.31
3.00
2.21
3.31
3.11
f1 (ppm)

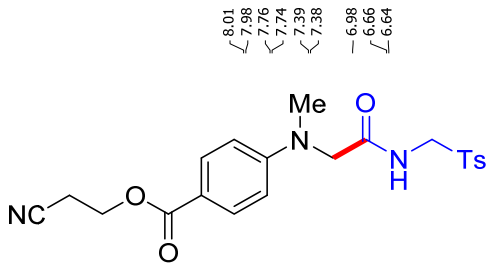

170.8
153.9
145.8
144.0
134.2
130.3
129.1
116.0
115.2
60.2
59.9
56.0
41.4
22.1
Me
O
N
N
H
Ts
MeO
(3ga)
f1 (ppm)


7.91
7.89
7.74
7.72
7.37
7.35
7.19
7.18
7.16
6.65
6.63
4.71
4.69
3.91
3.11
2.55
2.48
Me
O
N
N
H
Ts
Ac
(3ha)
1.94
1.92
1.85
1.06
1.92
2.25
2.07
3.00
2.84
3.43
f1 (ppm)


196.8
169.5
152.4
146.1
134.0
130.9
130.3
129.1
128.1
112.1
60.3
57.5
40.1
26.5
22.1
Me
O
N
N
H
Ts
Ac
(3ha)
f1 (ppm)

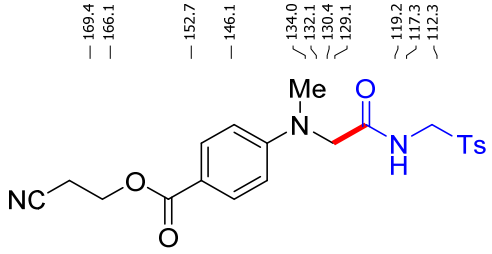

8.00 7.98 7.74 7.72 7.38 7.36 7.05 7.03 7.01 6.64 6.62 4.72 4.70 4.42 4.40 4.38 4.36 4.30 4.30 4.29 4.27 4.26 3.99 3.97 3.95 3.93 3.89 3.87 3.85 3.83 3.83 3.10 2.49 2.12 2.10 2.09 2.07 2.06 2.02 2.00 1.99 1.97 1.95 1.80 1.78 1.76 1.75 1.73
Me
N
O
N
H
Ts
O
O
O
(3ia)
1.72 1.70 1.54 1.05 2.05 2.18 1.09 1.91 1.01 1.97 1.39 3.00 2.96 1.19 1.93 1.34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.6 166.7 152.4 146.1 134.0 132.0 130.4 129.1 120.4 112.2 68.9 66.9 60.1 57.8 40.2 28.5 26.1 22.1
Me
N
O
N
H
Ts
O
O
O
(3ia)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Me
O
N
N
H
Ts
NC
O
O

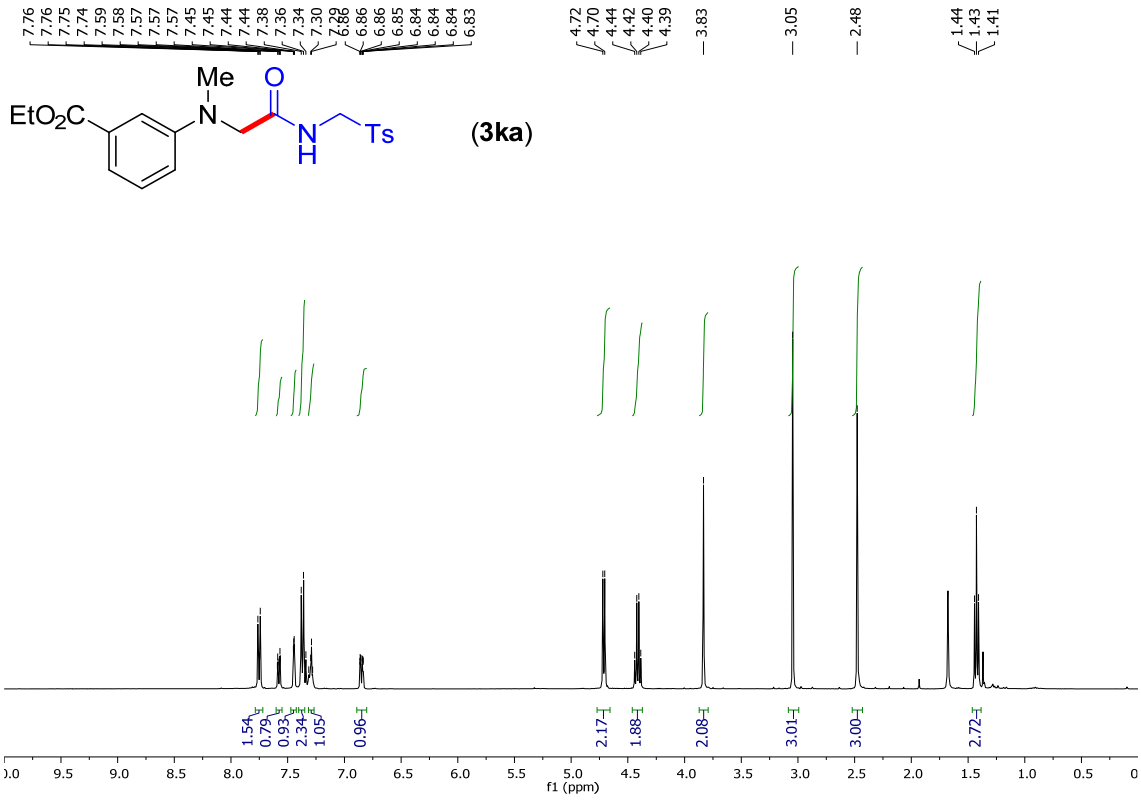
(3ja)

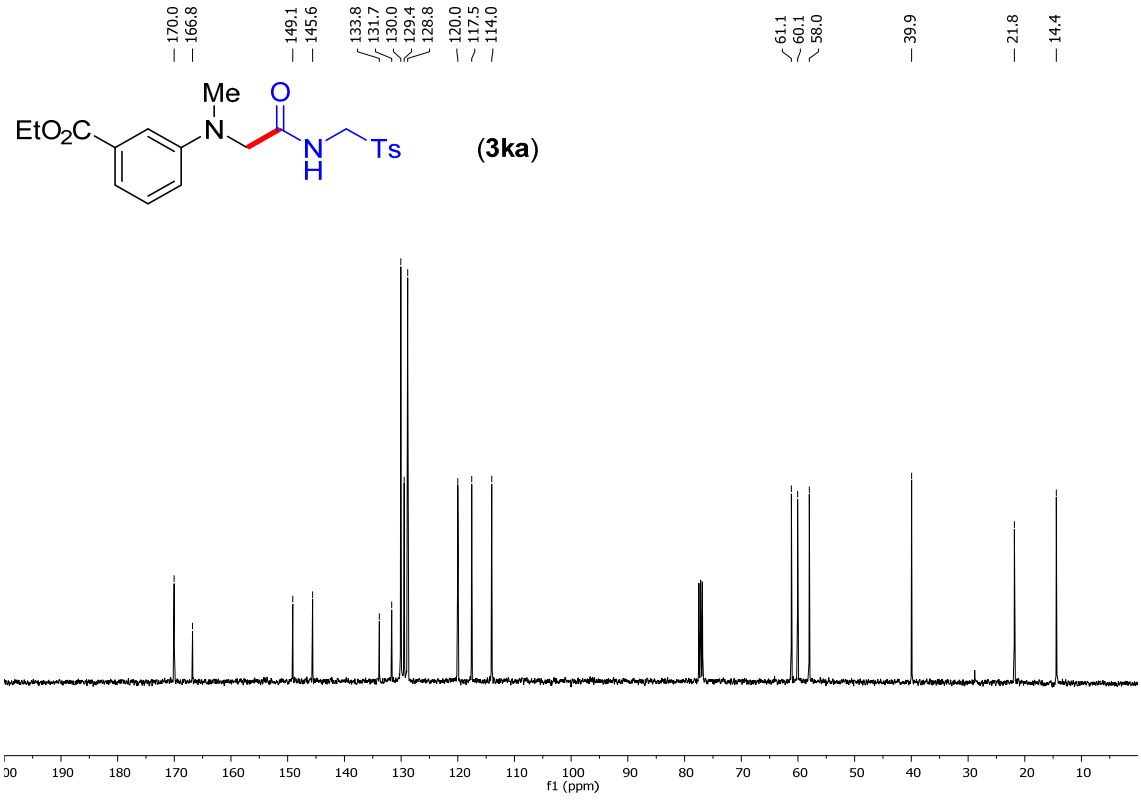
8.01
7.98
7.76
7.74
7.39
7.38
6.98
6.66
6.64
4.73
4.71
4.55
4.54
4.52
3.91
3.13
2.88
2.86
2.85
2.50
2.01
1.79
1.87
1.13
2.28
2.42
2.32
2.20
3.00
2.36
3.19
f1 (ppm)

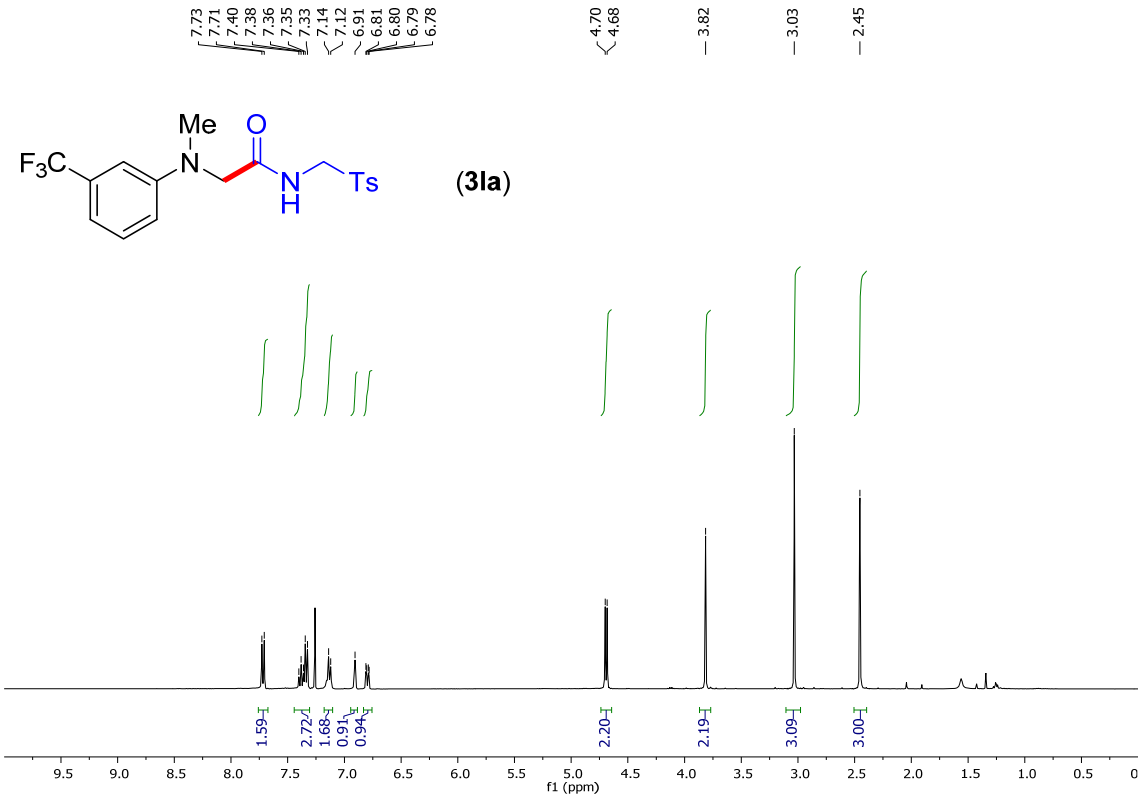

Me
O
N
N
H
Ts
NC
O
O

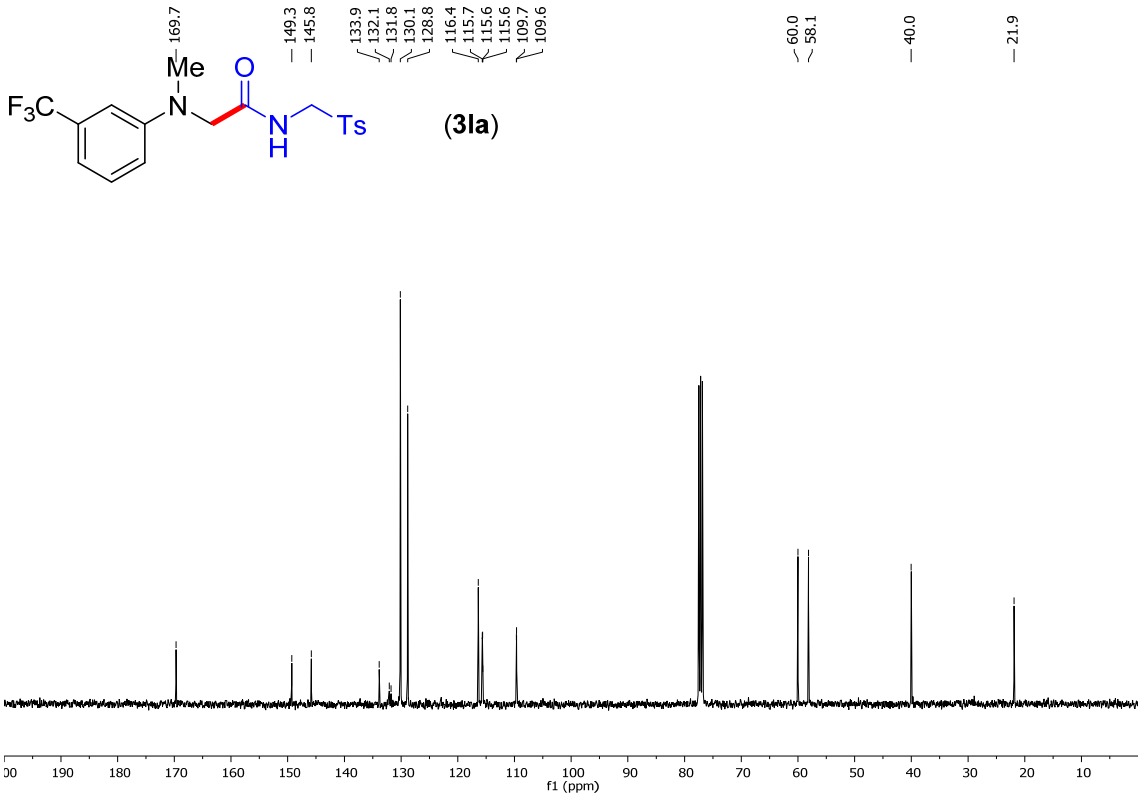
(3ja)

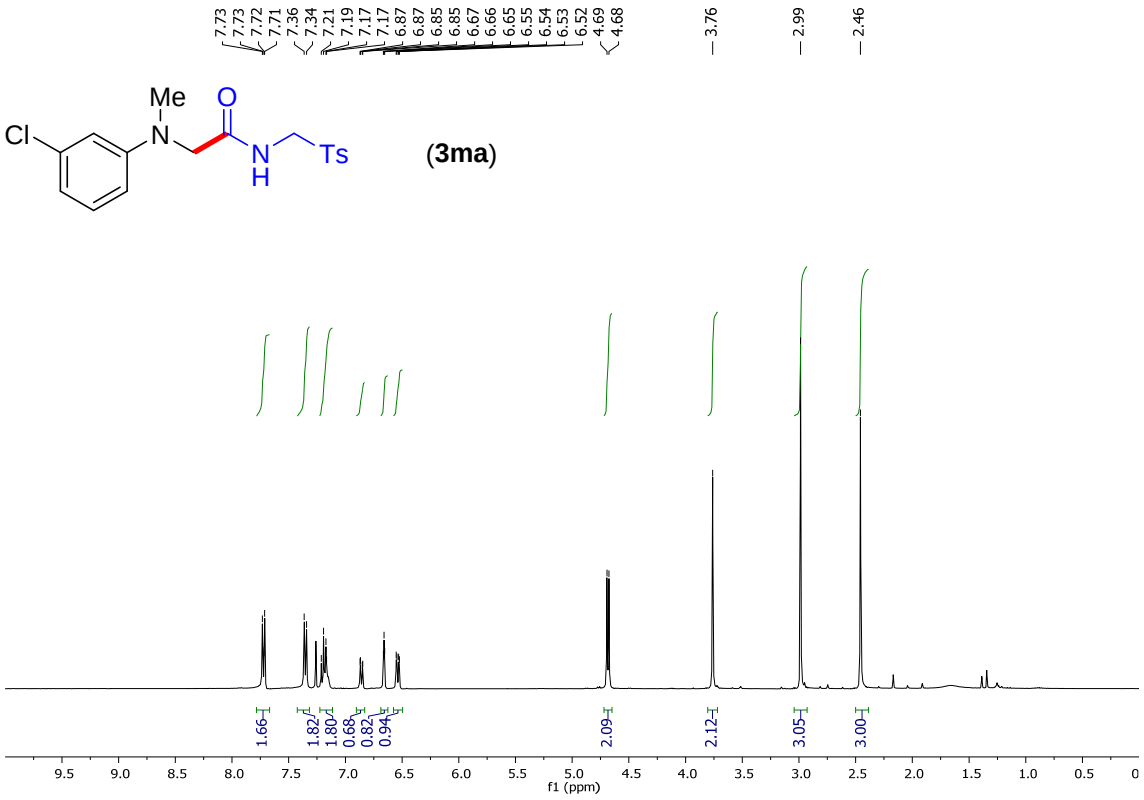
169.4
166.1
152.7
146.1
134.0
132.1
130.4
129.1
119.2
117.3
112.3
60.1
59.1
57.7
40.2
22.1
18.6
f1 (ppm)

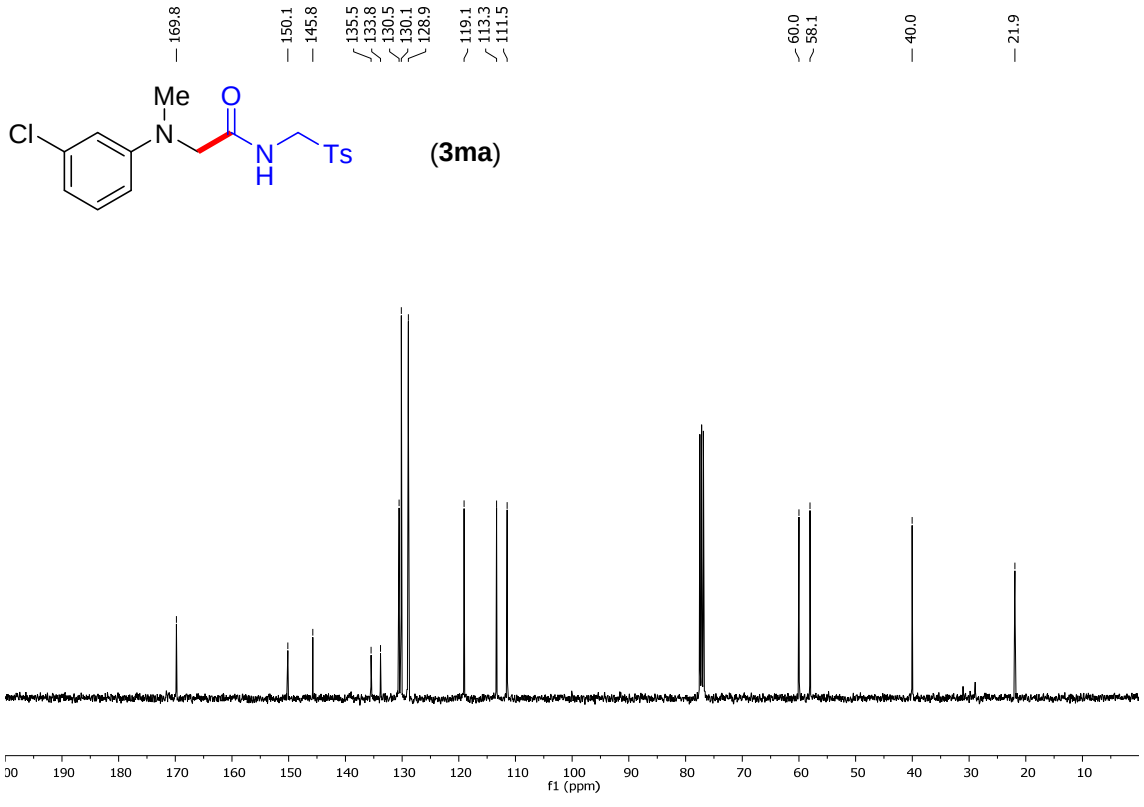

7.76
7.76
7.75
7.74
7.59
7.58
7.57
7.57
7.57
7.45
7.45
7.44
7.44
7.38
7.36
7.34
7.30
7.29
6.86
6.86
6.85
6.84
6.84
6.84
6.83
4.72
4.70
4.44
4.42
4.40
4.39
3.83
3.05
2.48
1.44
1.43
1.41
Me
O
EtO2C
N
N
H
Ts
(3ka)
1.54
0.79
0.93
2.34
1.05
0.96
2.17
1.88
2.08
3.01
3.00
2.72
f1 (ppm)

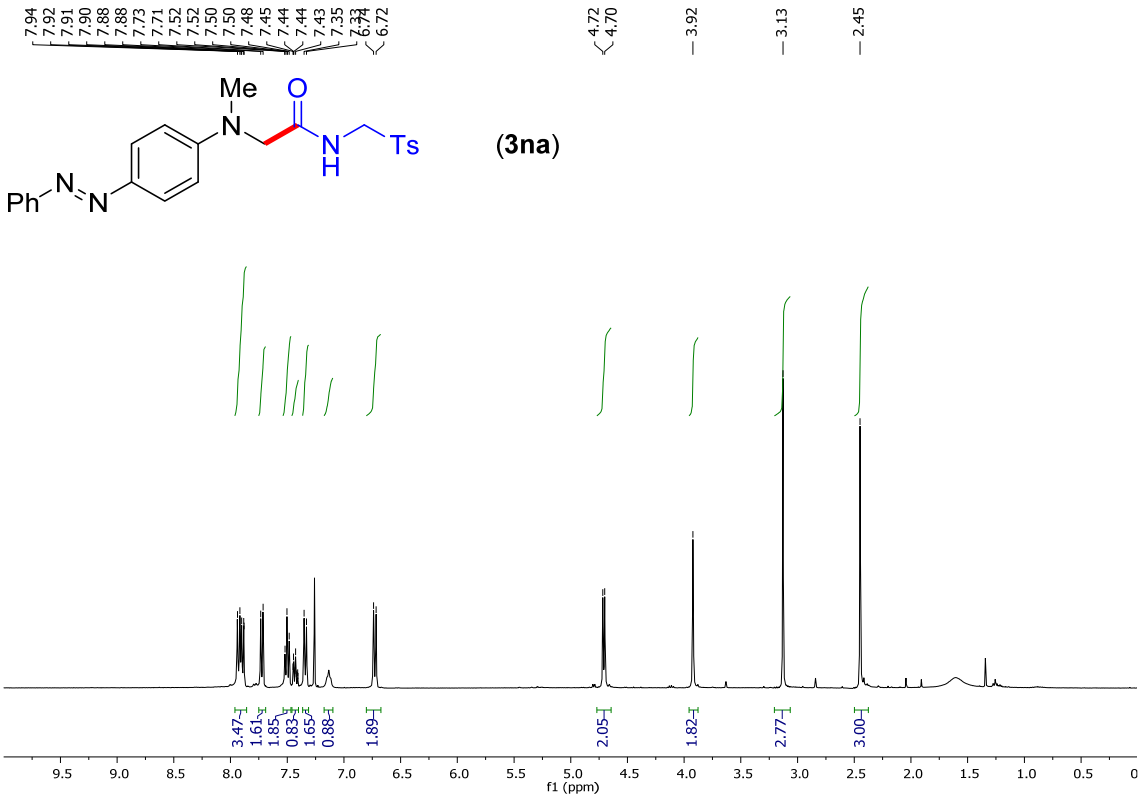

170.0
166.8
149.1
145.6
133.8
131.7
130.0
129.4
128.8
120.0
117.5
114.0
61.1
60.1
58.0
39.9
21.8
14.4
Me
O
EtO2C
N
N
H
Ts
(3ka)
f1 (ppm)

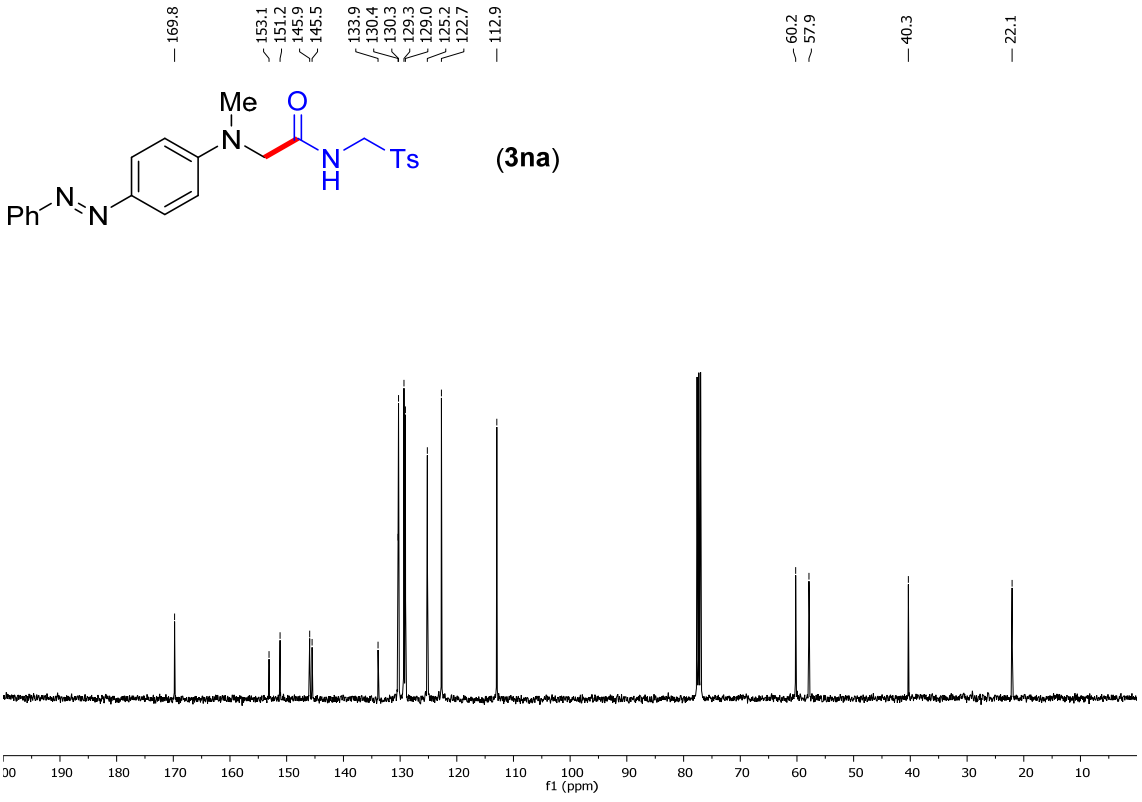

7.73
7.71
7.40
7.38
7.36
7.35
7.33
7.14
7.12
6.91
6.81
6.80
6.79
6.78
4.70
4.68
3.82
3.03
2.45
Me
O
F3C
N
N
H
Ts
(3la)
1.59
2.72
1.68
0.91
0.94
2.20
2.19
3.09
3.00
f1 (ppm)

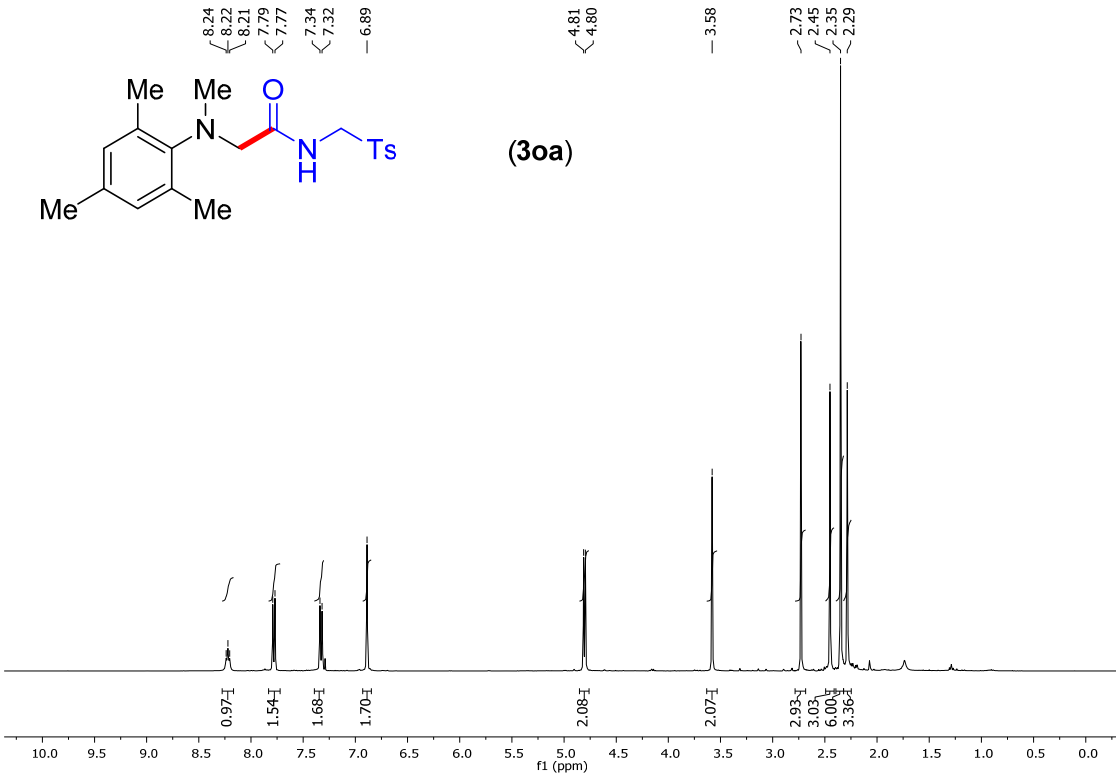

169.7
149.3
145.8
133.9
132.1
131.8
130.1
128.8
116.4
115.7
115.6
115.6
109.7
109.6
60.0
58.1
40.0
21.9
Me
O
F3C
N
N
H
Ts
(3la)
f1 (ppm)

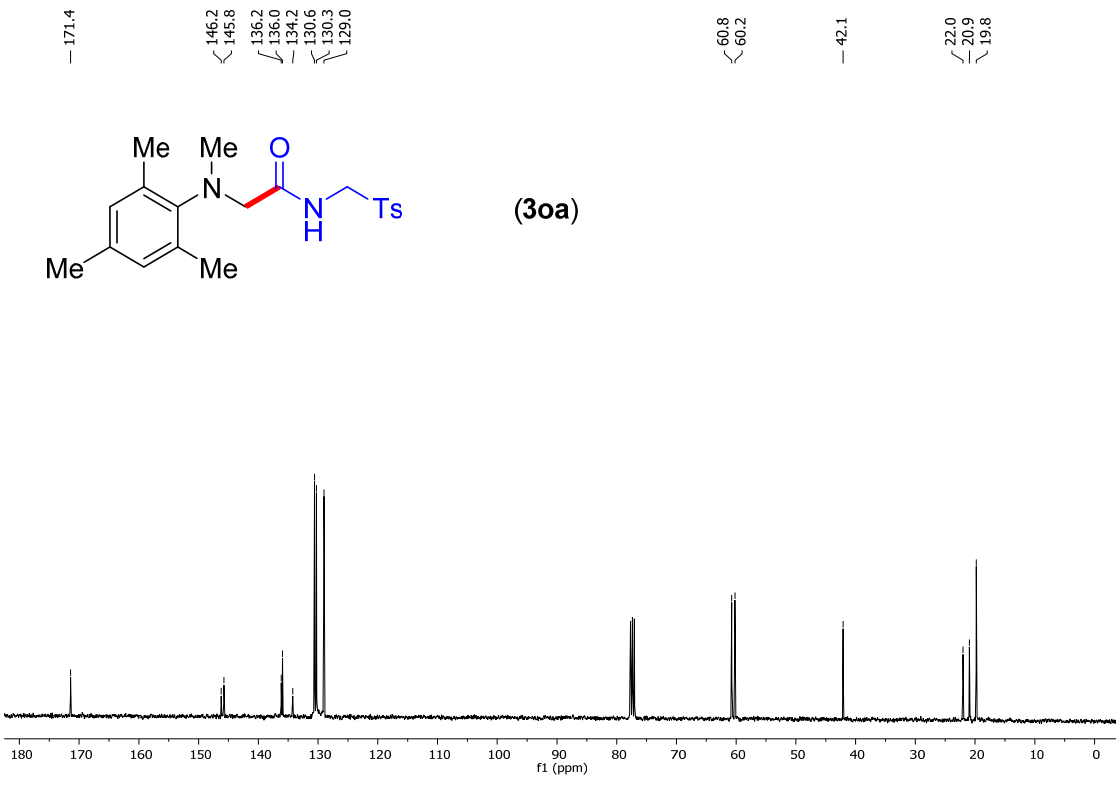

7.73
7.73
7.72
7.71
7.36
7.34
7.21
7.19
7.17
7.17
6.87
6.87
6.85
6.85
6.67
6.66
6.65
6.55
6.54
6.53
6.52
4.69
4.68
3.76
2.99
2.46
Me
O
Cl
N
N
H
Ts
(3ma)
1.66
1.82
1.80
0.68
0.82
0.94
2.09
2.12
3.05
3.00
f1 (ppm)

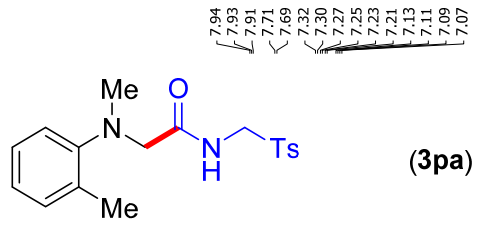

169.8
150.1
145.8
135.5
133.8
130.5
130.1
128.9
119.1
113.3
111.5
60.0
58.1
40.0
21.9
Me
O
Cl
N
N
H
Ts
(3ma)
f1 (ppm)


7.94
7.92
7.91
7.90
7.88
7.88
7.73
7.71
7.52
7.52
7.50
7.50
7.48
7.45
7.44
7.44
7.43
7.35
7.33
7.33
6.72
4.72
4.70
3.92
3.13
2.45
Me
O
N
N
H
Ts
Ph
N
N
(3na)
3.47
1.61
1.85
0.83
1.65
0.88
1.89
2.05
1.82
2.77
3.00
f1 (ppm)


169.8
153.1
151.2
145.9
145.5
133.9
130.4
130.3
129.3
129.0
125.2
122.7
112.9
60.2
57.9
40.3
22.1
Me
O
N
N
H
Ts
Ph
N
N
(3na)
f1 (ppm)

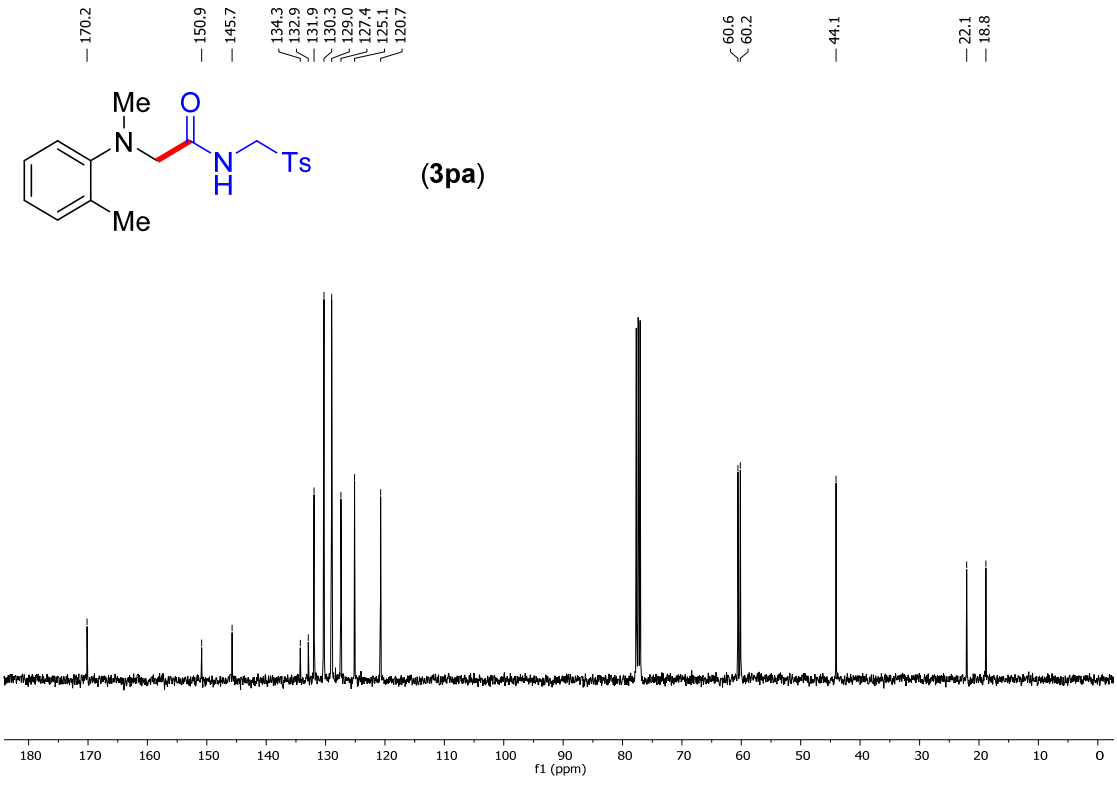

8.24
8.22
8.21
7.79
7.77
7.34
7.32
6.89
4.81
4.80
3.58
2.73
2.45
2.35
2.29
Me
Me
O
N
N
H
Ts
Me
Me
(3oa)
0.97
1.54
1.68
1.70
2.08
2.07
2.93
3.03
6.00
3.36
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.4
146.2
145.8
136.2
136.0
134.2
130.6
130.3
129.0
60.8
60.2
42.1
22.0
20.9
19.8
Me
Me
O
N
N
H
Ts
Me
Me
(3oa)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

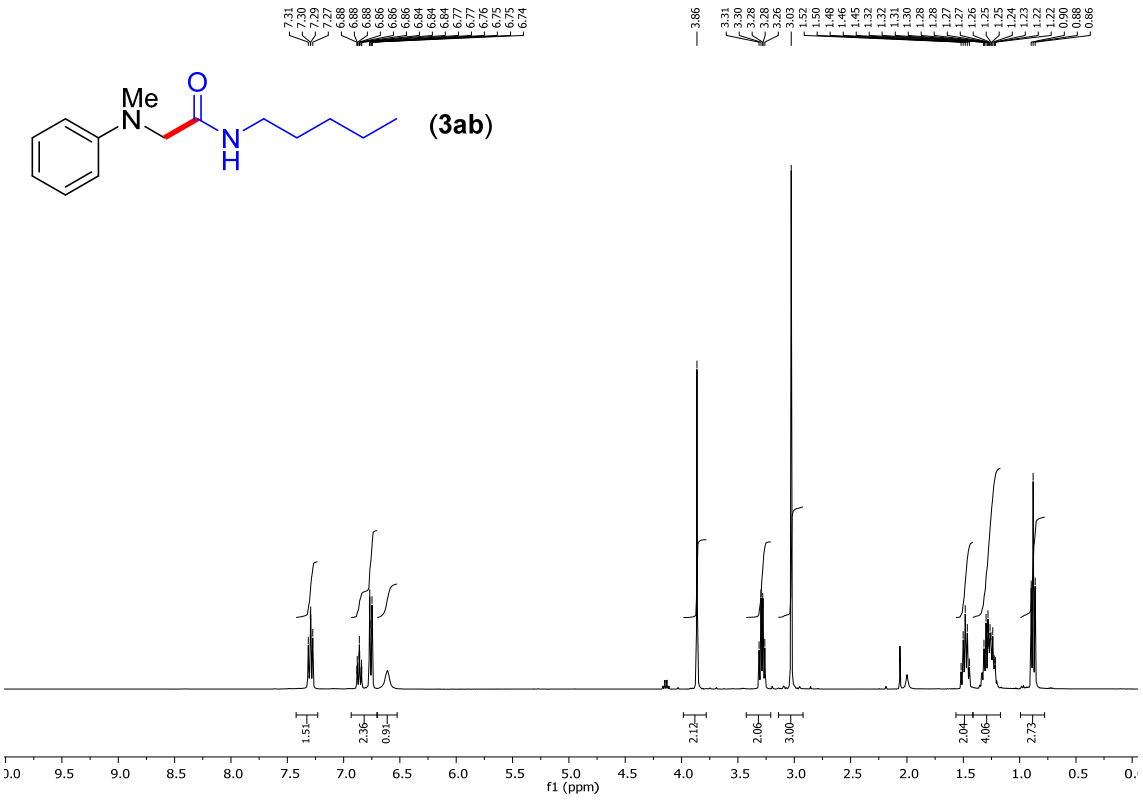

Me
O
N
N
H
Ts
Me

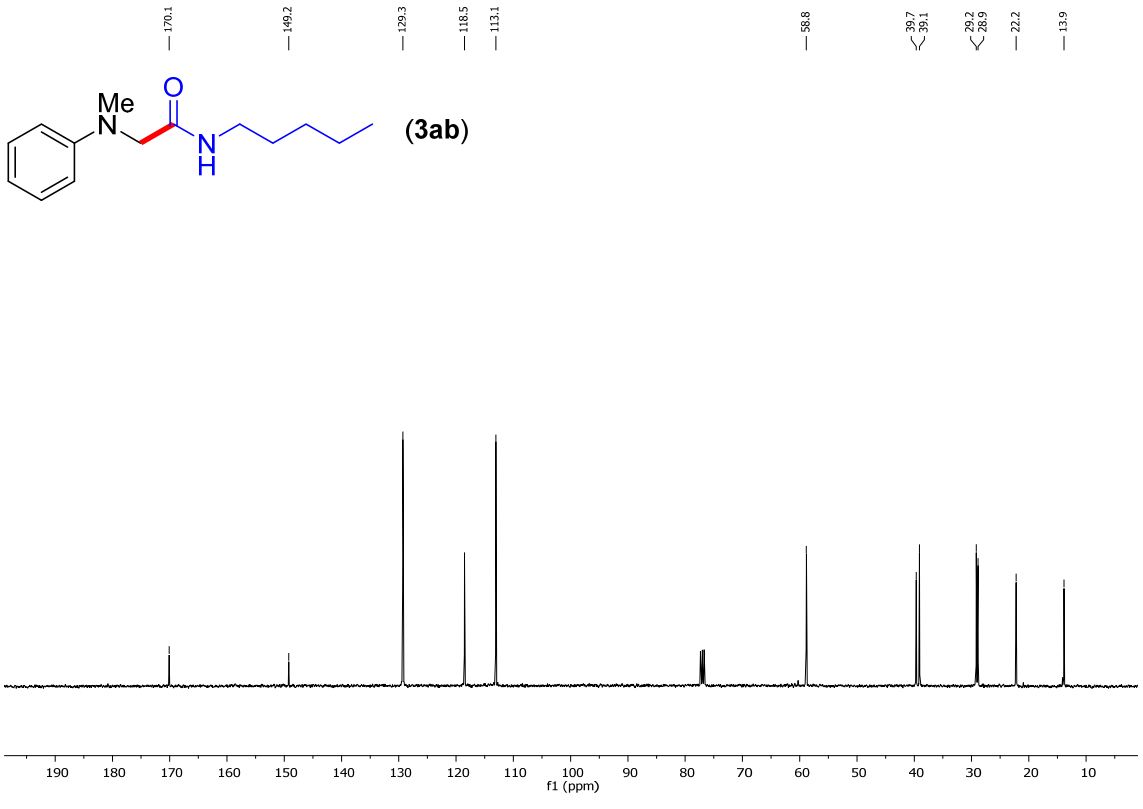
(**3pa**)

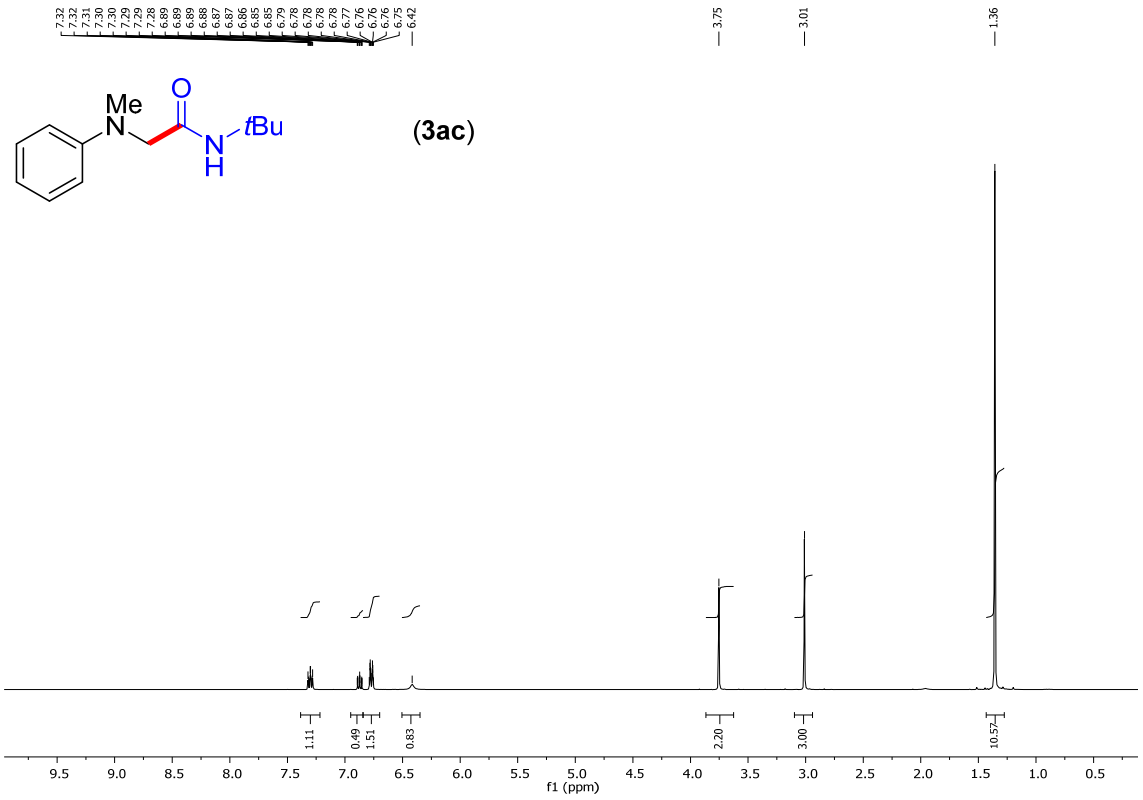
7.94
7.93
7.91
7.71
7.69
7.32
7.30
7.27
7.25
7.23
7.21
7.13
7.11
7.09
7.07
4.78
4.76
3.51
2.70
2.45
2.40
0.96
1.52
1.64
2.75
1.74
2.23
2.19
3.25
3.00
2.84
f1 (ppm)

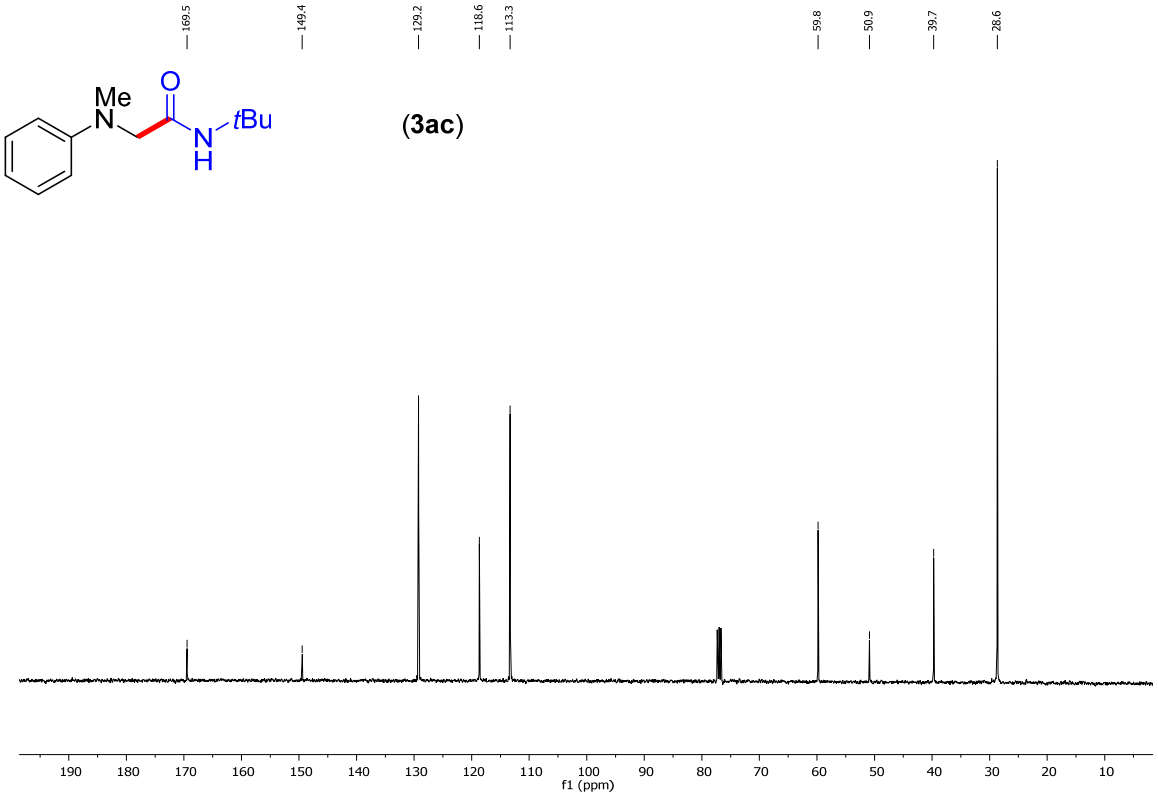

170.2
150.9
145.7
134.3
132.9
131.9
130.3
129.0
127.4
125.1
120.7
60.6
60.2
44.1
22.1
18.8
Me
O
N
N
H
Ts
Me
f1 (ppm)

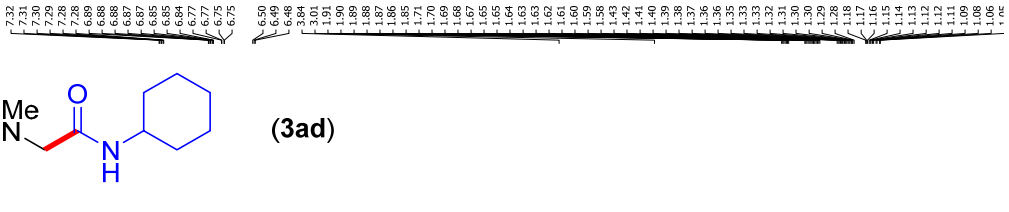
(**3pa**)


Me
N
O
N
H
(3ab)
f1 (ppm)

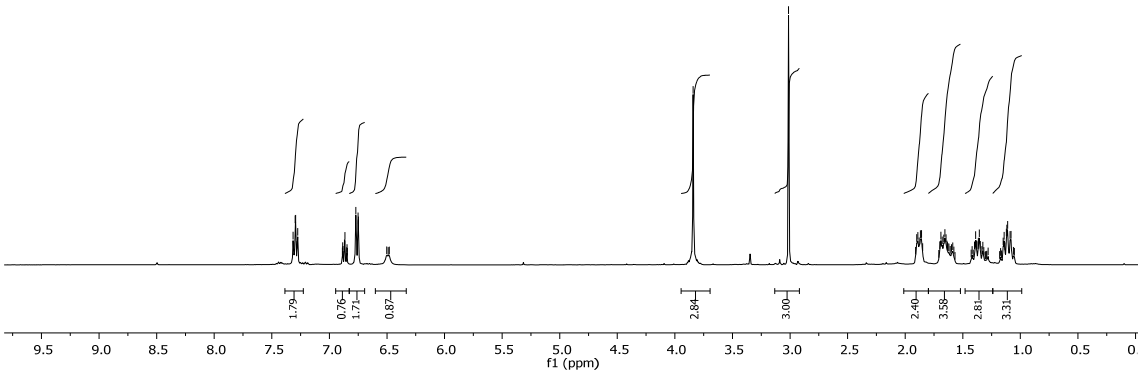

Me
N
O
N
H
(3ab)
f1 (ppm)

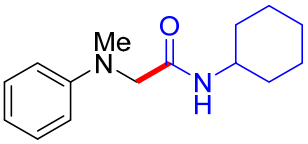

7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
6.89
6.89
6.88
6.87
6.87
6.86
6.85
6.79
6.78
6.78
6.78
6.77
6.76
6.76
6.76
6.75
6.42
3.75
3.01
1.36
Me
N
O
N
H
tBu
(3ac)
1.11
0.49
1.51
0.83
2.20
3.00
10.57
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


169.5
149.4
129.2
118.6
113.3
59.8
50.9
39.7
28.6
Me
N
O
N
H
tBu
(3ac)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

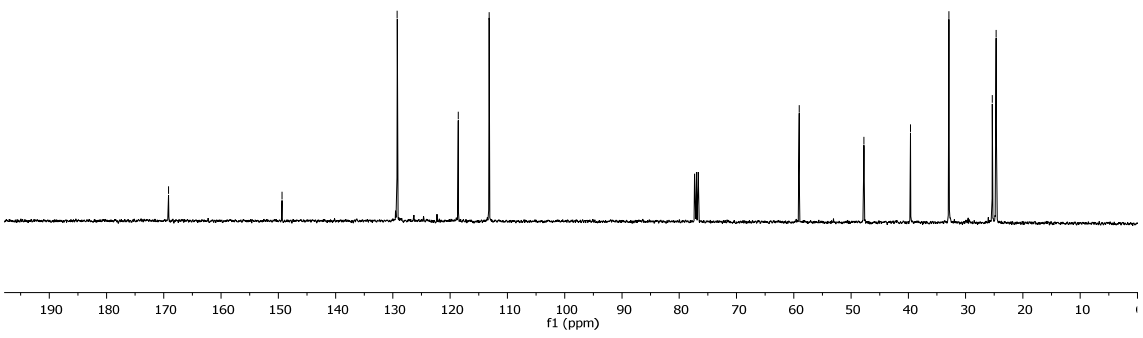


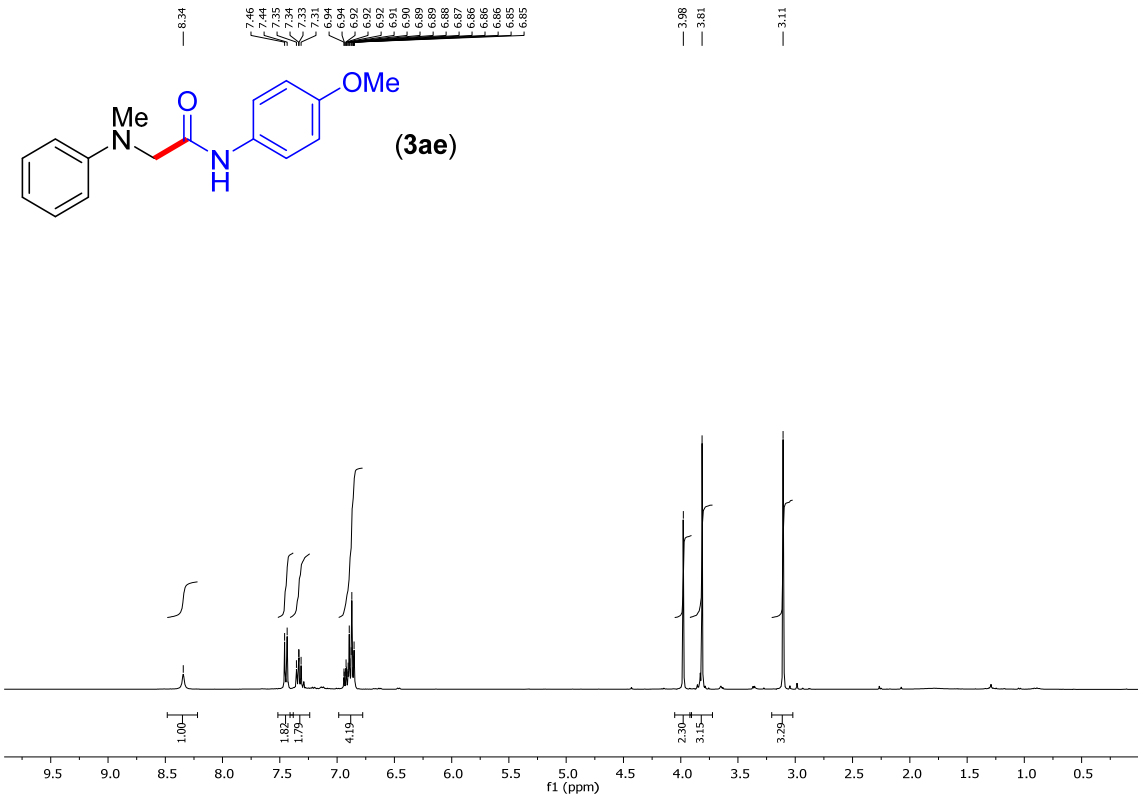
(3ad)

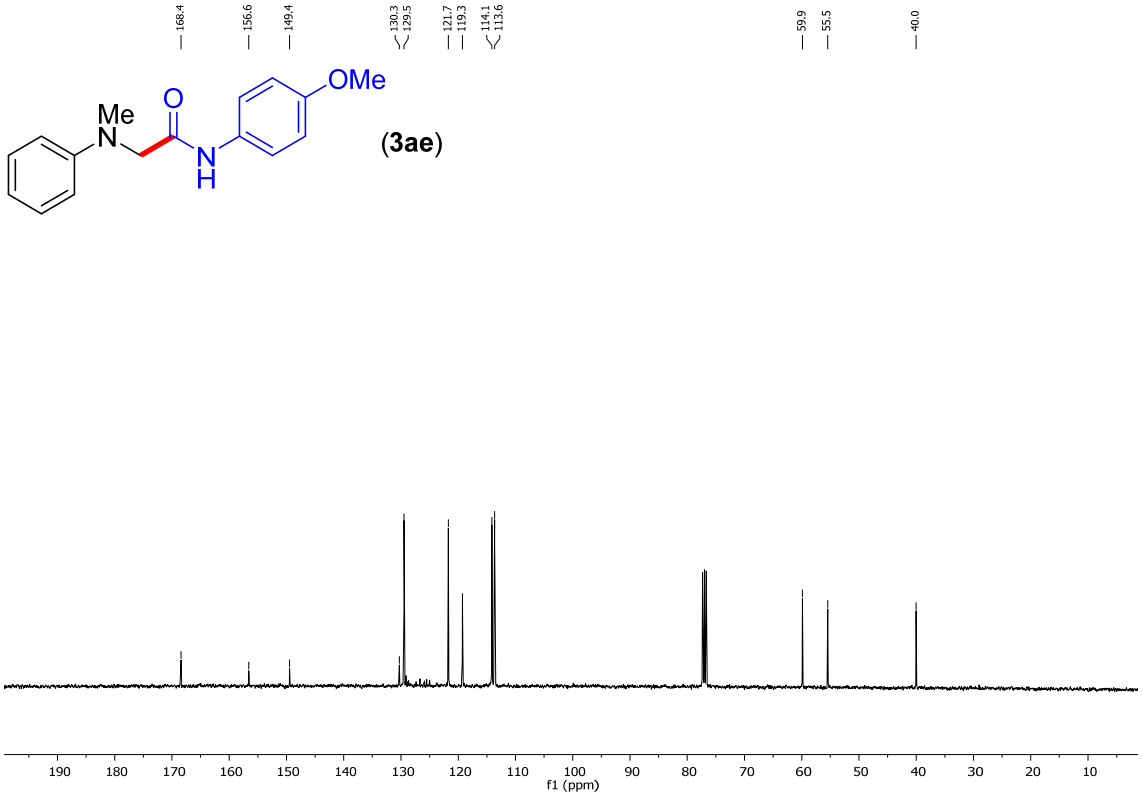


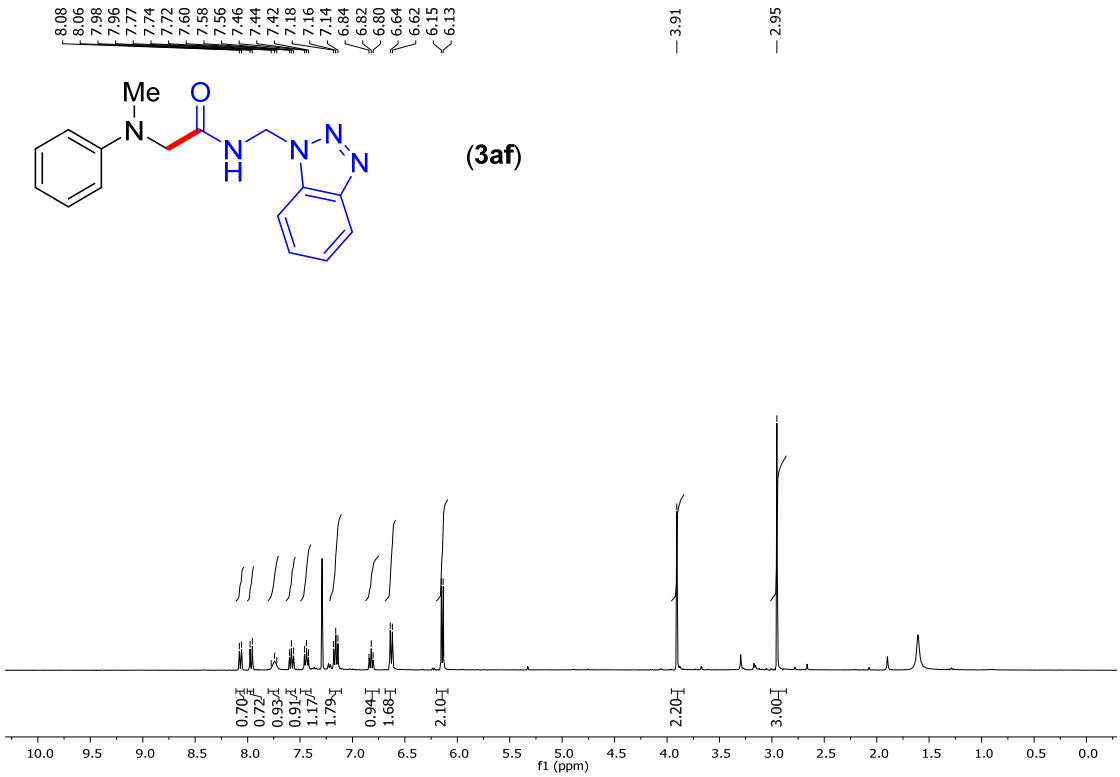


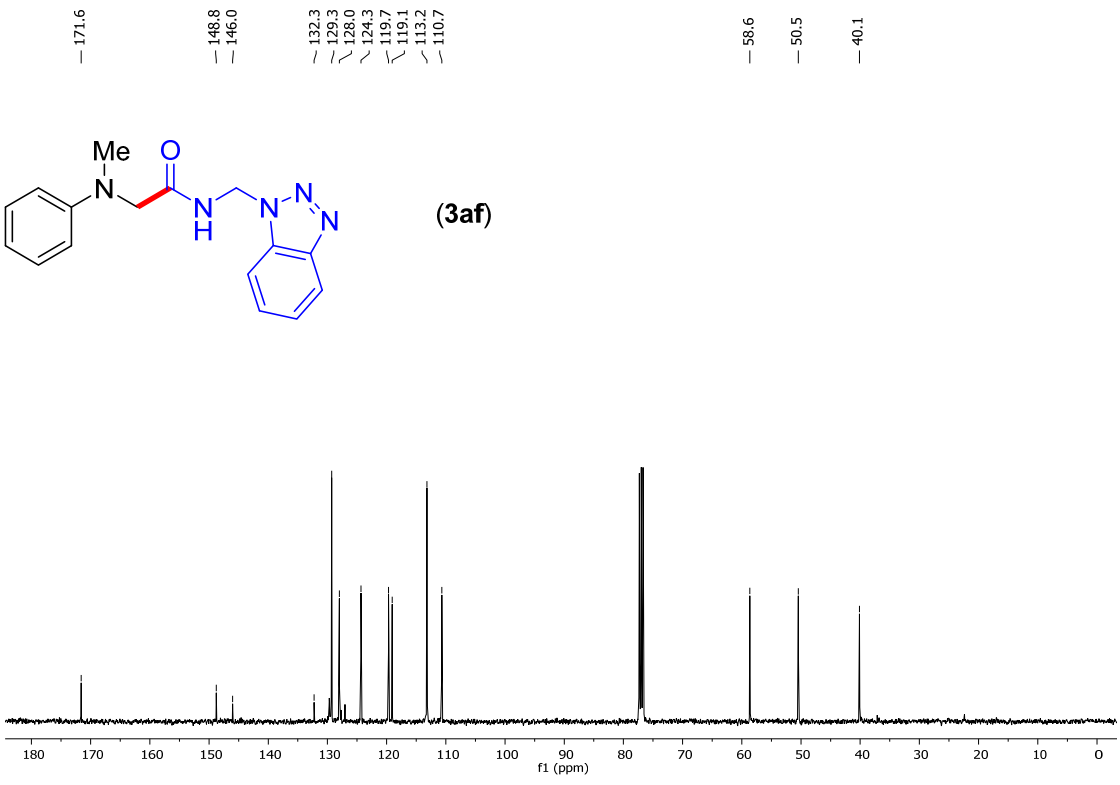
(3ad)

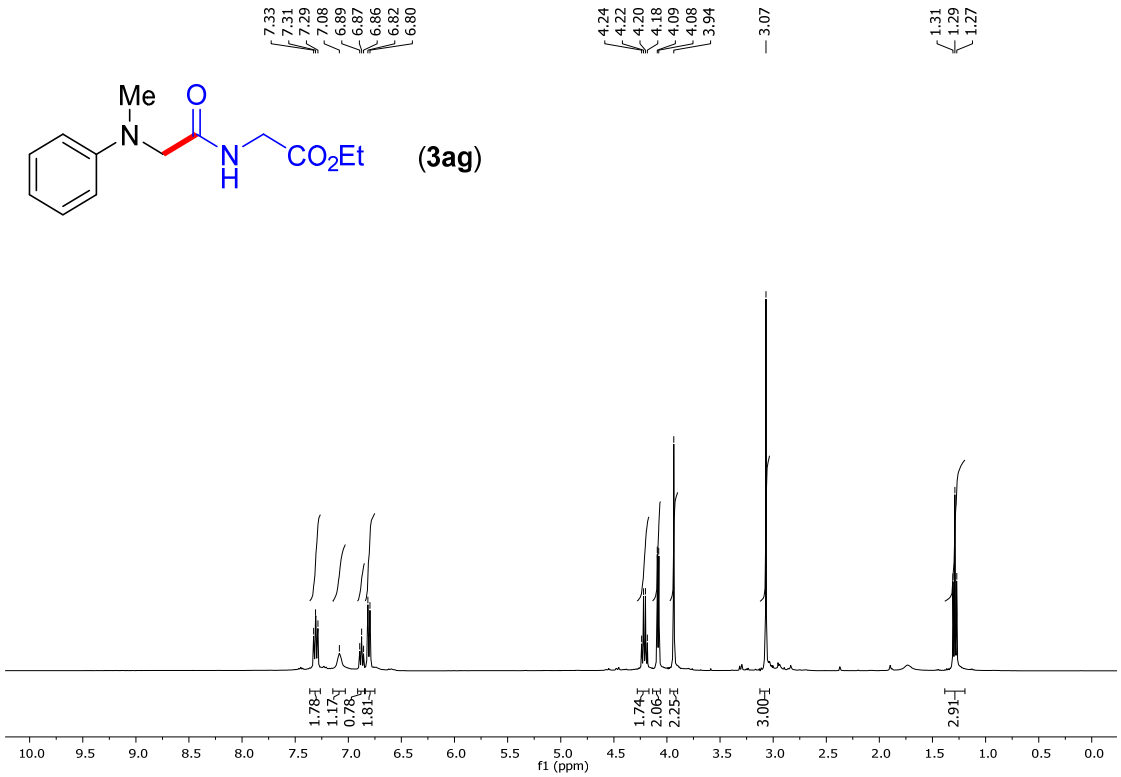


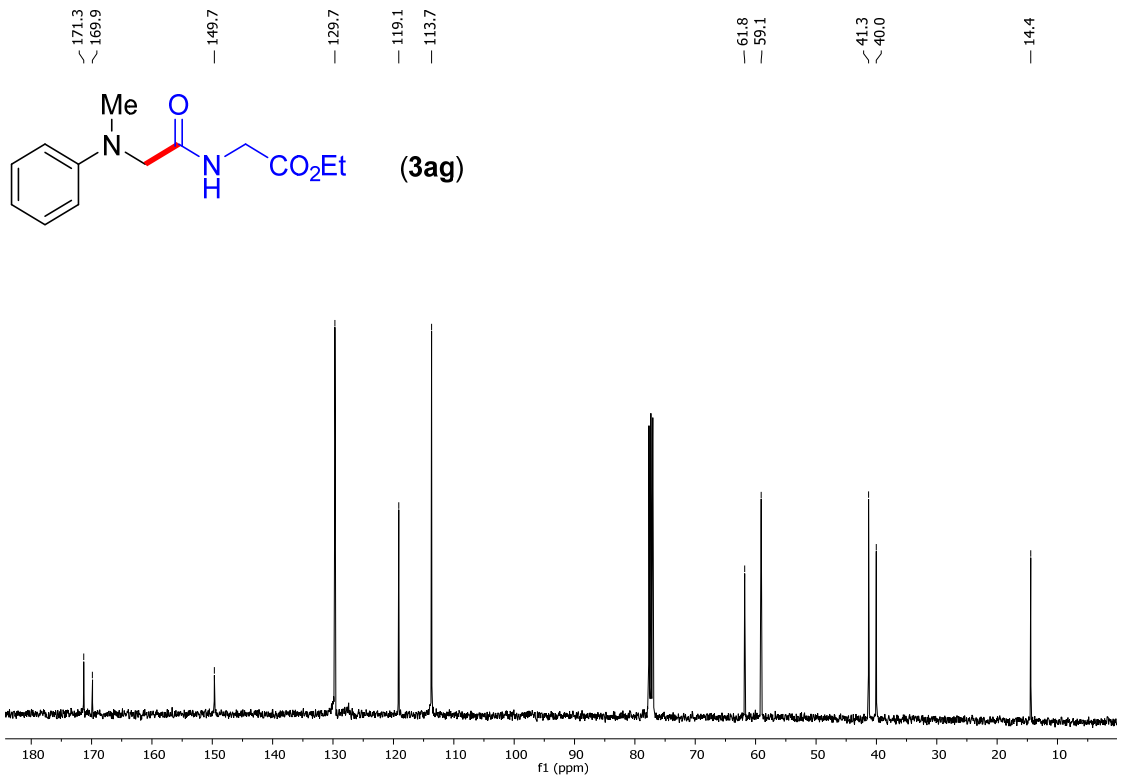

8.34
7.46
7.44
7.35
7.34
7.33
7.31
6.94
6.94
6.92
6.92
6.92
6.91
6.90
6.89
6.89
6.88
6.87
6.86
6.86
6.86
6.85
6.85
3.98
3.81
3.11
Me
N
O
N
H
OMe
(3ae)
1.00
1.82
1.79
4.19
2.30
3.15
3.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

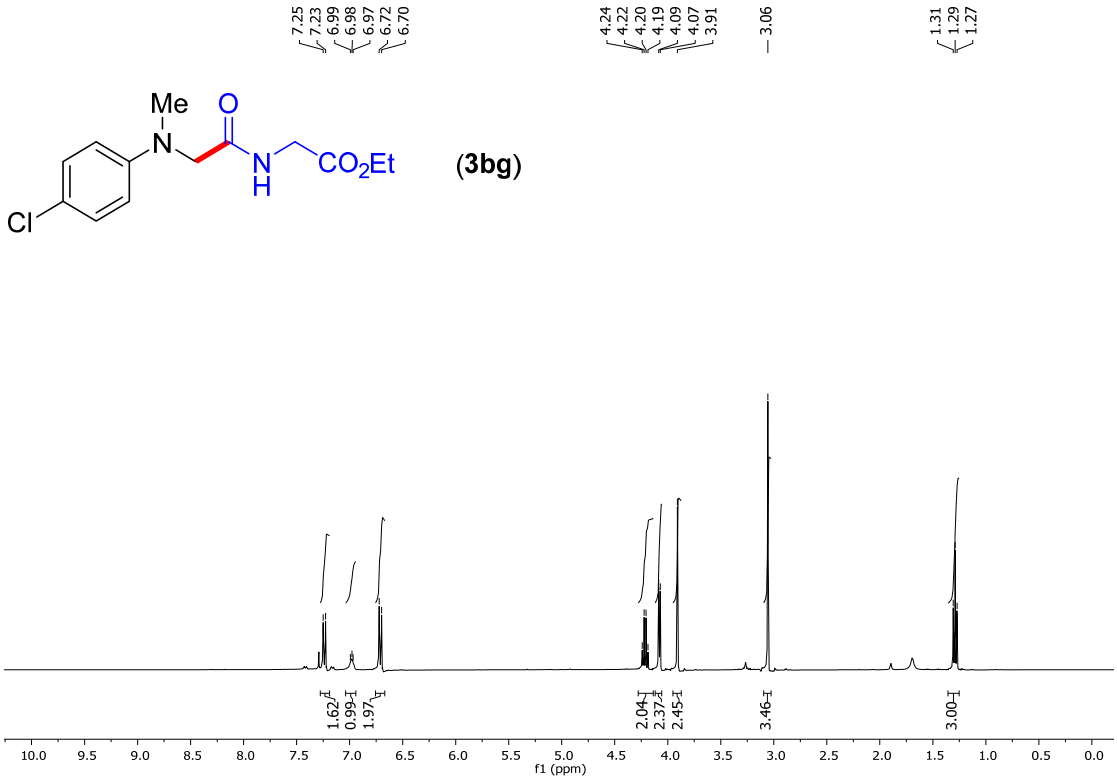

168.4
156.6
149.4
130.3
129.5
121.7
119.3
114.1
113.6
59.9
55.5
40.0
Me
N
O
N
H
OMe
(3ae)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

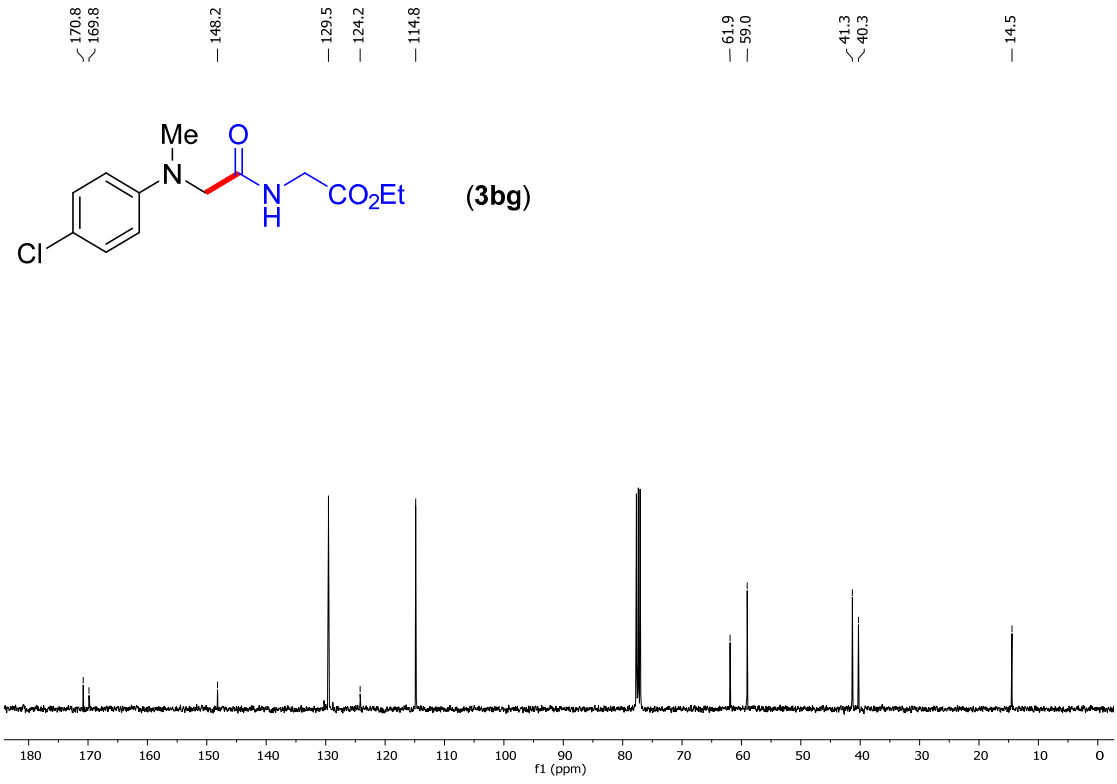

8.08
8.06
7.98
7.96
7.77
7.74
7.72
7.60
7.58
7.56
7.46
7.44
7.42
7.18
7.16
7.14
6.84
6.82
6.80
6.64
6.62
6.15
6.13
3.91
2.95
Me
O
N
N
H
N
N
N
(3af)
0.70
0.72
0.93
0.91
1.17
1.79
0.94
1.68
2.10
2.20
3.00
f1 (ppm)

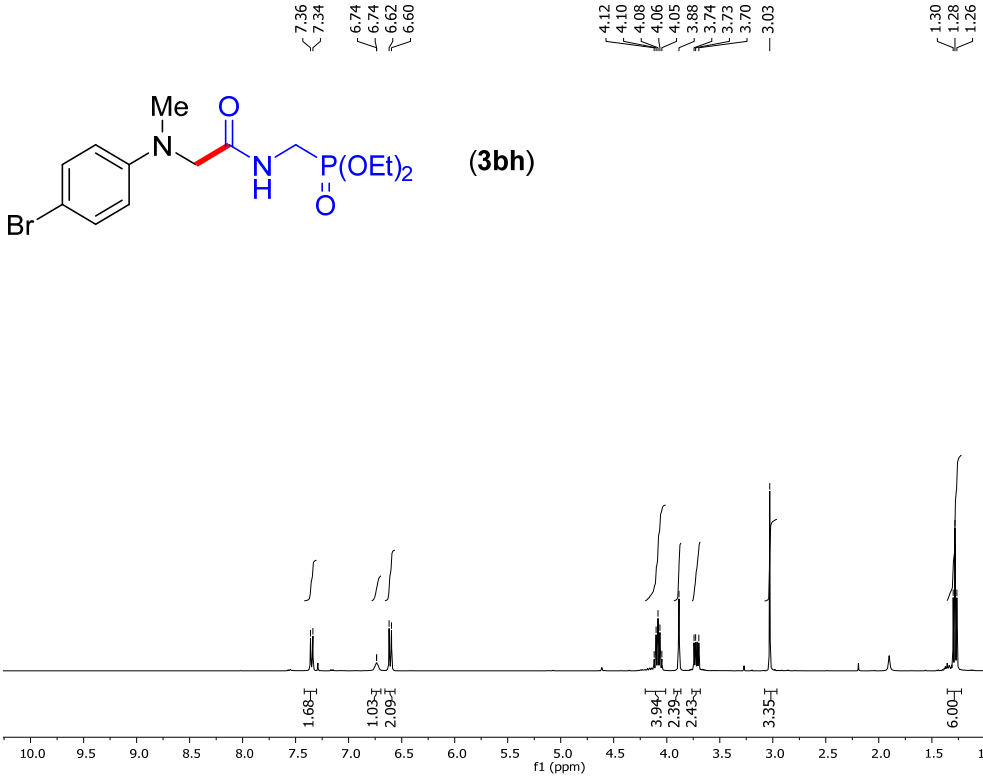

171.6
148.8
146.0
132.3
129.3
128.0
124.3
119.7
119.1
113.2
110.7
58.6
50.5
40.1
Me
O
N
N
H
N
N
N
(3af)
f1 (ppm)

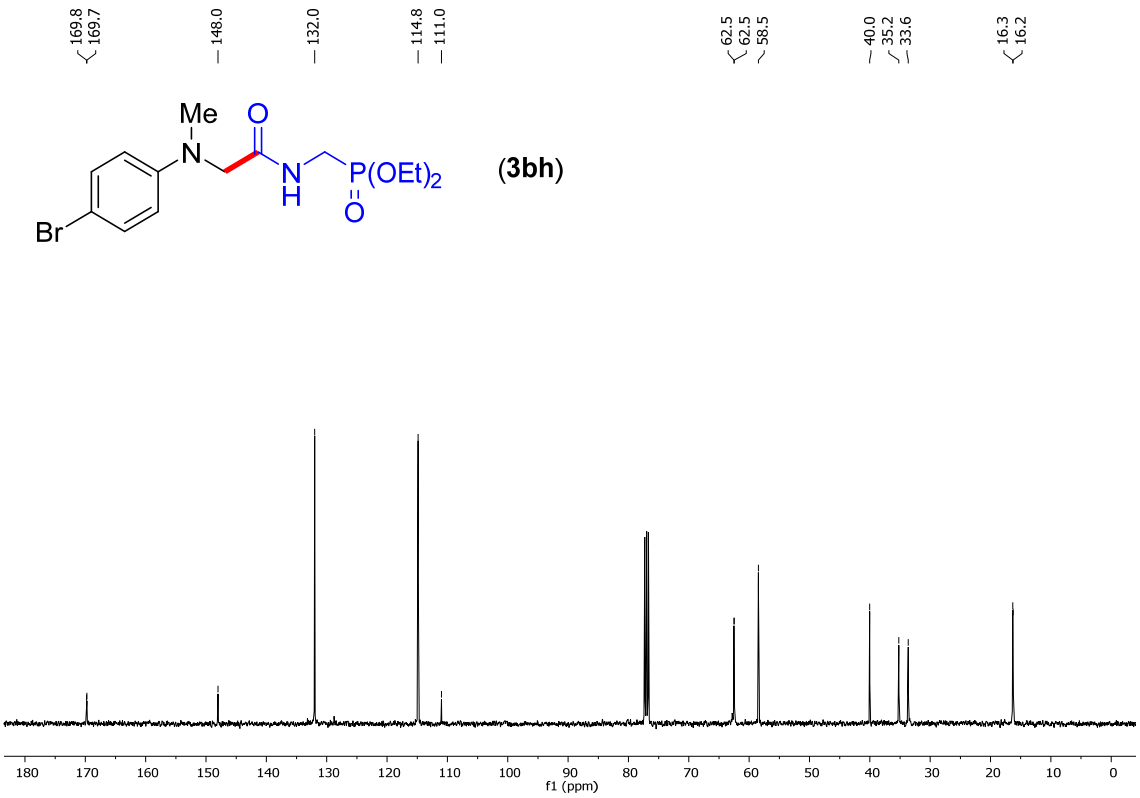

7.33
7.31
7.29
7.08
6.89
6.87
6.86
6.82
6.80
4.24
4.22
4.20
4.18
4.09
4.08
3.94
3.07
1.31
1.29
1.27
Me
O
N
N
H
CO2Et
(3ag)
1.78
1.17
0.78
1.81
1.74
2.06
2.25
3.00
2.91
f1 (ppm)

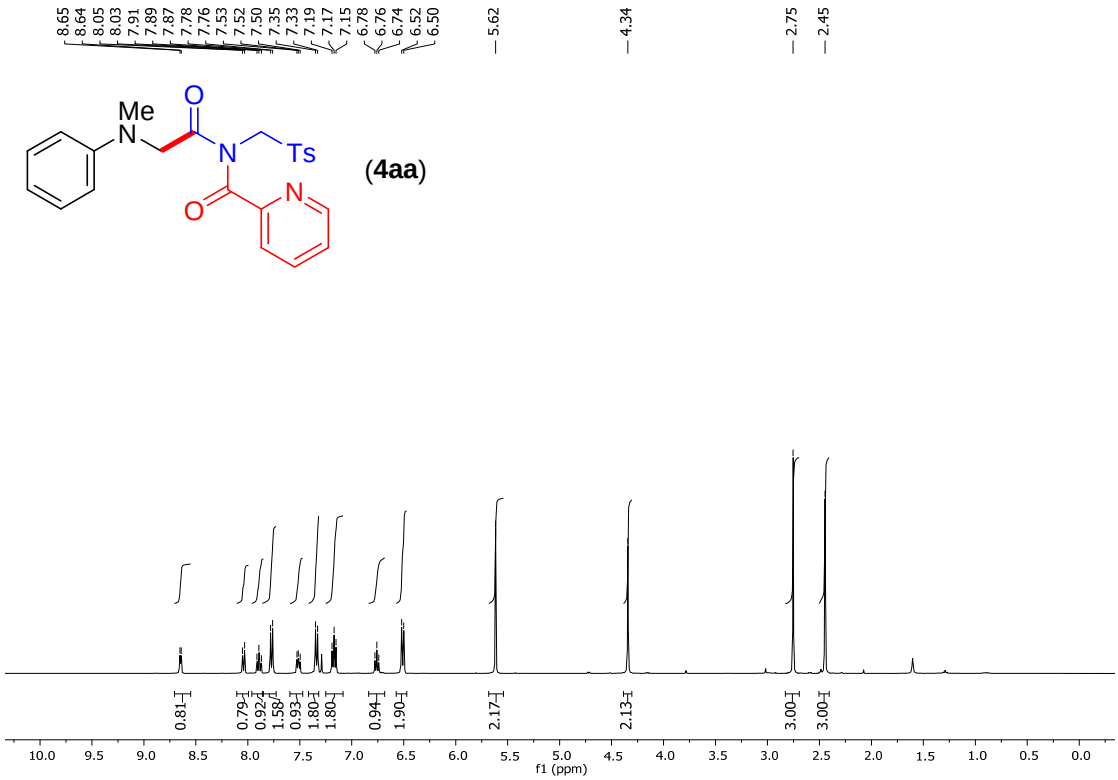

171.3
169.9
149.7
129.7
119.1
113.7
61.8
59.1
41.3
40.0
14.4
Me
O
N
N
H
CO2Et
(3ag)
f1 (ppm)

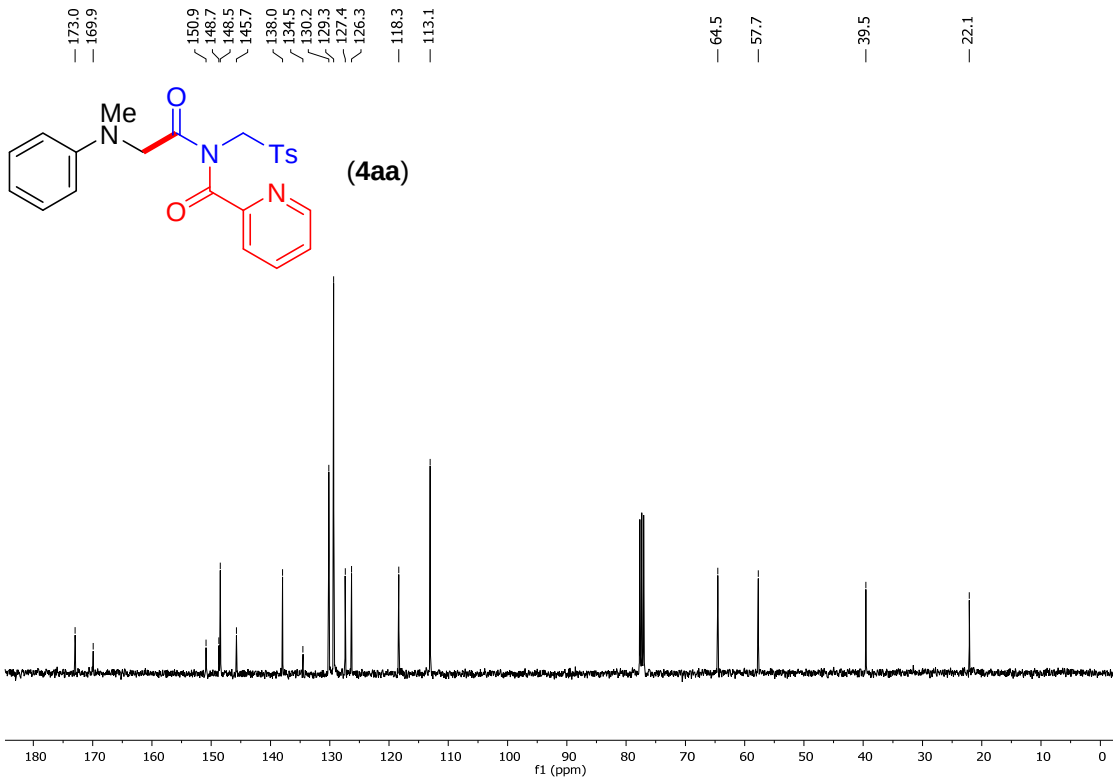

7.25
7.23
6.99
6.98
6.97
6.72
6.70
4.24
4.22
4.20
4.19
4.09
4.07
3.91
3.06
1.31
1.29
1.27
Me
N
O
N
H
CO2Et
Cl
(3bg)
1.62
0.99
1.97
2.04
2.37
2.45
3.46
3.00
f1 (ppm)

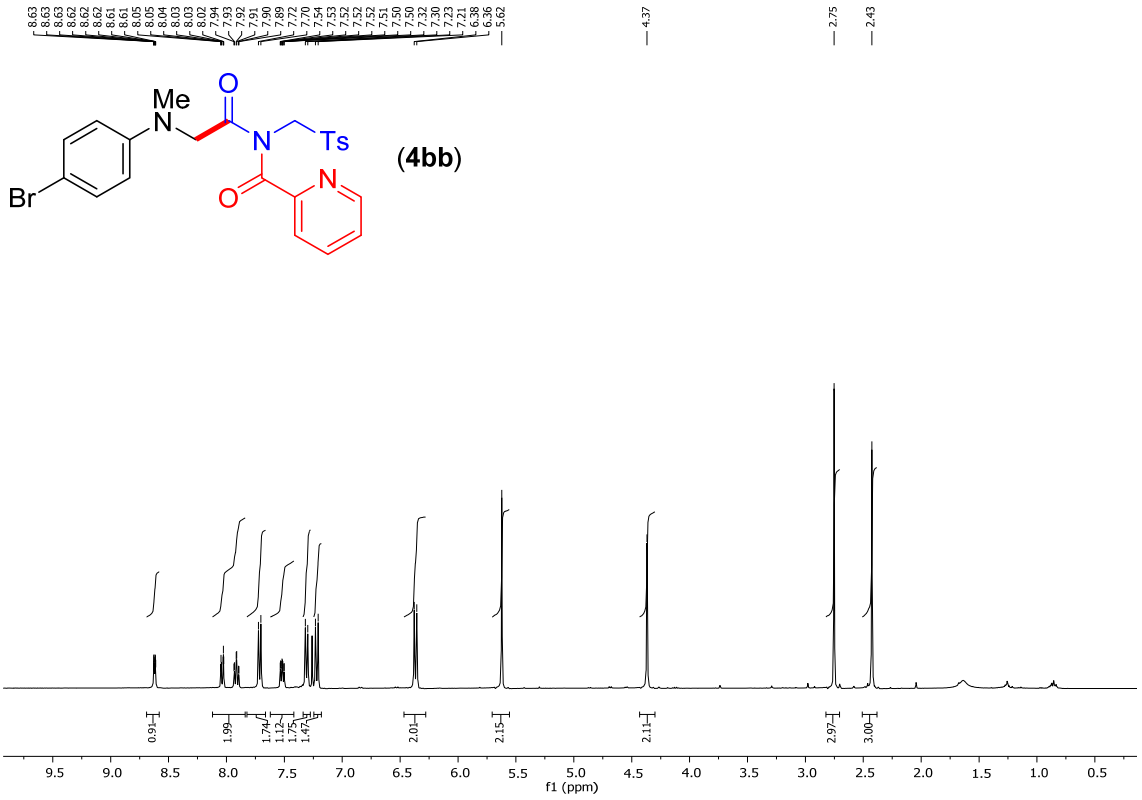

170.8
169.8
148.2
129.5
124.2
114.8
61.9
59.0
41.3
40.3
14.5
Me
N
O
N
H
CO2Et
Cl
(3bg)
f1 (ppm)

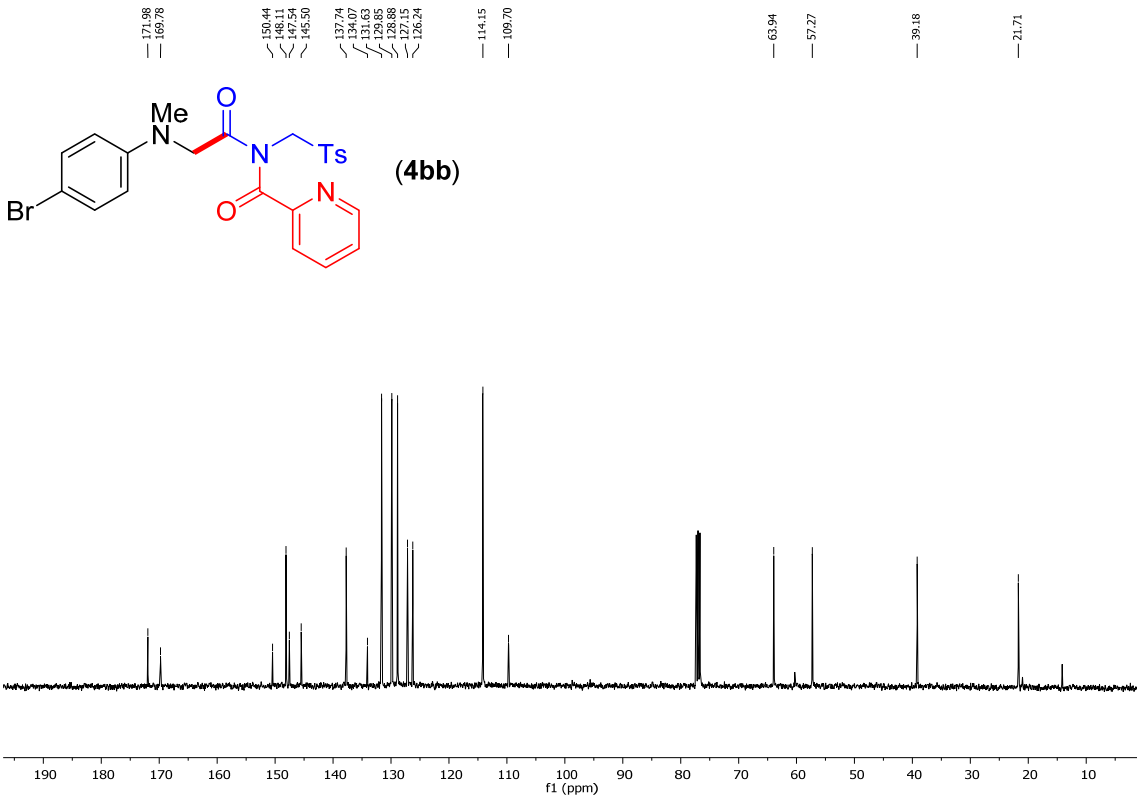

7.36
7.34
6.74
6.74
6.62
6.60
4.12
4.10
4.08
4.06
4.05
3.88
3.74
3.73
3.70
3.03
1.30
1.28
1.26
Me
N
O
N
H
P(OEt)2
O
Br
(3bh)
1.68
1.03
2.09
3.94
2.39
2.43
3.35
6.00
f1 (ppm)

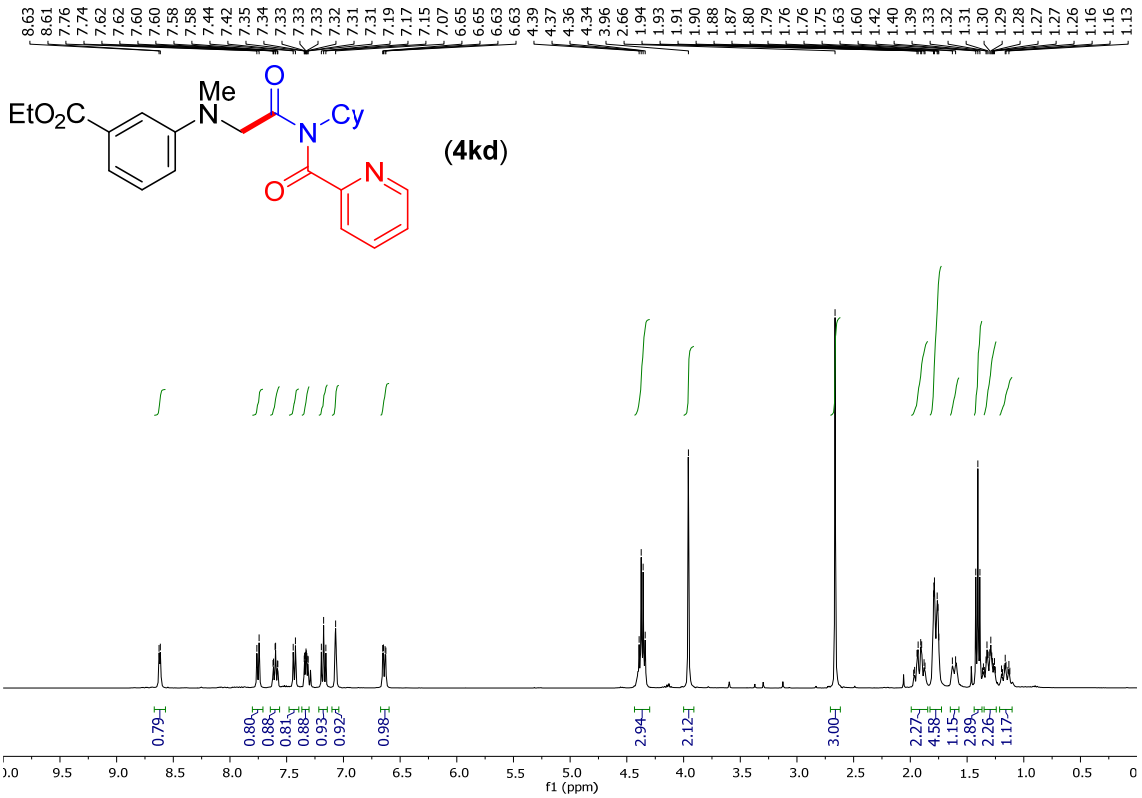

169.8
169.7
148.0
132.0
114.8
111.0
62.5
62.5
58.5
40.0
35.2
33.6
16.3
16.2
Me
N
O
N
H
P(OEt)2
O
Br
(3bh)
f1 (ppm)

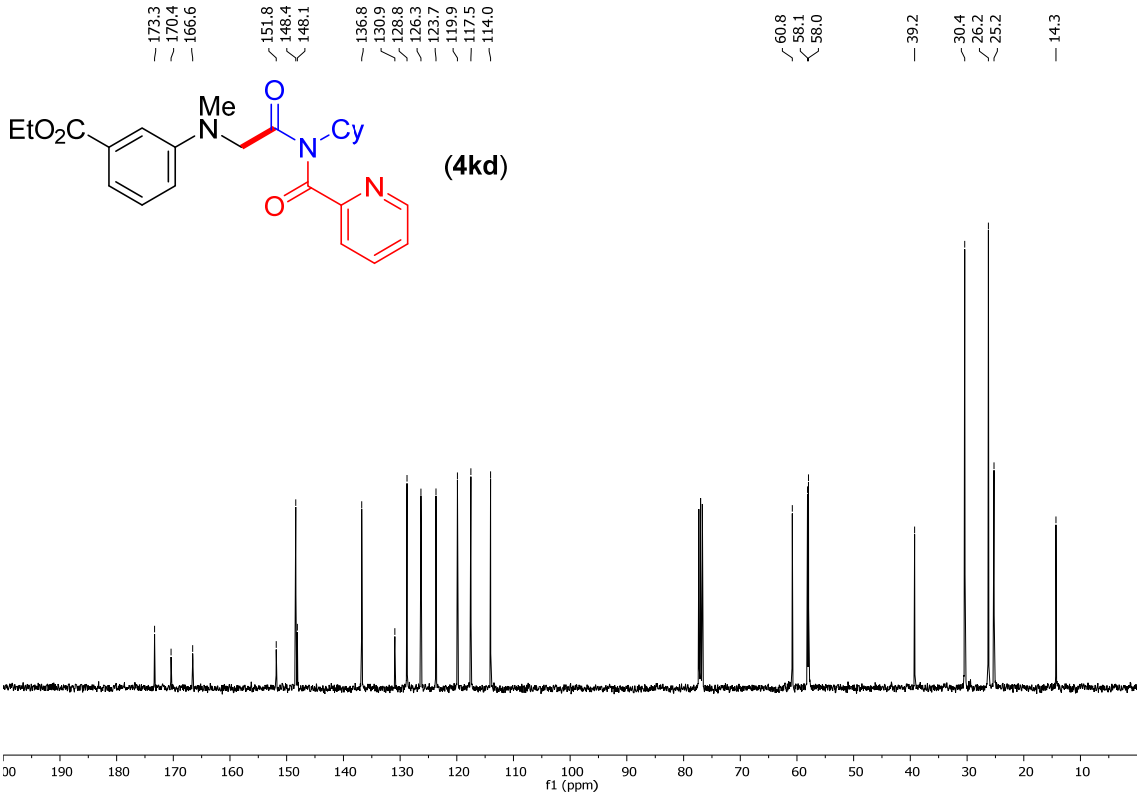

8.65
8.64
8.05
8.03
7.91
7.89
7.87
7.78
7.76
7.53
7.52
7.50
7.35
7.33
7.19
7.17
7.15
6.78
6.76
6.74
6.52
6.50
5.62
4.34
2.75
2.45
Me
N
O
N
Ts
O
N
(4aa)
0.81
0.79
0.92
1.58
0.93
1.80
1.80
0.94
1.90
2.17
2.13
3.00
3.00
f1 (ppm)

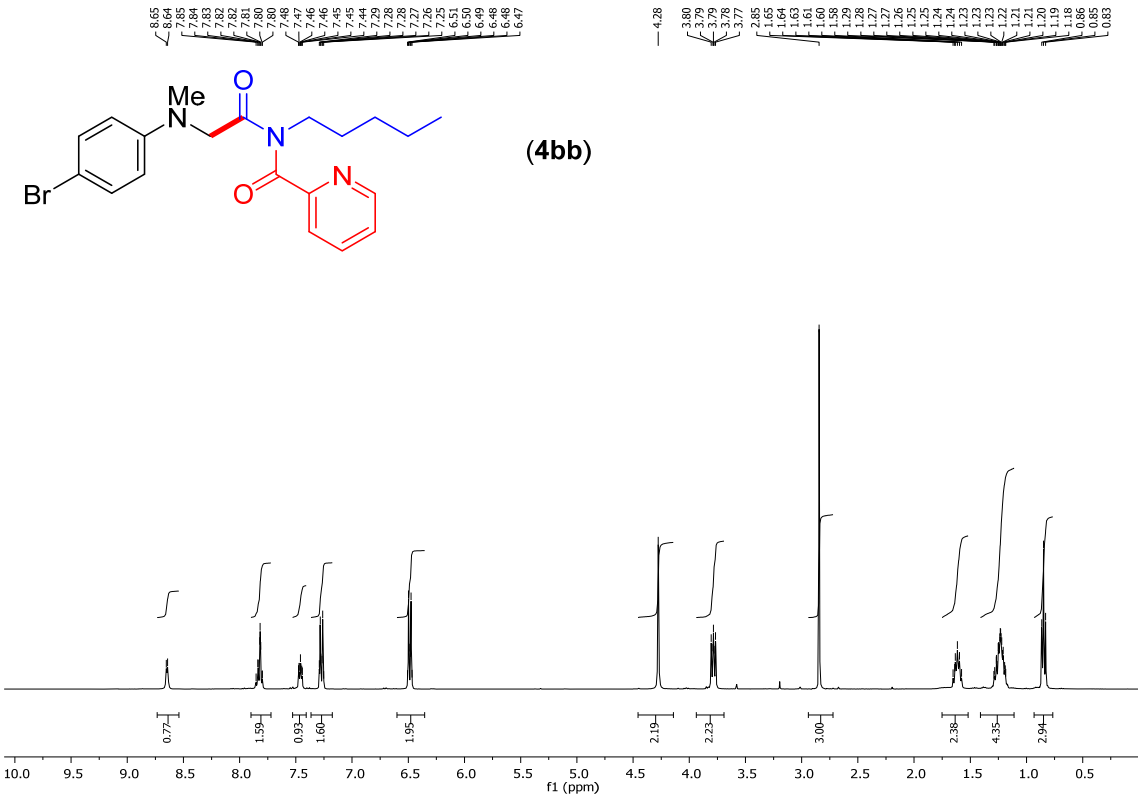

173.0
169.9
150.9
148.7
148.5
145.7
138.0
134.5
130.2
129.3
127.4
126.3
118.3
113.1
64.5
57.7
39.5
22.1
Me
N
O
N
Ts
O
N
(4aa)
f1 (ppm)


8.63
8.63
8.63
8.62
8.62
8.62
8.61
8.61
8.05
8.05
8.04
8.03
8.03
8.02
7.94
7.93
7.92
7.91
7.90
7.89
7.72
7.70
7.54
7.53
7.52
7.52
7.52
7.51
7.50
7.50
7.32
7.30
7.23
7.21
6.38
6.36
5.62
4.37
2.75
2.43
Me
N
O
N
Ts
Br
O
N
(4bb)
0.91
1.99
1.74
1.13
1.75
1.47
2.01
2.15
2.11
2.97
3.00
f1 (ppm)

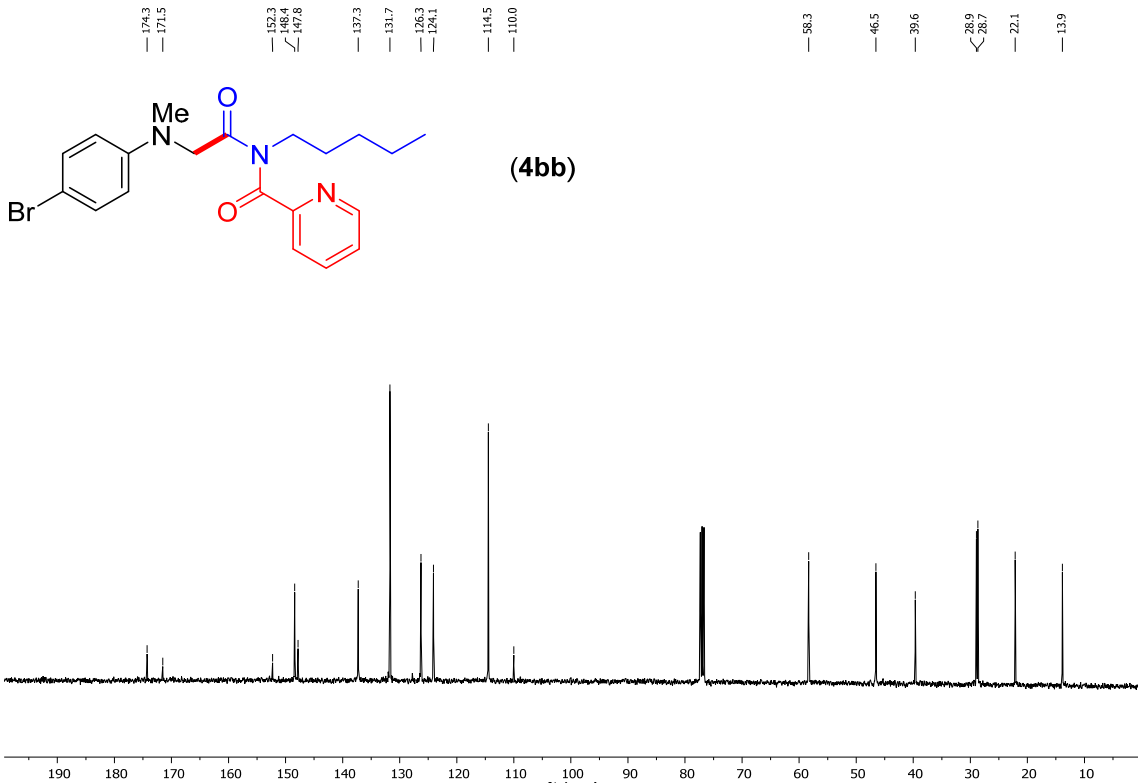

171.98
169.78
150.44
149.11
147.54
145.50
137.74
134.07
131.63
129.85
129.68
127.15
126.24
114.15
109.70
63.94
57.27
39.18
21.71
Me
N
O
N
Ts
Br
O
N
(4bb)
f1 (ppm)


8.63 8.61 7.76 7.74 7.62 7.62 7.60 7.60 7.58 7.58 7.44 7.42 7.35 7.34 7.33 7.33 7.33 7.32 7.31 7.31 7.19 7.17 7.15 7.07 6.65 6.63 6.63 4.39 4.37 4.36 4.34 3.96 2.66 1.94 1.93 1.91 1.90 1.88 1.87 1.80 1.79 1.76 1.76 1.75 1.63 1.60 1.42 1.40 1.39 1.33 1.32 1.31 1.30 1.29 1.28 1.27 1.27 1.26 1.16 1.16 1.13
EtO2C
Me
N
O
N
Cy
O
N
(4kd)
0.79 0.80 0.88 0.81 0.88 0.93 0.92 0.98 2.94 2.12 3.00 2.27 4.58 1.15 2.89 2.26 1.17
f1 (ppm)

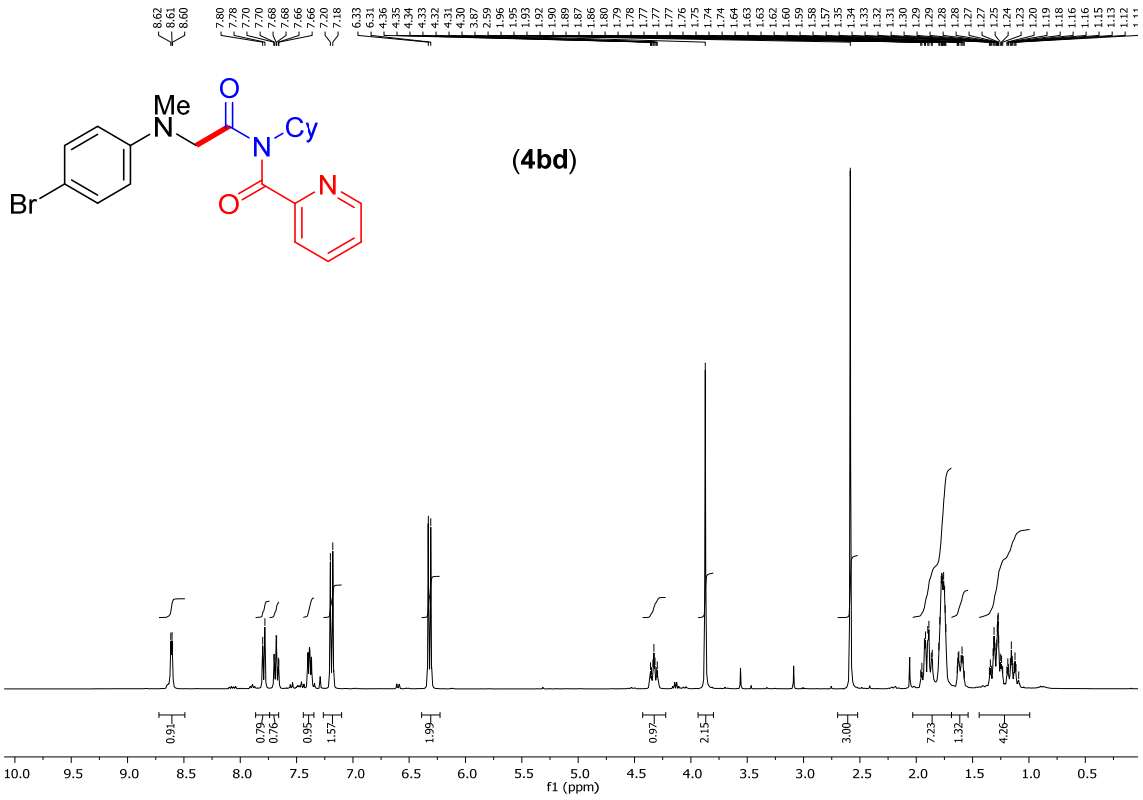

173.3 170.4 166.6 151.8 148.4 148.1 136.8 130.9 128.8 126.3 123.7 119.9 117.5 114.0 60.8 58.1 58.0 39.2 30.4 26.2 25.2 14.3
EtO2C
Me
N
O
N
Cy
O
N
(4kd)
f1 (ppm)

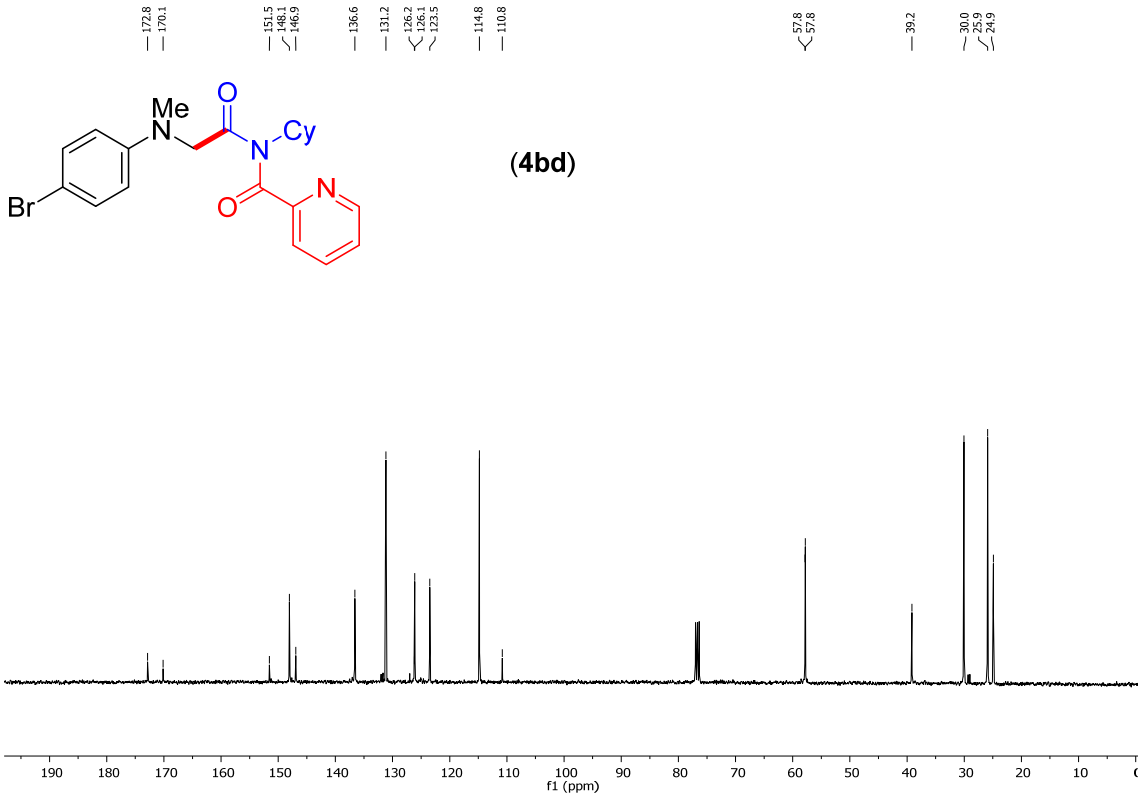


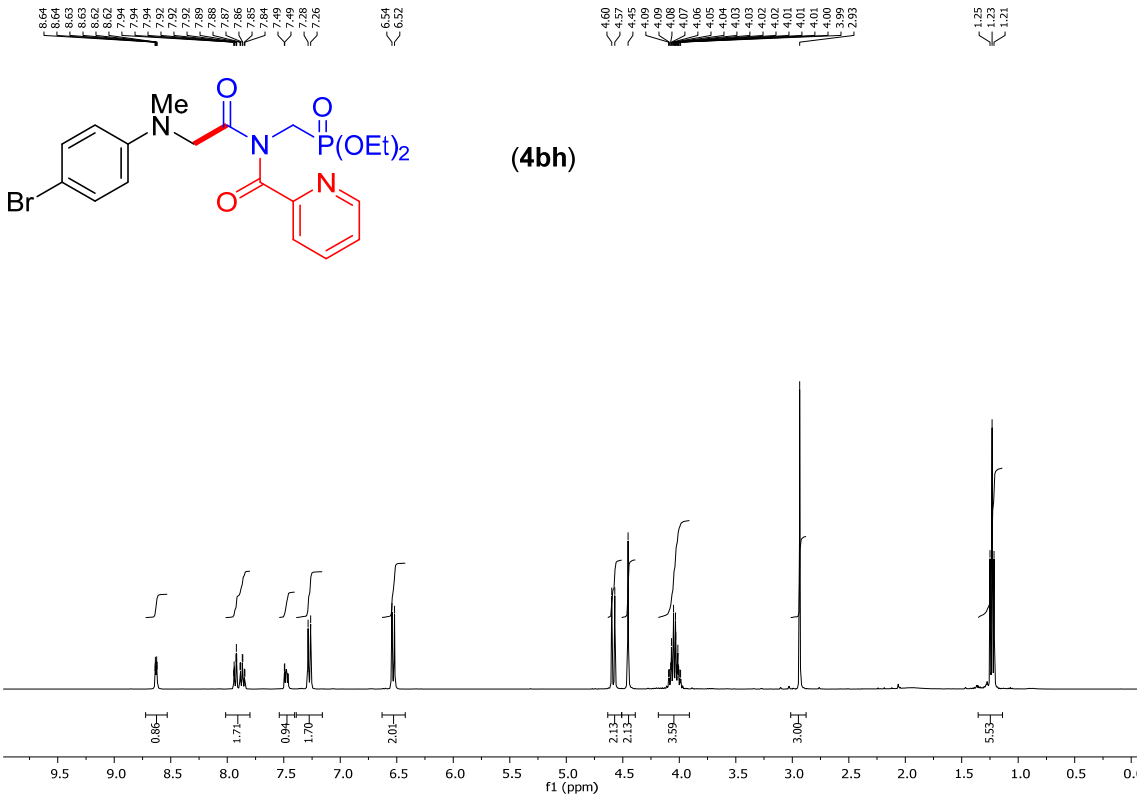
(**4bb**)



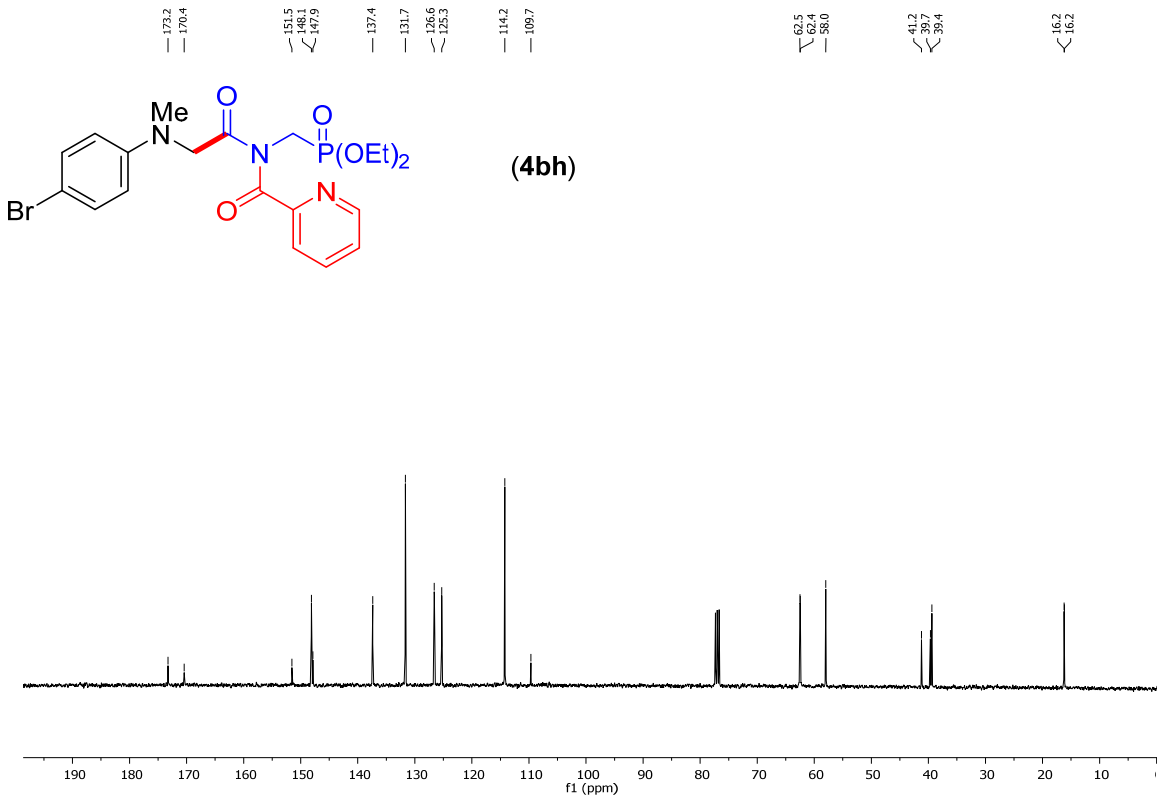
(**4bb**)


Me
N
O
N
Cy
O
N
Br
(4bd)
f1 (ppm)


Me
N
O
N
Cy
O
N
Br
(4bd)
f1 (ppm)


8.64
8.64
8.63
8.63
8.62
8.62
7.94
7.94
7.92
7.92
7.89
7.88
7.87
7.86
7.85
7.84
7.49
7.28
7.26
6.54
6.52
4.60
4.57
4.45
4.09
4.08
4.07
4.06
4.05
4.04
4.03
4.02
4.02
4.01
4.01
4.00
3.99
2.93
1.25
1.23
1.21
Me
N
O
N
O
P(OEt)2
O
N
Br
0.86
1.71
0.94
1.70
2.01
2.13
2.13
3.59
3.00
5.53
f1 (ppm)

(**4bh**)


173.2
170.4
151.5
148.1
147.9
137.4
131.7
126.6
125.3
114.2
109.7
62.5
62.4
58.0
41.2
39.7
39.4
16.2
16.2
Me
N
O
N
O
P(OEt)2
O
N
Br
f1 (ppm)

(**4bh**)