Electronic Supplementary Material (ESI) for ChemComm.

Homologation of α-Aryl Amino Acids through Quinone-Catalyzed Decarboxylation/Mukaiyama−Mannich Addition

Benjamin J. Haugeberg,[‡] Johnny, H. Phan,[‡†] Xinyun Liu, Thomas J. O'Connor and Michael D. Clift[*]

Department of Chemistry, The University of Kansas, 2010 Malott Hall, 1251 Wescoe Hall Drive, Lawrence, Kansas 66045, United States

Supporting Information

Part 1: General Methods

All reactions were carried out in 8 mL reaction vials with magnetic stirring unless otherwise stated. EtOH was used as purchased from Fisher Chemical (190 Proof). Other reagents were used as delivered from commercial sources. Purification of reaction products was carried out by flash chromatography using Fisher Chemical silica gel (230-400 Mesh, Grade 60). Analytical thin layer chromatography (TLC) was performed on EMD millipore TLC silica gel 60 – F 254: 25 glass plates. Visualization was accomplished with UV light and/or phosphomolybdic acid staining followed by heating. Melting point data were recorded using a Digimelt SRS. Film and KBr pellet infrared spectra were recorded using a Shimadzu FTIR-8400S. ^{1}H-NMR spectra were recorded on a Bruker Advance 400 (400 MHz) or a Bruker 500 (500 MHz) spectrometer and are reported in ppm using solvent as a reference ($CDCl_3$ at 7.26 ppm and D_2O at 4.79 ppm). Data are reported as (app = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad); integration; coupling constant(s) in Hz. Proton-decoupled ^{13}C-NMR spectra were recorded on a Bruker 500 (125 MHz) and are reported in ppm using solvent as a reference ($CDCl_3$ at 77.16 ppm). Mass spectra data were obtained on a Micromass Ltd. LCT Premier quadrupole and time-of-flight tandem mass analyzer.

Part 2: General Experimental Procedures for Sequential Oxidative Decaboxylation/ Mannich Addition

A: General procedure for glycine derivative decarboxylation/ silyl ketene (thio)acetal addition (9a-9j): To a solution of 2,6-di-*tert*-butyl-1,4-benzoquinone (11.0 mg, 0.050 mmol, unless otherwise noted) and p-anisidine (123.1 mg, 1.0 mmol) in ethanol (1.6 mL, 0.312 M) with respect to the glycine derivative substrate) was added the glycine derivative (0.50 mmol), followed by purging the reaction vial with a balloon of O_2. The reaction mixture was allowed to stir under O_2 at 70 ^oC for 24 hrs unless otherwise noted. The ethanol was removed by rotary evaporation and the oxidative decarboxylation product was further pumped for 0.5h with a high-vacuum pump. The remaining solid was dissolved in dry THF (1.6 mL, 0.312 M) and the solution was cooled to 0 ^oC. To this solution was added tetrafluoroboric acid solution (48 wt. % in H2O, 90.0 μL, 0.75 mmol) and silyl ketene (thio)acetal[1] (1.5 mmol). The resulting solution was allowed to stir for 1.5h under N_2 at 0 ^oC. Sodium phosphate buffer (PH = 7, 2 mL) was added followed by saturated aq. $NaHCO_3$ (0.5 mL). The mixture was transferred to a separatory funnel by aid of Et_2O, shaken vigorously and the organic phase was collected. The aqueous phase was further extracted with Et_2O (3 x 5.0 mL) and the combined organic extracts were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Flash chromatography on TEA neutralized silica gel (10% ethyl acetate in hexanes) provided the desired aryl amine thioesters (**9a-9j**).

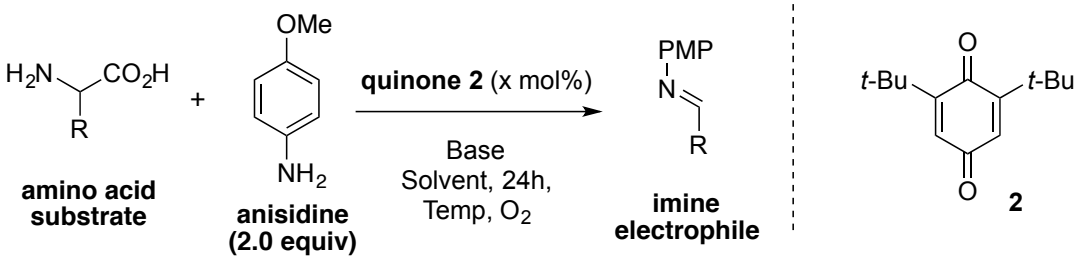
B: General procedure for glycine derivative decarboxylation/ silyl ketene acetal addition (11a-11j): To a solution of 2,6-di-*tert*-butyl-1,4-benzoquinone (11.0 mg, 0.050 mmol, unless otherwise noted) and p-anisidine (123.1 mg, 1.0 mmol) in ethanol (1.6 mL, 0.312 M) with respect to the glycine derivative substrate) was added the glycine derivative (0.50 mmol) , followed by purging the reaction vial with a balloon of O_2. The reaction mixture was allowed to stir under O_2 at 70 ^oC for 24 hrs unless otherwise noted. The ethanol was removed by rotary evaporation and the oxidative decarboxylation product was further pumped for 0.5h with a high-vacuum pump. The remaining solid was dissolved in dry THF (1.6 mL, 0.312 M) and the solution was cooled to 0 ^oC. To this solution was added tetrafluoroboric acid solution (48 wt. % in H_2O, 90.0 μL, 0.75 mmol) and silyl ketene (gem-dimethyl)acetal[2] (1.5 mmol) dropwise over 6 iterations by 15 min intervals. After 1.5 hrs, the solvent was removed under reduced pressure. Flash chromatography on TEA neutralized silica gel (5%-20% ethyl acetate in hexanes) followed by recrystallization in $CHCl_3$ and pentane provided the desired aryl amine methyl-esters (**11a-11j**).

[1] Prepared according to: Chua, S. S.; Alni, A.; Chan, L. T. J.; Yamane, M.; Loh T. P. *Tetrahedron*, **2011**, *67*, 5079.

[2] Prepared according to: Dong, S.; Parker, G. D.; Tei, T.; Paquette, L. A. *Org. Lett.,* **2006**, *8*, 2429.

Part 3: Optimization of Quinone-Catalyzed Oxidative Decarboxylation (Table S1) and Sequential Quinone-Catalyzed Oxidative Decarboxylation/Mukaiyama Mannich Addition (Table S2)

Table S1: NMR Yields for Optimization of Quinone-Catalyzed Oxidative Decarboxylation

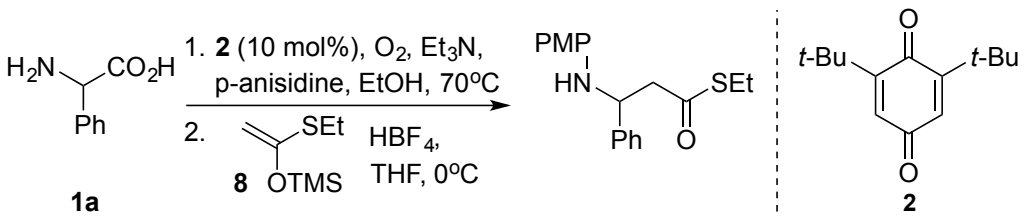


Entry	R	solvent	Temperature	catalyst	Base	yield[a]
1	Phenylglycine	1,4-Dioxane	50 ˚C	5%	-	0%
2	Phenylglycine	THF	50 ˚C	5%	-	0%
3	Phenylglycine	CH_3CN	50 ˚C	5%	-	0%
4	Phenylglycine	DMSO	50 ˚C	5%	-	39%
5	Phenylglycine	DMSO	50 ˚C	5%	Et_3N	42%
6	Phenylglycine	DMSO	80 ˚C	5%	Et_3N	68%
7	Phenylglycine	H_2O	80 ˚C	5%	Et_3N	63%
8	Phenylglycine	CH_3CN:H_2O (1:1)	80 ˚C	5%	Et_3N	74%
9	Phenylglycine	CH_3CN:H_2O (1:1)	80 ˚C	10%	Et_3N	90%
10	Phenylglycine	CH_3CN:H_2O (1:1)	80 ˚C	10%	Na_3PO_4	84%
11	Phenylglycine	CH_3CN:H_2O (1:1)	80 ˚C	10%	DIPEA	87%
12	Phenylglycine	CH_3CN:H_2O (1:1)	80 ˚C	10%	K_2PO_4	84%
13	Phenylglycine	CH_3CN:H_2O (1:1)	50 ˚C	5%	Et_3N	84%
14	Phenylglycine	CH_3CN:H_2O (1:1)	50 ˚C	10%	Et_3N	91%
15	Phenylglycine	EtOH	50 ˚C	10%	Et_3N	70%
16	**Phenylglycine**	**EtOH**	**70 ˚C**	**10%**	**Et_3N**	**92%**

17	Phenylglycine	*i*PrOH	70 ˚C	10%	Et_3N	10%
18	L-Serine	CH_3CN:H_2O (1:1)	50 ˚C	10%	Et_3N	0%
19	L-Tyrosine	CH_3CN:H_2O (1:1)	50 ˚C	10%	Et_3N	0%
20	L-Phenylalanine	CH_3CN:H_2O (1:1)	50 ˚C	10%	Et_3N	0%
21	L-Isoleucine	CH_3CN:H_2O (1:1)	50 ˚C	10%	Et_3N	0%
22	L-Alanine	CH_3CN:H_2O (1:1)	50 ˚C	10%	Et_3N	0%
23	L-Valine	CH_3CN:H_2O (1:1)	50 ˚C	10%	Et_3N	0%
24	L-Tryptophan	CH_3CN:H_2O (1:1)	50 ˚C	10%	Et_3N	0%
25	L-Valine	CH_3CN:H_2O (1:1)	70 ˚C	10%	Et_3N	0%
26	Phenylglycine	EtOH	70 ˚C	10%[b]	Et_3N	7%
27	L-Valine	EtOH	70 ˚C	10%[b]	Et_3N	0%
28	Phenylglycine	EtOH	70 ˚C	10%[c]	Et_3N	20%
29	L-Valine	EtOH	70 ˚C	10%[c]	Et_3N	0%
30	Phenylglycine	EtOH	70 ˚C	10%[d]	Et_3N	0%
31	L-Valine	EtOH	70 ˚C	10%[d]	Et_3N	0%
32	Phenylglycine	EtOH	70 ˚C	10%[e]	Et_3N	15%
33	L-Valine	EtOH	70 ˚C	10%[e]	Et_3N	0%
34	Phenylglycine	EtOH	70 ˚C	10%[f]	Et_3N	15%
35	L-Valine	EtOH	70 ˚C	10%[f]	Et_3N	0%
36	Phenylglycine	EtOH	70 ˚C	10[g]	Et_3N	5%
37	L-Valine	EtOH	70 ˚C	10[g]	Et_3N	0%
38	Phenylglycine	EtOH	70 ˚C	10%[h]	Et_3N	6%
39	L-Valine	EtOH	70 ˚C	10%[h]	Et_3N	0%

[a] Determined by ^1H NMR using methyl benzoate as an internal standard. [b] p-benzoquinone was used in lieu of quinone **2**. [c] 2,6-dimethyl-1,4-benzoquinone was used in lieu of quinone **2**. [d] 2,5-di-tert-butyl-1,4-benzoquinone was used in lieu of quinone **2**. [e] 3,5-Di-tert-butyl-o-benzoquinone was used in lieu of quinone **2**. [f] 2-anilino-5-methyl-1,4-benzoquinone was used in lieu of quinone **2**. [g] chloronill was used in lieu of quinone **2**. [h] DDQ was used in lieu of quinone **2**

Table S2: NMR Yields for Optimization of in situ Mukaiyama–Mannich Addition

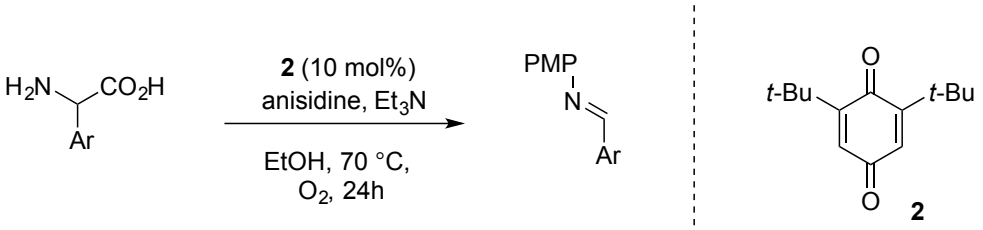


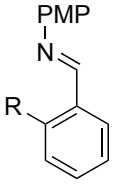
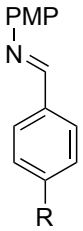
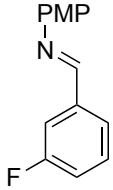
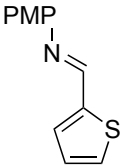
entry	**8**	HBF_4	yield[a]
1	2.0 equiv	1.5 equiv	0%
2	3.0 equiv	1.5 equiv	86%
3	4.0 equiv	1.5 equiv	84%
4	3.0 equiv	0 equiv	0%
5	3.0 equiv	0.5 equiv	8%
6	3.0 equiv	1.0 equiv	47%
7	3.0 equiv	2.0 equiv	82%

[a] NMR yields with methyl benzoate as the internal standard.

Part 4: NMR Yields for Quinone-Catalyzed Oxidative Decarboxylation Reactions

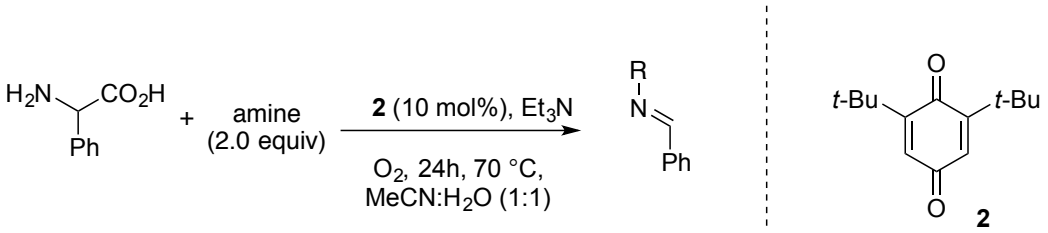
Table S3: NMR Yields for Quinone-Catalyzed Oxidative Decarboxylation Reactions with Aryl Glycine Derivatives and Anisidine



entry	product	yield[a]	entry	product	yield[a]
1		R = H, 92%	5		R = Me, 98%
2		R = Me, 97%	6		R = OMe[b], 88%
3		R = Cl, 97%	7		R = F, 98%
			8		R = Cl, 98%
			9		R = Br, 99%
4		97%	10		92%

[a] NMR yields with methyl benzoate as the internal standard. [b]48 h.

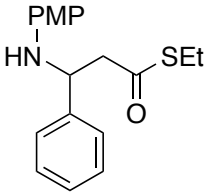
Table S4: NMR Yields for Quinone-Catalyzed Oxidative Decarboxylation Reactions with Phenylglycine and Various Amines



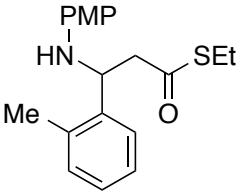
entry	amine	yield[a]	entry	amine	yield[a]
1	p-anisidine	91%	11	Benzhydrylamine	45%
2	3,5-dimethoxyaniline	37%	12	Di-p-anisylmethylamine	39%
3	4-Methylaniline	28%	13	2-picolylamine	0%
4	2-methylbenzylamine	75%	14	5-Methylfurfurylamine	39%
5	3-methylbenzylamine	47%	15	α-methylbenzylamine	77%
6	4-methylbenzylamine	37%	16	4−fluoro-α-methylbenzylamine	93%
7	3-methoxybenzylamine	30%	17	phenethylamine	0%
8	4-methoxybenzylamine	67%	18	tryptamine	32%
9	4-chlorobenzylamine	10%	19	t-butylamine	56%
10	1-Naphthylmethylamine	60%	20	allylamine	0%

[a] NMR yields with methyl benzoate as the internal standard.

Part 5: Experimental Procedures and Characterization Data for 9a−9j, 11a−11j, 13, 14, and 15

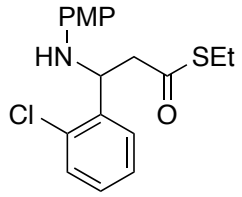


S-ethyl 3-((4-methoxyphenyl)amino)-3-phenylpropanethioate (9a): The reaction was carried out according to the general procedure **(A)** using 2-Phenylglycine (75.6 mg, 0.50 mmol) to provide after purification product **9a** (117.6 mg, 75%) as an orange solid. IR (film) 2928, 2056, 1992, 1676 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) 7.37 (d, 2H *, J* = 7.6 Hz), 7.34 – 7.30 (m, 2H), 6.69 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 8.5 Hz, 2H), 4.76 (t, J = 6.7 Hz, 1H), 3.69 (s, 3H), 2.99 (d, J = 6.2 Hz, 2H), 2.86 (q, J = 7.4 Hz, 2H), 1.20 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) 197.6, 152.4, 142.4, 141.1, 128.9, 127.6, 126.4, 115.2, 114.8, 56.7, 55.8, 51.8, 23.8, 14.7; HMRS (ESI): Exact mass calcd for $C_{18}H_{21}NO_2S$ $[M+H^+]$, 316.1371. Found 316.1383.

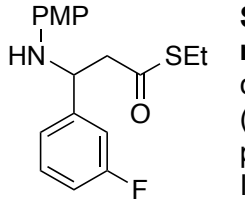


S-ethyl 3-((4-methoxyphenyl)amino)-3-(*o*-tolyl)propanethioate (9b): The reaction was carried out according to the general procedure **(A)** using 2-amino-2-(*o*-tolyl)acetic acid (82.6 mg, 0.50 mmol) to provide after purification product **9b** (92.8 mg, 56%) as an

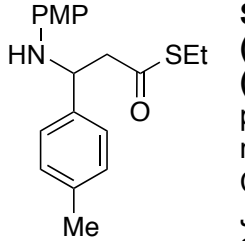
orange oil; IR (film) 3523, 3055, 2962, 1676 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 7.41 (d, 1H , *J* = 5.6 Hz), 7.21 – 7.11 (m, 3H), 6.68 (d, 2H, *J* = 8.3 Hz), 6.45 (d, 2H, *J* = 8.3 Hz), 4.94 (dd, 1H , J = 8.4, 5.0 Hz), 3.69 (s, 3H), 2.87 (m, 4H), 2.45 (s, 3H), 1.21 (t, 3H , *J* = 7.4 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) 197.7, 152.4, 141.2, 140.0, 134.9, 130.9, 127.4, 126.8, 125.4, 114.90, 114.87, 55.8, 53.1, 50.2, 23.8, 19.3, 14.7; HMRS (ESI): Exact mass calcd for $C_{19}H_{24}NO_2S$ [M+H^+], 330.1528. Found 330.1536.



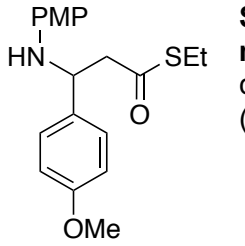
S-ethyl 3-(2-chlorophenyl)-3-((4-methoxyphenyl)amino)propanethioate (9c): The reaction was carried out according to the general procedure **(A)** using 2-amino-2-(2-chlorophenyl)acetic acid (92.8 mg, 0.50 mmol) while 1 equivalent of silyl ketene (thio)acetal (0.50 mmol) was added and the addition was repeated twice after each 30min to provide after purification product **9c** (166.6mg, 95%) as an orange oil. IR (film) 3390, 3062, 2966, 1674 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 7.45 – 7.41 (m, 1H), 7.40 – 7.37 (m, 1H), 7.22 – 7.14 (m, 2H), 6.72 – 6.63 (m, 2H), 6.47 – 6.38 (m, 2H), 5.13 (dd, 1H, *J* = 9.0, 3.7 Hz), 4.57 (bs, 1H), 3.68 (s, 3H), 3.09 (dd, 1H, *J* = 14.6, 3.7 Hz), 2.98 – 2.67 (m, 3H), 1.21 (t, 3H, *J* = 7.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) 197.7, 152.4, 140.6, 138.9, 132.7, 130.0, 128.7, 127.9, 127.4, 114.9, 114.8, 55.8, 53.6, 49.1, 23.8, 14.7; HMRS (ESI): Exact mass calcd for $C_{18}H_{21}NO_2SCl$ [M+H^+], 350.0982. Found 350.0975.



S-ethyl 3-(3-fluorophenyl)-3-((4-methoxyphenyl)amino)propanethioate (9d): The reaction was carried out according to the general procedure **(A)** using 2-amino-2-(3-fluorophenyl)acetic acid (84.6 mg, 0.50 mmol) to provide after purification product **9d** (130.1mg, 78%) as an orange solid, m.p. 84 °C. IR (KBr pellet) 3402, 3070, 2989, 1672 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 7.32 – 7.27 (m, 1H), 7.16 (d, 1H, *J* = 7.7 Hz,), 7.09 (dt, 1H, *J* = 9.8, 2.1 Hz), 6.93 (app td, 1H), 6.70 (d, 2H, J = 8.7 Hz, 1H), 6.51 (d, 2H, J = 8.3 Hz), 4.74 (t, 1H, *J* = 6.7 Hz), 3.70 (s, 3H), 2.98 (d, 2H, *J* = 6.6 Hz), 2.86 (q, 2H, *J* = 7.4 Hz), 1.21 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) 197.3, 163.3 (d, *J* = 247.0 Hz), 152.6, 145.2 (d, *J* = 6.3 Hz), 140.6, 130.4 (d, *J* = 7.6 Hz), 122.1 (d, *J* = 2.5 Hz), 115.3, 114.9, 114.5 (d, *J* = 21.4 Hz), 113.4 (d, *J* = 22.7 Hz), 56.4, 55.8, 51.5, 23.8, 14.7 ; HMRS (ESI): Exact mass calcd for $C_{18}H_{21}NO_2SF$ [M+H^+], 334.1277. Found 334.1281.

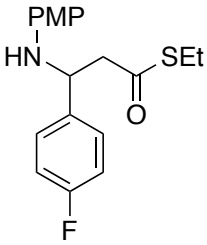


S-ethyl 3-((4-methoxyphenyl)amino)-3-(p-tolyl)propanethioate (9e): The reaction was carried out according to the general procedure **(A)** using 2-amino-2-(*p*-tolyl)acetic acid (82.6 mg, 0.50 mmol) to provide after purification product **9e** (146.2mg, 89%) as a brown solid, m.p. 68 °C. IR (KBr) 3398, 3041, 2904, 1681 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 7.25 (d, 2H, *J* = 8.1 Hz), 7.13 (d, 2H, *J* = 7.8 Hz), 6.69 (d, 2H, *J* = 9.0 Hz), 6.51 (d, 2H, *J* = 8.9 Hz), 4.73 (t, 1H, J = 6.8 Hz), 3.69 (s, 3H), 2.98 – 2.92 (m, 2H), 2.86 (q, 2H, *J* = 7.4 Hz), 2.32 (s, 3H), 1.21 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) 197.6, 152.4, 141.1, 139.3, 137.2, 129.6, 126.3, 115.3, 114.8, 56.5, 55.8, 51.9, 23.7, 21.2, 14.7; HMRS (ESI): Exact mass calcd for $C_{19}H_{24}NO_2S$ [M+H^+], 330.1528. Found 330. 1520.

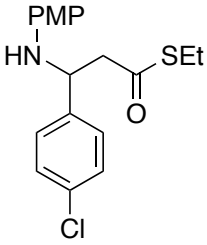


S-ethyl 3-(4-methoxyphenyl)-3-((4-methoxyphenyl)amino)propanethioate (9f): The reaction was carried out according to the general procedure **(A)** using 2-amino-2-(4-methoxyphenyl)acetic acid (120.6 mg, 0.50 mmol) while the

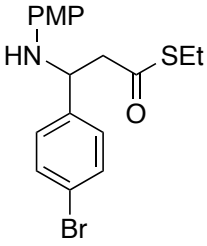
reaction was stirred for 48h in ethanol at 70°C to provide after purification product **9f** (151.8mg, 88%) as a lilac solid, m.p. 74 °C. IR (KBr pellet) 3384, 3068, 2929, 1676 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 7.29 (s, 1H), 6.87 – 6.82 (m, 2H), 6.71 – 6.67 (m, 2H), 6.52 (d, 2H, *J* = 8.9 Hz), 4.71 (dd, 1H, *J* = 7.8, 5.7 Hz), 3.78 (s, 3H), 3.69 (s, 3H), 3.00 – 2.91 (m, 2H), 2.89 – 2.81 (q, 2H, *J* = 7.4 Hz,), 1.20 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) 197.6, 158.8, 152.4, 140.8, 134.1, 127.4, 115.2, 114.7, 114.1, 56.1, 55.7, 55.3, 51.7, 23.6, 14.6; HMRS (ESI): Exact mass calcd for $C_{19}H_{24}NO_3S$ $[M+H^+]$, 346.1477. Found 346.1469. [i]



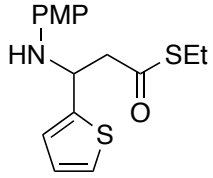
S-ethyl 3-(4-fluorophenyl)-3-((4-methoxyphenyl)amino)propanethioate (9g): The reaction was carried out according to the general procedure **(A)** using 2-amino-2-(4-fluorophenyl)acetic acid (84.6 mg, 0.50 mmol) to provide after purification product **9g** (139.8mg, 84%) as an orange solid, m.p. 90 °C. IR (KBr pellet) 3371, 3016, 2983, 1668 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 7.33 (m, 2H), 7.00 (app t, 2H), 6.69 (d, 2H, *J* = 8.9 Hz), 6.50 (d, 2H, *J* = 8.9 Hz), 4.76 – 4.70 (t, 1H, *J* = 6.7 Hz), 3.70 (s, 3H), 2.97 (m, 2H), 2.85 (q, 2H, J = 7.4 Hz), 1.20 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) 197.4, 162.2 (d, *J* = 243.8 Hz), 152.6, 140.7, 137.9, 128.1(d, *J* = 8.8 Hz), 115.8 (d, *J* = 21.4 Hz), 115.4, 114.8, 56.1, 55.8, 51.7, 23.8, 14.7; HMRS (ESI): Exact mass calcd for $C_{18}H_{21}NO_2SF$ $[M+H^+]$, 334.1277. Found 334.1281.



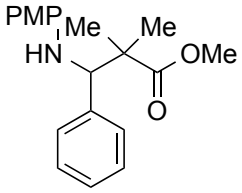
S-ethyl 3-(4-chlorophenyl)-3-((4-methoxyphenyl)amino)propanethioate (9h): The reaction was carried out according to the general procedure **(A)** using 2-amino-2-(4-chlorophenyl)acetic acid (92.8 mg, 0.50 mmol) to provide after purification product **9h** (164.5mg, 94%) as an orange oil. IR (film) 3382, 3060, 2929, 1666 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 7.33 – 7.27 (m, 4H), 6.69 (d, *J* = 8.9 Hz, 2H), 6.48 (d, *J* = 8.8 Hz, 2H), 4.72 (t, 1H, *J* = 6.7 Hz), 3.69 (s, 3H), 2.98 – 2.92 (m, 2H), 2.86 (q, *J* = 7.4 Hz, 2H), 1.21 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) 197.3, 152.6, 140.9, 140.7, 133.2, 129.1, 127.9, 115.3, 114.8, 56.1, 55.8, 51.6, 23.8, 14.7; HMRS (ESI): Exact mass calcd for $C_{18}H_{21}ClNO_2S$ $[M+H^+]$, 350.0982. Found 350.0984.



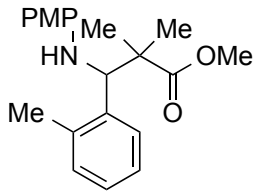
S-ethyl 3-(4-bromophenyl)-3-((4-methoxyphenyl)amino)propanethioate (9i): The reaction was carried out according to the general procedure **(A)** using 2-amino-2-(4-bromophenyl)acetic acid (115.0 mg, 0.50 mmol) to provide after purification product **9i** (142.0mg, 72%) as a dark orange solid, m.p. 70 °C. IR (KBr pellet) 3392, 3056, 2960, 1679 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 7.46 – 7.42 (m, 2H), 7.26 – 7.23 (m, 2H), 6.69 (d, 2H, *J* = 8.9 Hz), 6.48 (d, 2H, *J* = 8.9 Hz), 4.70 (t, 1H, *J* = 6.7 Hz), 3.69 (s, 3H), 2.97 – 2.92 (m, 2H), 2.86 (q, 2H, *J* = 7.5 Hz), 1.21 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) 197.3, 152.7, 141.3, 140.5, 132.0, 128.3, 121.4, 115.4, 114.9, 56.3, 55.8, 51.5, 23.8, 14.7; HMRS (ESI): Exact mass calcd for $C_{18}H_{21}BrNO_2S$ $[M+H^+]$, 394.0476. Found 394.0484



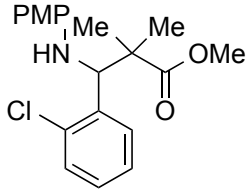
S-ethyl 3-((4-methoxyphenyl)amino)-3-(thiophen-2-yl)propanethioate (9j): The reaction was carried out according to the general procedure **(A)** using 2-amino-2-(thiophen-2-yl)acetic acid (78.6 mg, 0.50 mmol) to provide after purification product **9j** (123.3 mg, 77%) as an orange oil. IR (film) 3369, 3066, 2929, 1666 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 7.18 (dd, 1H, *J* = 5.0, 1.2 Hz), 6.98 (app dt, 1H), 6.93 (dd, 1H, J = 5.0, 3.5 Hz), 6.78 – 6.69 (m, 2H), 6.66 – 6.58 (m, 2H), 5.09 (dd, 1H, *J* = 7.1, 6.0Hz), 4.19 (bs, 1H), 3.72 (s, 3H), 3.13 (dd, 1H, *J* = 15.0, 7.4 Hz), 3.07 (dd, 1H, *J* = 14.9, 5.6 Hz), 2.88 (q, 2H, *J* = 7.4 Hz), 1.22 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) 197.1, 152.9, 147.1, 140.5, 126.9, 124.4, 124.0, 115.8, 114.8, 55.7, 52.8, 51.4, 23.7, 14.7; HMRS (ESI): Exact mass calcd for $C_{16}H_{20}NO_2S_2$ [M+H$^+$], 322.0935. Found 322.0906



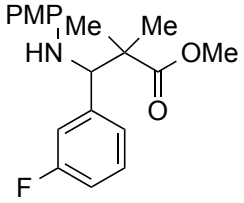
methyl 3-((4-methoxyphenyl)amino)-2,2-dimethyl-3-phenylpropanoate (11a): The reaction was carried out according to the general oxidation procedure **(B)** using 2-Phenylglycine (75.6 mg, 0.50 mmol) to provide after purification product **11a** (140.0. mg, 89%) as a white crystal; m.p. 87.7°C; IR (KBr) 3369, 2955, 1716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.32 – 7.22 (m, 4H), 7.24 – 7.18 (m, 1H), 6.63 (d, 2H, J = 8.9 Hz), 6.45 (d, 2H J = 8.8 Hz), 4.45 (s, 1H), 3.65 (s, 6H), 1.24 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 177.3, 152.1, 141.3, 139.5, 128.5, 128.1, 127.5, 114.9, 114.8, 65.4, 55.8, 52.2, 47.3, 24.6, 20.6; HMRS (ESI): Exact mass calcd for $C_{19}H_{23}NO_3$ [M+H], 314.1756. Found 314.1747.



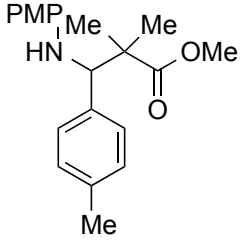
methyl 3-((4-methoxyphenyl)amino)-2,2-dimethyl-3-(*o*-tolyl) propanoate (11b): The reaction was carried out according to the general oxidation procedure **(B)** using 2-amino-2-(*o*-tolyl)acetic acid (82.6 mg, 0.50 mmol) to provide after purification product **11b**, 15% by NMR) as a white crystal; m.p. 87.4°C; IR (KBr) 3389, 3066, 2831, 1742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.24 (s, 1H), 7.15 – 7.08 (m, 3H), 6.64 (d, 2H, J = 8.9 Hz), 6.43 (d, 2H J = 8.4 Hz), 4.82 (s, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 2.50 (s, 3H), 1.26 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 177.5, 152.2, 136.7, 130.6, 130.6, 127.3, 127.2, 126.0, 126.0, 114.9, 114.9, 60.3, 55.8, 52.3, 48.4, 24.7, 20.6, 20.3; HMRS (ESI): Exact mass calcd for $C_{20}H_{25}NO_3$ [M+H$^+$], 328.1913. Found 328.1922.



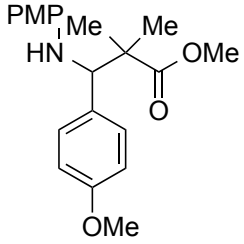
methyl 3-(2-chlorophenyl)-3-((4-methoxyphenyl)amino)-2,2-dimethylpropanoate (11c): The reaction was carried out according to the general oxidation procedure **(B)** using 2-amino-2-(2-chlorophenyl)acetic acid (92.8 mg, 0.50 mmol) to provide after purification product **11c** (112.3 mg, 65%) as a white crystal; m.p. 107.2 °C; IR (KBr) 3402, 2995, 2833, 1718 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.39 – 7.35 (m, 1H), 7.34 – 7.30 (m, 1H), 7.22 – 7.14 (m, 2H), 6.69 (d, 2H, J = 8.9 Hz), 6.51 (d, 2H, J = 8.9 Hz), 5.12 (s, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 1.39 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 177.2, 152.2, 140.9, 137.8, 135.2, 129.6, 128.9, 128.7, 127.0, 114.9, 114.5, 60.1, 55.8, 52.3, 48.0, 25.0, 20.5; HMRS (ESI): Exact mass calcd for $C_{19}H_{22}ClNO_3$ [M+H], 348.1366. Found 348.1356.



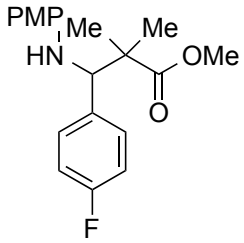
methyl 3-(3-fluorophenyl)-3-((4-methoxyphenyl)amino)-2,2-dimethylpropanoate (11d): The reaction was carried out according to the general oxidation procedure **(B)** using 2-amino-2-(3-fluorophenyl)acetic acid (84.6 mg, 0.50 mmol) to provide after purification product **11d (**155.0 mg, 94%) as a white crystal; m.p. 118.1 °C; IR (KBr) 3389, 3066, 2901, 1707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.28 – 7.22 (m, 1H), 7.07 (app dt, 1H), 7.00 (app dt, 1H), 6.93 (app tdd, 1H), 6.66 (d, 2H, J = 8.9 Hz), 6.45 (d, 2H, J = 8.9 Hz), 4.44 (s, 1H), 3.67 (s, 3H), 3.67 (s, 3H), 1.26 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 177.0, 162.9 (d, J = 245.9 Hz) , 152.3, 142.6 (d, J = 5.0 Hz), 141.0, 129.5 (d, J = 8.1 Hz), 124.3 (d, J = 2.9 Hz), 115.3 (d, J = 21.7 Hz), 114.872, 114.870, 114.6 (d, J = 21.2 Hz), 65.1, 55.8, 52.3, 47.2, 24.6, 20.8; HMRS (ESI): Exact mass calcd for $C_{19}H_{22}FNO_3$ [M+H], 332.1662. Found 332.1651.



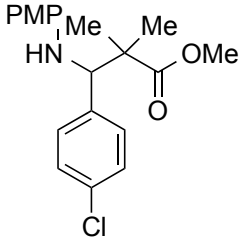
methyl 3-((4-methoxyphenyl)amino)-2,2-dimethyl-3-(*p*-tolyl) propanoate (11e): The reaction was carried out according to the general oxidation procedure **(B)** using 2-amino-2-(*p*-tolyl)acetic acid (82.6 mg, 0.50 mmol) to provide after purification product **11e** (131.0 mg, 80%) as a white crystal; m.p. 111.4 °C; IR (KBr) 3379, 2995, 2825, 1718 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.16 (d, 2H, J = 7.9 Hz), 7.09 (d, 2H, J = 7.9 Hz), 6.65 (d, 2H, J = 8.9 Hz), 6.47 (d, 2H, J = 8.9 Hz), 4.44 (s, 1H), 3.67 (s, 6H), 2.30 (s, 3H), 1.24 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 177.3, 152.0, 141.4, 137.1, 136.4, 128.8, 128.4, 114.9, 114.8, 65.1, 55.8, 52.2, 47.3, 24.6, 21.2, 20.6; HMRS (ESI): Exact mass calcd for $C_{20}H_{25}NO_3$ [M+], 327.1834. Found 327.1845.



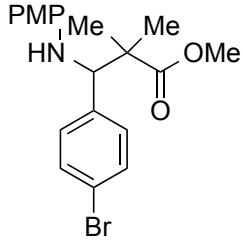
methyl 3-(4-methoxyphenyl)-3-((4-methoxyphenyl)amino)-2,2-dimethylpropanoate (11f): The reaction was carried out according to the general oxidation procedure **(B)** using 2-amino-2-(4-methoxyphenyl) acetic acid (120.6 mg, 0.50 mmol) to provide after purification product **11f (**142.5 mg, 83%) as a white crystal; m.p. 102.4 °C; IR (KBr) 3416, 2978, 2833, 1724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.21 (d, 2H, J = 8.7 Hz), 6.84 (d, 2H, J = 8.7 Hz), 6.67 (d, 2H, J = 8.9 Hz), 6.48 (d, 2H, J = 8.9 Hz), 4.43 (s, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 1.26 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 177.4, 159.0, 152.0, 141.4, 131.4, 129.5, 114.9, 114.8, 113.5, 64.7, 55.8, 55.3, 52.2, 47.4, 24.6, 20.6; HMRS (ESI): Exact mass calcd for $C_{20}H_{25}NO_4$ [M+], 343.1784. Found 343.1781.



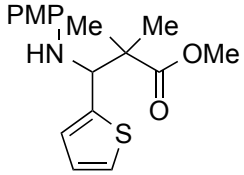
methyl 3-(4-fluorophenyl)-3-((4-methoxyphenyl)amino)-2,2-dimethylpropanoate (11g): The reaction was carried out according to the general oxidation procedure **(B)** using 2-amino-2-(4-fluorophenyl)acetic acid (84.6 mg, 0.50 mmol) to provide after purification product **11g (**132.7 mg, 80%) as a white crystal; m.p. 99.1 °C; IR (KBr) 3371, 2983, 1714 cm^{-1};-^1H NMR (400 MHz, $CDCl_3$) 7.25 (dd, 2H, J = 8.5, 5.4 Hz), 6.98 (app t, 2H), 6.66 (d, 2H, J = 8.8 Hz), 6.44 (d, 2H, J = 8.8 Hz), 4.44 (s, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 1.25 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 177.1, 163.5, 161.0, 152.2, 141.1, 135.3 (d, J = 3.3 Hz), 129.9 (d, J = 8.0 Hz), 115.1 (d, J = 21.3 Hz), 114.8 (d, J = 2.3 Hz), 64.8, 55.8, 52.3, 47.2, 24.5, 20.7; HMRS (ESI): Exact mass calcd for $C_{19}H_{22}FNO_3$ [M+H], 332.1662. Found 332.1653.



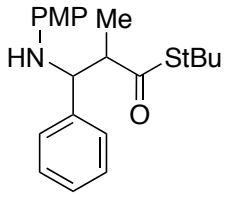
methyl 3-(4-chlorophenyl)-3-((4-methoxyphenyl)amino)-2,2-dimethylpropanoate (11h): The reaction was carried out according to the general oxidation procedure **(B)** using 2-amino-2-(4-chlorophenyl)acetic acid (92.8 mg, 0.50 mmol) to provide after purification product **11h (**151.7 mg, 87%) as a white crystal; m.p. 137.0 °C; IR (KBr) 3373, 2953, 2926, 1718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.30 – 7.20 (m, 4H), 6.66 (d, 2H, J = 8.9 Hz), 6.44 (d, 2H, J = 8.9 Hz), 4.43 (s, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 1.26 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 177.0, 152.3, 141.0, 138.2, 133.3, 129.8, 128.4, 114.9, 114.9, 64.9, 55.8, 52.3, 47.1, 24.5, 20.7; HMRS (ESI): Exact mass calcd for $C_{19}H_{22}ClNO_3$ [M+], 347.1288. Found 347.1223.



methyl 3-(4-bromophenyl)-3-((4-methoxyphenyl)amino)-2,2-dimethylpropanoate (11i): The reaction was carried out according to the general oxidation procedure **(B)** using 2-amino-2-(4-bromophenyl)acetic acid (115.0 mg, 0.50 mmol) to provide after purification product **11i** (166.0. mg, 85%) as a white crystal; m.p. 144.3 °C; IR (KBr) 3379, 2978, 2825, 1716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.44 (d, 2H, J = 8.5 Hz), 7.19 (d, 2H, J = 8.4 Hz), 6.68 (d, 2H, J = 8.9 Hz), 6.45 (d, 2H, J = 9.0 Hz), 4.43 (s, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 1.27 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 177.0, 152.2, 140.9, 138.8, 131.3, 130.2, 121.5, 114.9, 114.9, 65.0, 55.8, 52.3, 47.1, 24.6, 20.7; HMRS (ESI): Exact mass calcd for $C_{19}H_{22}BrNO_3$ [M+], 391.0783. Found 391.0787.



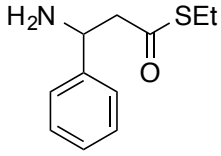
methyl 3-((4-methoxyphenyl)amino)-2,2-dimethyl-3-(thiophen-2-yl)propanoate (11j): The reaction was carried out according to the general oxidation procedure **(B)** using 2-amino-2-(thiophen-2-yl)acetic acid (78.6 mg, 0.50 mmol) to provide after purification product **11j** (131.0. mg, 82%) as a white crystal; m.p. 85.9 °C; IR (KBr) 3356, 3109, 2910, 1716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.18 – 7.14 (m, 1H), 6.94 – 6.90 (m, 2H), 6.70 (d, 2H, J = 8.9 Hz), 6.56 (d, 2H, J = 8.9 Hz), 4.77 (s, 1H), 3.69 (s, 6H), 1.31 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 177.0, 152.6, 144.5, 141.1, 126.6, 126.1, 124.5, 115.3, 114.8, 61.9, 55.8, 52.3, 47.6, 24.1, 21.3; HMRS (ESI): Exact mass calcd for $C_{17}H_{21}SNO_3$ [M+], 319.1242. Found 319.1252.



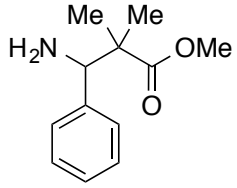
S-(tert-butyl) 3-((4-methoxyphenyl)amino)-2-methyl-3-phenylpropanethioate (13): To a solution of 2,6-di-*tert*-butyl-1,4-benzoquinone (11.0 mg, 0.050 mmol and p-anisidine (123.1 mg, 1.0 mmol) in ethanol (1.6 mL, 0.312 M with respect to phenylglycine) was added phenylglycine (0.50 mmol), followed by purging the reaction vial with a balloon of O_2. The reaction mixture was allowed to stir under O_2 at 70 °C for 24 hrs. The ethanol was removed by rotary evaporation and the oxidative decarboxylation product was further pumped for 0.5h with a high-vacuum pump. The remaining solid was dissolved in dry THF (1.6 mL, 0.312 M) and the solution was cooled to 0 °C. To this solution was added tetrafluoroboric acid solution (48 wt. % in H_2O, 90.0 μL, 0.75 mmol) and (Z)-((1-(tert-butylthio)prop-1-en-1-yl)oxy)trimethylsilane[3] (1.5 mmol). The resulting solution was warmed up to room temperature and allowed to

[3] Prepared according to: Chua, S. S.; Alni, A.; Chan, L. T. J.; Yamane, M.; Loh T. P. *Tetrahedron*, **2011**, *67*, 5079.

stir for 1.5h under Ar. Saturated aq. $NaHCO_3$ (0.5 mL) was added to quench the reaction and the two layers were separated. The organic phase was collected and dried (Na_2SO_4), filtered and concentrated under reduced pressure. Flash chromatography on basic alumina (5% ethyl acetate in hexanes with 1% TEA) provided product **13** (125.1mg, 70%) as inseparable diastereomers (d.r. = 4:1). IR (film) 3400, 3140, 2962, 1512 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) Key overlapping signals 7.31 – 7.17 (m, Ar H, obscured by $CHCl_3$), 6.67 – 6.59 (m, 2H), 6.49 – 6.40 (m, 2H), key signals for the major diastereomer 4.27 (d, 1H, *J* = 7.6 Hz), 3.64 (s, 3H), 2.83 (m, 1H), 1.39 (s, 9H), 1.09 (d, 3H, *J* = 7.0 Hz), key signals for the minor diastereomer 4.57 (d, 1H, *J* = 5.3 Hz), 3.65 (s, 3H), 2.91 (m, 1H), 1.35 (s, 9H), 1.14 (d, 3H, *J* = 7.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) 203.3, 202.9, 152.2, 152.0, 141.6, 141.4, 128.6, 128.6, 127.5, 127.3, 127.2, 127.2, 115.1, 114.8, 114.7, 114.6, 62.2, 61.4, 55.8, 55.8, 55.1, 54.9, 48.5, 48.3, 29.8, 16.0, 12.1; HMRS (ESI): Exact mass calcd for $C_{21}H_{28}NO_2S$ [$M+H^+$], 358.1841. Found 358.1702.



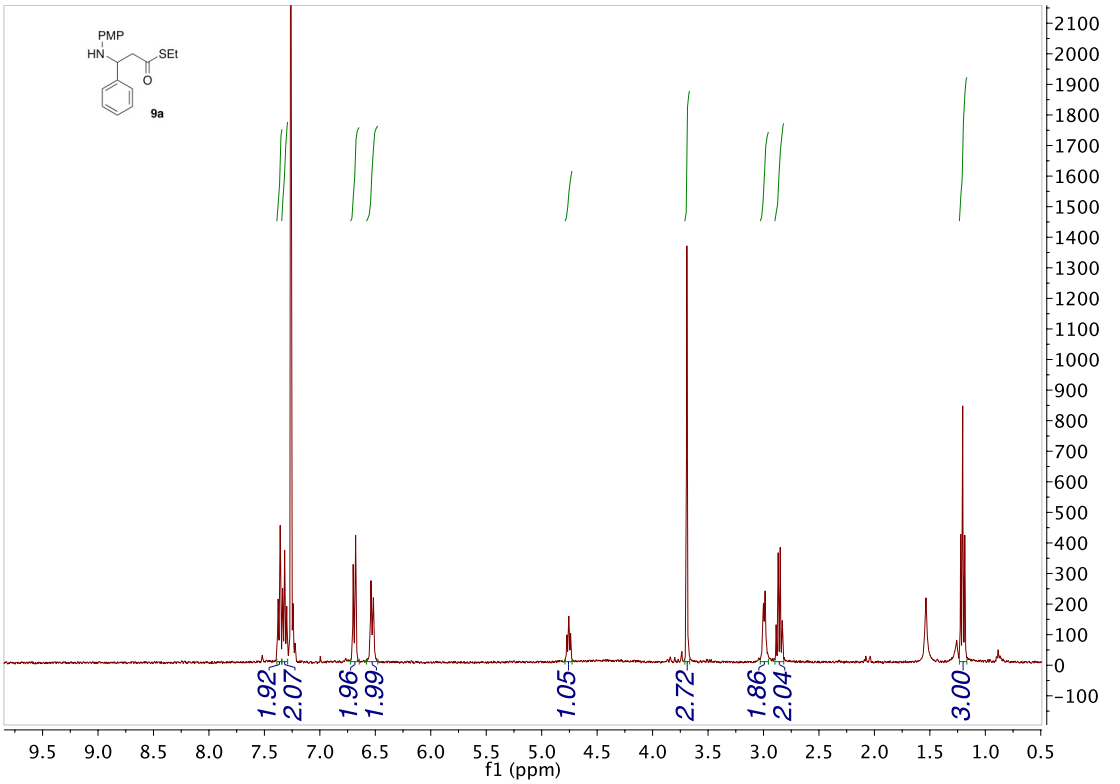
S-ethyl 3-((4-methoxyphenyl)amino)-3-phenylpropanethioate hydrochloride (14)[4]: 9a (0.5 mmol) was dissolved in CH_3CN (11 mL) and an aqueous solution of CAN (1.37g, 2.5 mmol in 8mL water) was added dropwise. The reaction mixture was stirred for 2 h. $NaHCO_3$ was added until pH 6 was reached. Sodium sulfite was then added until the mixture became brown. The product was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over sodium sulfate, evaporated and the obtained free amine **14** was provided (98.6 mg, 94%) as a brown oil. IR (film) 3413, 3388,3037, 2927, 1673 cm^{-1}. ^1H NMR (400 MHz, D_2O) 7.55 – 7.43 (m, 5H), 4.85 (t, *J* = 7.3 Hz, 1H), 3.42 (d, *J* = 7.3 Hz, 2H), 2.86 (q, *J* = 7.5 Hz, 2H), 1.15 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, D_2O) 199.6, 134.6, 129.6, 129.3, 127.0, 51.8, 46.2, 23.4, 13.5; HMRS (ESI): Exact mass calcd for $C_{11}H_{16}NOS$ [$M+H^+$], 210.0953. Found 210.0954.

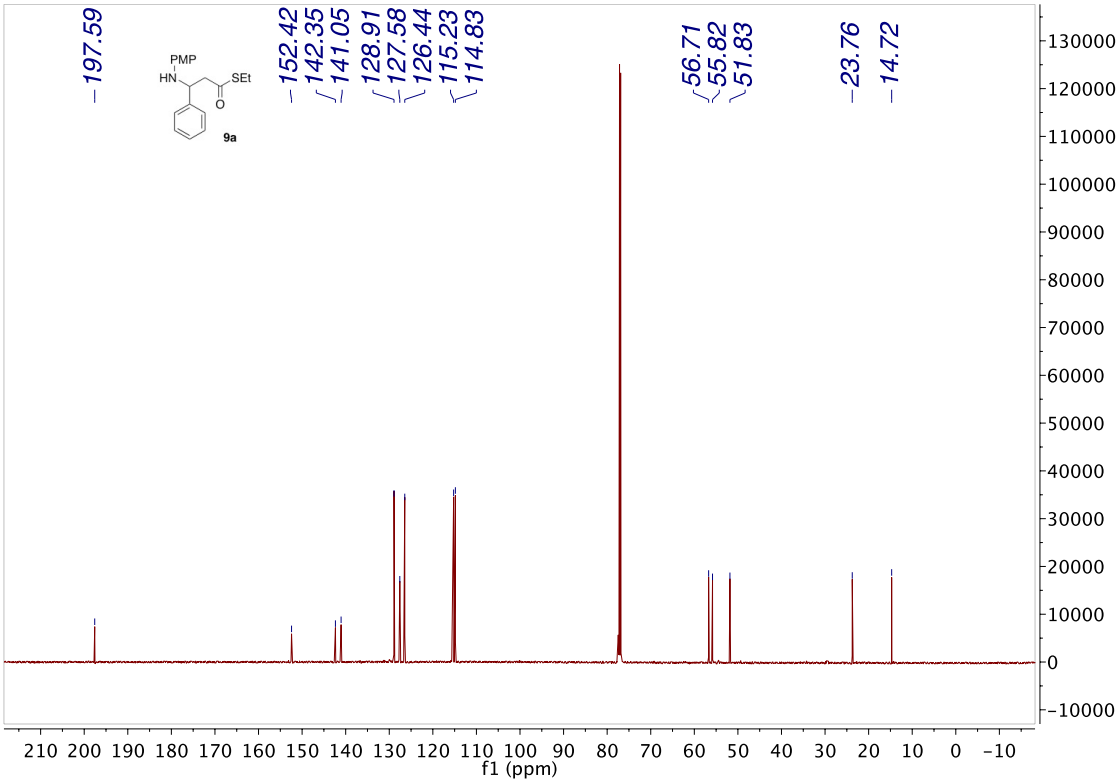


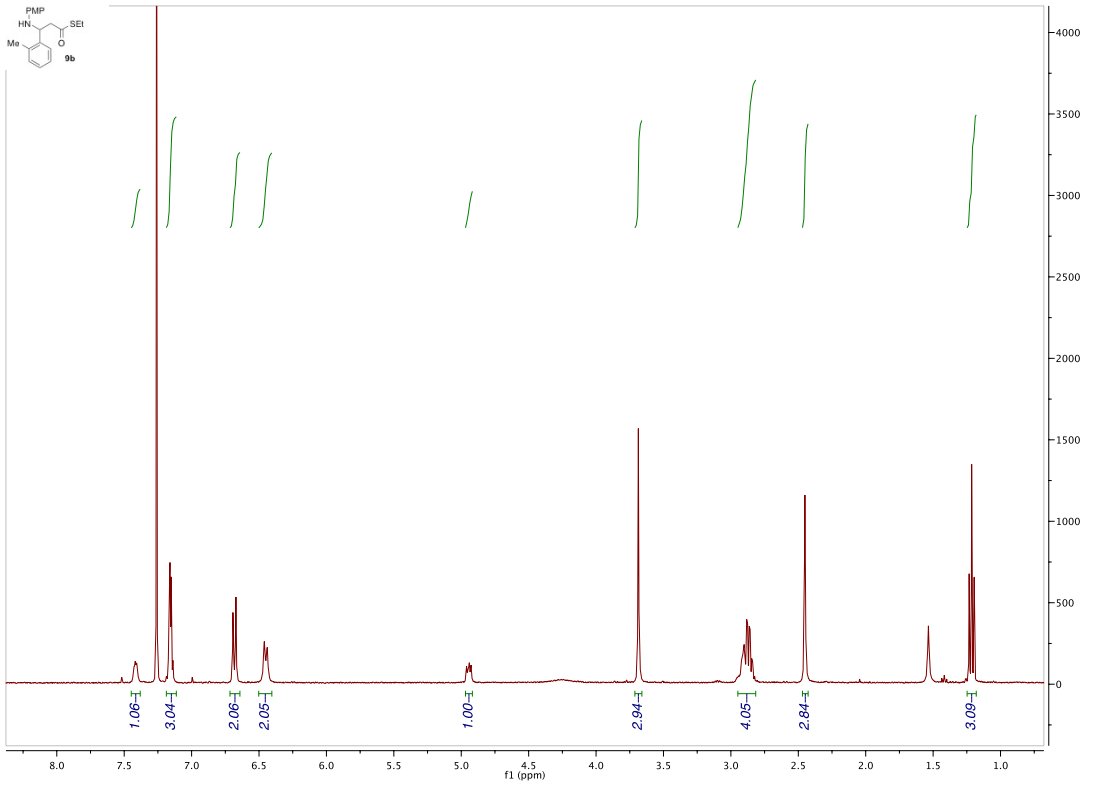
methyl 3-amino-2,2-dimethyl-3-phenylpropanoate (15)[4]: 11a (0.5 mmol) was dissolved in CH_3CN (11 mL) and an aqueous solution of CAN (1.37g, 2.5 mmol in 8mL water) was added dropwise. The reaction mixture was stirred for 2 h. $NaHCO_3$ was added until pH 6 was reached. Sodium sulfite was then added until the mixture became brown. The product was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over sodium sulfate, evaporated and the obtained free amine **15** was provided (92.6 mg, 89%) as a brown solid. IR (film) 2982, 2947, 2085, 1973, 1720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 7.35 – 7.22 (m, Ar H, obscured by $CHCl_3$), 4.24 (s, 1H), 3.69 (s, 3H), 1.15 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) 177.9, 141.6, 128.2, 128.0, 127.5, 62.0, 52.1, 47.8, 23.8, 19.6; HMRS (ESI): Exact mass calcd for $C_{12}H_{17}NO_2$ [$M+H^+$], 208.1338. Found 208.1358.

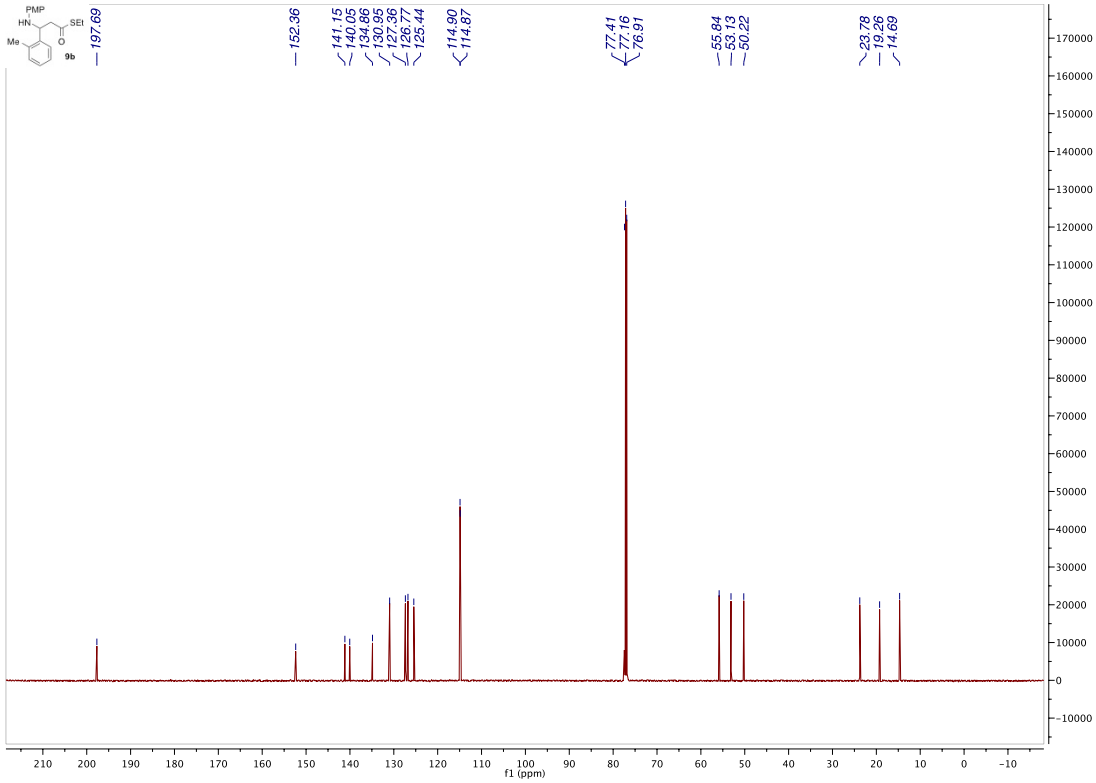
[4] Onodera, G.; Toeda, T.; Toda, N.; Shibagishi, D.; Takeuchi, R. *Tetrahedron*, **2010**, *66,* 9021

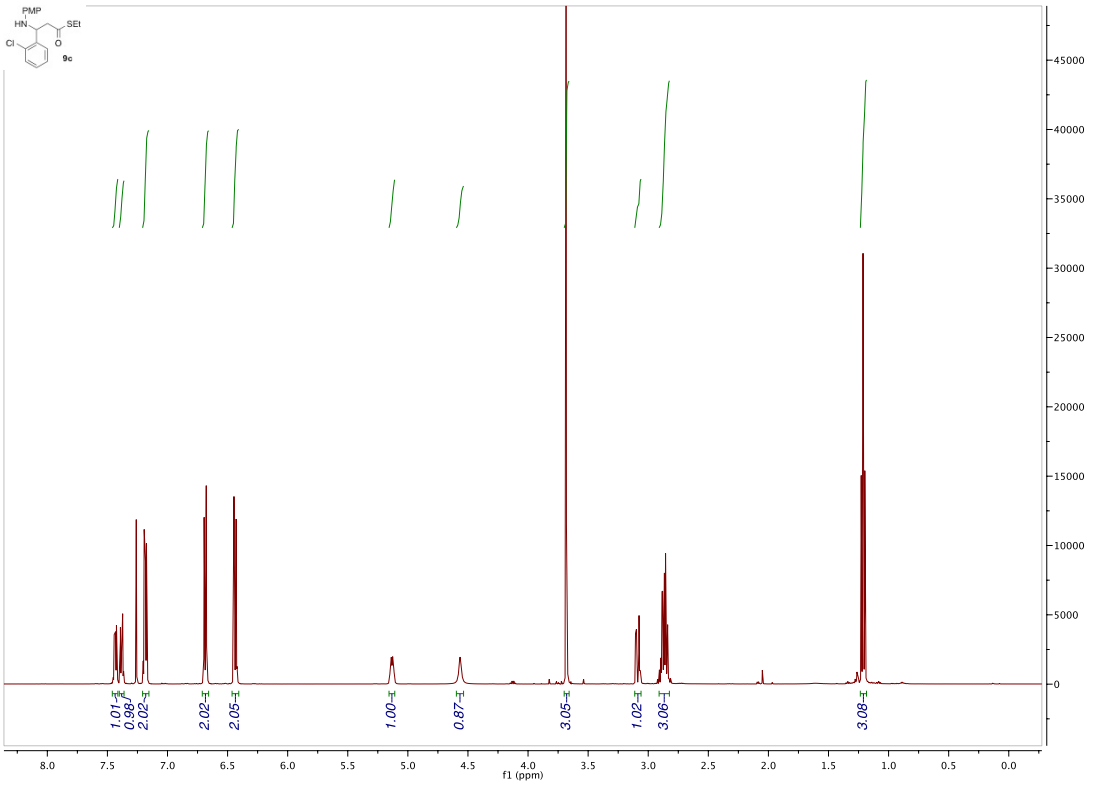
Part 6: ^{1}H and ^{13}C-NMR Spectra:

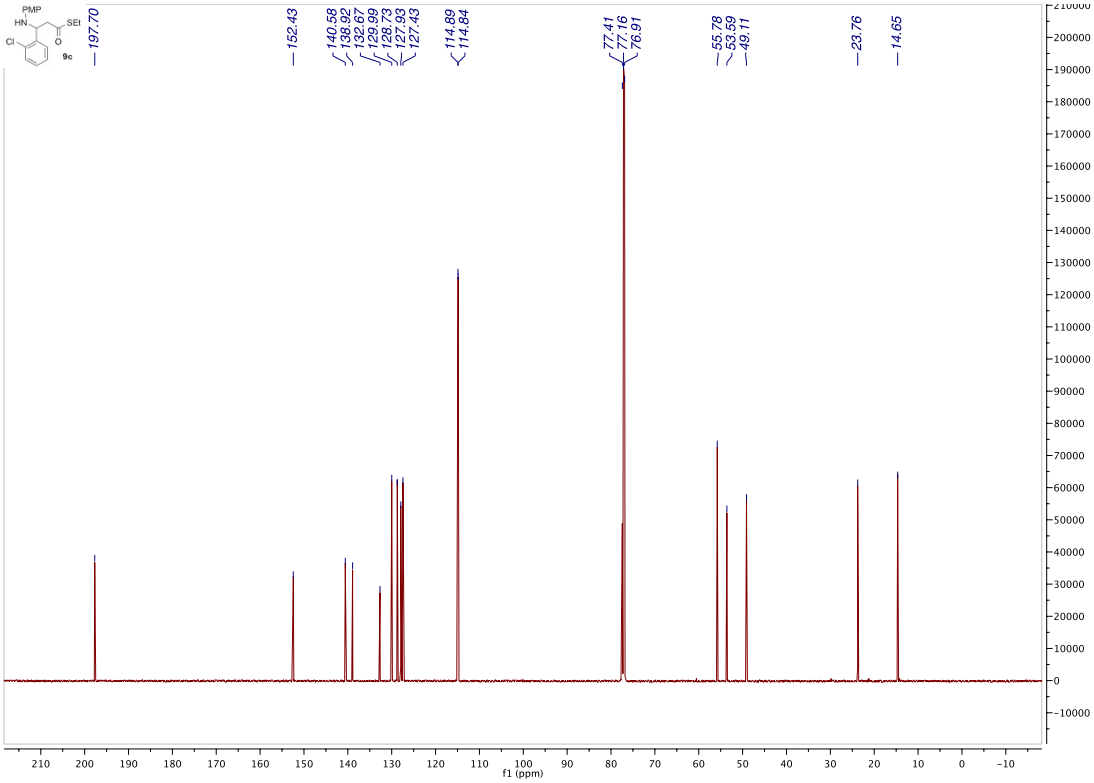


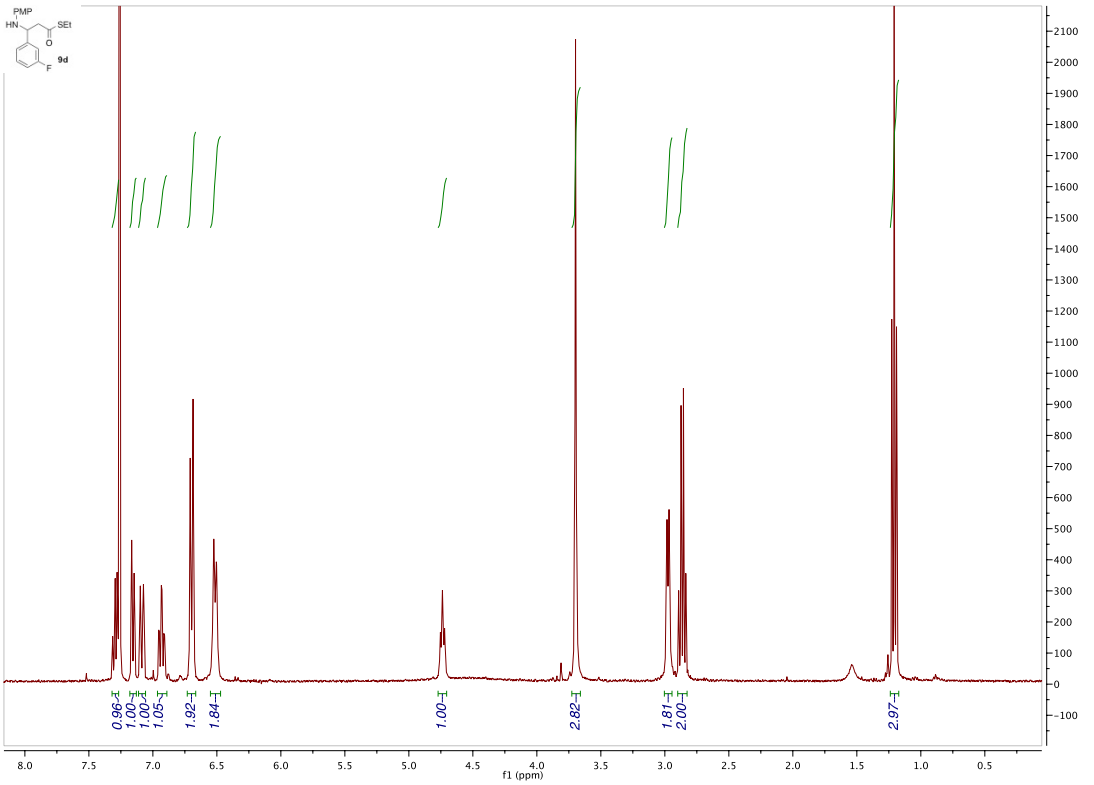


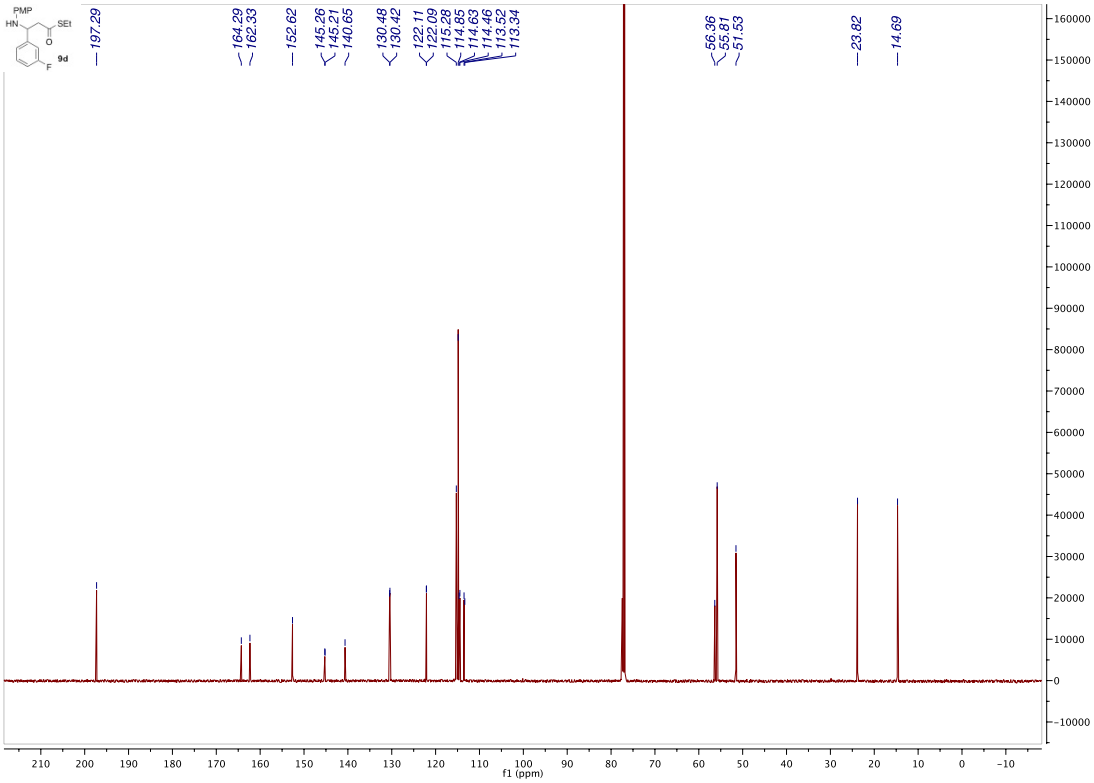

PMP
HN
SEt
Me
O
9b
1.06
3.04
2.06
2.05
1.00
2.94
4.05
2.84
3.09
f1 (ppm)

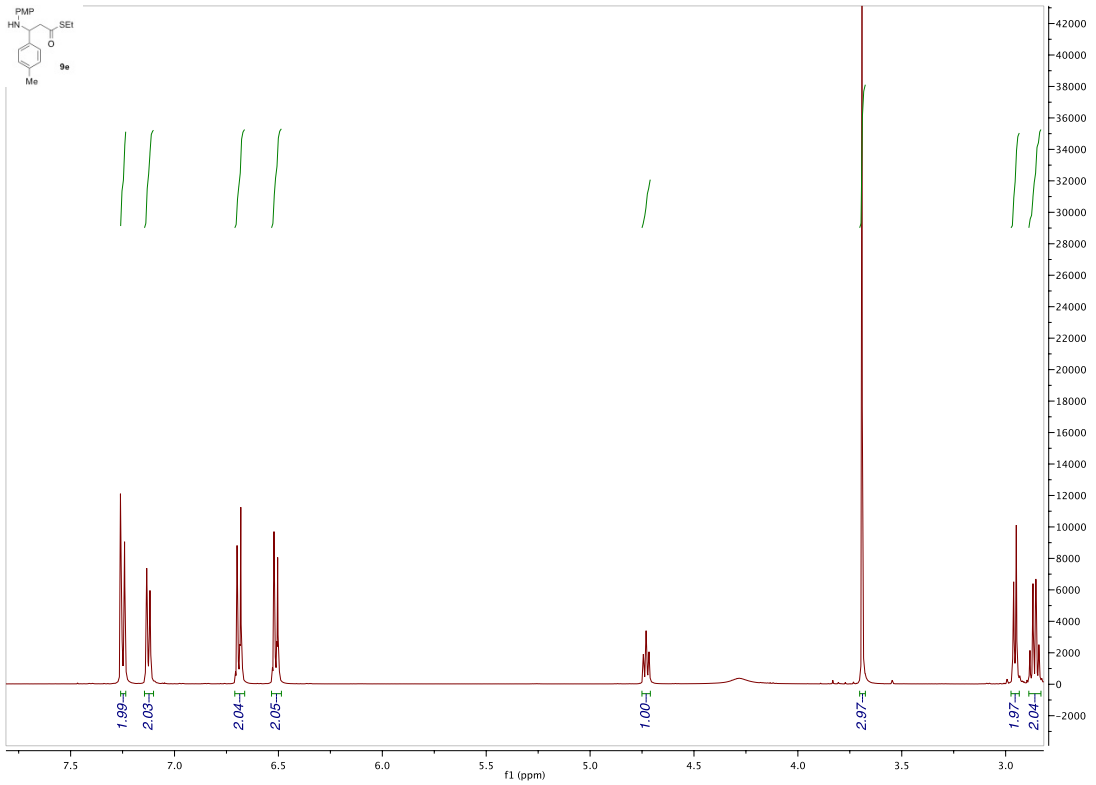

PMP
HN
SEt
Me
O
9b
197.69
152.36
141.15
140.05
134.86
130.95
127.36
126.77
125.44
114.90
114.87
77.41
77.16
76.91
55.84
53.13
50.22
23.78
19.26
14.69
f1 (ppm)

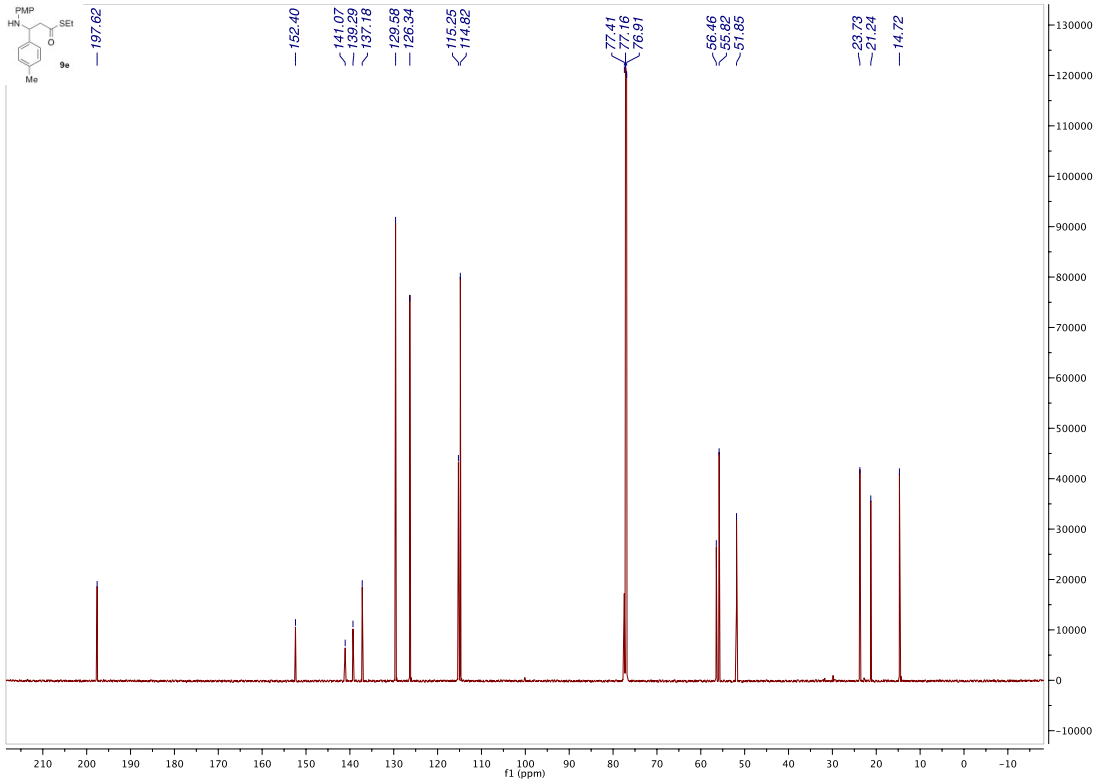

PMP
HN
SEt
O
Cl
9c
1.01
0.98
2.02
2.02
2.05
1.00
0.87
3.05
1.02
3.06
3.08
f1 (ppm)

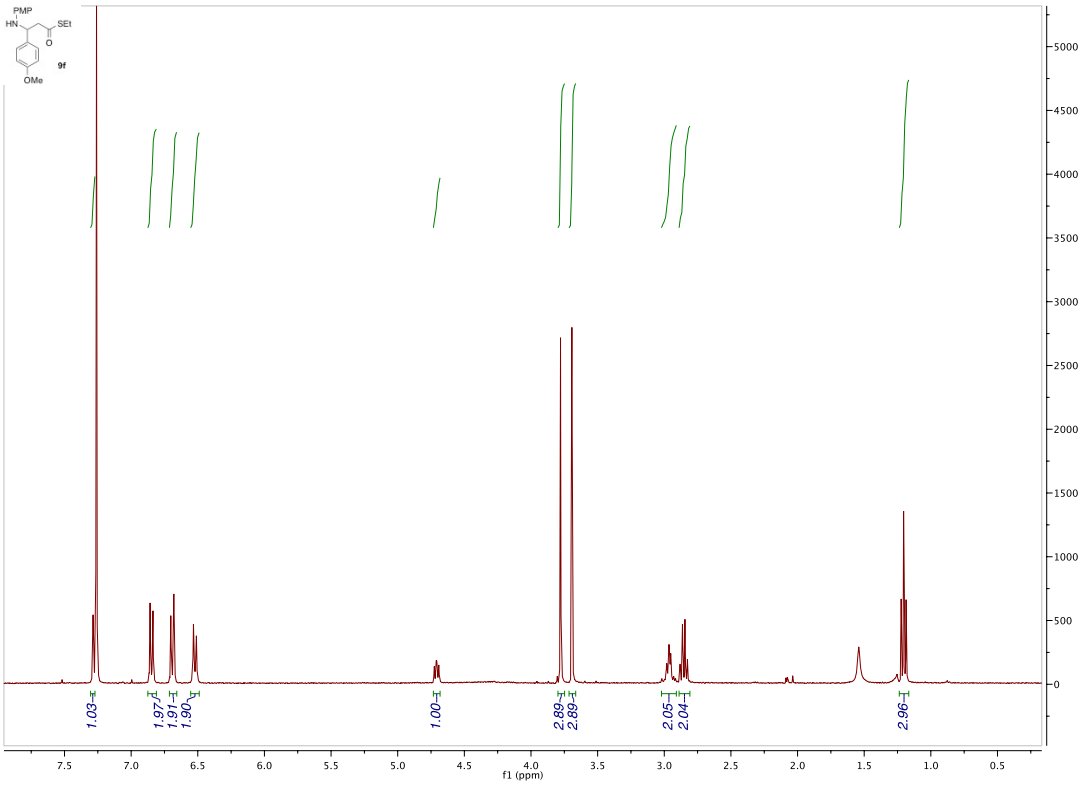

PMP
HN
SEt
O
Cl
9c
197.70
152.43
140.58
138.92
132.67
129.99
128.73
127.93
127.43
114.89
114.84
77.41
77.16
76.91
55.78
53.59
49.11
23.76
14.65
f1 (ppm)

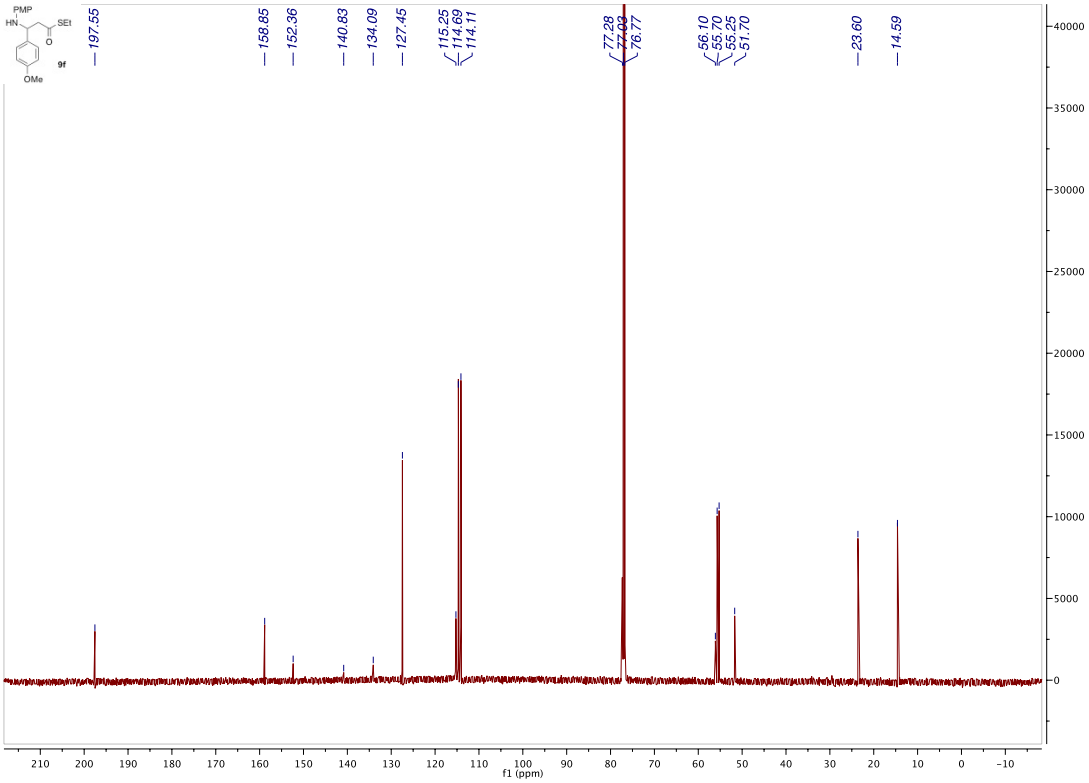

PMP
HN
SEt
O
F
9d
0.96
1.00
1.00
1.05
1.92
1.84
1.00
2.82
1.81
2.00
2.97
f1 (ppm)

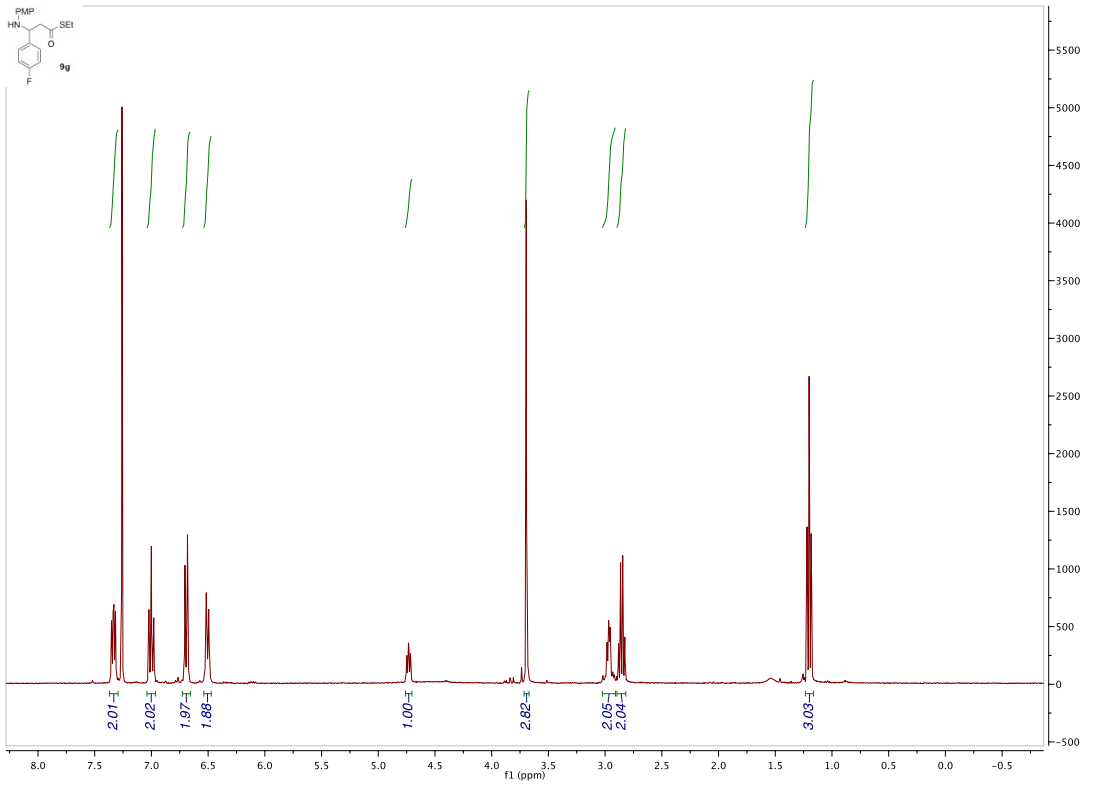

PMP
HN
SEt
O
F
9d
197.29
164.29
162.33
152.62
145.26
145.21
140.65
130.48
130.42
122.11
122.09
115.28
114.85
114.63
114.46
113.52
113.34
56.36
55.81
51.53
23.82
14.69
f1 (ppm)

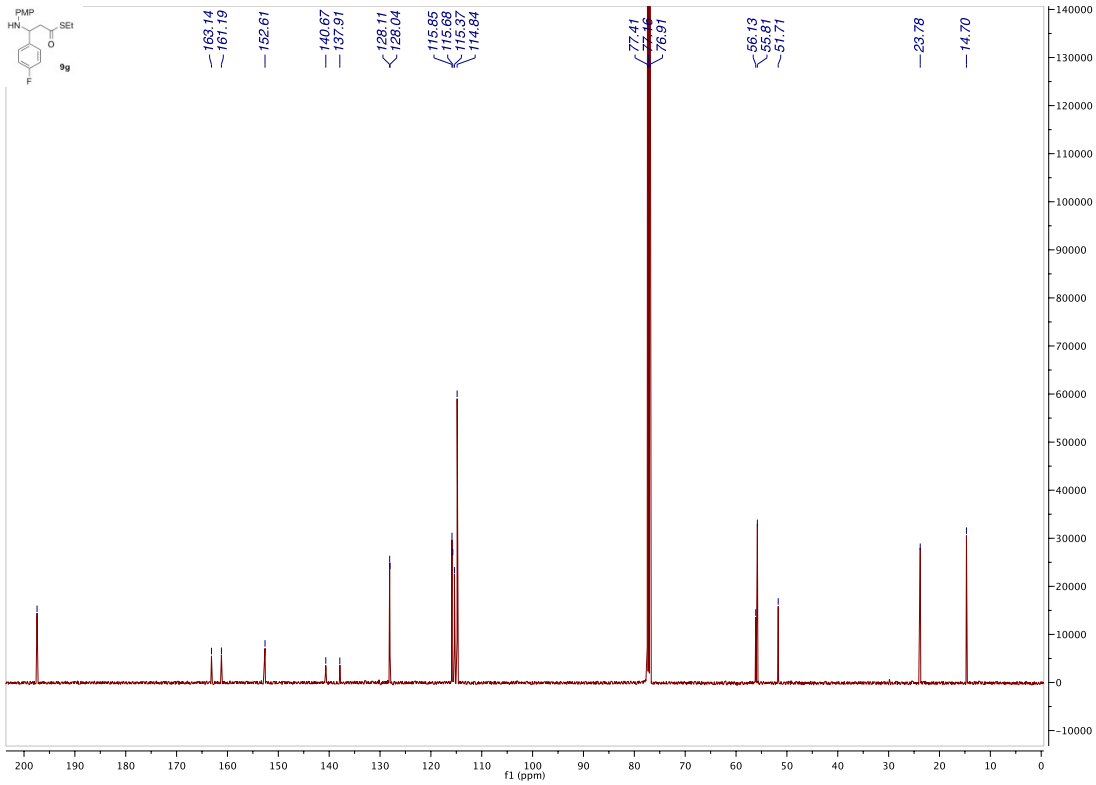

PMP
HN
SEt
O
9e
Me
1.99
2.03
2.04
2.05
1.00
2.97
1.97
2.04
f1 (ppm)

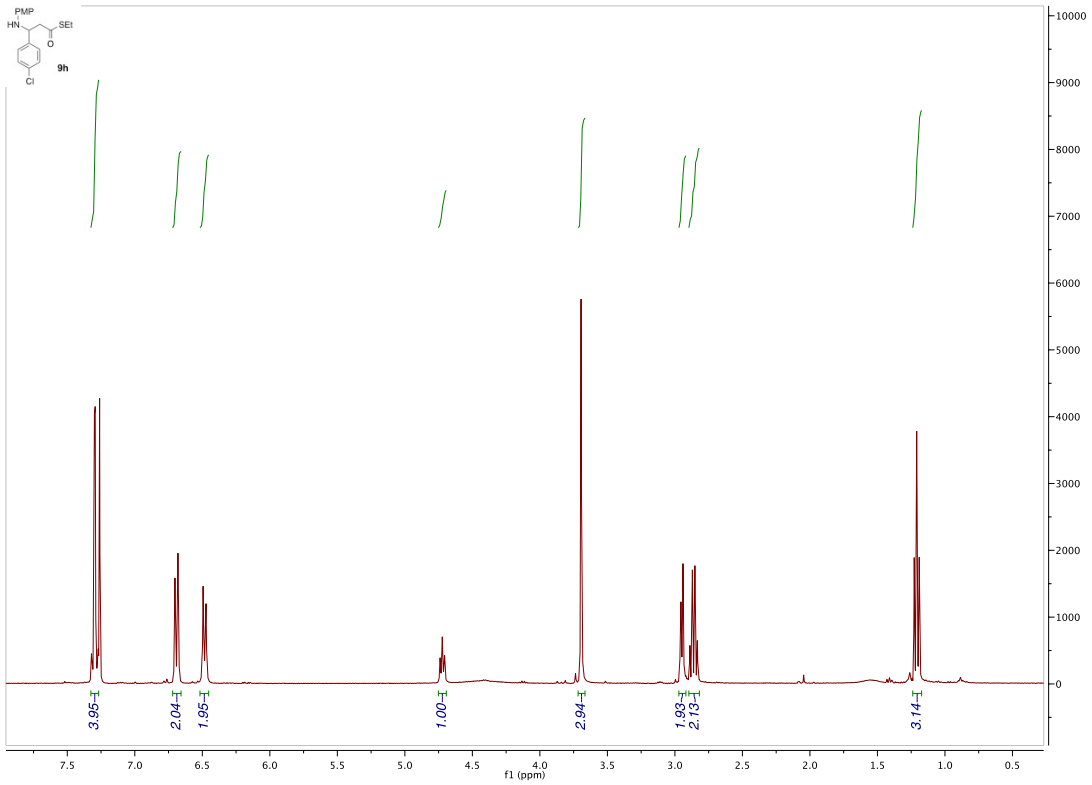

PMP
HN
SEt
O
9e
Me
197.62
152.40
141.07
139.29
137.18
129.58
126.34
115.25
114.82
77.41
77.16
76.91
56.46
55.82
51.85
23.73
21.24
14.72
f1 (ppm)

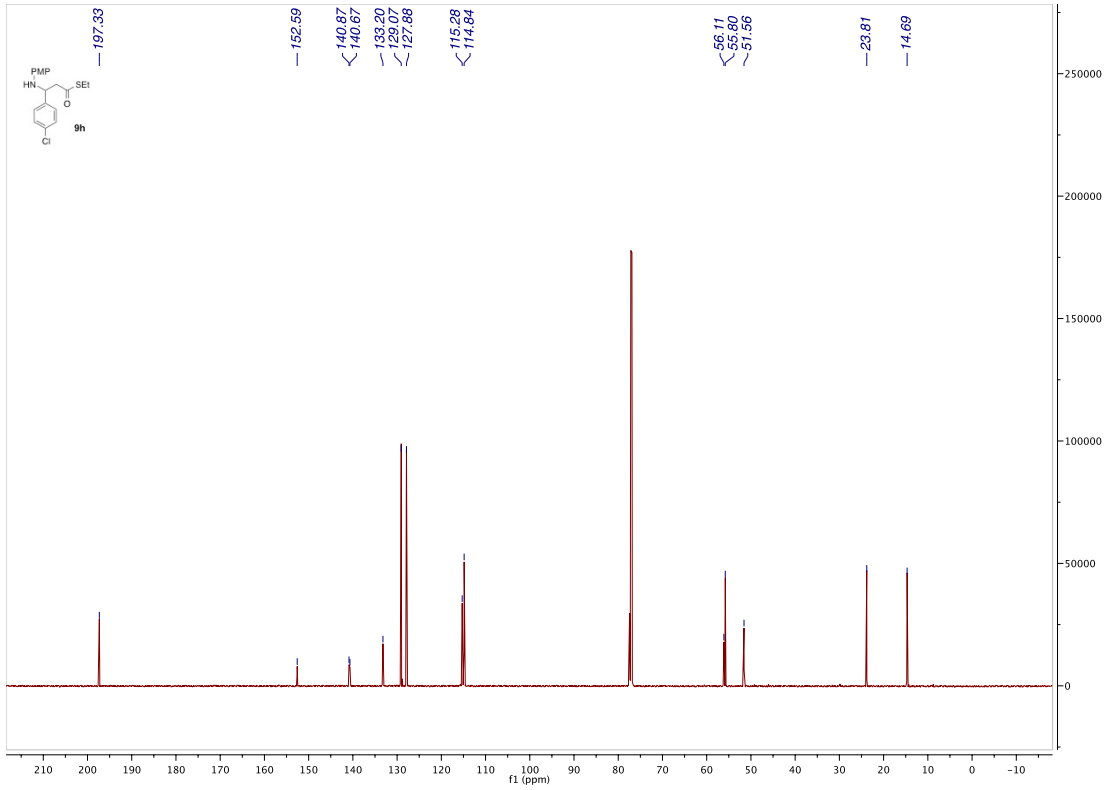

PMP
HN
SEt
O
9f
OMe
1.03
1.97
1.91
1.90
1.00
2.89
2.89
2.05
2.04
2.96
f1 (ppm)

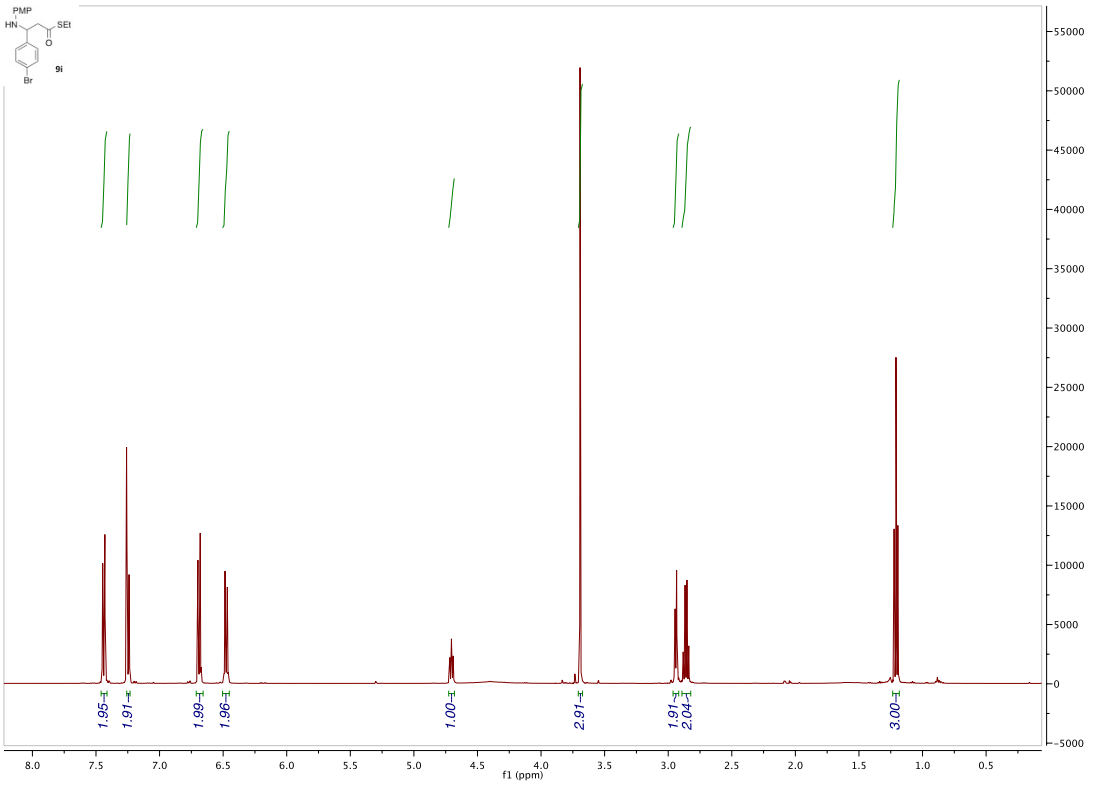

PMP
HN
SEt
O
9f
OMe
197.55
158.85
152.36
140.83
134.09
127.45
115.25
114.69
114.11
77.28
77.02
76.77
56.10
55.70
55.25
51.70
23.60
14.59
f1 (ppm)

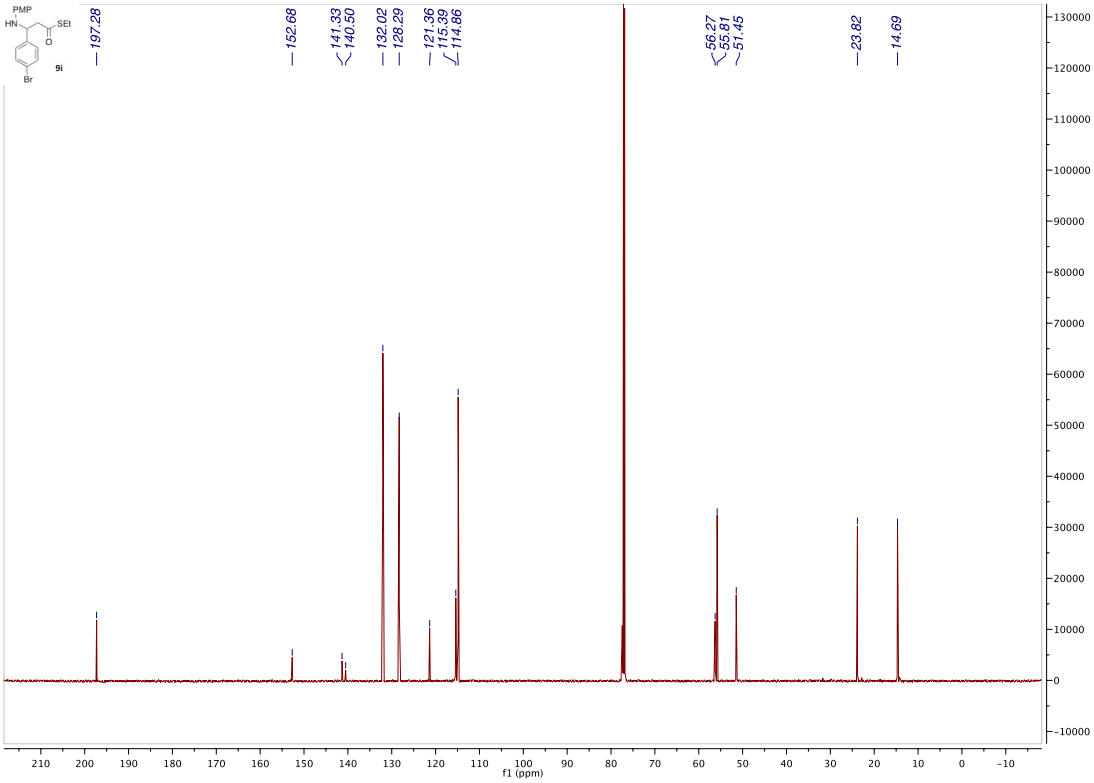

PMP
HN
SEt
O
F
9g
2.01
2.02
1.97
1.88
1.00
2.82
2.05
2.04
3.03
f1 (ppm)

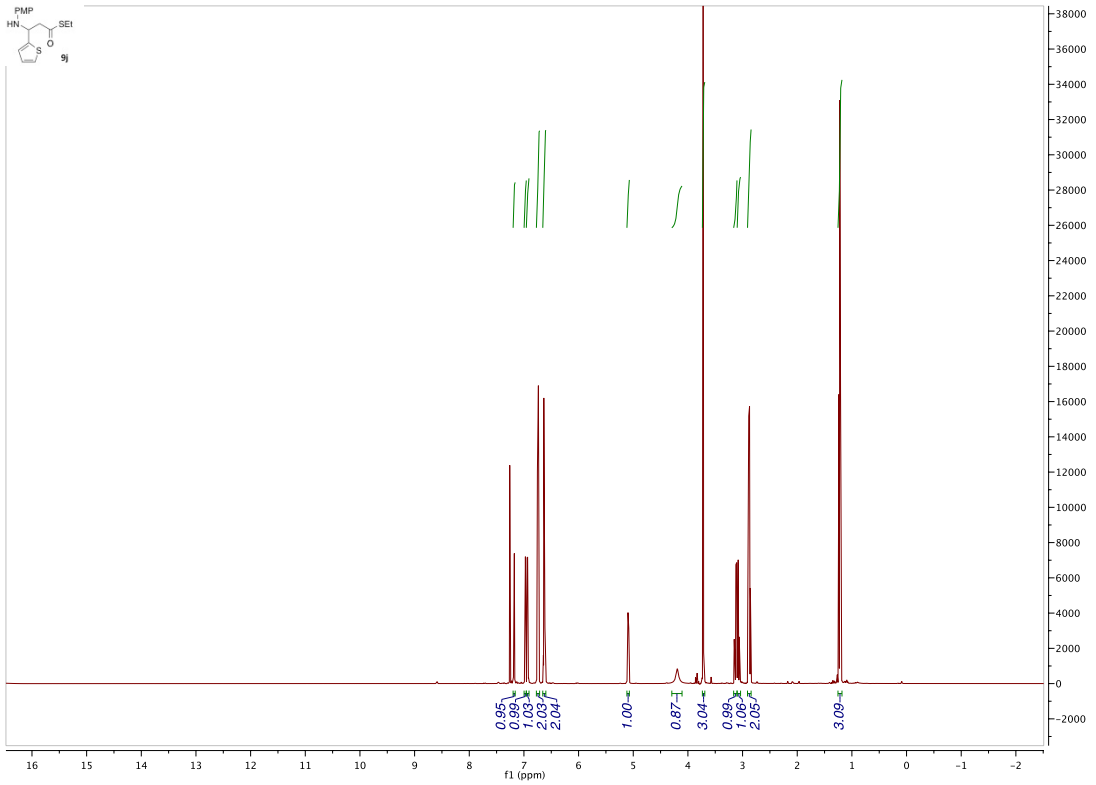

PMP
HN
SEt
O
F
9g
163.14
161.19
152.61
140.67
137.91
128.11
128.04
115.85
115.68
115.37
114.84
77.41
77.16
76.91
56.13
55.81
51.71
23.78
14.70
f1 (ppm)

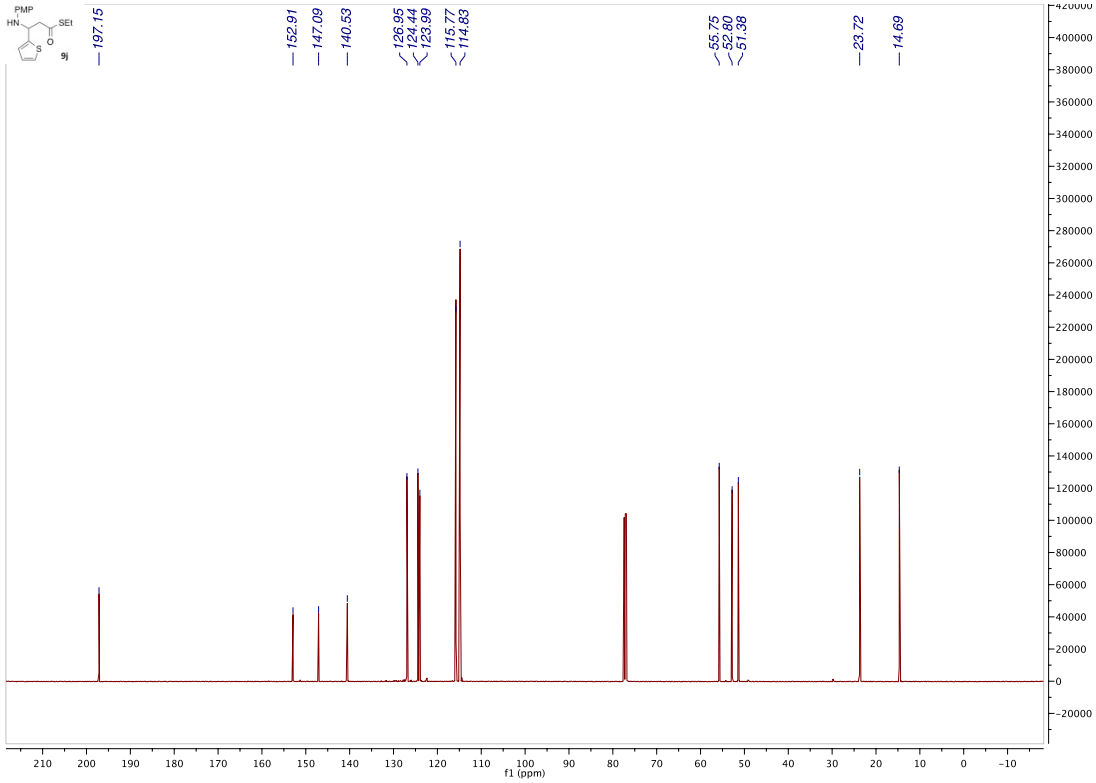

PMP
HN
SEt
O
Cl
9h
3.95
2.04
1.95
1.00
2.94
1.93
2.13
3.14
f1 (ppm)

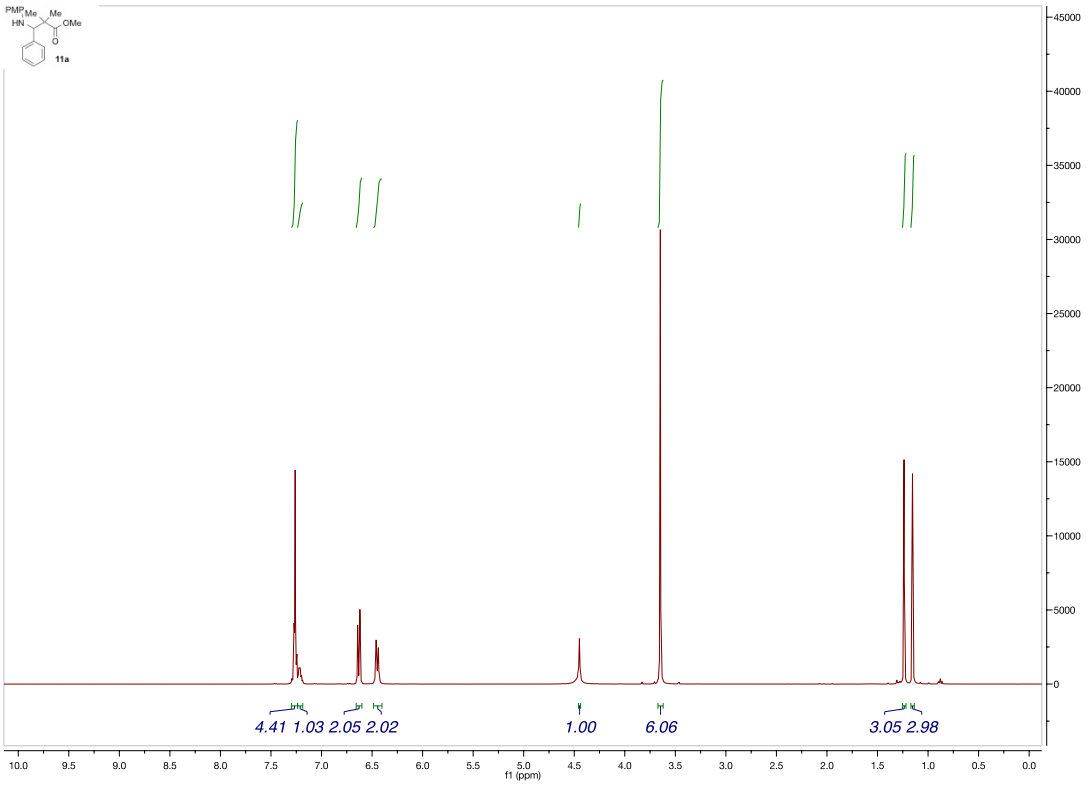

197.33
152.59
140.87
140.67
133.20
129.07
127.88
115.28
114.84
56.11
55.80
51.56
23.81
14.69
PMP
HN
SEt
O
Cl
9h
f1 (ppm)

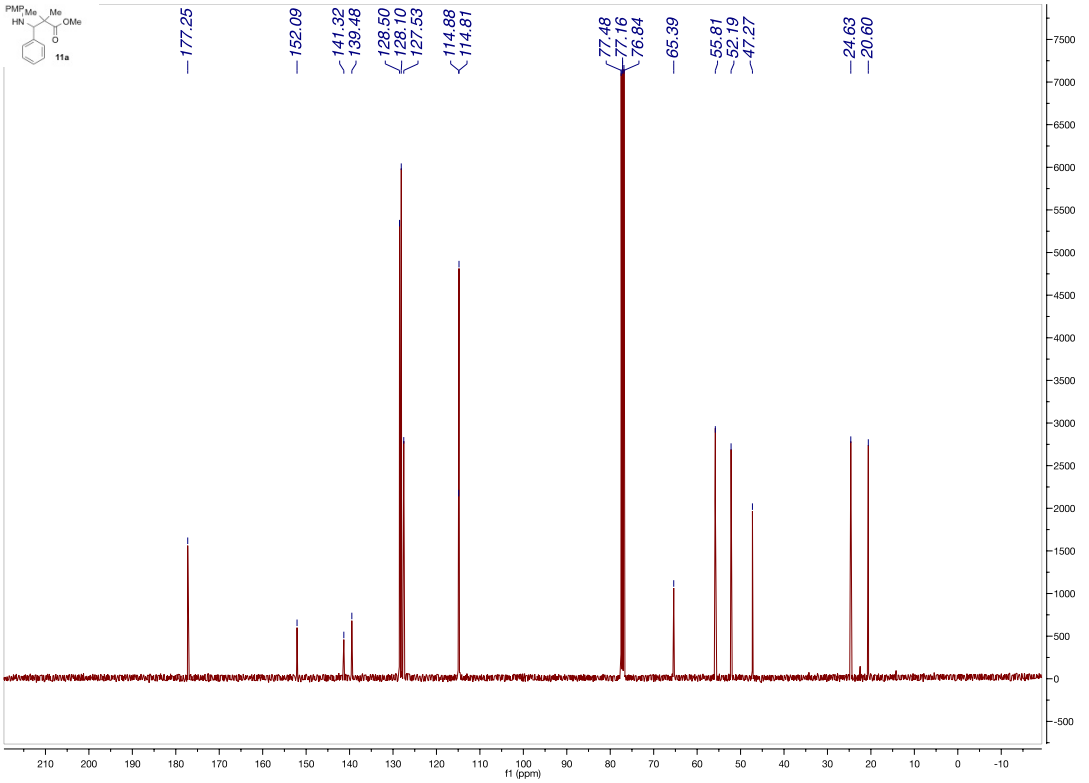

PMP
HN
SEt
O
Br
9i
1.95
1.91
1.99
1.96
1.00
2.91
1.91
2.04
3.00
f1 (ppm)

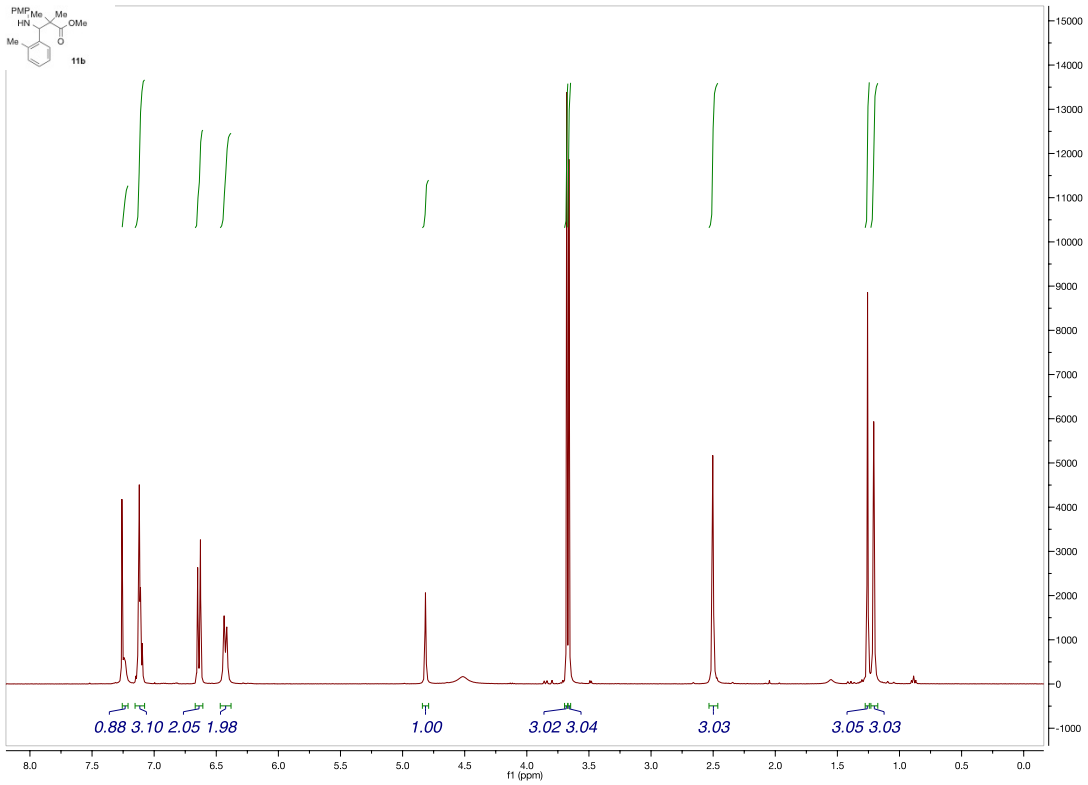

PMP
HN
SEt
O
Br
9i
197.28
152.68
141.33
140.50
132.02
128.29
121.36
115.39
114.86
56.27
55.61
51.45
23.82
14.69
f1 (ppm)

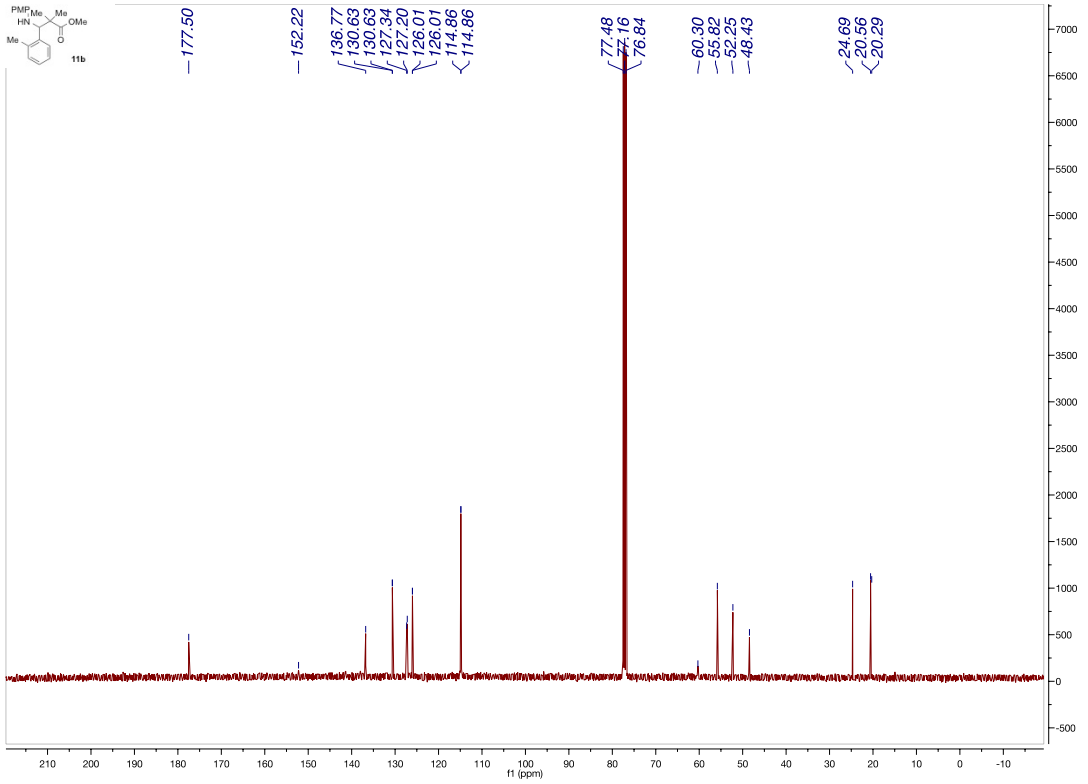

PMP
HN
SEt
O
S
9j
0.95
0.99
1.03
2.03
2.04
1.00
0.87
3.04
0.99
1.06
2.05
3.09
f1 (ppm)

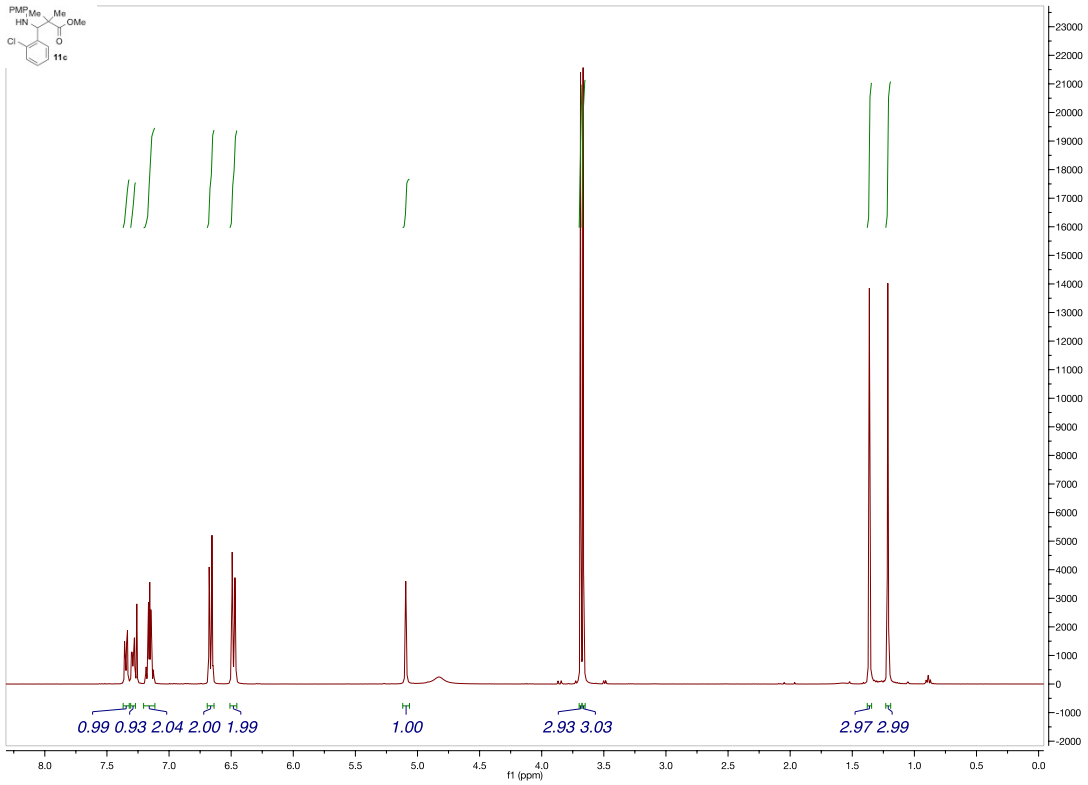

PMP
HN
SEt
O
S
9j
197.15
152.91
147.09
140.53
126.95
124.44
123.99
115.77
114.83
55.75
52.80
51.38
23.72
14.69
f1 (ppm)

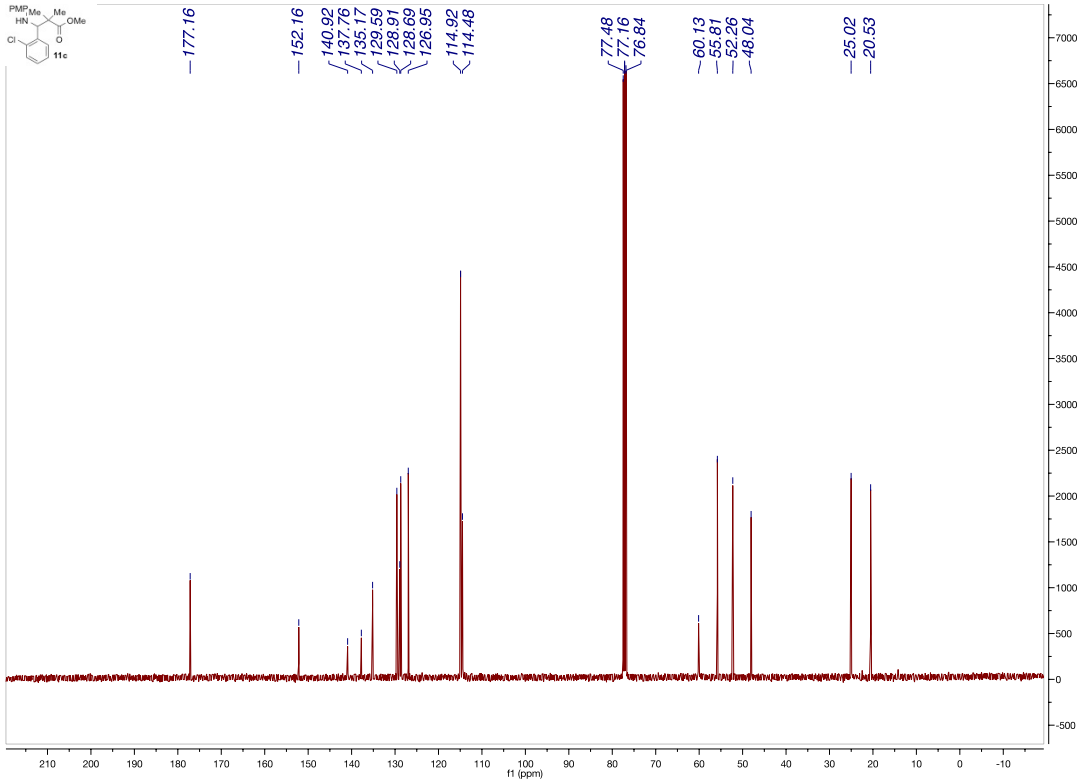

PMP
Me
HN
Me
OMe
O
11a
4.41 1.03 2.05 2.02
1.00
6.06
3.05 2.98
f1 (ppm)

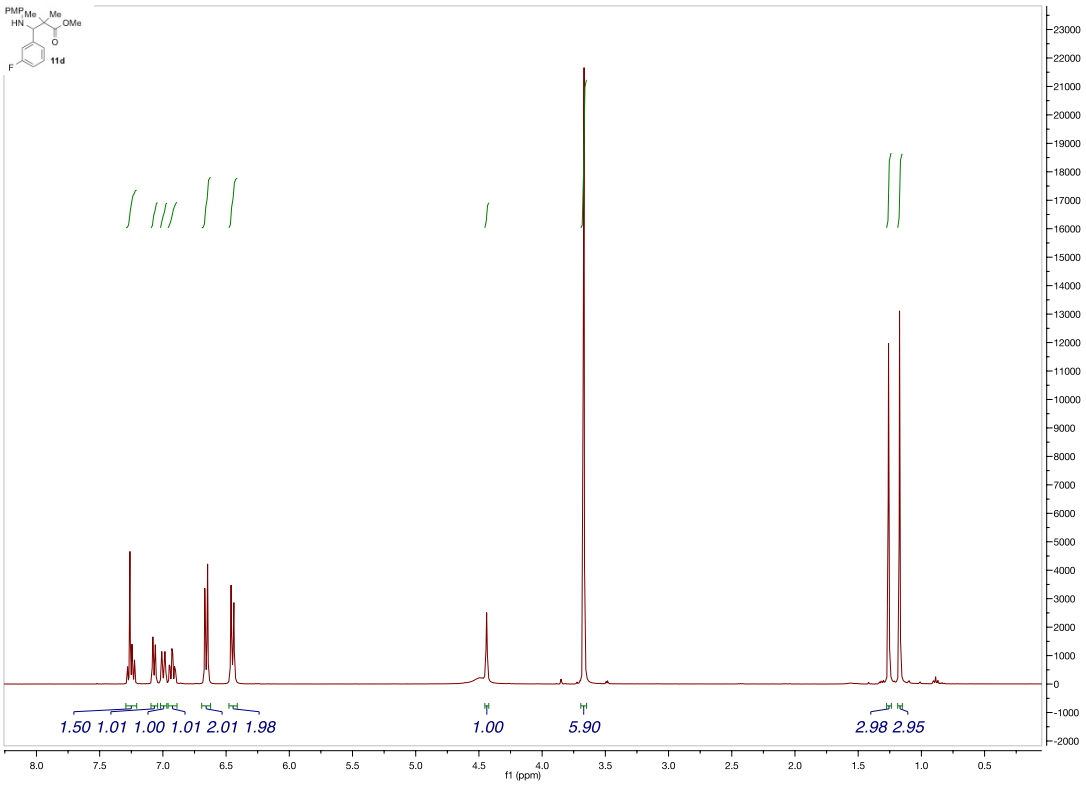

PMP
Me
HN
Me
OMe
O
11a
177.25
152.09
141.32
139.48
128.50
128.10
127.53
114.88
114.81
77.48
77.16
76.84
65.39
55.81
52.19
47.27
24.63
20.60
f1 (ppm)

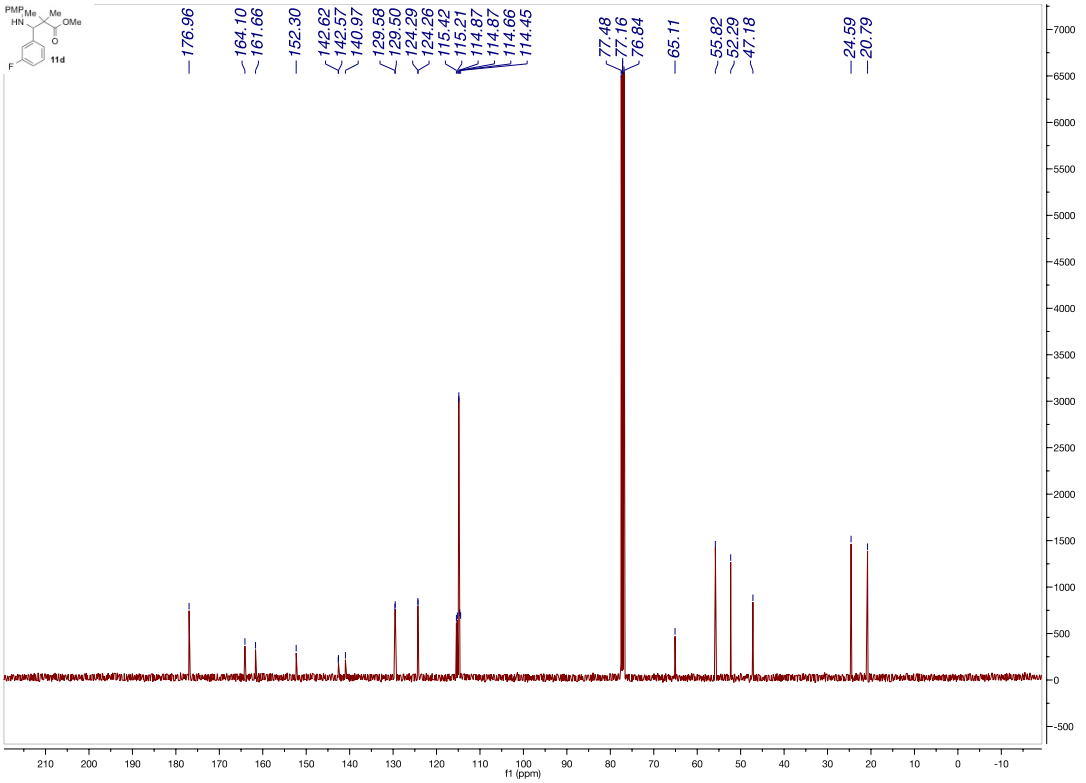

11b
0.88 3.10 2.05 1.98
1.00
3.02 3.04
3.03
3.05 3.03
f1 (ppm)

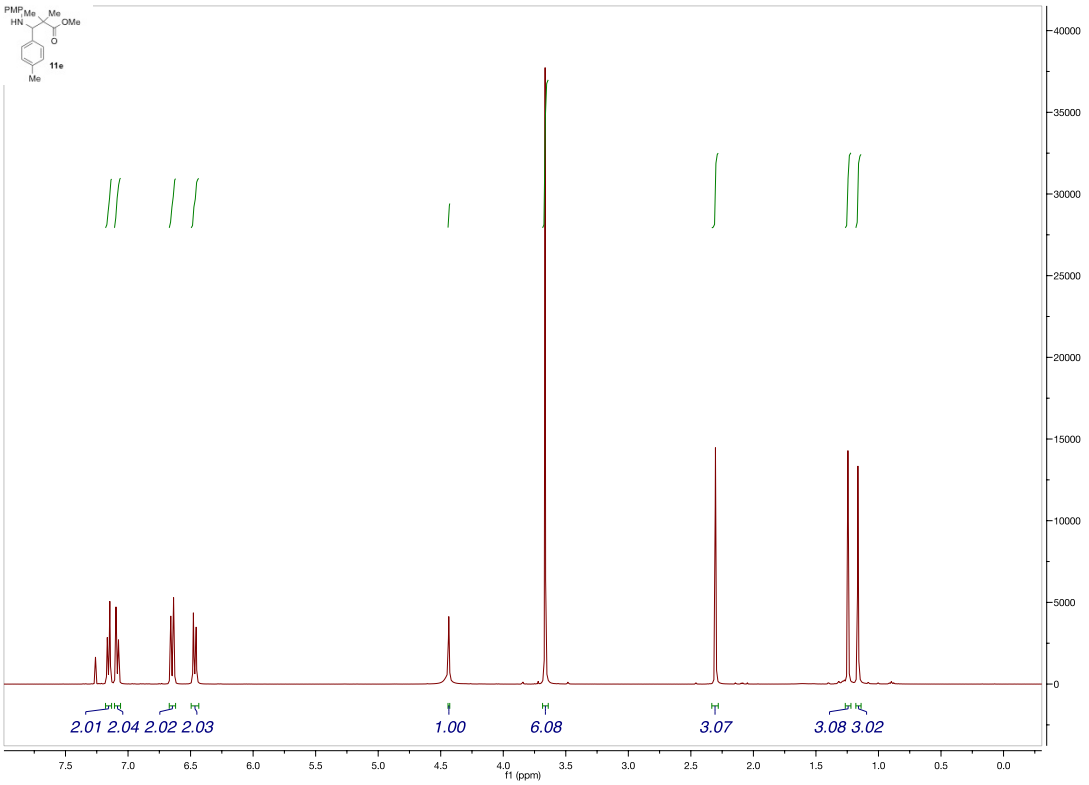

11b
177.50
152.22
136.77
130.63
130.63
127.34
127.20
126.01
126.01
114.86
114.86
77.48
77.16
76.84
60.30
55.82
52.25
48.43
24.69
20.56
20.29
f1 (ppm)

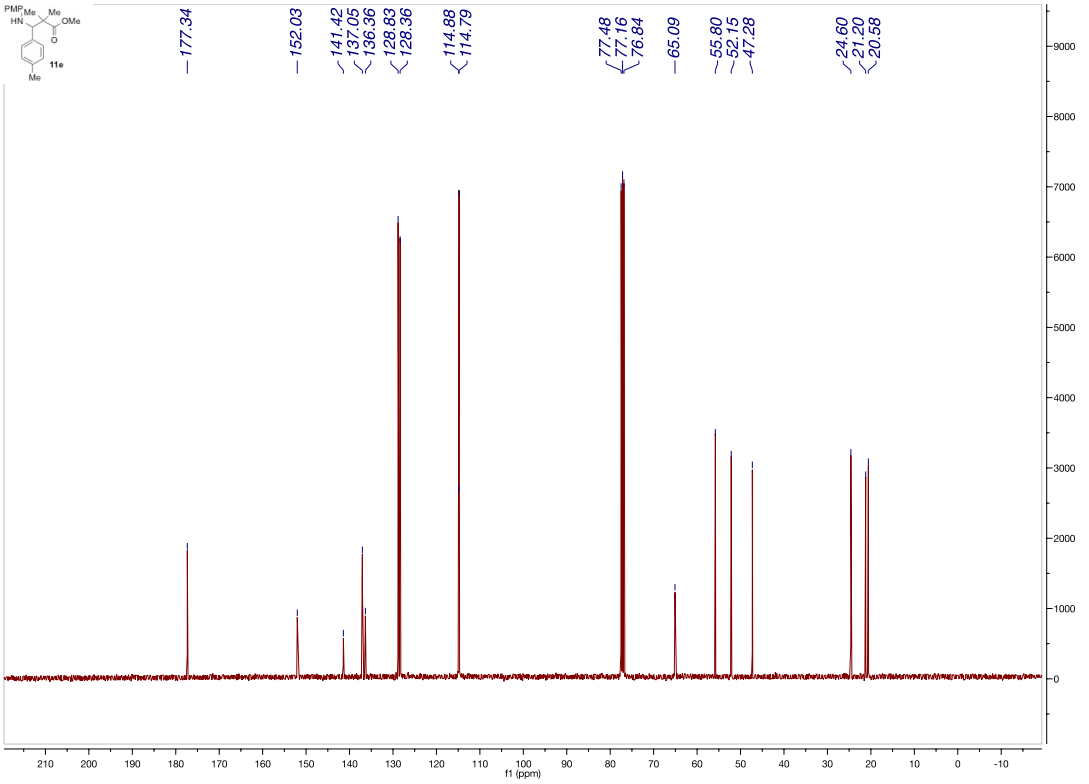

PMP
Me
HN
Me
OMe
O
Cl
11c
0.99 0.93 2.04 2.00 1.99
1.00
2.93 3.03
2.97 2.99
f1 (ppm)

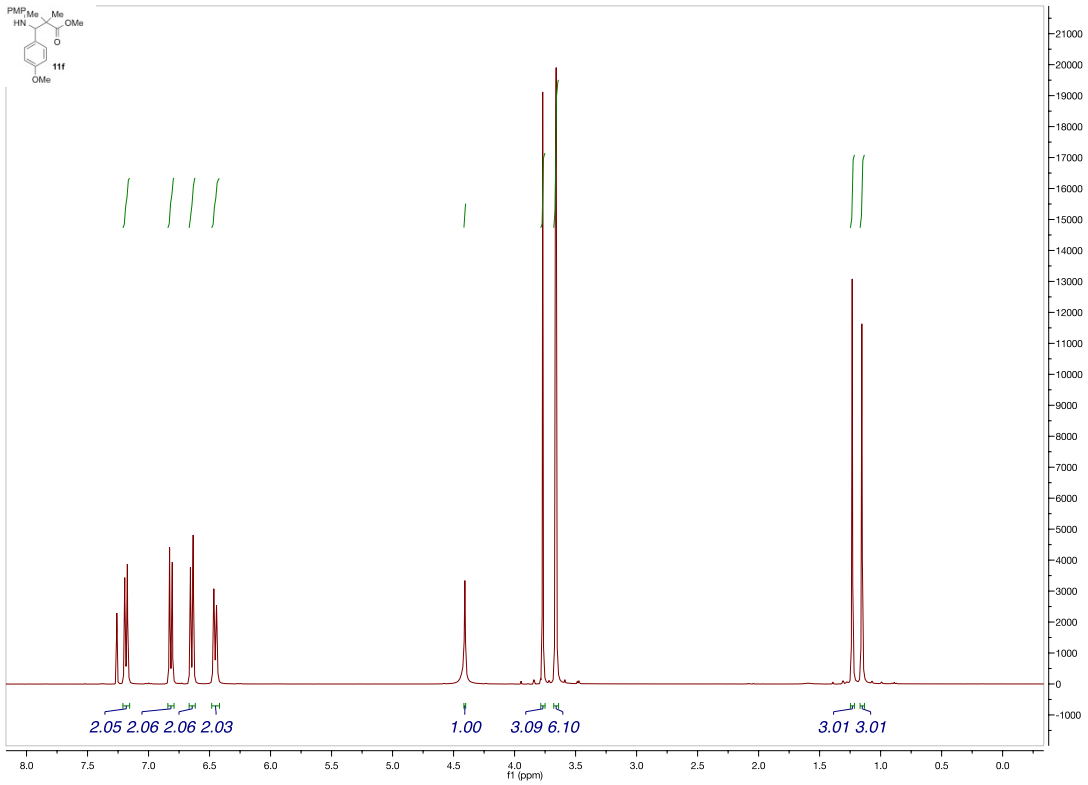

PMP
Me
HN
Me
OMe
O
Cl
11c
177.16
152.16
140.92
137.76
135.17
129.59
128.91
128.69
126.95
114.92
114.48
77.48
77.16
76.84
60.13
55.81
52.26
48.04
25.02
20.53
f1 (ppm)

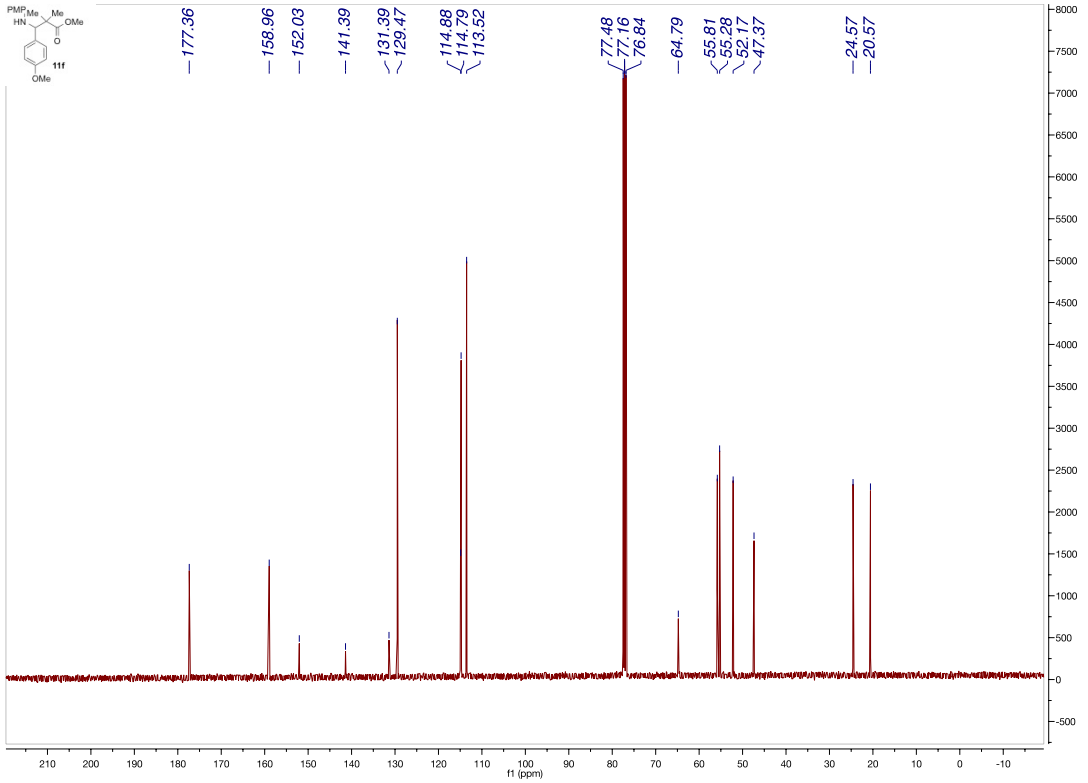

PMP
HN
Me
Me
OMe
O
F
11d
1.50 1.01 1.00 1.01 2.01 1.98
1.00
5.90
2.98 2.95
f1 (ppm)

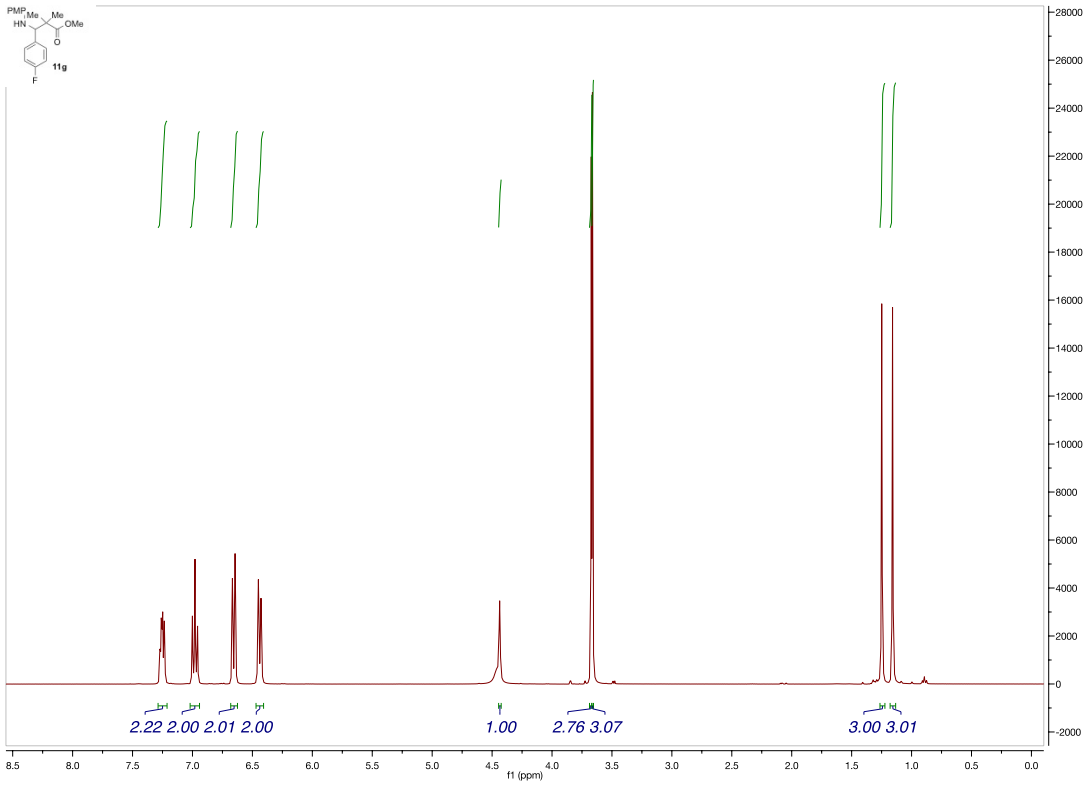

PMP
HN
Me
Me
OMe
O
F
11d
176.96
164.10
161.66
152.30
142.62
142.57
140.97
129.58
129.50
124.29
124.26
115.42
115.21
114.87
114.87
114.66
114.45
77.48
77.16
76.84
65.11
55.82
52.29
47.18
24.59
20.79
f1 (ppm)

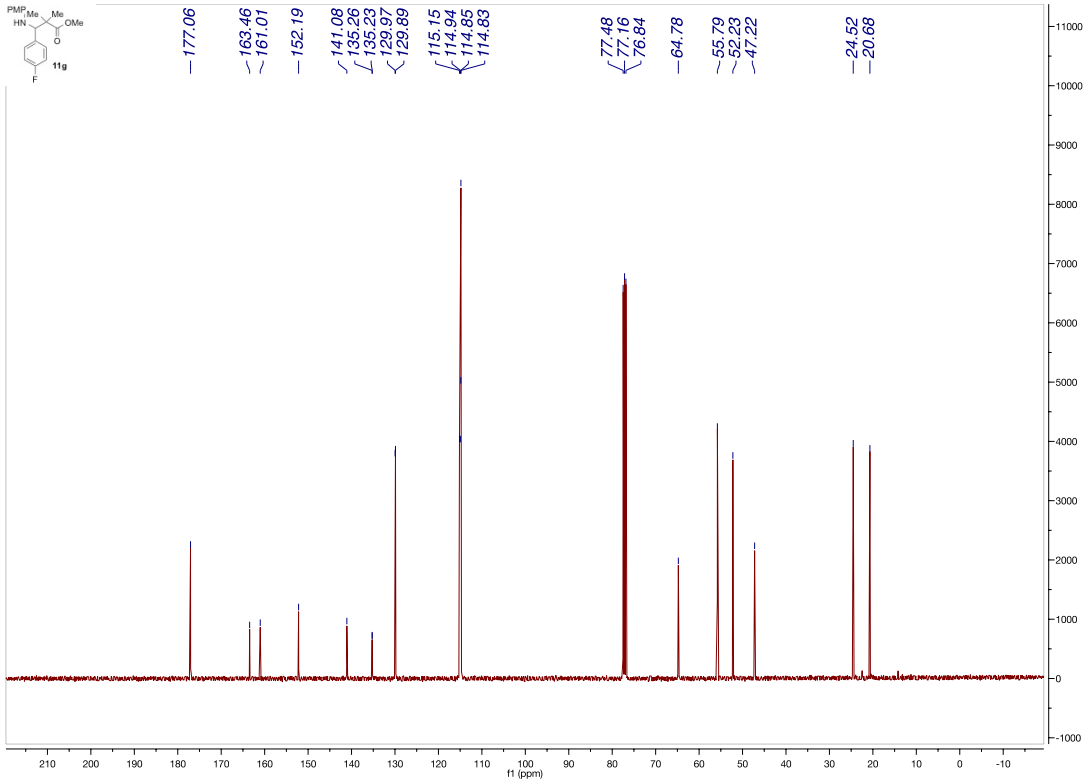

11e
2.01 2.04 2.02 2.03
1.00
6.08
3.07
3.08 3.02
f1 (ppm)

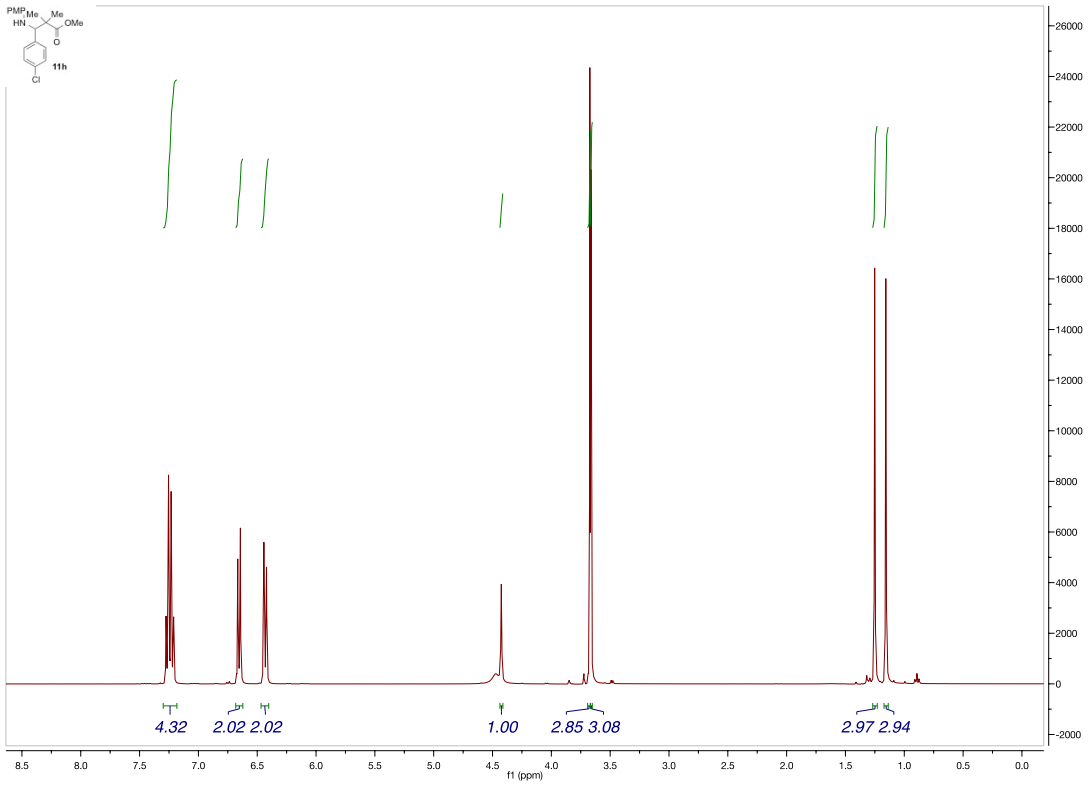

11e
177.34
152.03
141.42
137.05
136.36
128.83
128.36
114.88
114.79
77.48
77.16
76.84
65.09
55.80
52.15
47.28
24.60
21.20
20.58
f1 (ppm)

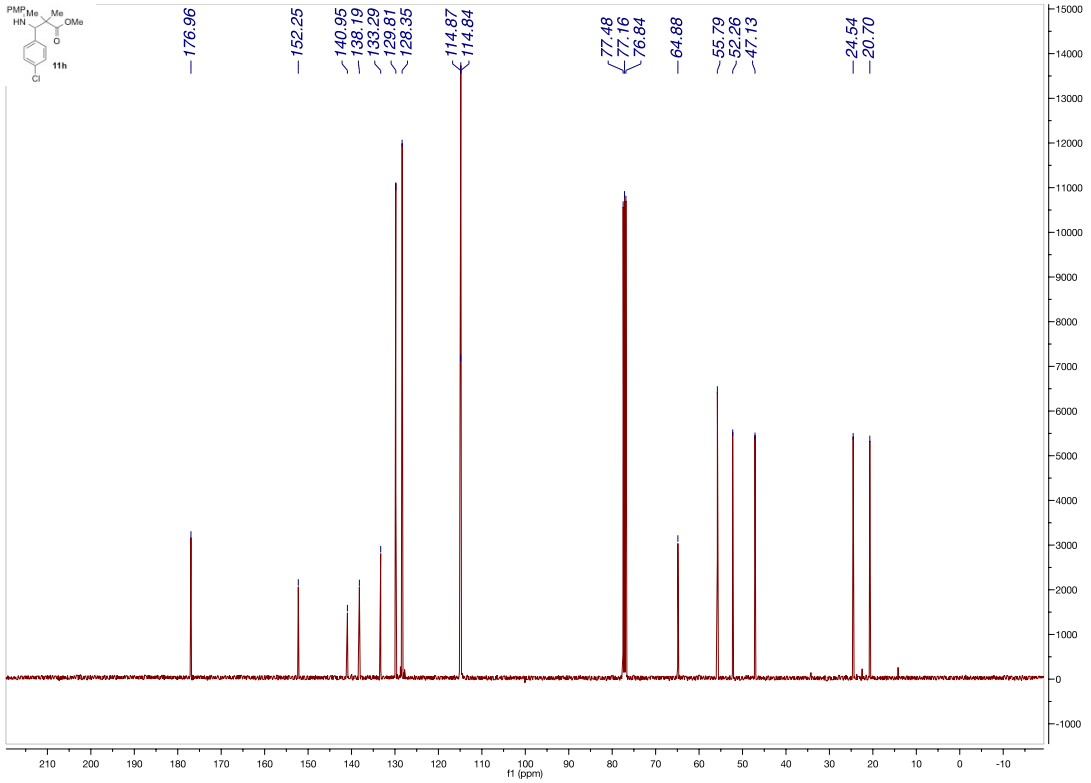

PMP
HN
Me
Me
OMe
O
11f
OMe
2.05 2.06 2.06 2.03
1.00
3.09 6.10
3.01 3.01
f1 (ppm)

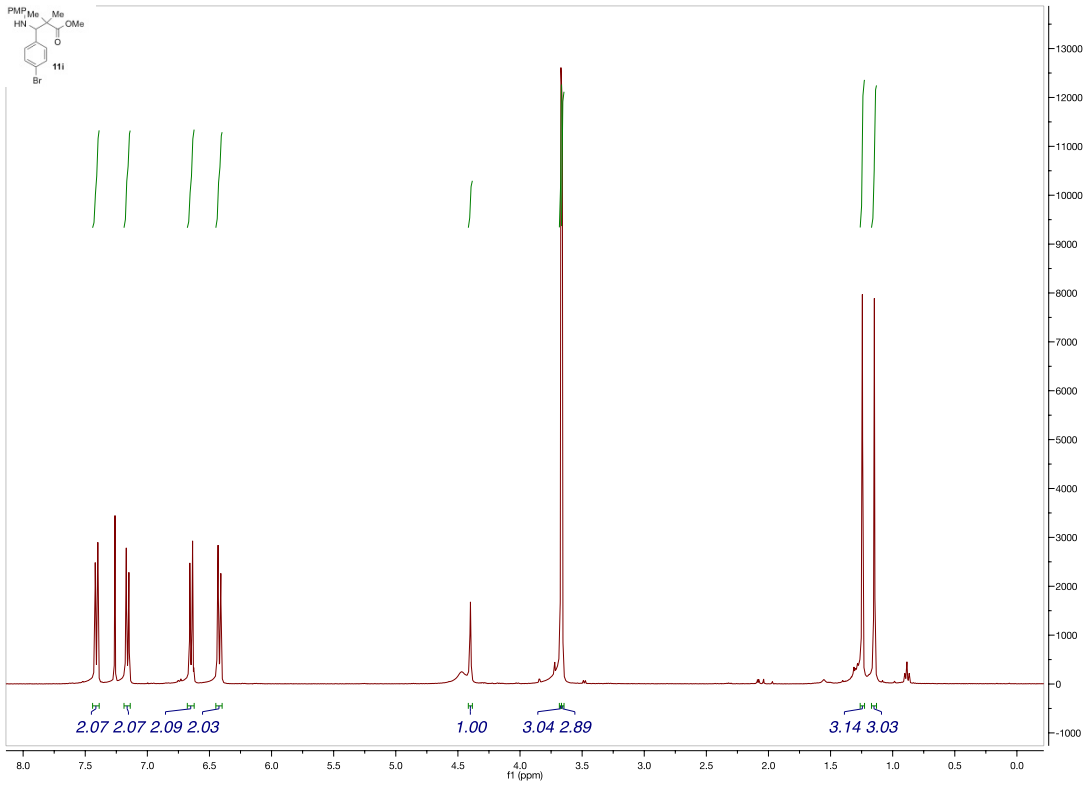

PMP
HN
Me
Me
OMe
O
11f
OMe
177.36
158.96
152.03
141.39
131.39
129.47
114.88
114.79
113.52
77.48
77.16
76.84
64.79
55.81
55.28
52.17
47.37
24.57
20.57
f1 (ppm)

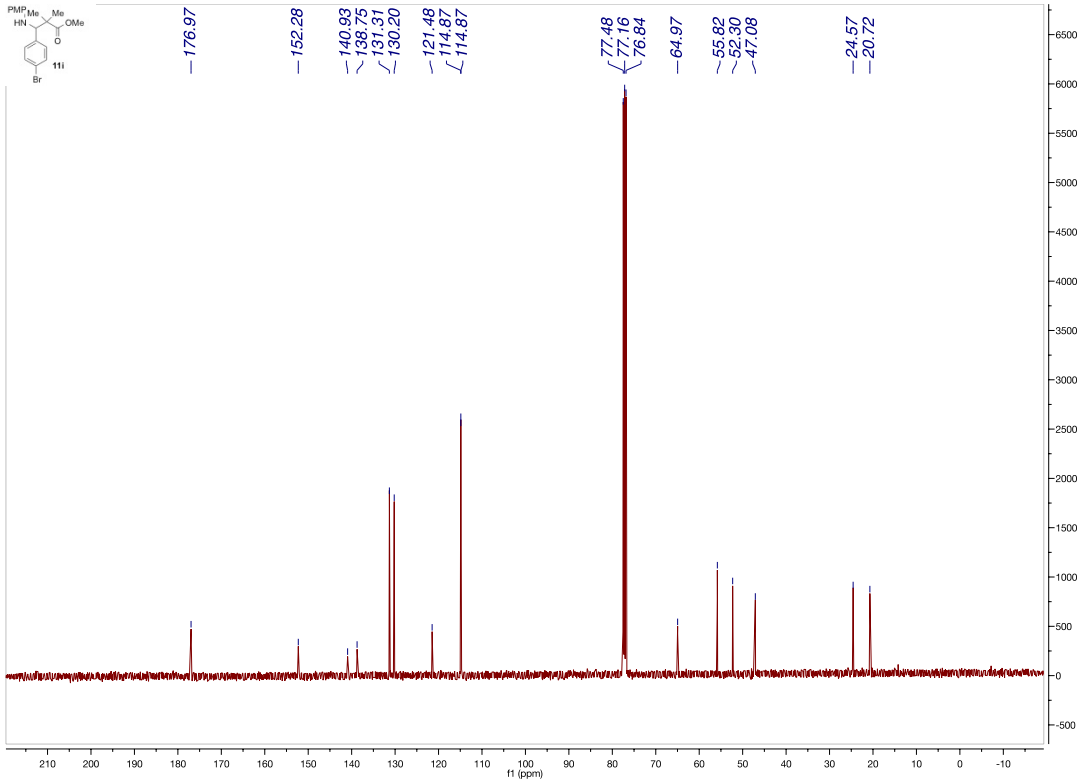

PMP
HN
Me
Me
OMe
O
11g
F
2.22 2.00 2.01 2.00
1.00
2.76 3.07
3.00 3.01
f1 (ppm)

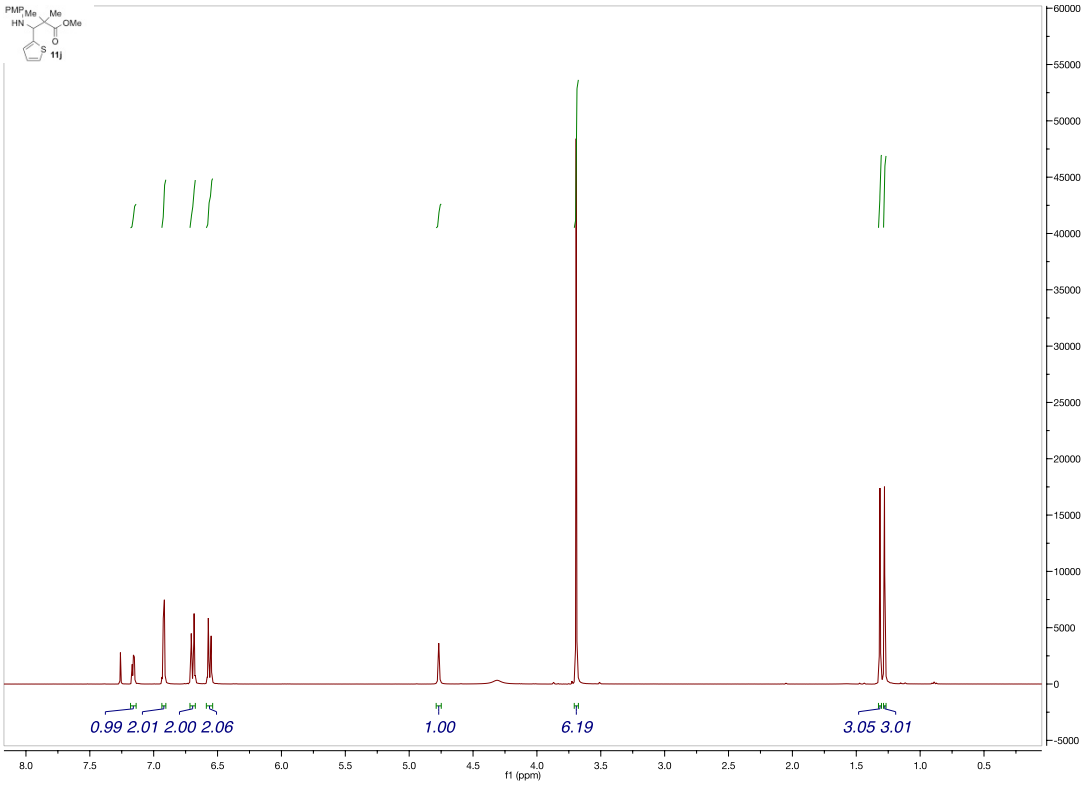

PMP
HN
Me
Me
OMe
O
11g
F
177.06
163.46
161.01
152.19
141.08
135.26
135.23
129.97
129.89
115.15
114.94
114.85
114.83
77.48
77.16
76.84
64.78
55.79
52.23
47.22
24.52
20.68
f1 (ppm)

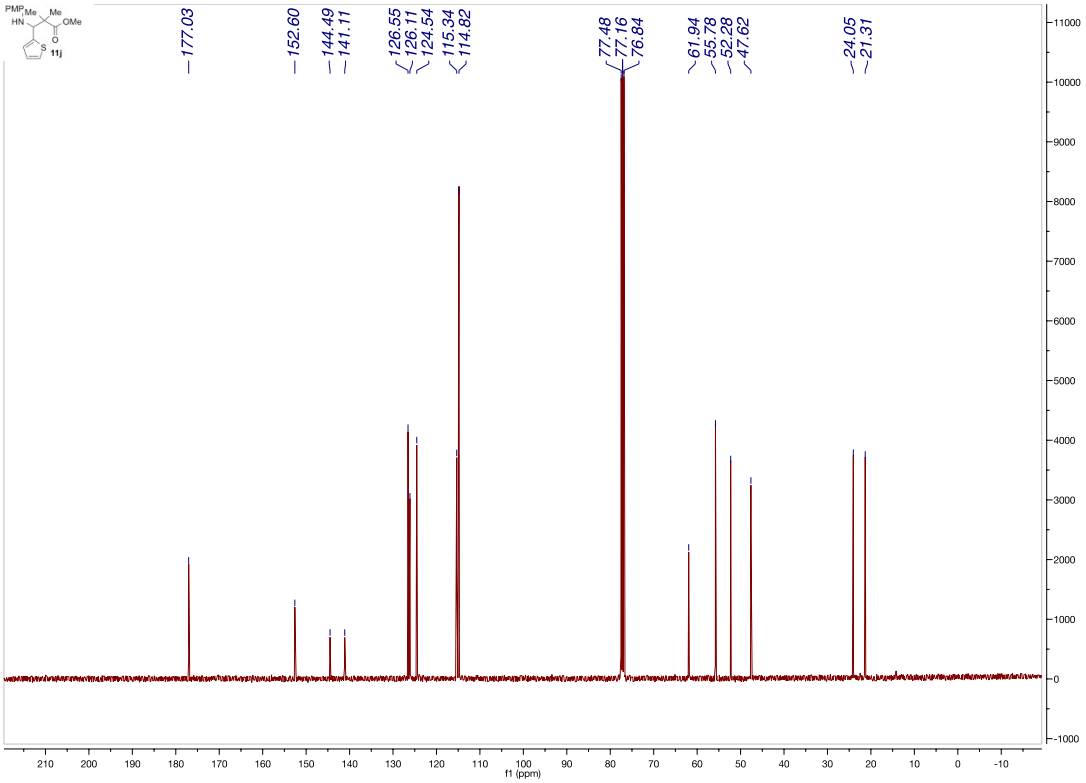

PMP
HN
Me
Me
OMe
O
11h
Cl
4.32
2.02 2.02
1.00
2.85 3.08
2.97 2.94
f1 (ppm)

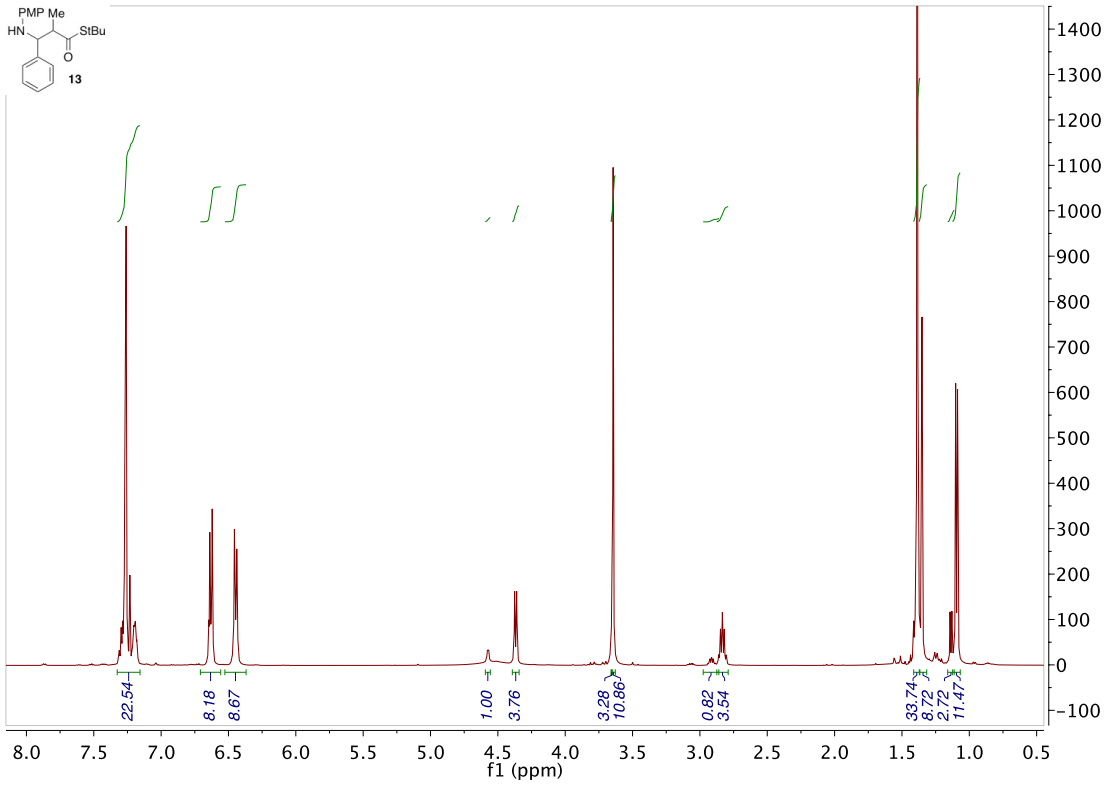

PMP
HN
Me
Me
OMe
O
11h
Cl
176.96
152.25
140.95
138.19
133.29
129.81
128.35
114.87
114.84
77.48
77.16
76.84
64.88
55.79
52.26
47.13
24.54
20.70
f1 (ppm)

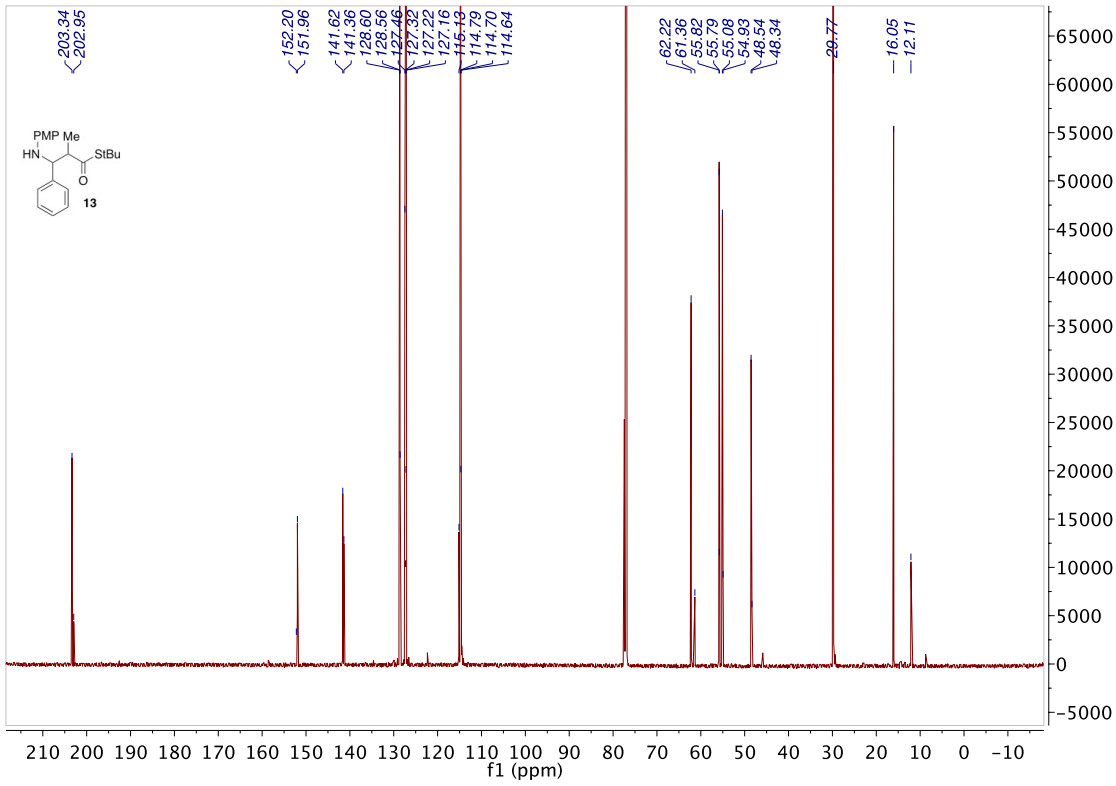

PMP
HN
Me
Me
OMe
O
11i
Br
2.07 2.07 2.09 2.03
1.00
3.04 2.89
3.14 3.03
f1 (ppm)

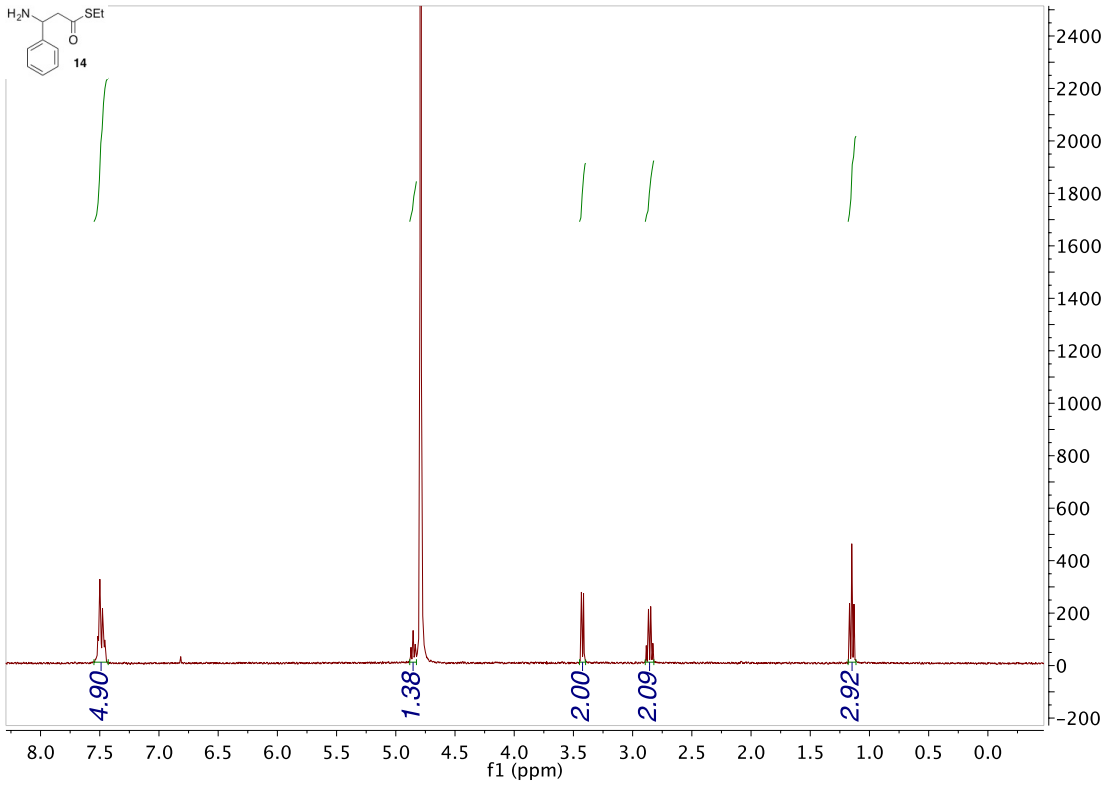

PMP
HN
Me
Me
OMe
O
11i
Br
176.97
152.28
140.93
138.75
131.31
130.20
121.48
114.87
114.87
77.48
77.16
76.84
64.97
55.82
52.30
47.08
24.57
20.72
f1 (ppm)

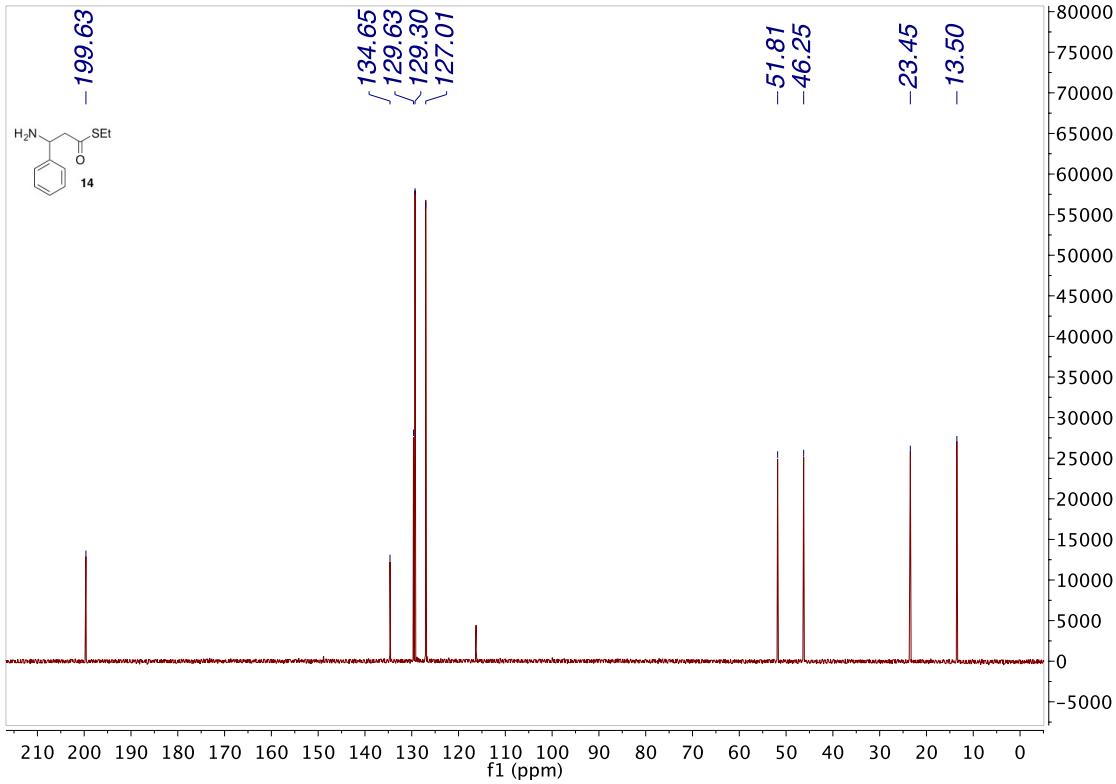

PMP
Me
HN
Me
OMe
O
S
11j
0.99 2.01 2.00 2.06
1.00
6.19
3.05 3.01
f1 (ppm)

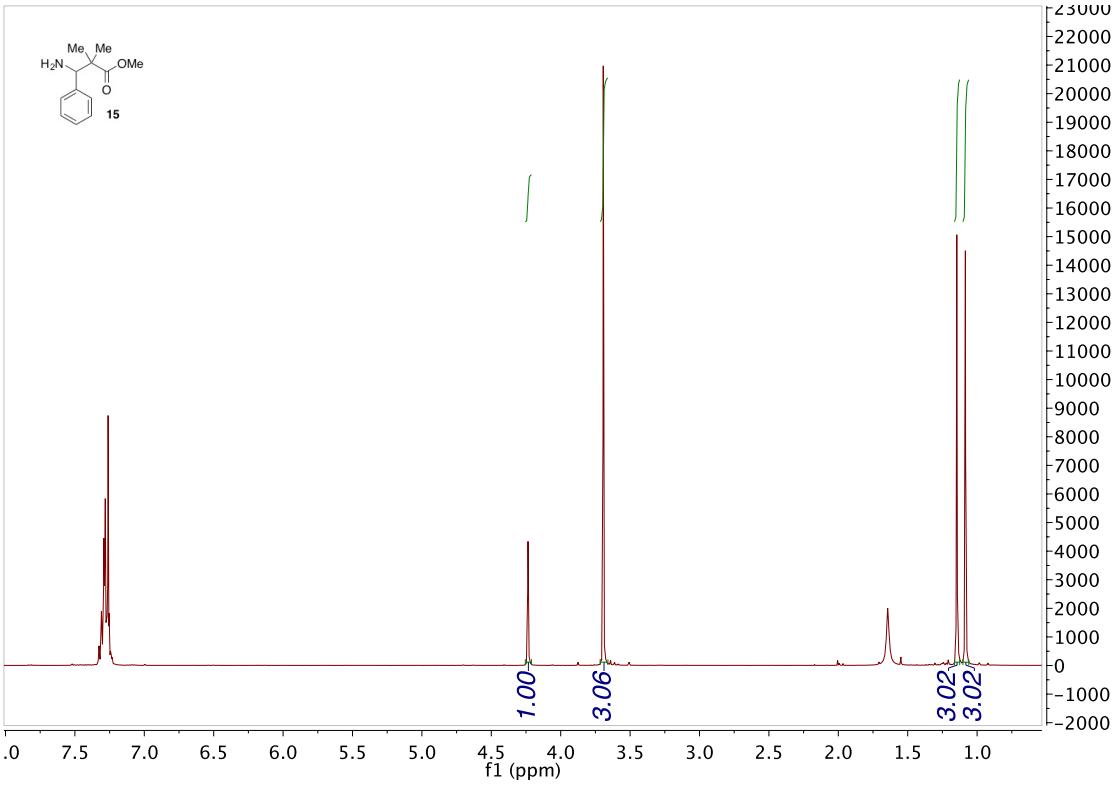

PMP
Me
HN
Me
OMe
O
S
11j
177.03
152.60
144.49
141.11
126.55
126.11
124.54
115.34
114.82
77.48
77.16
76.84
61.94
55.78
52.28
47.62
24.05
21.31
f1 (ppm)

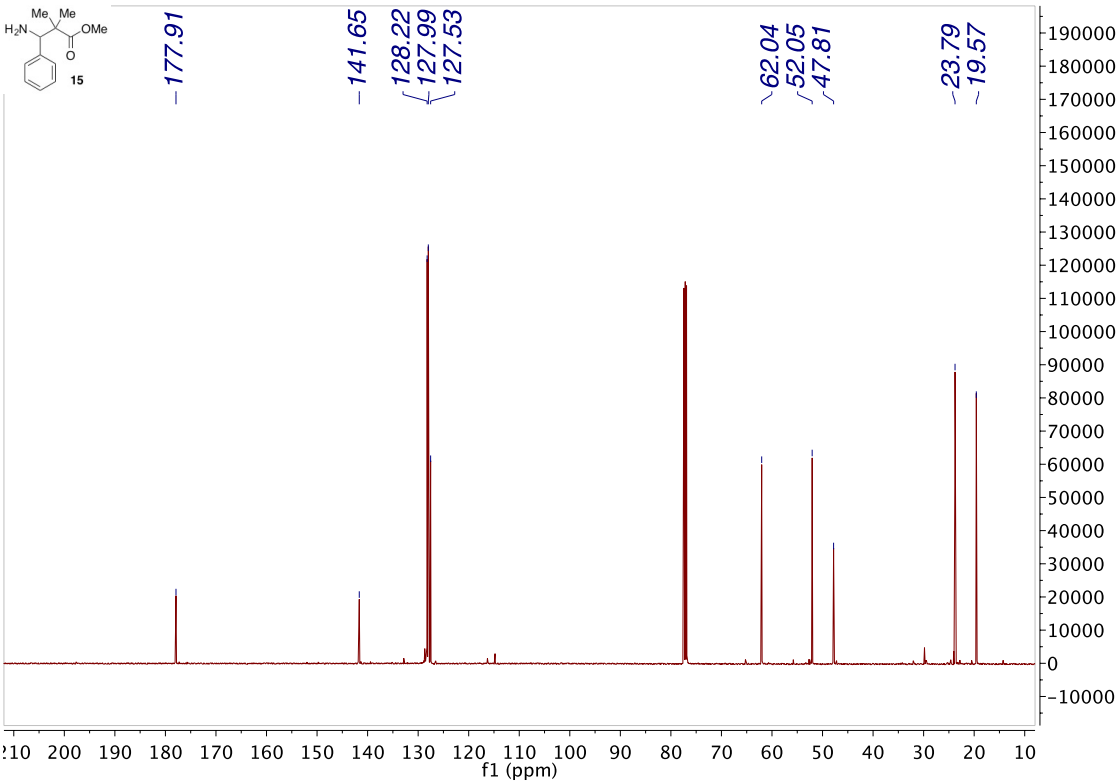

PMP Me
HN
StBu
O
13
22.54
8.18
8.67
1.00
3.76
3.28
10.86
0.82
3.54
33.74
8.72
2.72
11.47
f1 (ppm)


203.34
202.95
152.20
151.96
141.62
141.36
128.60
128.56
127.46
127.32
127.22
127.16
115.18
114.79
114.70
114.64
62.22
61.36
55.82
55.79
55.08
54.93
48.54
48.34
29.77
16.05
12.11
PMP Me
HN
StBu
O
13
f1 (ppm)


14
4.90
1.38
2.00
2.09
2.92
f1 (ppm)


199.63
134.65
129.63
129.30
127.01
51.81
46.25
23.45
13.50
14
f1 (ppm)


Me
Me
H2N
OMe
O
15
1.00
3.06
3.02
3.02
f1 (ppm)


Me
Me
H2N
OMe
O
15
177.91
141.65
128.22
127.99
127.53
62.04
52.05
47.81
23.79
19.57
f1 (ppm)