Catalytic Divergent Synthesis of 3*H* or 1*H* Pyrroles by [3+2] Cyclization of Allenoates with Activated Isocyanides

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Supporting Information

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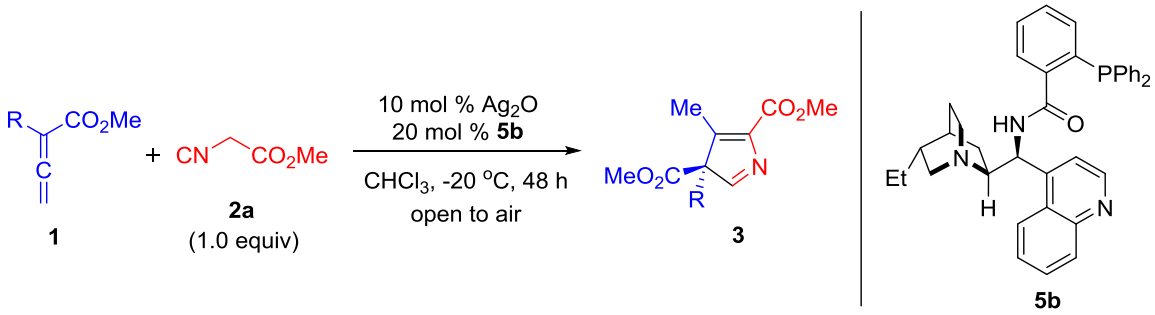
I. General information

^{1}H and **^{13}C NMR** spectra were recorded on a Bruker AFC 300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: ^{1}H (chloroform δ 7.26; DMSO δ 2.50; Acetone δ 2.05), ^{13}C (chloroform δ 77.0; DMSO δ 39.5; Acetone δ 29.8, 206.3). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets), coupling constants (Hz) and integration. ^{19}F NMR was measured at 282 MHz, and $CFCl_3$ (0 ppm) was used as an external standard. Melting point (**MP**) was obtained on Buchi B-540. For thin layer chromatography (**TLC**), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. High resolution mass spectra (**HRMS**) were obtained on a Finnigan/MAT 95XL-T spectrometer. **Optical rotations** were recorded on an mrc AP81 automatic polarimeter. Enantiomeric excesses (**ee**) were determined by HPLC analysis on Agilent HPLC units, including the following instruments: pump, LC-20AD; detector, SPD-20A; column, Chiralcel OD-H, Chiralpak AD-H, AS-H and IA, IB, IC, IE.

Unless otherwise noted, all the reactions were carried out open to air. Dichloromethane (DCM), diethyl ether (Et_2O), tetrahydrofuran (THF), and toluene were dried over a Pure Solv solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received without further purification. Methyl isocyanoacetate (**2a**), ethyl isocyanoacetate and *p*-toluenesulfonylmethyl isocyanide were purchased from Alfa Aesar company and used without further purification. *tert*-Butyl isocyanoacetate[1] and all allenoates were prepared according to literature procedures.[2] Other chemicals were purchased from commercial suppliers and used as received without further purification.

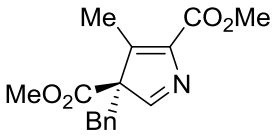
II. Ag-catalyzed enantioselective [3+2] cyclization of 1 and 2a



General procedure. To a 10 mL vial charged with **5b**[3] (12 mg, 0.020 mmol) and Ag_2O (2.3 mg, 0.010 mmol) was added anhydrous $CHCl_3$ (0.5 mL). The mixture was allowed to stir at ambient temperature for 5 min, then allenoate **1** (0.10 mmol) was added in one portion. After the mixture was cooled to -20 °C, isocyanoacetate **2a** (0.10 mmol) in anhydrous $CHCl_3$ (0.5 mL) was added via syringe pump over 2 h. The reaction mixture was stirred at -20 °C for 48 h, concentrated and purified by flash chromatography (hexanes/ethyl acetate) to afford the product **3**.

III. Characterization of compounds 3

(*S*)-dimethyl 3-benzyl-4-methyl-3*H*-pyrrole-3,5-dicarboxylate (3a)

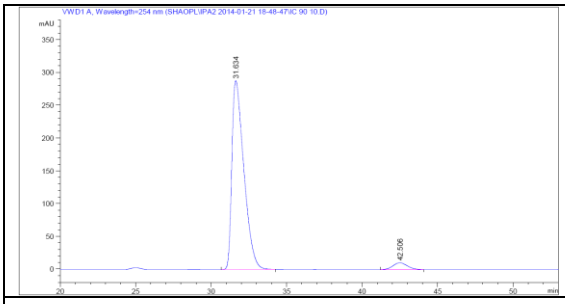


3a

The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 84% yield. **^{1}H NMR** (500 MHz, DMSO): δ 8.21 (s, 1H), 7.21-7.17 (m, 3H), 7.10-7.09 (m, 2H), 3.69 (s, 3H), 3.63 (d, *J* = 13.9 Hz, 1H), 3.63 (s, 3H), 3.19 (d, *J* = 13.9 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR** (125 MHz, DMSO): δ 170.4, 167.3, 162.7, 148.0, 141.9, 134.3, 129.2, 127.9, 127.0, 74.5, 53.0, 51.4, 36.5, 11.4; **HRMS** (ESI): m/z calcd. for $[C_{16}H_{16}NO_4, M\text{-}H]^-$: 286.1085; found: 286.1071.

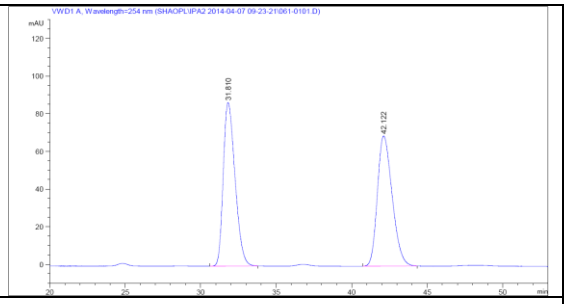
Optical Rotation: $[\alpha]^{25}_D$ = 86.5 (c = 0.4, $CHCl_3$). The absolute configuration of **3a** was assigned by analogy to **6a**. 92% ee (HPLC condition: Chiralpak IC column,

n-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 31.6 min for major isomer, t_R = 42.5 min for minor isomer).



Signal 1: VWD1 A, Wavelength=254 nm

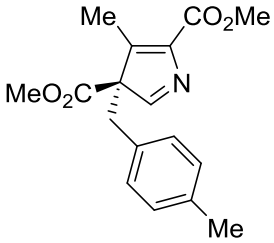
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.634	BB	0.7456	1.58397e4	287.81726	95.9517
2	42.506	BB	0.7651	668.29987	10.25111	4.0483



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.810	BB	0.6368	4713.68213	86.90087	50.0736
2	42.122	BB	0.7943	4699.83398	69.16246	49.9264

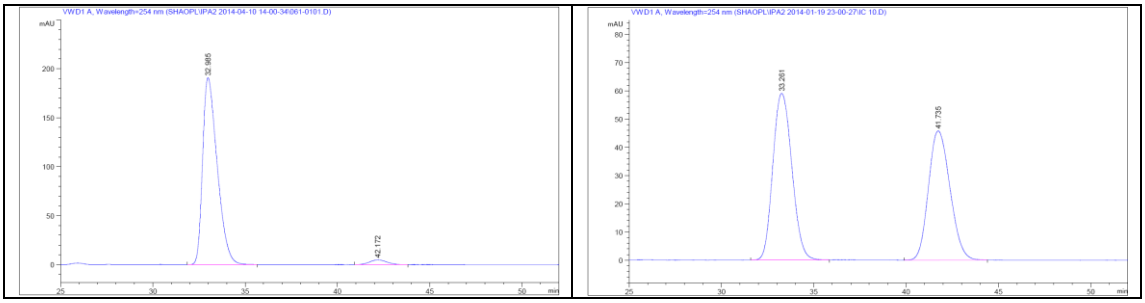
(*S*)-dimethyl 4-methyl-3-(4-methylbenzyl)-3*H*-pyrrole-3,5-dicarboxylate (**3b**)



3b

The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 92% yield. **^{1}H NMR** (500 MHz, DMSO): δ 7.19 (s, 1H), 7.01-6.96 (m, 4H), 3.69 (s, 3H), 3.63 (s, 3H), 3.58 (d, *J* = 13.9 Hz, 1H), 3.13 (d, *J* = 13.9 Hz, 1H), 2.28 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.5, 167.3, 162.7, 148.1, 141.8, 136.1, 131.2, 129.1, 128.5, 74.6, 53.0, 51.5, 36.2, 20.6, 11.4; **HRMS** (ESI): m/z calcd. for [$C_{17}H_{18}NO_4$, M-H]$^-$: 300.1241; found: 300.1243.

Optical Rotation: $[\alpha]^{25}_D$ = 82.8 (c = 0.3, $CHCl_3$). The absolute configuration of **3b** was assigned by analogy to **3a**. 94% ee (HPLC condition: Chiralcel IC column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 33.0 min for major isomer, t_R = 42.2 min for minor isomer).



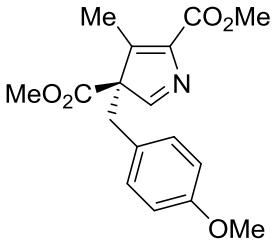
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.985	BB	0.7958	1.04640e4	190.81758	97.0669
2	42.172	BB	0.7611	316.18893	4.86621	2.9331

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.261	BB	1.0634	4229.10645	59.06289	53.2572
2	41.735	BB	1.2138	3711.79834	45.78618	46.7428

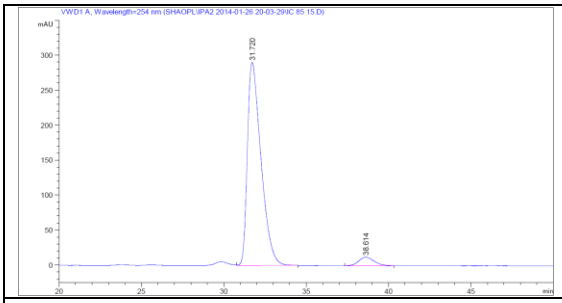
(*S*)-dimethyl 3-(4-methoxybenzyl)-4-methyl-3*H*-pyrrole-3,5-dicarboxylate (**3c**)

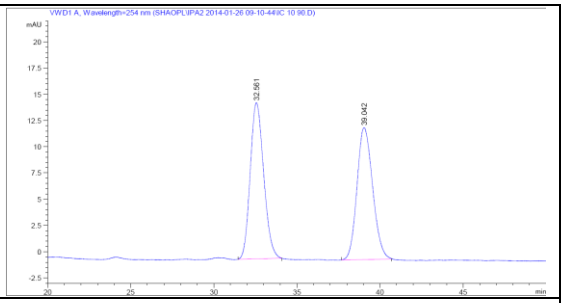


3c

The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 74% yield. **^{1}H NMR** (500 MHz, DMSO): δ 8.19 (s, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 3.70 (s, 3H), 3.68 (s, 3H), 3.63 (s, 3H), 3.56 (d, *J* = 13.8 Hz, 1H), 3.11 (d, *J* = 13.8 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.5, 167.3, 162.7, 158.1, 148.1, 141.8, 130.3, 126.1, 113.3, 74.7, 54.9, 53.0, 51.5, 35.8, 11.4; **HRMS** (ESI): m/z calcd. for $[C_{17}H_{18}NO_5, M\text{-}H]^-$: 316.1190; found: 316.1191.

Optical Rotation: $[\alpha]^{25}_D$ = 62.2 (c = 0.3, $CHCl_3$). The absolute configuration of **3c** was assigned by analogy to **3a**. 91% ee (HPLC condition: Chiralpak IC column, *n*-hexane/*i*-PrOH = 85:15, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 31.7 min for major isomer, t_R = 38.6 min for minor isomer).





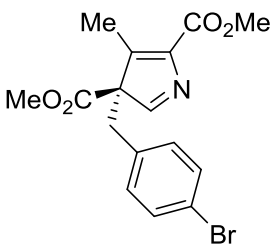
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.720	VB	0.7740	1.66209e4	290.27914	95.5570
2	38.614	VB	0.7531	772.80615	11.99587	4.4430

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.561	BB	0.6573	836.99536	14.87837	50.3487
2	39.042	BV	0.7671	825.40228	12.59414	49.6513

(*S*)-dimethyl 3-(4-bromobenzyl)-4-methyl-3*H*-pyrrole-3,5-dicarboxylate (**3d**)

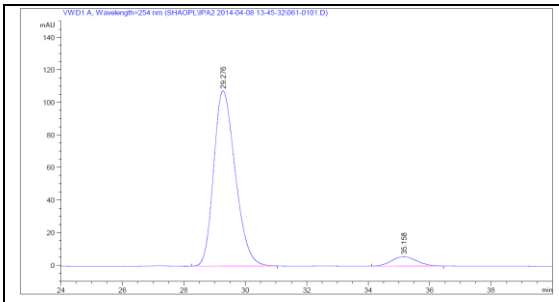


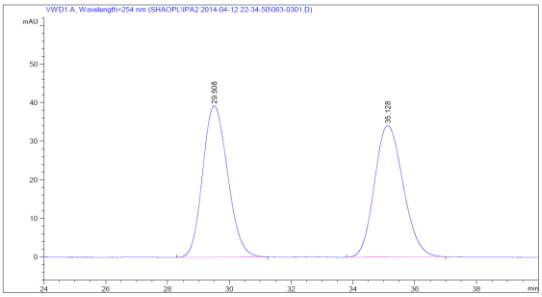
3d

The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 87% yield. **^{1}H NMR** (500 MHz, DMSO): δ 8.22 (s, 1H), 7.38 (d, *J*

= 8.3 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 3.70 (s, 3H), 3.63 (s, 3H), 3.61 (d, *J* = 13.8 Hz, 1H), 3.20 (d, *J* = 13.5 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR** (125 MHz, DMSO): δ 170.3, 167.1, 162.6, 147.8, 142.0, 133.7, 131.5, 130.8, 120.3, 74.2, 53.1, 51.5, 35.5, 11.4; **HRMS** (ESI): m/z calcd. for $[C_{16}H_{16}BrNNaO_4, M+Na]^+$: 388.0155; found: 388.0165.

Optical Rotation: $[\alpha]^{25}_D$ = 64.3 (c = 0.3, $CHCl_3$). The absolute configuration of **3d** was assigned by analogy to **3a**. 88% ee (HPLC condition: Chiralpak IC column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 29.3 min for major isomer, t_R = 35.2 min for minor isomer).





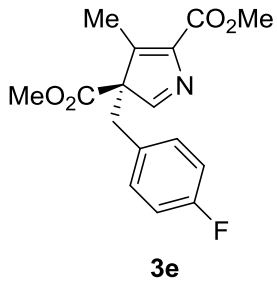
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.276	BB	0.5883	5255.60645	107.80663	94.1710
2	35.158	BB	0.6601	325.31232	5.76726	5.8290

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.508	BB	0.6565	2200.97900	39.26047	50.0668
2	35.128	BB	0.7533	2195.10376	34.06339	49.9332

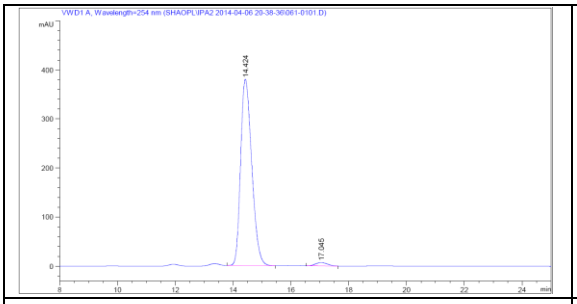
(*S*)-dimethyl 3-(4-fluorobenzyl)-4-methyl-3*H*-pyrrole-3,5-dicarboxylate (**3e**)



3e

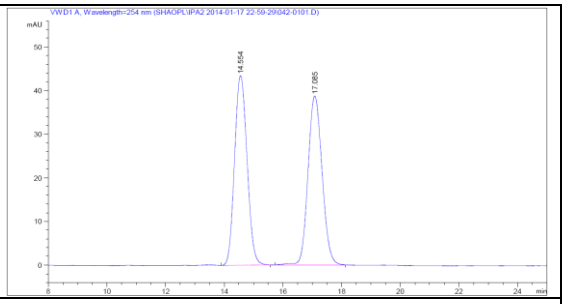
The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1.5:1). Colorless syrup, 92% yield. **^{1}H NMR** (500 MHz, DMSO): δ 8.22 (s, 1H), 7.15-7.12 (m, 1H), 7.03-6.99 (m, 1H), 3.69 (s, 3H), 3.63 (d, *J* = 13.9 Hz, 1H), 3.63 (s, 3H), 3.20 (d, *J* = 13.9 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR** (125 MHz, DMSO): δ 170.4, 167.2, 162.7, 161.2 (d, *J* = 241.4 Hz), 147.8, 142.0, 131.2 (d, *J* = 8.2 Hz), 130.4 (d, *J* = 2.7 Hz), 114.6 (d, *J* = 21.0 Hz), 74.4, 53.0, 51.5, 35.5, 11.4; **^{19}F NMR** (DMSO, 282 MHz): δ -115.52; **HRMS** (ESI): m/z calcd. for $[C_{16}H_{16}FNNaO_4, M+Na]^+$: 328.0956; found: 328.0971.

Optical Rotation: $[\alpha]^{25}_{D}$ = 39.4 (c = 0.7, $CHCl_3$). The absolute configuration of **3e** was assigned by analogy to **3a**. 96% ee (HPLC condition: Chiralpak IC column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 14.4 min for major isomer, t_R = 17.0 min for minor isomer).



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.424	VV	0.3722	1.01607e4	379.69833	98.0730
2	17.045	VV	0.3357	199.64679	6.96355	1.9270

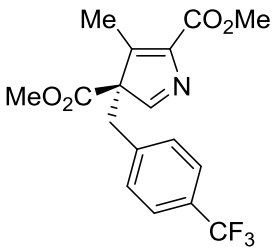


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.554	BB	0.3528	1283.29382	43.42076	49.8580
2	17.085	BB	0.3940	1290.60278	38.70964	50.1420

(*S*)-dimethyl

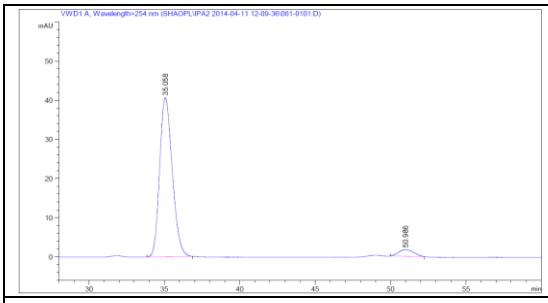
4-methyl-3-(4-(trifluoromethyl)benzyl)-3*H*-pyrrole-3,5-dicarboxylate (3f)



3f

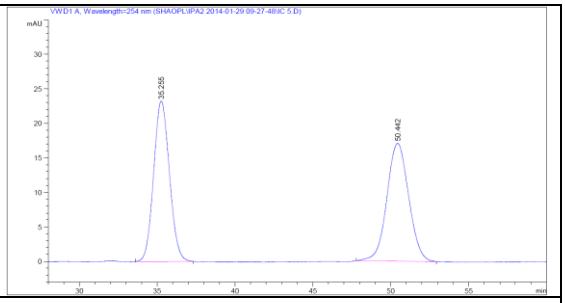
The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 88% yield. **^{1}H NMR** (500 MHz, DMSO): δ 8.26 (s, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 3.73 (d, *J* = 13.2 Hz, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 3.32 (d, *J* = 14.5 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR** (125 MHz, DMSO): δ 170.2, 167.1, 162.6, 147.7, 142.1, 139.2, 130.1, 127.6 (q, *J* = 31.9 Hz), 124.7 (q, *J* = 4.6 Hz), 124.2 (q, *J* = 270.5 Hz), 74.2, 53.1, 51.5, 35.7, 11.3; **^{19}F NMR** (282 MHz, DMSO): δ -60.94; **HRMS** (ESI): m/z calcd. for $[C_{17}H_{16}F_3NNaO_4, M+Na]^+$: 378.0924; found: 378.0932.

Optical Rotation: $[\alpha]^{25}_{D}$ = 50.2 (c = 0.3, $CHCl_3$). The absolute configuration of **3f** was assigned by analogy to **3a**. 91% ee (HPLC condition: Chiralpak IC column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 35.1 min for major isomer, t_R = 51.0 min for minor isomer).



Signal 1: VWD1 A, Wavelength=254 nm

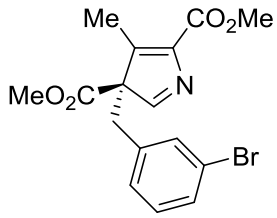
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.058	BB	0.6813	2367.87354	40.64016	95.2682
2	50.986	BB	0.8120	117.60919	1.70441	4.7318



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.255	BB	0.8260	1637.85962	23.24649	49.6986
2	50.442	BB	1.1438	1657.72803	17.07239	50.3014

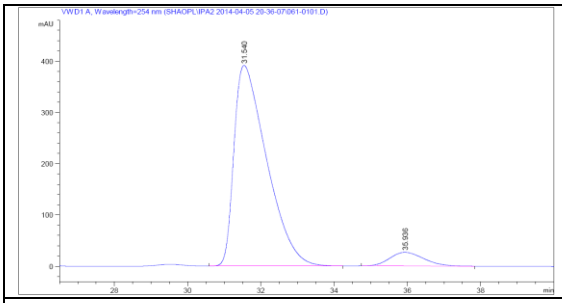
(*S*)-dimethyl 3-(3-bromobenzyl)-4-methyl-3*H*-pyrrole-3,5-dicarboxylate (3g)



3g

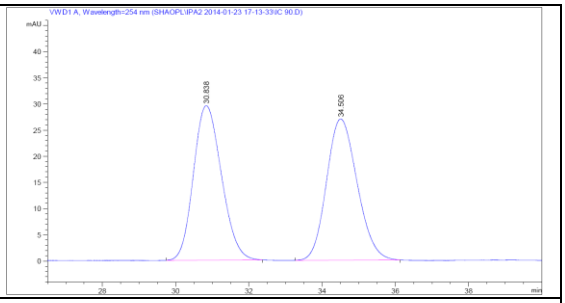
The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 94% yield. **^{1}H NMR** (500 MHz, DMSO): δ 8.24 (s, 1H), 7.38-7.33 (m, 2H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 3.70 (s, 3H), 3.63 (d, *J* = 13.9 Hz, 1H), 3.64 (s, 3H), 3.23 (d, *J* = 13.3 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR** (125 MHz, DMSO): δ 170.2, 167.1, 162.6, 147.7, 142.1, 137.0, 132.0, 130.0, 128.3, 121.0, 74.2, 53.1, 51.5, 35.5, 11.4; **HRMS** (ESI): m/z calcd. for $[C_{16}H_{16}BrNNaO_4, M+Na]^+$: 388.0155; found: 388.0159.

Optical Rotation: $[\alpha]^{25}_D$ = 48.2 (c = 0.3, $CHCl_3$). The absolute configuration of **3g** was assigned by analogy to **3a**. 87% ee (HPLC condition: Chiralpak IC column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 31.5 min for major isomer, t_R = 35.9 min for minor isomer).



Signal 1: VWD1 A, Wavelength=254 nm

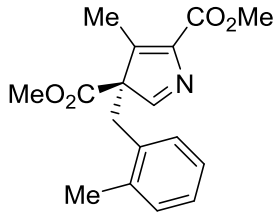
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.540	BB	0.8147	2.42107e4	391.13046	93.3785
2	35.936	BB	0.7560	1716.79358	26.63470	6.6215



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.838	BB	0.6224	1567.05066	29.51832	50.0318
2	34.506	BB	0.6783	1565.05554	26.97815	49.9682

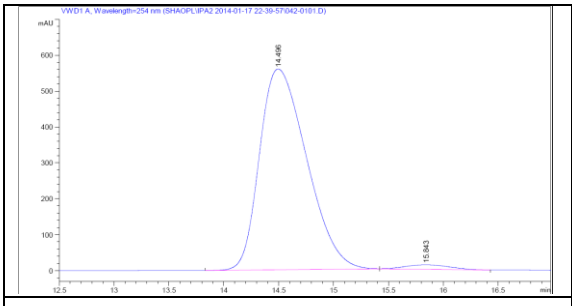
(*S*)-dimethyl 4-methyl-3-(2-methylbenzyl)-3*H*-pyrrole-3,5-dicarboxylate (3h)



3h

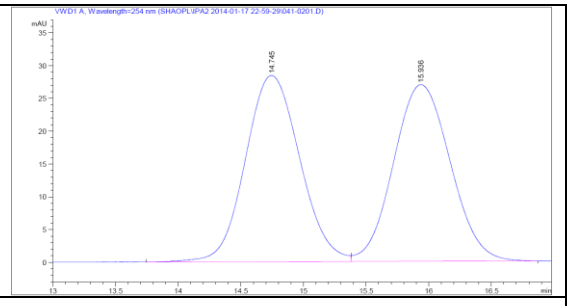
The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 84% yield. **^{1}H NMR** (500 MHz, DMSO): δ 8.06 (s, 1H), 7.13-7.08 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 3.62 (d, *J* = 14.4 Hz, 1H), 3.07 (d, *J* = 14.2 Hz, 1H), 2.32 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** (125 MHz, DMSO): δ 170.1, 167.5, 162.8, 148.2, 141.6, 136.1, 133.1, 130.4, 129.2, 127.2, 125.5, 74.5, 53.1, 51.5, 33.4, 19.4, 11.5; **HRMS** (ESI): m/z calcd. for [$C_{17}H_{18}NO_4$, M-H]$^-$: 300.1241; found: 300.1233.

Optical Rotation: $[\alpha]^{25}_D$ = 52.5 (c = 0.3, $CHCl_3$). The absolute configuration of **3h** was assigned by analogy to **3a**. 96% ee (HPLC condition: Chiralpak IC column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 14.5 min for major isomer, t_R = 15.8 min for minor isomer).



Signal 1: VWD1 A, Wavelength=254 nm

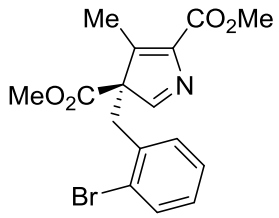
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.496	BB	0.4175	1.66658e4	559.06122	97.9664
2	15.843	BB	0.3237	345.96002	12.49807	2.0336



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.745	BV	0.3617	855.85681	28.39102	50.2045
2	15.936	VB	0.3712	848.88342	26.93318	49.7955

(*S*)-dimethyl 3-(2-bromobenzyl)-4-methyl-3*H*-pyrrole-3,5-dicarboxylate (**3i**)

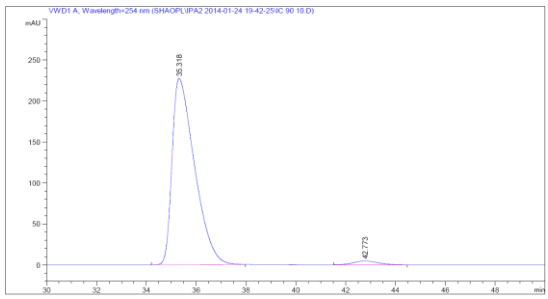


3i

The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 90% yield. **^{1}H NMR** (500 MHz, DMSO): δ 8.15 (s, 1H), 7.56 (dd, *J* = 7.8 Hz, 0.9 Hz, 1H), 7.26-7.22 (m, 1H), 7.17-7.14 (m, 1H),

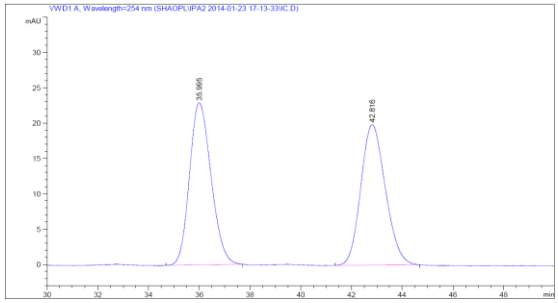
7.11 (dd, *J* = 7.6 Hz, 1.7 Hz, 1H), 3.80 (d, *J* = 14.0 Hz, 1H), 3.72 (s, 3H), 3.65 (s, 3H), 3.35 (d, *J* = 14.0 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR** (125 MHz, DMSO): δ 169.1, 167.0, 162.7, 147.7, 142.0, 134.0, 132.8, 131.0, 129.4, 127.5, 124.4, 74.3, 53.3, 51.6, 36.0, 11.6; **HRMS** (ESI), m/z calcd. for $[C_{16}H_{16}BrNNaO_4, M+Na]^+$: 388.0155; found: 388.0148.

Optical Rotation: $[\alpha]^{25}_D$ = 71.3 (c = 0.4, $CHCl_3$). The absolute configuration of **3i** was assigned by analogy to **3a**. 96% ee (HPLC condition: Chiralpak IC column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 35.3 min for major isomer, t_R = 42.8 min for minor isomer).



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.318	BB	0.7422	1.42154e4	227.28114	97.8621
2	42.773	BB	0.7938	310.54532	4.57593	2.1379

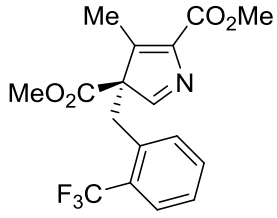


Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.995	VB	0.6902	1355.59167	22.94728	50.3227
2	42.816	BB	0.7874	1338.20361	19.89107	49.6773

(*S*)-dimethyl

4-methyl-3-(2-(trifluoromethyl)benzyl)-3*H*-pyrrole-3,5-dicarboxylate (**3j**)

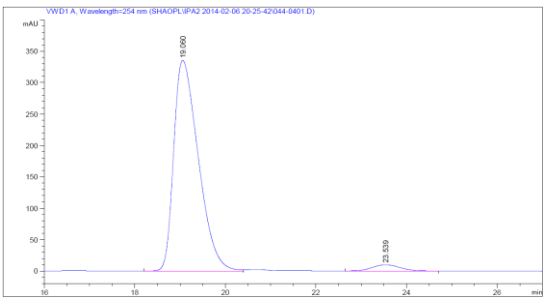


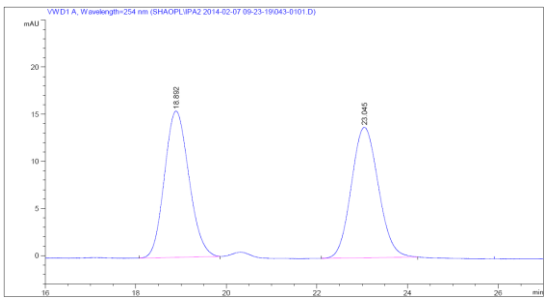
3j

The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 85% yield. **^{1}H NMR** (500 MHz, DMSO): δ 7.90 (s, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 3.82 (d, *J* = 14.8 Hz, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 3.35 (d, *J* = 14.8 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR** (125 MHz, DMSO): δ 169.5, 167.1, 162.7, 148.1, 142.3, 133.2, 132.3, 130.3, 127.9, 127.1 (q, *J* = 29.2 Hz), 126.1 (q, *J* = 5.5 Hz), 124.3 (q, *J* = 272.4 Hz), 73.7, 53.4, 51.6, 31.7, 11.3;

^{19}F NMR (282 MHz, DMSO): δ -56.90; **HRMS** (ESI): m/z calcd. for [$C_{17}H_{16}F_3NO_4$, M-H]$^-$: 354.0959; found: 354.0952.

Optical Rotation: $[\alpha]^{25}_D$ = -31.6 (c = 0.3, $CHCl_3$). The absolute configuration of **3j** was assigned by analogy to **3a**. 94% ee (HPLC condition: Chiralpak IC column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 19.1 min for major isomer, t_R = 23.5 min for minor isomer).





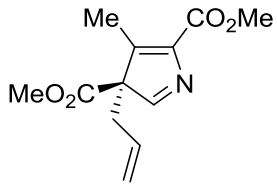
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.060	BV	0.5726	1.26316e4	335.23303	96.8317
2	23.539	BB	0.4947	413.29828	9.86670	3.1683

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.892	BB	0.4418	582.71259	15.52738	50.3647
2	23.045	BB	0.4851	574.27374	13.85384	49.6353

(*S*)-dimethyl 3-allyl-4-methyl-3*H*-pyrrole-3,5-dicarboxylate (3k)

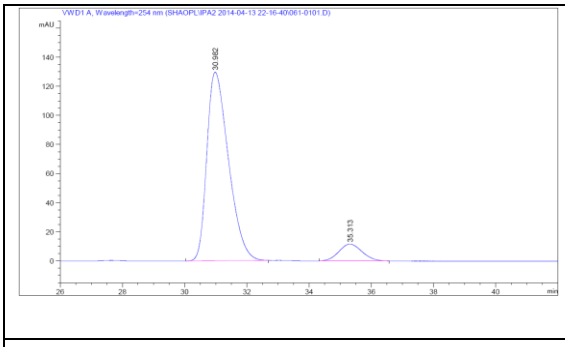


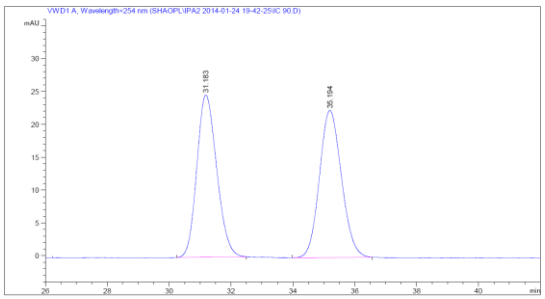
3k

The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 88% yield. **^{1}H NMR** (500 MHz, DMSO): δ 8.11 (s, 1H), 5.30-5.22 (m, 1H), 5.12 (dd, *J* = 17.0 Hz, 1.2 Hz, 1H), 4.98-4.96 (m, 1H), 3.76 (s, 3H), 3.61 (s, 3H), 2.99 (dd, *J* = 13.8 Hz, 6.7 Hz, 1H), 2.61 (dd, *J* = 13.8 Hz, 7.6 Hz, 1H), 2.16 (s, 3H); **^{13}C NMR** (125 MHz, DMSO): δ 170.4, 167.1, 162.9, 148.4, 141.6, 130.5, 119.5, 73.3, 53.0, 51.5, 34.4, 11.0; **HRMS** (ESI), m/z calcd. for [$C_{12}H_{15}NNaO_4$, M+Na]$^+$: 260.0893; found: 260.0900.

Optical Rotation: $[\alpha]^{25}_D$ = 5.1 (c = 0.2, $CHCl_3$). The absolute configuration of **3k** was assigned by analogy to **3a**. 83% ee (HPLC condition: Chiralpak IC column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 31.0 min

for major isomer, t_R = 35.3 min for minor isomer).





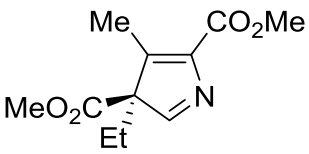
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.982	BB	0.5979	6260.72607	129.64581	91.3071
2	35.313	BB	0.6045	596.05530	11.54218	8.6929

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.183	BV	0.5227	1101.27893	24.69826	49.8963
2	35.194	BB	0.5778	1105.85596	22.38541	50.1037

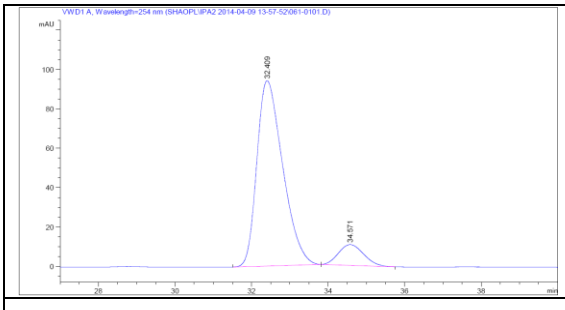
(*S*)-dimethyl 3-ethyl-4-methyl-3*H*-pyrrole-3,5-dicarboxylate (3l)

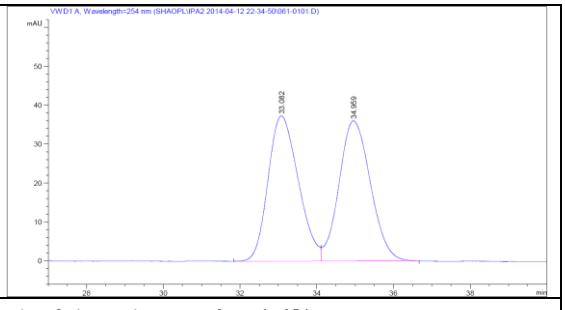


3l

The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 73% yield. **^{1}H NMR** (500 MHz, DMSO): δ 8.12 (s, 1H), 3.78 (s, 3H), 3.61 (s, 3H), 2.31-2.24 (m, 1H), 2.14 (s, 3H), 1.88-1.81 (m, 1H), 0.58 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO): δ 171.0, 167.7, 162.9, 148.5, 141.5, 74.3, 52.9, 51.5, 23.9, 10.8, 7.9; **HRMS** (ESI): m/z calcd. for $[C_{11}H_{15}NNaO_4, M+Na]^+$: 248.0893; found: 248.0905.

Optical Rotation: $[\alpha]^{25}_D$ = 6.5 (c = 0.2, $CHCl_3$). The absolute configuration of **3l** was assigned by analogy to **3a**. 80% ee (HPLC condition: Chiralpak IC column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 32.4 min for major isomer, t_R = 34.6 min for minor isomer).





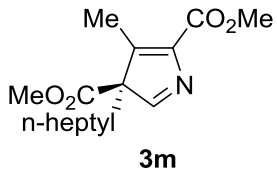
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.409	BB	0.5500	4408.55322	94.11761	90.1395
2	34.571	BB	0.5357	482.25842	10.53631	9.8605

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.082	BV	0.6426	2048.76660	37.34404	49.9184
2	34.959	VB	0.6665	2055.46509	36.06234	50.0816

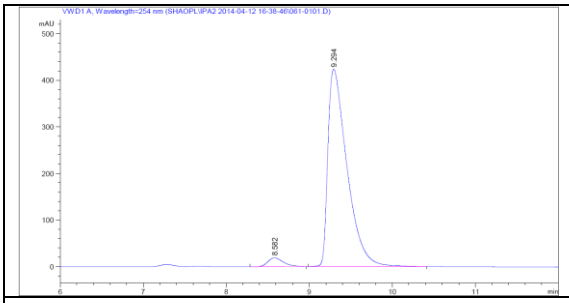
(*S*)-dimethyl 3-heptyl-4-methyl-3*H*-pyrrole-3,5-dicarboxylate (3m)



3m

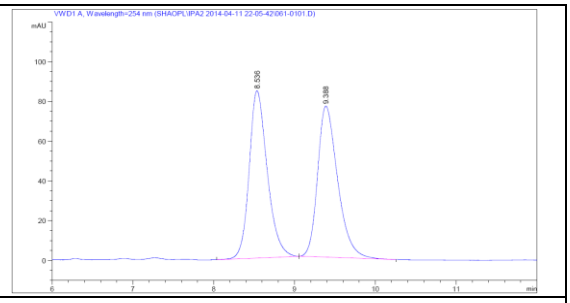
The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 1:1). Colorless syrup, 89% yield. **^{1}H NMR** (500 MHz, DMSO): δ 8.14 (s, 1H), 3.78 (s, 3H), 3.61 (s, 3H), 2.24-2.18 (m, 1H), 2.15 (s, 3H), 1.81-1.75 (m, 1H), 1.25-1.18 (m, 8H), 0.91-0.86 (m, 2H), 0.83 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, DMSO): δ 171.1, 167.6, 162.9, 148.6, 141.3, 73.9, 52.9, 51.5, 31.1, 30.6, 28.9, 28.2, 23.2, 22.0, 13.8, 10.9; **HRMS** (ESI), m/z calcd. for [$C_{16}H_{25}NNaO_4$, M+Na]$^{+}$: 318.1676; found: 318.1679.

Optical Rotation: $[\alpha]^{25}_{D}$ = +21.1 (c = 0.3, $CHCl_3$). The absolute configuration of **3m** was assigned by analogy to **3a**. 93% ee (HPLC condition: Chiralcel IB column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 8.6 min for minor isomer, t_R = 9.3 min for major isomer).



Signal 1: VWD1 A, Wavelength=254 nm

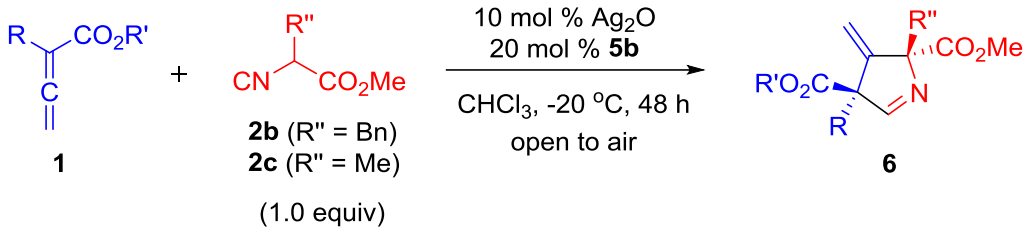
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.582	BB	0.1613	241.54588	18.80792	3.4665
2	9.294	BB	0.2308	6726.39209	423.50473	96.5335



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.536	BB	0.2189	1307.48840	84.11266	49.9077
2	9.388	BB	0.2259	1312.32678	76.00854	50.0923

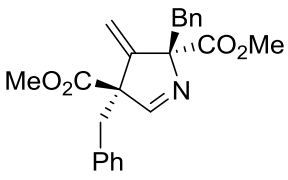
IV. Ag-Catalyzed enantioselective cyclization of substituted isocyanoacetate



General procedure. To a 10 mL vial charged with **5b** (12 mg, 0.020 mmol) and Ag_2O (2.3 mg, 0.010 mmol) was added anhydrous $CHCl_3$ (0.5 mL). The mixture was allowed to stir at ambient temperature for 5 min, then allenoate **1** (0.10 mmol) was added in one portion. After the mixture was cooled to -20 °C, isocyanoacetate **2b** or **2c** (0.10 mmol) in anhydrous $CHCl_3$ (0.5 mL) was added via syringe pump over 2 h. The reaction mixture was stirred at -20 °C for 48 h, concentrated and purified by flash chromatography (hexanes/ethyl acetate) to afford the product **6**. The pure major diastereomer was isolated and characterized.

V. Characterization of compounds 6

(2*R*,4*S*)-dimethyl 2,4-dibenzyl-3-methylene-3,4-dihydro-2*H*-pyrrole-2,4-dicarboxylate (6a)

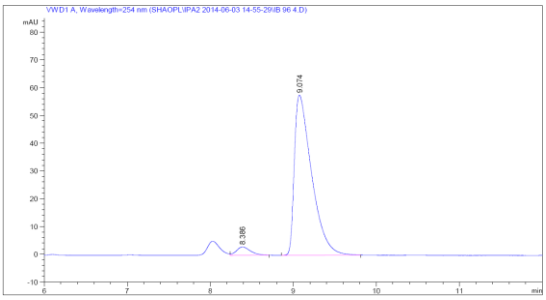


6a

6:1 dr (of crude). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). White solid, 85% yield. **MP**: 87-89 °C; **^{1}H NMR** (500 MHz, DMSO): δ 7.65 (s, 1H), 7.23-7.18 (m, 3H), 7.17-7.14 (m, 3H), 7.01-6.98 (m, 4H), 5.65 (s, 1H), 5.60 (s, 1H), 3.36 (s, 3H), 3.32 (s, 3H), 3.31 (d, *J* = 15.1 Hz, 1H), 3.26 (d, *J* = 13.2 Hz, 1H), 3.00 (d, *J* = 13.9 Hz, 1H), 2.91 (d, *J* = 13.3 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO): δ 170.9,

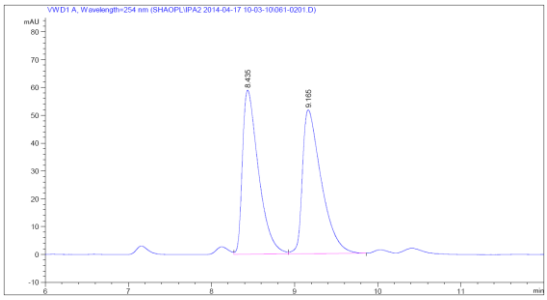
170.1, 166.9, 147.3, 135.3, 135.2, 130.8, 130.0, 128.0, 127.3, 126.7, 126.2, 112.5, 84.9, 66.4, 52.6, 52.4, 44.1, 42.7; **HRMS** (ESI): m/z calcd. for $[C_{23}H_{24}NO_4, M+H]^+$: 378.1700; found: 378.1711.

Optical Rotation: $[\alpha]^{25}_D$ = 51.6 (c = 1.0, $CHCl_3$). 92% ee (HPLC condition: Chiralpak IB column, *n*-hexane/*i*-PrOH = 96:4, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 8.4 min for minor isomer, t_R = 9.1 min for major isomer).



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.386	VV	0.1386	34.94751	2.99643	4.0403
2	9.074	BV	0.1942	830.03448	57.65868	95.9597



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.435	VV	0.1914	791.58527	58.97248	49.2947
2	9.165	VB	0.2054	814.23706	51.72694	50.7053

The *trans* relative configuration of **6a** was determined by the NOE (Figure S1), and reconfirmed by X-ray crystallographic analysis of a single crystal of **6a** (Figure S2).

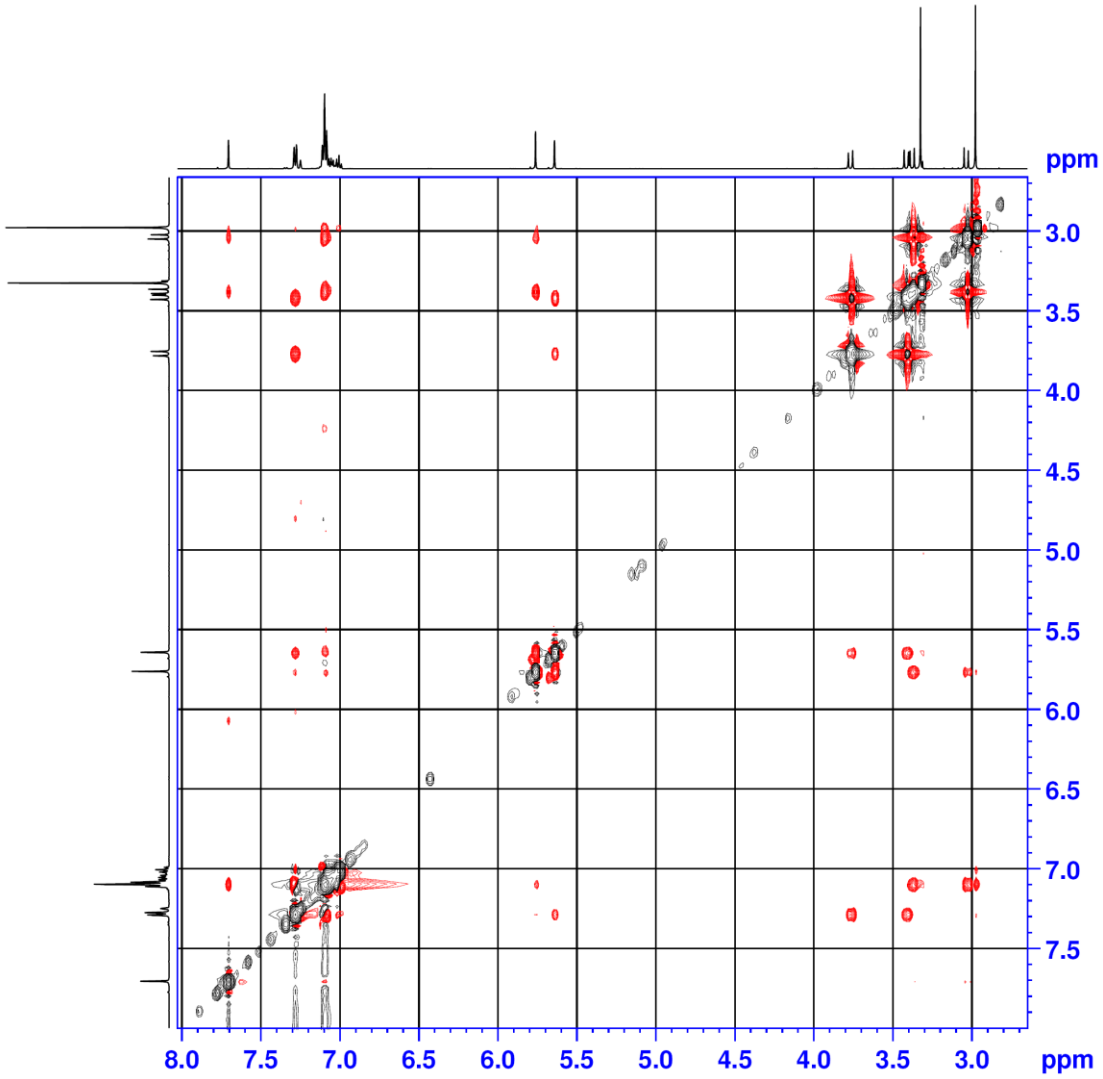
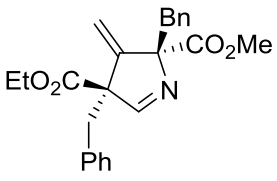


Figure S1. NOESY spectra of **6a**.

(2*R*,4*S*)-4-ethyl-2-methyl-2,4-dibenzyl-3-methylene-3,4-dihydro-2*H*-pyrrole-2,4-dicarboxylate (6b)

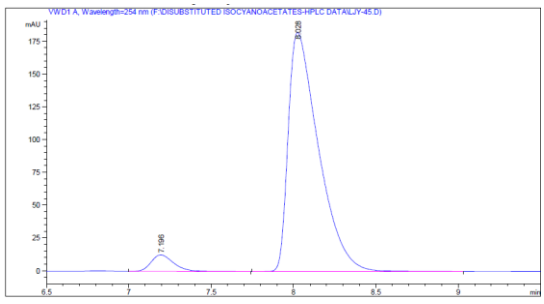


6b

11:1 dr (of crude). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 90% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.23-7.01 (m, 10H), 5.74 (s, 1H), 5.71 (s, 1H), 3.99-3.88 (m, 1H), 3.75-3.65 (m, 1H), 3.52 (s, 3H), 3.43 (d, *J* = 13.5 Hz, 1H), 3.29 (d, *J* = 13.4 Hz, 1H), 3.10 (d, *J* = 13.5 Hz, 1H), 2.92 (d, *J* = 13.4 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.6, 170.0, 167.5, 147.5, 135.3, 135.1, 131.2, 130.1, 128.2, 127.5, 126.9, 126.4, 112.9, 85.3, 66.7, 61.6, 52.7, 45.0, 44.4, 13.7; **HRMS**

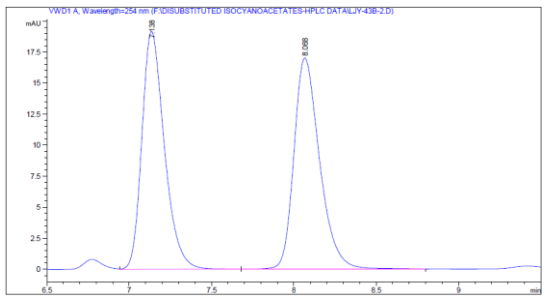
(ESI): m/z calcd. for $[C_{24}H_{26}NO_4, M+H]^+$: 392.1856; found: 392.1867.

Optical Rotation: $[\alpha]^{23}_D$ = 38.2 (c = 0.5, $CHCl_3$). The absolute configuration of **6b** was assigned by analogy to **6a**. 90% ee (HPLC condition: Chiralpak IB column, *n*-hexane/*i*-PrOH = 96:4, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 7.2 min for minor isomer, t_R = 8.0 min for major isomer).



Signal 1: VWD1 A, Wavelength=254 nm

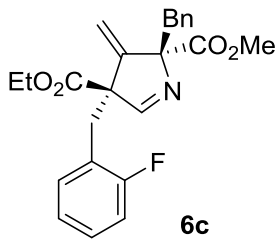
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.196	VB	0.1464	120.59810	12.63223	4.9254
2	8.028	BV	0.1900	2327.91309	182.03169	95.0746



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.138	VB	0.1458	181.94548	19.15106	49.6595
2	8.068	BB	0.1645	184.44064	16.99959	50.3405

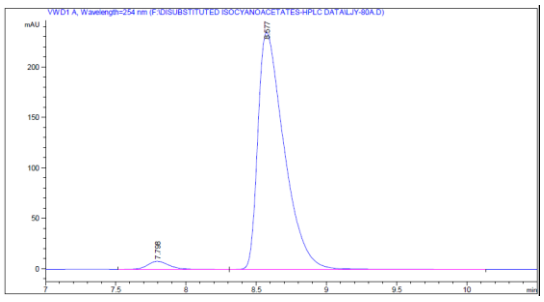
(2*R*,4*S*)-4-ethyl 2-methyl 2-benzyl-4-(2-fluorobenzyl)-3-methylene-3,4-dihydro-2*H*-pyrrole-2,4-dicarboxylate (6c)



6c

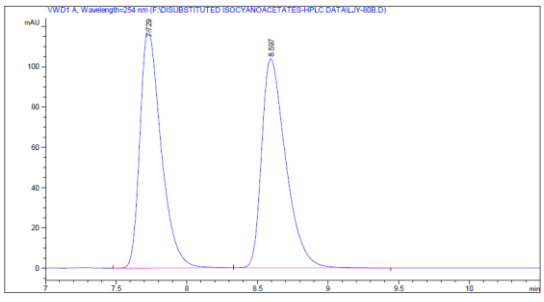
8:1 dr (of crude). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 78% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 2.6 Hz, 1H), 7.20-6.90 (m, 9H), 5.78 (s, 1H), 5.71 (s, 1H), 4.03-3.92 (m, 1H), 3.84-3.73 (m, 1H), 3.46-3.27 (m, 5H), 3.12-2.99 (m, 2H), 1.10 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.6, 169.8, 166.9, 161.1 (d, *J* = 246.2 Hz), 147.0, 135.3, 132.7 (d, *J* = 4.1 Hz), 131.1, 129.0 (d, *J* = 8.3 Hz), 127.6, 126.5, 123.7 (d, *J* = 3.7 Hz), 122.3 (d, *J* = 15.8 Hz), 115.4 (d, *J* = 22.5 Hz), 113.4, 85.3, 66.7, 61.8, 52.7, 45.5, 36.3, 13.7; **HRMS** (ESI): m/z calcd. for $[C_{24}H_{25}FNO_4, M+H]^+$: 410.1762; found: 410.1777.

Optical Rotation: $[\alpha]^{25}_{D}$ = 37.6 (c = 0.3, $CHCl_3$). The absolute configuration of **6c** was assigned by analogy to **6a**. 94% ee (HPLC condition: Chiralpak IB column, *n*-hexane/*i*-PrOH = 96:4, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 7.8 min for minor isomer, t_R = 8.6 min for major isomer).



Signal 1: VWD1 A, Wavelength=254 nm

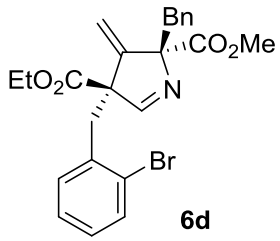
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.798	VV	0.1635	86.97683	8.08093	2.7800
2	8.577	VB	0.1949	3041.72290	234.71327	97.2200



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.729	BB	0.1577	1223.94080	117.80592	49.9724
2	8.597	BB	0.1802	1225.29333	103.65217	50.0276

(2*R*,4*S*)-4-ethyl 2-methyl 2-benzyl-4-(2-bromobenzyl)-3-methylene-3,4-dihydro-2*H*-pyrrole-2,4-dicarboxylate (6d)

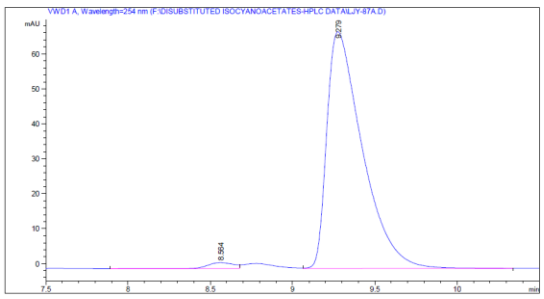


6d

7:1 dr (of crude). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 70% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.56-7.43 (m, 1H), 7.16-7.06 (m, 8H), 5.78 (d, *J* = 3.3 Hz, 2H), 4.02-3.91 (m, 1H), 3.78-3.66 (m, 1H), 3.52 (s, 3H), 3.45 (dd, *J* = 13.6, 6.2 Hz, 2H), 3.24 (d, *J* = 13.7 Hz, 1H), 3.10 (d, *J* = 13.5 Hz, 1H), 1.06 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.6, 169.9, 166.8, 147.4, 135.2, 133.1, 132.0, 131.1, 128.7, 127.5, 127.1, 126.4, 125.4, 113.5, 85.2, 77.2, 66.8, 61.8, 52.6, 45.2, 42.9, 13.7; **HRMS** (ESI): m/z calcd. for $[C_{24}H_{25}BrNO_4, M+H]^+$: 470.0961; found: 470.0964.

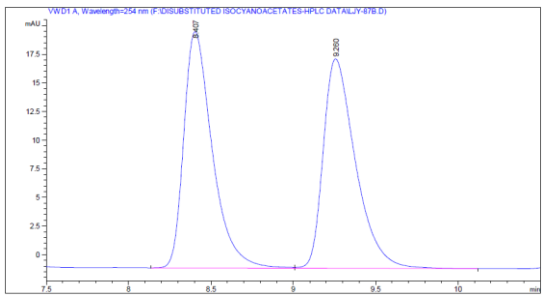
Optical Rotation: $[\alpha]^{22}_{D}$ = 22.1 (c = 0.3, $CHCl_3$). The absolute configuration of **6d** was assigned by analogy to **6a**. 96% ee (HPLC condition: Chiralpak IB column,

n-hexane/*i*-PrOH = 96:4, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 8.6 min for minor isomer, t_R = 9.3 min for major isomer).



Signal 1: VWD1 A, Wavelength=254 nm

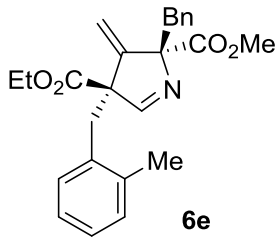
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.564	BV	0.1687	19.25164	1.71770	1.8614
2	9.279	VB	0.2245	1015.00482	67.67448	98.1386



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.407	BV	0.1842	248.20226	20.61120	49.9459
2	9.260	VB	0.2055	248.73956	18.26922	50.0541

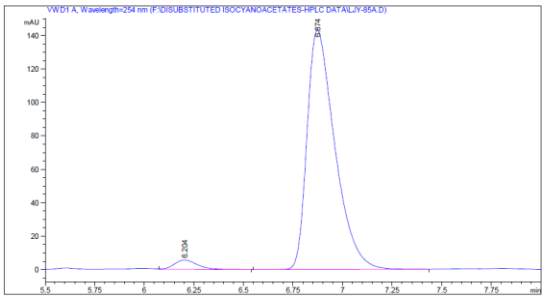
(2*R*,4*S*)-4-ethyl 2-methyl 2-benzyl-4-(2-methylbenzyl)-3-methylene-3,4-dihydro-2*H*-pyrrole-2,4-dicarboxylate (6e)



6e

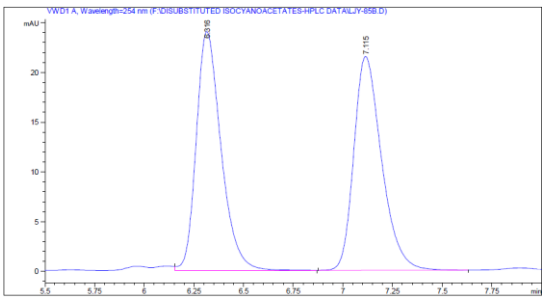
>20:1 dr (of crude). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 4:1). Colorless wax, 67% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.22-6.98 (m, 9H), 5.75 (s, 1H), 5.69 (s, 1H), 4.00-3.89 (m, 1H), 3.72-3.55 (m, 4H), 3.48 (d, *J* = 13.5 Hz, 1H), 3.30 (d, *J* = 13.8 Hz, 1H), 3.15 (d, *J* = 13.6 Hz, 1H), 3.02 (d, *J* = 13.8 Hz, 1H), 2.25 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.8, 170.3, 168.0, 148.3, 136.6, 135.3, 133.9, 131.3, 130.6, 130.2, 127.5, 127.2, 126.4, 125.8, 112.7, 85.3, 66.7, 61.6, 52.7, 44.4, 41.3, 19.7, 13.7; **HRMS** (ESI): m/z calcd. for $[C_{25}H_{28}NO_4, M+H]^+$: 406.2013; found: 406.2024.

Optical Rotation: $[\alpha]^{24}_D$ = 36.5 (c = 0.3, $CHCl_3$). The absolute configuration of **6e** was assigned by analogy to **6a**. 94% ee (HPLC condition: Chiralpak IB column, *n*-hexane/*i*-PrOH = 96:4, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 6.2 min for minor isomer, t_R = 6.9 min for major isomer).



Signal 1: VWD1 A, Wavelength=254 nm

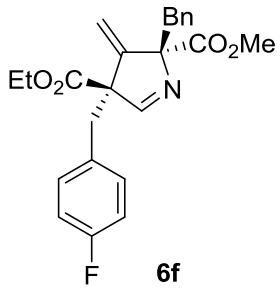
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.204	VB	0.1237	45.94837	5.66917	3.1898
2	6.874	BV	0.1486	1394.52600	143.15509	96.8102



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.316	VB	0.1316	207.96281	24.02143	49.8745
2	7.115	BB	0.1483	209.00940	21.51010	50.1255

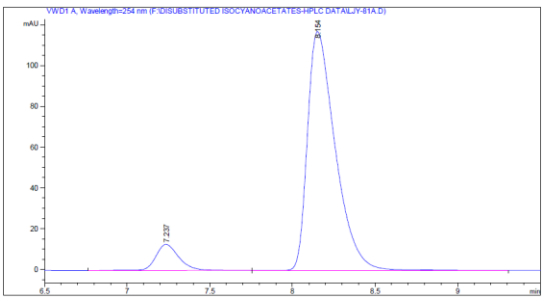
(2*R*,4*S*)-4-ethyl 2-methyl 2-benzyl-4-(4-fluorobenzyl)-3-methylene-3,4-dihydro-2*H*-pyrrole-2,4-dicarboxylate (6f)

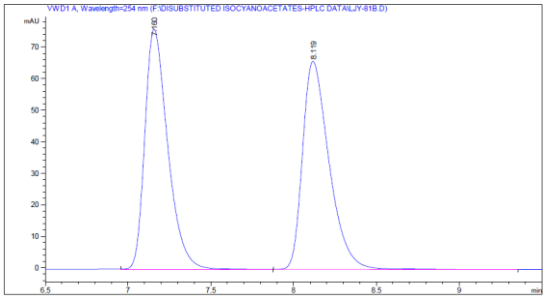


6f

8:1 dr (of crude). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 87% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.21-6.97 (m, 7H), 6.92-6.86 (m, 2H), 5.75 (s, 1H), 5.69 (s, 1H), 4.00-3.90 (m, 1H), 3.80-3.66 (m, 1H), 3.52 (s, 3H), 3.42 (d, *J* = 13.5 Hz, 1H), 3.26 (d, *J* = 13.6 Hz, 1H), 3.08 (d, *J* = 13.5 Hz, 1H), 2.92 (d, *J* = 13.6 Hz, 1H), 1.06 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.6, 169.9, 167.2, 162.0 (d, *J* = 245.5 Hz), 147.3, 135.2, 131.8 (d, *J* = 8.0 Hz), 131.1, 130.9 (d, *J* = 3.3 Hz), 127.6, 126.5, 115.1 (d, *J* = 21.3 Hz), 113.1, 85.4, 66.8, 61.7, 52.7, 45.3, 43.3, 13.8; **HRMS** (ESI): m/z calcd. for $[C_{24}H_{25}FNO_4, M+H]^+$: 410.1762; found: 410.1769.

Optical Rotation: $[\alpha]^{25}_D$ = 23.1 (c = 0.4, $CHCl_3$). The absolute configuration of **6f** was assigned by analogy to **6a**. 83% ee (HPLC condition: Chiralpak IB column, *n*-hexane/*i*-PrOH = 96:4, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 7.2 min for minor isomer, t_R = 8.2 min for major isomer).





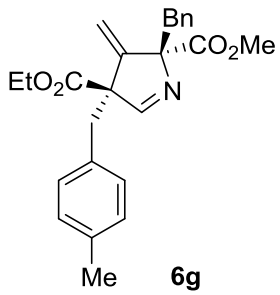
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.237	BB	0.1497	125.51192	12.76538	8.4047
2	8.154	BB	0.1773	1367.84045	116.96004	91.5953

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.160	VB	0.1471	732.23383	76.16946	49.8703
2	8.119	BB	0.1711	736.04211	65.92499	50.1297

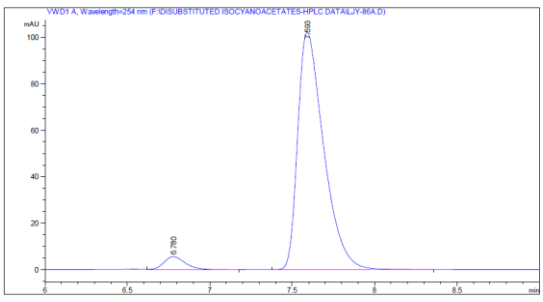
(2*R*,4*S*)-4-ethyl 2-methyl 2-benzyl-4-(4-methylbenzyl)-3-methylene-3,4-dihydro-2*H*-pyrrole-2,4-dicarboxylate (6g)

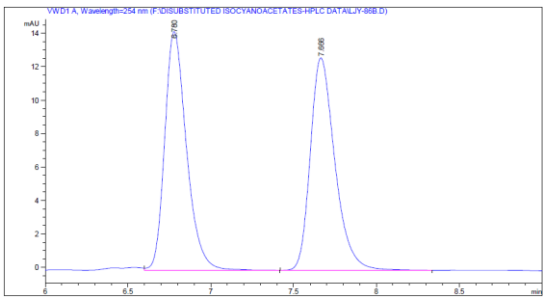


6g

7:1 dr (of crude). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 4:1). Colorless wax, 58% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.19-7.05 (m, 5H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 5.73 (s, 1H), 5.70 (s, 1H), 3.99-3.89 (m, 1H), 3.77-3.66 (m, 1H), 3.51 (s, 3H), 3.42 (d, *J* = 13.5 Hz, 1H), 3.25 (d, *J* = 13.5 Hz, 1H), 3.09 (d, *J* = 13.5 Hz, 1H), 2.88 (d, *J* = 13.5 Hz, 1H), 2.27 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.7, 170.1, 167.7, 147.6, 136.5, 135.3, 132.0, 131.2, 130.0, 128.9, 127.6, 126.4, 112.8, 85.3, 66.8, 61.6, 52.7, 45.1, 44.0, 21.0, 13.7; **HRMS** (ESI): m/z calcd. for $[C_{25}H_{28}NO_4, M+H]^+$: 406.2013; found: 406.2020.

Optical Rotation: $[\alpha]^{24}_D$ = 50.1 (c = 0.2, $CHCl_3$). The absolute configuration of **6g** was assigned by analogy to **6a**. 91% ee (HPLC condition: Chiralpak IB column, *n*-hexane/*i*-PrOH = 96:4, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 6.8 min for minor isomer, t_R = 7.6 min for major isomer).





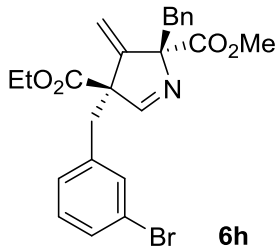
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.780	VB	0.1378	50.58162	5.57980	4.3302
2	7.593	VV	0.1654	1117.53906	102.27230	95.6698

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.780	VB	0.1417	130.41873	14.26197	49.8791
2	7.666	BB	0.1584	131.05101	12.69028	50.1209

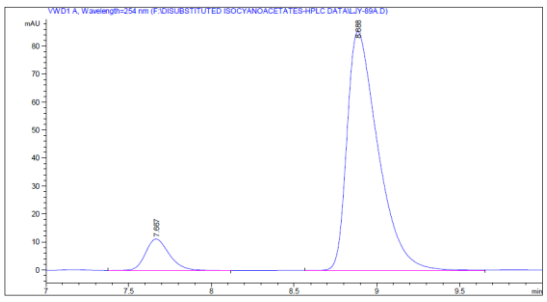
(2*R*,4*S*)-4-ethyl 2-methyl 2-benzyl-4-(3-bromobenzyl)-3-methylene-3,4-dihydro-2*H*-pyrrole-2,4-dicarboxylate (6h)

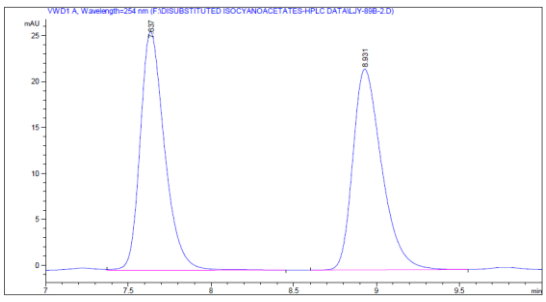


6h

10:1 dr (of crude). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 74% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.36-7.30 (m, 1H), 7.20-7.19 (m, 1H), 7.17-7.04 (m, 6H), 7.00-6.97 (m, 1H), 5.75 (s, 1H), 5.70 (s, 1H), 4.02-3.91 (m, 1H), 3.77-3.66 (m, 1H), 3.56 (s, 3H), 3.44 (d, *J* = 13.5 Hz, 1H), 3.25 (d, *J* = 13.5 Hz, 1H), 3.10 (d, *J* = 13.5 Hz, 1H), 2.88 (d, *J* = 13.5 Hz, 1H), 1.06 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.5, 169.8, 167.0, 147.3, 137.5, 135.2, 133.0, 131.2, 130.2, 129.8, 128.9, 127.6, 126.5, 122.3, 113.1, 85.4, 66.6, 61.8, 52.8, 45.0, 43.7, 13.8; **HRMS** (ESI): m/z calcd. for $[C_{24}H_{25}BrNO_4, M+H]^+$: 470.0961; found: 470.0974.

Optical Rotation: $[\alpha]^{22}_D$ = 29.8 (c = 0.4, $CHCl_3$). The absolute configuration of **6h** was assigned by analogy to **6a**. 82% ee (HPLC condition: Chiralpak IB column, *n*-hexane/*i*-PrOH = 96:4, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 7.7 min for minor isomer, t_R = 8.9 min for major isomer).





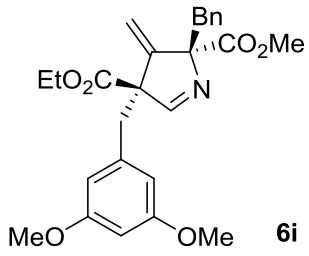
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.667	VB	0.1534	112.85846	11.25551	9.2130
2	8.888	BV	0.1957	1112.12939	85.37704	90.7870

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.637	VB	0.1559	265.85214	25.96662	50.0371
2	8.931	BV	0.1854	265.45810	21.85609	49.9629

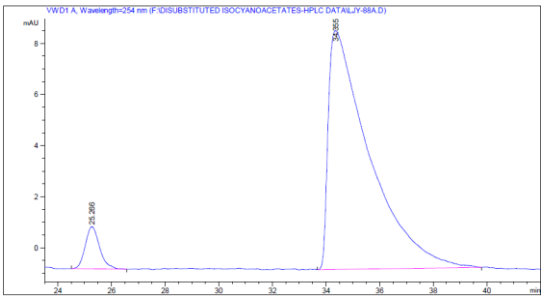
(2*R*,4*S*)-4-ethyl 2-methyl 2-benzyl-4-(3,5-dimethoxybenzyl)-3-methylene-3,4-dihydro-2*H*-pyrrole-2,4-dicarboxylate (6i)

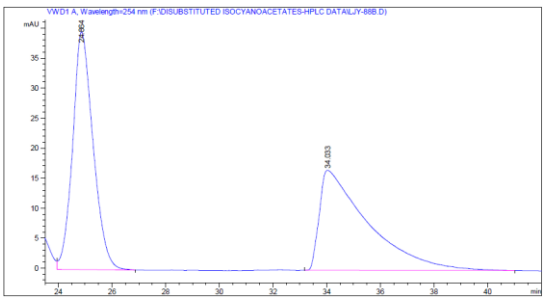


6i

11:1 dr (of crude). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 86% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.17-7.12 (m, 3H), 7.10-7.06 (m, 2H), 6.28 (t, *J* = 2.2 Hz, 1H), 6.19 (d, *J* = 2.2 Hz, 2H), 5.74 (s, 1H), 5.72 (s, 1H), 3.98-3.92 (m, 1H), 3.73-3.69 (m, 7H), 3.58 (s, 3H), 3.44 (d, *J* = 13.6 Hz, 1H), 3.23 (d, *J* = 13.4 Hz, 1H), 3.10 (d, *J* = 13.6 Hz, 1H), 2.85 (d, *J* = 13.4 Hz, 1H), 1.05 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.8, 170.0, 167.6, 160.6, 147.8, 137.4, 135.3, 131.2, 127.6, 126.5, 112.9, 108.0, 99.2, 85.4, 66.6, 61.6, 55.2, 52.7, 45.1, 44.8, 13.8; **HRMS** (ESI): m/z calcd. for $[C_{26}H_{30}NO_6, M+H]^+$: 452.2068; found: 452.2084.

Optical Rotation: $[\alpha]^{23}_D$ = 52.5 (c = 0.2, $CHCl_3$). The absolute configuration of **6i** was assigned by analogy to **6a**. 88% ee (HPLC condition: Chiralpak IE column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 25.3 min for minor isomer, t_R = 34.4 min for major isomer).





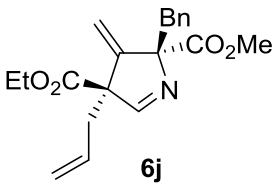
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.266	BB	0.5828	61.31674	1.64788	5.8156
2	34.355	BB	1.4259	993.03467	9.34848	94.1844

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.864	VB	0.7902	2098.56079	39.60702	50.1750
2	34.033	BB	1.6324	2083.92188	16.64777	49.8250

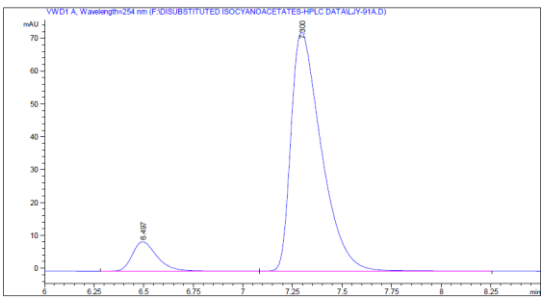
(2*R*,4*S*)-4-ethyl 2-methyl 4-allyl-2-benzyl-3-methylene-3,4-dihydro-2*H*-pyrrole-2,4-dicarboxylate (6j)



6j

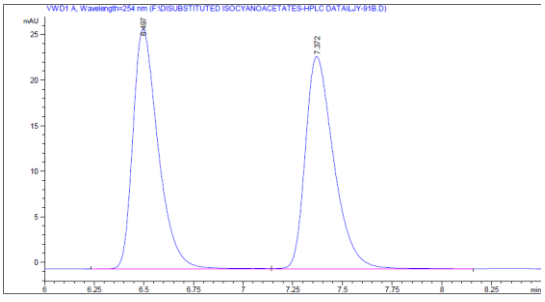
4:1 dr (of crude). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 67% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.18-7.09 (m, 5H), 5.71-5.47 (m, 3H), 5.11-5.06 (m, 1H), 5.04-4.99 (m, 1H), 4.02-3.91 (m, 1H), 3.82-3.64 (m, 4H), 3.46 (d, *J* = 13.6 Hz, 1H), 3.16 (d, *J* = 13.6 Hz, 1H), 2.66 (dd, *J* = 13.8, 7.1 Hz, 1H), 2.37 (dd, *J* = 13.8, 7.7 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.7, 169.8, 167.7, 147.4, 135.3, 131.7, 131.2, 127.6, 126.5, 119.5, 112.5, 85.5, 65.5, 61.6, 52.6, 44.7, 42.6, 13.8; **HRMS** (ESI): m/z calcd. for $[C_{20}H_{24}NO_4, M+H]^+$: 342.1700; found: 342.1710.

Optical Rotation: $[\alpha]^{22}_D$ = 20.3 (c = 0.2, $CHCl_3$). The absolute configuration of **6j** was assigned by analogy to **6a**. 82% ee (HPLC condition: Chiralpak IB column, *n*-hexane/*i*-PrOH = 96:4, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 6.5 min for minor isomer, t_R = 7.3 min for major isomer).



Signal 1: VWD1 A, Wavelength=254 nm

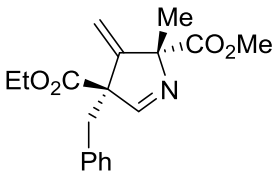
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.497	BV	0.1339	78.06826	8.94640	9.1760
2	7.300	VV	0.1621	772.71698	72.60119	90.8240



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.497	BV	0.1353	232.79108	26.31088	49.9599
2	7.372	VV	0.1516	233.16481	23.32430	50.0401

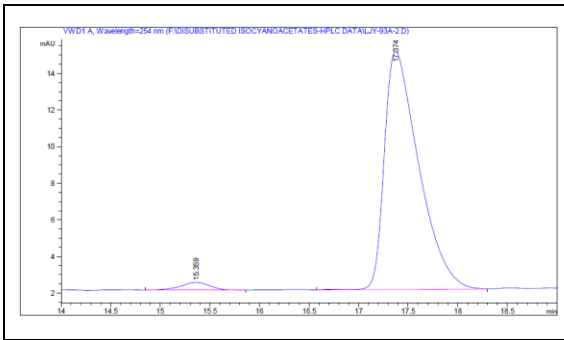
(2*R*,4*S*)-4-ethyl 2-methyl 4-benzyl-2-methyl-3-methylene-3,4-dihydro-2*H*-pyrrole-2,4-dicarboxylate (6k)

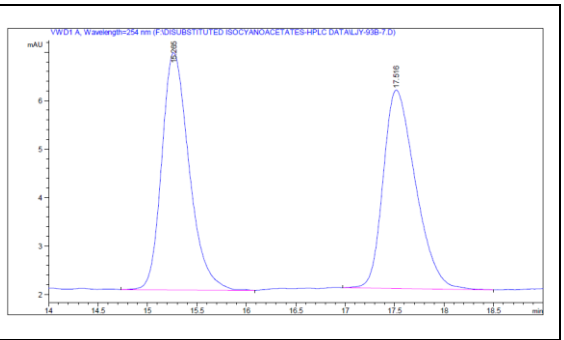


6k

11:1 dr (of crude). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 79% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.32-7.20 (m, 3H), 7.18-7.08 (m, 2H), 5.49 (s, 2H), 4.23-4.03 (m, 2H), 3.59 (s, 3H), 3.42 (d, *J* = 13.6 Hz, 1H), 2.99 (d, *J* = 13.6 Hz, 1H), 1.55 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 172.2, 170.4, 166.8, 150.6, 135.5, 130.2, 128.3, 127.0, 111.1, 81.5, 67.0, 61.7, 52.8, 43.2, 26.2, 13.9; **HRMS** (ESI): m/z calcd. for $[C_{18}H_{22}NO_4, M+H]^+$: 316.1543; found: 316.1550.

Optical Rotation: $[\alpha]^{23}_D$ = -55.8 (c = 0.3, $CHCl_3$). The absolute configuration of **6k** was assigned by analogy to **6a**. 94% ee (HPLC condition: Chiralpak IE column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, t_R = 15.4 min for minor isomer, t_R = 17.4 min for major isomer).





Signal 1: VWD1 A, Wavelength=254 nm						
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.359	BB	0.3102	8.88352	4.31435e-1	2.7630
2	17.374	BB	0.3624	312.63379	12.98880	97.2370

Signal 1: VWD1 A, Wavelength=254 nm						
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.265	BB	0.2972	94.05493	4.89152	50.3094
2	17.516	BB	0.3494	92.89819	4.09208	49.6906

VI. X-ray crystallographic analysis and determination of configuration of 6a

The absolute configuration of **6a** (**2*R***, **4*S***) was assigned by X-ray crystallographic analysis of a single crystal of **6a** (Figure S2). The crystal was prepared from the solution of **6a** in hexanes/ethyl acetate (8:1) at ambient temperature.

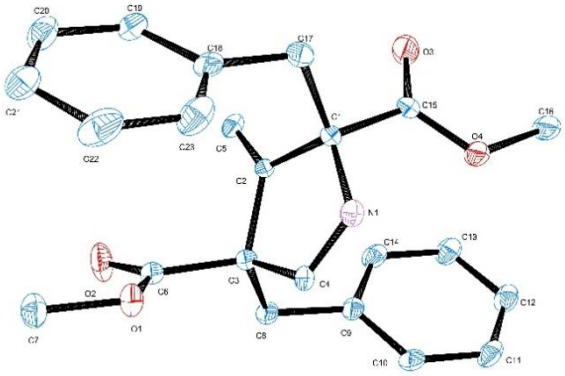


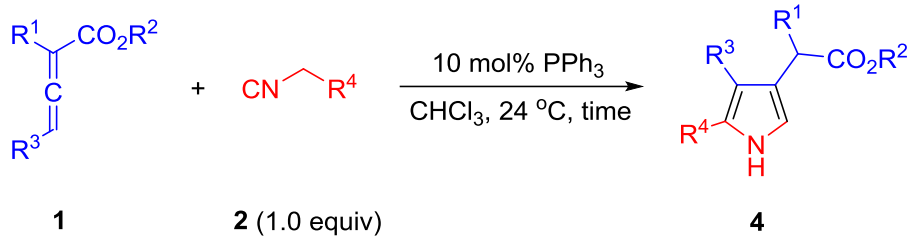
Figure S2. X-ray structure of **6a**

Table S1. Crystal data and structure refinement for e477

Identification code	e477	
Empirical formula	$C_{23}H_{23}NO_4$	
Formula weight	377.42	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 9.2073(5) Å	α= 90°

	b = 8.4035(4) Å	β= 90.524(2)°
	c = 12.6305(7) Å	γ = 90°
Volume	977.23(9) $Å^3$	
Z	2	
Density (calculated)	1.283 Mg/m^3	
Absorption coefficient	0.711 mm^{-1}	
F(000)	400	
Crystal size	0.329 x 0.025 x 0.014 mm^3	
Theta range for data collection	3.499 to 72.628°	
Index ranges	-9<=h<=11, -10<=k<=10, -15<=l<=15	
Reflections collected	12788	
Independent reflections	3778 [R(int) = 0.0558]	
Completeness to theta = 67.679°	99.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3778 / 1 / 323	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.1349	
R indices (all data)	R1 = 0.0518, wR2 = 0.1352	
Absolute structure parameter	0.32(9)	
Largest diff. peak and hole	0.409 and -0.248 $e.Å^{-3}$	

VII. Pyrrole synthesis by PPh_3-catalyzed [3+2] cyclization of 1 and 2

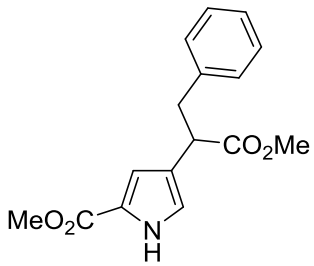


1 **2** (1.0 equiv) **4**

General procedure. To a 4 mL vial charged with PPh_3 (3.2 mg, 0.012 mmol) was added anhydrous $CHCl_3$ (0.5 mL). Allenoate **1** (0.12 mmol, 1.2 equiv) and activated isocyanide **2** (0.10 mmol, 1.0 equiv) were added in one portion. The reaction mixture was allowed to stir at ambient temperature for the given time and then concentrated. The residue was purified by flash chromatography (hexanes/ethyl acetate) to afford the product **4**.

VIII. Characterization of compounds 4

Methyl 4-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-1*H*-pyrrole-2-carboxylate (4a)



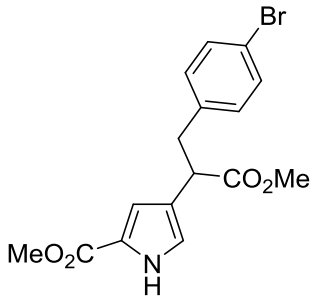
4a

The general procedure outlined above was followed (using 1.0 equiv of allenoate, 24 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 90% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.42 (br s, 1H), 7.28-7.16 (m, 3H), 7.16-7.09 (m, 2H), 6.92-6.86 (m, 1H), 6.81 (dd, *J* = 2.8, 1.7 Hz, 1H), 3.86-3.79 (m, 4H), 3.62 (s, 3H), 3.30 (dd, *J* = 13.6, 8.5 Hz, 1H), 3.01 (dd, *J* = 13.6, 7.0 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.1, 161.6, 138.9, 128.8, 128.3, 126.3, 122.9, 122.5, 121.3, 114.3, 51.9, 51.5, 46.0, 39.8; **HRMS** (ESI): m/z calcd. for $[C_{16}H_{16}NO_4, M\text{-}H]^-$: 286.1085; found: 286.1078.

Methyl

4-(3-(4-bromophenyl)-1-methoxy-1-oxopropan-2-yl)-1*H*-pyrrole-2-carboxylate

(4b)



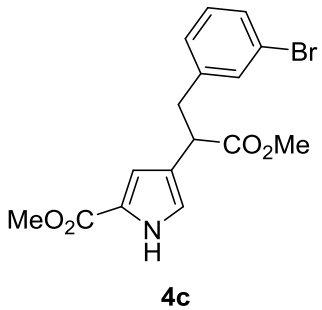
4b

The general procedure outlined above was followed (17 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 90% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.17 (br s, 1H), 7.40-7.32 (m, 2H), 7.02-6.95 (m, 2H), 6.90-6.84 (m, 1H), 6.79 (dd, *J* = 2.8, 1.7 Hz, 1H), 3.84 (s, 3H), 3.80-3.73 (m, 1H), 3.62 (s, 3H), 3.24 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.95 (dd, *J* = 13.7, 7.2 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.9, 161.4, 137.9, 131.4, 130.6, 122.7, 122.6, 121.2, 120.3, 114.2, 52.0, 51.5, 45.8, 39.1; **HRMS** (ESI): m/z calcd. for [$C_{16}H_{15}BrNO_4$, M-H]$^-$: 364.0190; found: 364.0188.

Methyl

4-(3-(3-bromophenyl)-1-methoxy-1-oxopropan-2-yl)-1*H*-pyrrole-2-carboxylate

(4c)



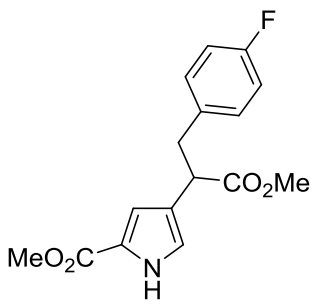
4c

The general procedure outlined above was followed (17 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 90% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.30 (br s, 1H), 7.35-7.25 (m, 2H), 7.13-7.00 (m, 2H), 6.87 (s, 1H), 6.81 (d, *J* = 2.2 Hz, 1H), 3.86-3.74 (m, 4H), 3.62 (s, 3H), 3.26 (dd, *J* = 13.7, 8.5 Hz, 1H), 2.96 (dd, *J* = 13.7, 7.0 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.8, 161.5, 141.3, 131.9, 129.8, 129.5, 127.6, 122.7, 122.6, 122.3, 121.2, 114.1, 52.0, 51.5, 45.7, 39.3; **HRMS** (ESI): m/z calcd. for [$C_{16}H_{15}BrNO_4$, M-H]$^-$: 364.0190; found: 364.0186.

Methyl

4-(3-(4-fluorophenyl)-1-methoxy-1-oxopropan-2-yl)-1*H*-pyrrole-2-carboxylate

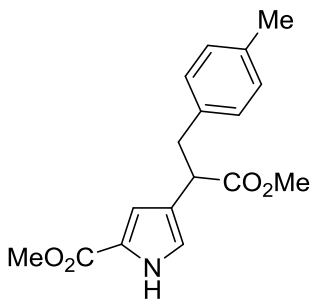
(**4d**)



4d

The general procedure outlined above was followed (17 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 94% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.21 (br s, 1H), 7.10-7.02 (m, 2H), 6.97-6.89 (m, 2H), 6.88-6.84 (m, 1H), 6.82-6.78 (m, 1H), 3.84 (s, 3H), 3.80-3.73 (m, 1H), 3.62 (s, 3H), 3.25 (dd, *J* = 13.7, 8.5 Hz, 1H), 2.97 (dd, *J* = 13.7, 7.1 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.0, 161.5 (d, *J* = 242.7 Hz), 161.4, 134.6 (d, *J* = 3.2 Hz), 130.3 (d, *J* = 7.8 Hz), 122.8, 122.6, 121.2, 115.1 (d, *J* = 21.3 Hz), 114.2, 52.0, 51.5, 46.1, 39.0; **HRMS** (ESI): m/z calcd. for $[C_{22}H_{28}N_3O_6, M+H]^+$: 430.1973; found: 430.1981.

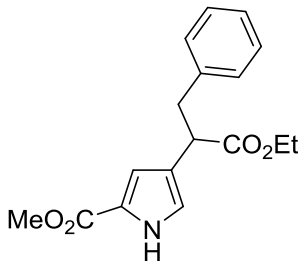
Methyl 4-(1-methoxy-1-oxo-3-(*p*-tolyl)propan-2-yl)-1*H*-pyrrole-2-carboxylate (4e)



4e

The general procedure outlined above was followed (17 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 91% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.26 (br s, 1H), 7.10-6.97 (m, 4H), 6.93-6.86 (m, 1H), 6.82 (dd, *J* = 2.8, 1.7 Hz, 1H), 3.87-3.75 (m, 4H), 3.62 (s, 3H), 3.26 (dd, *J* = 13.7, 8.6 Hz, 1H), 2.97 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.2, 161.5, 135.8, 129.0, 128.7, 123.1, 122.5, 121.2, 114.3, 51.9, 51.5, 46.1, 39.4, 21.0; **HRMS** (ESI), m/z calcd. for $[C_{17}H_{18}NO_4, M-H]^-$: 300.1241; found: 300.1244.

Methyl 4-(1-ethoxy-1-oxo-3-phenylpropan-2-yl)-1*H*-pyrrole-2-carboxylate (**4f**)

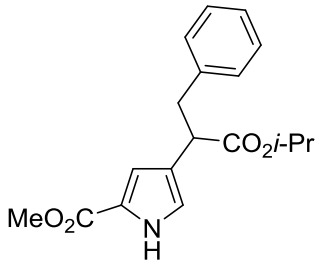


4f

The general procedure outlined above was followed (18 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 95%

yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.16 (br s, 1H), 7.28-7.17 (m, 3H), 7.17-7.10 (m, 2H), 6.93-6.85 (m, 1H), 6.82 (dd, *J* = 2.7, 1.7 Hz, 1H), 4.15-3.99 (m, 2H), 3.87-3.75 (m, 4H), 3.28 (dd, *J* = 13.6, 8.7 Hz, 1H), 3.01 (dd, *J* = 13.6, 7.0 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.7, 161.5, 139.0, 128.9, 128.2, 126.3, 123.2, 122.5, 121.2, 114.3, 60.7, 51.5, 46.1, 39.9, 14.1; **HRMS** (ESI): m/z calcd. for $[C_{17}H_{18}NO_4, M\text{-}H]^-$: 300.1241; found: 300.1233.

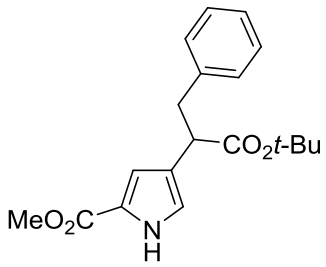
Methyl 4-(1-isopropoxy-1-oxo-3-phenylpropan-2-yl)-1*H*-pyrrole-2-carboxylate (4g)



4g

The general procedure outlined above was followed (16 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 4:1). Colorless wax, 93% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.28 (br s, 1H), 7.29-7.11 (m, 5H), 6.94-6.87 (m, 1H), 6.83 (dd, *J* = 2.5, 1.9 Hz, 1H), 5.04-4.80 (m, 1H), 3.88-3.72 (m, 4H), 3.26 (dd, *J* = 13.6, 9.0 Hz, 1H), 3.00 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.13 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.2, 161.6, 139.0, 128.9, 128.2, 126.3, 123.3, 122.4, 121.2, 114.3, 68.0, 51.4, 46.3, 40.0, 21.6, 21.6; **HRMS** (ESI): m/z calcd. for $[C_{18}H_{20}NO_4, M\text{-}H]^-$: 314.1398; found: 314.1392.

Methyl 4-(1-*tert*-butoxy-1-oxo-3-phenylpropan-2-yl)-1*H*-pyrrole-2-carboxylate (4h)



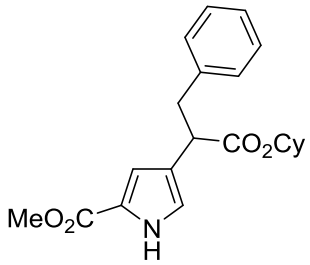
4h

The general procedure outlined above was followed (72 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 4:1). Colorless wax, 95% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.20 (br s, 1H), 7.27-7.13 (m, 5H), 6.92-6.85 (m, 1H), 6.85-6.79 (m, 1H), 3.84 (s, 3H), 3.72 (dd, *J* = 8.9, 6.8 Hz, 1H), 3.23 (dd, *J* = 13.6, 9.0 Hz, 1H), 2.97 (dd, *J* = 13.7, 6.8 Hz, 1H), 1.33 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 172.88, 161.6, 139.2, 129.0, 128.2, 126.2, 123.7, 122.4, 121.1, 114.3, 80.7,

51.4, 46.9, 40.0, 27.9; **HRMS** (ESI): m/z calcd. for [$C_{19}H_{22}NO_4$, M-H]$^-$: 328.1554; found: 328.1546.

Methyl

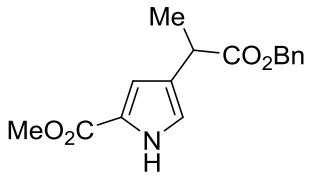
4-(1-(cyclohexyloxy)-1-oxo-3-phenylpropan-2-yl)-1*H*-pyrrole-2-carboxylate (**4i**)



4i

The general procedure outlined above was followed (36 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 4:1). Colorless wax, 93% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.14 (br s, 1H), 7.27-7.12 (m, 5H), 6.93-6.87 (m, 1H), 6.83 (dd, *J* = 2.8, 1.6 Hz, 1H), 4.69 (dd, *J* = 8.2, 4.3 Hz, 1H), 3.87-3.73 (m, 4H), 3.27 (dd, *J* = 13.6, 9.0 Hz, 1H), 3.00 (dd, *J* = 13.7, 6.8 Hz, 1H), 1.85-1.55 (m, 5H), 1.36-1.18 (m, 5H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.1, 161.5, 139.1, 128.9, 128.2, 126.3, 123.5, 122.4, 121.1, 114.3, 72.9, 51.5, 46.3, 40.0, 31.3, 31.3, 25.3, 23.6; **HRMS** (ESI): m/z calcd. for [$C_{21}H_{24}NO_4$, M-H]$^-$: 354.1711; found: 354.1706.

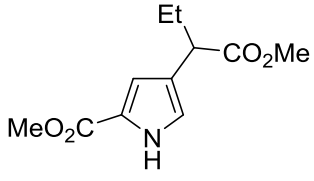
Methyl 4-(1-(benzyloxy)-1-oxopropan-2-yl)-1*H*-pyrrole-2-carboxylate (4j)



4j

The general procedure outlined above was followed (using 2.0 equiv of allenoate, 23 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 4:1). Colorless oil, 75% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.21 (br s, 1H), 7.40-7.27 (m, 5H), 6.87 (d, *J* = 2.8 Hz, 2H), 5.12 (d, *J* = 1.9 Hz, 2H), 3.84 (s, 3H), 3.73 (q, *J* = 7.2 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.6, 161.5, 136.0, 128.5, 128.1, 128.0, 124.8, 122.4, 120.7, 114.1, 66.4, 51.4, 38.0, 18.2; **HRMS** (ESI): m/z calcd. for [$C_{16}H_{16}NO_4$, M-H]$^-$: 286.1085; found: 286.1073.

Methyl 4-(1-methoxy-1-oxobutan-2-yl)-1*H*-pyrrole-2-carboxylate (4k)

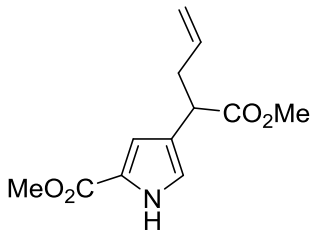


4k

The general procedure outlined above was followed (using

2.0 equiv of allenoate, 23 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 4:1). Colorless oil, 84% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.15 (br s, 1H), 6.96-6.78 (m, 2H), 3.83 (s, 3H), 3.67 (s, 3H), 3.42 (t, *J* = 7.6 Hz, 1H), 2.06-1.89 (m, 1H), 1.84-1.72 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.9, 161.5, 123.6, 122.5, 121.1, 114.4, 51.9, 51.5, 45.7, 26.8, 12.0; **HRMS** (ESI), m/z calcd. for $[C_{11}H_{14}NO_4, M\text{-}H]^-$: 224.0928; found: 224.0922.

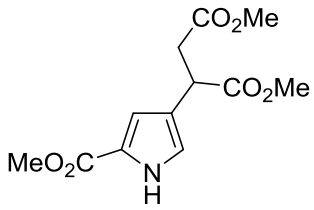
Methyl 4-(1-methoxy-1-oxopent-4-en-2-yl)-1*H*-pyrrole-2-carboxylate (4l)



4l

The general procedure outlined above was followed (16 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 4:1). Colorless oil, 81% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.31 (br s, 1H), 6.92-6.83 (m, 2H), 5.82-5.66 (m, 1H), 5.11-4.97 (m, 2H), 3.83 (s, 3H), 3.70-3.57 (m, 4H), 2.80-2.62 (m, 1H), 2.56-2.41 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.2, 161.5, 135.2, 123.0, 122.5, 121.1, 117.0, 114.3, 51.9, 51.5, 43.8, 37.6; **HRMS** (ESI), m/z calcd. for $[C_{12}H_{14}NO_4, M\text{-}H]^-$: 236.0928; found: 236.0923.

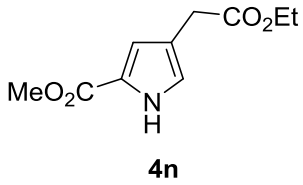
Dimethyl 2-(5-(methoxycarbonyl)-1*H*-pyrrol-3-yl)succinate (4m)



4m

The general procedure outlined above was followed (using 2.0 equiv of allenoate, 16 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 86% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.27 (br s, 1H), 6.88 (s, 1H), 6.82 (s, 1H), 4.04 (dd, *J* = 9.5, 5.8 Hz, 1H), 3.83 (s, 3H), 3.68 (d, *J* = 6.7 Hz, 6H), 3.10 (dd, *J* = 16.9, 9.6 Hz, 1H), 2.68 (dd, *J* = 16.8, 5.7 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.6, 172.0, 161.4, 122.8, 122.0, 121.0, 113.9, 52.3, 51.9, 51.5, 39.6, 37.3; **HRMS** (ESI): m/z calcd. for $[C_{12}H_{14}NO_6, M\text{-}H]^-$: 268.0827; found: 268.0827.

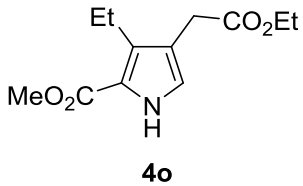
Methyl 4-(2-ethoxy-2-oxoethyl)-1*H*-pyrrole-2-carboxylate (4n)



4n

The general procedure outlined above was followed (using 2.0 equiv of allenoate, 20 mol % PPh_3, 43 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Pale brown oil, 56% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.15 (br s, 1H), 6.91 (dd, *J* = 2.1, 1.5 Hz, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 3.49 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 171.8, 161.5, 122.6, 121.9, 117.8, 115.7, 60.8, 51.4, 32.8, 14.2; **HRMS** (ESI), m/z calcd. for $[C_{10}H_{12}NO_4, M\text{-}H]^-$: 210.0772; found: 210.0764.

Methyl 4-(2-ethoxy-2-oxoethyl)-3-ethyl-1*H*-pyrrole-2-carboxylate (4o)

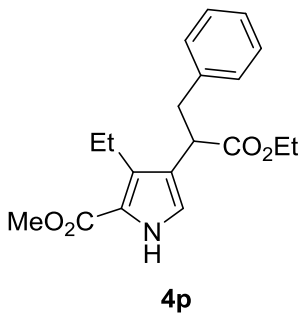


4o

The general procedure outlined above was followed (using 1.5 equiv of allenoate, 20 mol % PPh_3, 41 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 59% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.98 (br s, 1H), 6.85 (d, *J* = 3.0 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.45 (s, 2H), 2.75 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 172.0, 161.7, 133.1, 121.4, 118.6, 116.7, 60.8, 51.1, 30.8, 18.0, 15.2, 14.2; **HRMS** (ESI), m/z calcd. for $[C_{12}H_{16}NO_4, M\text{-}H]^-$: 238.1085; found: 238.1082.

Methyl

4-(1-ethoxy-1-oxo-3-phenylpropan-2-yl)-3-ethyl-1*H*-pyrrole-2-carboxylate (4p)

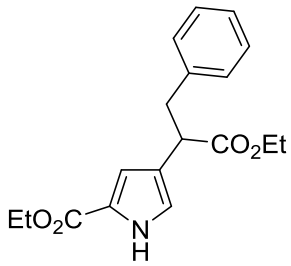


4p

The general procedure outlined above was followed (using 2.0 equiv of allenoate, 50 mol % PPh_3, 95 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 39% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.95 (br s, 1H),

7.28-7.11 (m, 5H), 6.95 (d, *J* = 3.1 Hz, 1H), 4.13-3.94 (m, 2H), 3.86-3.74 (m, 4H), 3.28 (dd, *J* = 13.5, 9.2 Hz, 1H), 2.97 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.83-2.57 (m, 2H), 1.16-0.98 (m, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.1, 161.6, 139.2, 132.7, 128.9, 128.3, 126.4, 122.3, 120.2, 118.3, 60.7, 51.1, 44.1, 40.4, 17.8, 15.5, 14.0; **HRMS** (ESI), m/z calcd. for $[C_{19}H_{22}NO_4, M\text{-}H]^-$: 328.1554; found: 328.1552.

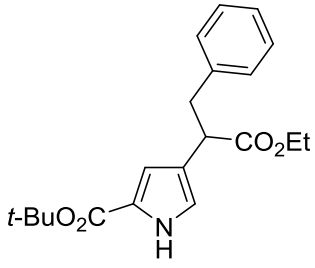
Ethyl 4-(1-ethoxy-1-oxo-3-phenylpropan-2-yl)-1*H*-pyrrole-2-carboxylate (4q)



4q

The general procedure outlined above was followed (20 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 97% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.28 (br s, 1H), 7.31-7.09 (m, 5H), 6.95-6.86 (m, 1H), 6.82 (dd, *J* = 2.8, 1.7 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.16-3.98 (m, 2H), 3.81 (dd, *J* = 8.7, 6.9 Hz, 1H), 3.29 (dd, *J* = 13.6, 8.8 Hz, 1H), 3.01 (dd, *J* = 13.6, 6.9 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.7, 161.2, 139.0, 128.9, 128.2, 126.3, 123.1, 122.8, 121.0, 114.1, 60.7, 60.4, 46.1, 39.9, 14.4, 14.0; **HRMS** (ESI), m/z calcd. for $[C_{18}H_{20}NO_4, M\text{-}H]^-$: 314.1398; found: 314.1392.

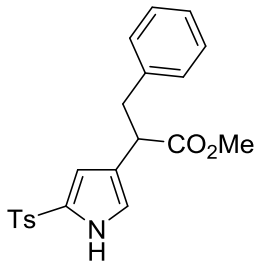
***tert*-Butyl 4-(1-ethoxy-1-oxo-3-phenylpropan-2-yl)-1*H*-pyrrole-2-carboxylate (4r)**



4r

The general procedure outlined above was followed (20 mol % PPh_3, 89 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 4:1). Colorless wax, 82% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.07 (br s, 1H), 7.33-7.09 (m, 5H), 6.92-6.71 (m, 2H), 4.18-3.98 (m, 2H), 3.80 (dd, *J* = 8.9, 6.7 Hz, 1H), 3.28 (dd, *J* = 13.6, 9.0 Hz, 1H), 3.00 (dd, *J* = 13.6, 6.6 Hz, 1H), 1.56 (s, 9H), 1.13 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.8, 160.6, 139.1, 128.9, 128.2, 126.3, 124.3, 123.0, 120.3, 113.5, 80.9, 60.7, 46.2, 40.0, 28.3, 14.0; **HRMS** (ESI), m/z calcd. for $[C_{20}H_{24}NO_4, M\text{-}H]^-$: 342.1711; found: 342.1694.

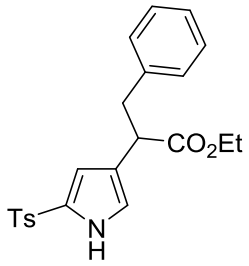
Methyl 3-phenyl-2-(5-tosyl-1*H*-pyrrol-3-yl)propanoate (4s)



4s

The general procedure outlined above was followed (23 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 79% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.30 (br s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.33-7.00 (m, 7H), 6.81 (d, *J* = 2.5 Hz, 1H), 6.77 (d, *J* = 1.9 Hz, 1H), 3.80-3.73 (m, 1H), 3.59 (s, 3H), 3.23 (dd, *J* = 13.5, 8.6 Hz, 1H), 2.94 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.7, 143.9, 139.3, 138.6, 129.8, 128.8, 128.4, 128.3, 126.9, 126.5, 123.7, 121.5, 114.3, 52.0, 46.0, 40.0, 21.6; **HRMS** (ESI), m/z calcd. for $[C_{21}H_{20}NO_4S, M\text{-}H]^-$: 382.1119; found: 382.1112.

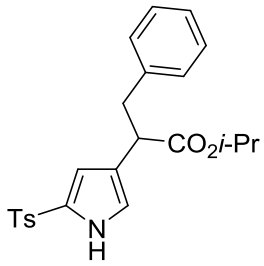
Ethyl 3-phenyl-2-(5-tosyl-1*H*-pyrrol-3-yl)propanoate (4t)



4t

The general procedure outlined above was followed (18 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Colorless wax, 83% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.58 (br s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.32-7.24 (m, 2H), 7.23-7.12 (m, 3H), 7.11-7.02 (m, 2H), 6.87-6.74 (m, 2H), 4.11-3.95 (m, 2H), 3.76 (dd, *J* = 8.7, 7.0 Hz, 1H), 3.22 (dd, *J* = 13.5, 8.8 Hz, 1H), 2.94 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.40 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.3, 143.9, 139.3, 138.6, 129.8, 128.9, 128.2, 128.1, 126.8, 126.4, 123.7, 121.7, 114.5, 60.8, 46.1, 40.0, 21.5, 14.0; **HRMS** (ESI), m/z calcd. for $[C_{22}H_{22}NO_4S, M\text{-}H]^-$: 396.1275; found: 396.1268.

Isopropyl 3-phenyl-2-(5-tosyl-1*H*-pyrrol-3-yl)propanoate (4u)

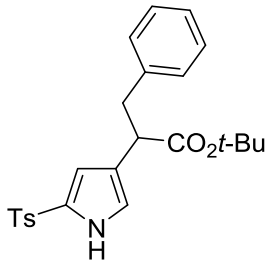


4u

The general procedure outlined above was followed (23 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 4:1). Colorless wax, 86%

yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.52 (br s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.31-7.04 (m, 7H), 6.89-6.82 (m, 1H), 6.82-6.74 (m, 1H), 5.00-4.82 (m, 1H), 3.73 (dd, *J* = 9.0, 6.8 Hz, 1H), 3.21 (dd, *J* = 13.6, 9.0 Hz, 1H), 2.95 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.40 (s, 3H), 1.11 (d, *J* = 6.3 Hz, 3H), 1.05 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 172.8, 143.8, 139.4, 138.7, 129.8, 128.9, 128.2, 128.1, 126.8, 126.4, 123.9, 121.7, 114.5, 68.1, 46.2, 40.0, 21.5; **HRMS** (ESI), m/z calcd. for $[C_{23}H_{24}NO_4S, M\text{-}H]^-$: 410.1432; found: 410.1420.

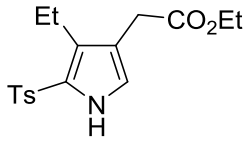
tert-Butyl 3-phenyl-2-(5-tosyl-1*H*-pyrrol-3-yl)propanoate (4v)



4v

The general procedure outlined above was followed (20 mol % PPh_3, 47 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). White solid, 71% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.46 (br s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.28-7.08 (m, 7H), 6.83 (s, 1H), 6.78 (d, *J* = 1.7 Hz, 1H), 3.68 (dd, *J* = 8.8, 7.0 Hz, 1H), 3.18 (dd, *J* = 13.6, 9.0 Hz, 1H), 2.92 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.41 (s, 3H), 1.31 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 172.5, 143.8, 139.5, 138.8, 129.8, 129.0, 128.1, 128.0, 126.8, 126.3, 124.3, 121.6, 114.5, 80.9, 46.9, 40.0, 27.8, 21.5; **HRMS** (ESI), m/z calcd. for $[C_{24}H_{26}NO_4S, M\text{-}H]^-$: 424.1588; found: 424.1595.

Ethyl 2-(4-ethyl-5-tosyl-1*H*-pyrrol-3-yl)acetate (4w)



4w

The general procedure outlined above was followed (using 2.0 equiv of allenoate, 30 mol % PPh_3, 95 h). The crude reaction mixture was purified by flash column chromatography (hexane/EtOAc 3:1). Pale brown wax, 58% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.20 (br s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.32-7.23 (m, 2H), 6.92 (d, *J* = 3.0 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.38 (s, 2H), 2.62 (q, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.5, 143.7, 139.9, 130.7, 129.7, 126.7, 123.5, 121.8, 117.5, 60.9, 30.8, 21.5, 17.3, 14.9, 14.1; **HRMS** (ESI), m/z calcd. for $[C_{17}H_{20}NO_4S, M\text{-}H]^-$: 334.1119; found:

334.1112.

IX. X-ray crystallographic analysis of 4v

The conformation of **4v** was determined by X-ray crystallographic analysis of a single crystal of **4v** (Figure S3). The crystal was prepared from the solution of **4v** in hexanes/ethyl acetate at ambient temperature.

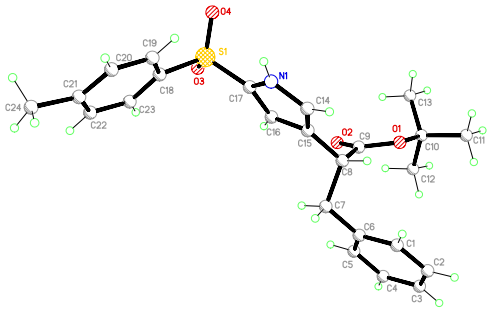


Figure S3. X-ray structure of **4v**

Table S2. Crystal data and structure refinement for E351

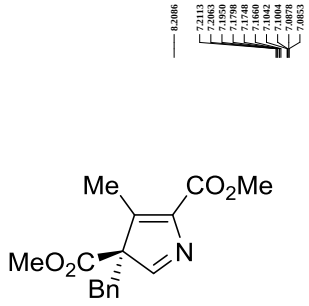
Identification code	E351	
Empirical formula	$C_{24}H_{27}NO_4S$	
Formula weight	425.52	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 24.358(3) Å	α=90°
	b = 8.0579(9) Å	β=100.201(3)°
	c = 11.2629(13) Å	γ=90°
Volume	2175.7(4) $Å^3$	
Z	4	
Density (calculated)	1.299 Mg/m^3	

Absorption coefficient	0.179 mm^{-1}
F(000)	904
Crystal size	0.260 x 0.200 x 0.100 mm^3
Theta range for data collection	1.699 to 27.518°
Index ranges	-31<=h<=27, -10<=k<=10, -13<=l<=14
Reflections collected	14979
Independent reflections	4999 [R(int) = 0.0578]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6607
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4999 / 0 / 279
Goodness-of-fit on F^2	0.990
Final R indices [I>2sigma(I)]	R1 = 0.0581, wR2 = 0.1484
R indices (all data)	R1 = 0.0772, wR2 = 0.1615
Extinction coefficient	n/a
Largest diff. peak and hole	0.500 and -0.385 e.$Å^{-3}$

X. References

1. Waki, M.; Meienhofer, J. *J. Org. Chem.* **1977**, *42*, 2019.
2. (a) Buono, G. *Tetrahedron Lett.* **1972**, *13*, 3257. (b) Zhu, X.-F.; Lan, J.; Kwon, O. *J. Am. Chem. Soc.* **2003**, *125*, 4716. (c) Na, R.; Jing, C.; Xu, Q.; Jiang, H.; Wu, X.; Shi, J.; Zhong, J.; Wang, M.; Benitez, D.; Tkatchouk, E.; Goddard III, W. A.; Guo, H.; Kwon, O. *J. Am. Chem. Soc.* **2011**, *133*, 13337.
3. Sladojevich, F.; Trabocchi, A.; Guarna, A.; Dixon, D. J. *J. Am. Chem. Soc.* **2011**, *133*, 1710.

XI. NMR spectra of the products



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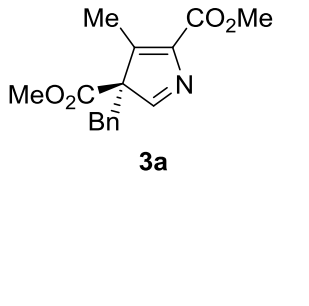

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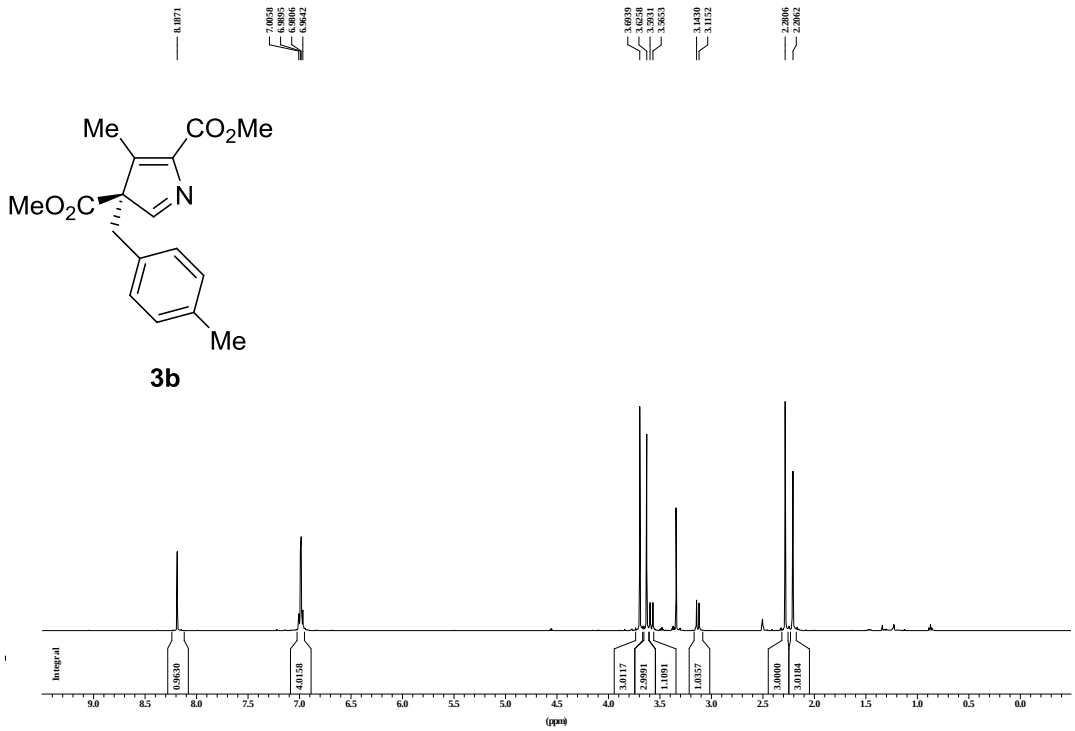
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6.9895
6.9806
6.9642
3.6939
3.6258
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3.1430
3.1152
2.2806
2.2062
Me
CO2Me
MeO2C
N
Me
3b
Integral
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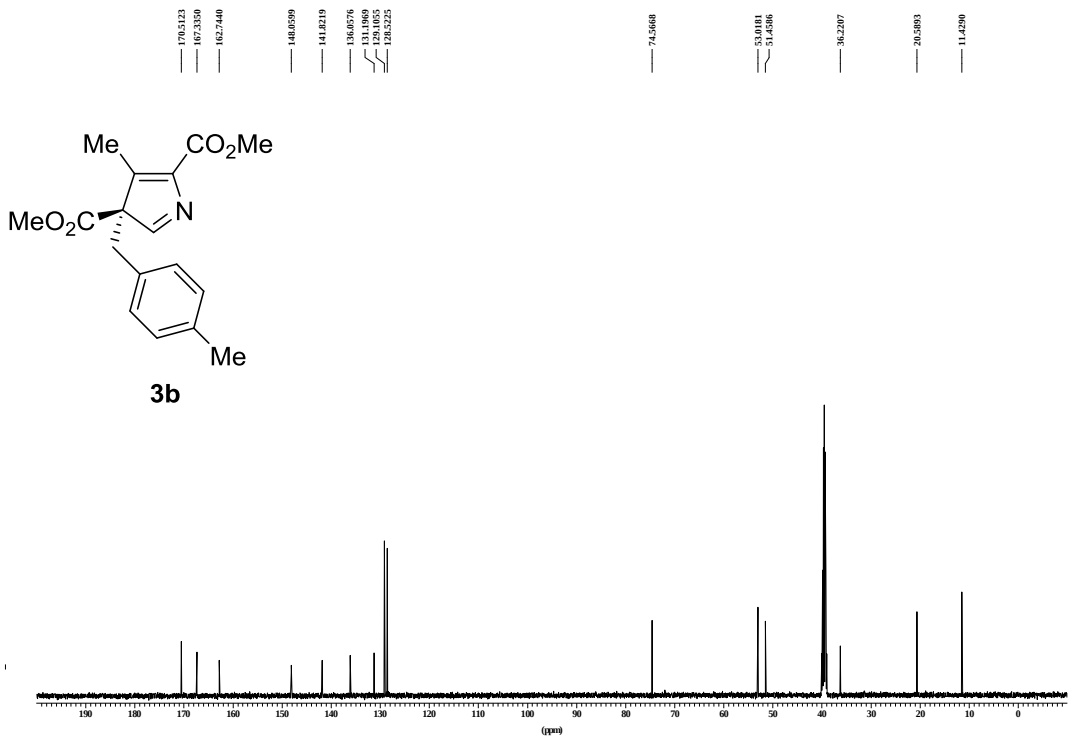
3.0117
2.9991
1.1091
1.0357
3.0000
3.0184
(ppm)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148.0599
141.0219
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74.5668
53.0181
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36.2207
20.5893
11.4290
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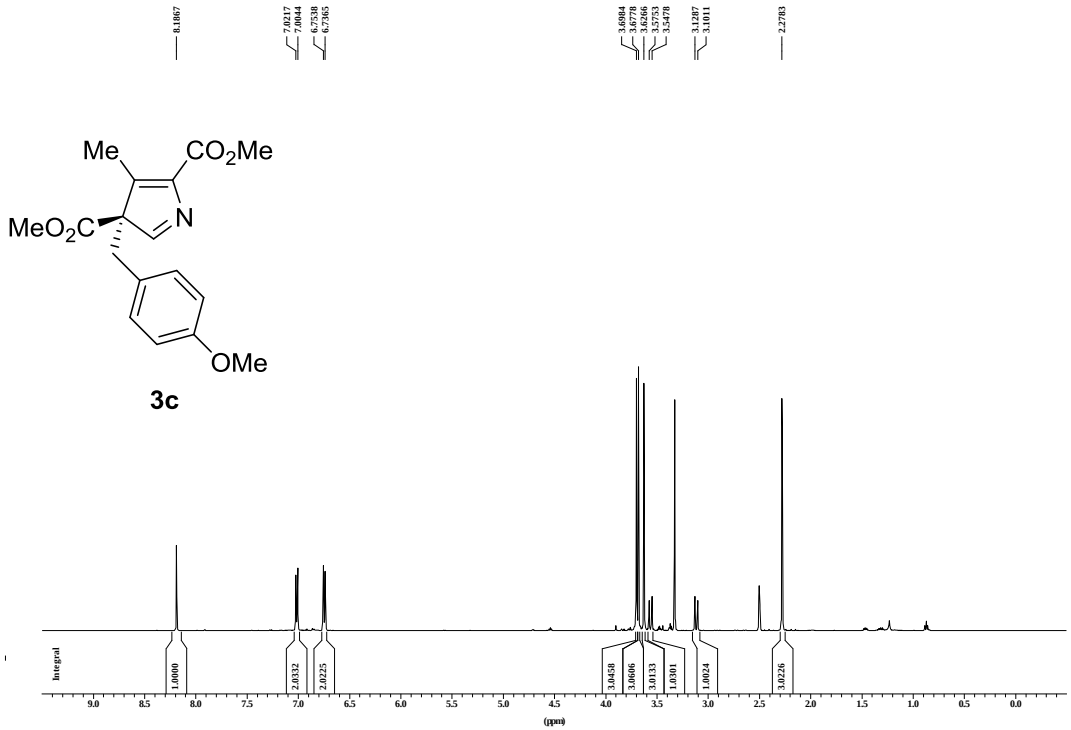
CO2Me
MeO2C
N
Me
3b
(ppm)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7.0044
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6.7365
3.6984
3.6778
3.6286
3.5253
3.5478
3.1287
3.1011
2.2783
Me
CO2Me
MeO2C
N
OMe
Integral
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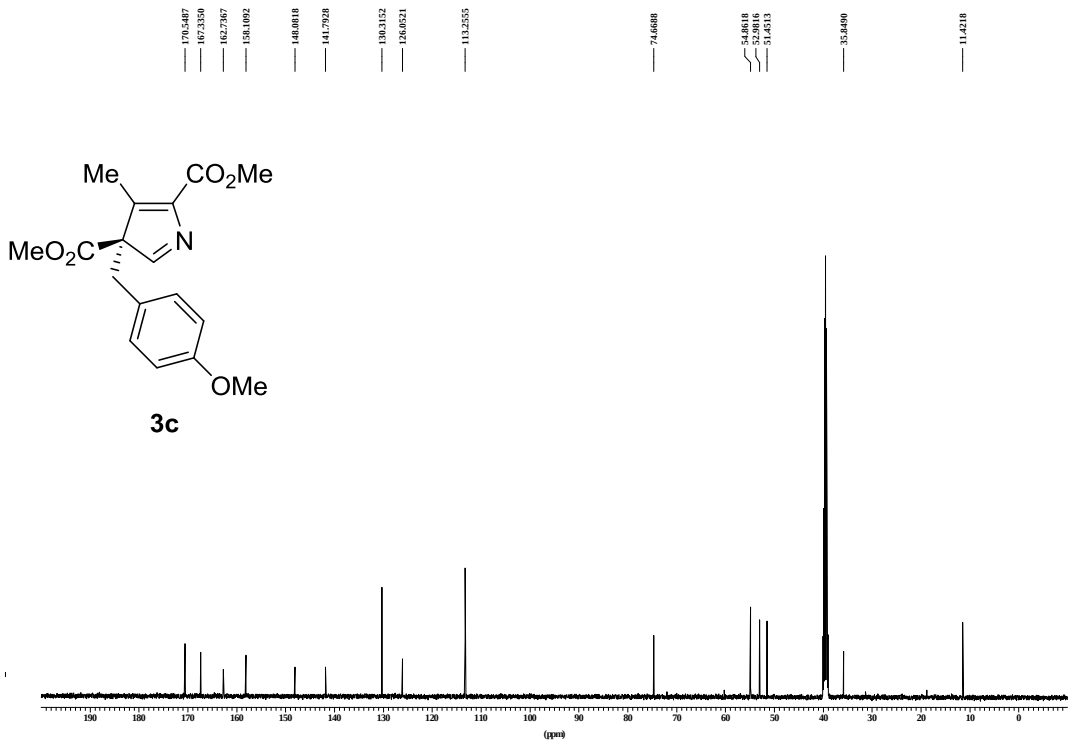
2.0225
3.0458
3.0606
3.0133
1.0301
1.0024
3.0226
(ppm)

3c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130.3152
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113.2555
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51.4315
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11.4218
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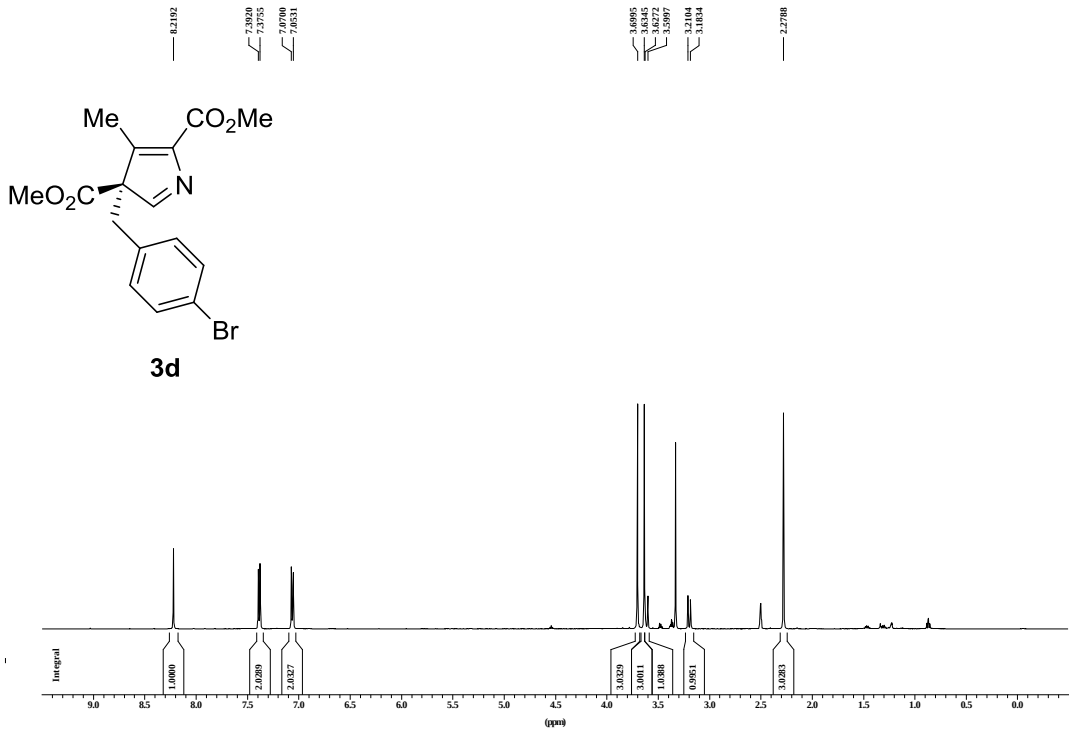
MeO2C
N
OMe
(ppm)

3c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3.6345
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2.2708
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N
Br
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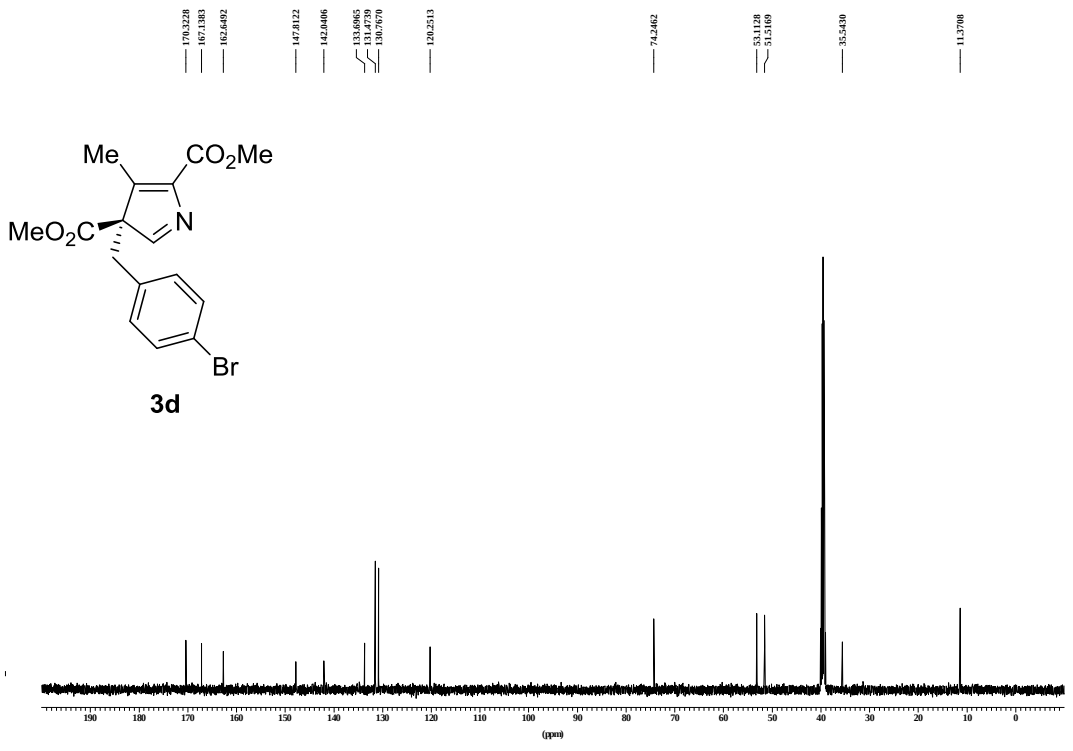
(ppm)

3d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51.5169
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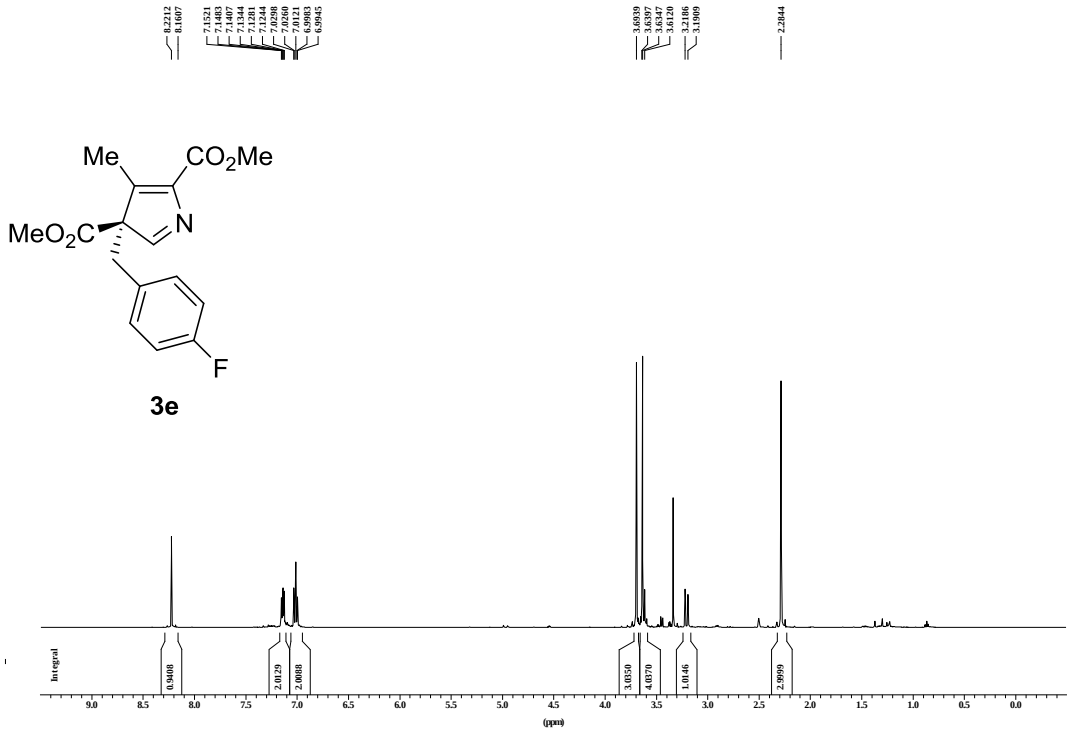
N
Br
(ppm)

3d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6.9983
6.9945
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3.6397
3.6347
3.6140
3.2186
3.1909
2.2844
Me
CO2Me
MeO2C
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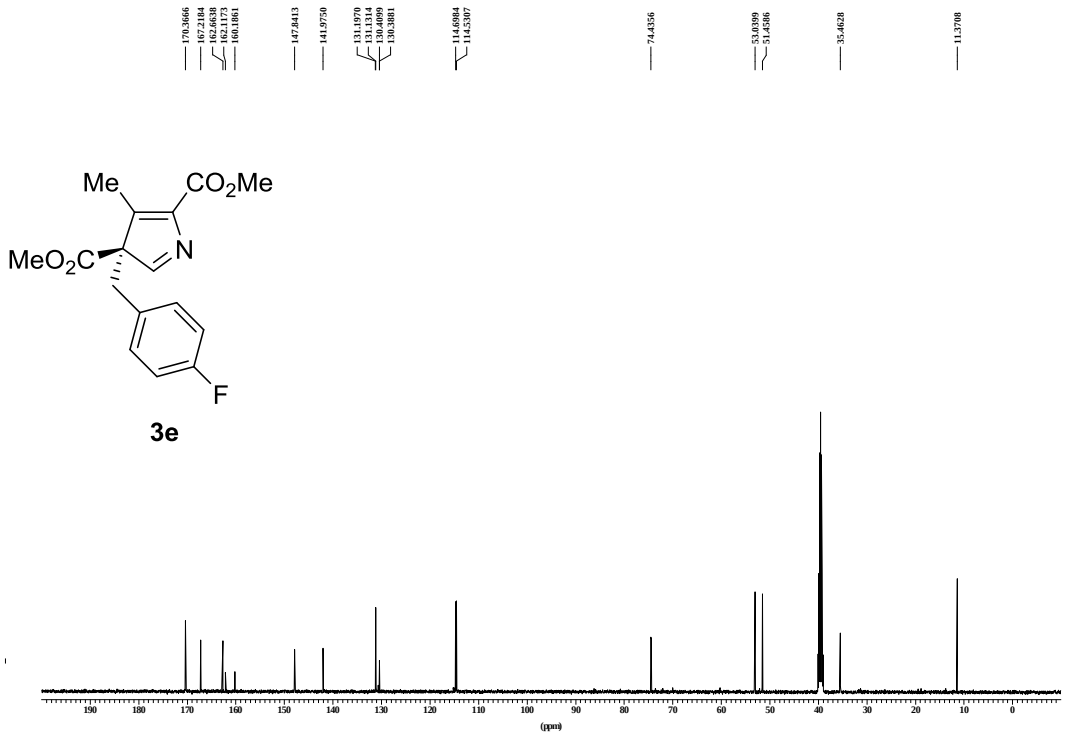
2.9099
(ppm)

3e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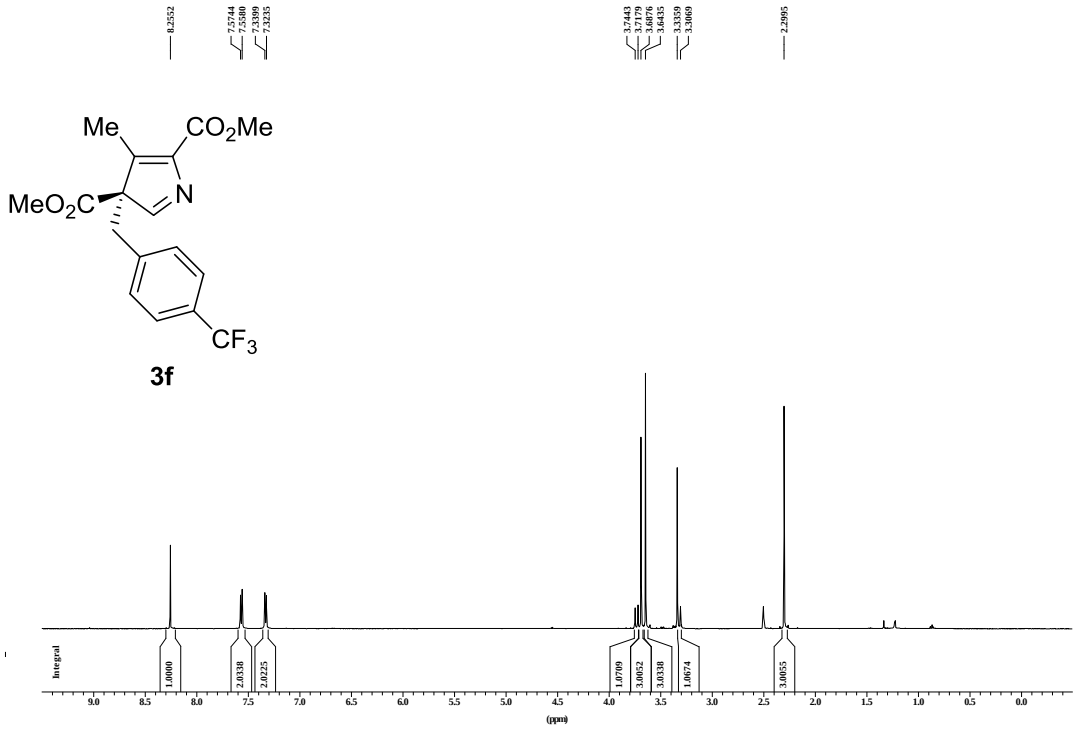
CO2Me
MeO2C
N
F
(ppm)

3e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MeO2C
N
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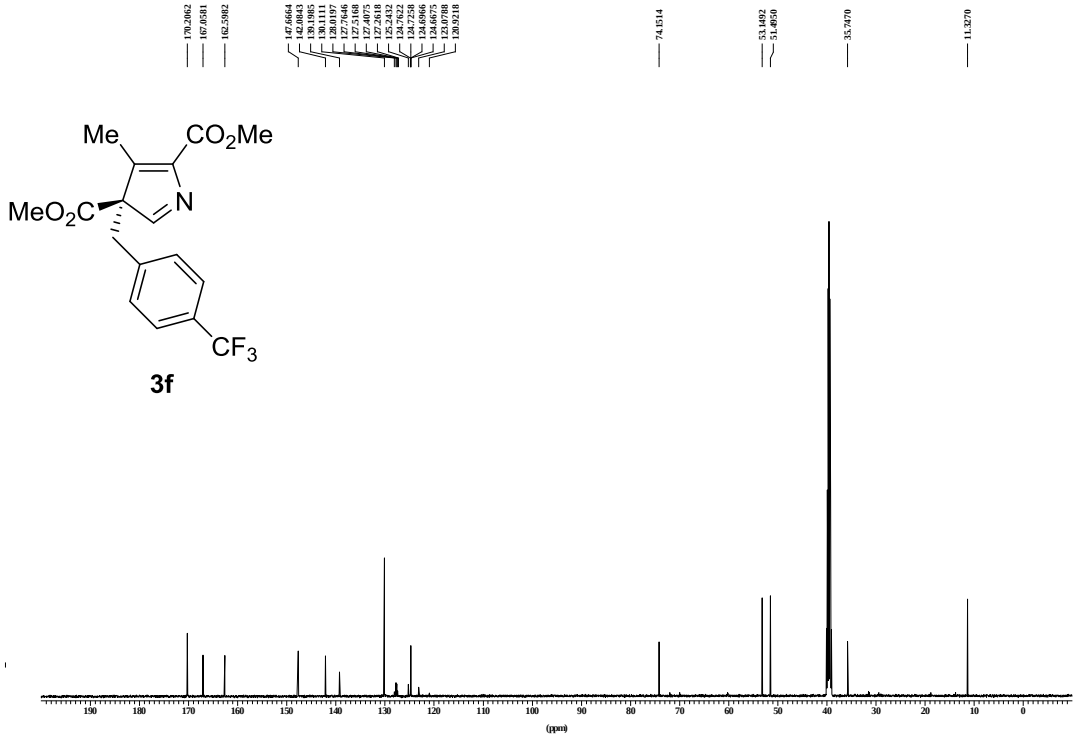
(ppm)

3f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124.6966
124.6675
123.0788
120.9218
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MeO2C
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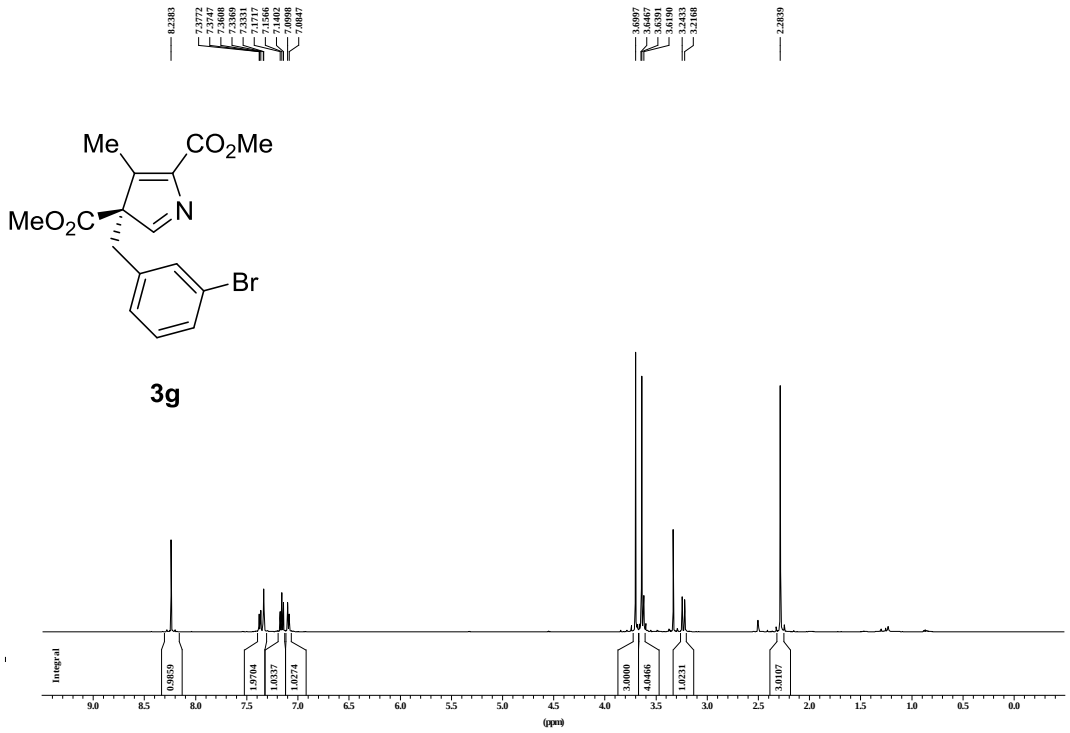
CF3
(ppm)

3f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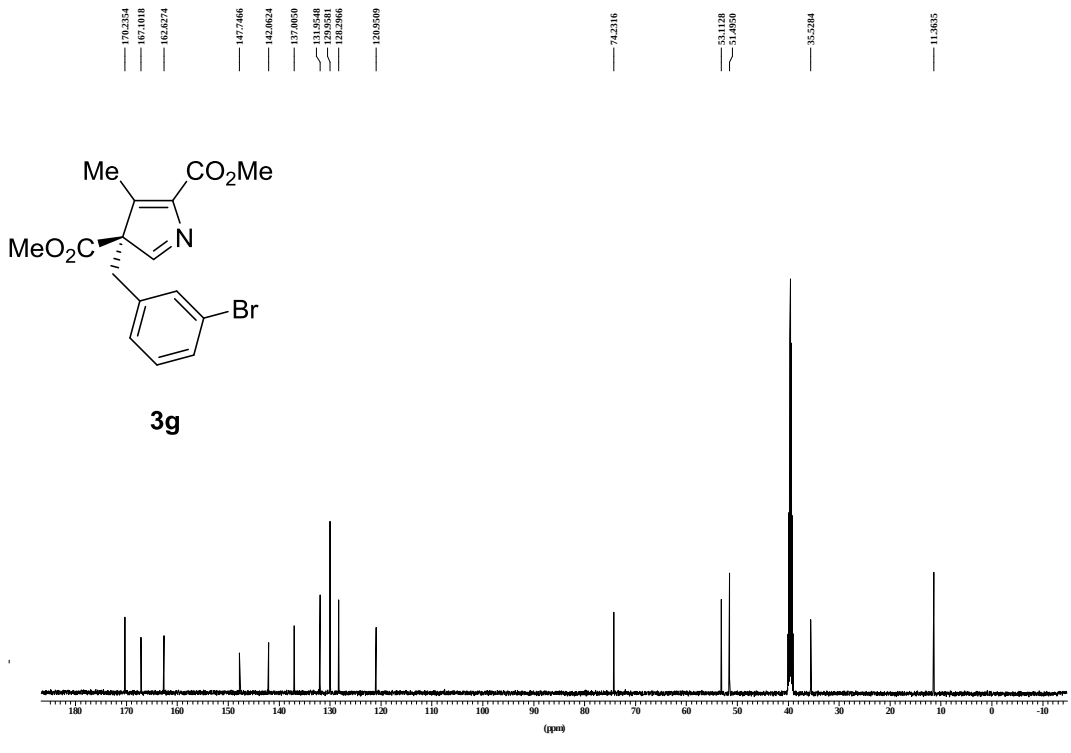
3.0107
(ppm)

3g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11.3635
Me
CO2Me
MeO2C
N
Br
(ppm)

3g


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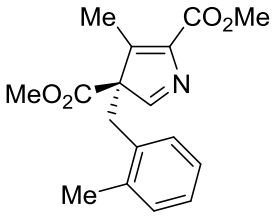
2.3154
2.2536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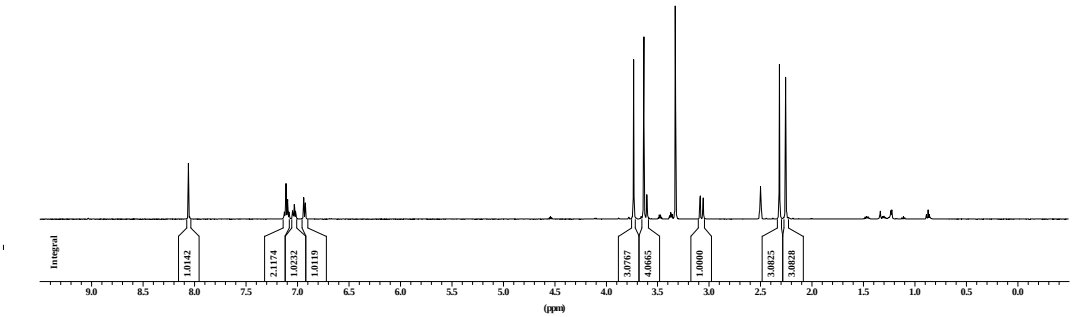
MeO2C
N
Me

3h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(ppm)


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148.1911
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133.1208
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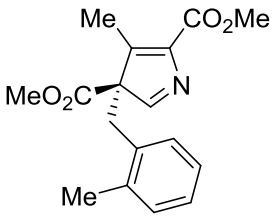
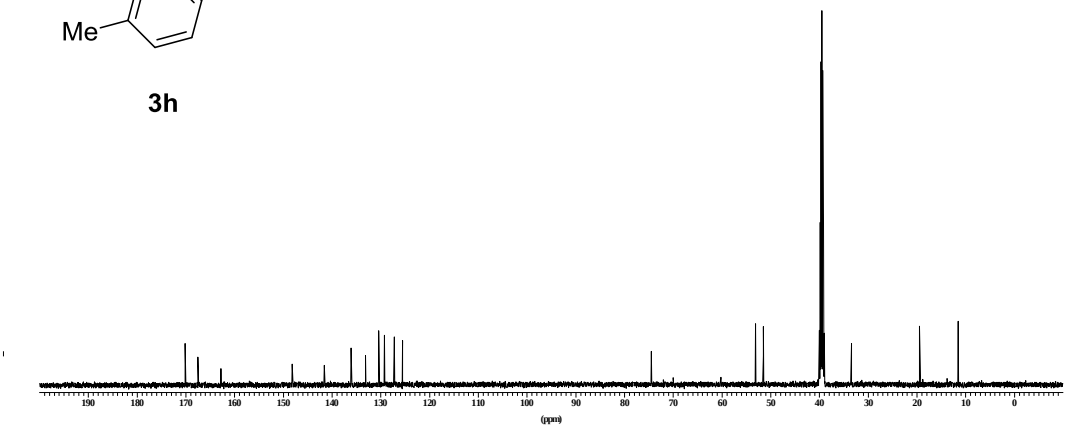

Me
CO2Me
MeO2C
N
Me

3h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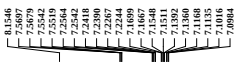
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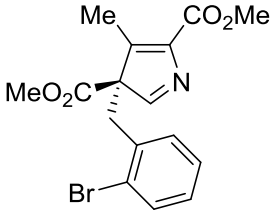
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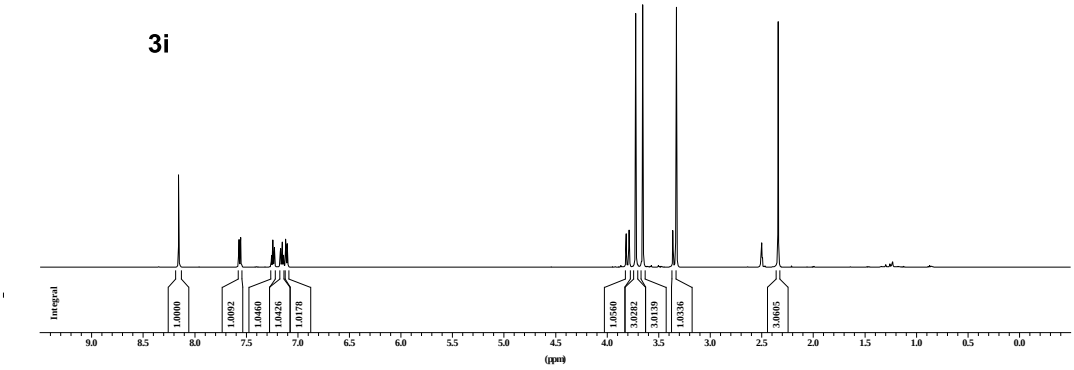
MeO2C
N
Br

3i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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
(ppm)


169.1423
166.9925
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147.6883
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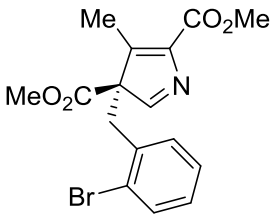
35.9802
11.6404


Me
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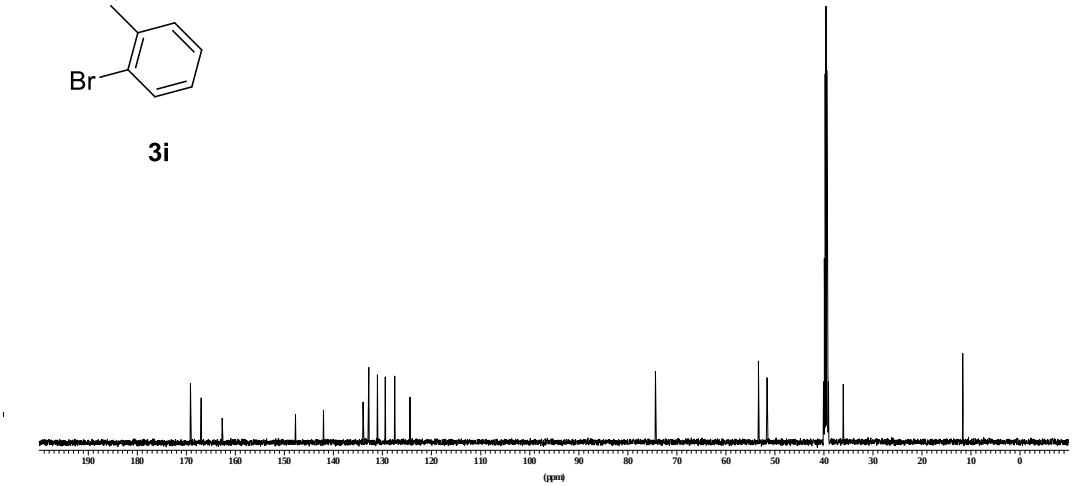
MeO2C
N
Br

3i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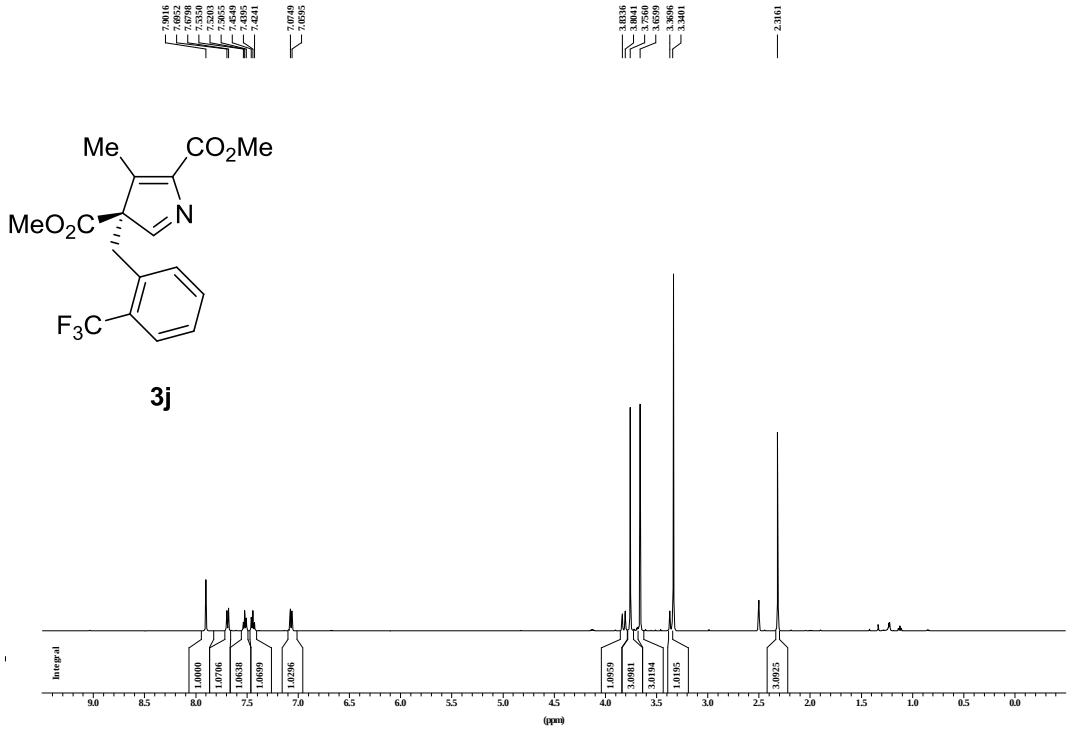
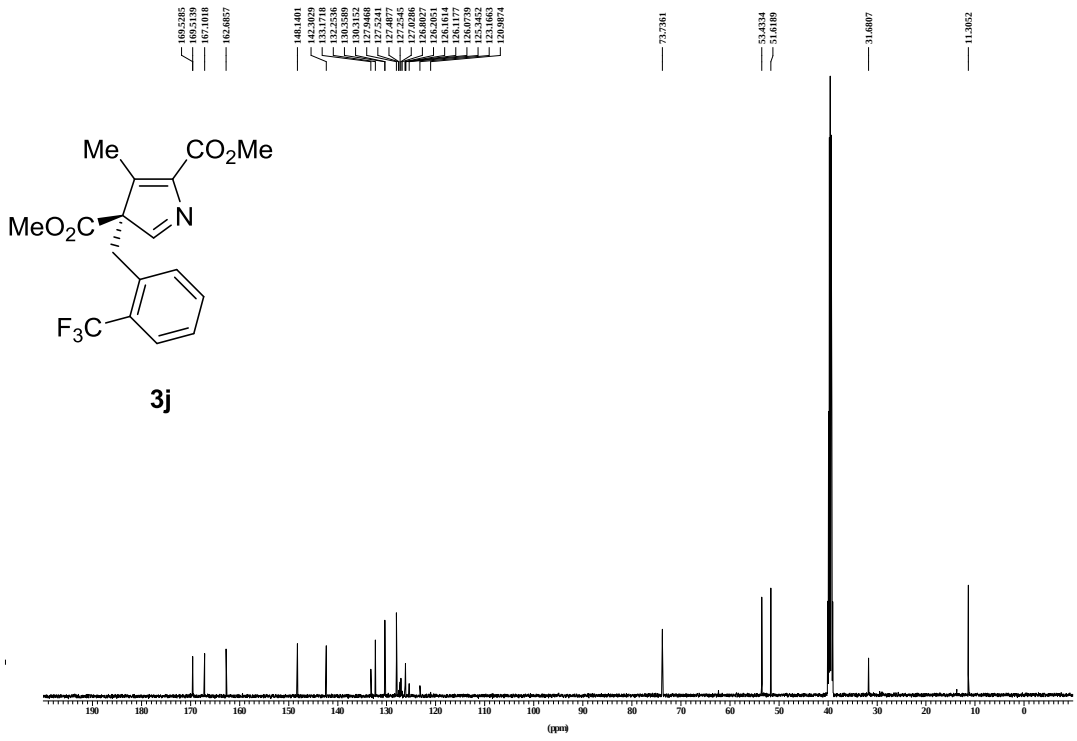
30
20
10
0
(ppm)

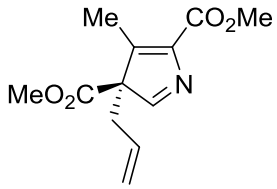

7.9016
7.6952
7.6798
7.5350
7.5203
7.4655
7.4549
7.4395
7.4241
7.0749
7.0595
3.8836
3.8041
3.7560
3.6599
3.3696
3.3401
2.3161
Me
CO2Me
MeO2C
N
F3C
Integral
1.0000
1.0706
1.0638
1.0699
1.0296
1.0959
3.0981
3.0194
1.0195
3.0925
(ppm)

3j

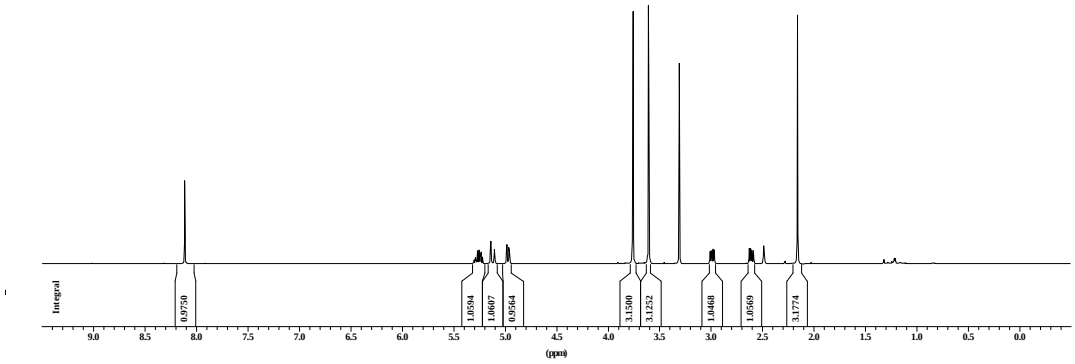

169.5205
169.3139
167.1018
162.6857
148.1401
142.3029
133.1718
132.2536
130.3589
130.3152
127.9468
127.5341
127.4497
127.2545
127.0286
126.8027
126.7651
126.1614
126.1177
126.0739
125.3452
123.1663
120.9874
73.7361
53.4334
51.6189
31.6807
11.3052
Me
CO2Me
MeO2C
N
F3C
(ppm)

3j

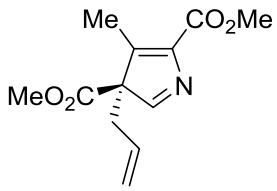

8.1134
5.3016
5.2879
5.2820
5.2720
5.2682
5.2540
5.2481
5.2394
5.2343
5.2192
5.1395
5.1372
5.1056
5.1013
4.9824
4.9806
4.9708
4.9627
4.9044
4.9591
3.7577
3.6065
3.0084
2.9951
2.9809
2.9672
2.9529
2.6140
2.6017
2.5866
2.1583


Me
CO2Me
MeO2C
N

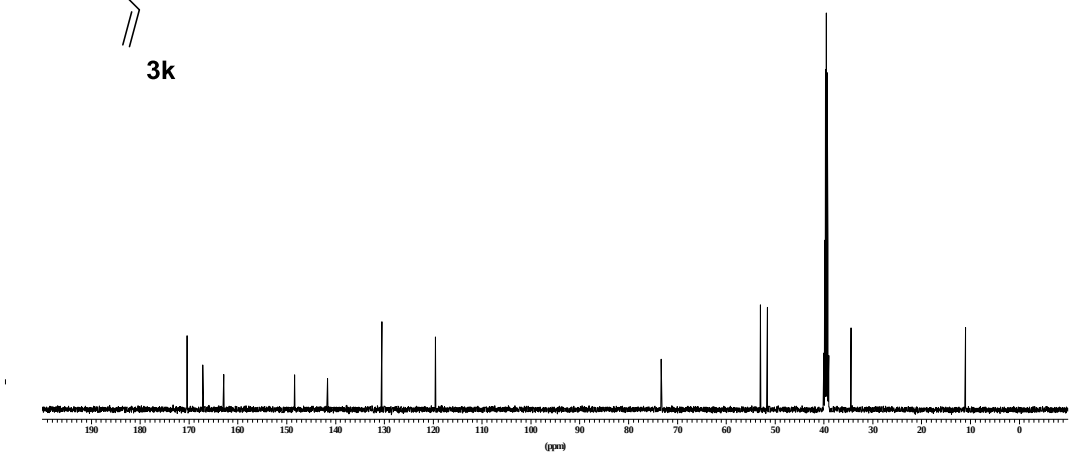
3k

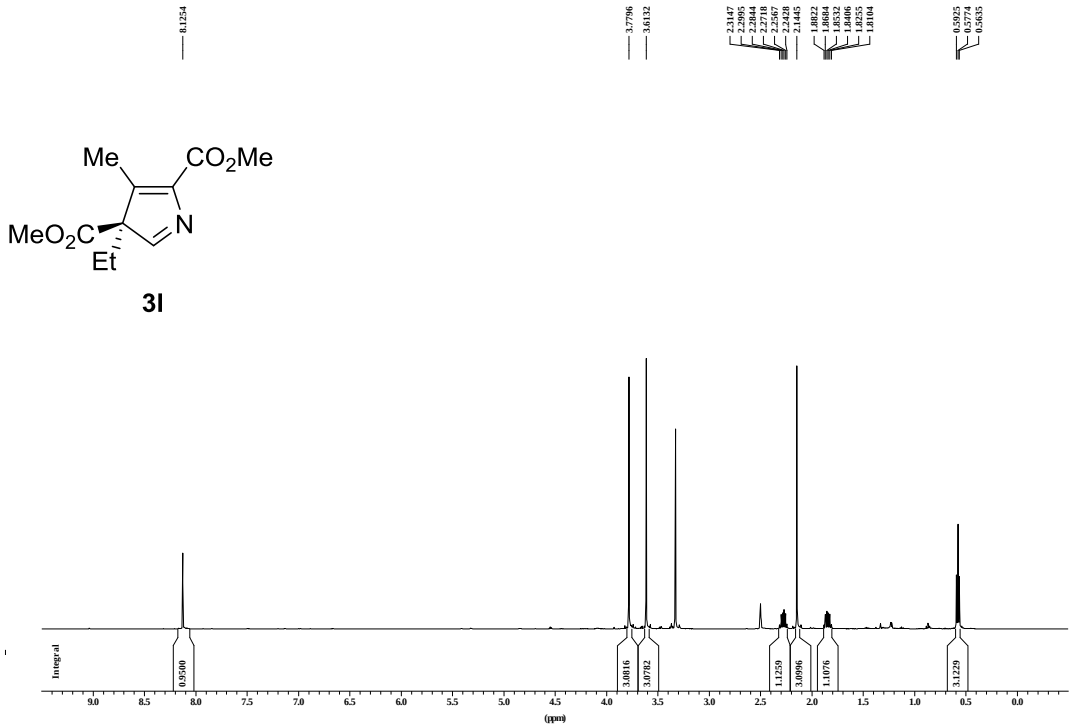

Integral
0.9750
1.0594
1.0607
0.9564
3.1560
3.1252
1.0468
1.0569
3.1774
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

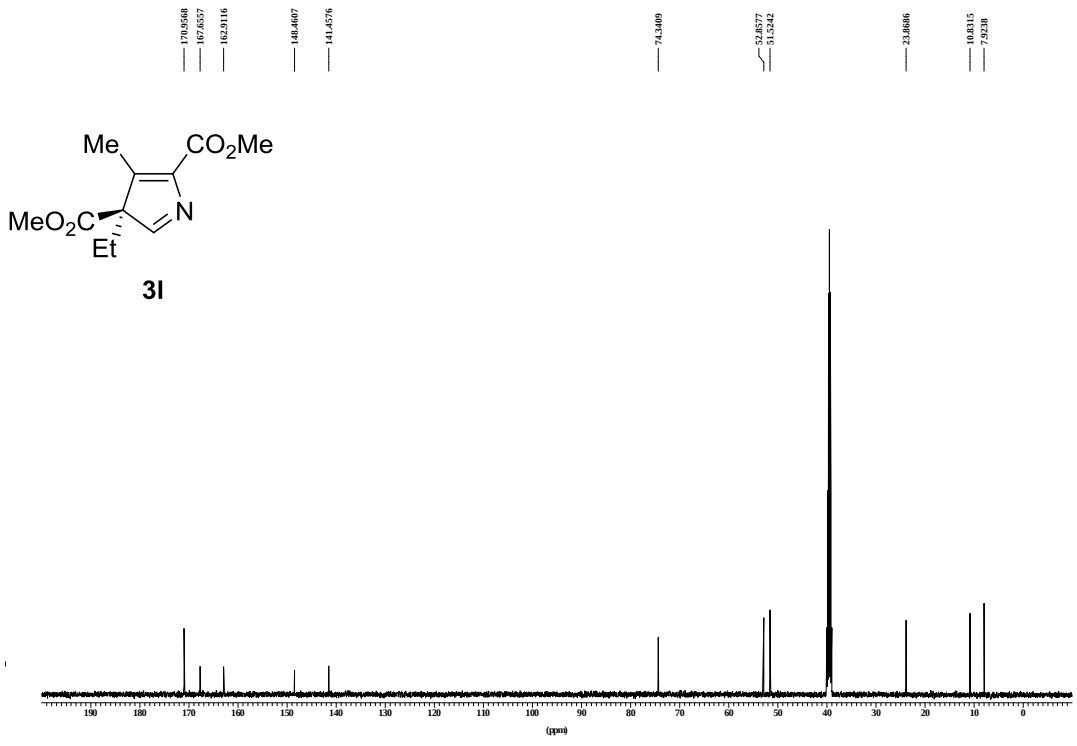

170.3811
167.1237
162.8824
148.3733
141.6325
130.5047
119.5153
73.2915
52.9816
51.5460
34.4061
10.9700


Me
CO2Me
MeO2C
N

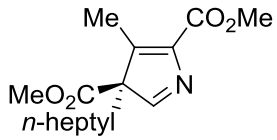
3k


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

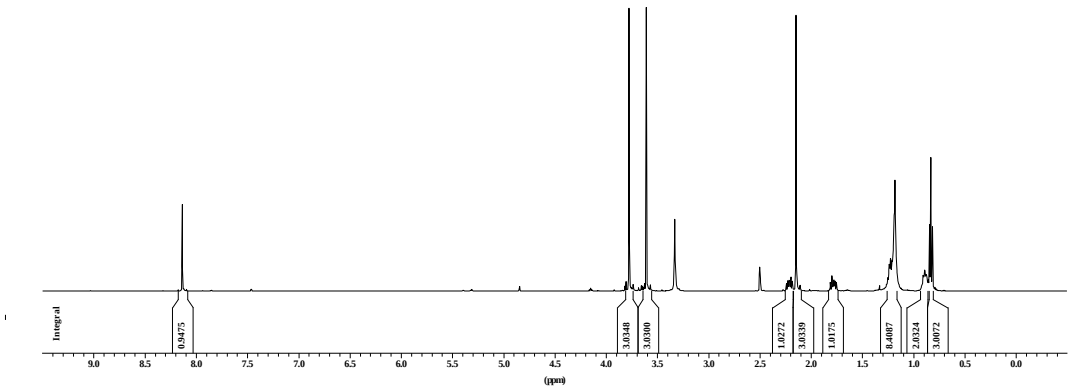

8.1254
3.7796
3.6132
2.3147
2.2995
2.2844
2.2718
2.2567
2.2428
2.1445
1.8822
1.8684
1.8552
1.8406
1.8255
1.8104
0.5925
0.5774
0.5635
Me
CO2Me
MeO2C
N
Et
3I
Integral
0.9500
3.0816
3.0782
1.1259
3.0996
1.1076
3.1229
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


170.3568
167.6557
162.9116
148.4607
141.4576
74.3409
52.8577
51.5242
23.8686
10.8315
7.9238
Me
CO2Me
MeO2C
N
Et
3I
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

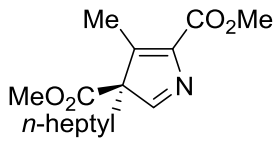

8.1355
3.7759
3.6069
2.2415
2.2277
2.2226
2.2151
2.2088
2.1974
2.1861
2.1823
2.1457
1.8129
1.7965
1.7864
1.7789
1.7733
1.7663
1.7524
1.2519
1.2367
1.2254
1.2090
1.1838
0.9064
0.8926
0.8749
0.8575
0.8447
0.8308
0.8169


Me
CO2Me
MeO2C
N
n-heptyl

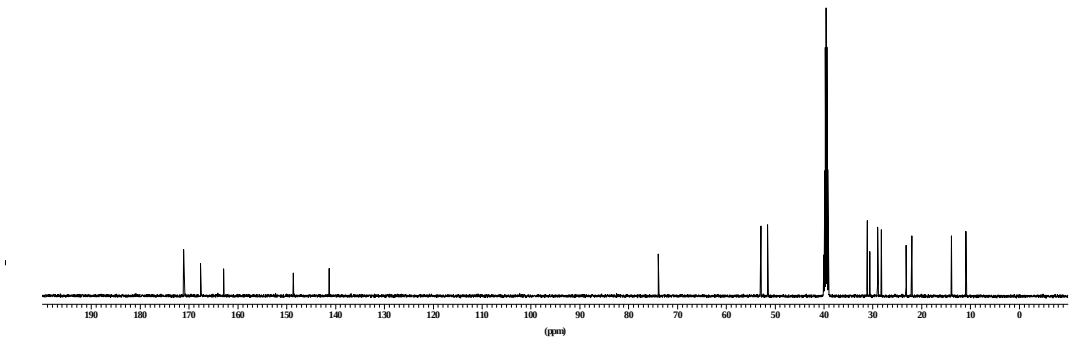
3m

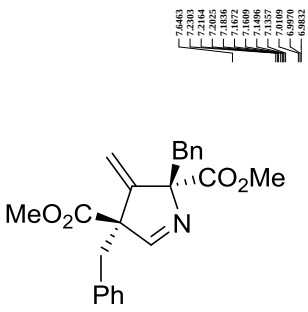

Integral
0.9475
3.0348
3.0300
1.0272
3.0339
1.0175
8.4087
2.0324
3.0072
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


171.1026
167.6192
162.9189
148.6429
141.2972
73.8891
52.8577
51.4950
31.0758
30.5530
28.9479
28.2337
23.1763
21.9593
13.8485
10.8679


Me
CO2Me
MeO2C
N
n-heptyl

3m


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

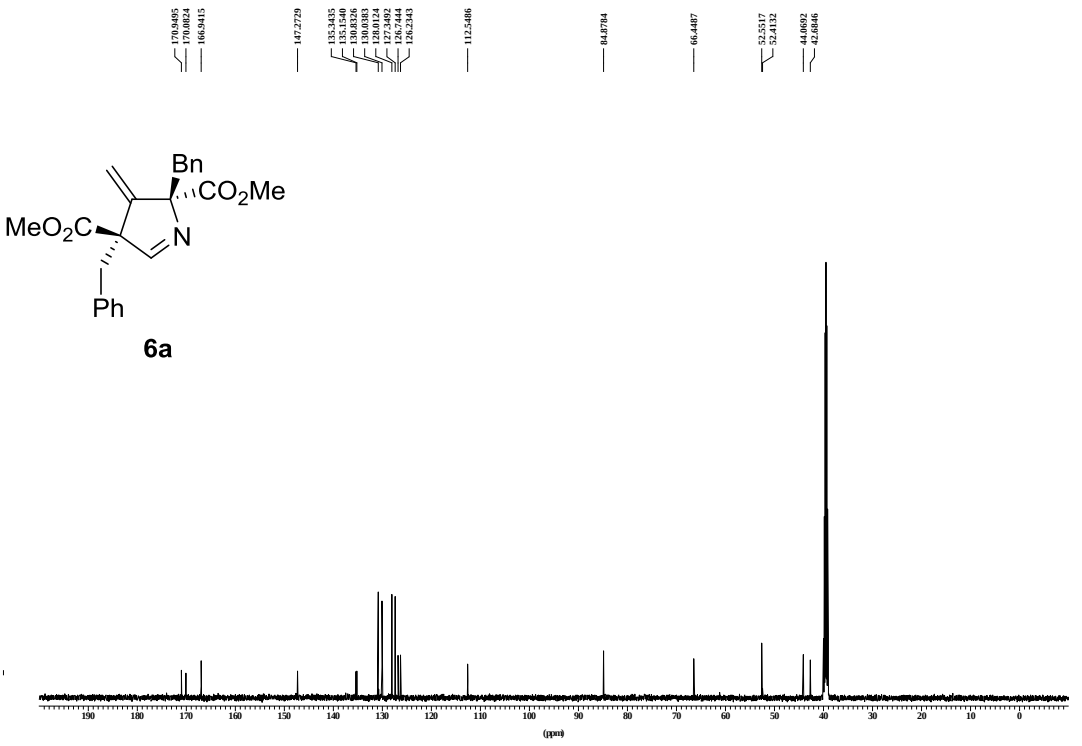

Bn
CO2Me
MeO2C
N
Ph

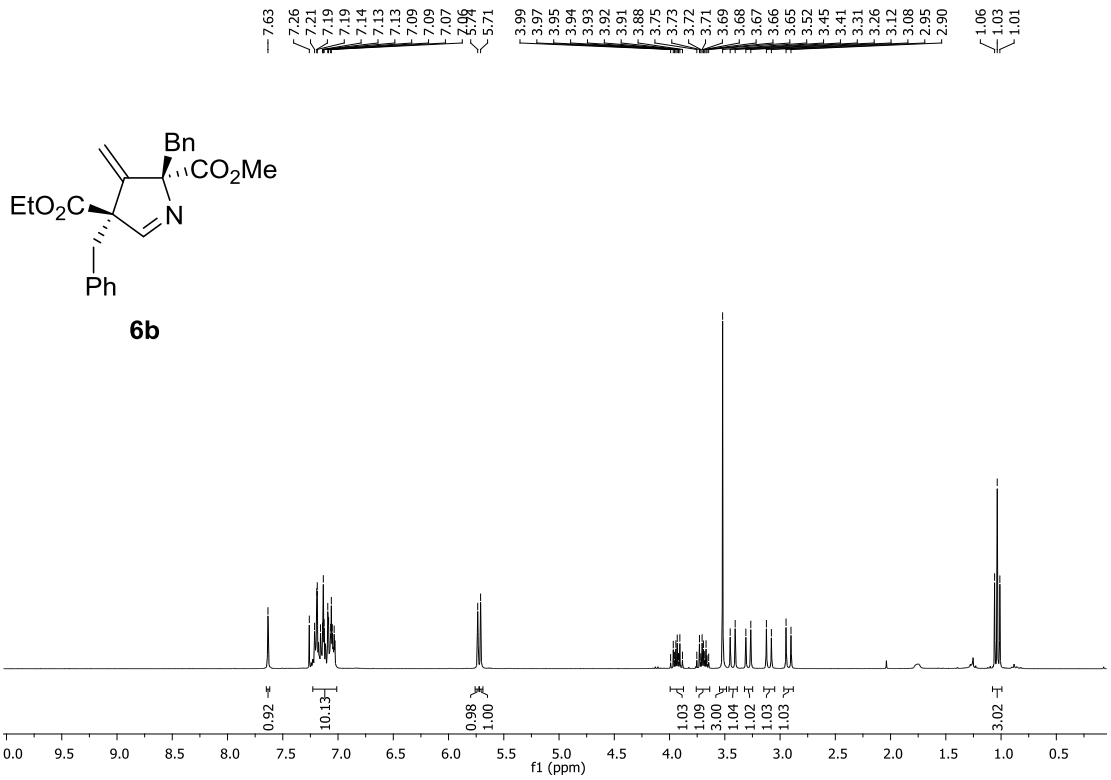
6a

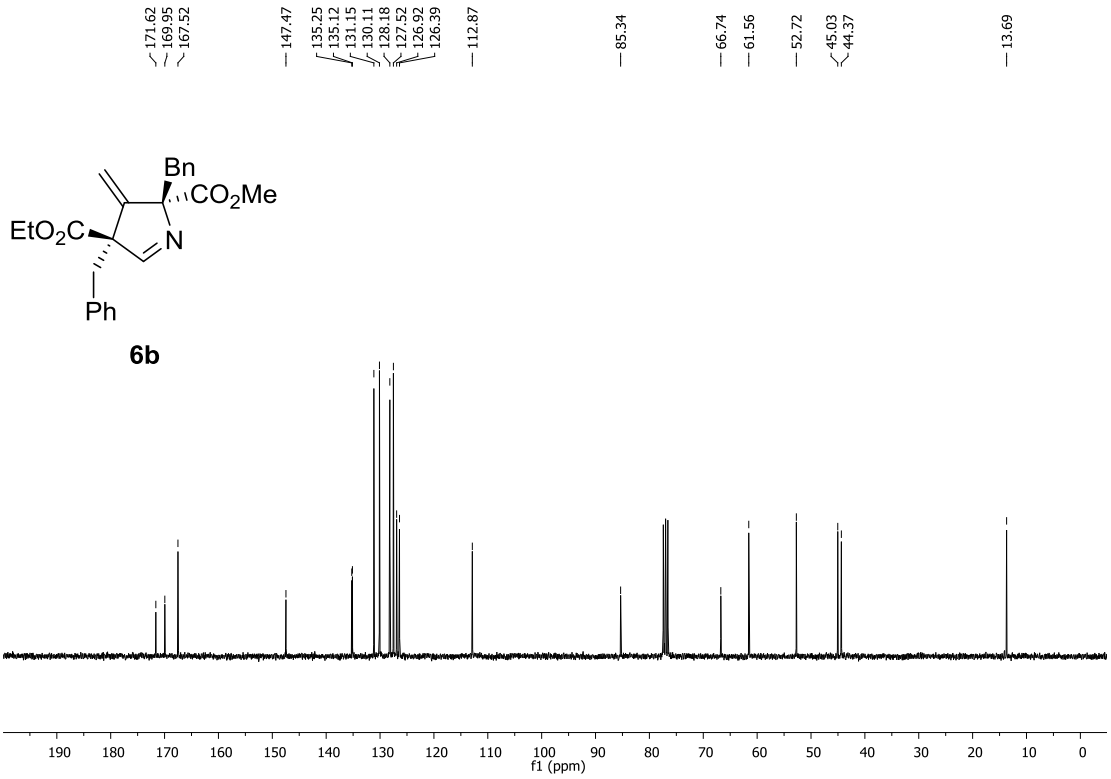
7.6463
7.2303
7.2164
7.2025
7.1836
7.1672
7.1609
7.1496
7.1357
7.0109
6.9899
6.9832
5.6493
5.5976
3.3649
3.3207
3.2965
3.2723
3.2480
3.0156
2.9879
2.9311
2.8946
Integral
1.0064
3.0632
3.0272
4.0521
1.0199
1.0331
3.0093
4.0283
1.0628
1.0000
1.0140
(ppm)

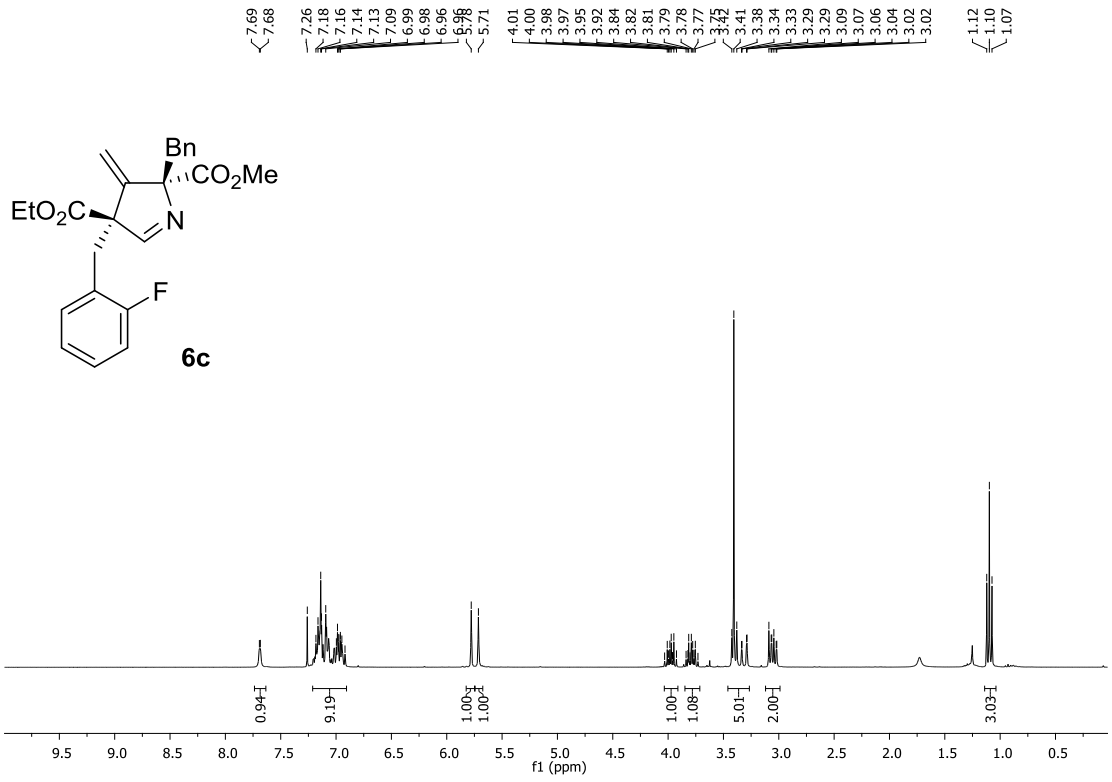
Bn
CO2Me
MeO2C
N
Ph

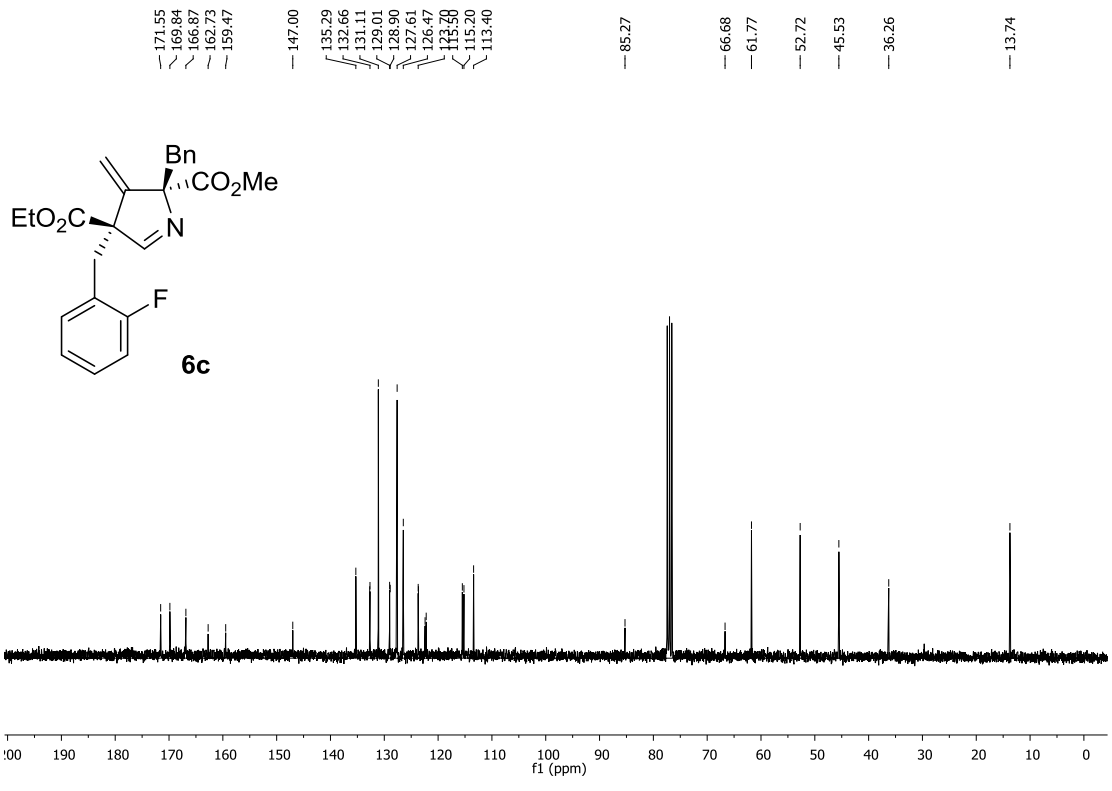
6a

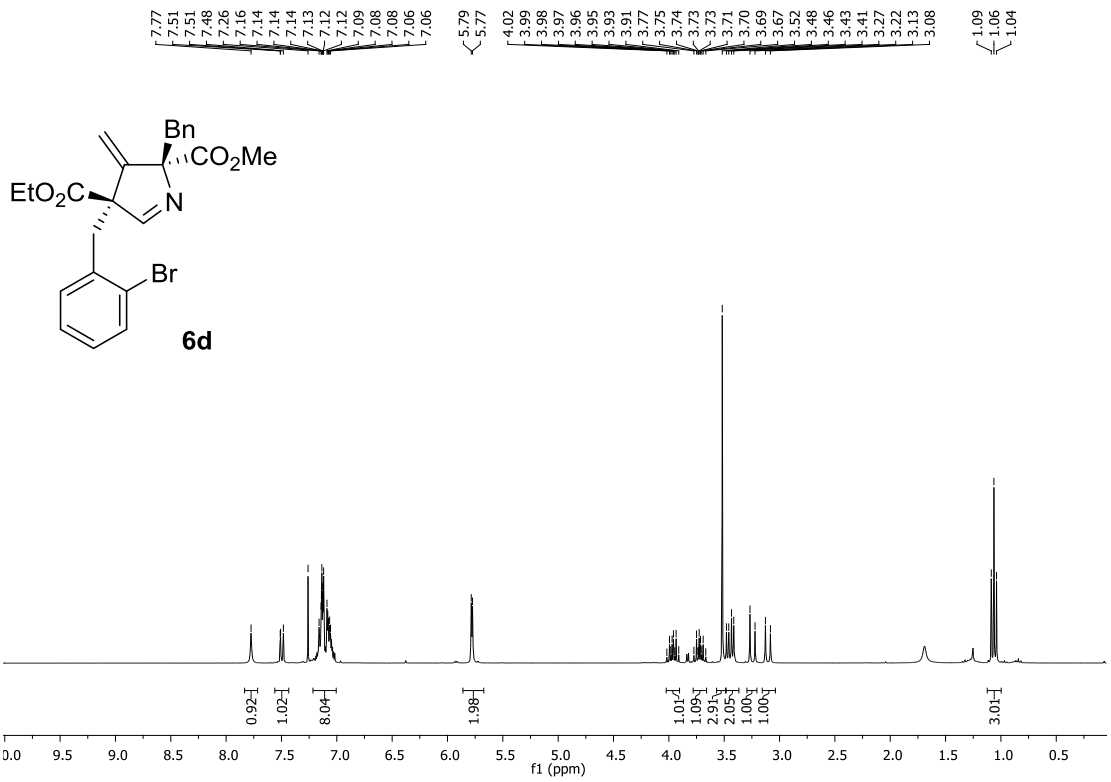

170.9495
170.0824
166.9415
147.2729
135.3435
135.1540
130.8326
130.0383
129.0124
127.2440
126.7444
126.2343
112.5486
84.8784
66.4487
52.5517
52.4132
44.0692
42.6846
(ppm)

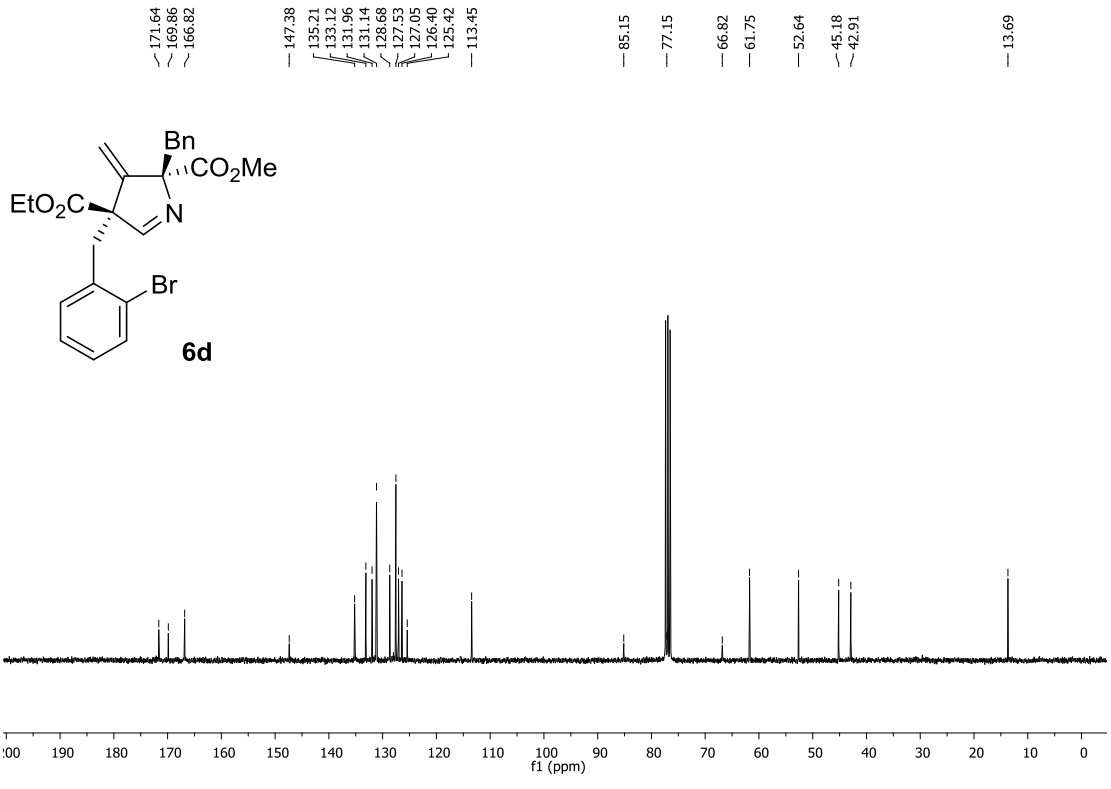

7.63
7.26
7.21
7.19
7.19
7.14
7.13
7.13
7.09
7.09
7.07
7.06
5.74
5.71
3.99
3.97
3.95
3.94
3.93
3.92
3.91
3.88
3.75
3.73
3.72
3.71
3.69
3.68
3.67
3.66
3.65
3.52
3.45
3.41
3.31
3.26
3.12
3.08
2.95
2.90
1.06
1.03
1.01
Bn
CO2Me
EtO2C
N
Ph
6b
0.92
10.13
0.98
1.00
1.03
1.09
3.00
1.04
1.02
1.03
1.03
3.02
f1 (ppm)


171.62
169.95
167.52
147.47
135.25
135.12
131.15
130.11
128.18
127.52
126.92
126.39
112.87
85.34
66.74
61.56
52.72
45.03
44.37
13.69
Bn
CO2Me
EtO2C
N
Ph
6b
f1 (ppm)


7.69
7.68
7.26
7.18
7.16
7.14
7.13
7.09
6.99
6.98
6.96
6.96
5.78
5.71
4.01
4.00
3.98
3.97
3.95
3.92
3.84
3.82
3.81
3.79
3.78
3.77
3.75
3.42
3.41
3.38
3.34
3.33
3.29
3.29
3.09
3.07
3.06
3.04
3.02
3.02
1.12
1.10
1.07
Bn
CO2Me
EtO2C
N
F
6c
0.94
9.19
1.00
1.00
1.00
1.08
5.01
2.00
3.03
f1 (ppm)


171.55
169.84
166.87
162.73
159.47
147.00
135.29
132.66
131.11
129.01
128.90
127.61
126.47
115.20
113.40
85.27
66.68
61.77
52.72
45.53
36.26
13.74
Bn
CO2Me
EtO2C
N
F
6c
f1 (ppm)


7.77
7.51
7.51
7.48
7.26
7.16
7.14
7.14
7.14
7.13
7.12
7.12
7.09
7.08
7.08
7.06
7.06
5.79
5.77
4.02
3.99
3.98
3.97
3.96
3.95
3.93
3.91
3.77
3.75
3.74
3.73
3.73
3.71
3.70
3.69
3.67
3.52
3.48
3.46
3.43
3.41
3.27
3.22
3.13
3.08
1.09
1.06
1.04
Bn
CO2Me
EtO2C
N
Br
6d
0.92
1.02
8.04
1.98
1.01
1.09
2.91
2.05
1.00
1.00
3.01
f1 (ppm)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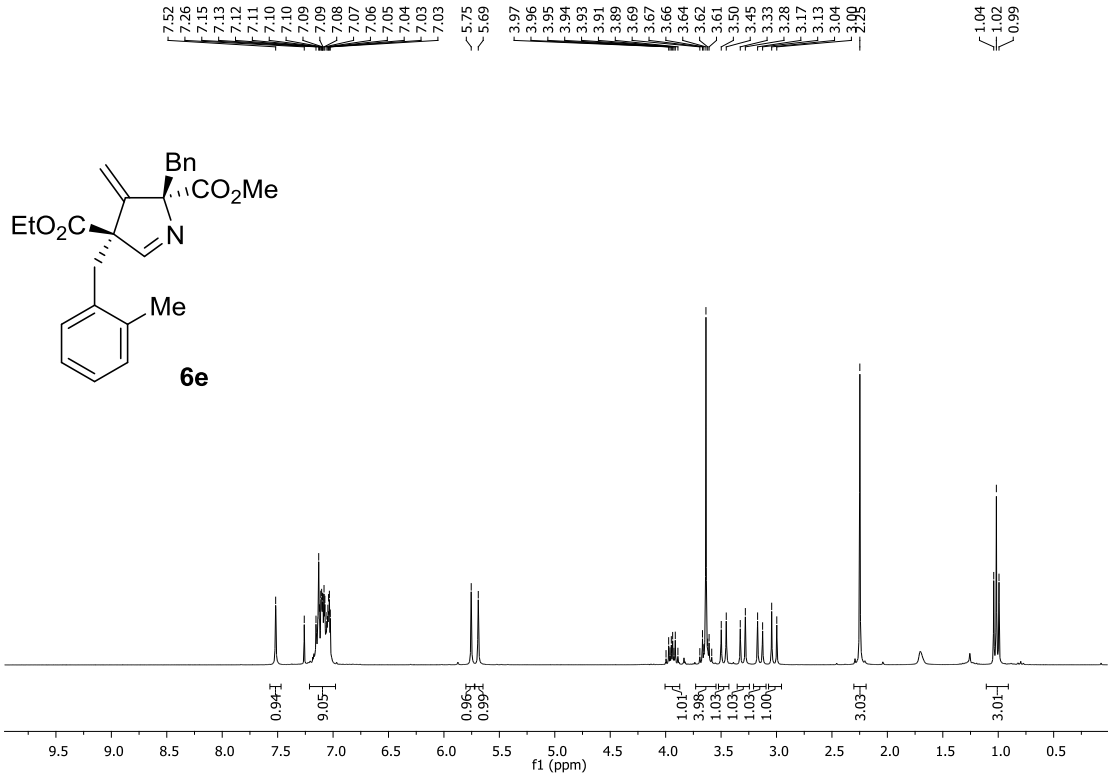
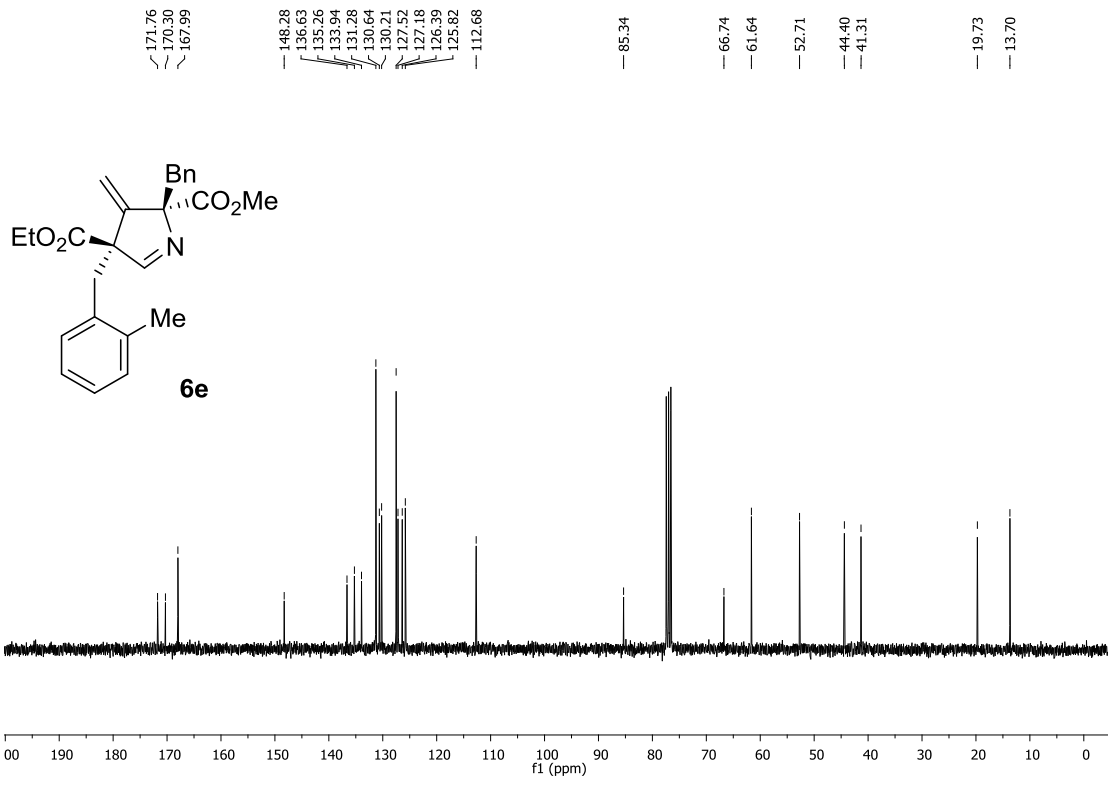
147.38
135.21
133.12
131.96
131.14
128.68
127.53
127.05
126.40
125.42
113.45
85.15
77.15
66.82
61.75
52.64
45.18
42.91
13.69
Bn
CO2Me
EtO2C
N
Br
6d
f1 (ppm)


7.52
7.26
7.15
7.13
7.12
7.11
7.10
7.10
7.09
7.09
7.08
7.07
7.06
7.05
7.04
7.03
7.03
5.75
5.69
3.97
3.96
3.95
3.94
3.93
3.91
3.89
3.69
3.67
3.66
3.64
3.62
3.61
3.50
3.45
3.33
3.28
3.17
3.13
3.04
3.00
2.25
1.04
1.02
0.99
Bn
CO2Me
EtO2C
N
Me
6e
0.94
9.05
0.96
0.99
1.01
3.98
1.03
1.03
1.00
3.03
3.01
f1 (ppm)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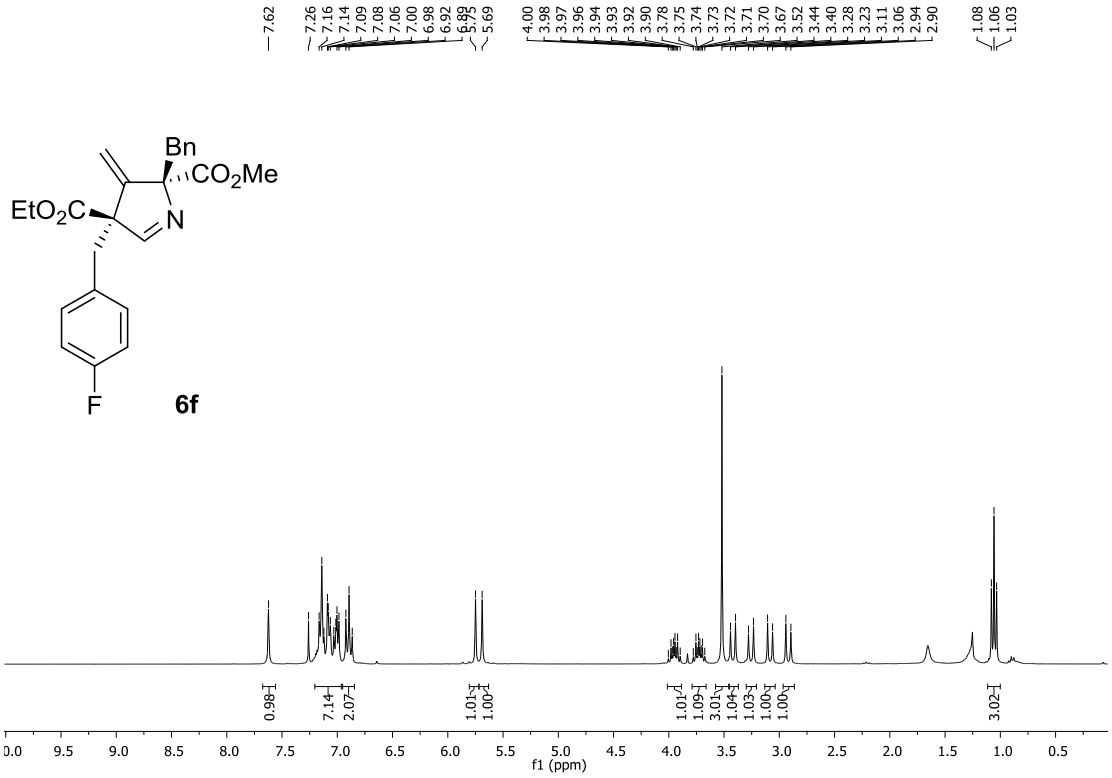
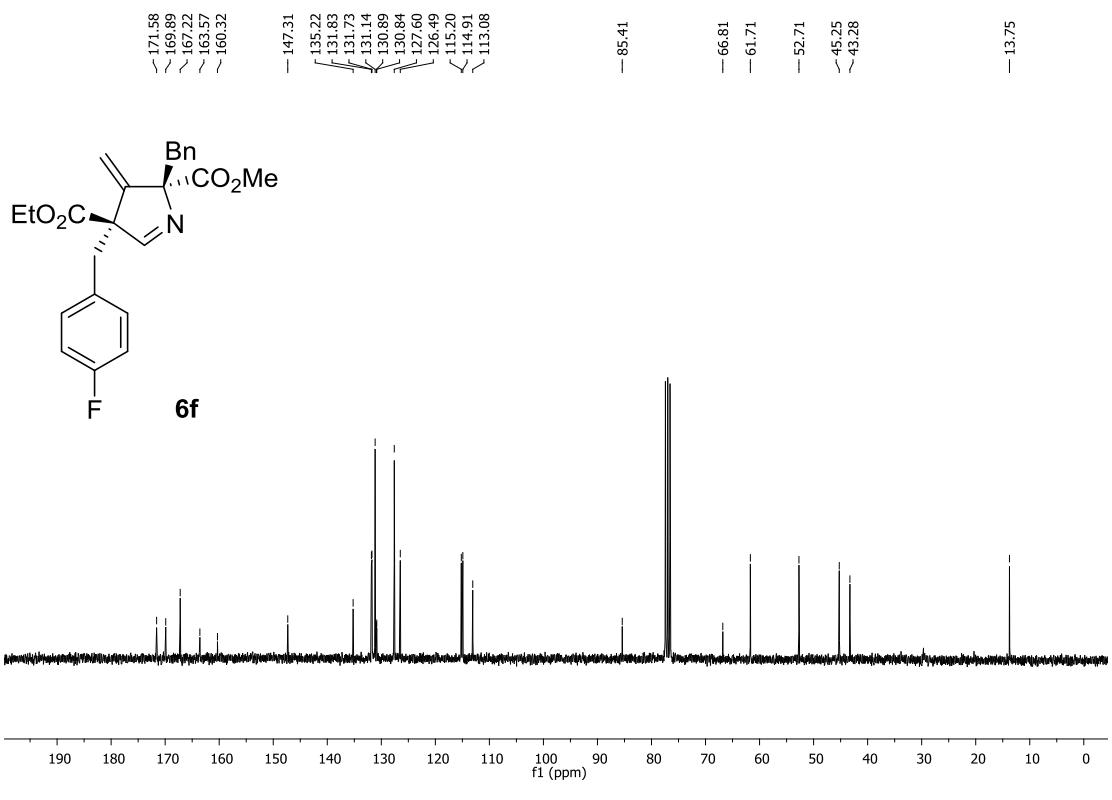
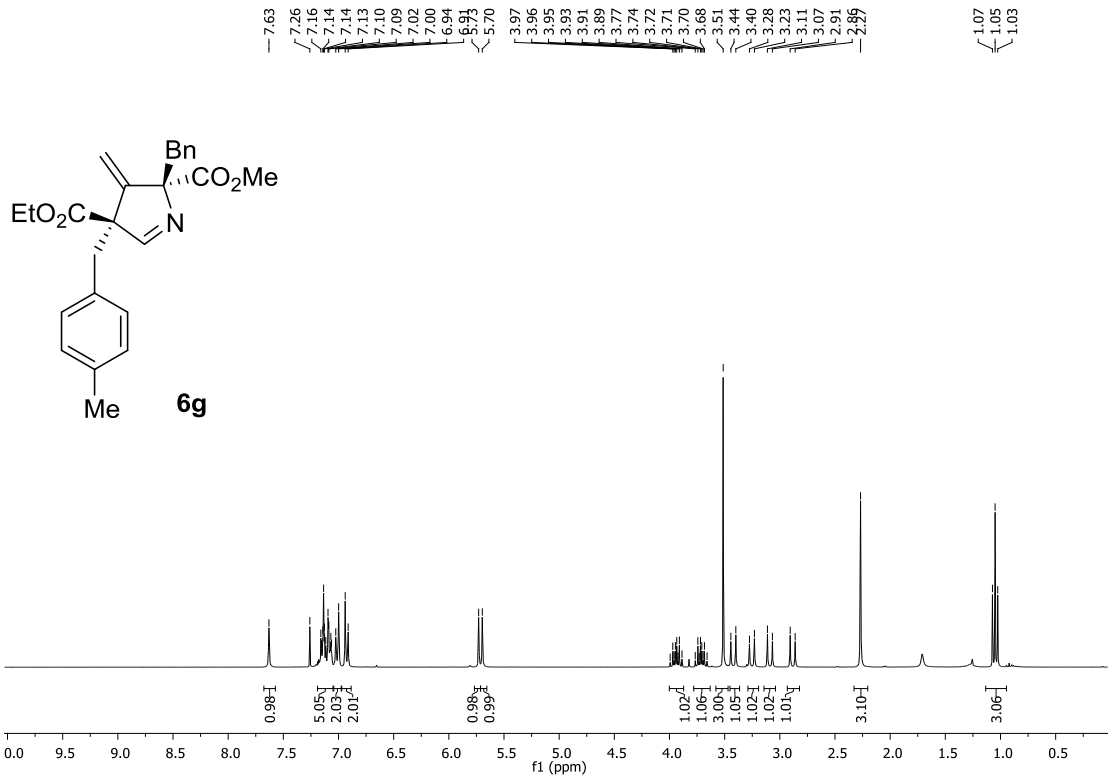
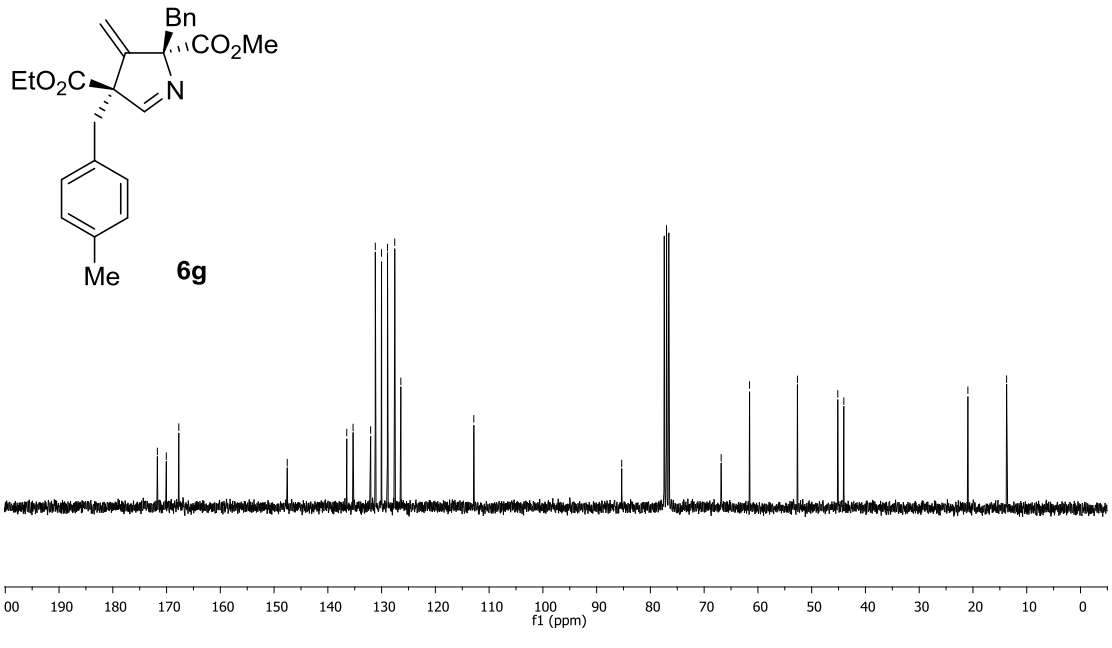
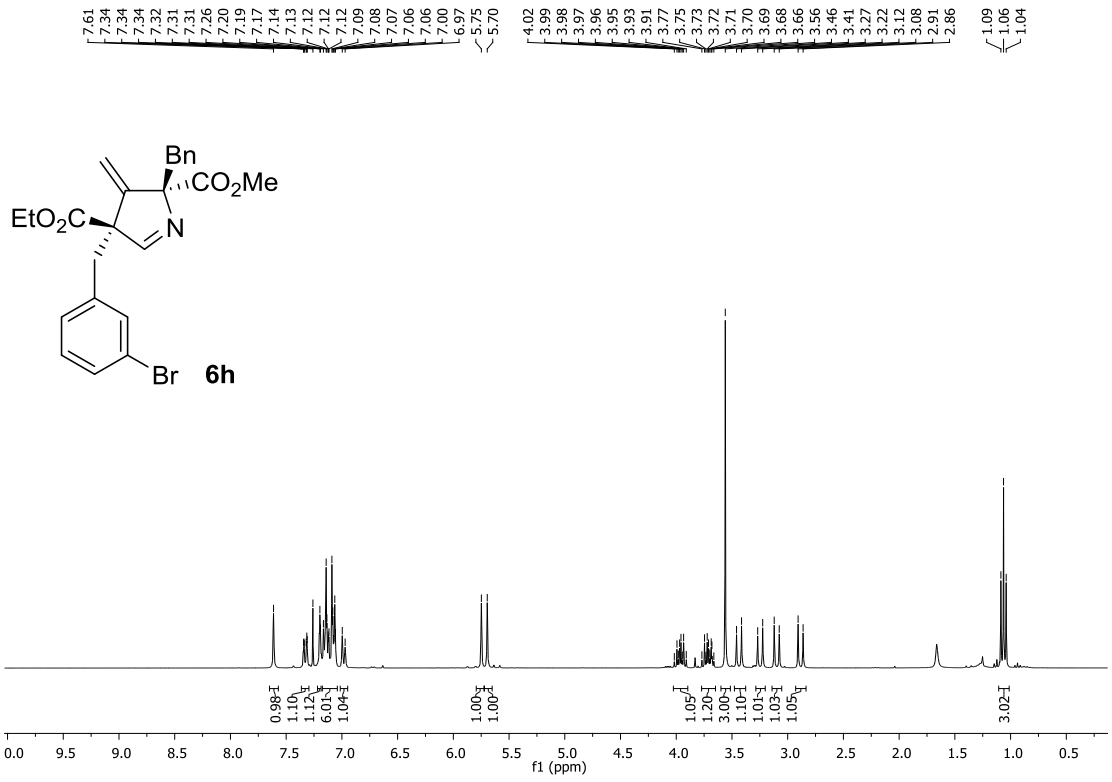
170.30
167.99
148.28
136.63
135.26
133.94
131.28
130.64
130.21
127.52
127.18
126.39
125.82
112.68
85.34
66.74
61.64
52.71
44.40
41.31
19.73
13.70
Bn
CO2Me
EtO2C
N
Me
6e
f1 (ppm)


7.62
7.26
7.16
7.14
7.09
7.08
7.06
7.00
6.98
6.92
6.89
5.75
5.69
4.00
3.98
3.97
3.96
3.94
3.93
3.92
3.90
3.78
3.75
3.74
3.73
3.72
3.71
3.70
3.67
3.52
3.44
3.40
3.28
3.23
3.11
3.06
2.94
2.90
1.08
1.06
1.03
Bn
CO2Me
EtO2C
N
F
6f
0.98
7.14
2.07
1.01
1.00
1.01
1.09
3.01
1.04
1.03
1.00
1.00
3.02
f1 (ppm)


171.58
169.89
167.22
163.57
160.32
147.31
135.22
131.83
131.73
131.14
130.89
130.84
127.60
126.49
115.20
114.91
113.08
85.41
66.81
61.71
52.71
45.25
43.28
13.75
Bn
CO2Me
EtO2C
N
F
6f
f1 (ppm)


Bn
CO2Me
EtO2C
N
Me
6g
f1 (ppm)


Bn
CO2Me
EtO2C
N
Me
6g
f1 (ppm)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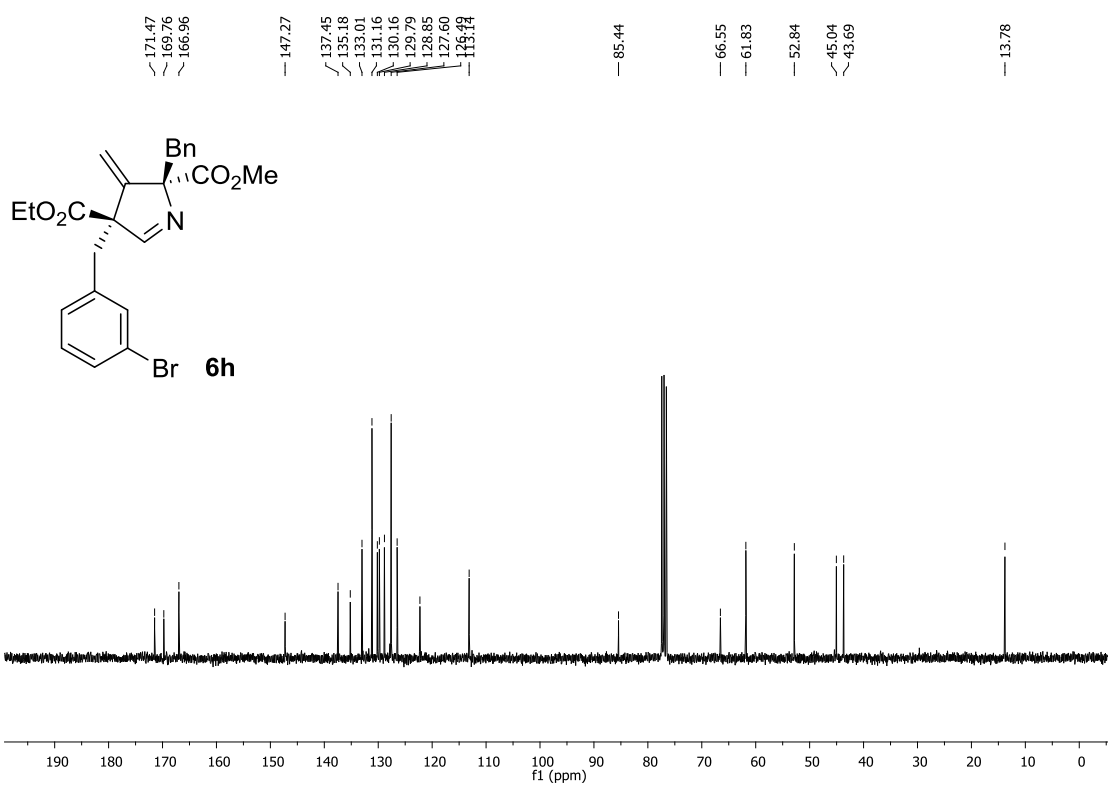
4.02 3.99 3.98 3.97 3.96 3.95 3.93 3.91 3.77 3.75 3.73 3.72 3.71 3.70 3.69 3.68 3.66 3.56 3.46 3.41 3.27 3.22 3.12 3.08 2.91 2.86
1.09 1.06 1.04
Bn
CO2Me
EtO2C
N
Br
6h
0.98 1.10 1.12 6.01 1.04 1.00 1.00 1.05 1.20 3.00 1.10 1.01 1.03 1.05 3.02
f1 (ppm)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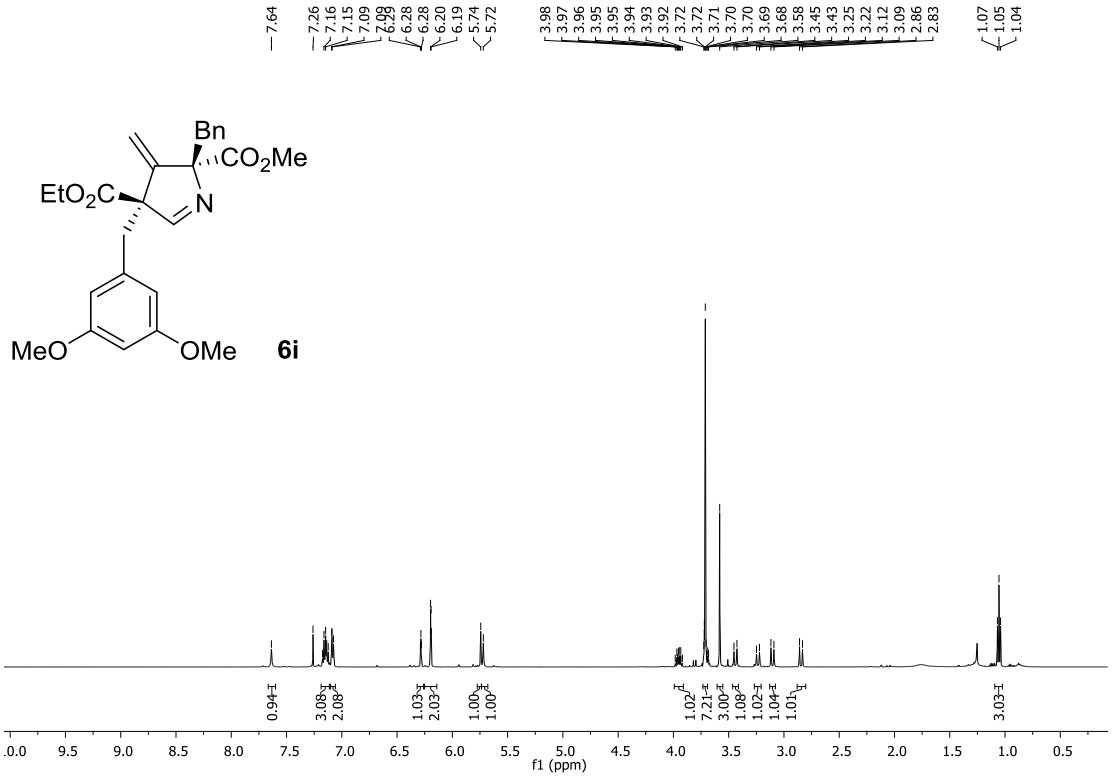
Bn
CO2Me
EtO2C
N
Br
6h
f1 (ppm)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6.28
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6.19
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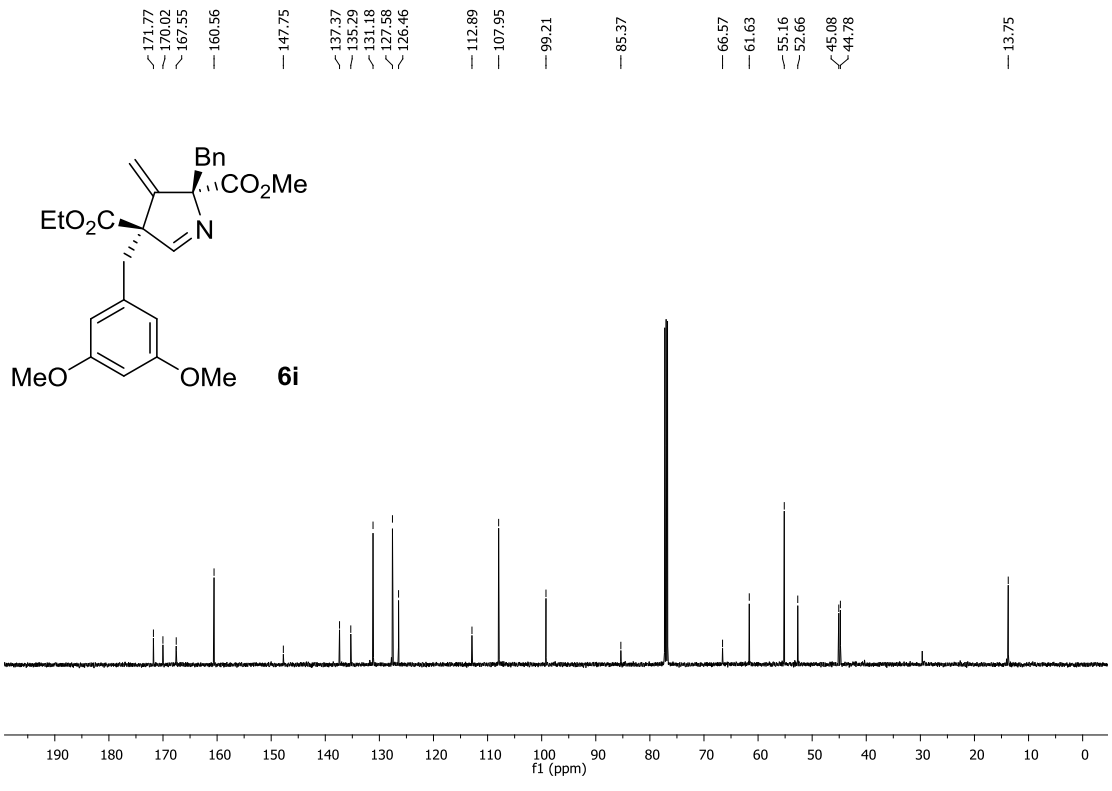
5.72
3.98
3.97
3.96
3.95
3.95
3.94
3.93
3.92
3.72
3.72
3.71
3.70
3.70
3.69
3.68
3.58
3.45
3.43
3.25
3.22
3.12
3.09
2.86
2.83
1.07
1.05
1.04
Bn
CO2Me
EtO2C
N
MeO
OMe
6i
0.94
3.08
2.08
1.03
2.03
1.00
1.00
1.02
7.21
3.00
1.08
1.02
1.04
1.01
3.03
f1 (ppm)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135.29
131.18
127.58
126.46
112.89
107.95
99.21
85.37
66.57
61.63
55.16
52.66
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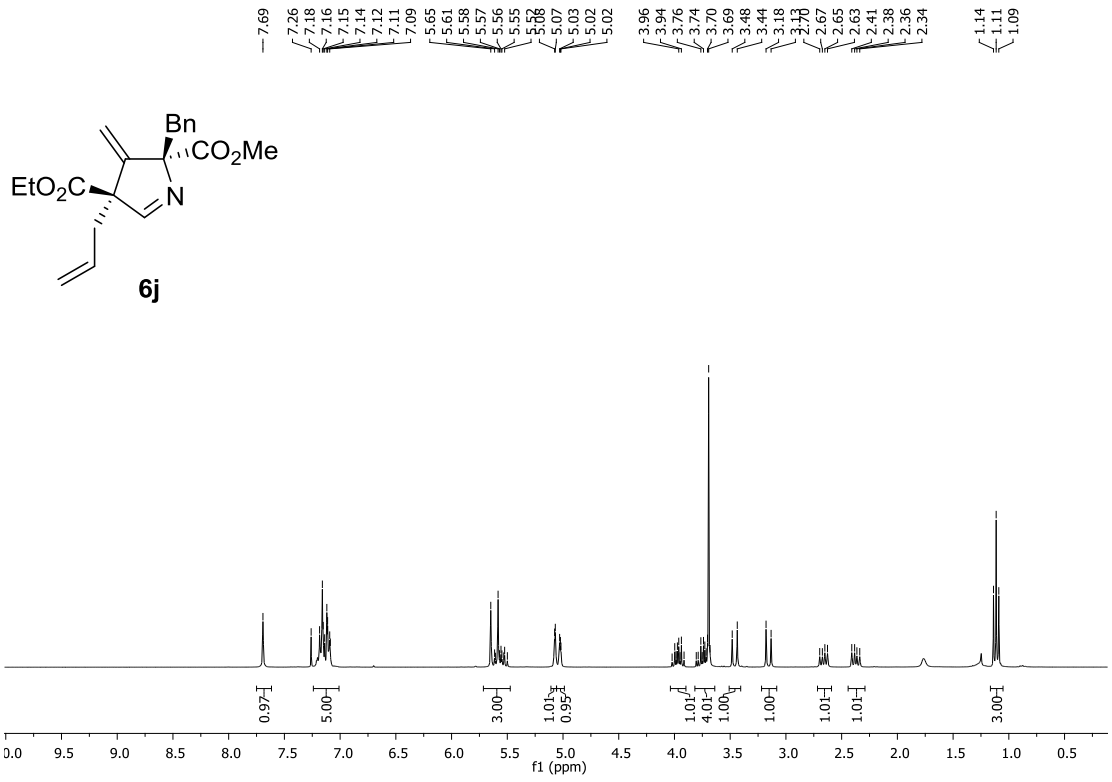
44.78
13.75
Bn
CO2Me
EtO2C
N
MeO
OMe
6i
f1 (ppm)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7.14
7.12
7.11
7.09
5.65
5.61
5.58
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5.56
5.55
5.52
5.08
5.07
5.03
5.02
5.02
3.96
3.94
3.76
3.74
3.70
3.69
3.48
3.44
3.18
3.13
2.70
2.67
2.65
2.63
2.41
2.38
2.36
2.34
1.14
1.11
1.09
Bn
CO2Me
EtO2C
N
6j
0.97
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3.00
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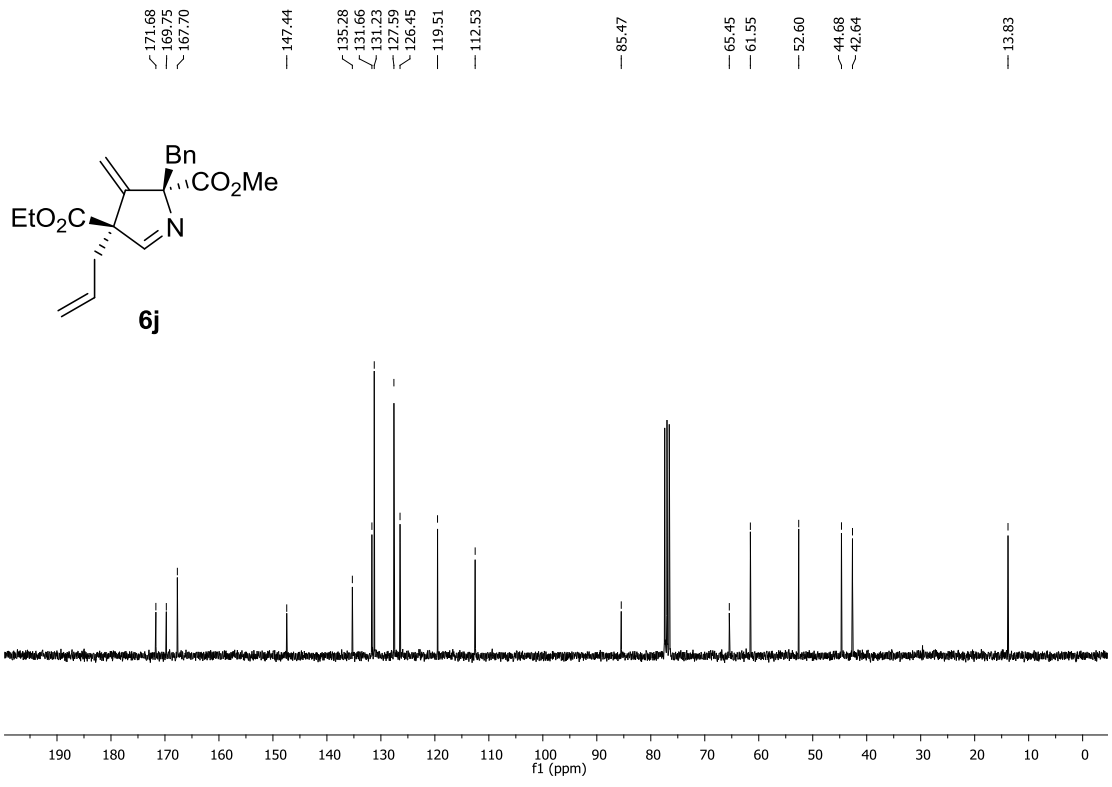
0.95
1.01
4.01
1.00
1.00
1.01
1.01
3.00
f1 (ppm)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131.23
127.59
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119.51
112.53
85.47
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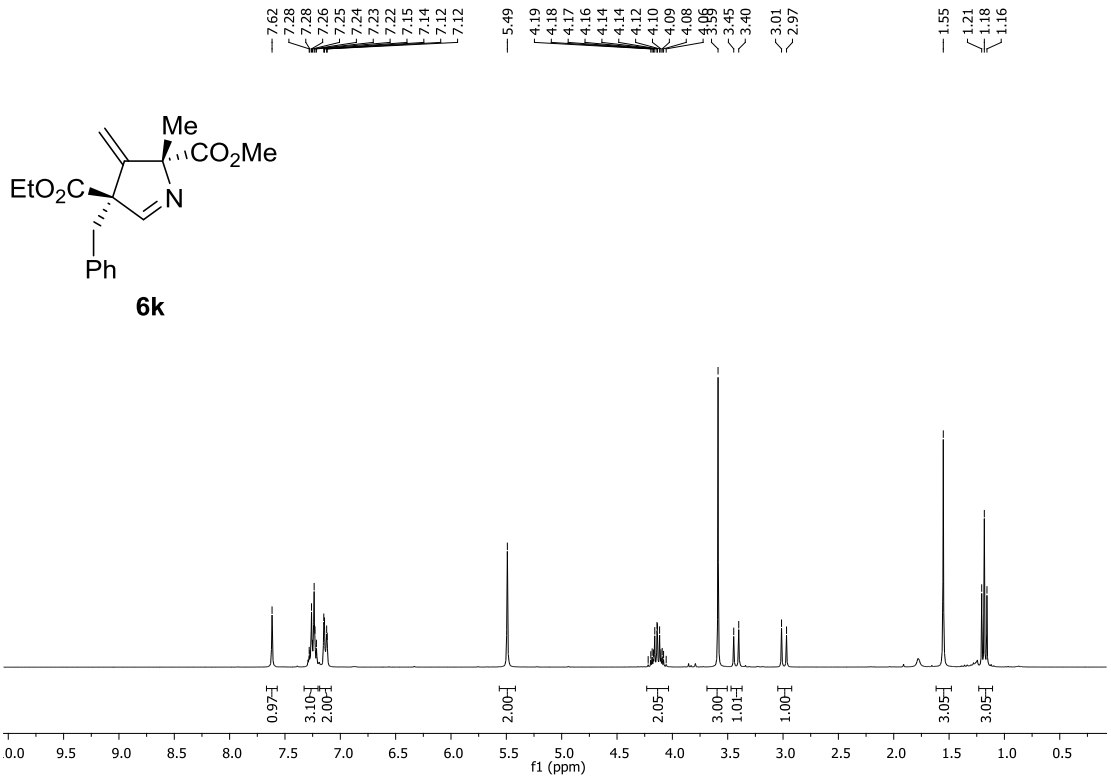
61.55
52.60
44.68
42.64
13.83
Bn
CO2Me
EtO2C
N
6j
f1 (ppm)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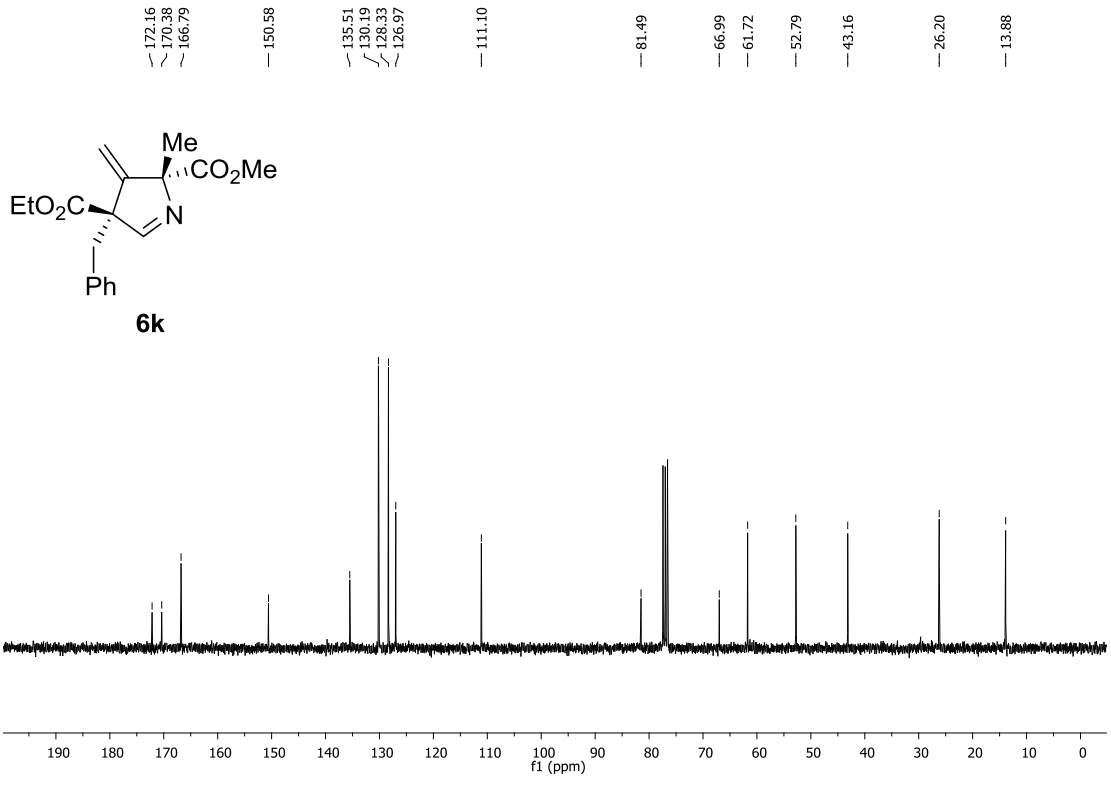
7.24
7.23
7.22
7.15
7.14
7.12
7.12
7.12
5.49
4.19
4.18
4.17
4.16
4.14
4.14
4.12
4.10
4.09
4.08
3.45
3.40
3.01
2.97
1.55
1.21
1.18
1.16
Me
CO2Me
EtO2C
N
Ph
6k
0.97
3.10
2.00
2.00
2.05
3.00
1.01
1.00
3.05
3.05
f1 (ppm)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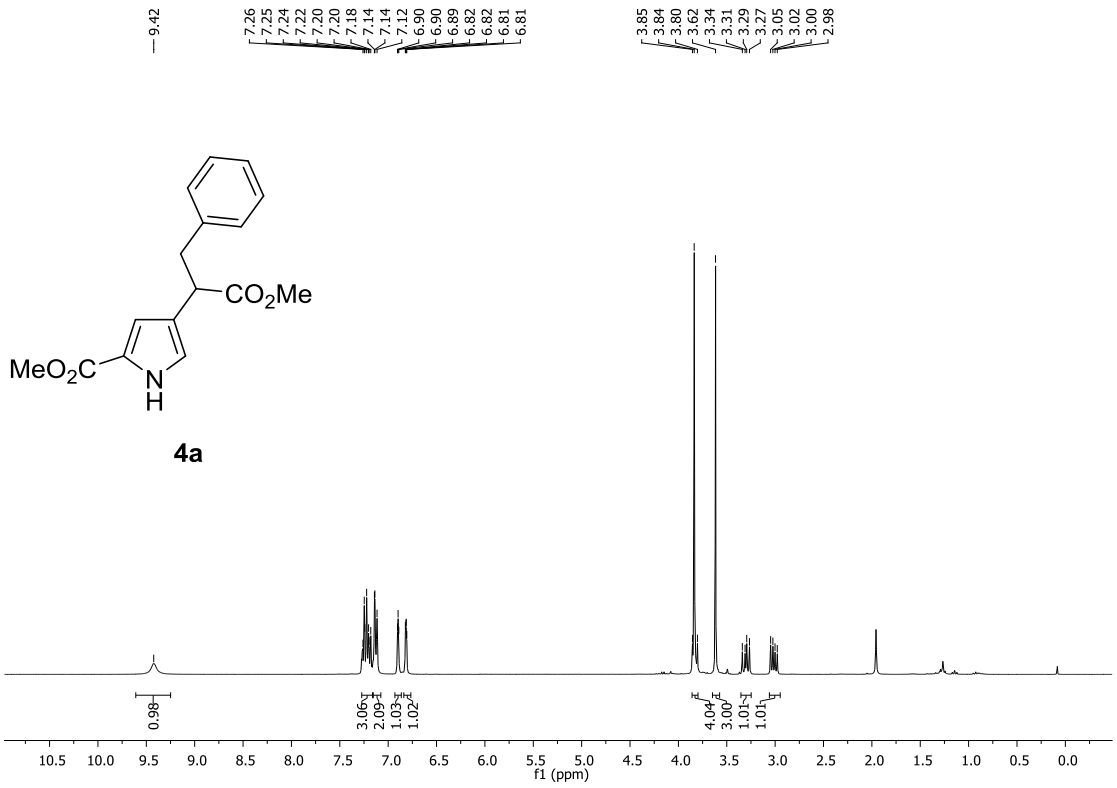
170.38
166.79
150.58
135.51
130.19
128.33
126.97
111.10
81.49
66.99
61.72
52.79
43.16
26.20
13.88
Me
CO2Me
EtO2C
N
Ph
6k
f1 (ppm)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7.18
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7.14
7.12
6.90
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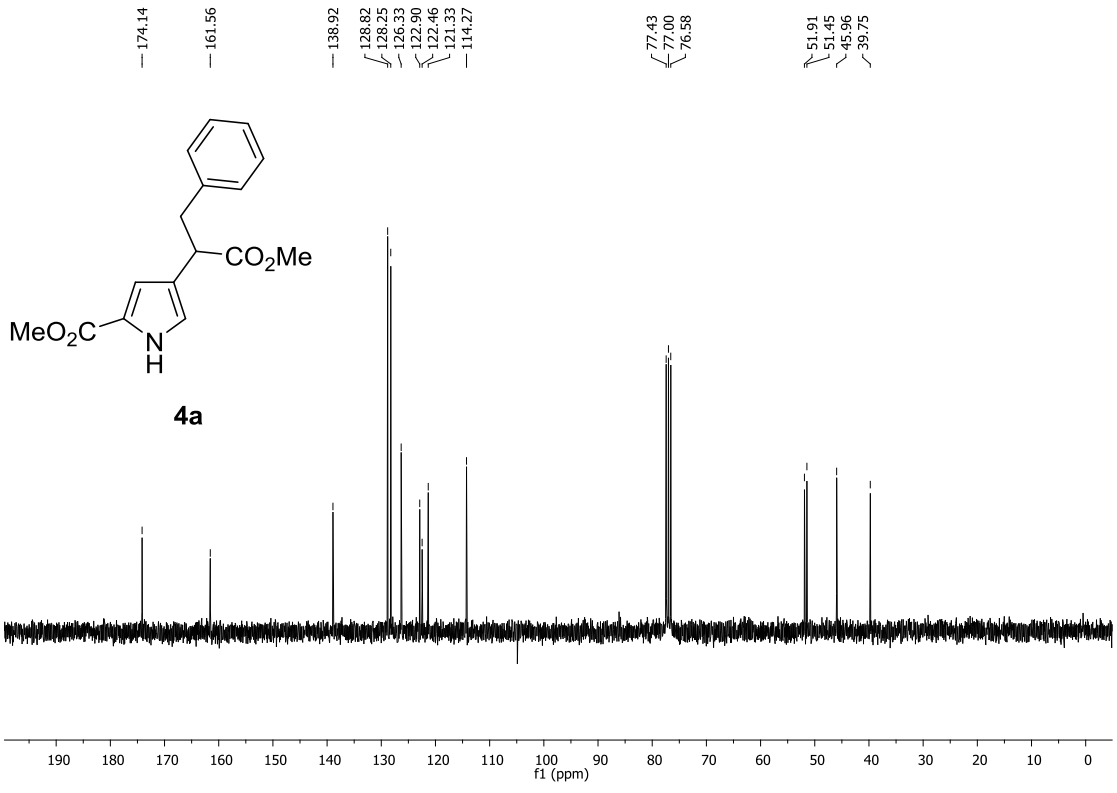
6.89
6.82
6.82
6.81
6.81
3.85
3.84
3.80
3.62
3.34
3.31
3.29
3.27
3.05
3.02
3.00
2.98
CO2Me
MeO2C
N
H
4a
0.98
3.06
2.09
1.03
1.02
4.04
3.00
1.01
1.01
f1 (ppm)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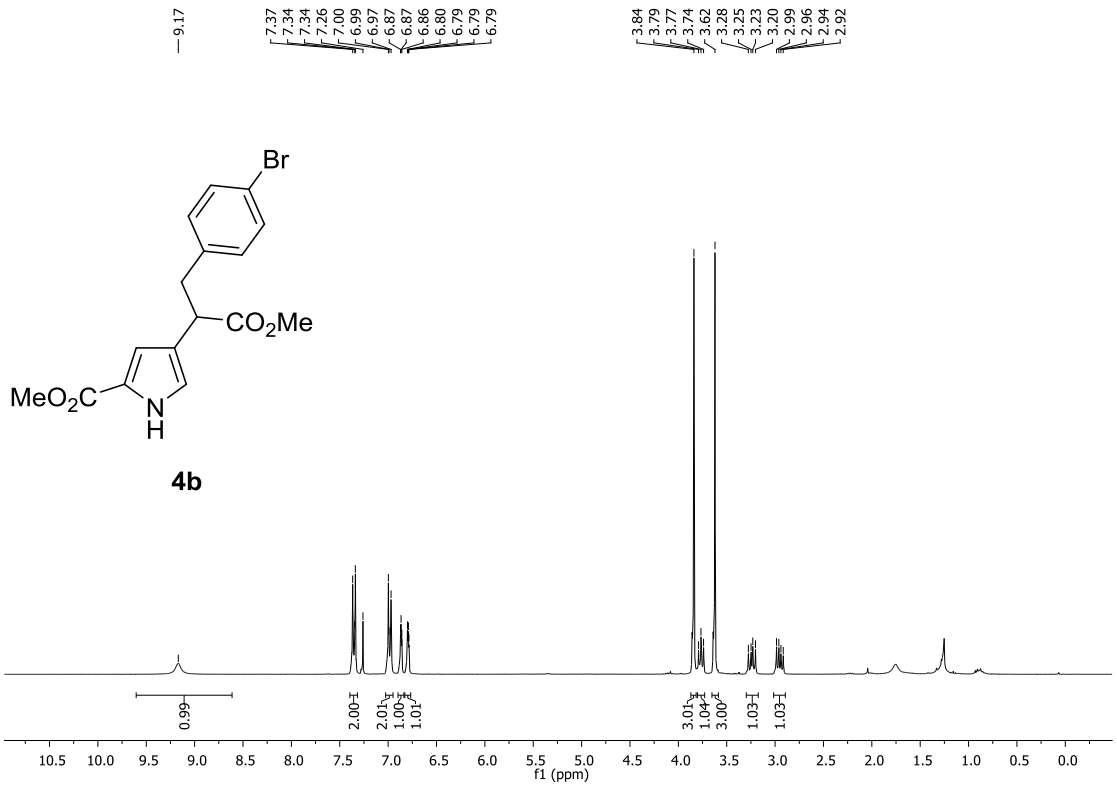
161.56
138.92
128.82
128.25
126.33
122.90
122.46
121.33
114.27
77.43
77.00
76.58
51.91
51.45
45.96
39.75
CO2Me
MeO2C
N
H
4a
f1 (ppm)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6.87
6.86
6.80
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6.79
3.84
3.79
3.77
3.74
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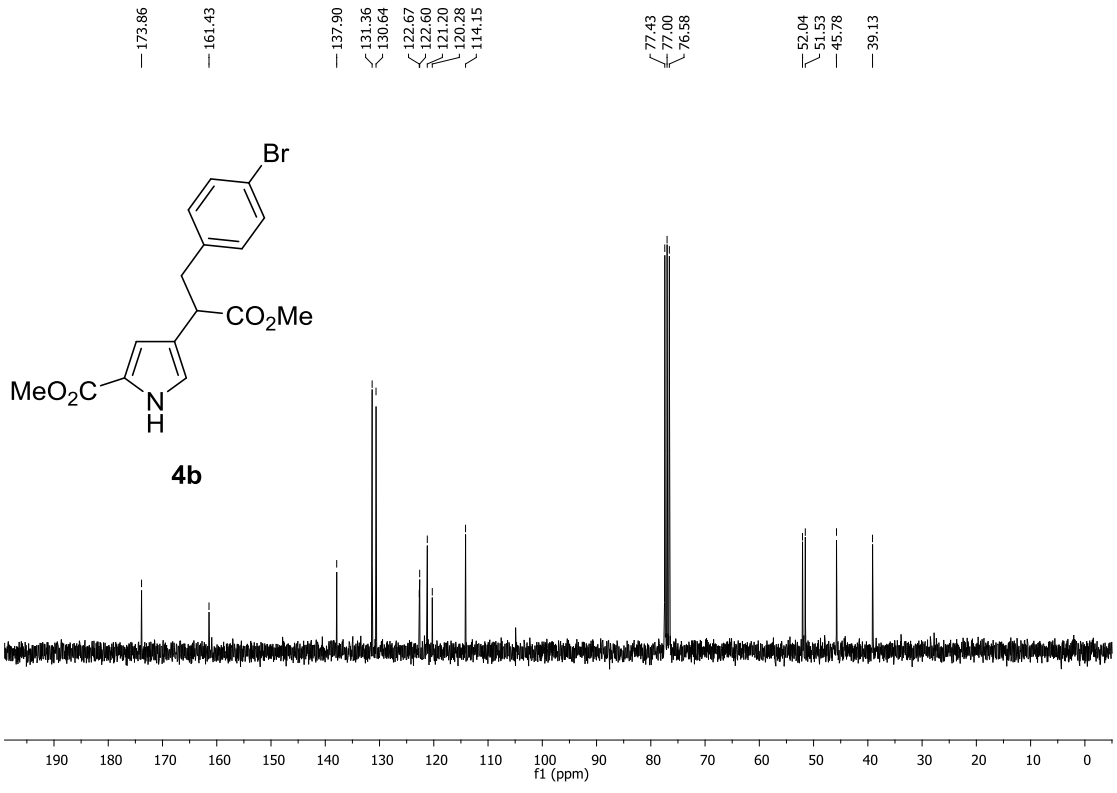
3.28
3.25
3.23
3.20
2.99
2.96
2.94
2.92
Br
CO2Me
MeO2C
N
H
4b
0.99
2.00
2.01
1.00
1.01
3.01
1.04
3.00
1.03
1.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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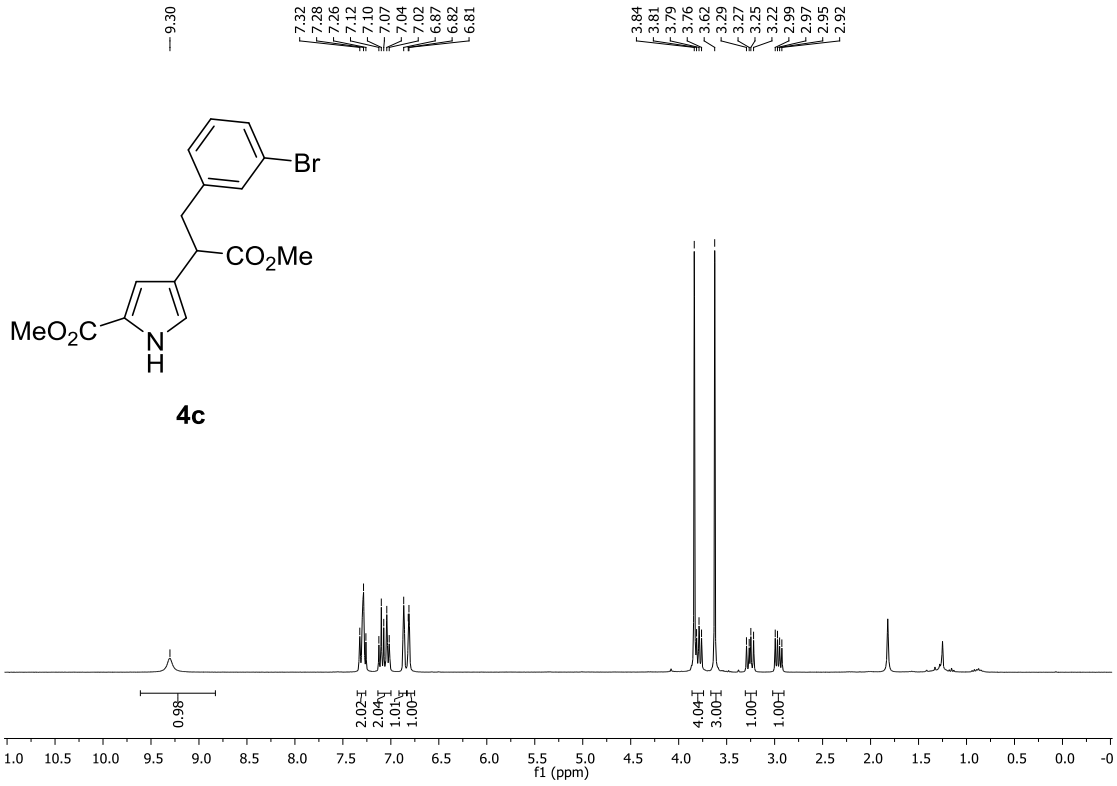
122.60
121.20
120.28
114.15
77.43
77.00
76.58
52.04
51.53
45.78
39.13
Br
CO2Me
MeO2C
N
H
4b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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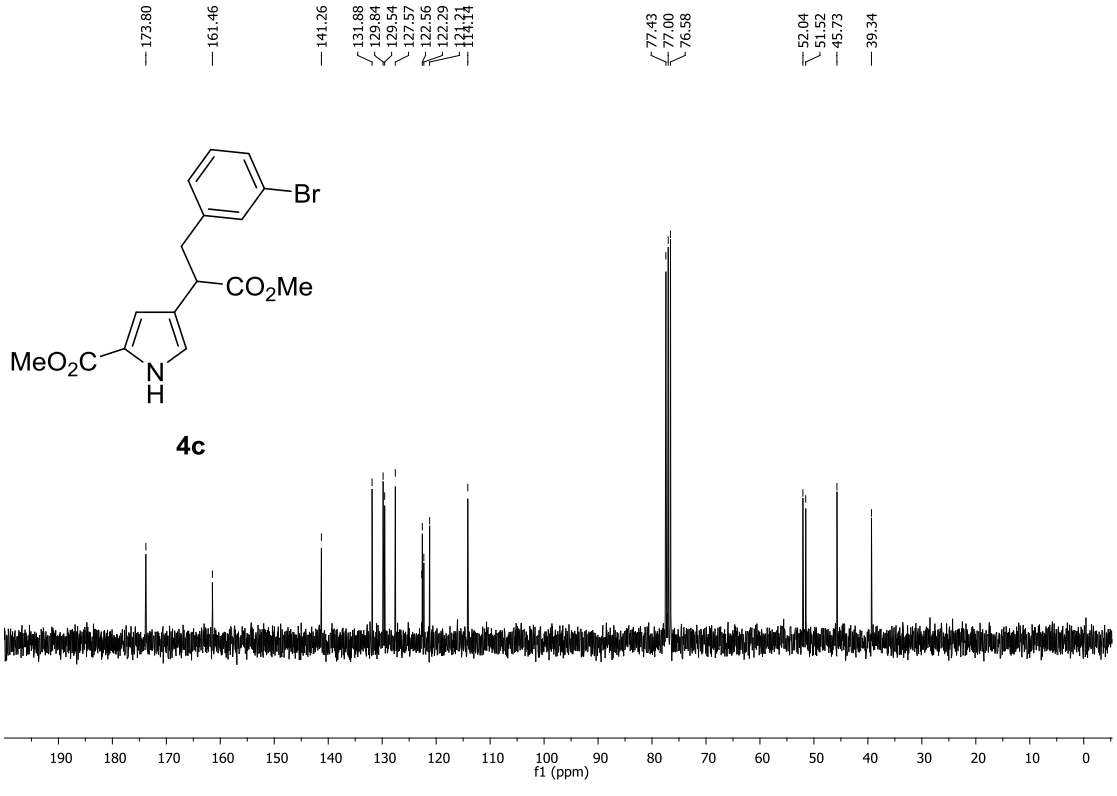
7.28
7.26
7.12
7.10
7.07
7.04
7.02
6.87
6.82
6.81
3.84
3.81
3.79
3.76
3.62
3.29
3.27
3.25
3.22
2.99
2.97
2.95
2.92
Br
CO2Me
MeO2C
N
H
0.98
2.02
2.04
1.01
1.00
4.04
3.00
1.00
1.00
f1 (ppm)

4c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141.26
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127.57
122.56
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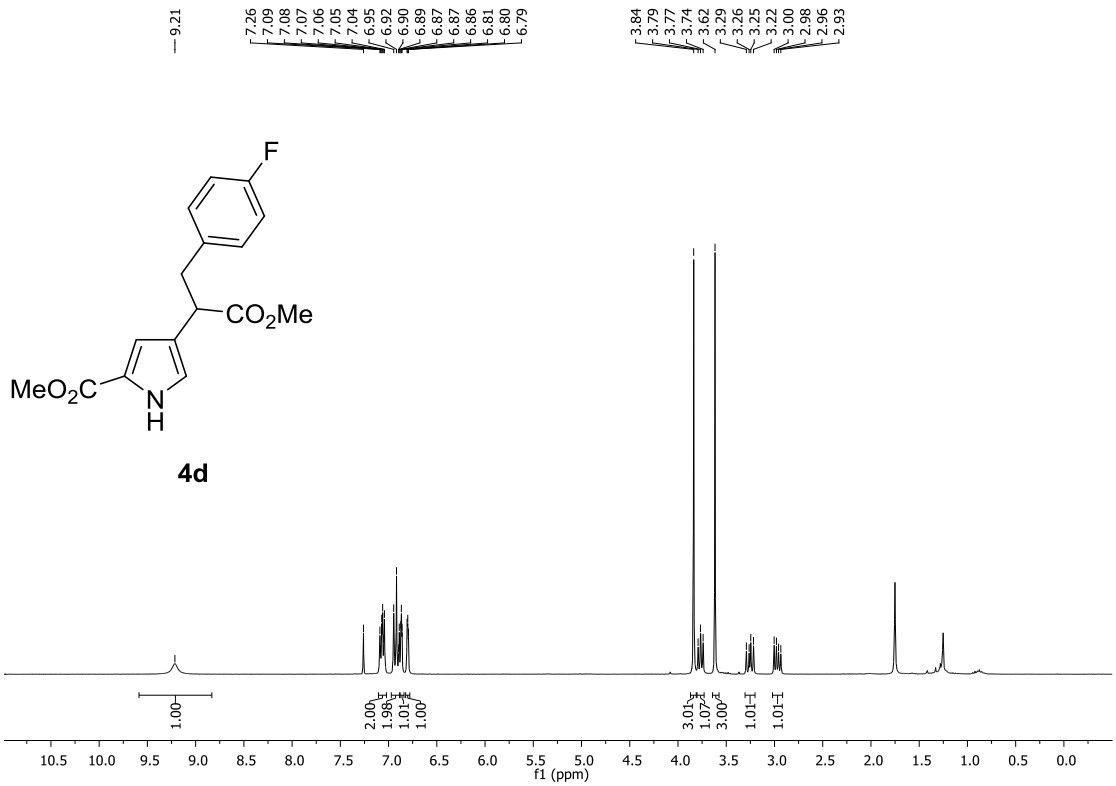
121.21
114.14
77.43
77.00
76.58
52.04
51.52
45.73
39.34
Br
CO2Me
MeO2C
N
H
f1 (ppm)

4c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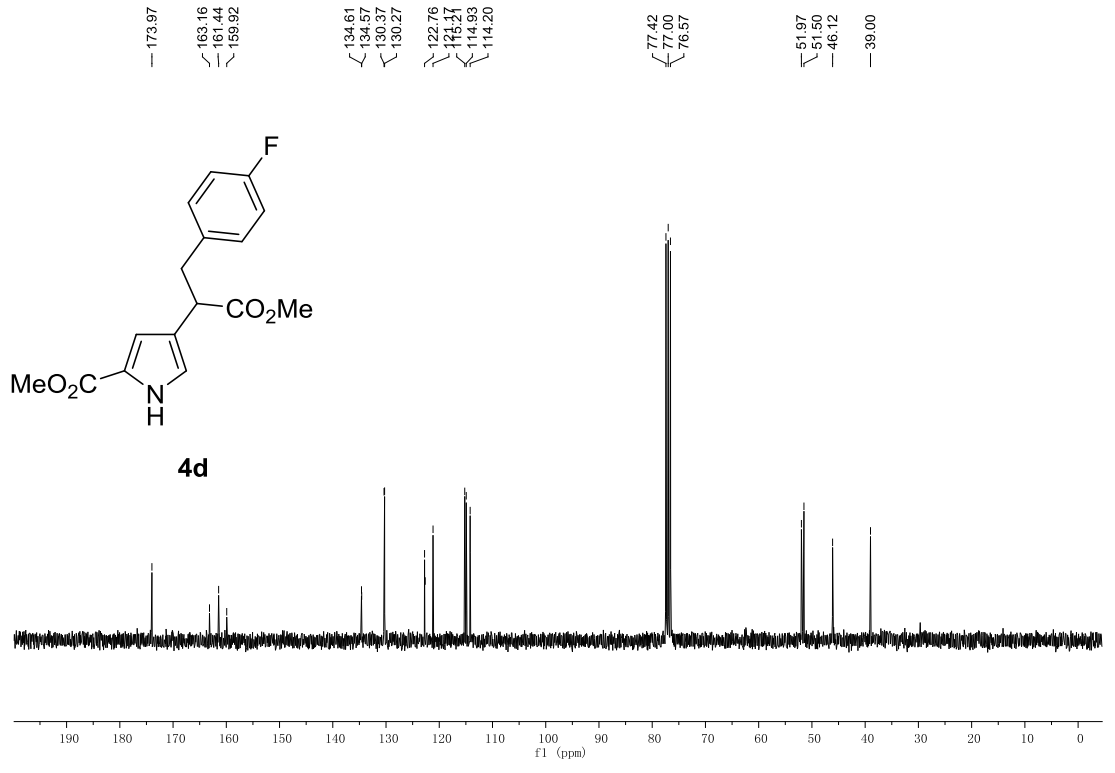
7.26
7.09
7.08
7.07
7.06
7.05
7.04
6.95
6.92
6.90
6.89
6.87
6.87
6.86
6.81
6.80
6.79
3.84
3.79
3.77
3.74
3.62
3.29
3.26
3.25
3.22
3.00
2.98
2.96
2.93
F
CO2Me
MeO2C
N
H
4d
1.00
2.00
1.98
1.01
1.00
3.01
1.07
3.00
1.01
1.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.27
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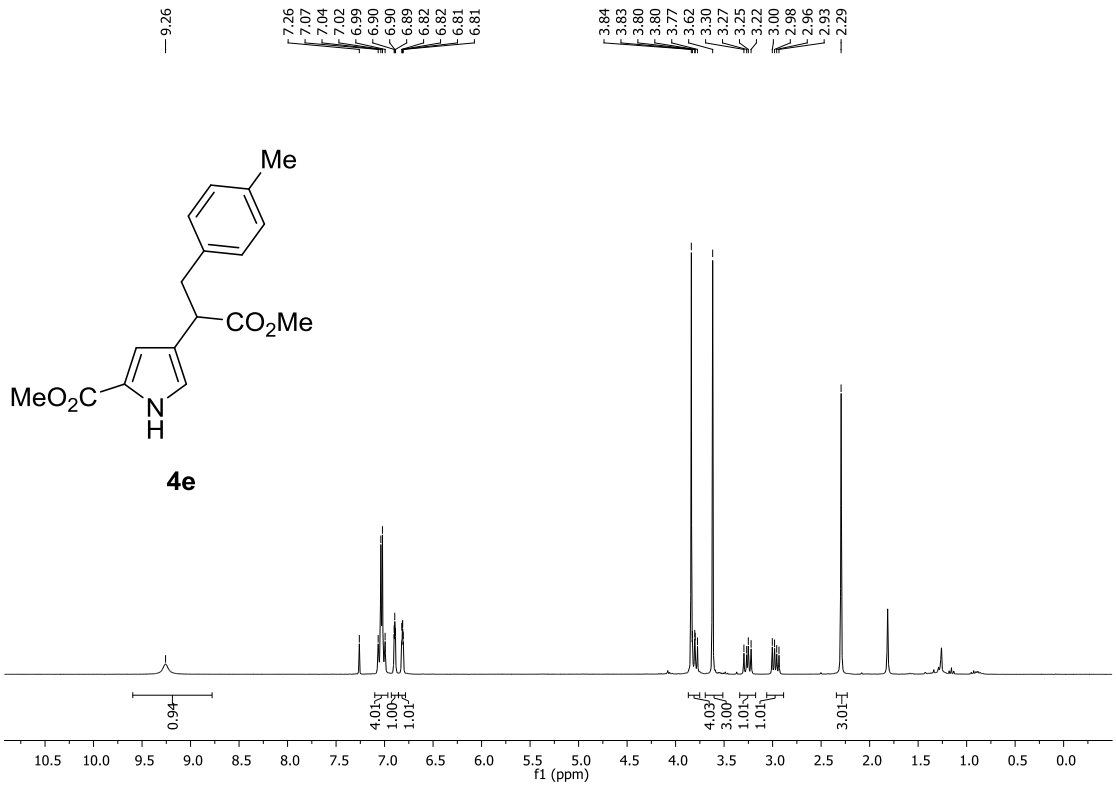
121.17
115.21
114.93
114.20
77.42
77.00
76.57
51.97
51.50
46.12
39.00
F
CO2Me
MeO2C
N
H
4d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.90
6.90
6.89
6.82
6.82
6.81
6.81
3.84
3.83
3.80
3.80
3.77
3.62
3.30
3.27
3.25
3.22
3.00
2.98
2.96
2.93
2.29
Me
CO2Me
MeO2C
N
H
4e
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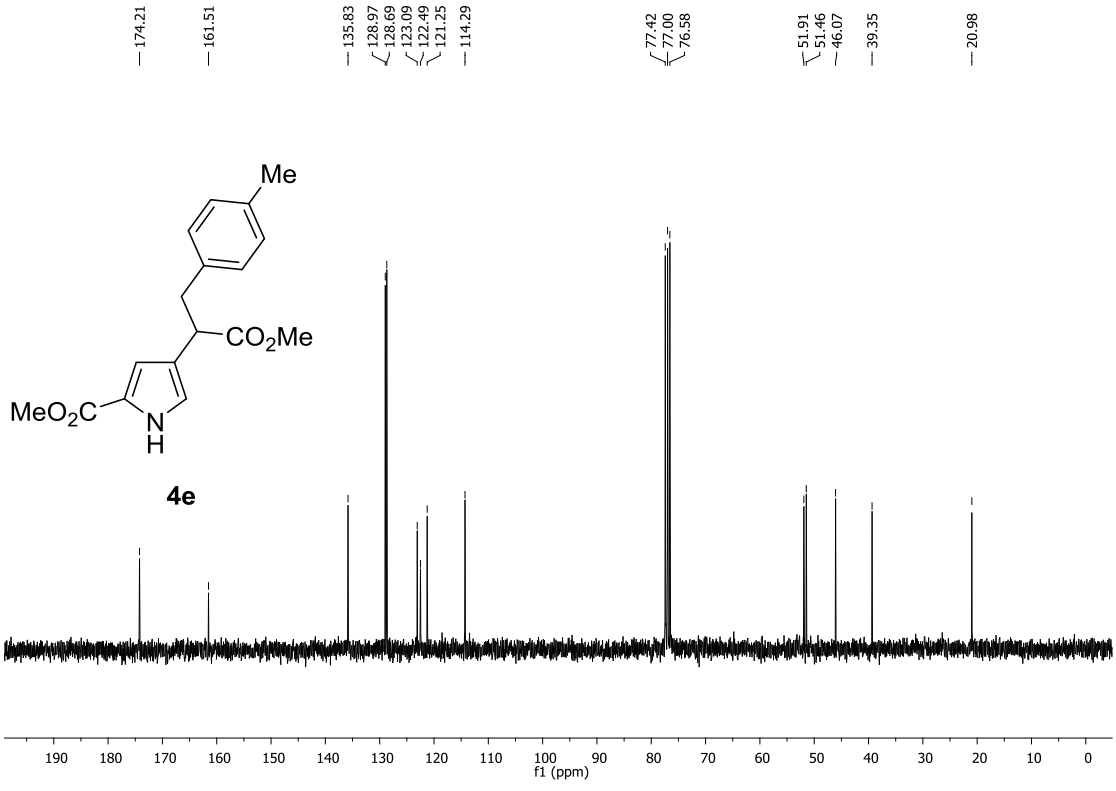
4.01
1.00
1.01
4.03
3.00
1.01
1.01
3.01
f1 (ppm)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114.29
77.42
77.00
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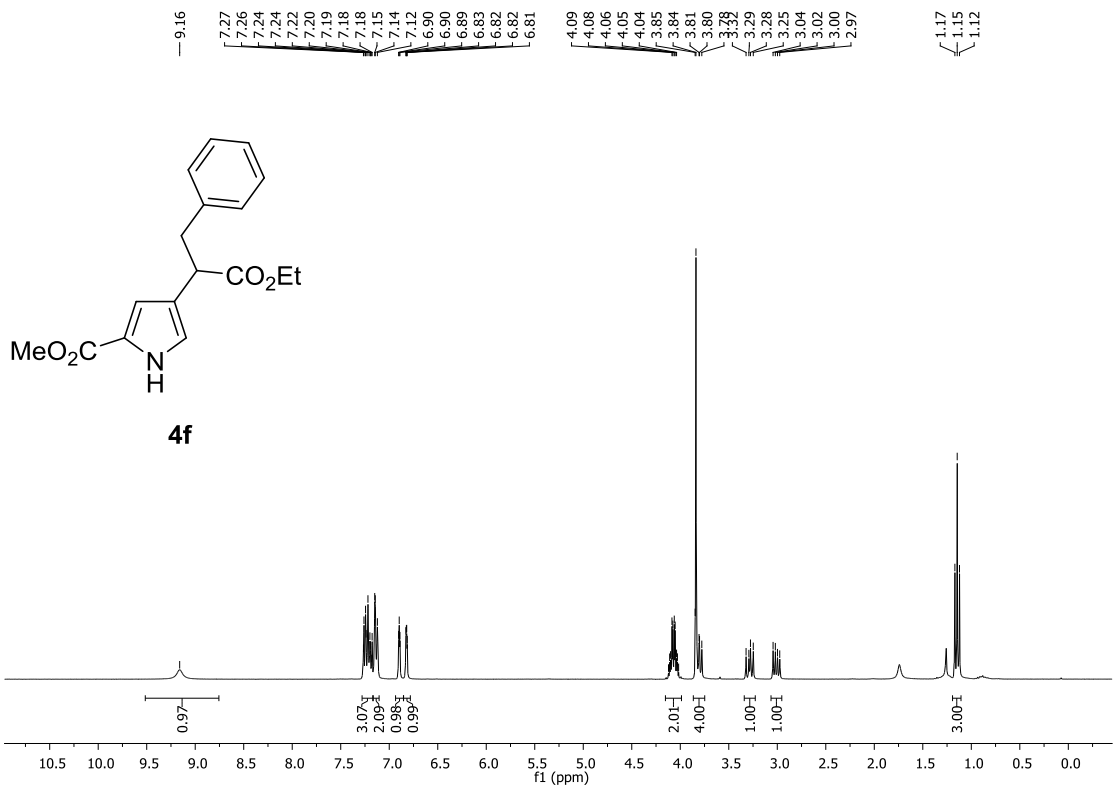
51.91
51.46
46.07
39.35
20.98
Me
CO2Me
MeO2C
N
H
4e
f1 (ppm)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7.24
7.24
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7.19
7.18
7.18
7.15
7.14
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6.89
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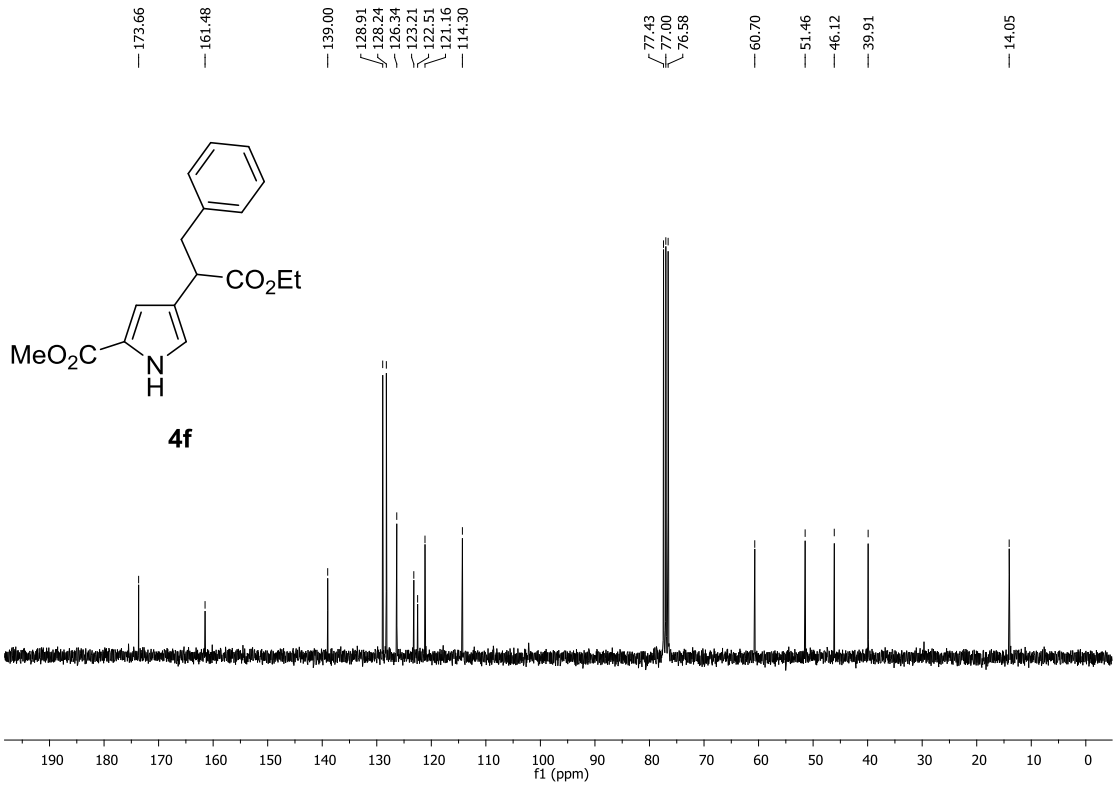
6.82
6.82
6.81
4.09
4.08
4.06
4.05
4.04
3.85
3.84
3.81
3.80
3.32
3.29
3.28
3.25
3.04
3.02
3.00
2.97
1.17
1.15
1.12
CO2Et
MeO2C
N
H
0.97
3.07
2.09
0.98
0.99
2.01
4.00
1.00
1.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

4f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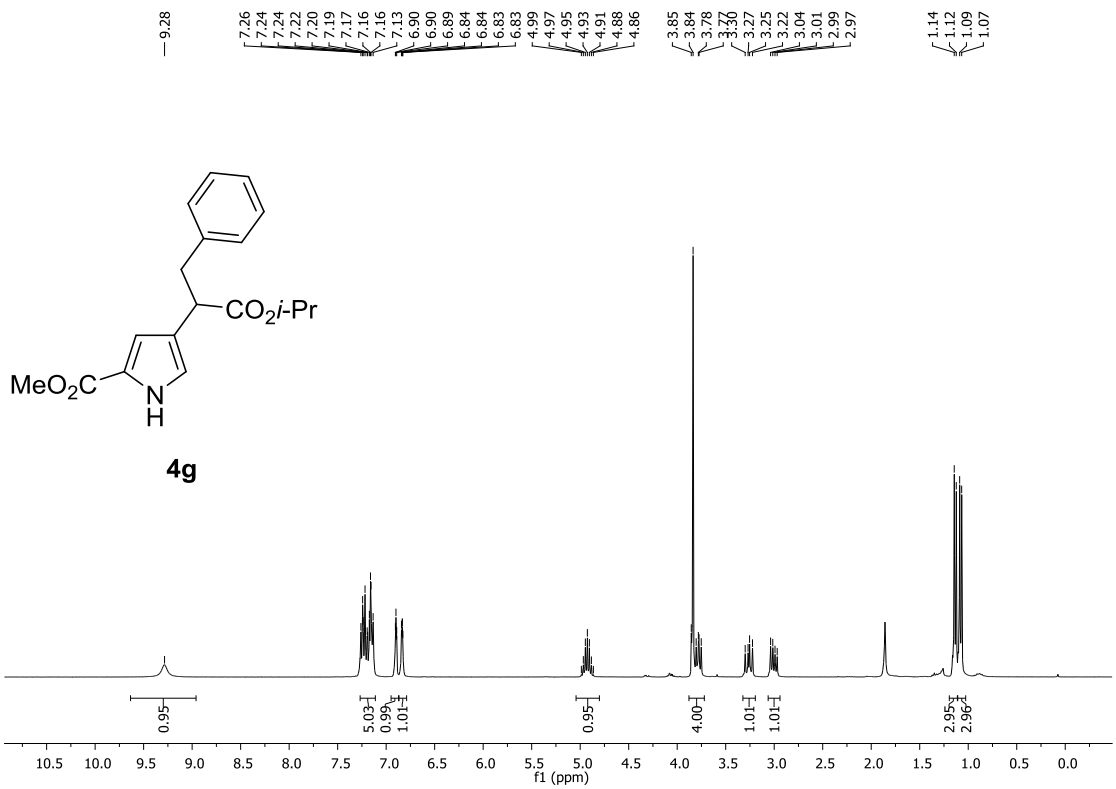
123.21
122.51
121.16
114.30
77.43
77.00
76.58
60.70
51.46
46.12
39.91
14.05
CO2Et
MeO2C
N
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4f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7.19
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7.16
7.16
7.13
6.90
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4.99
4.97
4.95
4.93
4.91
4.88
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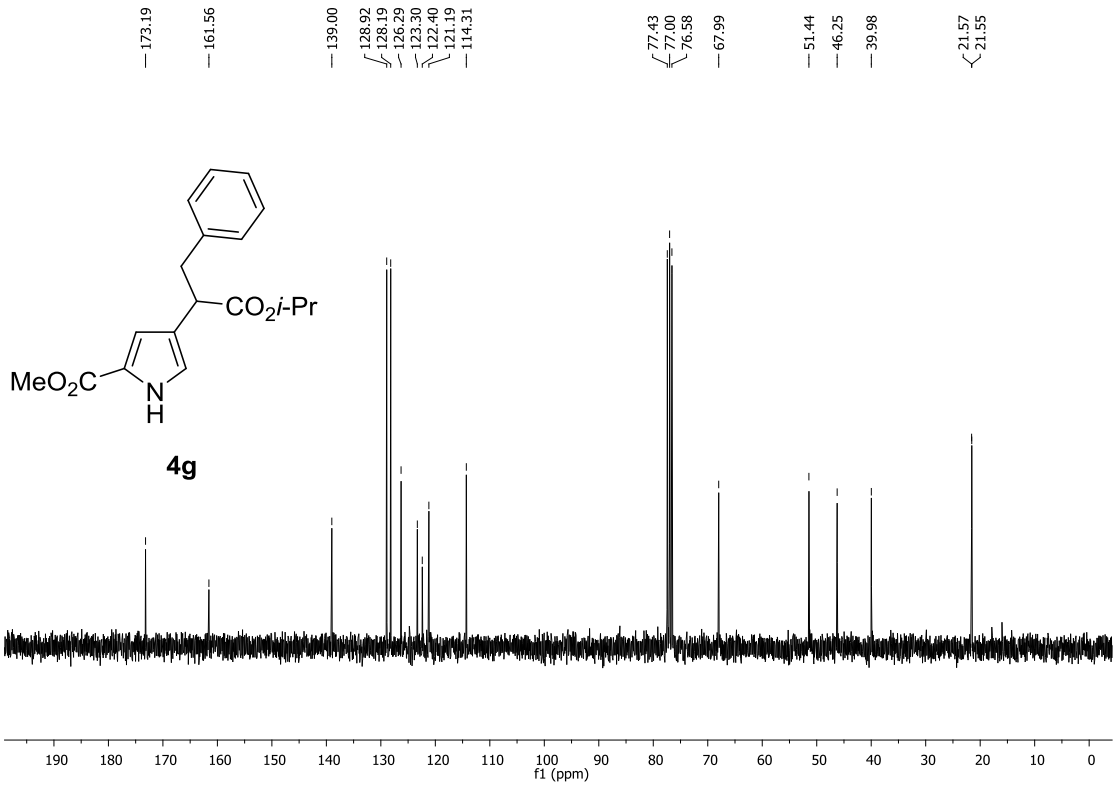
3.85
3.84
3.78
3.77
3.30
3.27
3.25
3.22
3.04
3.01
2.99
2.97
1.14
1.12
1.09
1.07
CO2i-Pr
MeO2C
N
H
4g
0.95
5.03
0.99
1.01
0.95
4.00
1.01
1.01
2.95
2.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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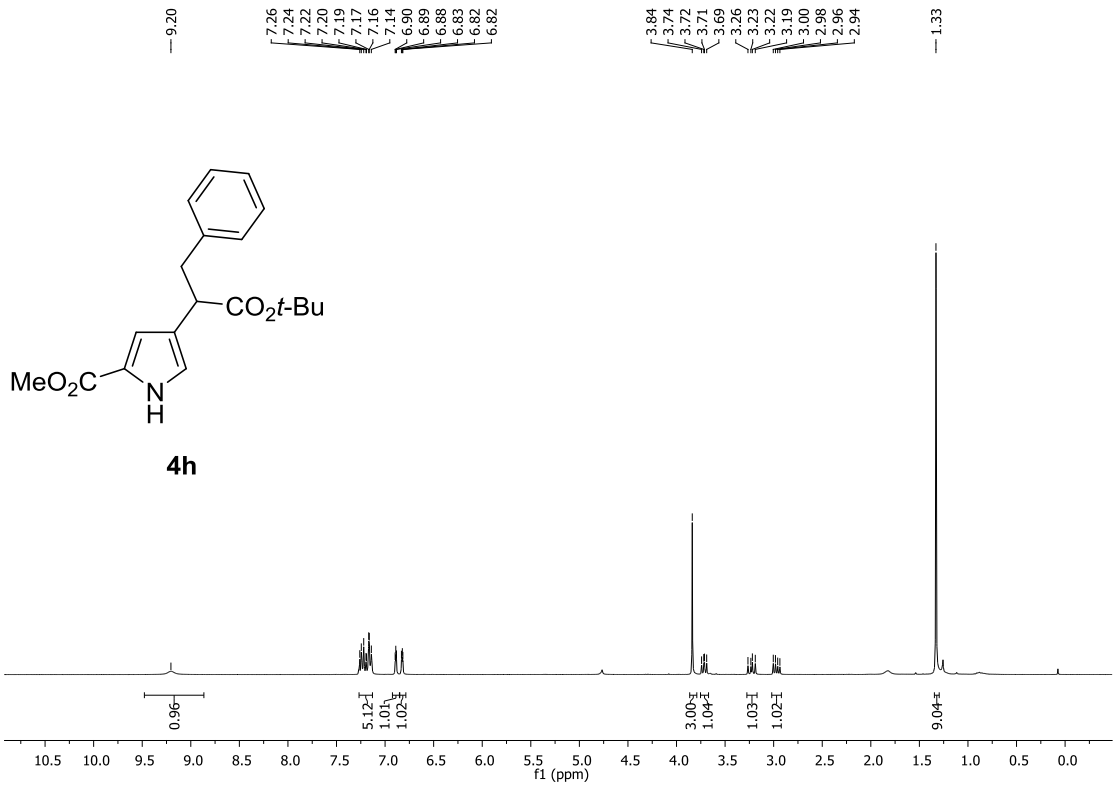
114.31
77.43
77.00
76.58
67.99
51.44
46.25
39.98
21.57
21.55
CO2i-Pr
MeO2C
N
H
4g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.19
7.17
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6.90
6.89
6.88
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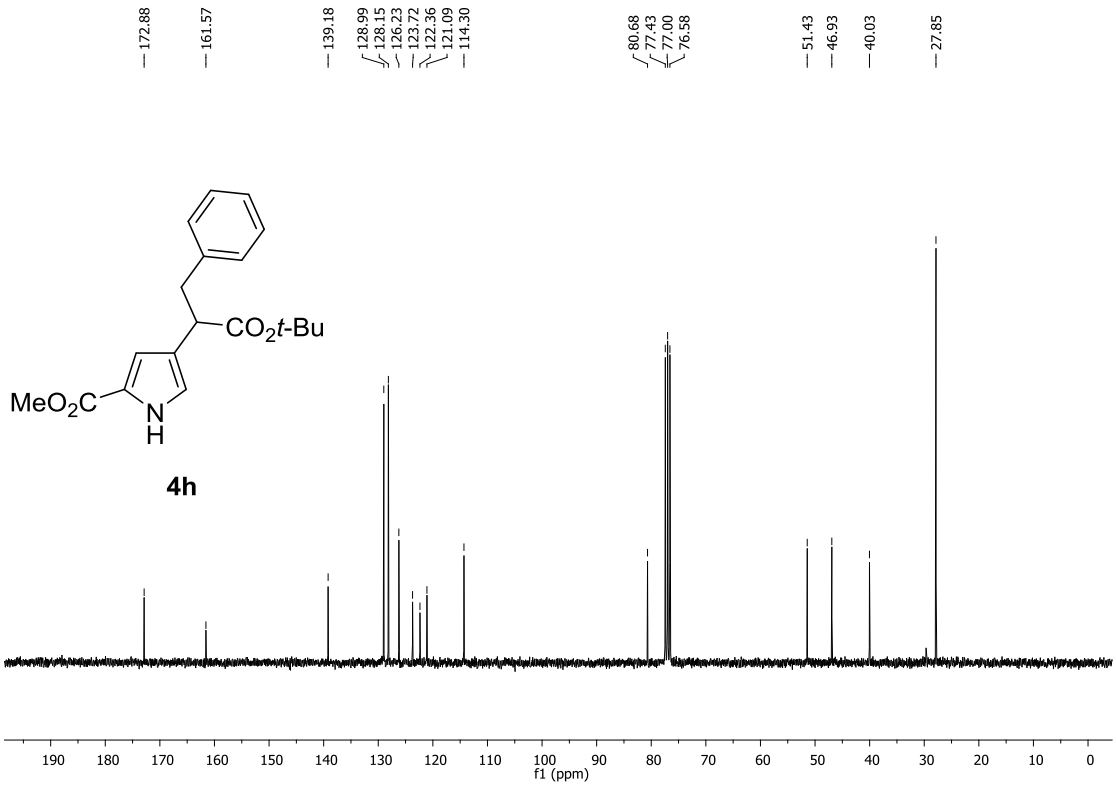
6.82
6.82
3.84
3.74
3.72
3.71
3.69
3.26
3.23
3.22
3.19
3.00
2.98
2.96
2.94
1.33
CO2t-Bu
MeO2C
N
H
4h
0.96
5.12
1.01
1.02
3.00
1.04
1.03
1.02
9.04
f1 (ppm)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77.43
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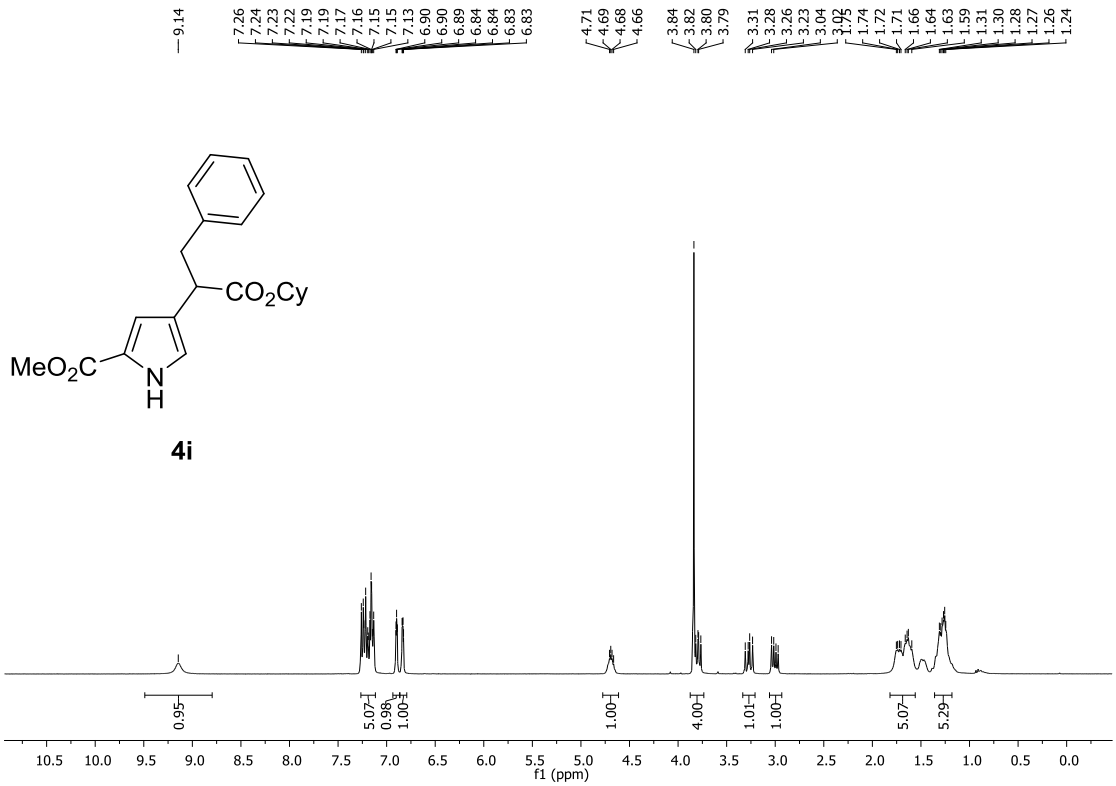
46.93
40.03
27.85
CO2t-Bu
MeO2C
N
H
4h
f1 (ppm)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7.22
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7.19
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7.15
7.15
7.13
6.90
6.90
6.89
6.84
6.84
6.83
6.83
4.71
4.69
4.68
4.66
3.84
3.82
3.80
3.79
3.31
3.28
3.26
3.23
3.04
3.02
1.75
1.74
1.72
1.71
1.66
1.64
1.63
1.59
1.31
1.30
1.28
1.27
1.26
1.24
CO2Cy
MeO2C
N
H
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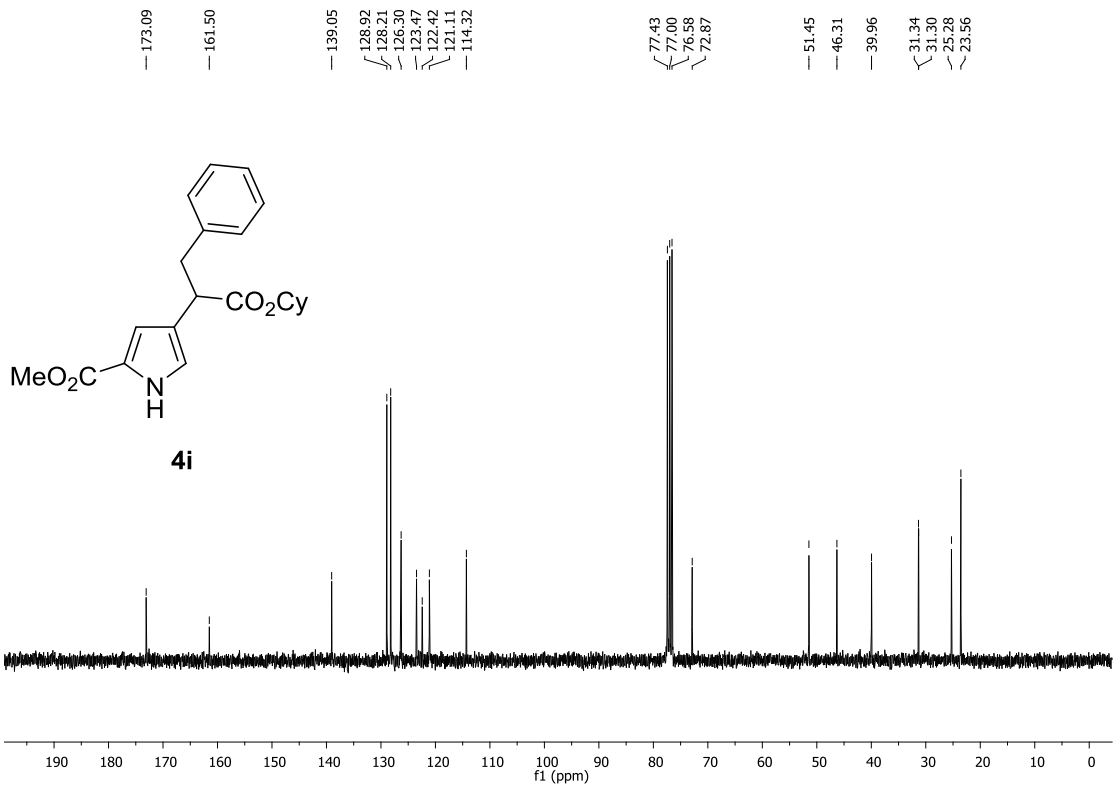
1.00
5.07
5.29
f1 (ppm)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122.42
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114.32
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77.00
76.58
72.87
51.45
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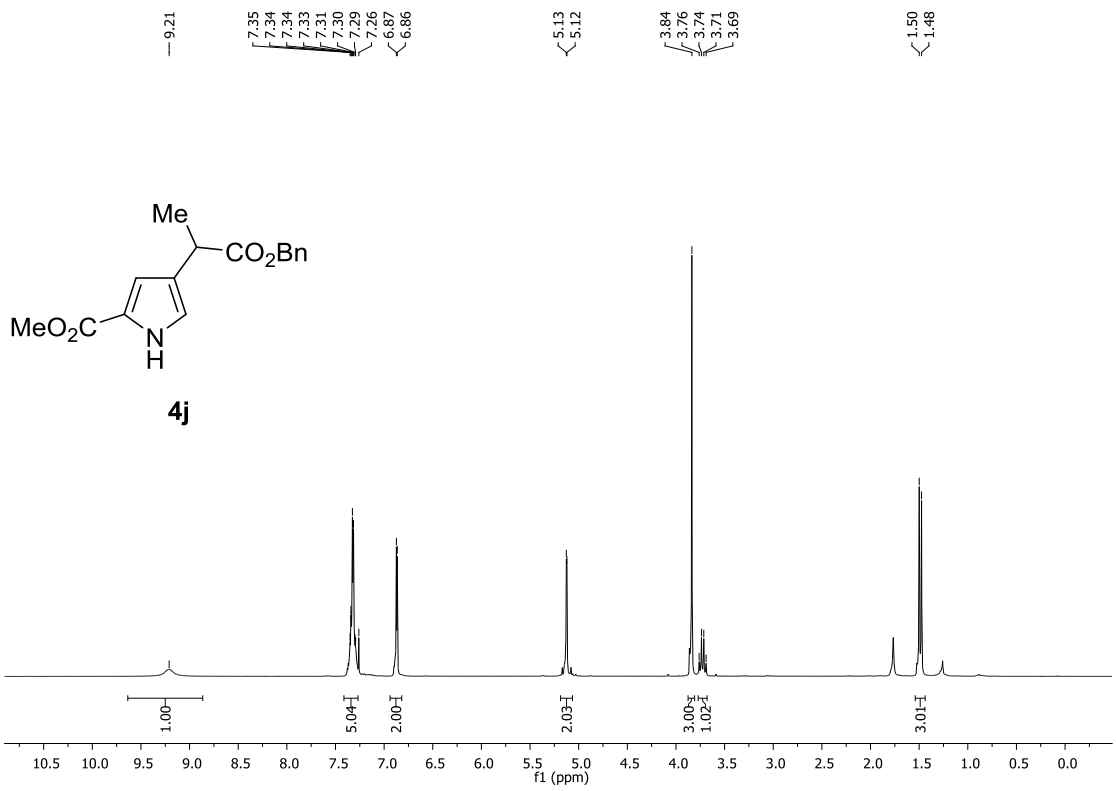
31.34
31.30
25.28
23.56
CO2Cy
MeO2C
N
H
4i
f1 (ppm)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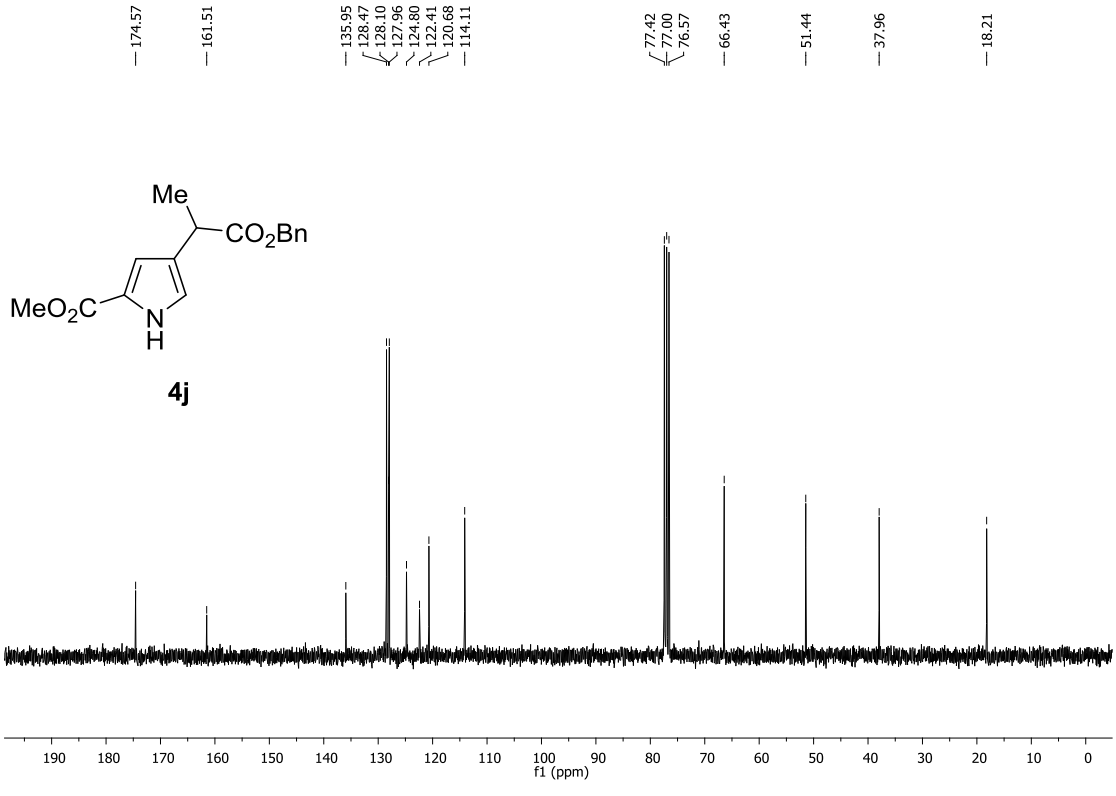
6.86
5.13
5.12
3.84
3.76
3.74
3.71
3.69
1.50
1.48
Me
CO2Bn
MeO2C
N
H
4j
1.00
5.04
2.00
2.03
3.00
1.02
3.01
f1 (ppm)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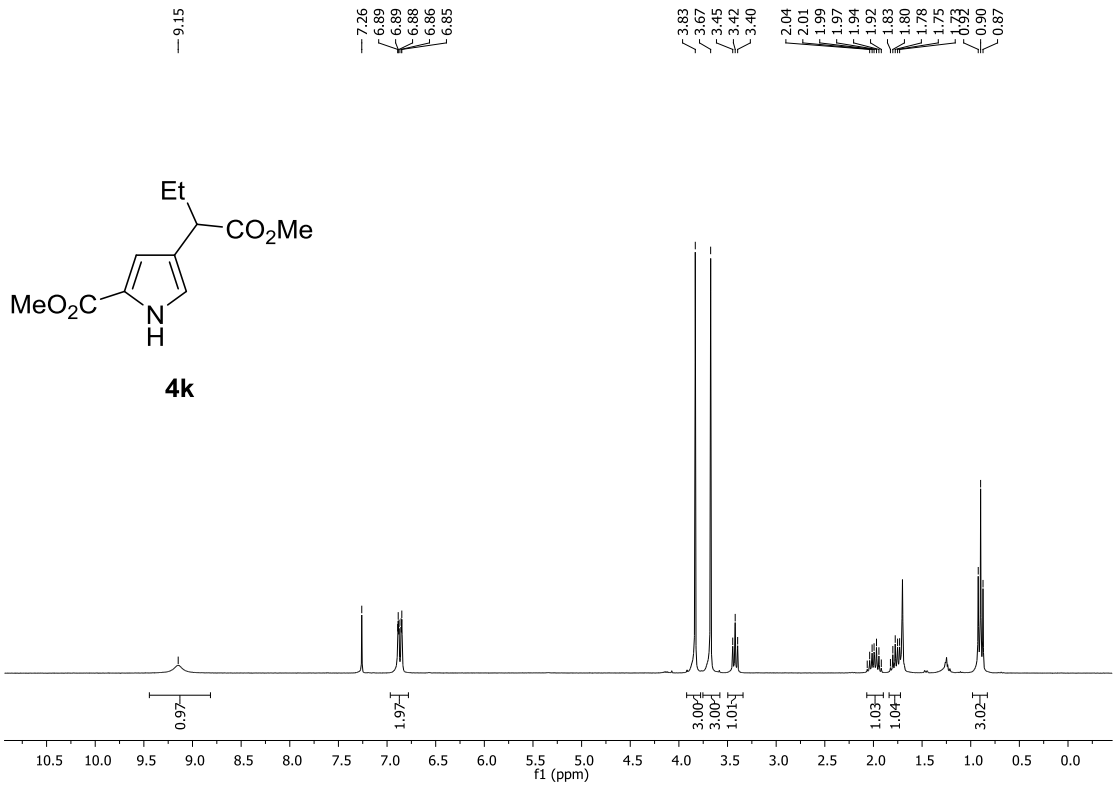
37.96
18.21
Me
CO2Bn
MeO2C
N
H
4j
f1 (ppm)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3.83
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3.45
3.42
3.40
2.04
2.01
1.99
1.97
1.94
1.92
1.83
1.80
1.78
1.75
0.90
0.87
Et
CO2Me
MeO2C
N
H
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3.00
3.00
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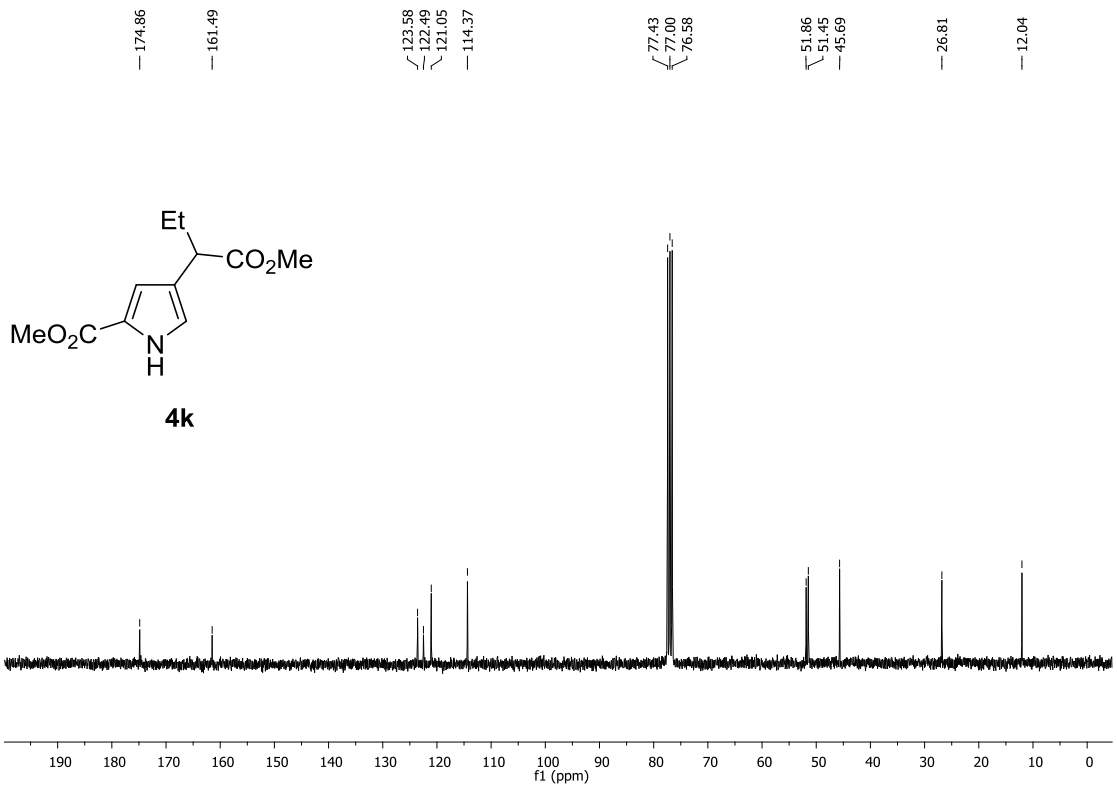
1.03
1.04
3.02
f1 (ppm)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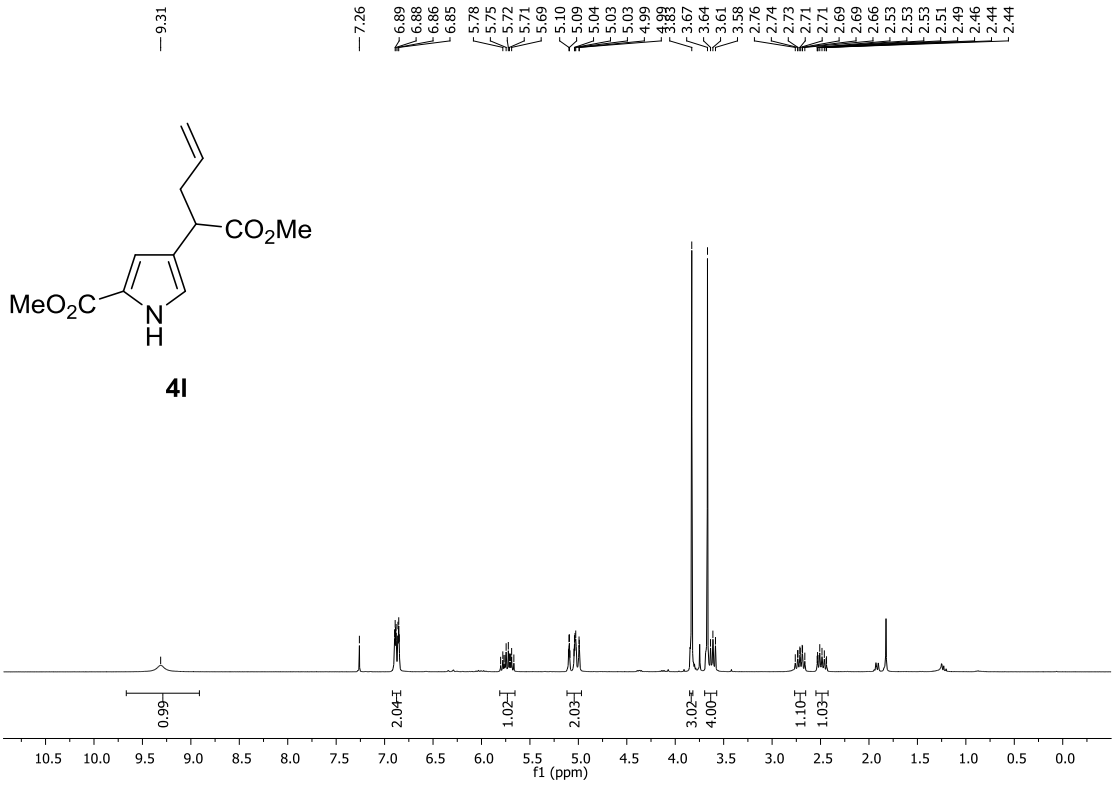
CO2Me
MeO2C
N
H
4k
f1 (ppm)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5.10
5.09
5.04
5.03
5.03
4.99
3.67
3.64
3.61
3.58
2.76
2.74
2.73
2.71
2.71
2.69
2.69
2.66
2.53
2.53
2.53
2.51
2.49
2.46
2.44
2.44
CO2Me
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H
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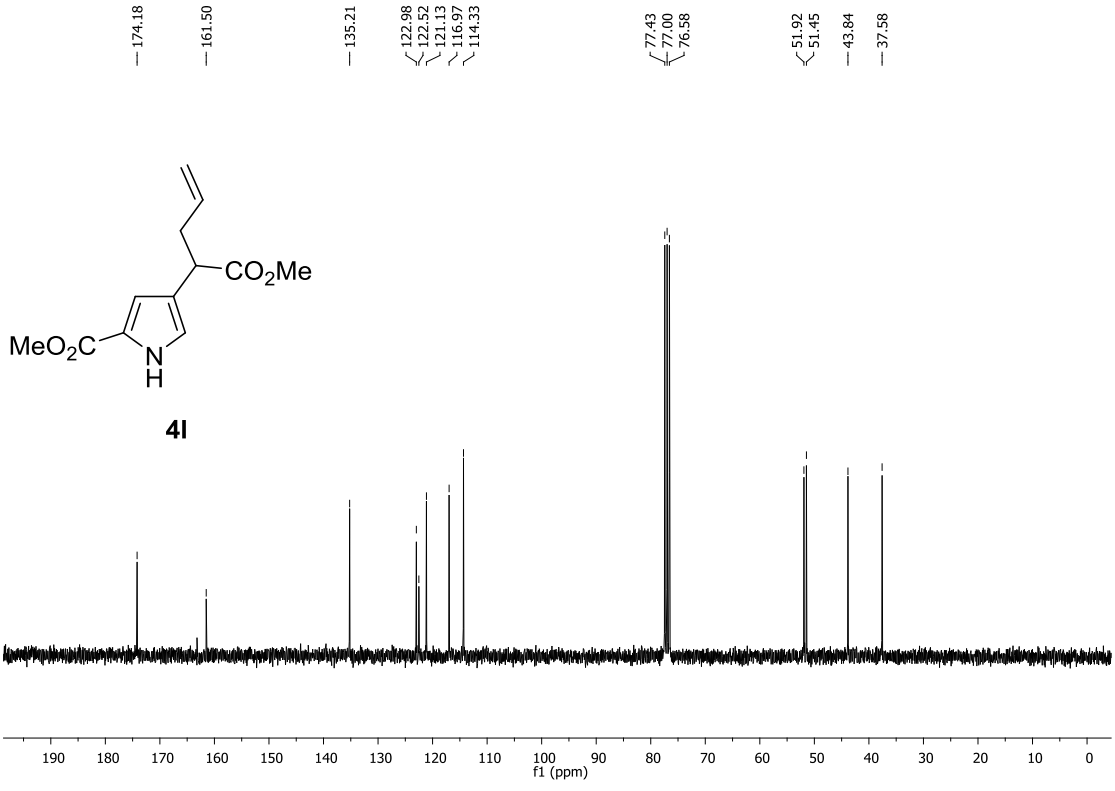
1.02
2.03
3.02
4.00
1.10
1.03
f1 (ppm)

4l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114.33
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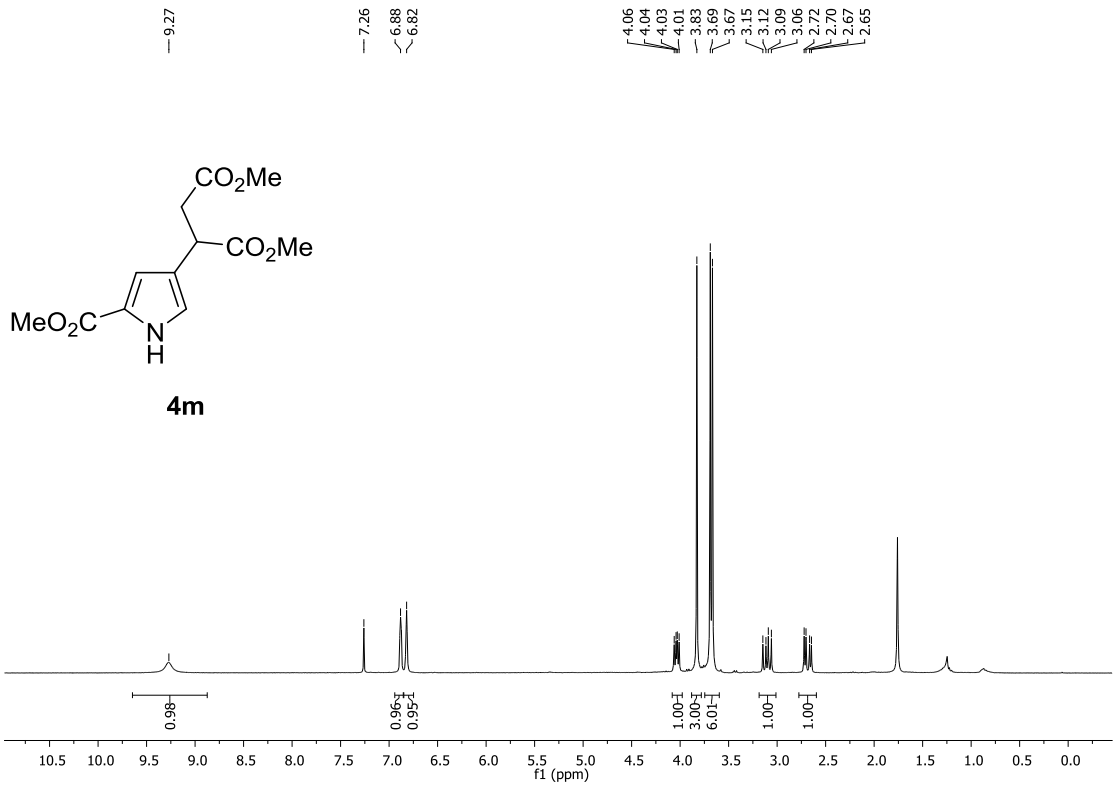
43.84
37.58
CO2Me
MeO2C
N
H
f1 (ppm)

4l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4.04
4.03
4.01
3.83
3.69
3.67
3.15
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3.09
3.06
2.72
2.70
2.67
2.65
CO2Me
CO2Me
MeO2C
N
H
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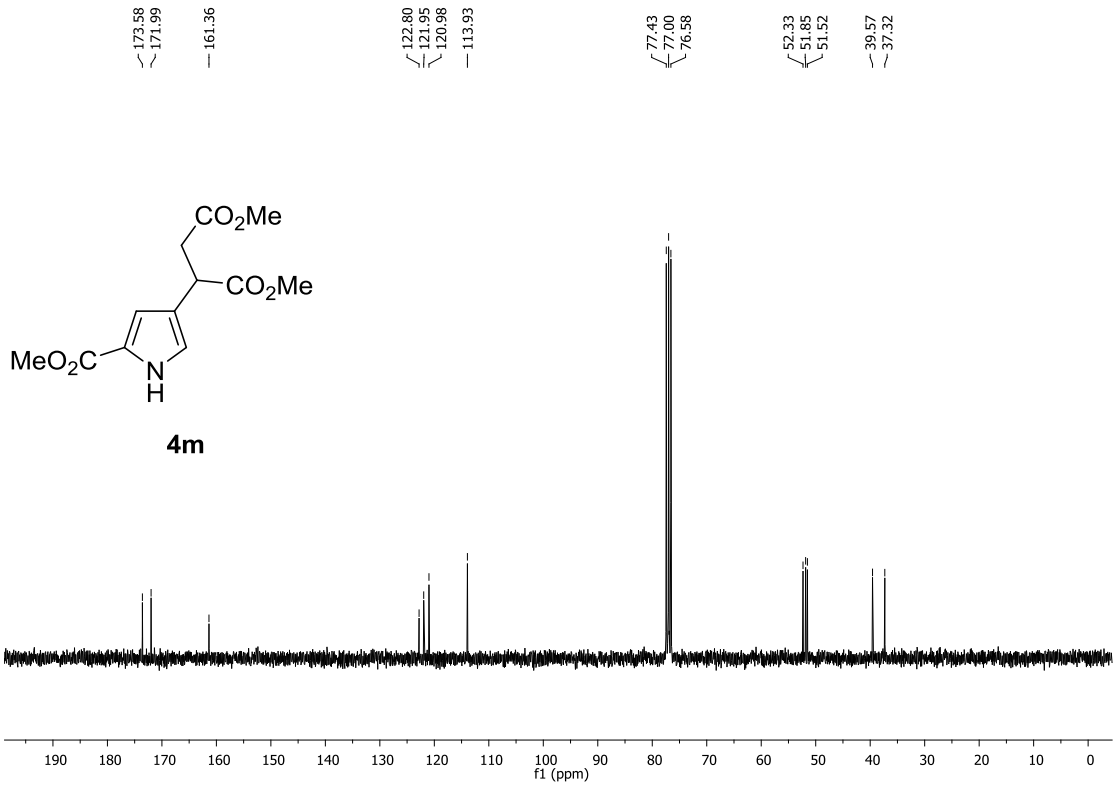
0.96
0.95
1.00
3.00
6.01
1.00
1.00
f1 (ppm)

4m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77.43
77.00
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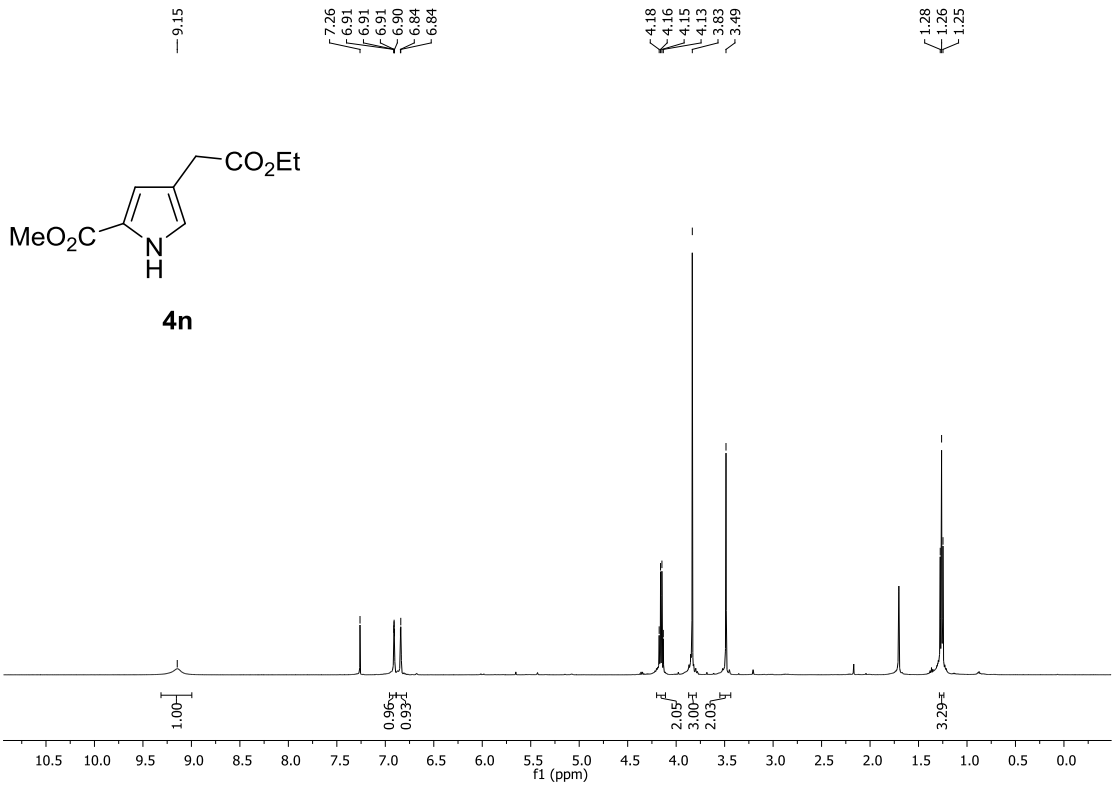
51.52
39.57
37.32
CO2Me
CO2Me
MeO2C
N
H
f1 (ppm)

4m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6.90
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6.84
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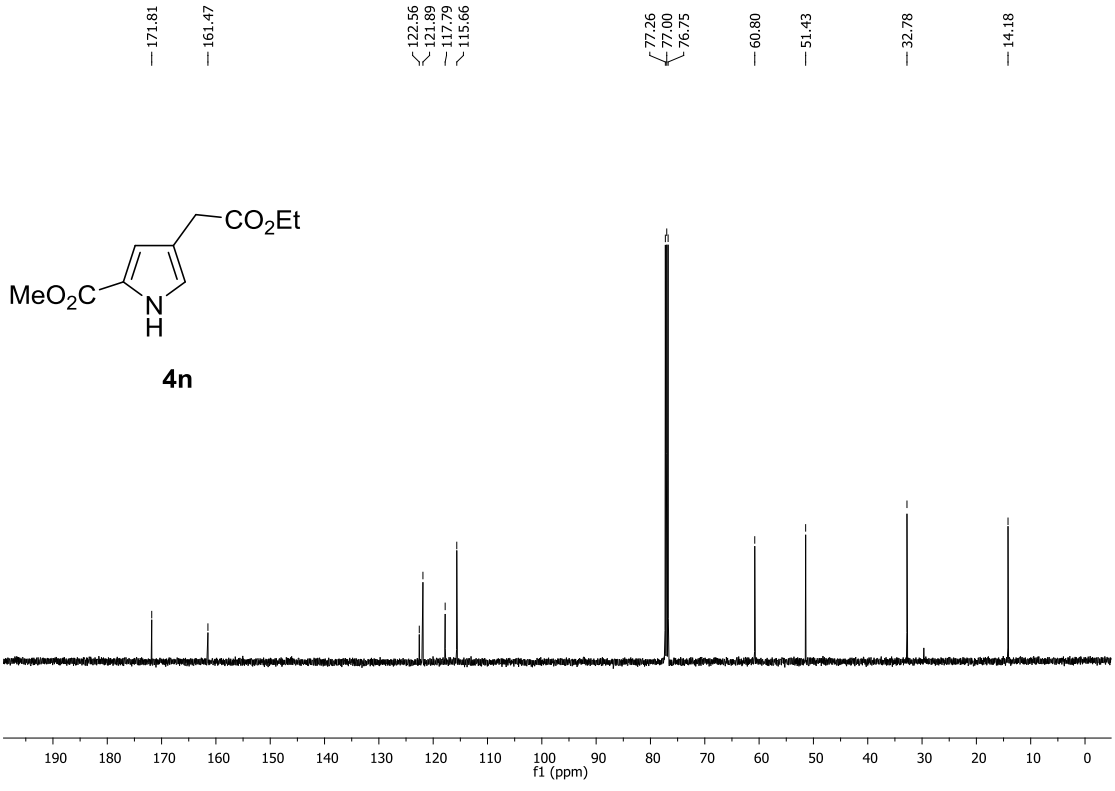
4.16
4.15
4.13
3.83
3.49
1.28
1.26
1.25
CO2Et
MeO2C
N
H
4n
1.00
0.96
0.93
2.05
3.00
2.03
3.29
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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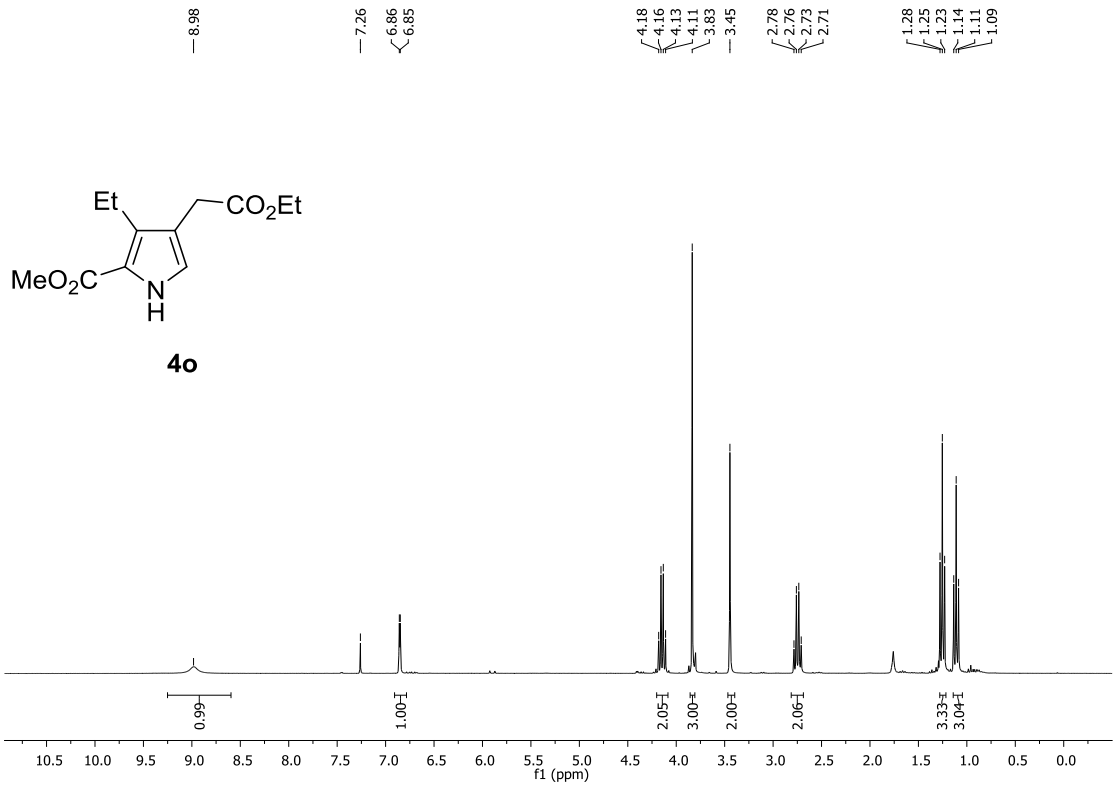
MeO2C
N
H
4n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3.45
2.78
2.76
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2.71
1.28
1.25
1.23
1.14
1.11
1.09
Et
CO2Et
MeO2C
N
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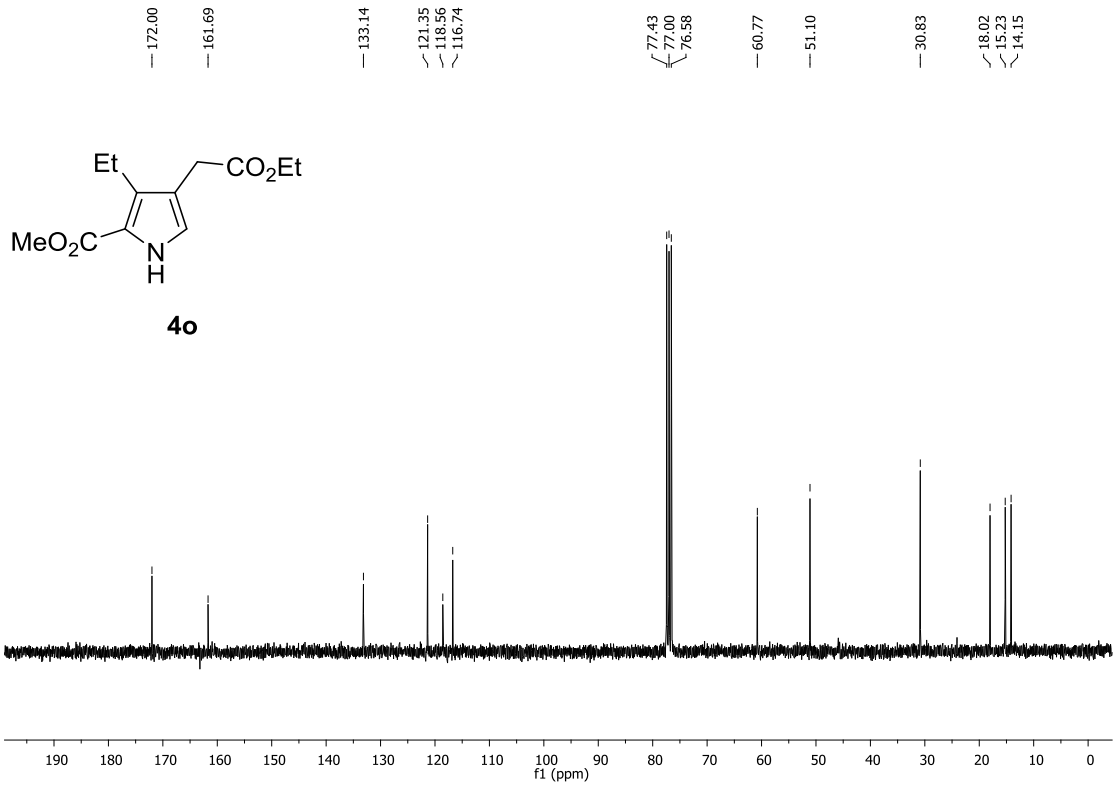
1.00
2.05
3.00
2.00
2.06
3.33
3.04
f1 (ppm)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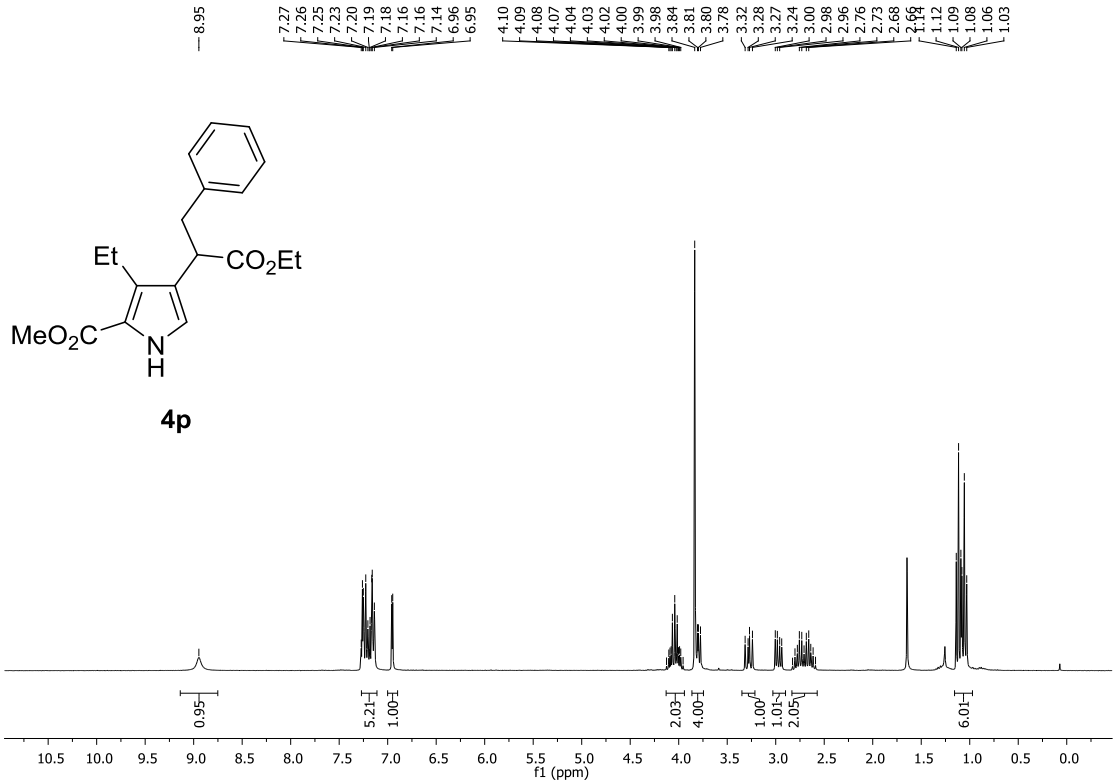
Et
CO2Et
MeO2C
N
H
4o
f1 (ppm)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4.07
4.04
4.03
4.02
4.00
3.99
3.98
3.84
3.81
3.80
3.78
3.32
3.28
3.27
3.24
3.00
2.98
2.96
2.76
2.73
2.68
2.66
1.14
1.12
1.09
1.08
1.06
1.03
Et
CO2Et
MeO2C
N
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2.03
4.00
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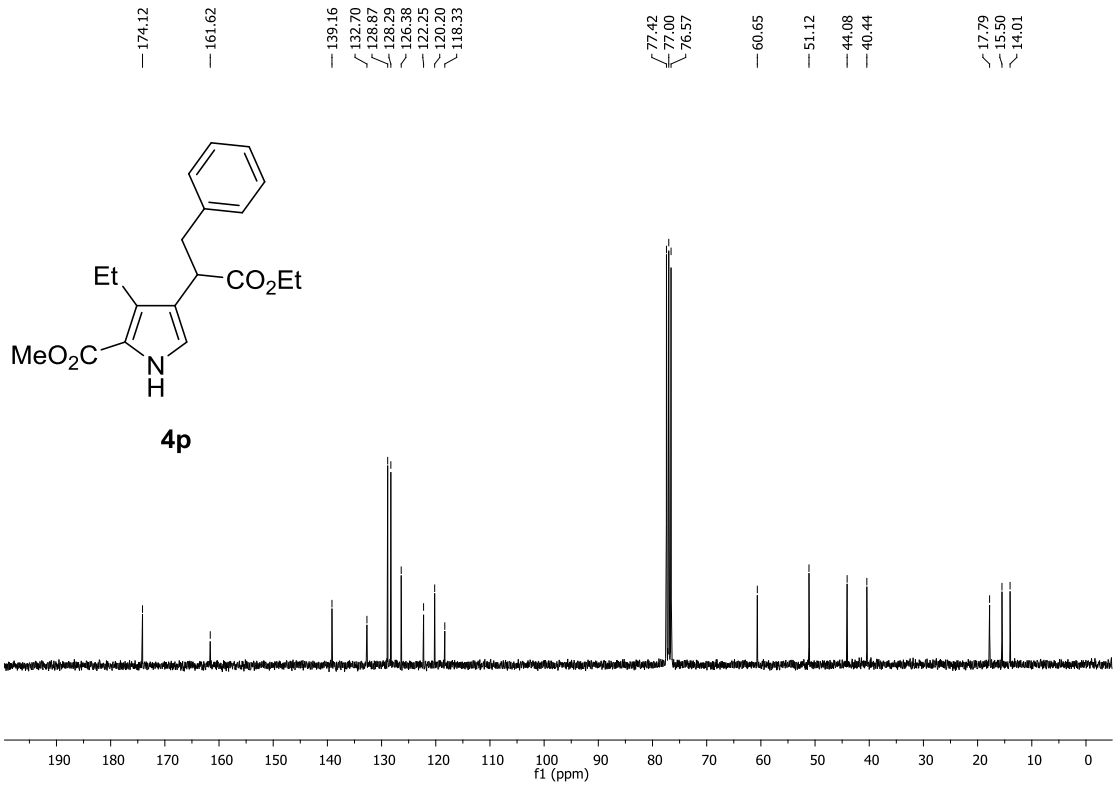
6.01
f1 (ppm)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76.57
60.65
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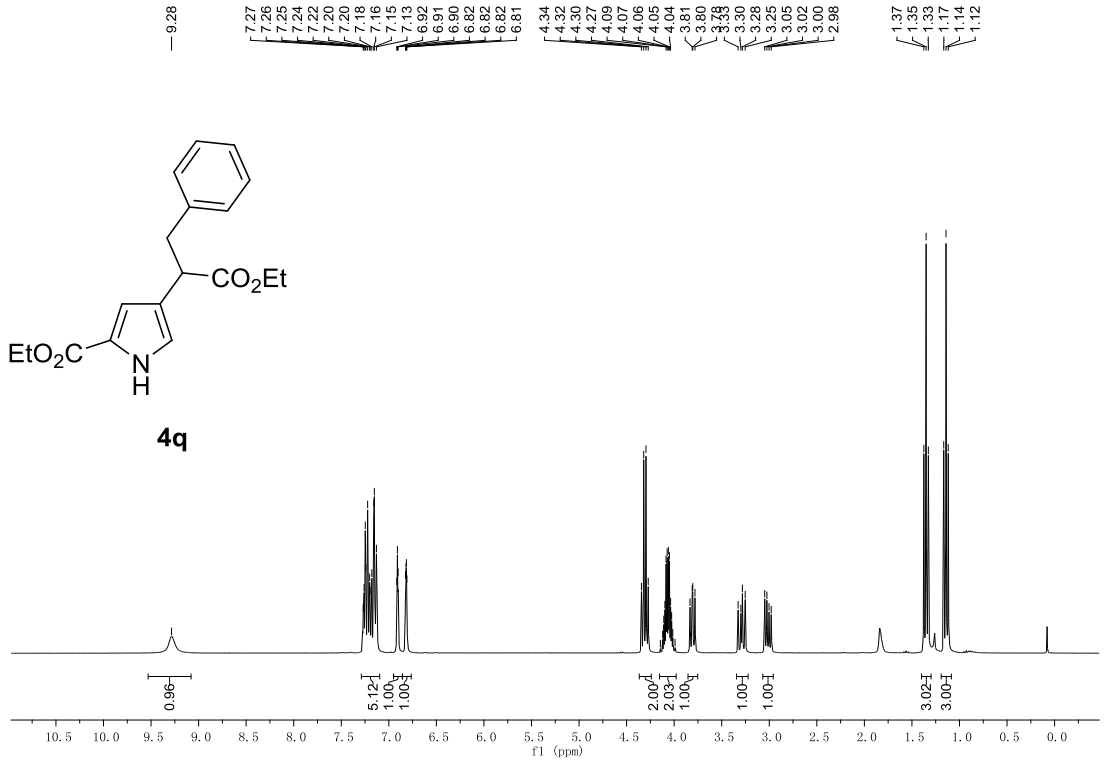
CO2Et
MeO2C
N
H
4p
f1 (ppm)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6.91
6.90
6.82
6.82
6.82
6.81
4.34
4.32
4.30
4.27
4.09
4.07
4.06
4.05
4.04
3.81
3.80
3.30
3.28
3.25
3.05
3.02
3.00
2.98
1.37
1.35
1.33
1.17
1.14
1.12
CO2Et
EtO2C
N
H
4q
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3.00
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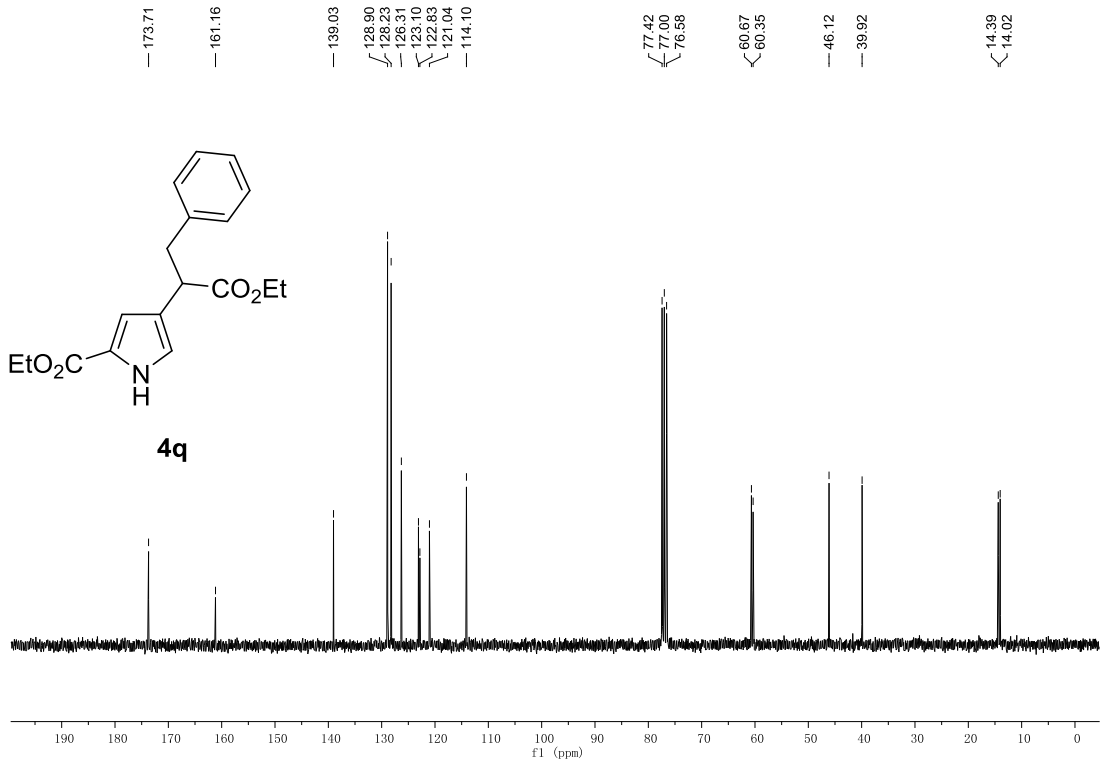
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14.39
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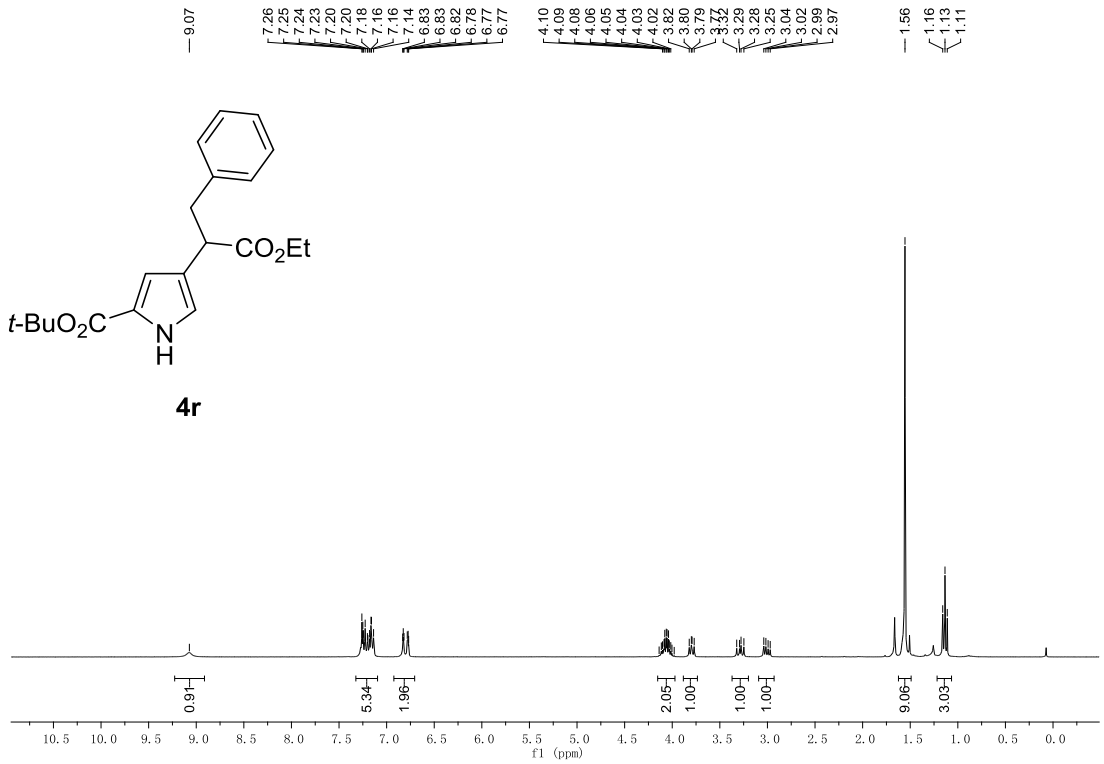
EtO2C
N
H
4q
f1 (ppm)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4.09
4.08
4.06
4.05
4.04
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4.02
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3.32
3.29
3.28
3.25
3.04
3.02
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1.56
1.16
1.13
1.11
CO2Et
t-BuO2C
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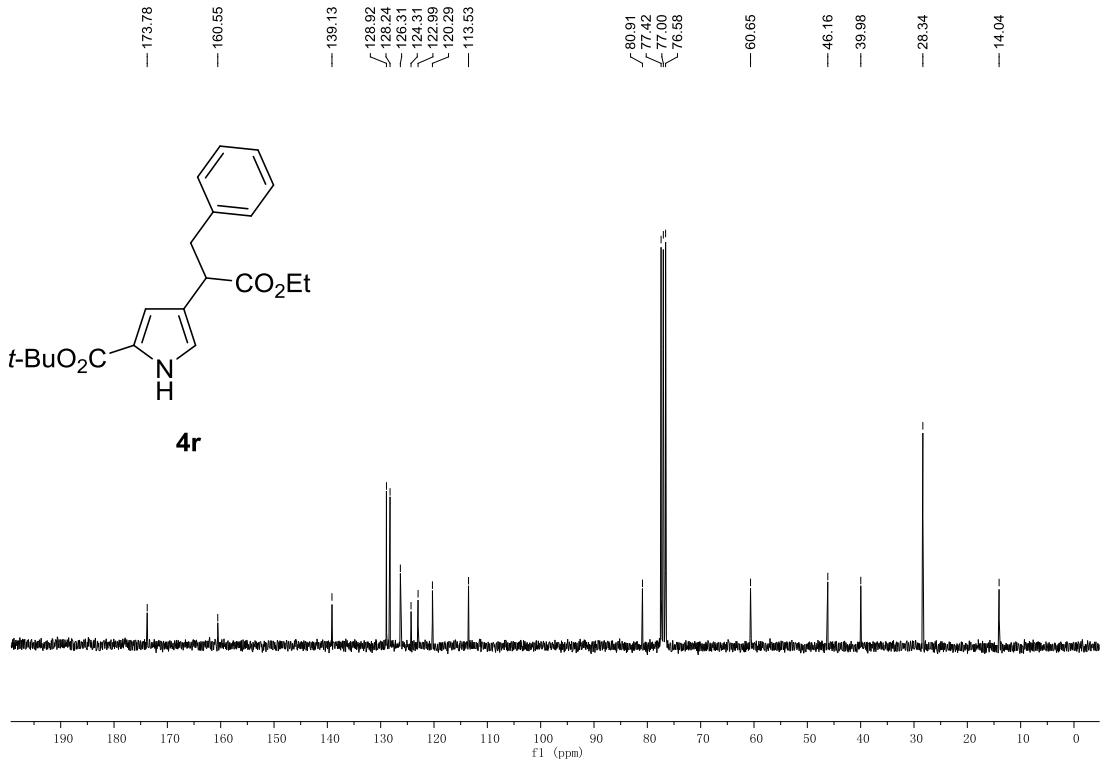
1.00
1.00
1.00
9.06
3.03
f1 (ppm)

4r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77.00
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39.98
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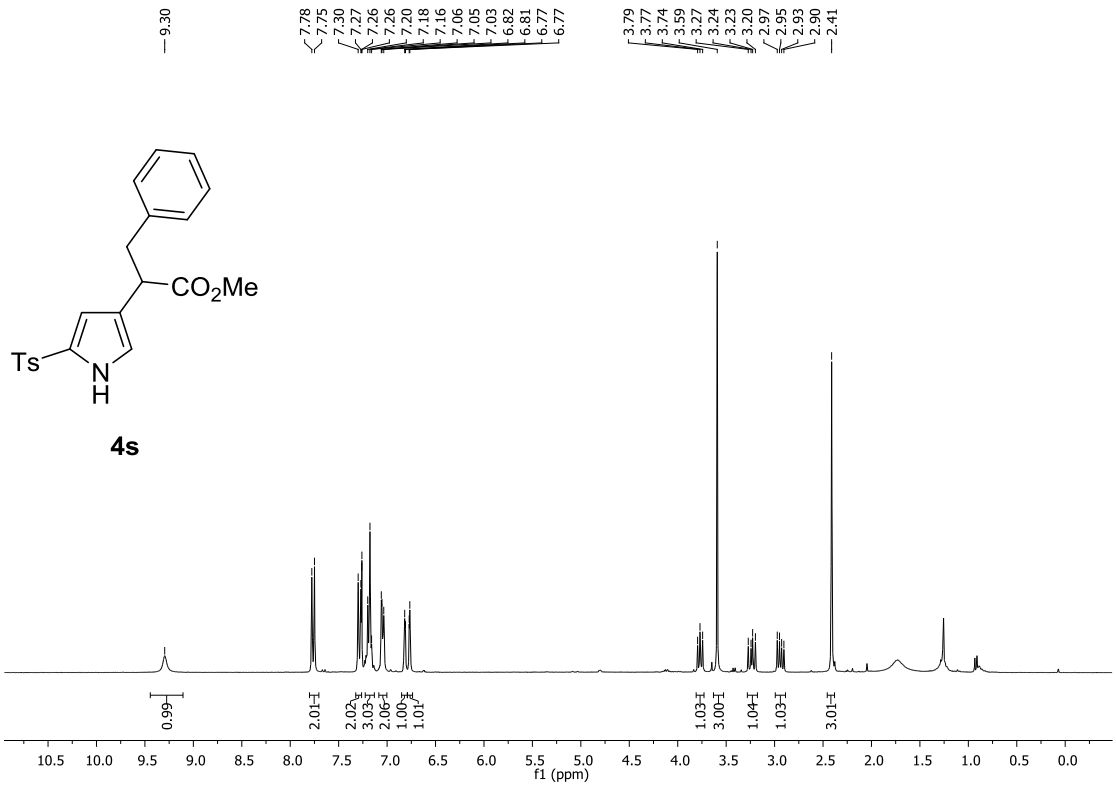
14.04
CO2Et
t-BuO2C
N
H
f1 (ppm)

4r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7.05
7.03
6.82
6.81
6.77
6.77
3.79
3.77
3.74
3.59
3.27
3.24
3.23
3.20
2.97
2.95
2.93
2.90
2.41
CO2Me
Ts
N
H
4s
0.99
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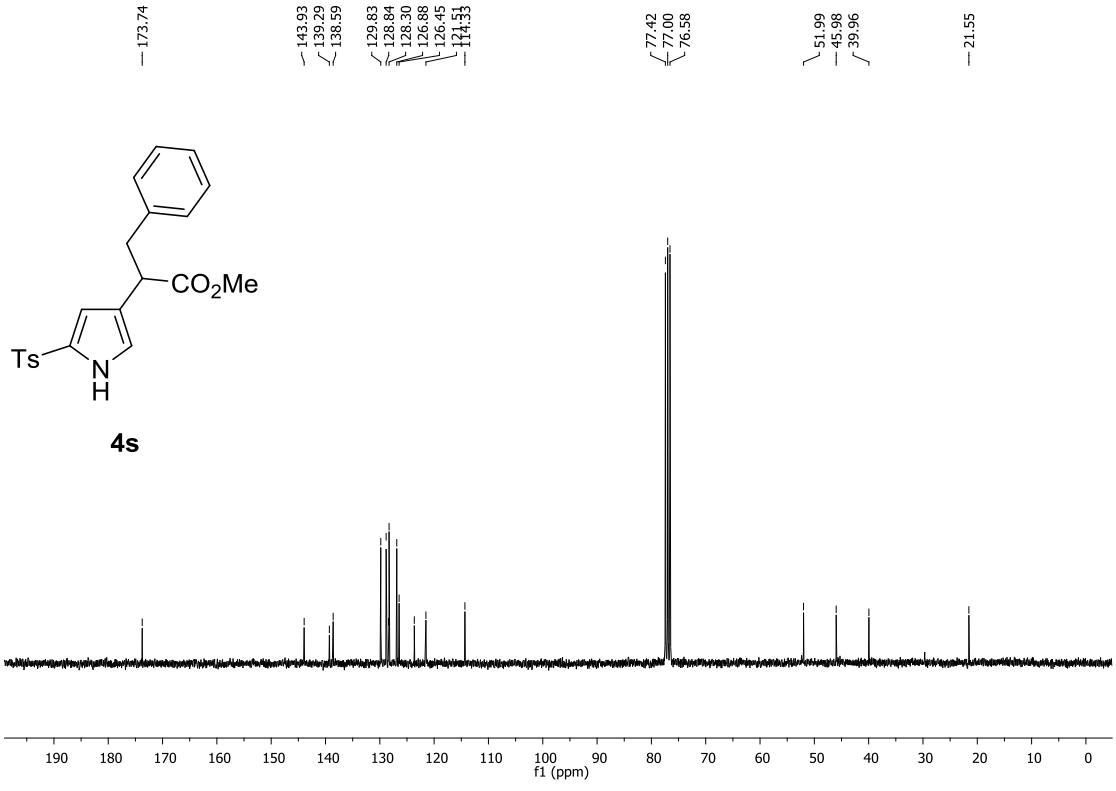
2.02
3.03
2.06
1.00
1.01
1.03
3.00
1.04
1.03
3.01
f1 (ppm)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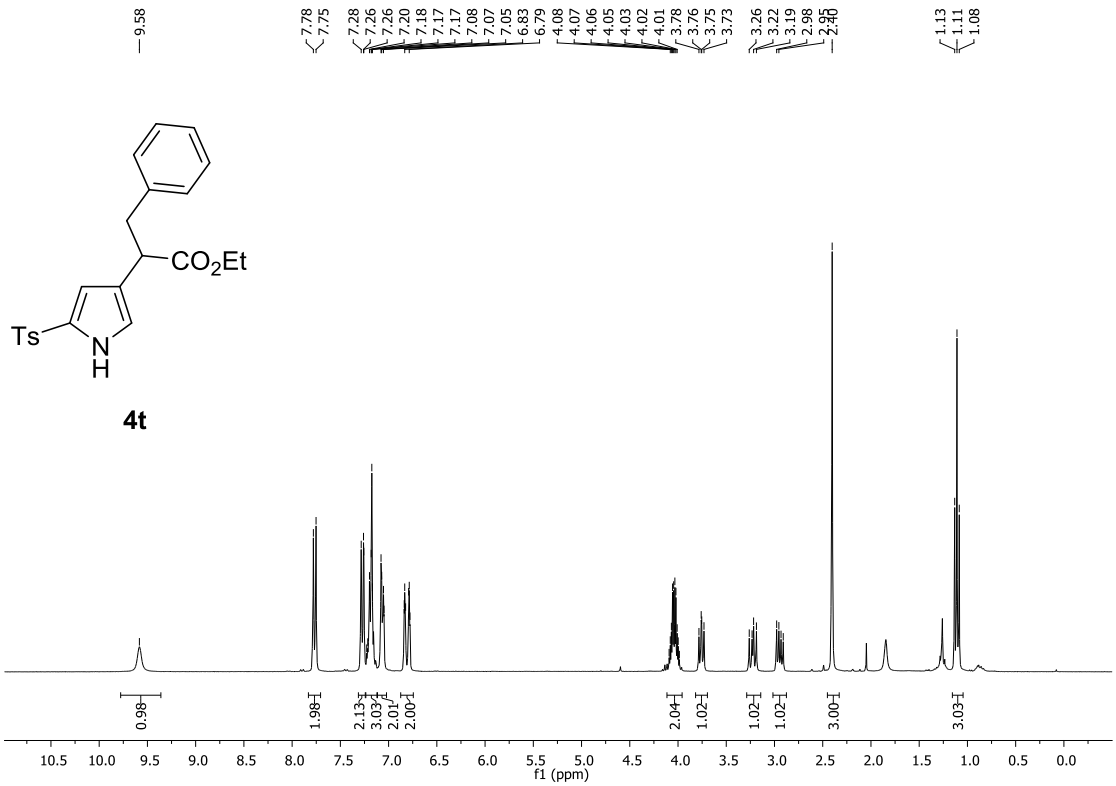
21.55
CO2Me
Ts
N
H
4s
f1 (ppm)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6.79
4.08
4.07
4.06
4.05
4.03
4.02
4.01
3.78
3.76
3.75
3.73
3.26
3.22
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2.40
1.13
1.11
1.08
CO2Et
Ts
N
H
4t
0.98
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2.01
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2.04
1.02
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1.02
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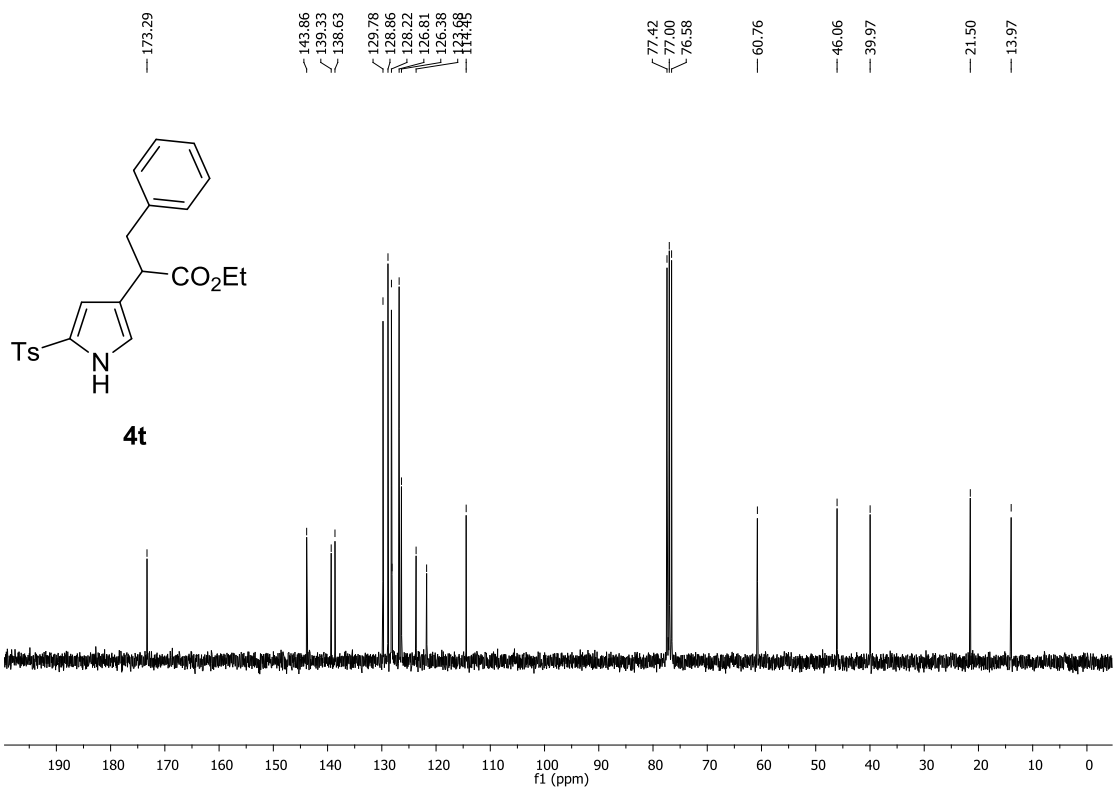
3.03
f1 (ppm)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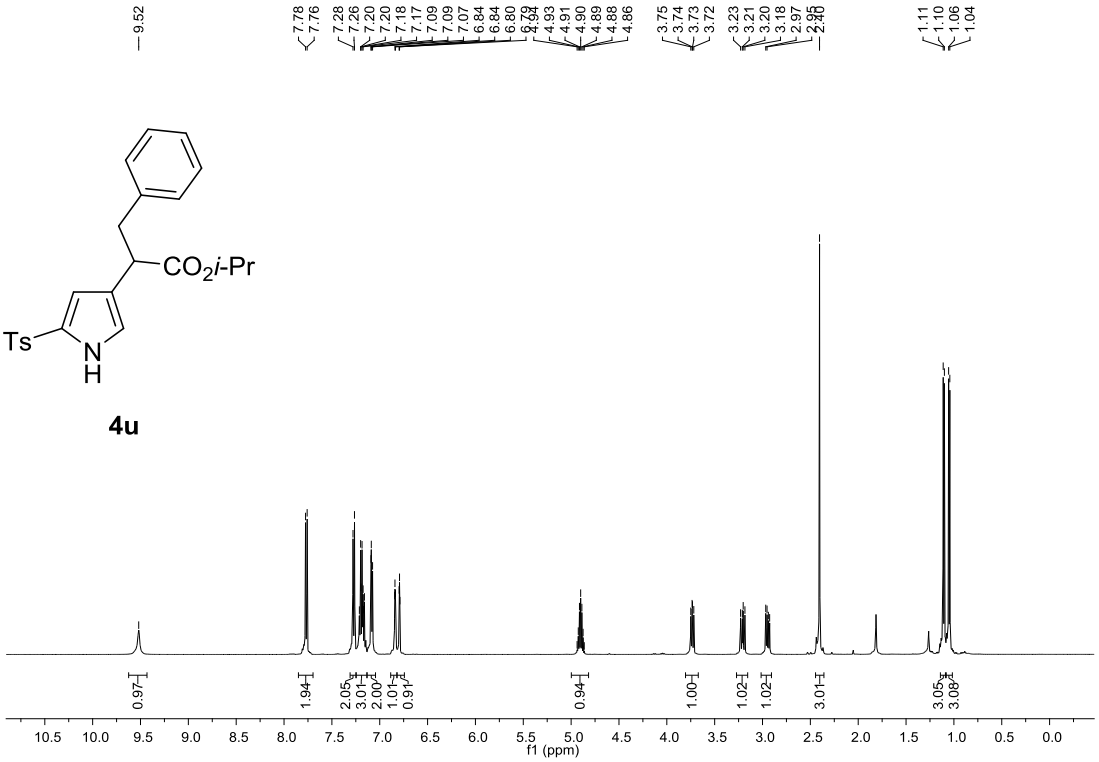
CO2Et
Ts
N
H
4t
f1 (ppm)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4.93
4.91
4.90
4.89
4.88
4.86
3.75
3.74
3.73
3.72
3.23
3.21
3.20
3.18
2.97
2.95
2.40
1.11
1.10
1.06
1.04
CO2i-Pr
Ts
N
H
4u
0.97
1.94
2.05
3.01
2.00
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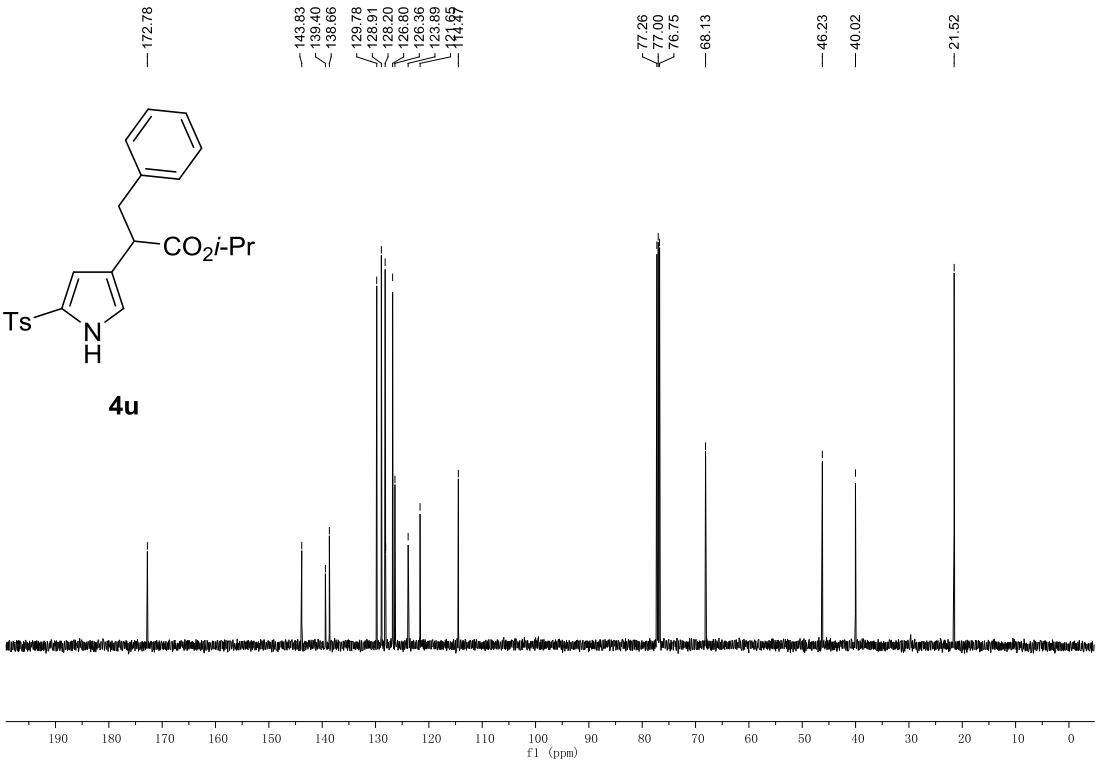
0.91
0.94
1.00
1.02
1.02
3.01
3.05
3.08
f1 (ppm)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121.65
114.47
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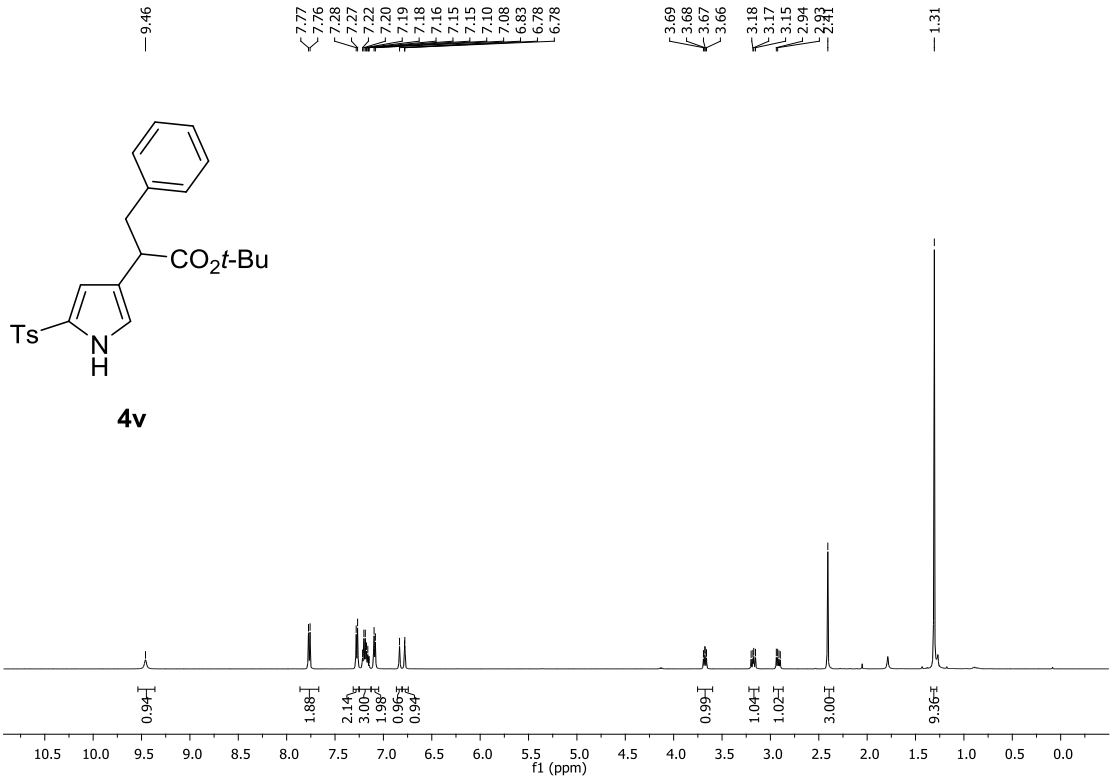
68.13
46.23
40.02
21.52
CO2i-Pr
Ts
N
H
4u
f1 (ppm)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7.10
7.08
6.83
6.78
6.78
3.69
3.68
3.67
3.66
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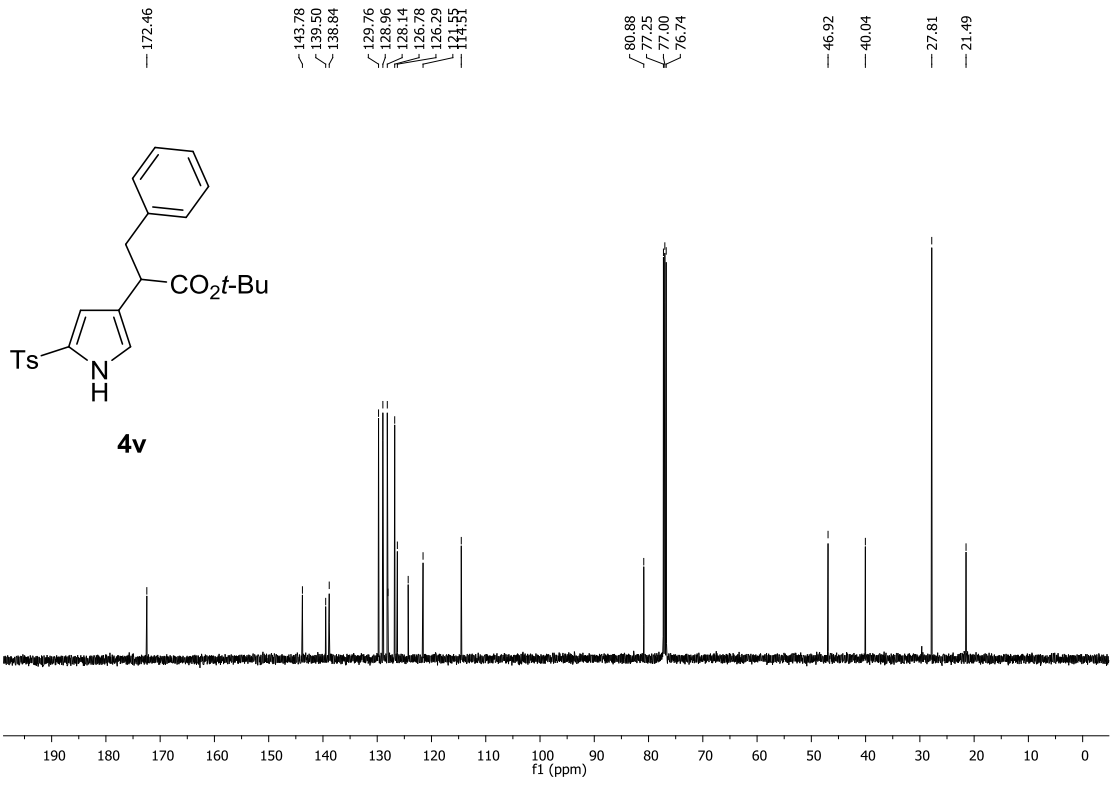
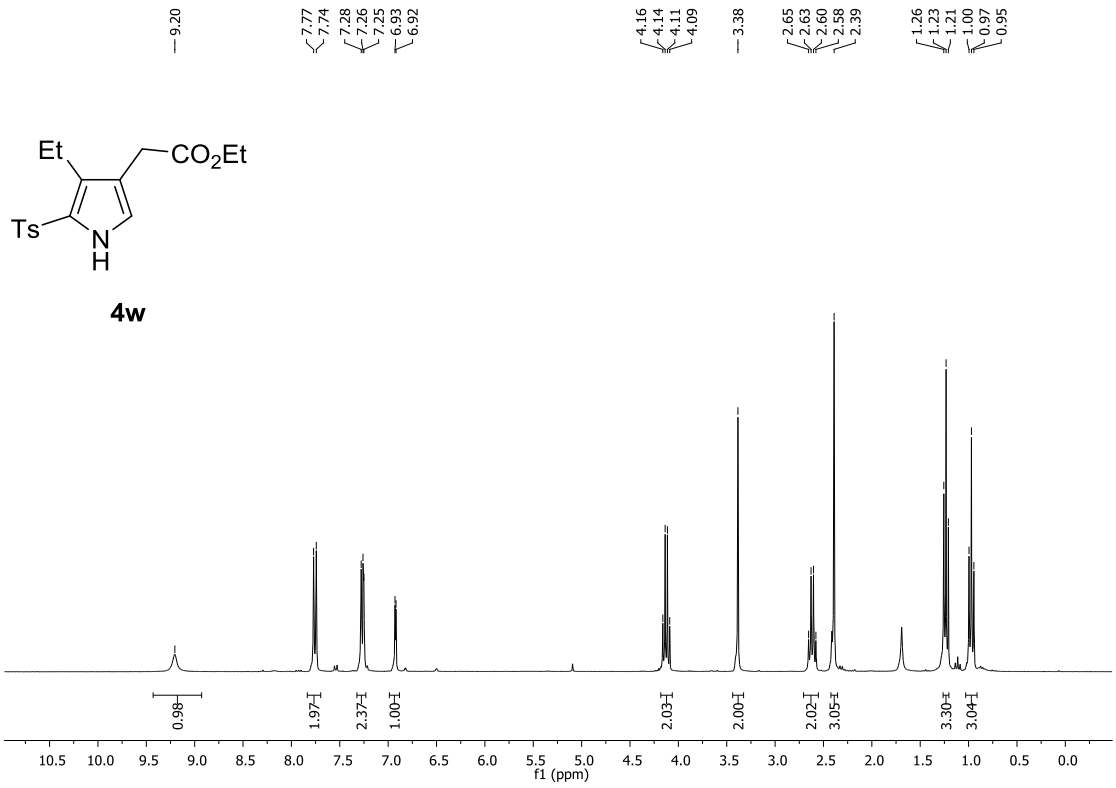
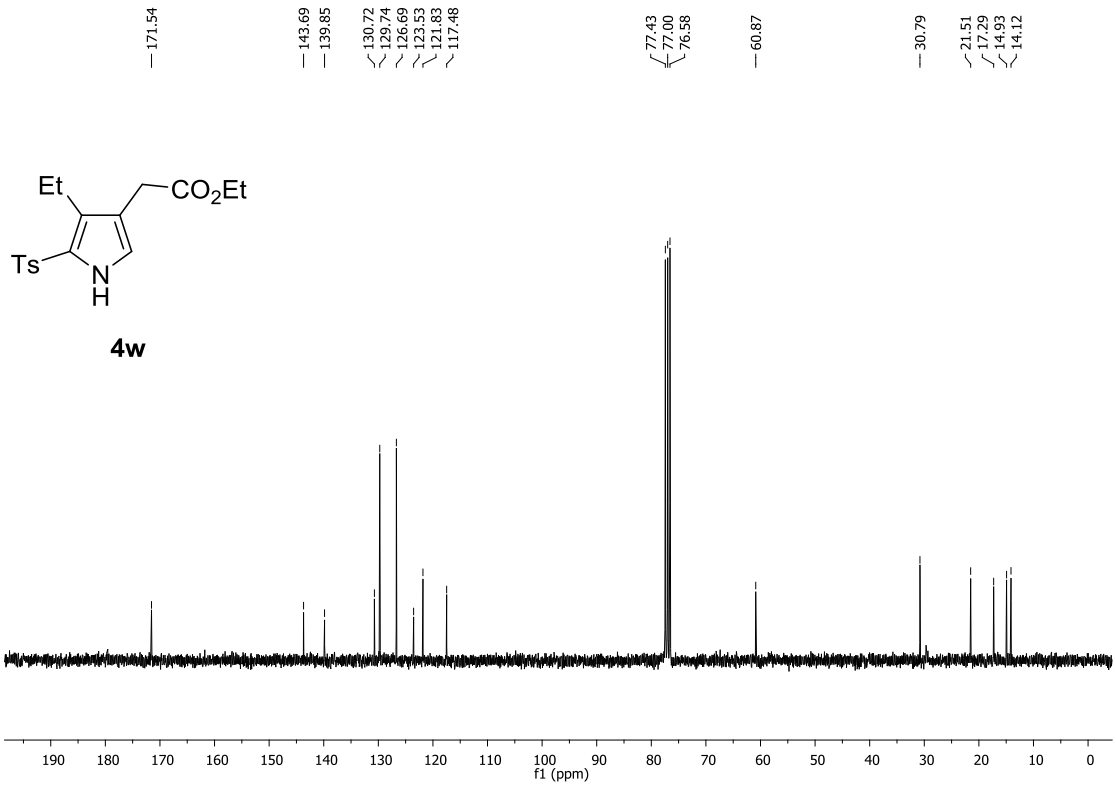
2.41
1.31
CO2t-Bu
Ts
N
H
4v
0.94
1.88
2.14
3.00
1.98
0.96
0.94
0.99
1.04
1.02
3.00
9.36
f1 (ppm)


172.46
143.78
139.50
138.84
129.76
128.96
128.14
126.78
126.29
121.55
114.51
80.88
77.25
77.00
76.74
46.92
40.04
27.81
21.49
CO2t-Bu
Ts
N
H
4v
f1 (ppm)


9.20
7.77
7.74
7.28
7.26
7.25
6.93
6.92
4.16
4.14
4.11
4.09
3.38
2.65
2.63
2.60
2.58
2.39
1.26
1.23
1.21
1.00
0.97
0.95
Et
CO2Et
Ts
N
H
4w
0.98
1.97
2.37
1.00
2.03
2.00
2.02
3.05
3.30
3.04
f1 (ppm)


171.54
143.69
139.85
130.72
129.74
126.69
123.53
121.83
117.48
77.43
77.00
76.58
60.87
30.79
21.51
17.29
14.93
14.12
Et
CO2Et
Ts
N
H
4w
f1 (ppm)