Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis of a flower-like Zr-based metal-organic framework and study of its catalytic performance in the Mannich reaction

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General Information.

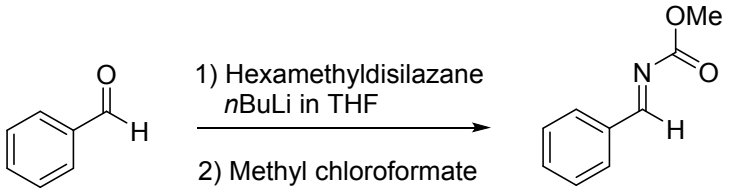
Characterization.

The phase composition of the samples was investigated by X-ray powder diffraction (XRD, M21X, Cu Kα radiation, λ=0.154178 nm). The morphology and structure of the as-obtained product were characterized by scanning electron microscopy (SEM, ZEISS SUPRA55). Thermogravimetric analysis (TG) was conducted by Netzsch STA449F at a heating rate of 10 ^{o}C/min under the N_2 flow. The specific surface areas were calculated by nitrogen sorption-desorption isotherms using a Micromeritics ASAP 2420 adsorption analyzer. The pore size distributions were derived from the adsorption branches of isotherms by using the Barrett-Joyner-Halenda (BJH) model. Fourier transform infrared spectroscopy (FTIR) was acquired on Nicolet 6700 using the KBr pellet technique. The results were analyzed by gas chromatography-mass spectrometry using an internal standard (GC-MS, Agilent7890/5975C-GC/MSD, HP5-MS column, Ar carrier gas, 200 ^{o} C). All ^{1}H NMR, and ^{13}C NMR spectra were recorded using Varian Unity Plus 400 MHz spectrometer at ambient temperature in $CDCl_3$. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant, and integration. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR ESP spectrophotometer. Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel.

Catalytic reaction conditions

For a general catalytic reaction, 0.5 mol% of the catalyst was added to 2.00 mL CH_2Cl_2, which was in an oven dried round bottom reaction vessel. 1.0 mmol of imine and 1.5 mmol of the nucleophile were added successively. The solution was stirred at 23 ºC for 3 h. The reaction mixture was passed through a silica gel plug and eluted with 5 mL of ethyl acetate. Then, the filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography over silica gel to afford the addition product. The yield was calculated based on the isolated product.

The synthesis procedure of acyl aldimine



To an oven-dried 250 mL round-bottom flask equipped with stir bar was added hexamethyldisilazane (5.54 mL, 26 mmol) under nitrogen. The flask was cooled to 0 ºC for drop-wise addition of *n*BuLi in hexanes (1.60 M, 15.60 mL, 25 mmol). The solution was stirred at room temperature for 15 minutes and cooled down to 0 ºC for slow addition of freshly distilled benaldehyde (25 mmol) in THF (10 mL) solution. Reaction was stirred for 30 minutes at room temperature then concentrated under reduced pressure for addition of CH_2Cl_2 (25 mL). Reaction mixture was cooled down to 0 ºC for slow addition of methyl chloroformate (125 mmol). Reaction was further stirred for 3 h at room temperature then concentrated under reduced pressure. The resulting acyl aldimine was distilled and stored under nitrogen before use.

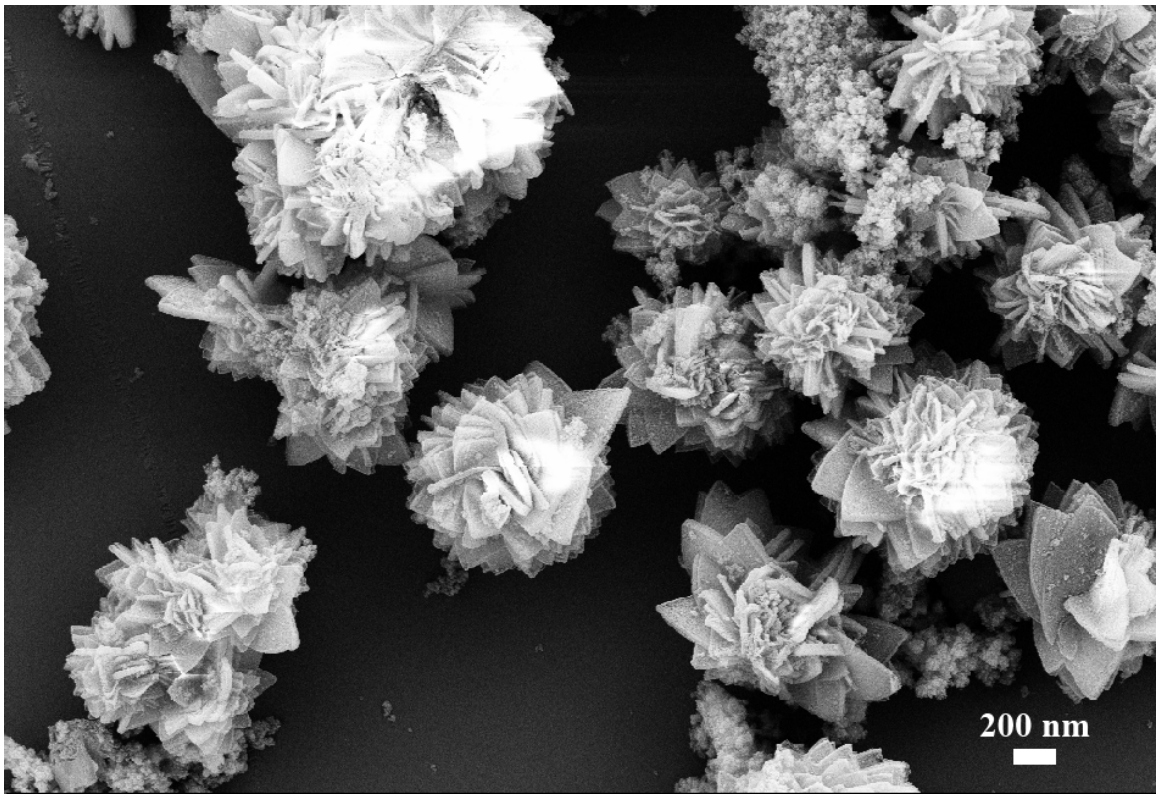


Figure S1. SEM of Recycled F-UiO-66-$(COOH)_2$

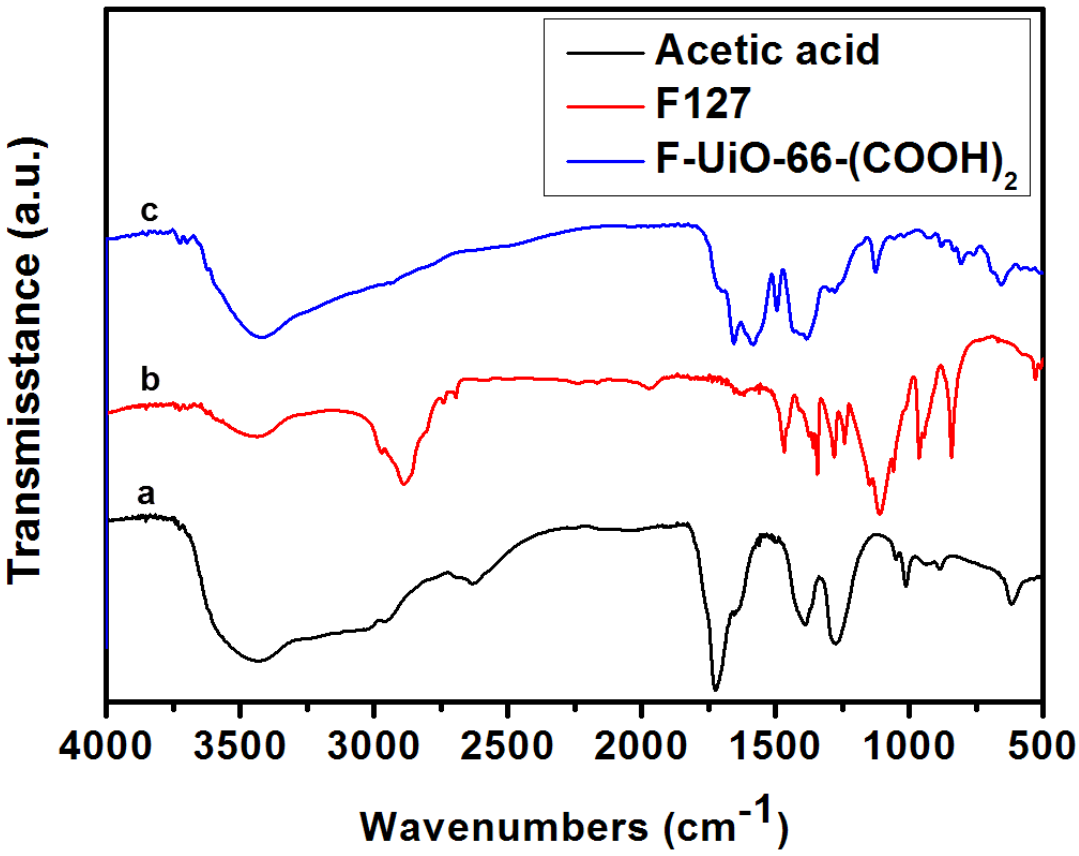


Figure S2. FTIR of (a) Acetic acid (b) F127 and (c) F-UiO-66-$(COOH)_2$

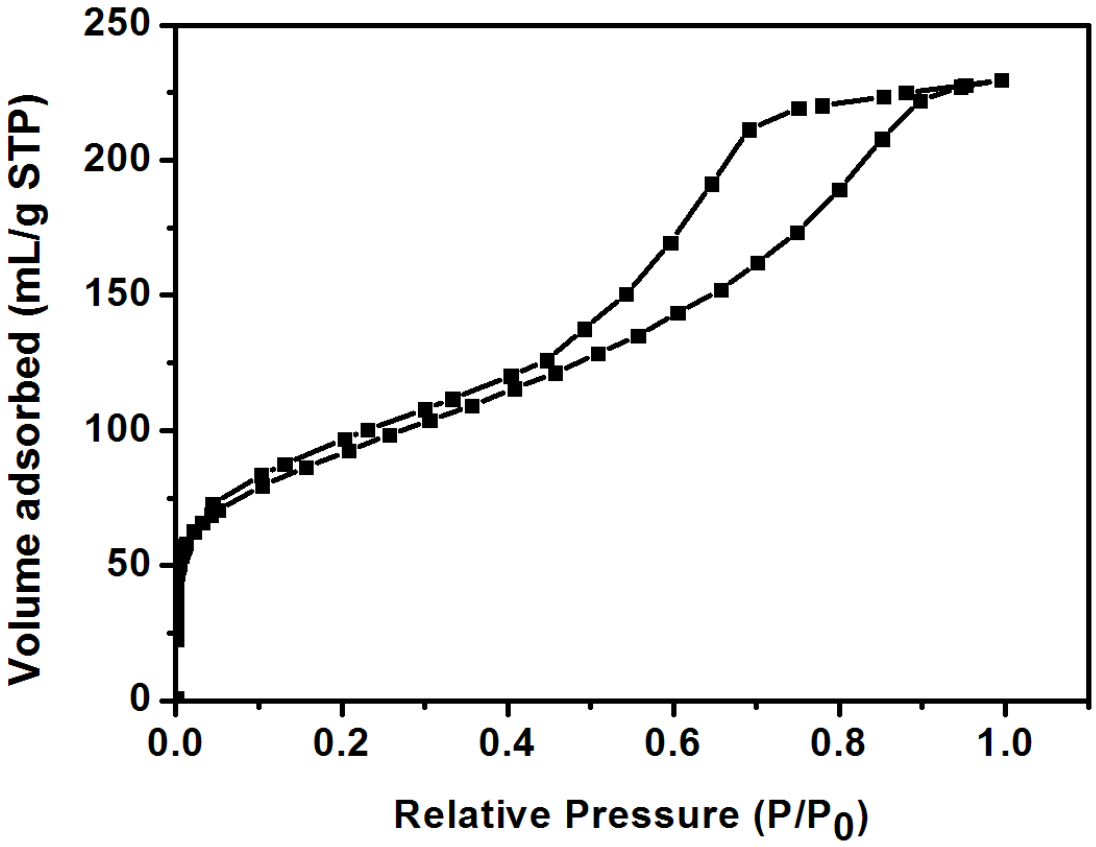


Figure S3. Nitrogen adsorption/desorption isotherms of F-UiO-66-$(COOH)_2$

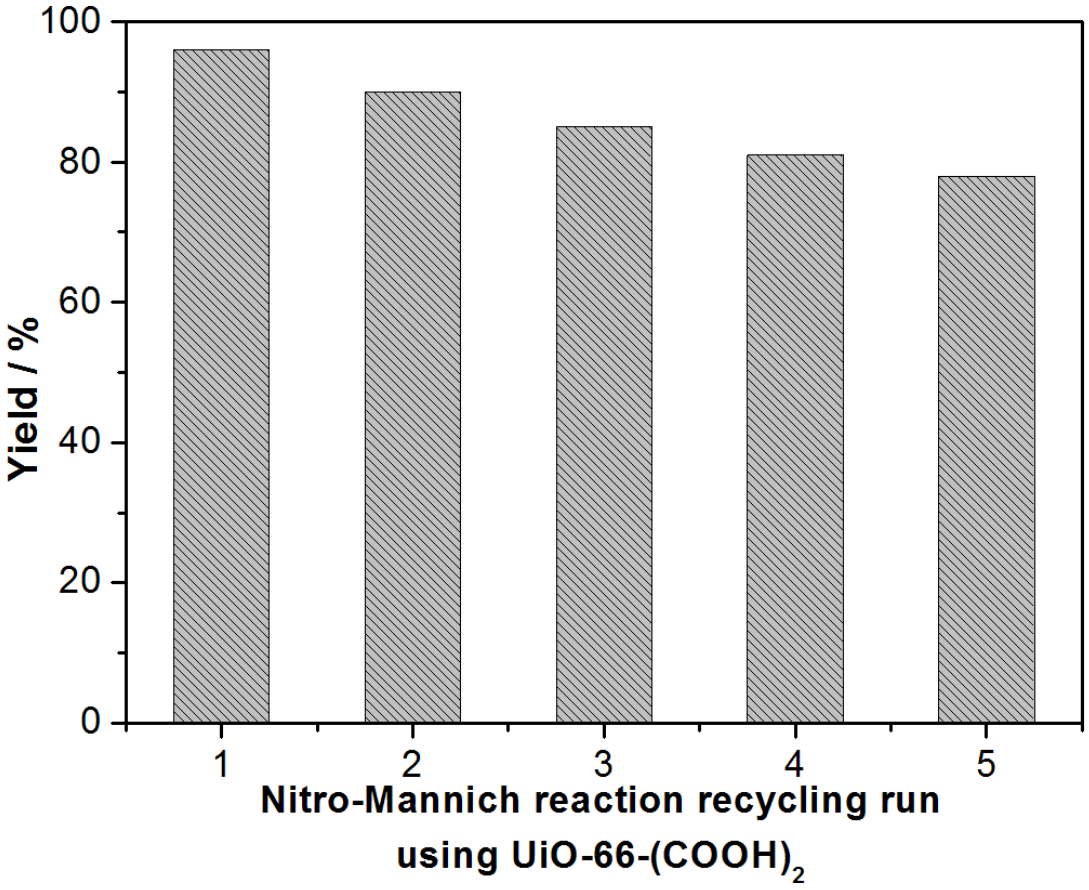
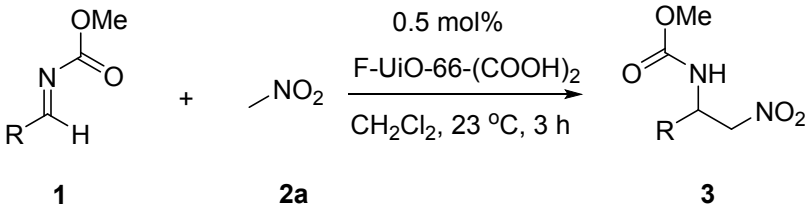


Figure S4. Parent UiO-66-$(COOH)_2$ in the catalyst recycle.



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

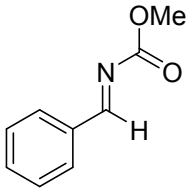
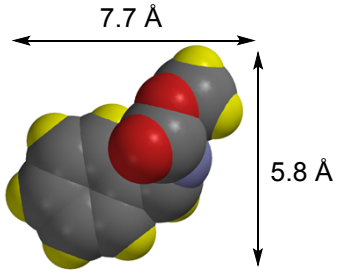
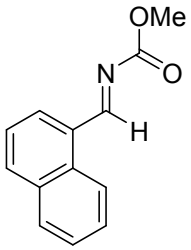
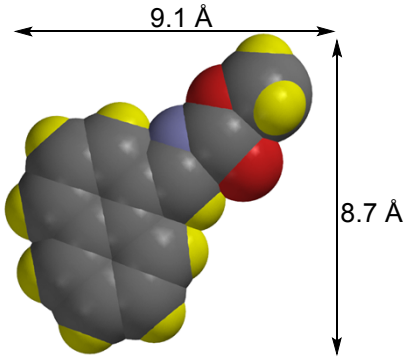
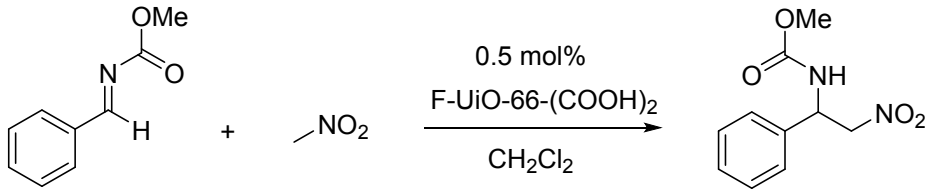
Entry	Substrate	Molecular size	Yield
1			99%
2			17%

Figure S5. Size selectivity test of acyl imines.

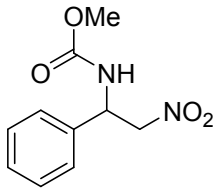
General procedure for Mannich addition of nitromethane 2a to acyl imine 1a.



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

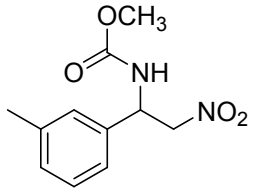
In an oven dried round bottom reaction vessel, 0.5 mol% F-UiO-66-$(COOH)_2$ (11 mg, 0.005 mmol based on the molecular weight of 2196) was added in 2.00 mL CH_2Cl_2. The imine **1a** (163 mg, 1.0 mmol) and nitromethane **2a** (91.5 mg, 1.50 mmol) were added successively. The solution was stirred at 23 °C for 3 h. The nitro-Mannich reaction mixture was passed through a silica gel plug and eluted with 5 mL of ethyl acetate. Then, the filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography over silica gel (elution with 15%-30% ethyl acetate in hexanes) to afford nitroamine **3a**-**3f**.

Methyl (2-nitro-1-phenylethyl)carbamate (3a)



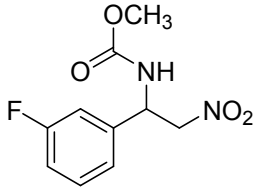
The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.222 g, 99%, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39-7.27 (m, 5H), 5.41 (m, 2H), 4.83 (s, 1H), 4.68 (m, 1H), 3.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 156.1, 136.6, 129.0, 128.7, 126.2, 78.5, 53.0, 52.5. **IR** (thin film, cm^{-1}): 3326, 2951, 1683, 1531, 1255, 1047; **HRMS**: (m/z) $(M+Na)^+$ calculated for $C_{10}H_{12}N_2O_4Na$ 247.0695, found 247.0694.□

Methyl (2-nitro-1-(m-tolyl)ethyl)carbamate (3b)



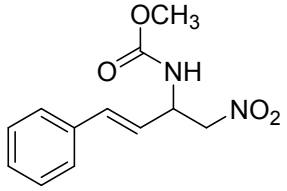
The crude mixture was purified by flash column chromatography with elution by 98:2–95:5, hexanes:EtOAc. **Yield:** 0.233 g, 98%, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26-6.98, (m, 4H), 5.42 (m, 1H), 4.89 (s, 1H), 4.70 (m, 1H), 3.68 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 156.0, 138.7, 136.5, 129.4, 128.8, 127.0, 123.1, 78.4, 76.7, 53.0, 52.3. 21.2; **IR** (thin film, cm^{-1}): 3311, 2956, 1701, 1550, 1459, 1374, 1260, 1063, 910, 787; **HRMS**: calc'd for $(M+H)^+$ $C_{11}H_{14}N_2O_4$: 239.1026; found 239.1038.

Methyl (1-(3-fluorophenyl)-2-nitroethyl)carbamate (3c)



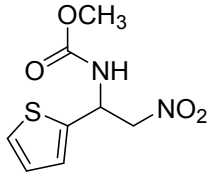
The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.237 g, 98%, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33-7.29 (m, 2H), 7.08-6.92 (m, 2H), 6.13 (d, J = 8.4 Hz, 1H), 5.54 (s , 1H), 5.08 (m, 1H), 3.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 164.2, 161.1, 155.8, 130.1, 122.2, 117.5, 113.6, 83.6, 55.5, 53.6; **IR** (thin film, cm^{-1}): 3654, 2934, 1703, 1594, 1531, 1352, 1256, 1057, 773; **HRMS**: calc'd for $(M+H)^+$ $C_{10}H_{11}FN_2O_4$: 243.0776; found 243.0771.

Methyl (*E*)-(1-nitro-4-phenylbut-3-en-2-yl)carbamate (3d)



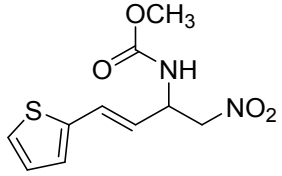
The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.220 g, 88%, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10-6.85 (m, 5H), 6.62 (d, *J* = 6.8 Hz, 1H), 6.13 (dd, *J* = 6.4, 6.8 Hz, 1H), 5.37 (s, 1H), 4.99-4.92 (m, 1H), 4.71-4.62 (m, 2H), 3.70 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 155.9, 133.5, 128.5, 128.40, 127.8, 127.0, 126.3, 123.1, 80.8, 52.6, 51.3; **IR** (thin film, cm^{-1}): 3320, 2936, 1714, 1555, 1445, 1241, 1065, 961, 756; **HRMS**: calc'd for $(M+H)^+$ $C_{12}H_{14}N_2O_4$: 251.1026; found 251.1002.

Methyl (2-nitro-1-(thiophen-2-yl)ethyl)carbamate (3e)

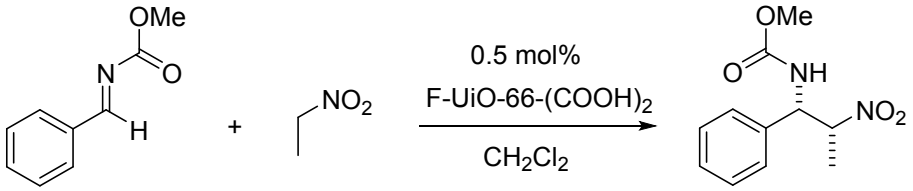


The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.166 g, 72%, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 1.6 Hz, 1H), 7.32 (dd, *J* = 3.4, 1.6 Hz, 1H), 6.29 (d, *J* = 2.8 Hz, 1H), 5.48 (m, 1H), 5.42 (s, 1H), 4.84 (dd, *J* = 16.0, 8.0 MHz, 1H), 4.70 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 155.9, 148.9, 142.8, 110.6, 107.8, 76.2, 52.6, 47.4; **IR** (thin film, cm^{-1}): 3310, 2952, 1704, 1546, 1259; **HRMS**: (m/z) $(M+Na)^+$ calculated for $C_8H_{10}N_2NaO_4S$ 253.0253, found 253.0237.

Methyl (*E*)-(1-nitro-4-(thiophen-2-yl)but-3-en-2-yl)carbamate (3f)



The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.230 g, 97%, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 2.0, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.34 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.26 (d, *J* = 3.2 Hz, 1H), 6.06 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.24 (br s, 1H), 4.90 (m, 1H), 4.64 (m, 1H), 4.56 (dd, *J* = 12.8, 4.8 Hz, 1H), 3.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 156.1, 151.1, 142.6, 121.8, 121.4, 111.4, 109.8, 78.1, 52.5, 51.1; **IR** (thin film, cm^{-1}): 3311, 2953, 2861, 1701, 1551, 1375, 1257; **HRMS:** (m/z) $(M+Na)^+$ calculated for $C_{10}H_{12}NaN_2O_4S$ 279.0410, found 279.0444.

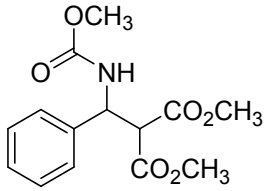


1a **4** **5**

Methyl (2-nitro-1-phenylpropyl)carbamate (5)

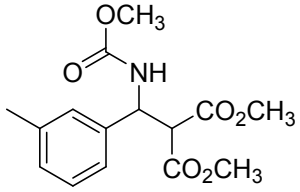
The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.231g, 97%, >95:5 dr, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39-7.31 (m, 3H), 7.22-7.19 (m, 2H), 5.49 (s, 1H), 5.22 (dd, *J* = 9.0, 5.8 Hz, 1H), 4.92 (m, 1H), 3.67 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 156.1, 136.1, 128.8, 128.6, 126.6, 85.4, 57.7, 52.4, 15.0. **IR** (thin film, cm^{-1}): 3311, 2924, 2853, 1691, 1544, 1291, 1018; **HRMS:** (m/z) $(M+Na)^+$ calculated for $C_{11}H_{14}N_2O_4Na$ 261.0846, found 261.0851.

Dimethyl 2-(((methoxycarbonyl)amino)(phenyl)methyl)malonate (7a)



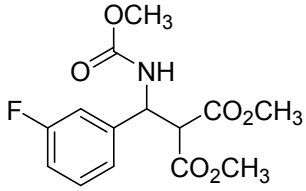
The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.292 g, 99%, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.23 (m, 5H), 6.34 (d, *J* = 8.0 Hz, 1H), 5.46 (m, 1H), 3.91 (d, *J* = 5.6 Hz, 1H), 3.73 (s, 3H), 3.64 (s, 3H), 3.62 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 168.5, 167.5, 156.4, 139.2, 128.8, 127.9, 126.3, 56.6, 54.0, 53.1, 52.8, 52.4; **IR** (thin film, cm^{-1}): 3278, 2945, 1752, 1736, 1685, 1552, 1433, 1291, 1262, 1146; **HRMS:** (m/z) $(M+Na)^+$ calculated for $C_{14}H_{17}NNaO_6$ 318.0948, found 318.0953.

Dimethyl 2-(((methoxycarbonyl)amino)(m-tolyl)methyl)malonate (7b)



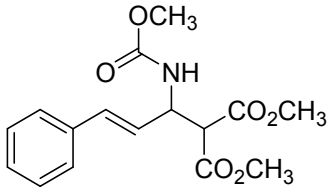
The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.303 g, 98%, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28-7.15 (m, 2H), 7.07-7.05 (m, 2H), 6.35 (d, *J* = 7.2 Hz, 1H), 5.45 (br s, 1H), 3.87 (s, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 3.62 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 168.1, 167.1, 156.1, 138.8, 138.1, 128.4, 128.3, 126.7, 122.9, 56.2, 53.7, 52.7, 52.3, 52.0, 21.2; **IR** (thin film, cm^{-1}): 3266, 2945, 2932, 1744, 1691, 1543, 1436, 1353, 1291, 1190, 1146, 1047, 1010, 911, 783; **HRMS**: calc'd for $(M+H)^+$ $C_{17}H_{21}NO_6$: 309.1212; found 309.1233.

Dimethyl 2-((3-fluorophenyl)((methoxycarbonyl)amino)methyl)malonate (7c)



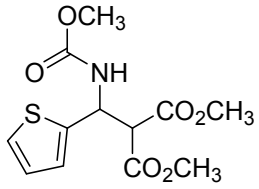
The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.310 g, 99%, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30-7.22 (m, 2H), 7.08-6.90 (m, 2H), 6.41 (d, *J* = 8.4 Hz, 1H), 5.47 (d , *J* = 4.4 Hz, 1H), 3.88 (d, *J* = 1.3 Hz, 1H), 3.72 (s, 3H), 3.63 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 164.4, 161.1, 142.0, 130.1, 121.9, 114.6, 113.4, 63.6, 62.1, 52.6, 52.5; **IR** (thin film, cm^{-1}): 3313, 2951, 1702, 1585, 1551, 1448, 1353, 1247, 1024, 874, 784; **HRMS**: calc'd for $(M+H)^+$ $C_{14}H_{17}FNO_6$: 314.1034; found 314.1038.

Dimethyl (*E*)-2-(1-((methoxycarbonyl)amino)-3-phenylallyl)malonate (7d)



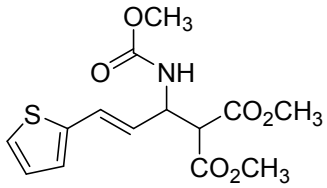
The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.315 g, 98%, **^{1}H NMR** (400 MHz, $CDCl_3$): 7.36-7.20 (m, 5H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 6.8, 6.8 Hz, 1H), 5.85 (s, 1H), 5.01 (m, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 168.1, 156.1, 135.9, 132.3, 128.4, 127.8, 126.5, 125.8, 55.2, 52.7, 52.5, 52.2; **IR** (thin film, cm^{-1}): 3385, 2944, 1731, 1522, 1431, 1348, 1243, 1192, 1066, 1031, 974, 748; **HRMS**: calc'd for $(M+H)^+$ $C_{16}H_{20}NO_6$: 322.1285; found 322.1279.

Dimethyl 2-(((methoxycarbonyl)amino)(thiophen-2-yl)methyl)malonate (7e)

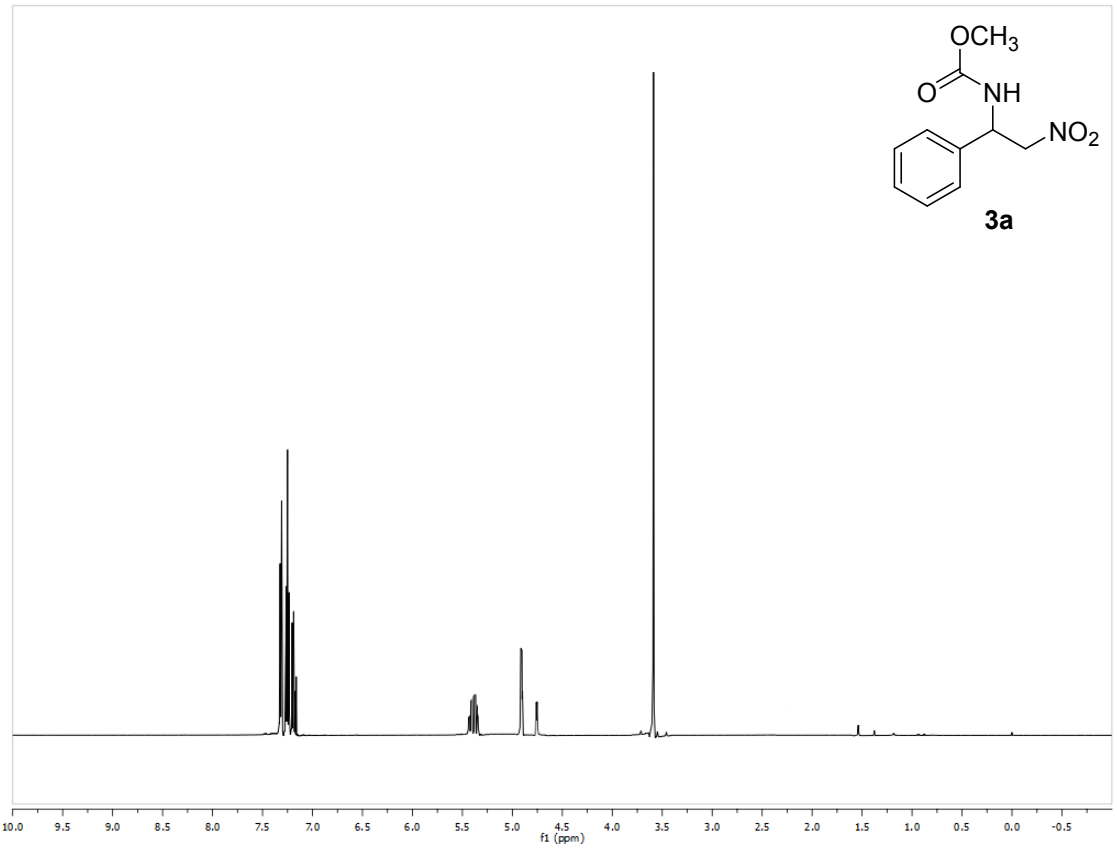


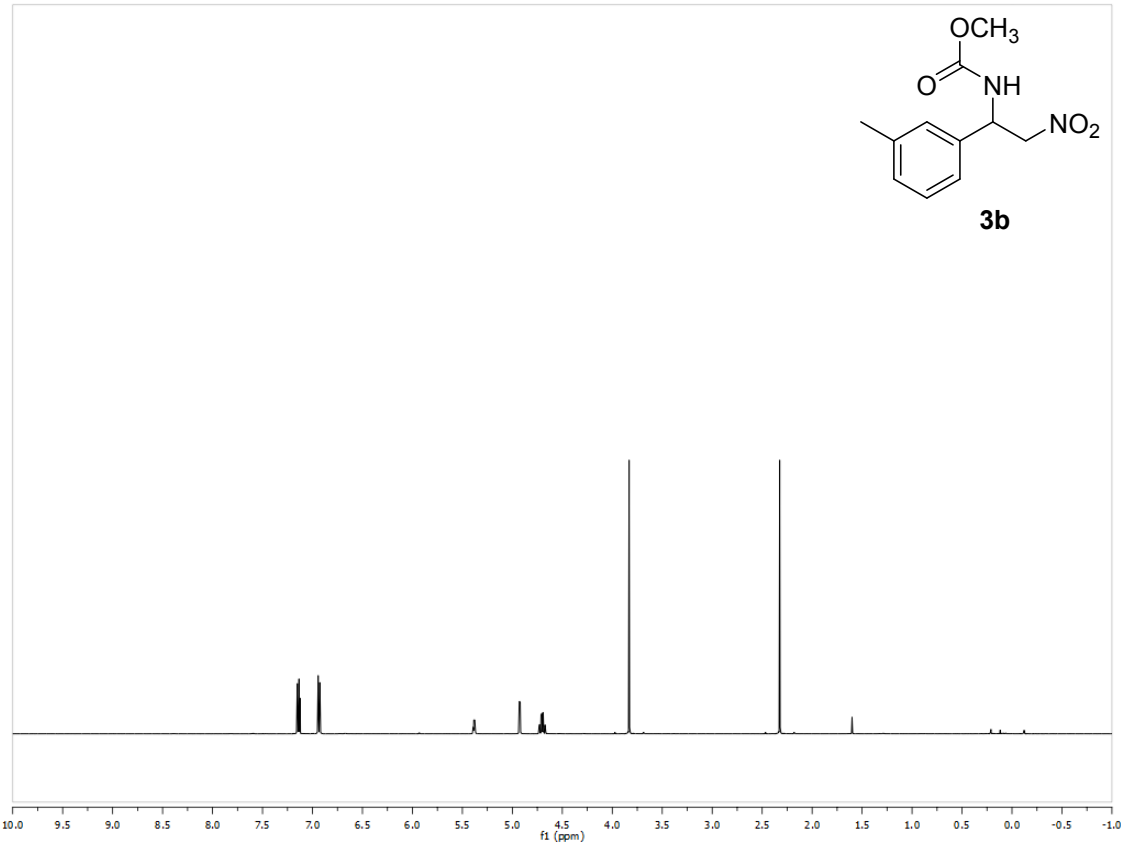
The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.274 g, 91%, **^{1}H NMR** (400 MHz, $CDCl_3$): 7.31 (dd, *J* = 1.8, 0.6 Hz, 1H), 6.27 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.20 (dd, *J* = 3.2, 1.2 Hz, 1H), 6.06 (d, *J* = 8.8 Hz, 1H), 5.53 (dd, *J* = 9.4, 4.2 Hz, 1H), 4.01 (d, *J* = 4.8 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 168.0, 167.0, 156.2, 151.7, 142.1, 110.4, 106.8, 53.7, 52.9, 52.6, 52.3, 48.6; **IR** (thin film, cm^{-1}): 3344, 2919, 2842, 1721, 1501, 1432, 1227, 1141; **HRMS**: (m/z) $(M+H)^+$ calculated for $C_{12}H_{16}SNO_6$ 302.0693, found 302.0706.

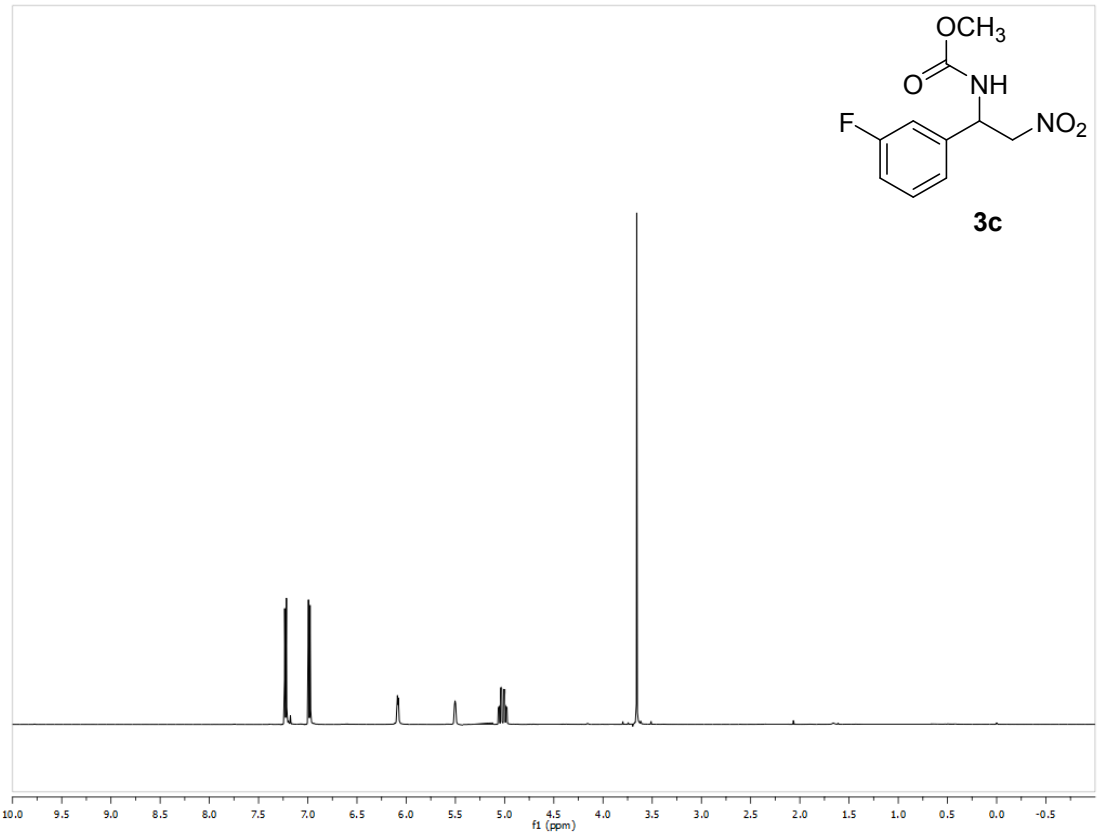
Dimethyl (*E*)-2-(1-((methoxycarbonyl)amino)-3-(thiophen-2-yl)allyl)malonate (7f)

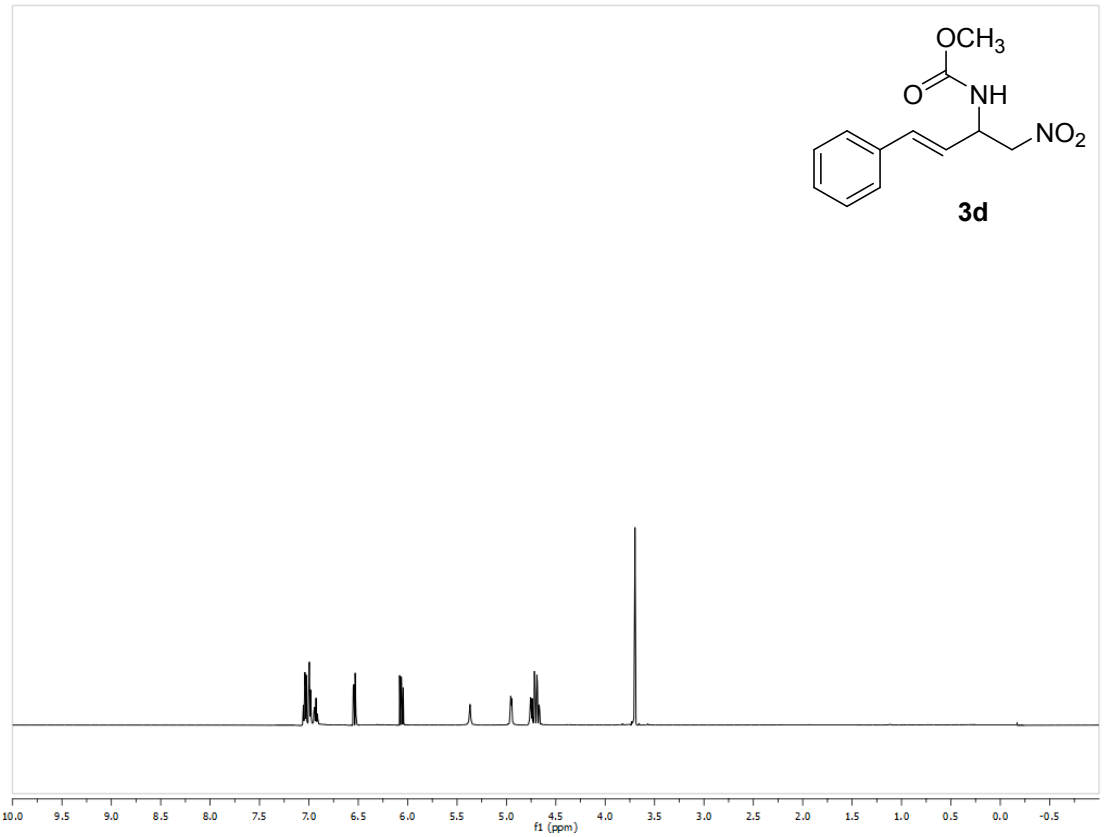


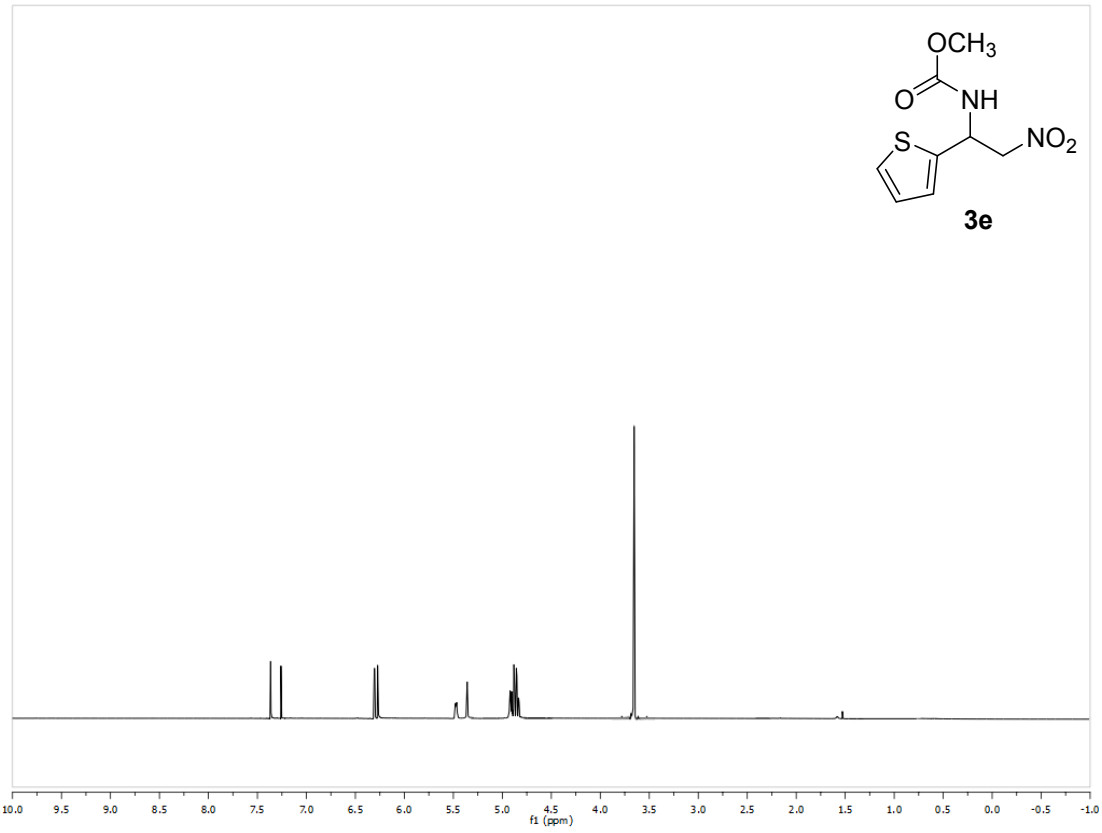
The crude mixture was purified by flash column chromatography with elution by 95:5–90:10, hexanes:EtOAc. **Yield:** 0.314 g, 96%, **^{1}H NMR** (400 MHz, $CDCl_3$): 7.39 (d, *J* = 1.5 Hz, 1H), 6.42 (d, *J* = 15.1 Hz, 1H), 6.32 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 6.07 (dd, *J* = 15.2, 6.4 Hz, 1H), 5.84 (d, *J* = 10.4 Hz, 1H), 4.97 (s, 1H), 3.72 (s, 6H), 3.64 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 167.2, 151.3, 142.0, 124.1, 124.1, 120.3, 111.1, 108.6, 55.0, 52.5, 52.3, 52.0. **IR** (thin film, cm^{-1}): 3371, 2950, 2850, 1723, 1510, 1434, 1230, 725; **HRMS**: (m/z) $(M+Na)^+$ calculated for $C_{14}H_{17}NNaO_6S$ 350.0669, found 350.0657.


OCH3
O
NH
NO2
3a
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 -0.5
f1 (ppm)


OCH3
O
NH
NO2
3b
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 -0.5 -1.0
f1 (ppm)


OCH3
O
NH
F
NO2
3c
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 -0.5
f1 (ppm)


OCH3
O
NH
NO2
3d
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 -0.5
f1 (ppm)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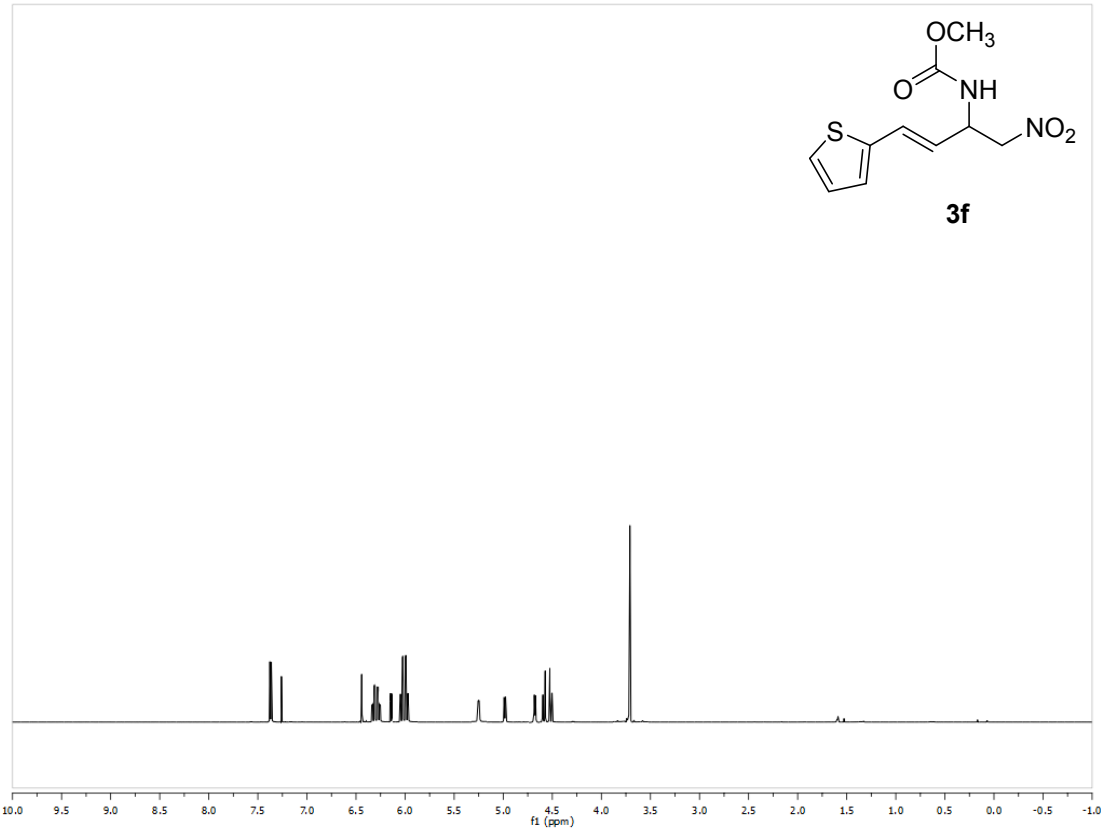
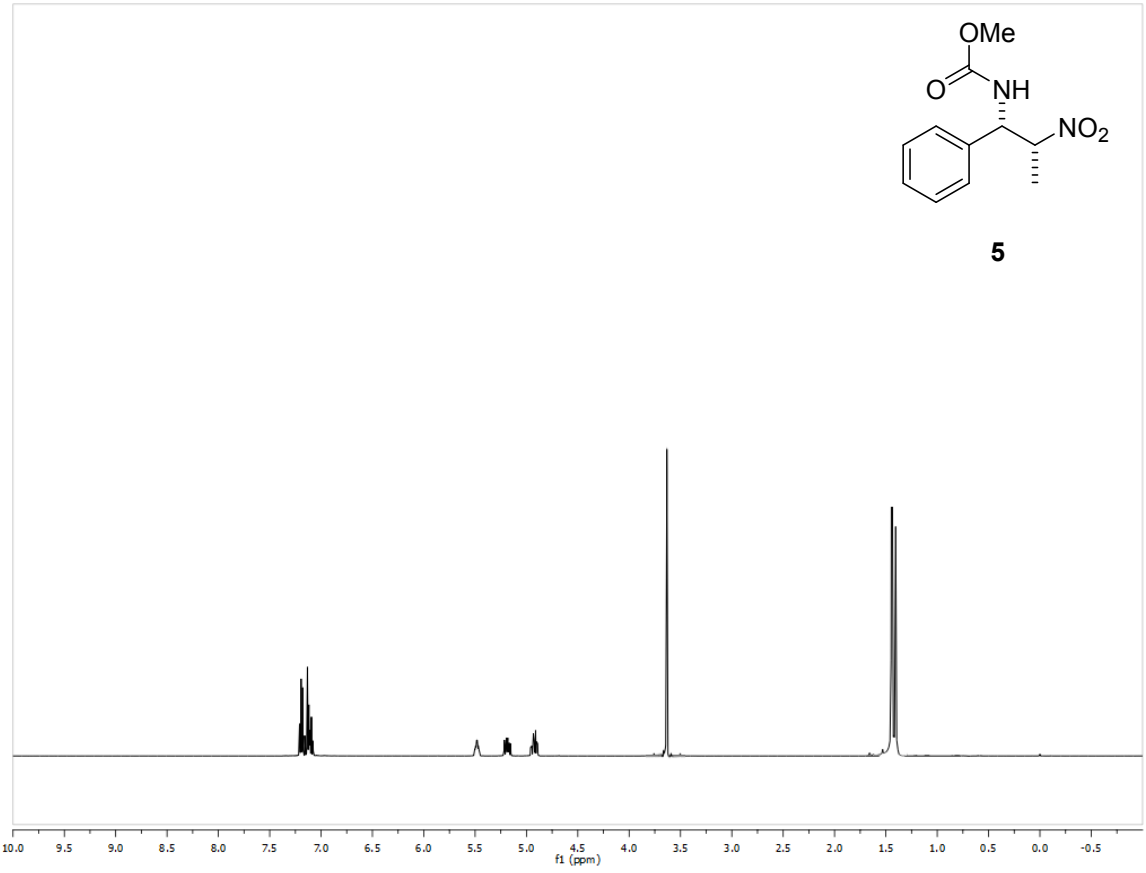
O
NH
S
NO2
3e
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


OCH3
O
NH
S
NO2
3f
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 -0.5 -1.0
f1 (ppm)


OMe
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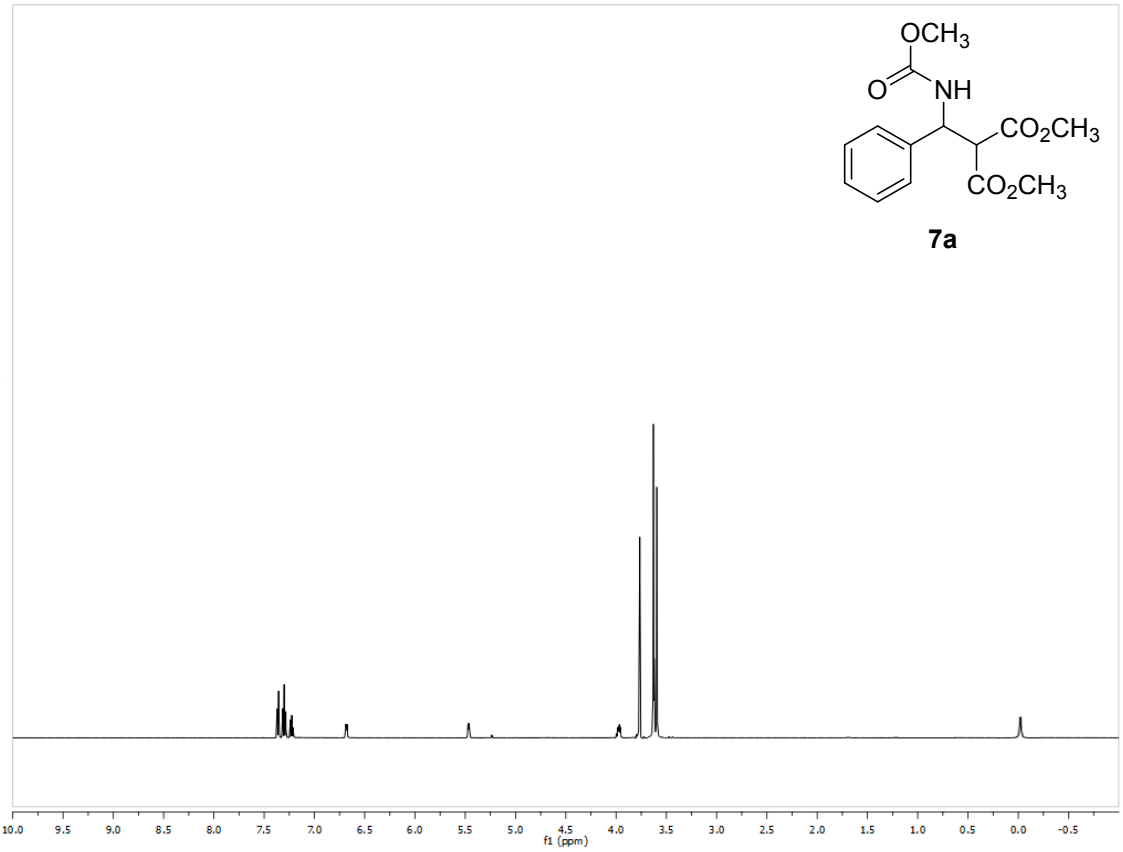
NH
NO2
5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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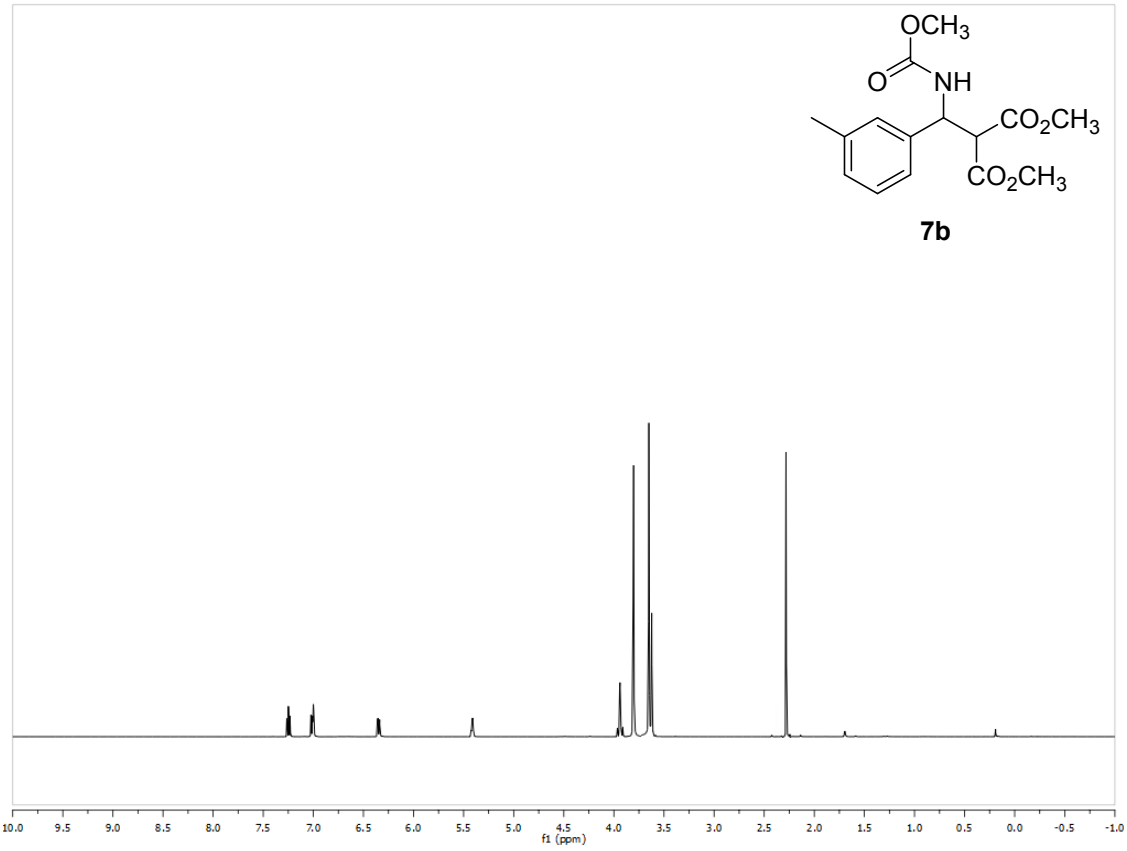
O
NH
CO2CH3
CO2CH3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

7a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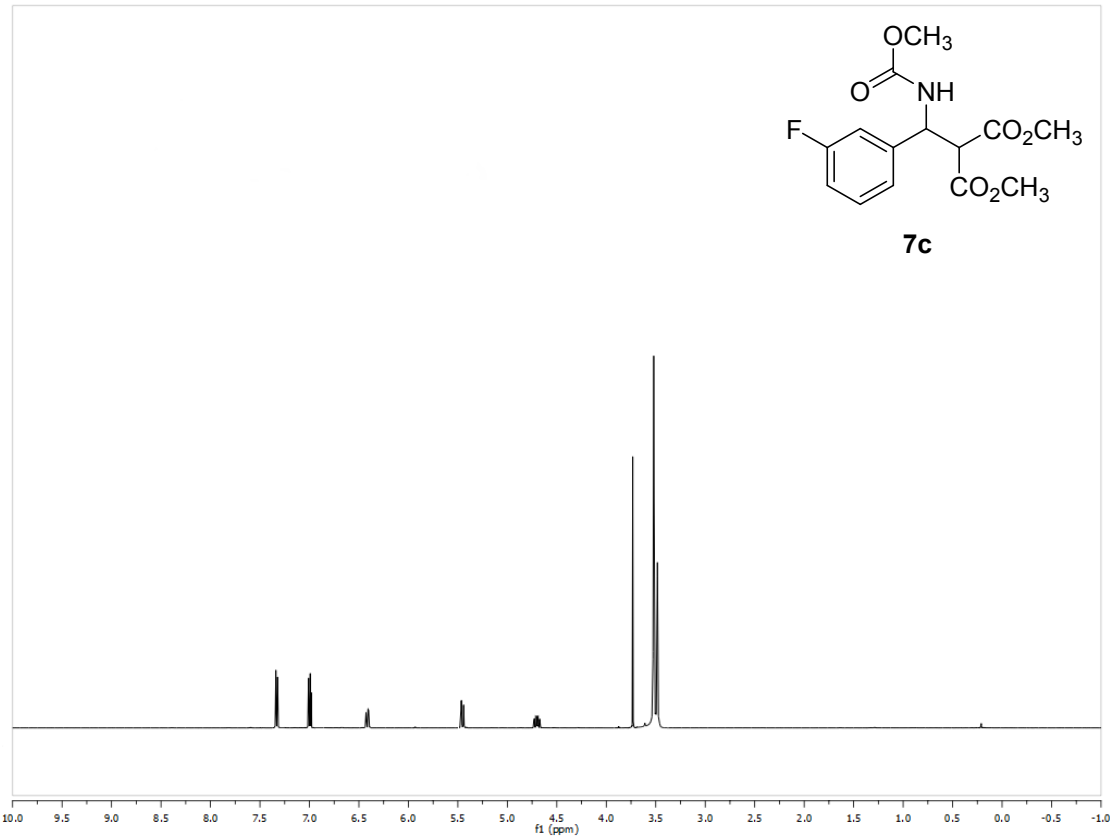
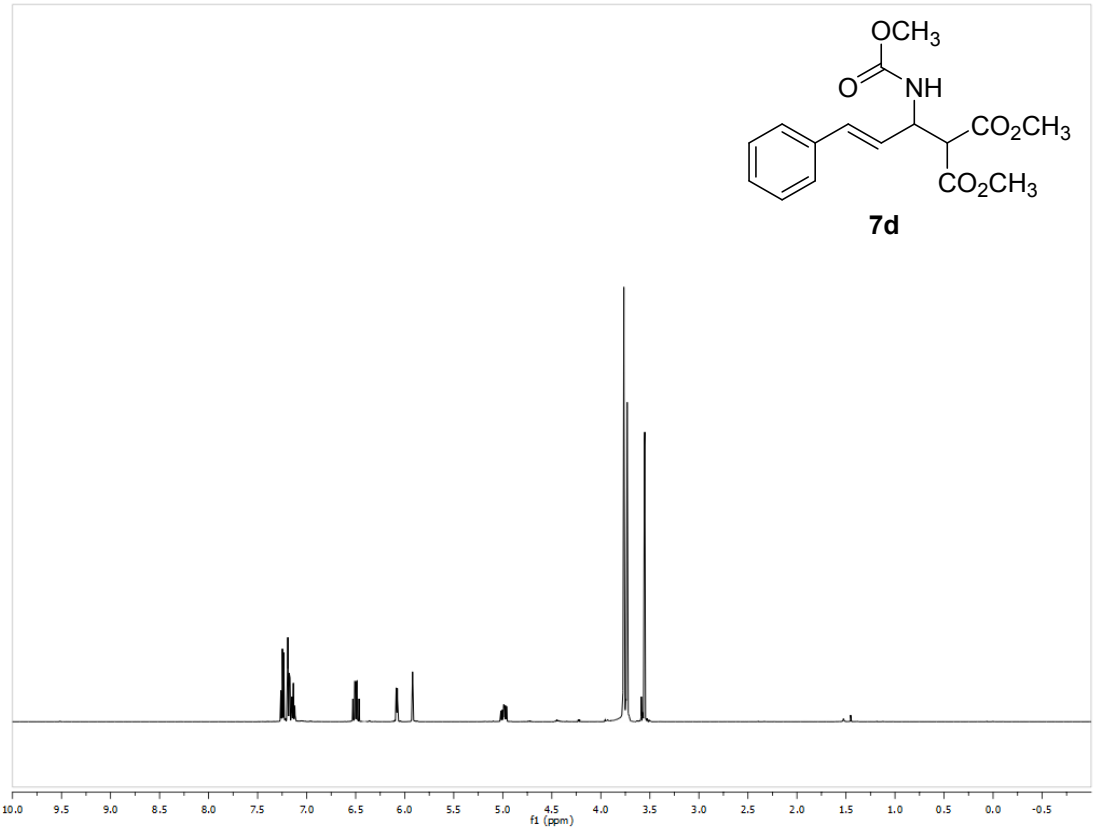
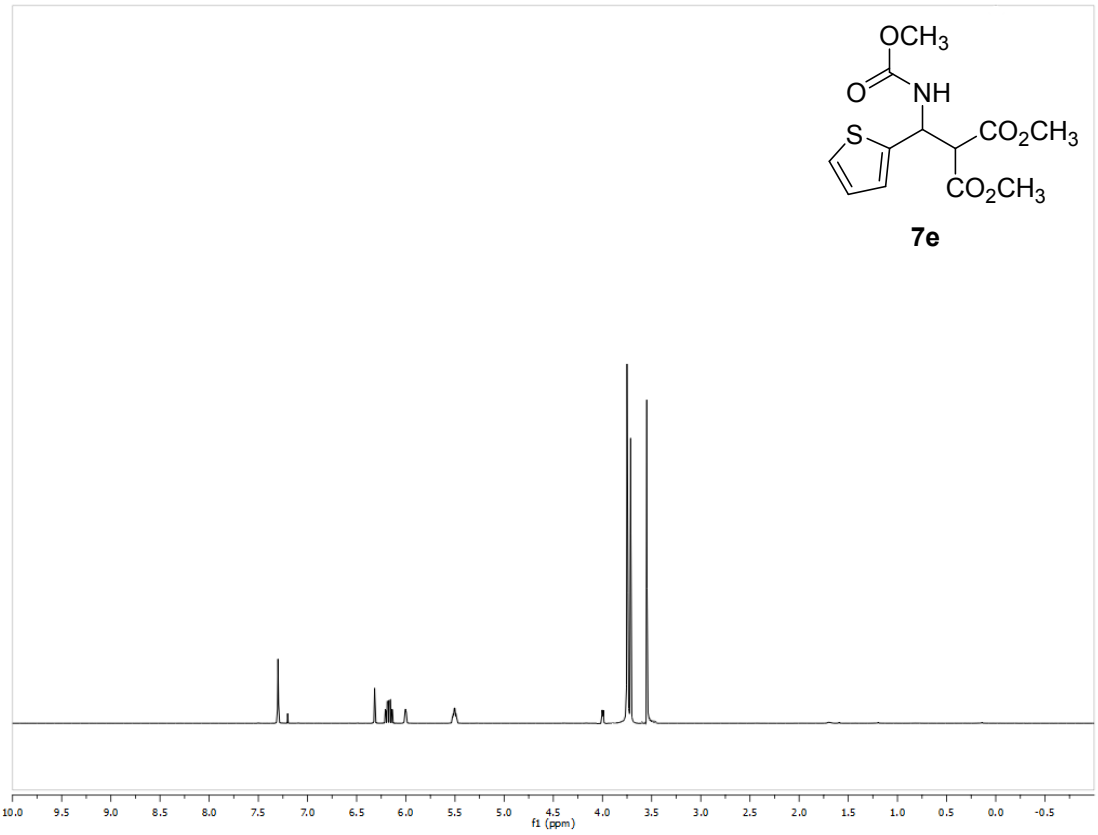
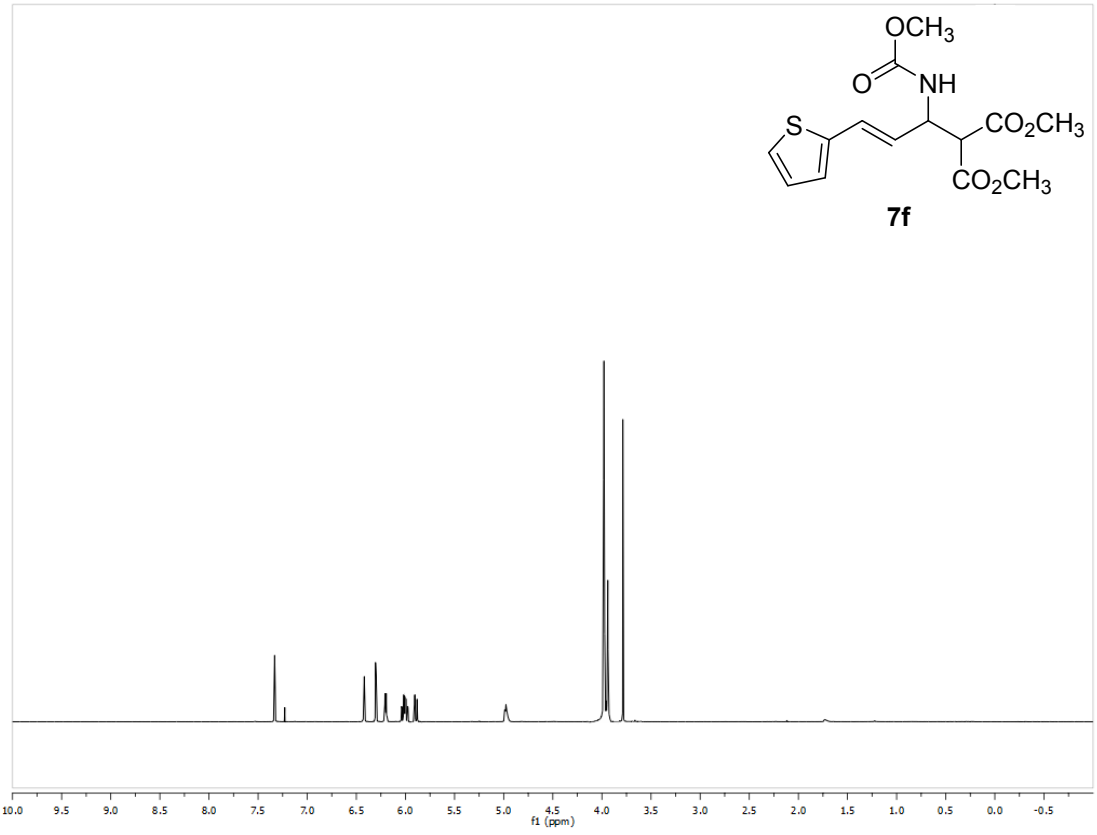
O
NH
CO2CH3
CO2CH3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

7b


OCH3
O
NH
F
CO2CH3
CO2CH3
7c
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 -0.5 -1.0
f1 (ppm)


OCH3
O
NH
CO2CH3
CO2CH3
7d
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 -0.5
f1 (ppm)


OCH3
O
NH
S
CO2CH3
CO2CH3
7e
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 -0.5
f1 (ppm)


OCH3
O
NH
S
CO2CH3
CO2CH3
7f
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 -0.5
f1 (ppm)