Invertible Enantioselectivity in 6'-Deoxy-6'-Acylamino-β-Isocupreidine-Catalyzed Asymmetric Aza-Morita-Baylis-Hillman Reaction: Key Role of Achiral Additive

SUPPORTING INFORMATION

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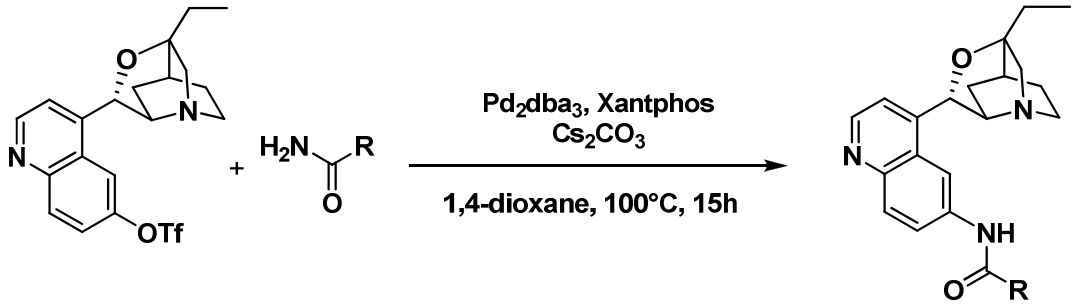
I] General Remarks:

All reactions were performed in dried glassware, under argon atmosphere and sealed with a rubber septum. Solvents were distilled by standard methods. Reagents were obtained from commercial supplier and used without further purification unless otherwise noted.
Flash column chromatography was carried out using kieselgel 35-70 μm particle sized silica gel (200-400 mesh). Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). TLC plates were analyzed by exposure to ultraviolet (UV) light and/or by submersion in ethanolic phosphomolybdic acid or in ninhydrin solution.
Melting points were recorded using Reichert melting point apparatus and are uncorrected.
Infrared spectra were recorded on neat samples, on a Perkin Elmer Spectrum BX FT-IR spectrometer and the characteristic IR absorption frequencies are reported in cm^{-1}.
Optical rotations were performed on a Jasco P-1010 polarimeter (589 nm) using a 700-μL cell with a path length of 1 dm.
^{1}H NMR spectra were recorded at 500 MHz on a Bruker AC-500 spectrometer and ^{13}C NMR spectra at 75 MHz on a Bruker AC-300 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) from internal tetramethylsilane. NMR experiments were carried out in deuterochloroform ($CDCl_3$). The following abbrevations are used for the multiplicities: s: singlet, d: doublet, t: triplet, dd: doublet of doublet, m: multiplets, br: broad signal for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).
Mass spectra were obtained from an AEI MS-9 using electron spray ionization (ESI). The HRMS data were measured on MALDI-TOF type of instrument for the high resolution mass spectra.
Analytical high performance liquid chromatography (HPLC) was performed on Hitachi LaChrom-Elite apparatus, equipped with diode array UV detectors, using Daicel Chiralpak AD-H column (0.46cm ØX15cm).
Racemic aza-MBH products were prepared with DABCO as catalyst.
Aromatic N-sulfonylated imines were prepared according to literature procedures.[1]
Aliphatic N-sulfonylated imines were prepared according to literature procedures.[2]
Catalyst **(1a)** β-ICD was prepared according to literature procedures.[3]
Catalyst **(1b)** has already been prepared.[4]

II] Preparation of catalysts

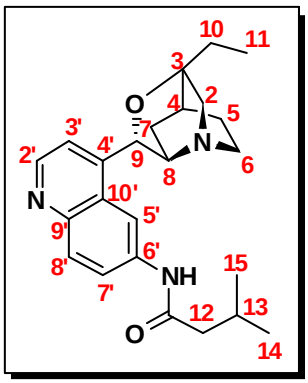
All catalysts were prepared by following the Buchwald amidation procedure (Scheme 1).[5]

[1] Palomo, C.; Oiarbide, M.; Halder, R.; Laso, A.; López, R. *Ang. Chem. Int. Ed*. **2006**, *45*, 117-120. Raheem, I. T.; Jacobsen, E. N. *Adv. Synth. Catal*. **2005**, *347*, 1701-1708.
[2] Chemla, F.; Hebbe, V.; Normant, J.-F. *Synthesis* **2000**, 75-77.
[3] Iwabuchi, Y.; Nakatani, M.; Yokoyama, N.; Hatakeyama, S. *J. Am. Chem. Soc*. **1999**, *121*, 10219-10220. Nakano, A.; Kawahara, S.; Akamatsu, S.; Morokuma, K.; Nakatani, M.; Iwabuchi, Y.; Takahashi, K.; Ishihara, J.; Hatakeyama, S. *Tetrahedron* **2006**, *62*, 381-389.
[4] Abermil, N.; Masson, G.; Zhu, J. *J. Am. Chem. Soc.* **2008**, *130*, 12596-12597.
[5] Yin, J.; Buchwald, S. L. *Org. Lett*. **2000**, *2*, 1101-1104. Yin, J.; Buchwald, S. L. *J. Am. Chem. Soc*. **2002**, *124*, 6043-6048.



Scheme 1

The synthesis of triflate β-ICD was accomplished by following the method described by Deng.[6] A flame-dried flask provided with a water-cooled reflux condenser was charged with Pd_2dba_3 (46.9 mg, 0.05 mmol, 0.04 eq), Xantphos (12.6 mg, 0.07 mmol, 0.06 eq) and 1,4-dioxane (1 mL). The condenser was capped with a rubber septum, evacuated and backfilled with argon. This evacuation/backfilled sequence was repeated one additional time. Carbonate cesium (514.6 mg, 1.6 mmol, 1.4 eq), corresponding amide (1.7 mmol, 1.5 eq) and triflate (500.0 mg, 1.1 mmol, 1 eq) in solution in 1,4-dioxane (1.5 mL) were added. The evacuation/backfilled sequence was performed two times. The mixture was then stirred at 100°C for 15 h until the starting triflate had been completely consumed, as judged by TLC. The reaction was then cooled to room temperature, diluted with ethyle acetate, filtered on celite and concentrated in vacuo. The crude material was purified by flash chromatography.



Compound (1c): Purification by flash chromatography using EtOAc/MeOH 95/5 to give 194.7 mg (45%) of **(1c)** as a yellow solid.

Formula $C_{24}H_{31}N_3O_2$ (393.2 g.mol^{-1}).

[α]$^{25}_D$ -5.3 (c 1.11, $CHCl_3$). **Melting point** 105-106°C.

IR (cm^{-1}) ν 3266 (N-H), 2958, 2930, 2880, 1670 (C=O), 1621, 1554, 1501, 1459, 1364, 1306.

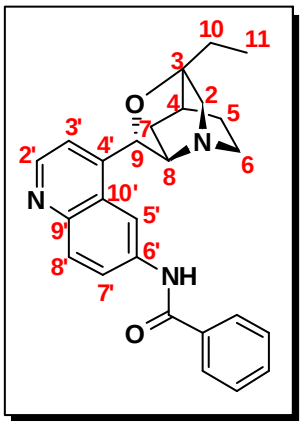
^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 1.05 (m, 9H, H11, H14, H15), 1.30 (m, 1H, H7), 1.59 (m, 1H, H5), 1.71 (m, 3H, H5, H10), 1.80 (m, 1H, H7), 2.20 (m, 1H, H4), 2.30 (m, 3H, H12, H13), 2.74 (d, *J* = 14.0 Hz, 1H, H2), 3.07 (m, 2H, H6), 3.60 (m, 1H, H8), 3.64 (d, *J* = 14.0 Hz, 1H, H2), 5.98 (s, 1H, H9), 7.73 (d, *J* = 4.5 Hz, 1H, H3'), 7.91 (br, 1H, NH), 7.96 (m, 1H, H5'), 8.10 (d, *J* = 9.0 Hz, 1H, H8'), 8.25 (d, *J* = 9.0 Hz, 1H, H7'), 8.86 (d, *J* = 4.5 Hz, 1H, H2').

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 7.3 (C11), 22.5 (C14, C15), 23.4 (C5), 24.0 (C7), 26.1 (C13), 27.4 (C10), 32.9 (C4), 46.5 (C6), 46.9 (C12), 54.6 (C2), 56.5 (C8), 73.0 (C9), 77.2 (C3), 110.7 (C5'), 119.4 (C3'), 123.2 (C7'), 125.7 (C10'), 131.0 (C8'), 136.9 (C6'), 143.7 (C4'), 145.1 (C9'), 149.0 (C2'), 171.6 (C=O).

MS (ESI) m/z 394.2 [M+H]$^+$

[6] Song, J.; Wang, Y.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 6048-6049.

HRMS (ESI) m/z 394.2491 $[M+H]^+$, $C_{24}H_{32}N_3O_2$ requires 394.2495.



Compound (1d): Purification by flash chromatography using EtOAc/MeOH 95/5 to give 258.8 mg (57%) of **(1d)** as a yellow solid.

Formula $C_{26}H_{27}N_3O_2$ (413.2 $g.mol^{-1}$).

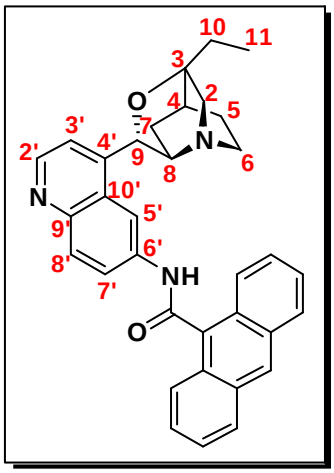
$[\alpha]^{25}_D$ +16.1 (c 1.06, $CHCl_3$). **Melting point** 127-128°C.

IR (cm^{-1}) ν 3256 (N-H), 2963, 2930, 2880, 1660 (C=O), 1622, 1548, 1504, 1455, 1361, 1305, 1276.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 1.06 (t, *J* = 7.5 Hz, 3H, H11), 1.29 (m, 1H, H7), 1.55 (m, 1H, H5), 1.70 (m, 3H, H5, H10), 1.79 (m, 1H, H7), 2.18 (m, 1H, H4), 2.70 (d, *J* = 13.0 Hz, 1H, H2), 3.03 (m, 2H, H6), 3.57 (m, 1H, H8), 3.59 (d, *J* = 13.0 Hz, 1H, H2), 6.00 (s, 1H, H9), 7.53 (m, 2H, Ar), 7.59 (m, 1H, Ar), 7.77 (d, *J* = 4.5 Hz, 1H, H3'), 7.98 (d, *J* = 7.5 Hz, 2H, Ar), 8.04 (m, 1H, H5'), 8.16 (d, *J* = 9.0 Hz, 1H, H8'), 8.36 (d, *J* = 9.0 Hz, 1H, H7'), 8.45 (br, 1H, NH), 8.89 (d, *J* = 4.5 Hz, 1H, H2').

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 7.3 (C11), 22.9 (C5), 23.5 (C7), 27.3 (C10), 32.7 (C4), 46.6 (C6), 54.5 (C2), 57.2 (C8), 72.5 (C9), 77.2 (C3), 111.1 (C5'), 119.3 (C3'), 123.7 (C7'), 125.5 (C10'), 127.4 (2*CHAr), 128.7 (2*CHAr), 131.3 (C8'), 132.0 (CHAr), 134.3 (CqAr), 137.2 (C6'), 142.6 (C4'), 145.3 (C9'), 149.2 (C2'), 166.2 (C=O).

MS (ESI) m/z 414.2 $[M+H]^+$
HRMS (ESI) m/z 414.2175 $[M+H]^+$, $C_{26}H_{28}N_3O_2$ requires 414.2182.



Compound (1e): Purification by flash chromatography using EtOAc/MeOH 95/5 to give 423.2 mg (75%) of **(1e)** as a yellow solid.

Formula $C_{34}H_{31}N_3O_2$ (513.2 $g.mol^{-1}$).

$[\alpha]^{25}_D$ +35.9 (c 1.03, $CHCl_3$). **Melting point** 132-133°C.

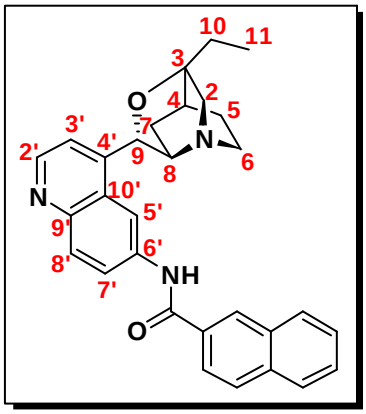
IR (cm^{-1}) ν 3250 (N-H), 2963, 2931, 2881, 1664 (C=O), 1621, 1552, 1499, 1454, 1363, 1301, 1256.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 1.04 (t, *J* = 7.5 Hz, 3H, H11), 1.30 (m, 1H, H7), 1.57 (m, 1H, H5), 1.66 (m, 3H, H5, H10), 1.80 (m, 1H, H7), 2.21 (m, 1H, H4), 2.66 (d, *J* = 13.5 Hz, 1H, H2), 2.99 (m, 2H, H6), 3.51 (d, *J* = 13.5 Hz, 1H, H2), 3.72 (m, 1H, H8), 5.82 (s, 1H, H9), 7.46 (m, 2H, Anth), 7.53 (m, 2H, Anth), 7.72 (d, *J* = 4.0 Hz, 1H, H3'), 7.99 (m, 2H, H5', Anth), 8.08 (m, 1H, H8'), 8.21 (m, 3H, Anth), 8.48 (s, 1H, Anth), 8.73 (m, 1H, H7'), 8.88 (br, 1H, NH), 8.91 (d, *J* = 4.0 Hz, 1H, H2').

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 7.3 (C11), 22.9 (C5), 23.5 (C7), 27.3 (C10), 32.8 (C4), 46.1 (C6), 53.9 (C2), 56.5 (C8), 72.7 (C9), 77.2 (C3), 111.0 (C5'), 119.3 (C3'), 123.0 (C7'),

125.1 (CHAnth), 125.5 (C10', 3*CHAnth), 127.0 (CHAnth, CqAnth), 128.1 (CqAnth), 128.6 (3*CHAnth, CqAnth), 128.7 (CHAnth), 131.1 (CqAnth), 131.4 (C8'), 131.5 (CqAnth), 137.4 (C6'), 142.9 (C4'), 145.4 (C9'), 149.3 (C2'), 168.2 (C=O).

MS (ESI) m/z 514.2 $[M+H]^+$
HRMS (ESI) m/z 514.2491 $[M+H]^+$, $C_{34}H_{32}N_3O_2$ requires 514.2495.



Compound (1f): Purification by flash chromatography using EtOAc/MeOH 95/5 to give 382.4 mg (75%) of **(1f)** as a yellow solid.

Formula $C_{30}H_{29}N_3O_2$ (463.2 $g.mol^{-1}$).

$[\alpha]^{25}_D$ +13.1 (c 1.05, $CHCl_3$). **Melting point** 126-127°C.

IR (cm^{-1}) ν 3252 (N-H), 2933, 2877, 1660 (C=O), 1621, 1547, 1499, 1456, 1362, 1305, 1284.

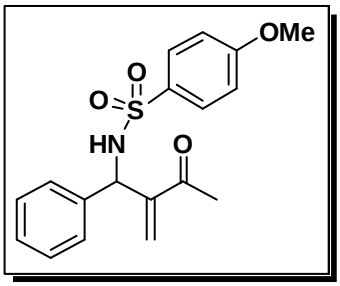
^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 1.07 (t, *J* = 7.5 Hz, 3H, H11), 1.32 (m, 1H, H7), 1.68 (m, 1H, H5), 1.72 (m, 3H, H5, H10), 1.86 (m, 1H, H7), 2.27 (m, 1H, H4), 2.81 (d, *J* = 13.5 Hz, 1H, H2), 3.15 (m, 2H, H6), 3.81 (m, 2H, H2, H8), 6.07 (s, 1H, H9), 7.56 (m, 2H, Naph), 7.70 (d, *J* = 4.5 Hz, 1H, H3'), 7.88 (d, *J* = 8.0 Hz, 1H, Naph), 7.95 (d, *J* = 8.5 Hz, 1H, Naph), 8.04 (d, *J* = 8.0 Hz, 1H, Naph), 8.13 (d, *J* = 8.5 Hz, 1H, Naph), 8.19 (d, *J* = 9.5 Hz, 1H, H8'), 8.31 (m, 1H, H5'), 8.69 (m, 2H, H7', Naph), 8.89 (d, *J* = 4.5 Hz, 1H, H2'), 9.14 (br, 1H, NH).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 7.3 (C11), 23.2 (C5), 23.8 (C7), 27.4 (C10), 32.8 (C4), 46.4 (C6), 54.4 (C2), 56.6 (C8), 72.9 (C9), 77.3 (C3), 111.4 (C5'), 119.3 (C3'), 123.5 (C7'), 123.9 (CHNaph), 125.6 (C10'), 126.8 (CHNaph), 127.7 (CHNaph), 127.9 (CHNaph), 128.1 (CHNaph), 128.5 (CHNaph), 129.1 (CHNaph), 131.2 (C8'), 131.7 (CqNaph), 132.5 (CqNaph), 134.9 (CqNaph), 137.2 (C6'), 143.3 (C4'), 145.3 (C9'), 149.2 (C2'), 166.3 (C=O).

MS (ESI) m/z 464.2 $[M+H]^+$
HRMS (ESI) m/z 464.2345 $[M+H]^+$, $C_{30}H_{30}N_3O_2$ requires 464.2338.

III] General procedure of aza-MBH reactions involving aromatic imines:

To a solution of corresponding imine (0.073 mmol, 1 eq) in dried dichloromethane (0.2 mL) at -50°C, catalyst **(1e)** (3.7 mg, 0.0073 mmol, 0.1 eq), β-naphthol (1.1 mg, 0.0073 mmol, 0.1 eq) and alkylvinylketone (0.15 mmol, 2 eq) were added. The reaction mixture was stirred under argon atmosphere at -50°C for 48 hours. The reaction was stopped by passing the mixture through a short pad of silica gel using ethyle acetate for the elution. Solvents were removed in vacuo and the residue was purified by flash chromatography on silica gel (*n*-Hept/EtOAc 90/10) to afford the corresponding pure product.



Compound (5a):

A white solid (25.1 mg, >99%).

Formula $C_{18}H_{19}NO_4S$ (345.1 g.mol^{-1}).

[α]$^{25}_{D}$ +39.1 (c 1.12, $CHCl_3$). **Melting point** 98-99°C.

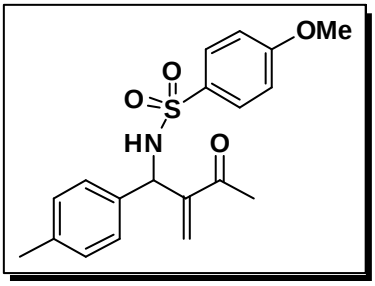
IR (cm^{-1}) ν 3228, 2919, 2849, 1672 (C=O), 1630, 1594, 1577, 1496, 1456, 1258, 1147.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 2.19 (s, 3H, CH_3), 3.87 (s, 3H, OMe), 5.29 (d, *J* = 8.5 Hz, 1H, CH), 5.68 (d, *J* = 8.5 Hz, 1H, NH), 6.12 (s, 1H, =CH), 6.14 (s, 1H, =CH), 6.92 (d, *J* = 9.0 Hz, 2H, PMP), 7.11 (m, 1H, Ar), 7.21 (m, 4H, Ar), 7.71 (d, *J* = 9.0 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 26.4 (CH_3), 55.6 (CH), 58.8 (OMe), 114.0 (2*CHPMP), 126.5 (2*CHAr), 127.6 (=CH_2), 128.1 (CHAr), 128.6 (2*CHAr), 129.4 (2*CHPMP), 132.1 (=Cq), 138.9 (CqAr), 146.7 (CqPMP), 162.8 (CqPMP), 198.8 (C=O).

MS (ESI) m/z 368.1 $[M+Na]^+$
HRMS (ESI) m/z 368.0931 $[M+Na]^+$, $C_{18}H_{19}NO_4NaS$ requires 368.0932.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 90/10, 1mL/mn, 254 nm, 25°C) **e.e.** 96%.



Compound (5b):

A white solid (26.2 mg, >99%).

Formula $C_{19}H_{21}NO_4S$ (359.1 g.mol^{-1}).

[α]$^{25}_{D}$ +59.8 (c 1.03, $CHCl_3$). **Melting point** 101-102°C.

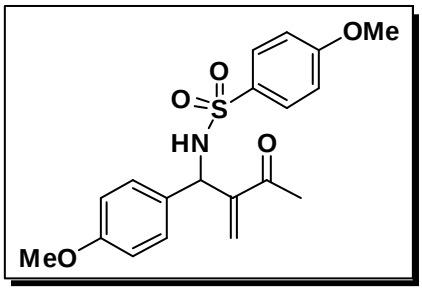
IR (cm^{-1}) ν 3262, 2919, 2846, 1670 (C=O), 1594, 1575, 1498, 1424, 1263, 1152.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 2.19 (s, 3H, CH_3), 2.28 (s, 3H, $ArCH_3$), 3.87 (s, 3H, OMe), 5.26 (d, *J* = 8.5 Hz, 1H, CH), 5.64 (d, *J* = 8.5 Hz, 1H, NH), 6.12 (s, 1H, =CH), 6.13 (s, 1H, =CH), 6.92 (d, *J* = 8.5 Hz, 2H, PMP), 6.98 (d, *J* = 8.0 Hz, 2H, Ar), 7.03 (d, *J* = 8.0 Hz, 2H, Ar), 7.71 (d, *J* = 8.5 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 21.0 ($ArCH_3$), 26.4 (CH_3), 55.6 (CH), 58.5 (OMe), 114.0 (2*CHPMP), 126.4 (2*CHAr), 127.9 (=CH_2), 129.2 (2*CHAr), 129.4 (2*CHPMP), 132.1 (=Cq), 136.0 (CqAr), 137.4 (CqAr), 146.8 (CqPMP), 162.8 (CqPMP), 198.8 (C=O).

MS (ESI) m/z 382.1 $[M+Na]^+$
HRMS (ESI) m/z 382.1083 $[M+Na]^+$, $C_{19}H_{21}NO_4NaS$ requires 382.1089.

HPLC analysis Chiralpak AD-H (*n*-Hept/EtOH 80/20, 1mL/mn, 254 nm, 25°C) **e.e.** 96%.



Compound (5c):

A white solid (17.1 mg, 62%).

Formula $C_{19}H_{21}NO_5S$ (375.1 g.mol^{-1}).

[α]$^{25}_D$ +61.8 (c 0.97, $CHCl_3$). **Melting point** 104-105°C.

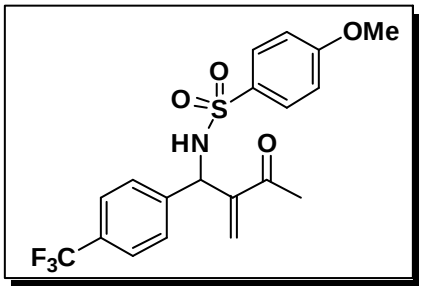
IR (cm^{-1}) ν 3324, 3241, 2945, 2841, 1673 (C=O), 1596, 1578, 1497, 1459, 1257, 1148.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 2.20 (s, 3H, CH_3), 3.76 (s, 3H, OMe), 3.88 (s, 3H, OMe), 5.23 (d, *J* = 8.5 Hz, 1H, CH), 5.51 (d, *J* = 8.5 Hz, 1H, NH), 6.12 (s, 1H, =CH), 6.13 (s, 1H, =CH), 6.75 (d, *J* = 9.0 Hz, 2H, Ar), 6.93 (d, *J* = 8.5 Hz, 2H, PMP), 7.01 (d, *J* = 9.0 Hz, 2H, Ar), 7.72 (d, *J* = 8.5 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 26.4 (CH_3), 55.2 (OMe), 55.6 (CH), 58.3 (OMe), 113.9 (2*CHPMP), 114,0 (2*CHAr), 127.7 (2*CHAr, $=CH_2$), 129.4 (2*CHPMP), 131.0 (CqAr), 132.1 (=Cq), 146.9 (CqPMP), 159.1 (CqAr), 162.8 (CqPMP), 198.9 (C=O).

MS (ESI) m/z 398.1 $[M+Na]^+$
HRMS (ESI) m/z 398.1043 $[M+Na]^+$, $C_{19}H_{21}NO_5NaS$ requires 398.1038.

HPLC analysis Chiralpak AD-H (*n*-Hept/EtOH 80/20, 1mL/mn, 254 nm, 25°C) **e.e.** 96%.



Compound (5d):

A white solid (30.1 mg, >99%).

Formula $C_{19}H_{18}NO_4F_3S$ (413.1 g.mol^{-1}).

[α]$^{25}_D$ +1.3 (c 1.03, $CHCl_3$). **Melting point** 115-116°C.

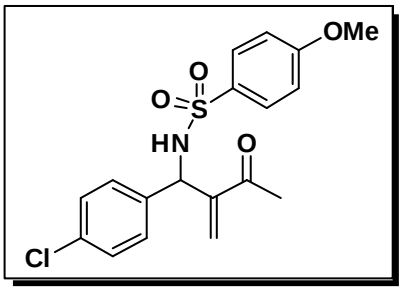
IR (cm^{-1}) ν 3274, 2970, 2847, 1674 (C=O), 1596, 1579, 1498, 1442, 1322, 1258, 1150.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 2.18 (s, 3H, CH_3), 3.86 (s, 3H, OMe), 5.34 (d, *J* = 9.0 Hz, 1H, CH), 5.99 (d, *J* = 9.0 Hz, 1H, NH), 6.10 (s, 1H, =CH), 6.14 (s, 1H, =CH), 6.88 (d, *J* = 9.0 Hz, 2H, PMP), 7.27 (d, *J* = 8.0 Hz, 2H, Ar), 7.46 (d, *J* = 8.0 Hz, 2H, Ar), 7.68 (d, *J* = 9.0 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 26.2 (CH_3), 55.6 (CH), 58.6 (OMe), 114.1 (2*CHPMP), 123.9 (q, *J* = 270 Hz, **C**F_3), 125,3 (CHAr), 125,4 (CHAr), 126.9 (2*CHAr), 128.9 ($=CH_2$), 129.3 (2*CHPMP), 129.7 (q, *J* = 33 Hz, **C**CF_3), 132.0 (=Cq), 143.0 (CqAr), 146.1 (CqPMP), 163.0 (CqPMP), 198.7 (C=O).

MS (ESI) m/z 436.1 $[M+Na]^+$
HRMS (ESI) m/z 436.0815 $[M+Na]^+$, $C_{19}H_{18}NO_4F_3NaS$ requires 436.0806.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 85/15, 1mL/mn, 254 nm, 25°C) **e.e.** 95%.



Compound (5e):

A white solid (27.6 mg, >99%).

Formula $C_{18}H_{18}NO_4SCl$ (379.1 g.mol^{-1}).

$[\alpha]^{25}_D$ +35.3 (c 1.04, $CHCl_3$). **Melting point** 97-98°C.

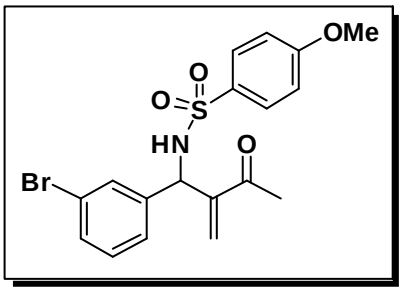
IR (cm^{-1}) ν 3216, 2918, 2839, 1682 (C=O), 1631, 1594, 1578, 1495, 1444, 1258, 1152.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 2.18 (s, 3H, CH_3), 3.87 (s, 3H, OMe), 5.25 (d, *J* = 9.0 Hz, 1H, CH), 5.81 (d, *J* = 9.0 Hz, 1H, NH), 6.08 (s, 1H, =CH), 6.12 (s, 1H, =CH), 6.91 (d, *J* = 9.0 Hz, 2H, PMP), 7.06 (d, *J* = 8.5 Hz, 2H, Ar), 7.18 (d, *J* = 8.5 Hz, 2H, Ar), 7.68 (d, *J* = 9.0 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 26.3 (CH_3), 55.7 (CH), 58.4 (OMe), 114.1 (2*CHPMP), 127.9 (2*CHAr), 128.4 (=CH_2), 128.6 (2*CHAr), 129.3 (2*CHPMP), 132.0 (=Cq), 133.5 (CqAr), 137.5 (CqAr), 146.4 (CqPMP), 162.9 (CqPMP), 198.8 (C=O).

MS (ESI) m/z 402.0, 404.1 $[M+Na]^+$
HRMS (ESI) m/z 402.0541 $[M+Na]^+$, $C_{18}H_{18}NO_4NaS^{35}Cl$ requires 402.0543.
404.0536 $[M+Na]^+$, $C_{18}H_{18}NO_4NaS^{37}Cl$ requires 404.0513.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 85/15, 1mL/mn, 254 nm, 25°C) **e.e.** 94%.



Compound (5f):

A white solid (30.8 mg, >99%).

Formula $C_{18}H_{18}NO_4SBr$ (423.0 g.mol^{-1}).

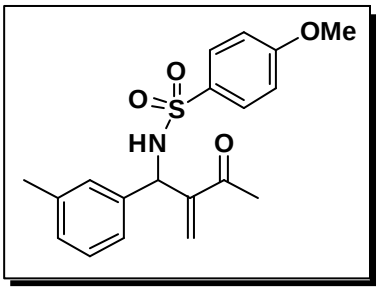
$[\alpha]^{25}_D$ +21.8 (c 1.02, $CHCl_3$). **Melting point** 107-108°C.

IR (cm^{-1}) ν 3368, 3186, 2918, 2848, 1673 (C=O), 1594, 1578, 1496, 1464, 1259, 1155.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 2.20 (s, 3H, CH_3), 3.88 (s, 3H, OMe), 5.24 (d, *J* = 9.0 Hz, 1H, CH), 5.79 (d, *J* = 9.0 Hz, 1H, NH), 6.10 (s, 1H, =CH), 6.15 (s, 1H, =CH), 6.91 (d, *J* = 9.0 Hz, 2H, PMP), 7.09 (m, 2H, Ar), 7.19 (m, 1H, Ar), 7.31 (m, 1H, Ar), 7.69 (d, *J* = 9.0 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 26.3 (CH_3), 55.7 (CH), 58.4 (OMe), 114.1 (2*CHPMP), 122.6 (CqAr), 125.1 (=CH_2), 128.7 (CHAr), 129.4 (2*CHPMP), 129.6 (CHAr), 130.0 (CHAr), 130.7 (CHAr), 132.0 (=Cq), 141.2 (CqAr), 146.1 (CqPMP), 163.0 (CqPMP), 198.7 (C=O).

MS (ESI) m/z 446.0, 448.0 $[M+Na]^+$
HRMS (ESI) m/z 446.0037 $[M+Na]^+$, $C_{18}H_{18}NO_4NaS^{79}Br$ requires 446.0038.
448.0017 $[M+Na]^+$, $C_{18}H_{18}NO_4NaS^{81}Br$ requires 448.0017.
HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 85/15, 1mL/mn, 254 nm, 25°C) **e.e.** 96%.



Compound (5g):

A white solid (26.2 mg, >99%).

Formula $C_{19}H_{21}NO_4S$ (359.1 g.mol^{-1}).

[α]$^{25}_{D}$ +47.3 (c 1.17, $CHCl_3$). **Melting point** 102-103°C.

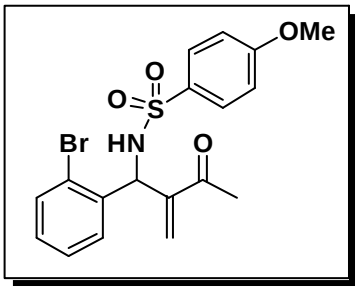
IR (cm^{-1}) ν 3325, 3014, 2968, 2939, 2834, 1673 (C=O), 1594, 1578, 1497, 1462, 1261, 1149.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 2.19 (s, 3H, CH_3), 2.24 (s, 3H, $ArCH_3$), 3.87 (s, 3H, OMe), 5.25 (d, *J* = 8.5 Hz, 1H, CH), 5.63 (m, 1H, NH), 6.12 (s, 1H, =CH), 6.14 (s, 1H, =CH), 6.88 (m, 2H, Ar), 6.92 (d, *J* = 8.5 Hz, 2H, PMP), 7.00 (m, 1H, Ar), 7.10 (m, 1H, Ar), 7.71 (d, *J* = 8.5 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 21.3 ($ArCH_3$), 26.4 (CH_3), 55.6 (CH), 58.7 (OMe), 114.0 (2*CHPMP), 123.4 (CHAr), 127.3 (=CH_2), 128.0 (CHAr), 128.4 (2*CHAr), 129.4 (2*CHPMP), 132.1 (=Cq), 138.2 (CqAr), 138.8 (CqAr), 146.8 (CqPMP), 162.8 (CqPMP), 198.8 (C=O).

MS (ESI) m/z 382.1 $[M+Na]^+$
HRMS (ESI) m/z 382.1096 $[M+Na]^+$, $C_{19}H_{21}NO_4NaS$ requires 382.1089.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 85/15, 1mL/mn, 254 nm, 25°C) **e.e.** 97%.



Compound (5h):

A white solid (30.8 mg, >99%).

Formula $C_{18}H_{18}NO_4SBr$ (423.0 g.mol^{-1}).

[α]$^{25}_{D}$ +15.3 (c 1.06, $CHCl_3$). **Melting point** 115-116°C.

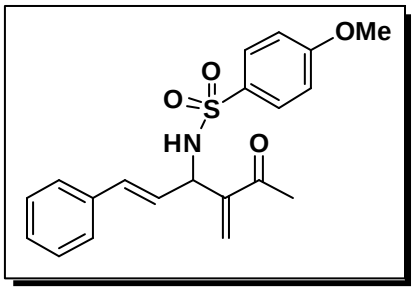
IR (cm^{-1}) ν 3242, 2968, 1676 (C=O), 1594, 1576, 1495, 1259, 1149.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 2.25 (s, 3H, CH_3), 3.84 (s, 3H, OMe), 5.71 (d, *J* = 8.5 Hz, 1H, CH), 5.79 (d, *J* = 8.5 Hz, 1H, NH), 6.15 (s, 1H, =CH), 6.19 (s, 1H, =CH), 6.86 (d, *J* = 9.0 Hz, 2H, PMP), 7.05 (t, *J* = 7.5 Hz, 1H, Ar), 7.17 (t, *J* = 7.5 Hz, 1H, Ar), 7.36 (d, *J* = 7.5 Hz, 1H, Ar), 7.44 (d, *J* = 7.5 Hz, 1H, Ar), 7.70 (d, *J* = 9.0 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 26.5 (CH_3), 55.6 (CH), 57.8 (OMe), 114.0 (2*CHPMP), 123.2 (CqAr), 127.5 (=CH_2), 129.1 (CHAr), 129.4 (2*CHPMP, 2*CHAr), 131.8 (=Cq), 133.1 (CHAr), 137.6 (CqAr), 145.7 (CqPMP), 162.8 (CqPMP), 198.9 (C=O).

MS (ESI) m/z 446.0, 448.0 $[M+Na]^+$
HRMS (ESI) m/z 446.0033 $[M+Na]^+$, $C_{18}H_{18}NO_4NaS^{79}Br$ requires 446.0038.
448.0020 $[M+Na]^+$, $C_{18}H_{18}NO_4NaS^{81}Br$ requires 448.0017.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 85/15, 1mL/mn, 254 nm, 25°C) **e.e.** 98%.



Compound (5i):

A white solid (23.1 mg, 85%).

Formula $C_{20}H_{21}NO_4S$ (371.1 g.mol^{-1}).

[α]$^{25}_{D}$ +8.2 (c 1.08, $CHCl_3$). **Melting point** 102-103°C.

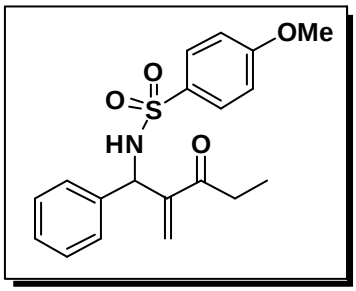
IR (cm^{-1}) ν 3277, 3020, 2964, 2838, 1668 (C=O), 1595, 1578, 1496, 1462, 1260, 1152.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 2.23 (s, 3H, CH_3), 3.79 (s, 3H, OMe), 4.79 (t, *J* = 9.0 Hz, 1H, CH), 5.63 (d, *J* = 9.0 Hz, 1H, NH), 6.00 (s, 1H, =CH), 6.02 (t, *J* = 9.0 Hz, 1H, CH), 6.03 (s, 1H, =CH), 6.31 (d, *J* = 9.0 Hz, 1H, =CH), 6.89 (d, *J* = 8.5 Hz, 2H, PMP), 7.19 (m, 2H, Ar), 7.25 (m, 3H, Ar), 7.75 (d, *J* = 8.5 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 26.3 (CH_3), 55.5 (CH), 58.7 (OMe), 114.0 (2*CHPMP), 126.5 (2*CHAr), 127.2 (=CH), 127.9 (=CH_2), 128.1 (CHAr), 128.5 (2*CHAr), 129.5 (2*CHPMP), 132.0 (=CH), 132.5 (=Cq), 136.0 (CqAr), 146.4 (CqPMP), 162.8 (CqPMP), 199.2 (C=O).

MS (ESI) m/z 394.1 $[M+Na]^+$
HRMS (ESI) m/z 394.1089 $[M+Na]^+$, $C_{20}H_{21}NO_4NaS$ requires 394.1089.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 85/15, 1mL/mn, 254 nm, 25°C) **e.e.** 96%.



Compound (5j):

A white solid (26.2 mg, >99%).

Formula $C_{19}H_{21}NO_4S$ (359.1 g.mol^{-1}).

[α]$^{25}_{D}$ +29.6 (c 1.08, $CHCl_3$). **Melting point** 82-83°C.

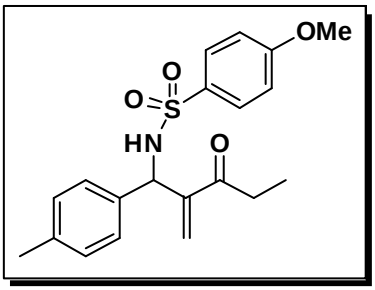
IR (cm^{-1}) ν 3281, 2937, 1673 (C=O), 1596, 1579, 1496, 1454, 1257, 1152.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 0.95 (t, *J* = 7.5 Hz, 3H, CH_3), 2.54 (m, 2H, CH_2), 3.86 (s, 3H, OMe), 5.29 (d, *J* = 8.5 Hz, 1H, CH), 5.75 (d, *J* = 8.5 Hz, 1H, NH), 6.06 (s, 1H, =CH), 6.12 (s, 1H, =CH), 6.90 (d, *J* = 8.5 Hz, 2H, PMP), 7.11 (m, 2H, Ar), 7.22 (m, 3H, Ar), 7.71 (d, *J* = 8.5 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 7.8 (CH_3), 31.4 (CH_2), 55.6 (CH), 59.1 (OMe), 114.0 (2*CHPMP), 126.4 (2*CHAr), 126.8 (CHAr), 127.6 (=CH_2), 128.5 (2*CHAr), 129.4 (2*CHPMP), 132.2 (=Cq), 139.0 (CqAr), 146.2 (CqPMP), 162.8 (CqPMP), 201.6 (C=O).

MS (ESI) m/z 382.2 $[M+Na]^+$
HRMS (ESI) m/z 382.1075 $[M+Na]^+$, $C_{19}H_{21}NO_4NaS$ requires 382.1089.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 90/10, 0.9 mL/mn, 254 nm, 15°C) **e.e.** 98%.



Compound (5k):

A white solid (27.2 mg, >99%).

Formula $C_{20}H_{23}NO_4S$ (373.1 g.mol^{-1}).

[α]$^{25}_{D}$ +47.4 (c 0.84, $CHCl_3$). **Melting point** 96-97°C.

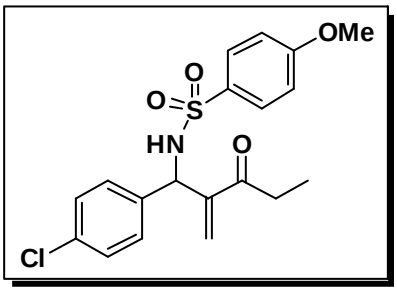
IR (cm^{-1}) ν 3225, 2935, 1682 (C=O), 1594, 1578, 1496, 1443, 1257, 1157.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 0.96 (t, *J* = 7.0 Hz, 3H, CH_3), 2.28 (s, 3H, $ArCH_3$), 2.55 (m, 2H, CH_2), 3.87 (s, 3H, OMe), 5.25 (d, *J* = 8.5 Hz, 1H, CH), 5.64 (d, *J* = 8.5 Hz, 1H, NH), 6.08 (s, 1H, =CH), 6.12 (s, 1H, =CH), 6.91 (d, *J* = 9.0 Hz, 2H, PMP), 6.99 (d, *J* = 8.0 Hz, 2H, Ar), 7.03 (d, *J* = 8.0 Hz, 2H, Ar), 7.72 (d, *J* = 9.0 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 7.8 (CH_3), 21.0 ($ArCH_3$), 31.4 (CH_2), 55.6 (CH), 58.9 (OMe), 114.0 (2*CHPMP), 126.4 (2*CHAr), 126.6 (=CH_2), 129.2 (2*CHAr), 129.4 (2*CHPMP), 132.1 (=Cq), 136.1 (CqAr), 137.4 (CqAr), 146.3 (CqPMP), 162.8 (CqPMP), 201.6 (C=O).

MS (ESI) m/z 396.1 $[M+Na]^+$
HRMS (ESI) m/z 396.1245 $[M+Na]^+$, $C_{20}H_{23}NO_4NaS$ requires 396.1245.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 90/10, 0.9 mL/mn, 254 nm, 15°C) **e.e.** 98%.



Compound (5l):

A white solid (28.6 mg, >99%).

Formula $C_{19}H_{20}NO_4SCl$ (393.1 g.mol^{-1}).

[α]$^{25}_{D}$ +30.8 (c 0.84, $CHCl_3$). **Melting point** 86-87°C.

IR (cm^{-1}) ν 3277, 2977, 2940, 2841, 1674 (C=O), 1595, 1579, 1494, 1457, 1258, 1151.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 0.95 (t, *J* = 7.0 Hz, 3H, CH_3), 2.53 (m, 2H, CH_2), 3.87 (s, 3H, OMe), 5.25 (d, *J* = 8.5 Hz, 1H, CH), 5.83 (d, *J* = 8.5 Hz, 1H, NH), 6.04 (s, 1H, =CH), 6.11 (s, 1H, =CH), 6.90 (d, *J* = 9.0 Hz, 2H, PMP), 7.07 (d, *J* = 8.5 Hz, 2H, Ar), 7.18 (d, *J* = 8.5 Hz, 2H, Ar), 7.68 (d, *J* = 9.0 Hz, 2H, PMP).

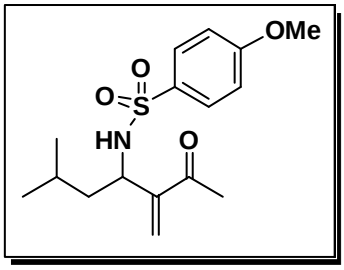
^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 7.8 (CH_3), 31.4 (CH_2), 55.7 (CH), 58.8 (OMe), 114.0 (2*CHPMP), 127.2 (=CH_2), 127.9 (2*CHAr), 128.6 (2*CHAr), 129.4 (2*CHPMP), 132.0 (=Cq), 133.4 (CqAr), 137.6 (CqAr), 145.8 (CqPMP), 162.9 (CqPMP), 201.5 (C=O).

MS (ESI) m/z 416.1 $[M+Na]^+$
HRMS (ESI) m/z 416.0705 $[M+Na]^+$, $C_{19}H_{20}NO_4NaS^{35}Cl$ requires 416.0699.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 85/15, 1 mL/mn, 254 nm, 25°C) **e.e.** 97%.

IV] General procedure of aza-MBH reactions involving aliphatic imines:

To a solution of corresponding imine freshly prepared (0.073 mmol, 1 eq) in dried dichloromethane at 0°C, catalyst **(1e)** (3.7 mg, 0.0073 mmol, 0.1 eq), β-naphthol (1.1 mg, 0.0073 mmol, 0.1 eq), alkylvinylketone (0.15 mmol, 2 eq) and 50 mg of molecular sieves were added. The reaction mixture was stirred under argon atmosphere at 0°C for 12 hours. The reaction was stopped by passing the mixture through a short pad of silica gel using ethyle acetate for the elution. Solvents were removed in vacuo and the residue was purified by flash chromatography on silica gel (*n*-Hept/EtOAc 90/10) to afford the corresponding pure product.



Compound (5m):

A white solid (14.1 mg, 59%).

Formula $C_{16}H_{23}NO_4S$ (325.1 g.mol^{-1}).

$[\alpha]^{25}_D$ +4.8 (c 1.02, $CHCl_3$). **Melting point** 105-106°C.

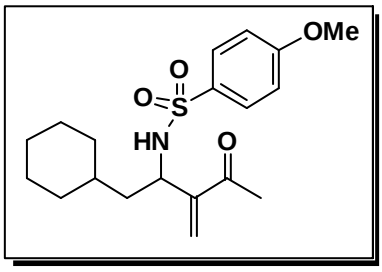
IR (cm^{-1}) ν 3242, 3074, 2950, 2866, 1673 (C=O), 1596, 1579, 1499, 1462, 1260, 1145.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 0.82 (d, *J* = 6.0 Hz, 3H, CH_3), 0.85 (d, *J* = 6.0 Hz, 3H, CH_3), 1.31 (m, 1H, CH), 1.57 (m, 2H, CH_2), 2.09 (s, 3H, CH_3), 3.87 (s, 3H, OMe), 4.05 (m, 1H, CH), 5.41 (d, *J* = 9.5 Hz, 1H, NH), 5.75 (s, 1H, =CH), 5.83 (s, 1H, =CH), 6.92 (d, *J* = 8.5 Hz, 2H, PMP), 7.70 (d, *J* = 8.5 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 21.7 (CH_3), 22.5 (CH_3), 24.7 (CH), 26.3 (CH_3), 44.5 (CH_2), 55.5 (CH), 55.6 (OMe), 113.9 (2*CHPMP), 127.6 (=CH_2), 129.4 (2*CHPMP), 132.8 (=Cq), 147.0 (CqPMP), 162.6 (CqPMP), 199.6 (C=O).

MS (ESI) m/z 348.2 $[M+Na]^+$
HRMS (ESI) m/z 348.1234 $[M+Na]^+$, $C_{16}H_{23}NO_4NaS$ requires 348.1245.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 85/15, 0.8 mL/mn, 254 nm, 10°C) **e.e.** 81%.



Compound (5n):

A white solid (18.9 mg, 71%).

Formula $C_{19}H_{27}NO_4S$ (365.2 g.mol^{-1}).

$[\alpha]^{25}_D$ +2.7 (c 1.04, $CHCl_3$). **Melting point** 110-112°C.

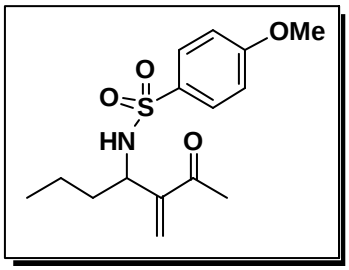
IR (cm^{-1}) ν 3194, 2925, 2843, 1654 (C=O), 1596, 1579, 1498, 1462, 1256, 1150.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 0.80 (m, 2H, CH_2), 1.19 (m, 5H, 2*CH_2, CH), 1.55 (m, 6H, 3*CH_2), 2.10 (s, 3H, CH_3), 3.86 (s, 3H, OMe), 4.09 (m, 1H, CH), 5.42 (d, *J* = 9.5 Hz, 1H, NH), 5.78 (s, 1H, =CH), 5.86 (s, 1H, =CH), 6.92 (d, *J* = 9.0 Hz, 2H, PMP), 7.70 (d, *J* = 9.0 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 26.0 (CH_2), 26.1 (CH_2), 26.3 (CH_3), 26.4 (CH_2), 32.3 (CH_2), 33.3 (CH_2), 34.0 (CH_2), 43.2 (CH_2), 54.2 (CH), 55.6 (OMe), 113.9 (2*CHPMP), 127.4 (=CH_2), 129.4 (2*CHPMP), 132.6 (=Cq), 147.4 (CqPMP), 162.7 (CqPMP), 199.5 (C=O).

MS (ESI) m/z 388.2 $[M+Na]^+$
HRMS (ESI) m/z 388.1561 $[M+Na]^+$, $C_{19}H_{27}NO_4NaS$ requires 388.1559.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 90/10, 0.8 mL/mn, 254 nm, 10°C) **e.e.** 85%.



Compound (5o):

A white solid (9.5 mg, 42%).

Formula $C_{15}H_{21}NO_4S$ (311.1 g.mol^{-1}).

$[\alpha]^{25}_D$ -2.3 (c 0.96, $CHCl_3$). **Melting point** 90-91°C.

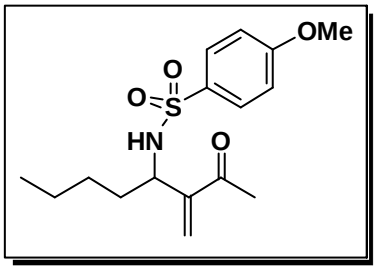
IR (cm^{-1}) ν 3258, 2962, 2926, 2874, 1678 (C=O), 1596, 1579, 1498, 1446, 1259, 1154.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 0.84 (t, *J* = 7.5 Hz, 3H, CH_3), 1.24 (m, 2H, CH_2), 1.56 (m, 2H, CH_2), 2.10 (s, 3H, CH_3), 3.87 (s, 3H, OMe), 3.96 (m, 1H, CH), 5.43 (d, *J* = 10.0 Hz, 1H, NH), 5.74 (s, 1H, =CH), 5.86 (s, 1H, =CH), 6.92 (d, *J* = 9.0 Hz, 2H, PMP), 7.70 (d, *J* = 9.0 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 13.4 (CH_3), 19.5 (CH_2), 26.3 (CH_3), 37.4 (CH_2), 55.6 (CH), 57.0 (OMe), 113.9 (2*CHPMP), 127.8 (=CH_2), 129.4 (2*CHPMP), 132.8 (=Cq), 146.7 (CqPMP), 162.6 (CqPMP), 199.6 (C=O).

MS (ESI) m/z 334.1 $[M+Na]^+$
HRMS (ESI) m/z 334.1095 $[M+Na]^+$, $C_{15}H_{21}NO_4NaS$ requires 334.1089.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 90/10, 1 mL/mn, 254 nm, 25°C) **e.e.** 90%.



Compound (5p):

A white solid (10.9 mg, 46%).

Formula $C_{16}H_{23}NO_4S$ (325.1 g.mol^{-1}).

$[\alpha]^{25}_D$ +0.9 (c 0.94, $CHCl_3$). **Melting point** 81-82°C.

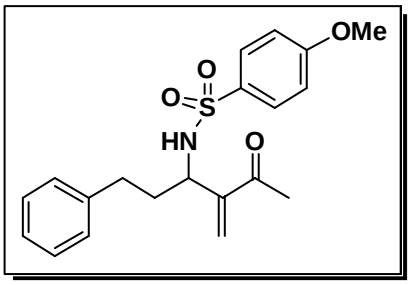
IR (cm^{-1}) ν 3241, 2955, 2868, 1661 (C=O), 1595, 1577, 1496, 1459, 1256, 1146.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 0.83 (t, *J* = 7.0 Hz, 3H, CH_3), 1.17 (m, 2H, CH_2), 1.23 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 2.10 (s, 3H, CH_3), 3.87 (s, 3H, OMe), 3.95 (m, 1H, CH), 5.44 (d, *J* = 9.5 Hz, 1H, NH), 5.74 (s, 1H, =CH), 5.86 (s, 1H, =CH), 6.92 (d, *J* = 8.5 Hz, 2H, PMP), 7.70 (d, *J* = 8.5 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 13.9 (CH_3), 22.0 (CH_2), 26.3 (CH_3), 28.4 (CH_2), 35.0 (CH_2), 55.6 (CH), 57.2 (OMe), 113.9 (2*CHPMP), 127.8 (=CH_2), 129.4 (2*CHPMP), 132.8 (=Cq), 146.8 (CqPMP), 162.7 (CqPMP), 199.6 (C=O).

MS (ESI) m/z 348.1 $[M+Na]^+$
HRMS (ESI) m/z 348.1247 $[M+Na]^+$, $C_{16}H_{23}NO_4NaS$ requires 348.1245.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 90/10, 0.8 mL/mn, 254 nm, 10°C) **e.e.** 92%.



Compound (5q):

A white solid (9.8 mg, 36%).

Formula $C_{20}H_{23}NO_4S$ (373.1 g.mol^{-1}).

$[\alpha]^{25}_D$ +6.6 (c 0.98, $CHCl_3$). **Melting point** 113-114°C.

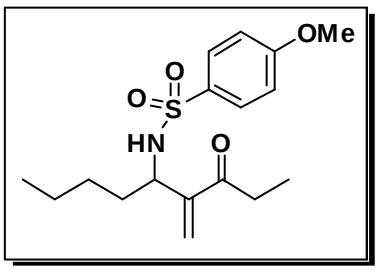
IR (cm^{-1}) ν 3268, 3024, 2938, 2841, 1678 (C=O), 1594, 1578, 1496, 1455, 1263, 1162.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 1.93 (m, 2H, CH_2), 2.08 (s, 3H, CH_3), 2.59 (m, 2H, $ArCH_2$), 3.87 (s, 3H, OMe), 4.00 (m, 1H, CH), 5.58 (d, *J* = 10.0 Hz, 1H, NH), 5.71 (s, 1H, =CH), 5.85 (s, 1H, =CH), 6.92 (d, *J* = 9.0 Hz, 2H, PMP), 7.10 (m, 2H, Ar), 7.19 (m, 1H, Ar), 7.26 (m, 2H, Ar), 7.70 (d, *J* = 9.0 Hz, 2H, PMP).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 26.3 (CH_3), 32.4 ($ArCH_2$), 36.8 (CH_2), 55.6 (CH), 57.1 (OMe), 114.0 (2*CHPMP), 126.0 (CHAr), 128.3 (=CH_2), 128.4 (4*CHAr), 129.4 (2*CHPMP), 132.7 (=Cq), 140.8 (CqAr), 146.4 (CqPMP), 162.7 (CqPMP), 199.7 (C=O).

MS (ESI) m/z 396.1 $[M+Na]^+$
HRMS (ESI) m/z 396.1244 $[M+Na]^+$, $C_{20}H_{23}NO_4NaS$ requires 396.1245.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 75/25, 0.8 mL/mn, 254 nm, 10°C) **e.e.** 93%.



Compound (5r):

A colorless oil (9.2 mg, 37%).

Formula $C_{17}H_{25}NO_4S$ (339.2 g.mol^{-1}).

$[\alpha]^{25}_D$ -2.2 (c 0.92, $CHCl_3$).

IR (cm^{-1}) ν 3292, 2956, 2934, 2878, 1673 (C=O), 1596, 1579, 1497, 1459, 1256, 1147.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 0.83 (t, *J* = 7.0 Hz, 3H, CH_3), 0.98 (t, *J* = 7.5 Hz, 3H, CH_3), 1.17 (m, 4H, 2*CH_2), 1.59 (m, 2H, CH_2), 2.43 (m, 2H, CH_2), 3.87 (s, 3H, OMe), 3.94

(m, 1H, CH), 5.45 (d, *J* = 9.5 Hz, 1H, NH), 5.70 (s, 1H, =CH), 5.85 (s, 1H, =CH), 6.92 (d, *J* = 9.0 Hz, 2H, PMP), 7.69 (d, *J* = 9.0 Hz, 2H, PMP).

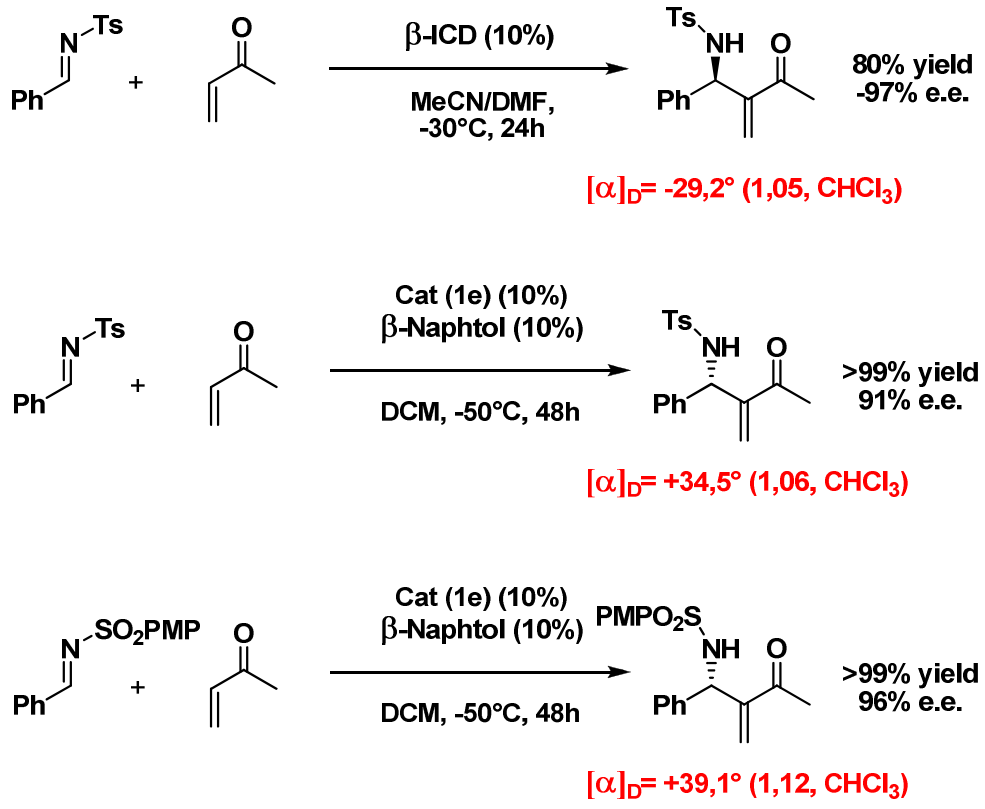
^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 7.9 (CH_3), 13.9 (CH_3), 22.0 (CH_2), 28.4 (CH_2), 31.3 (CH_2), 35.0 (CH_2), 55.6 (CH), 57.6 (OMe), 113.8 (2*CHPMP), 126.5 (=CH_2), 129.4 (2*CHPMP), 132.8 (=Cq), 146.1 (CqPMP), 162.6 (CqPMP), 202.3 (C=O).

MS (ESI) m/z 362.1 $[M+Na]^+$
HRMS (ESI) m/z 362.1401 $[M+Na]^+$, $C_{17}H_{25}NO_4NaS$ requires 362.1402.

HPLC analysis Chiralpak AD-H (*n*-Hept/*i*PrOH 90/10, 0.8 mL/mn, 254 nm, 10°C) **e.e.** 93%.

V] Absolute configuration assignments of aza-MBH adducts (5):

By comparison of the optical rotation with the literature value[7], the absolute configuration was determined to be (*S*) (Scheme 2).

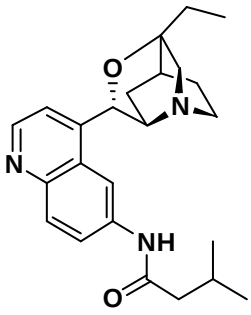


Scheme 2

VI] ^{1}H and ^{13}C NMR data of compounds 1(c) to 5(r)

[7] Shi, M.; Xu, Y.-M. *Angew. Chem. Int. Ed.* **2002**, *41*, 4507-4510.

Compound 1c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NH
O

ppm
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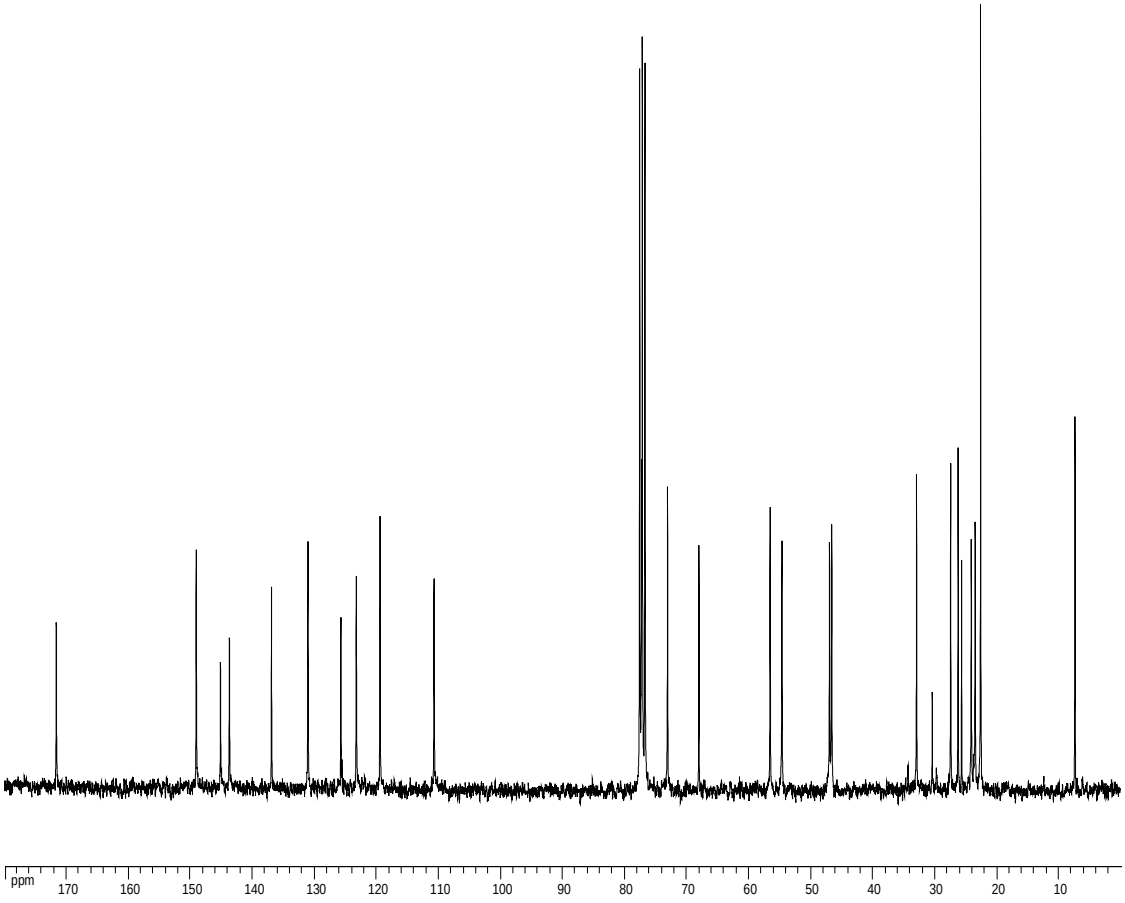
7
6
5
4
3
2
1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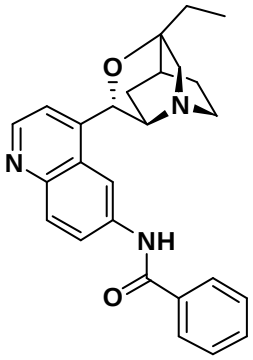
30
20
10

Compound 1d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NH
O

ppm
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6
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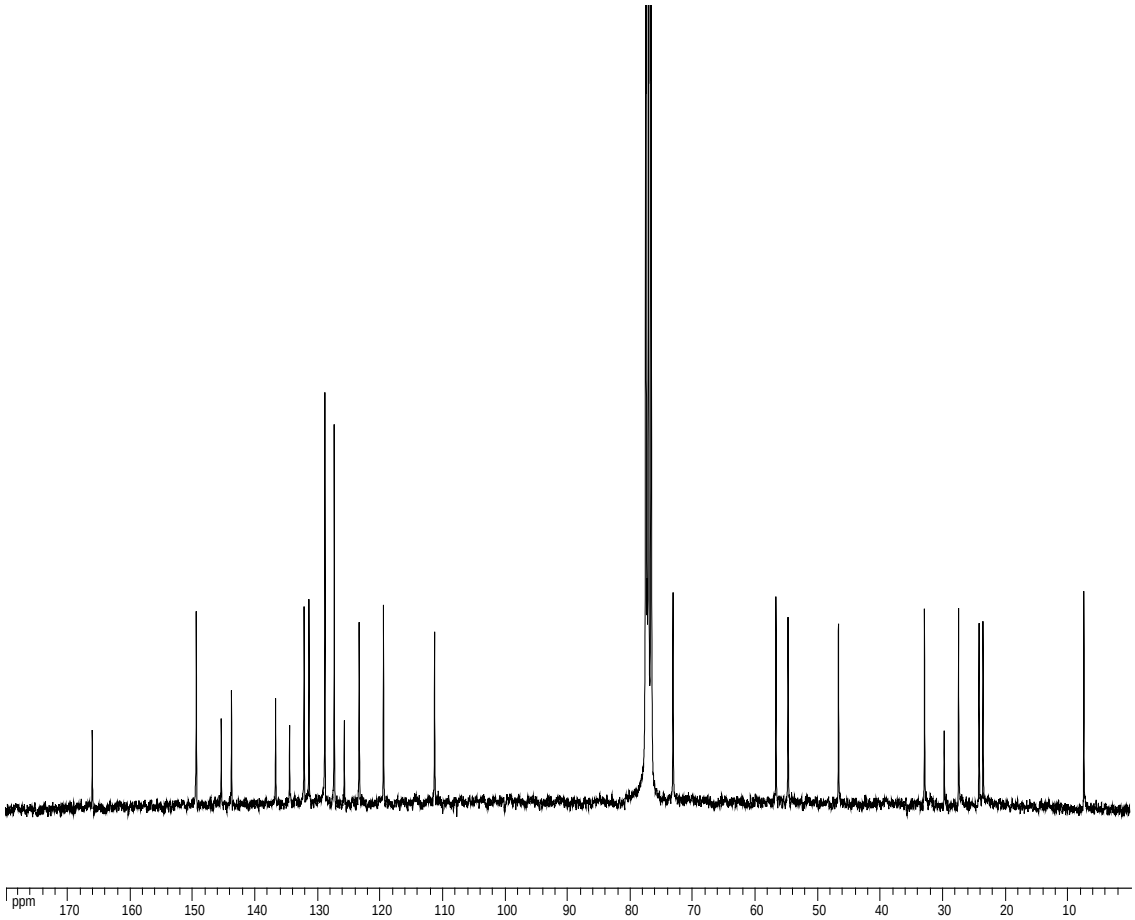
4
3
2
1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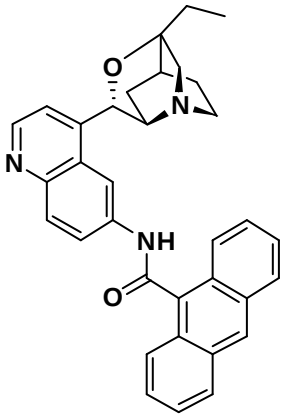
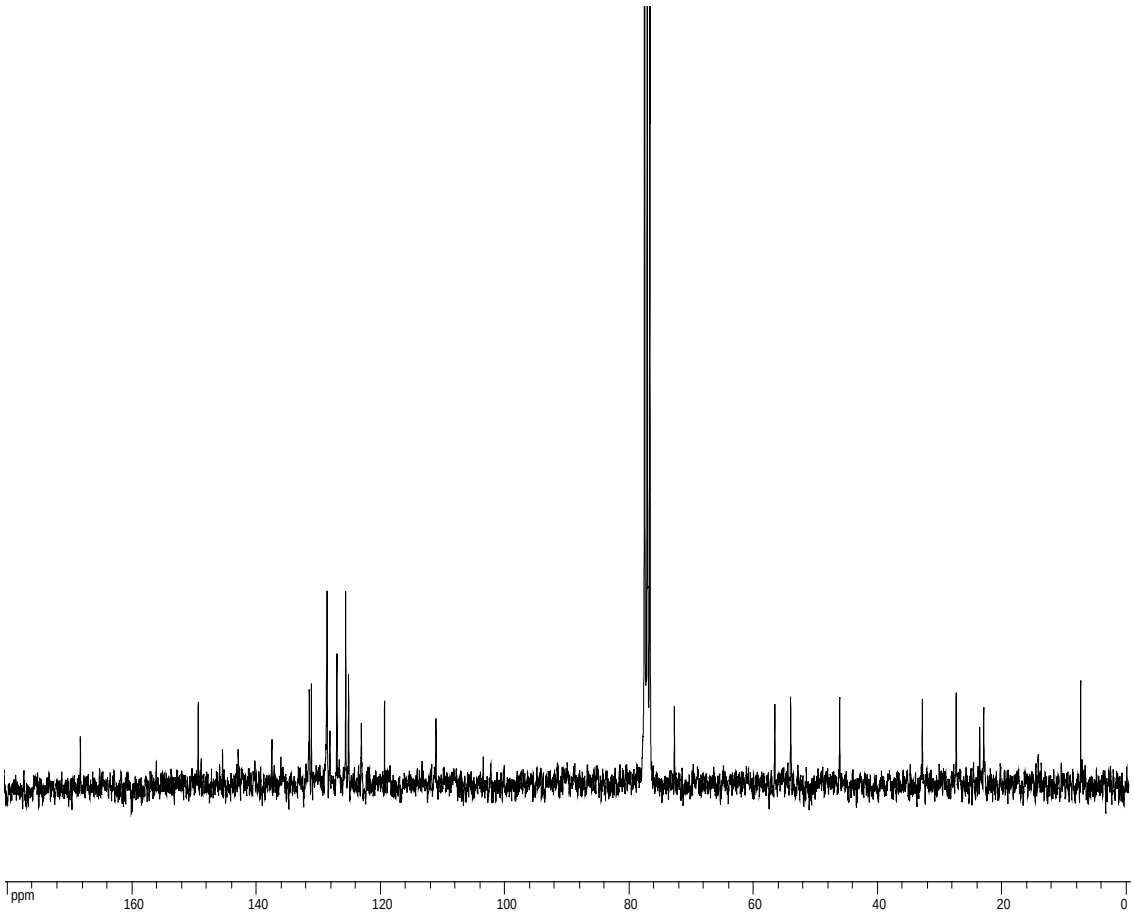
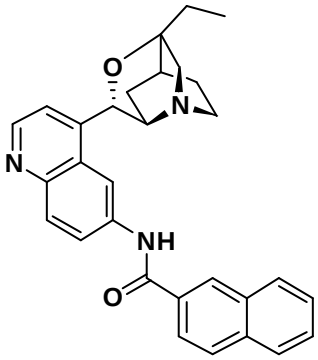
40
30
20
10

Compound 1e





Compound 1f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N
NH
O

ppm
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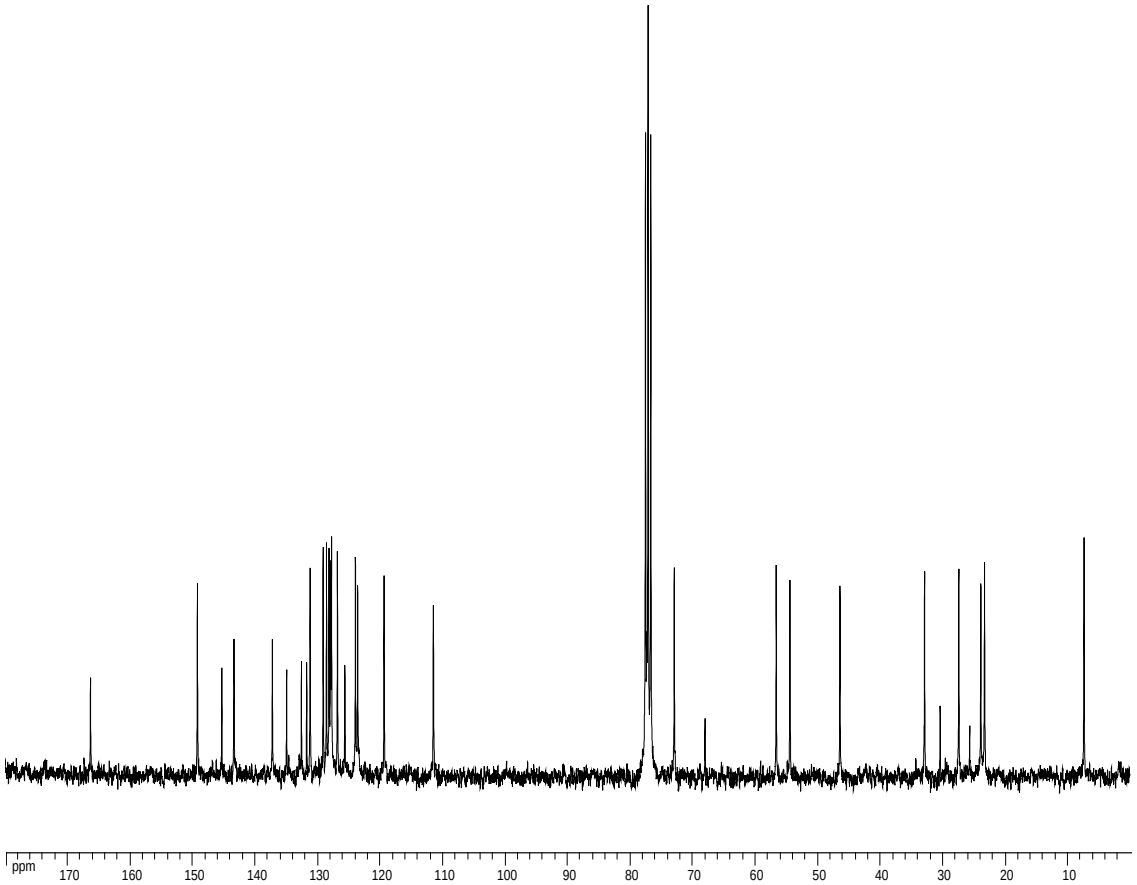
7
6
5
4
3
2
1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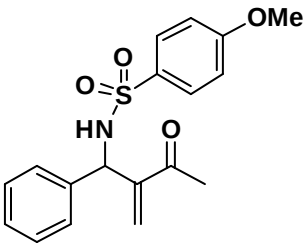
OMe
O
O
S
HN
O

Compound 5a

ppm
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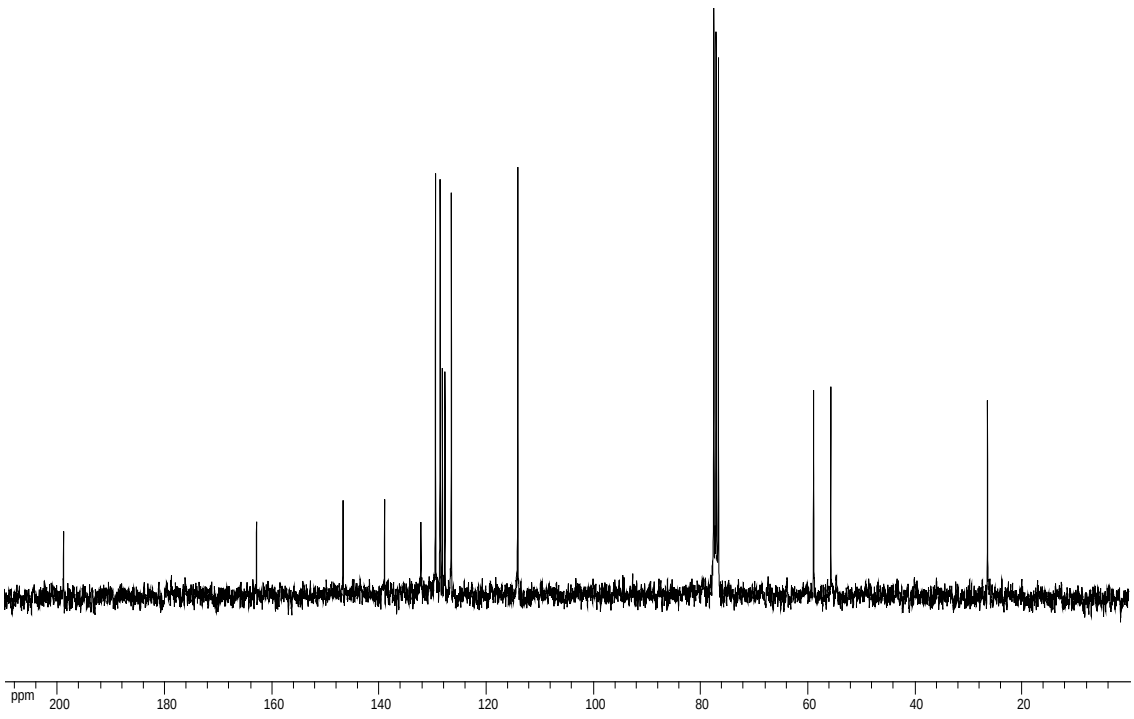
6
5
4
3
2
1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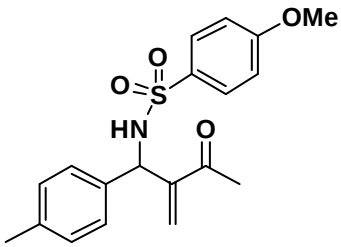
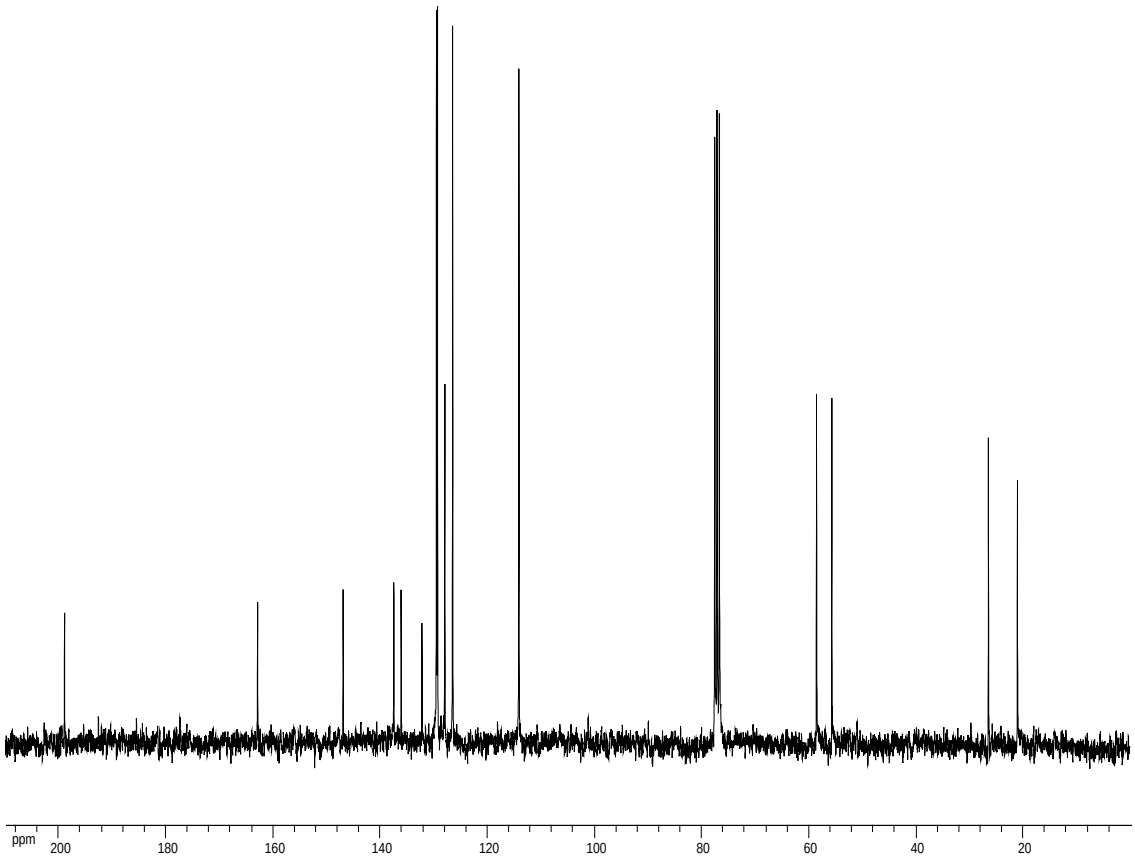
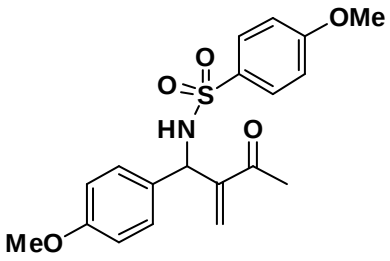


Compound 5b



Compound 5c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S
HN
O
MeO

ppm
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4
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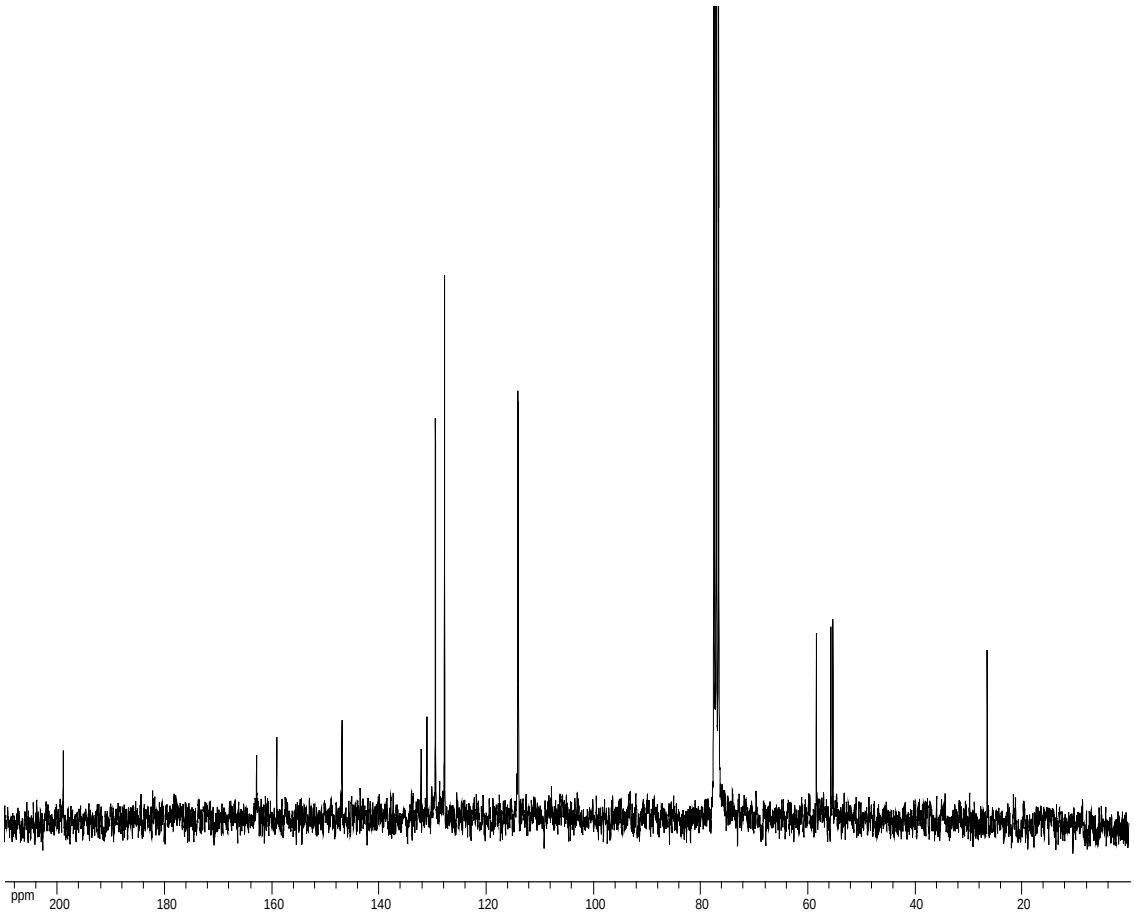
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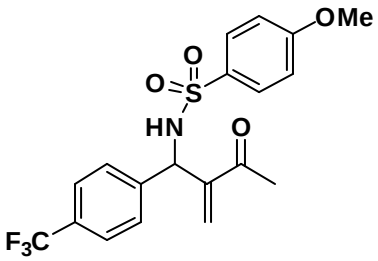
OMe
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O
S
HN
O
F3C

Compound 5d

ppm
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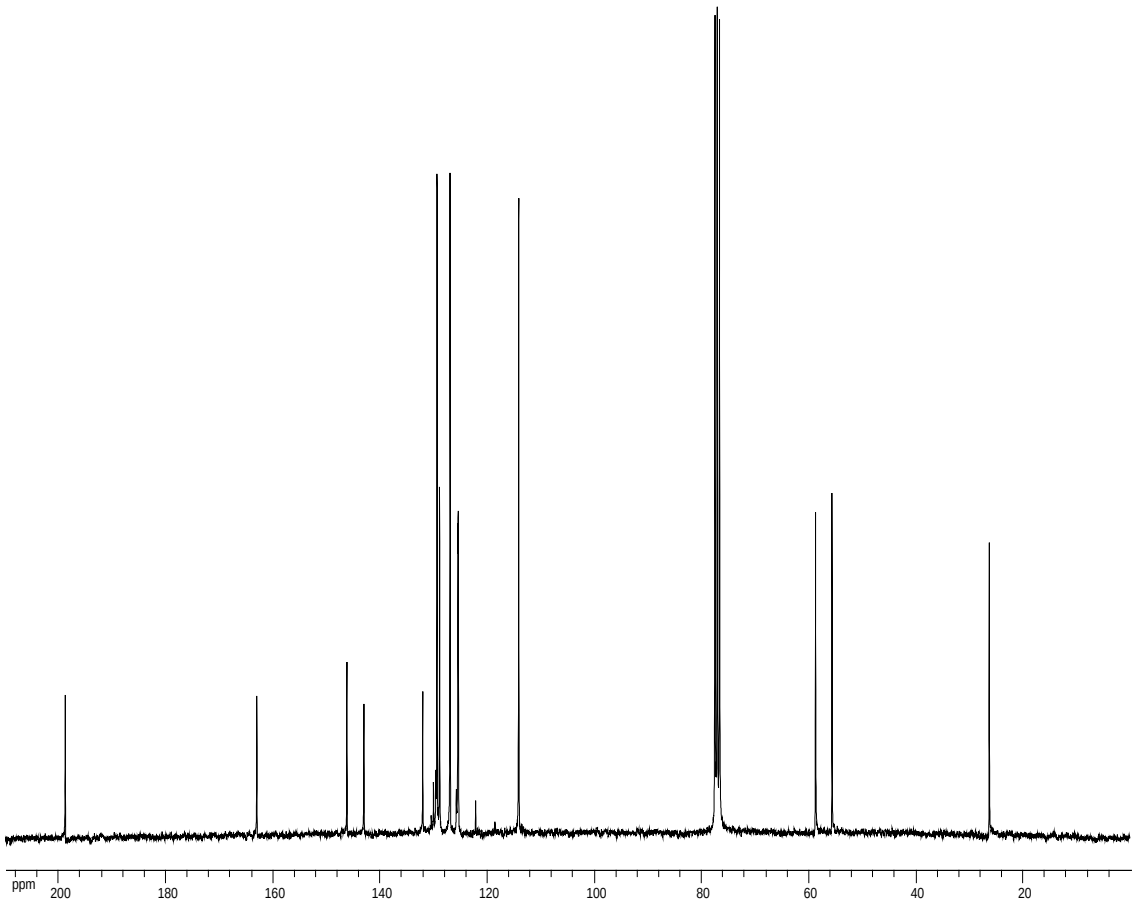
5
4
3
2
1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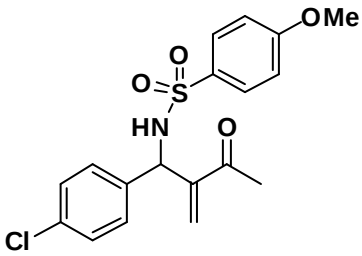
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O
S
HN
O
Cl

Compound 5e

ppm
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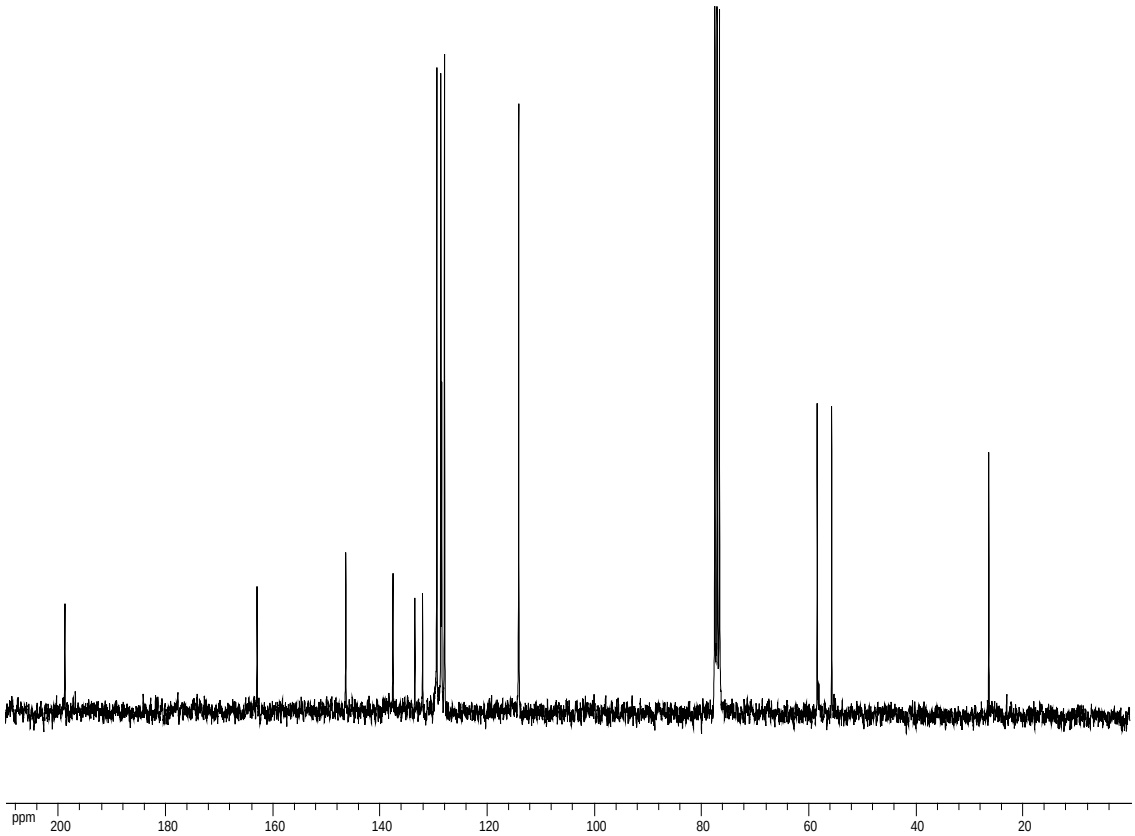
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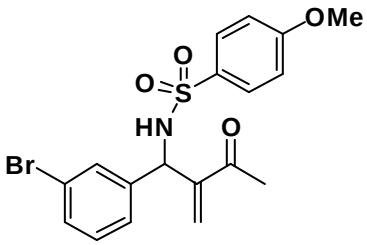
OMe
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O
S
HN
O
Br

Compound 5f

ppm
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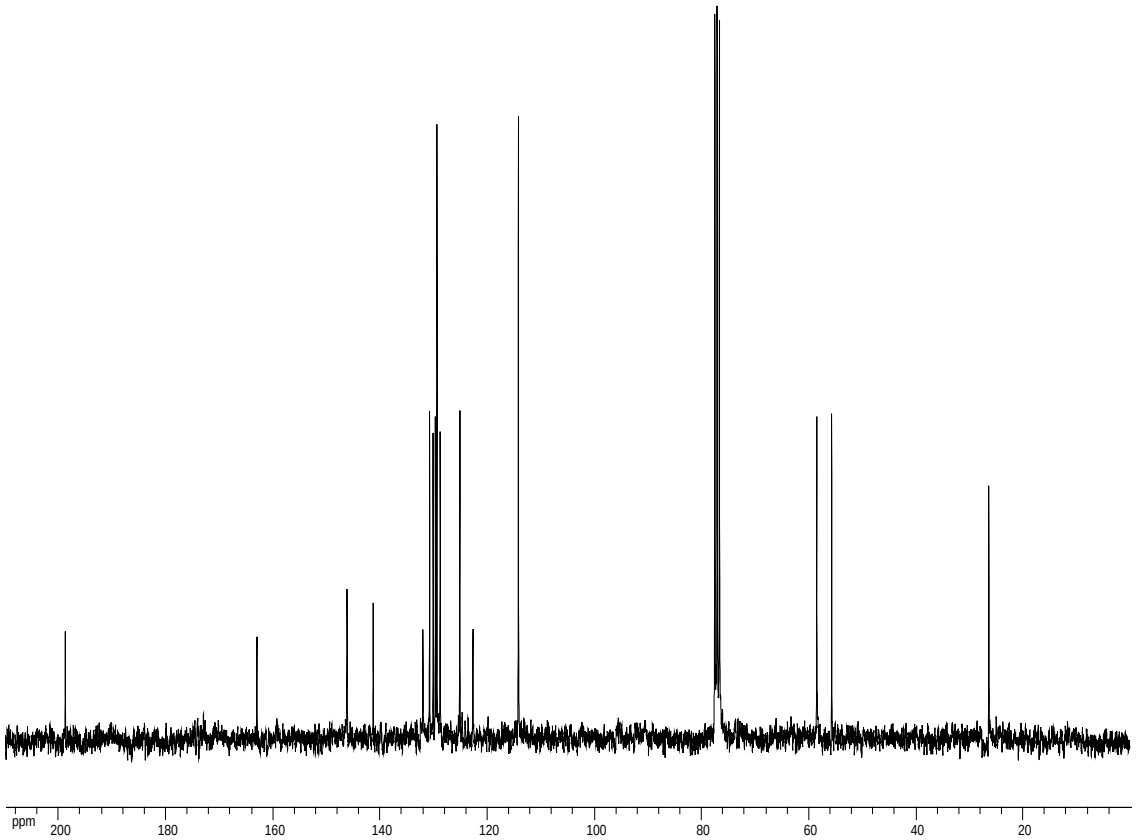
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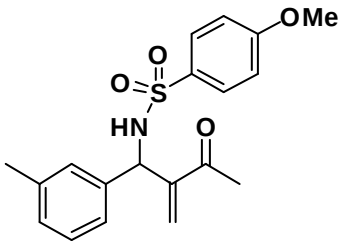
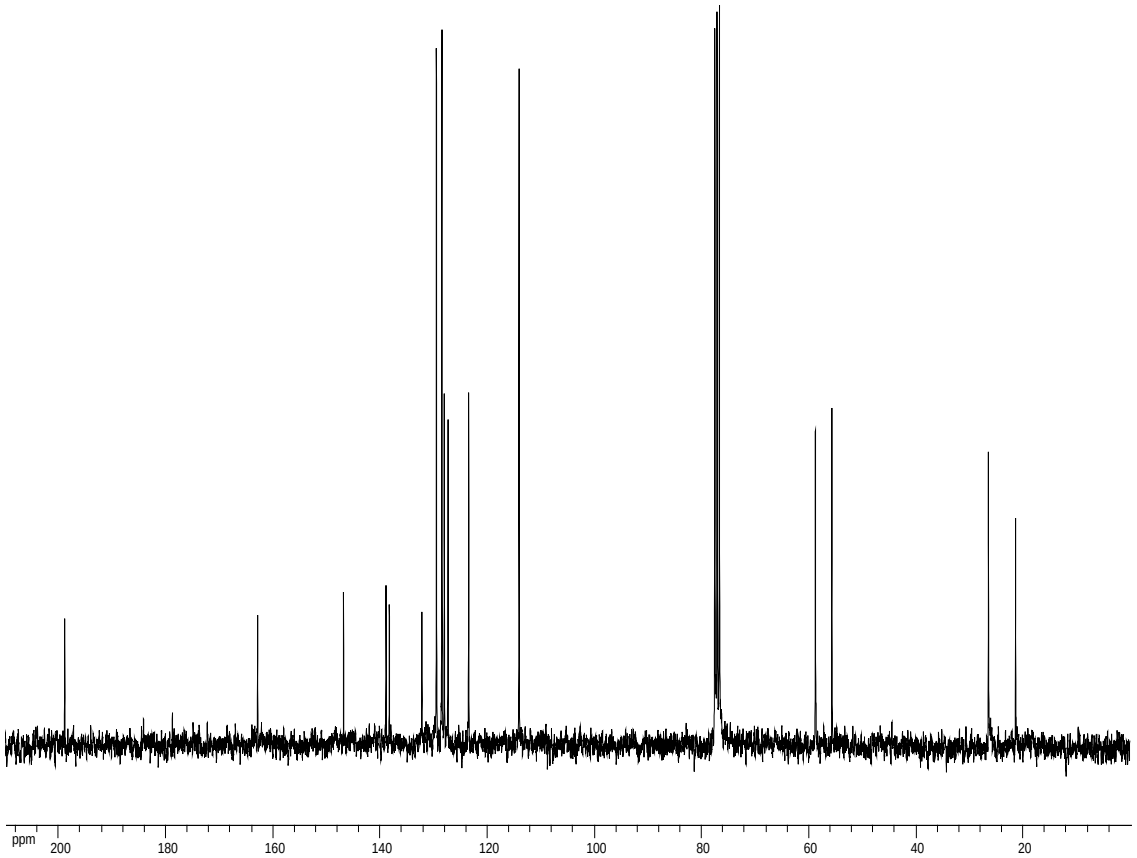
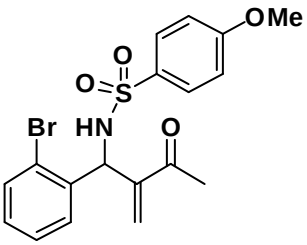


Compound 5g




OMe
O
O
S
Br
HN
O

Compound

5h

ppm
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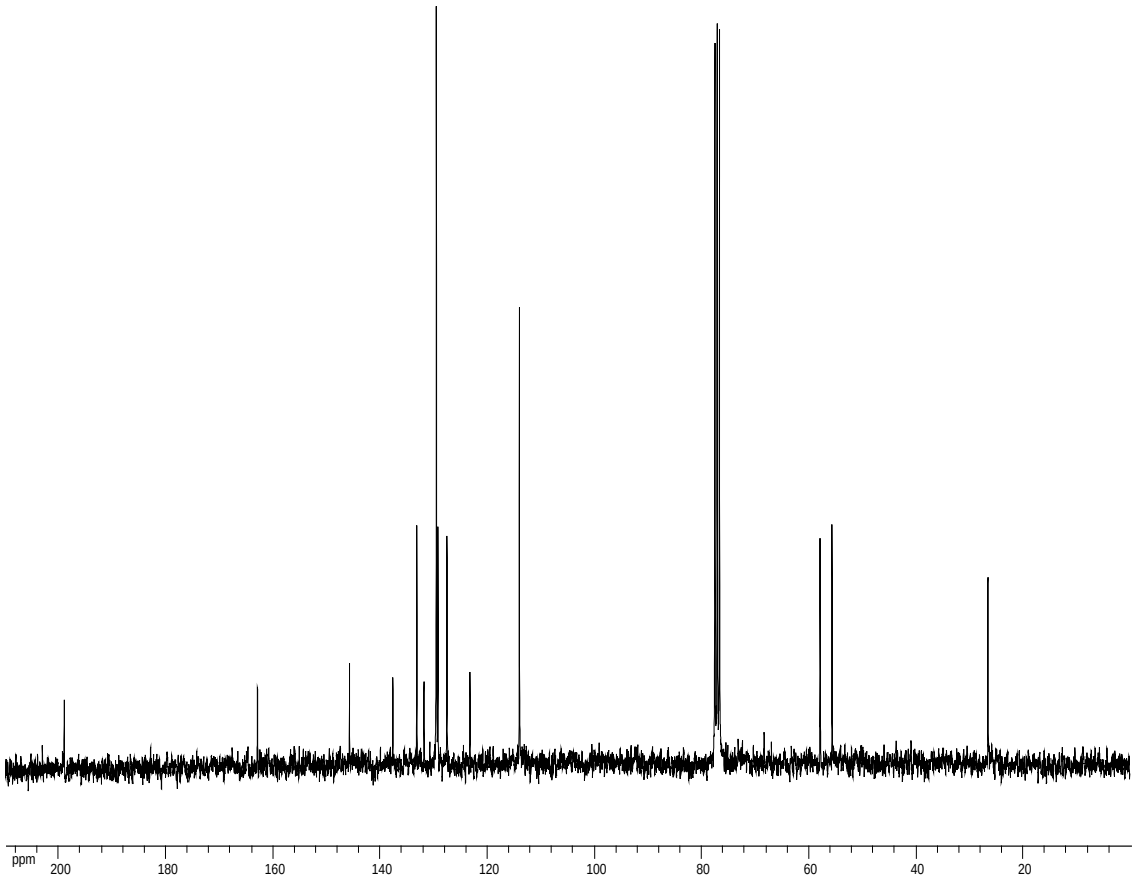
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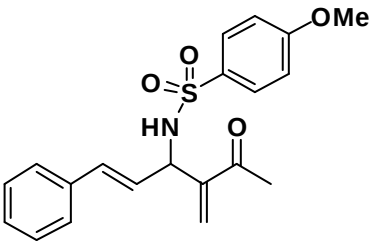
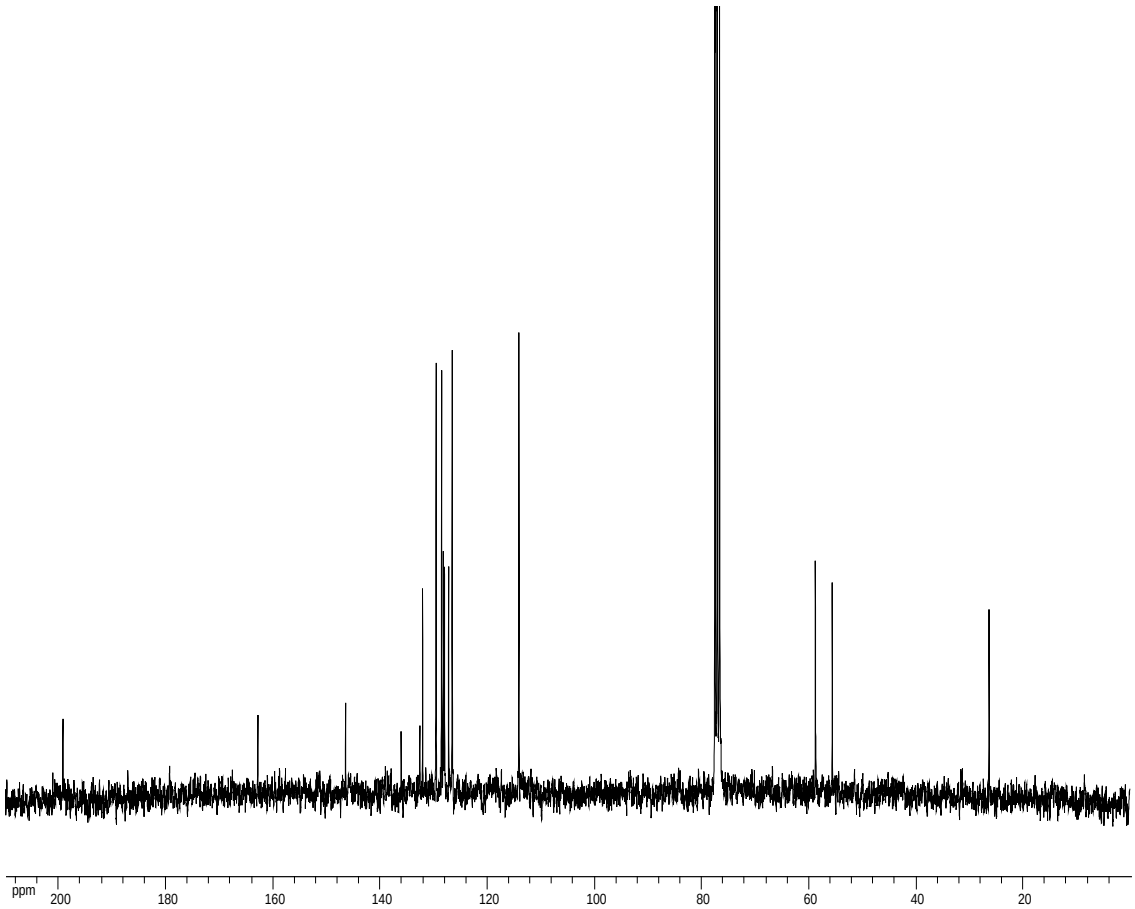
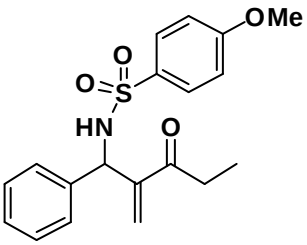
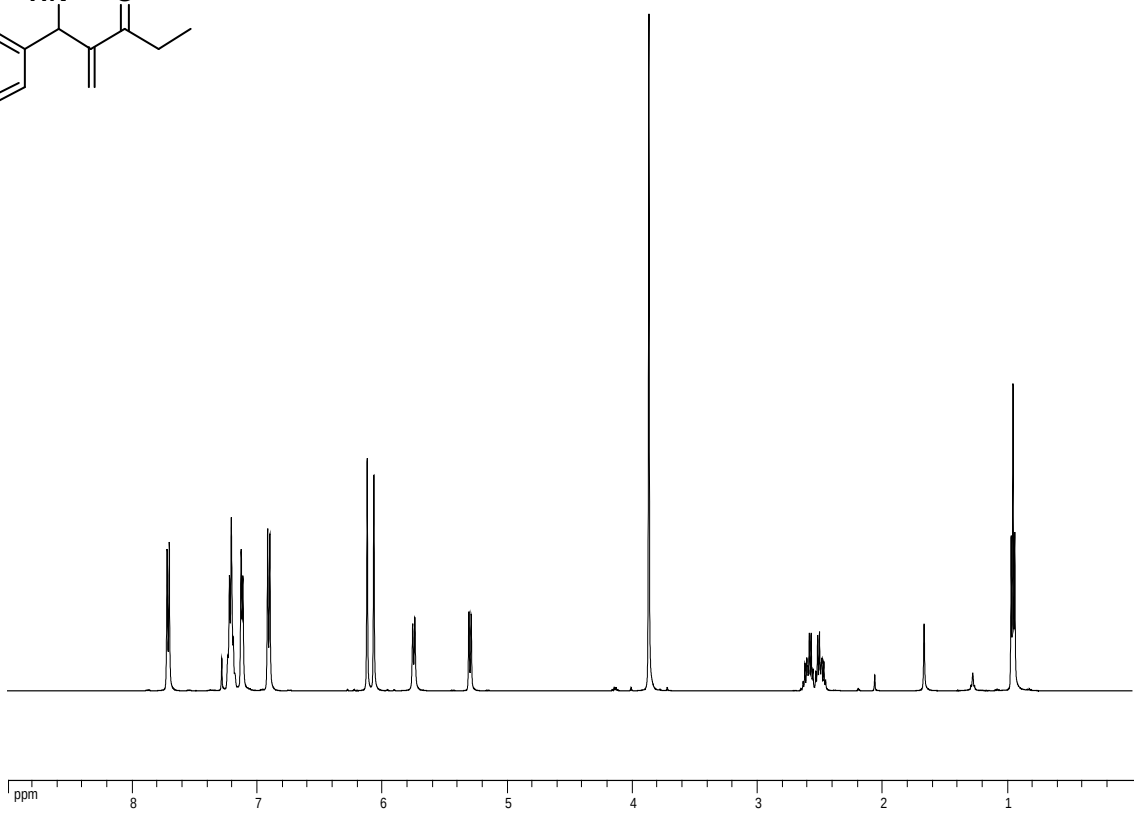


Compound 5i

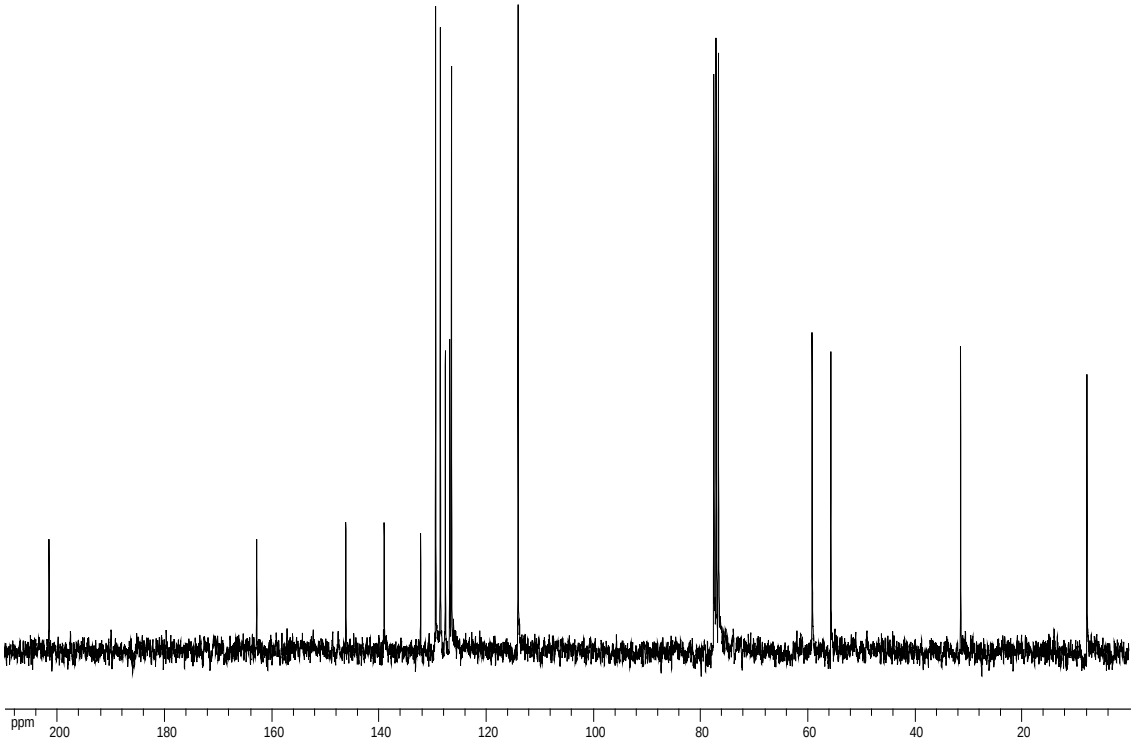


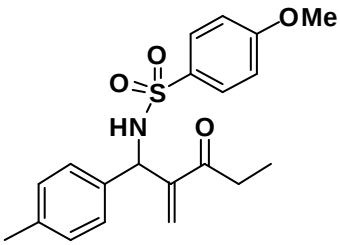
Compound



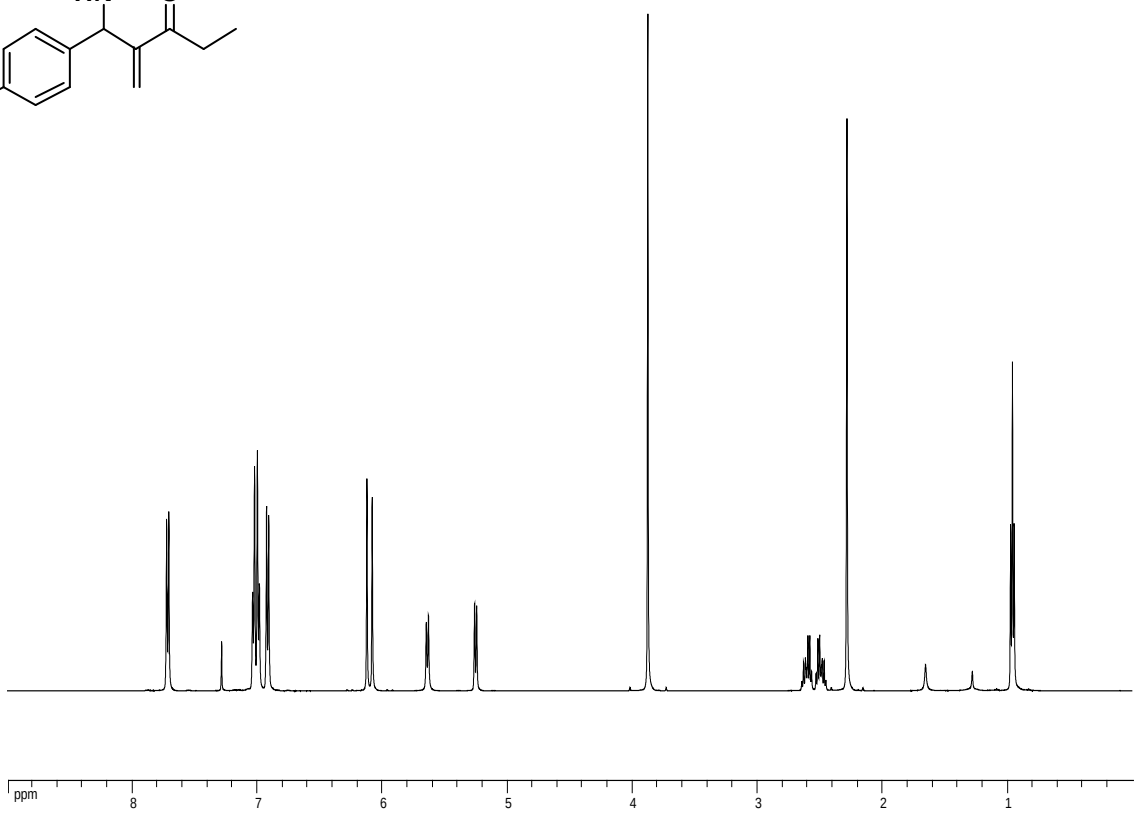


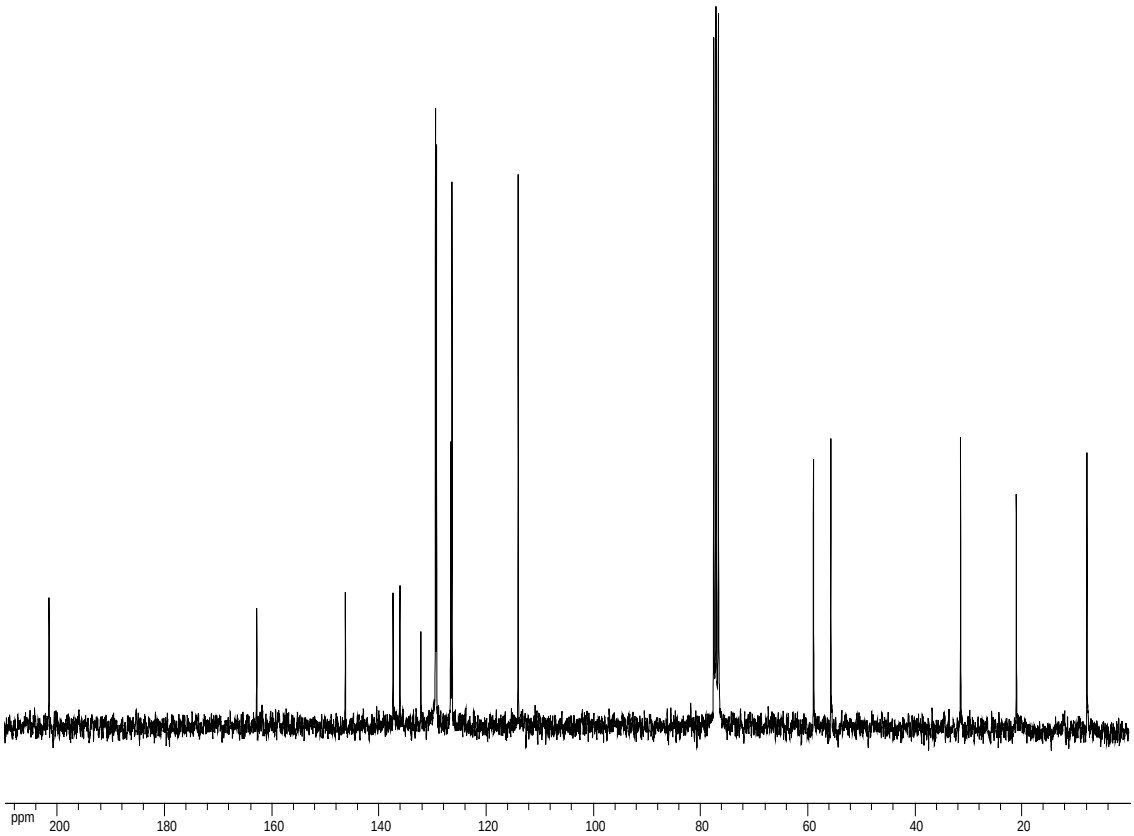
5i

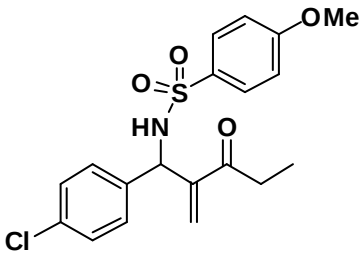




Compound 5k

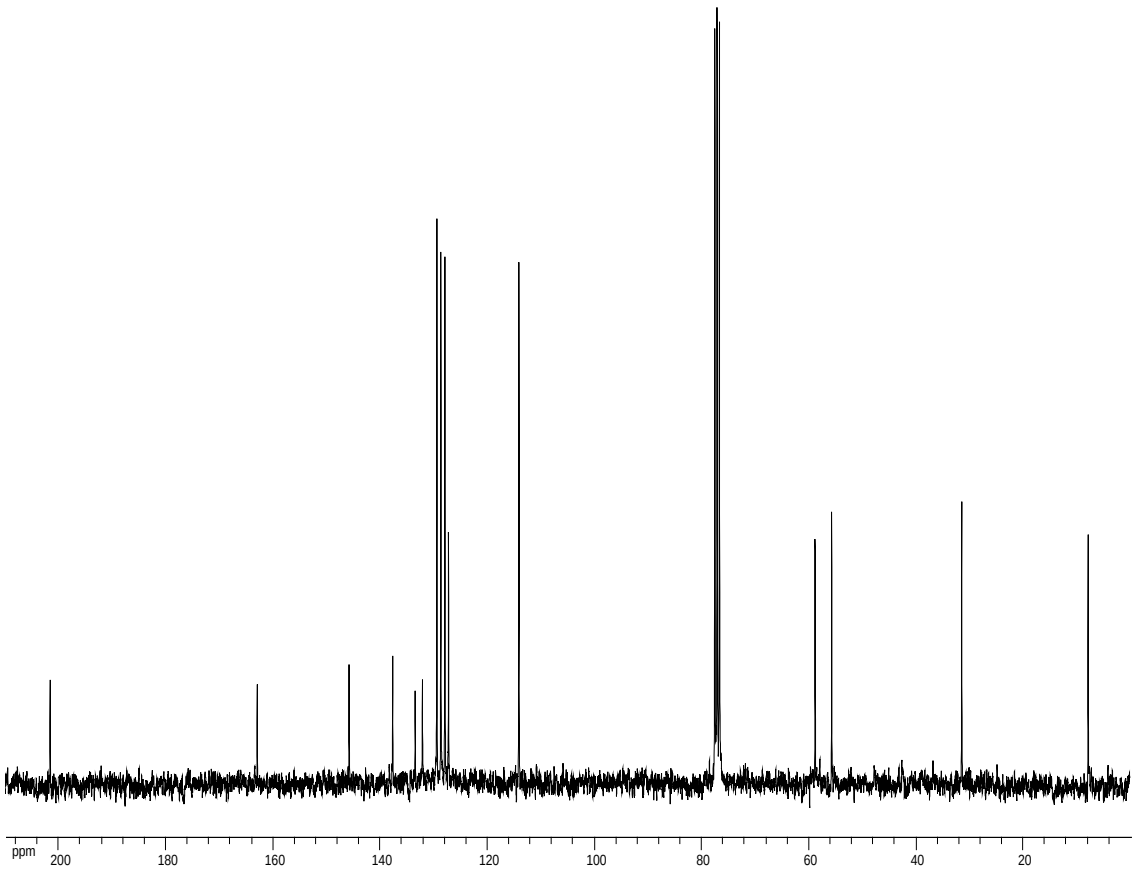


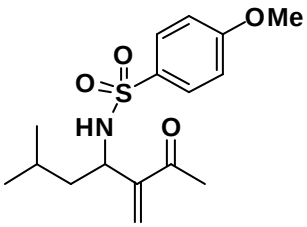



OMe
O
O
S
HN
O
Cl

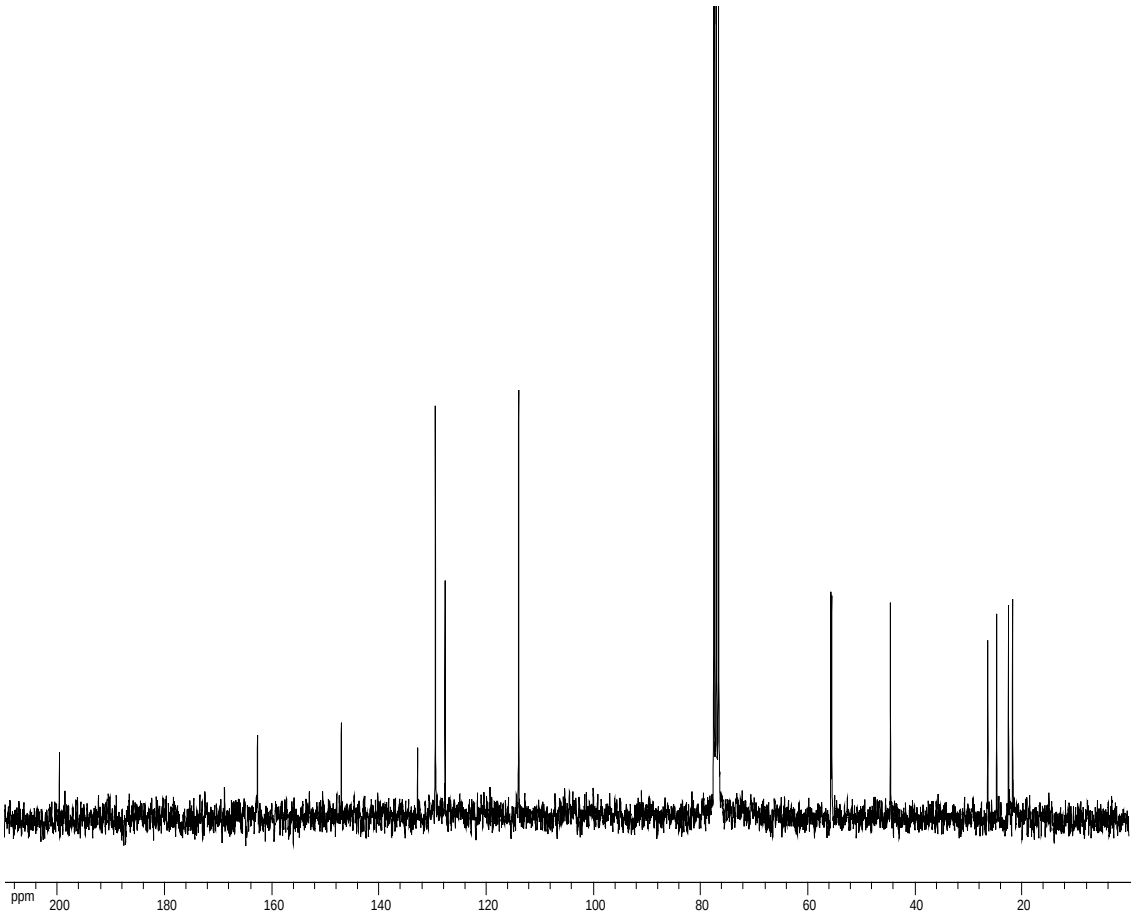
Compound 5l

ppm
8
7
6
5
4
3
2
1

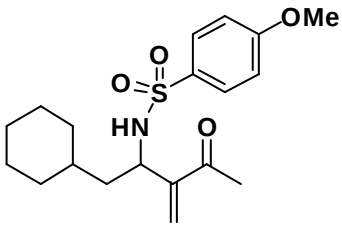

ppm
200
180
160
140
120
100
80
60
40
20

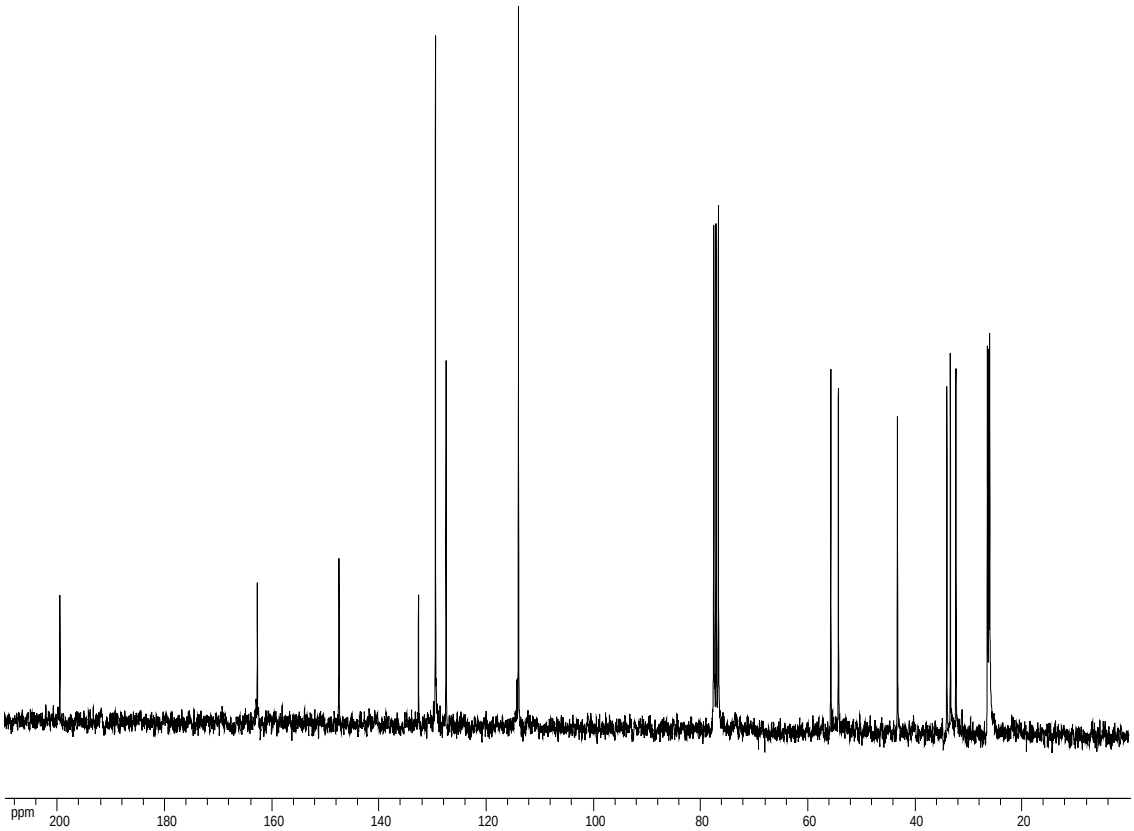


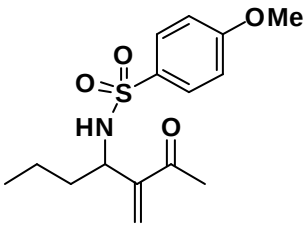
Compound 5m



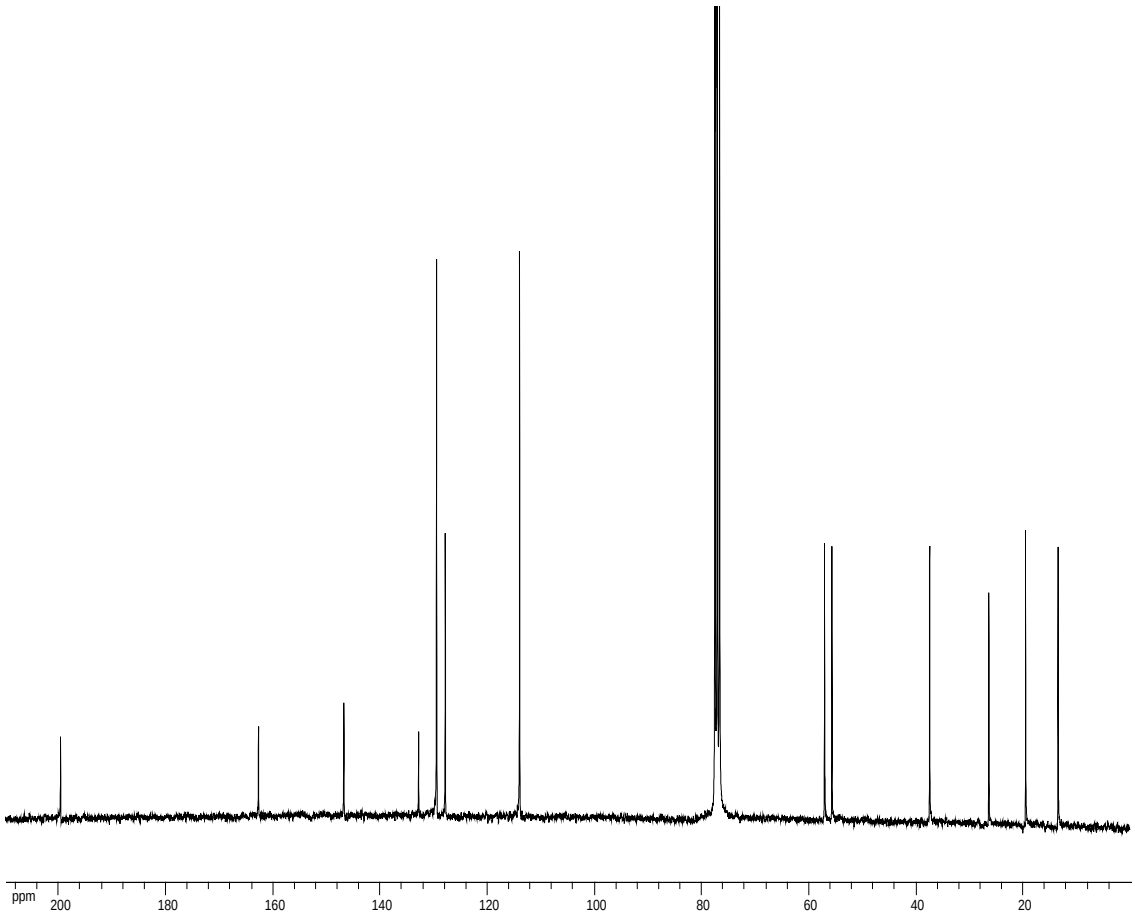
Compound 5n

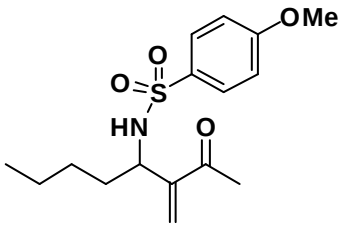




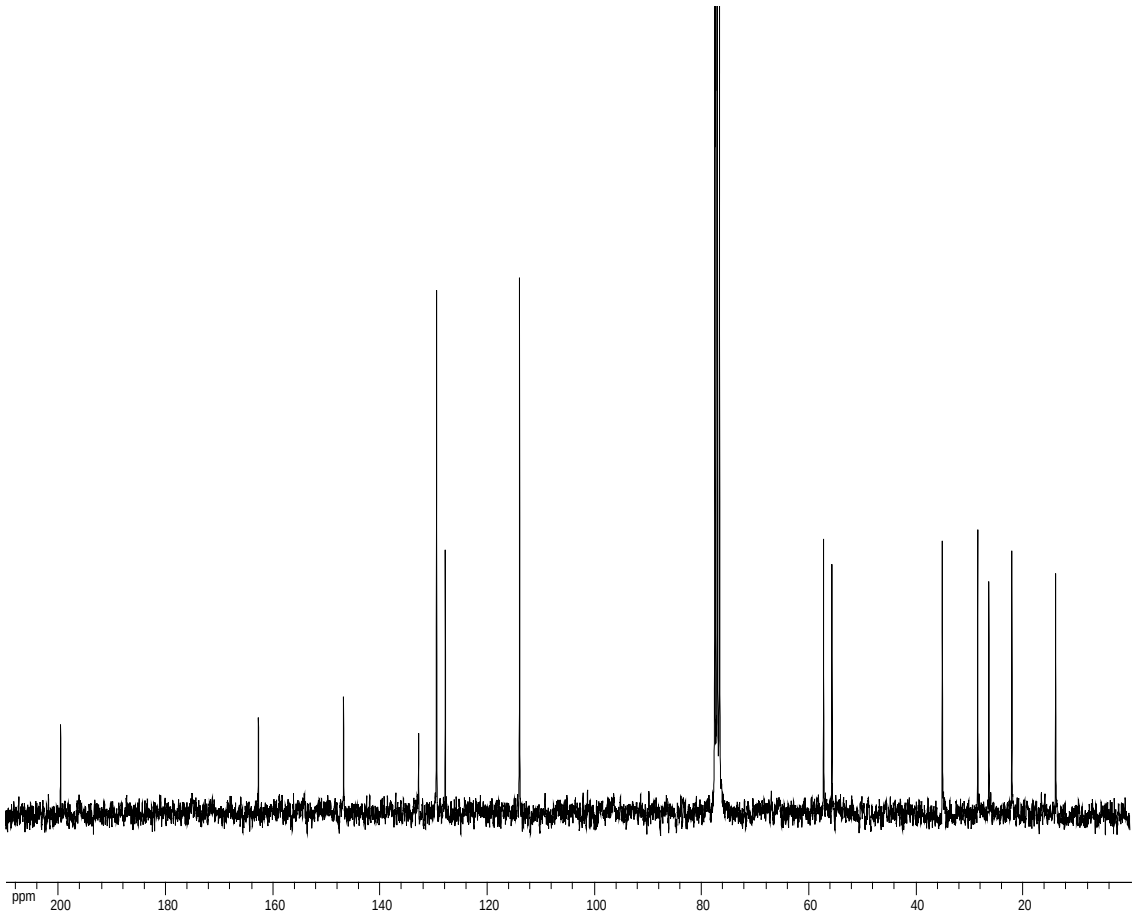


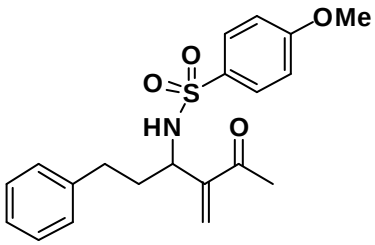
Compound 5o



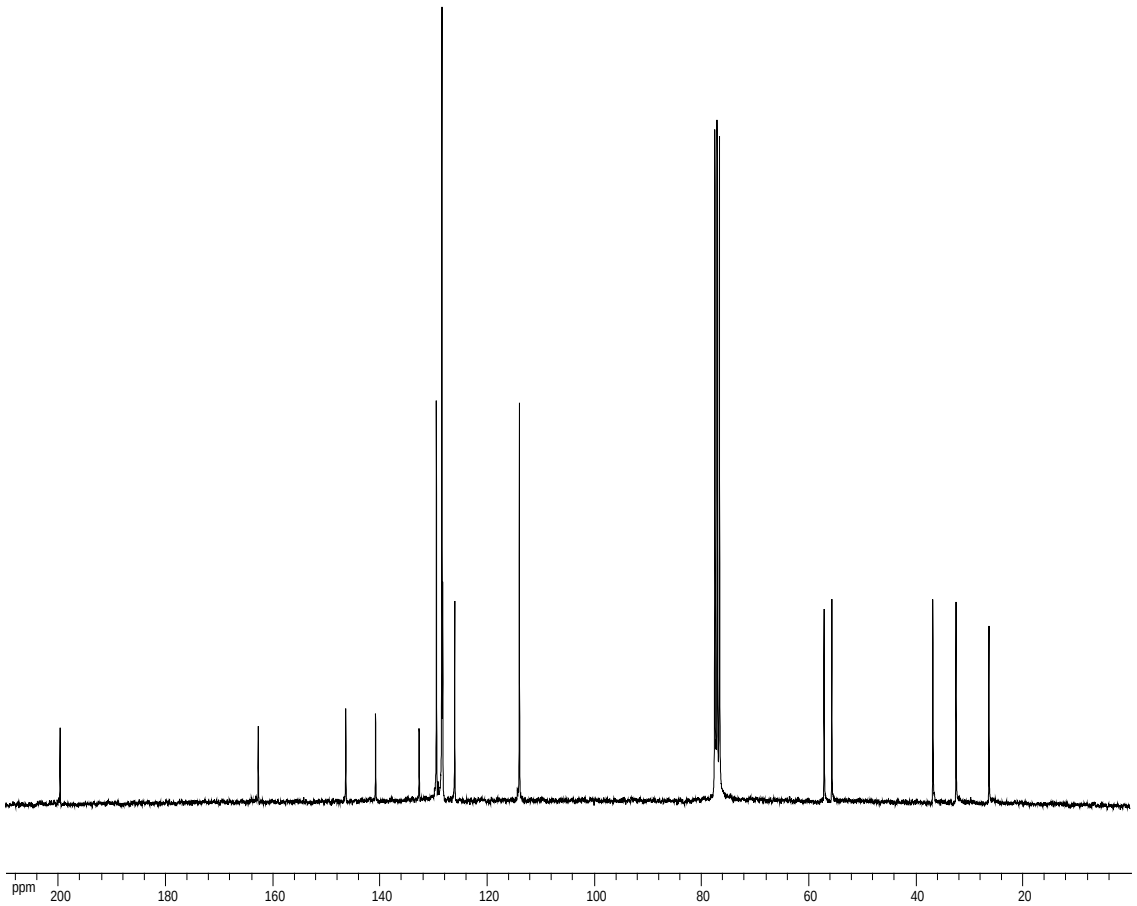


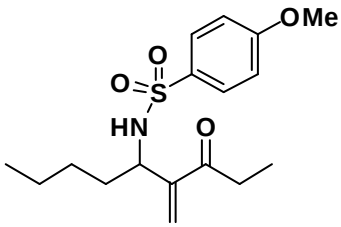
Compound 5p



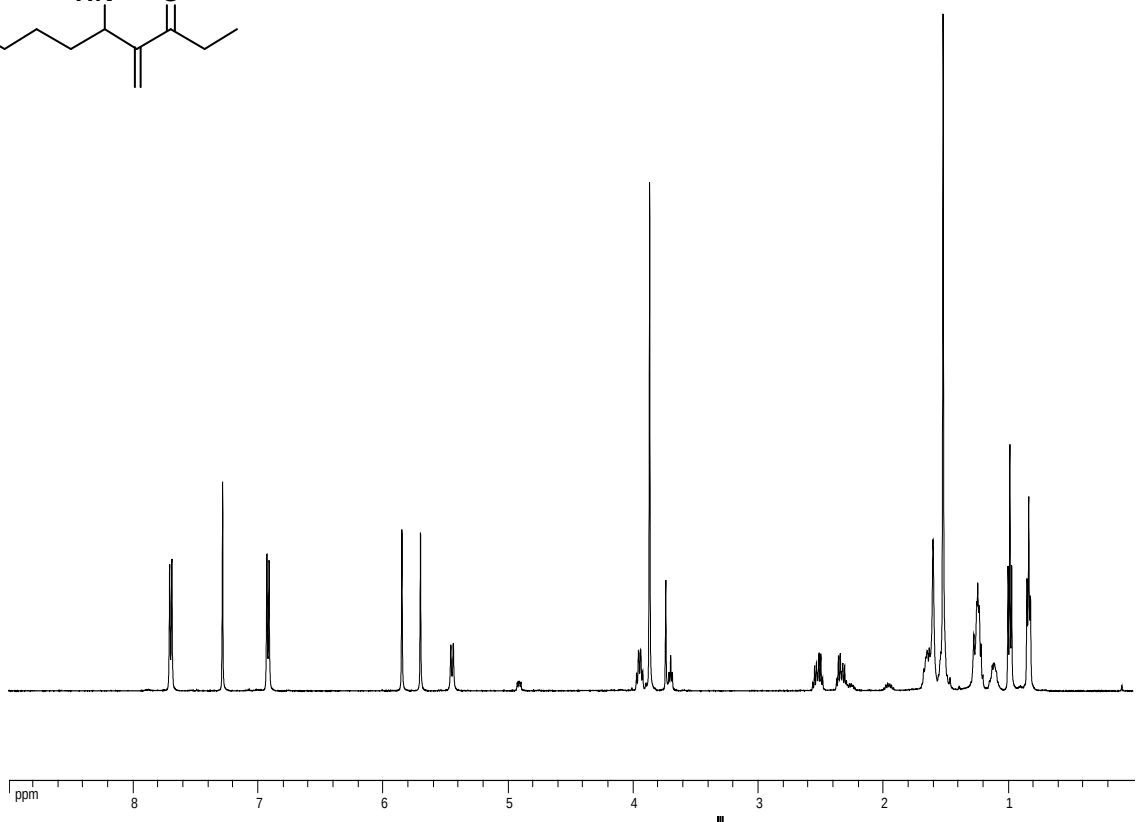


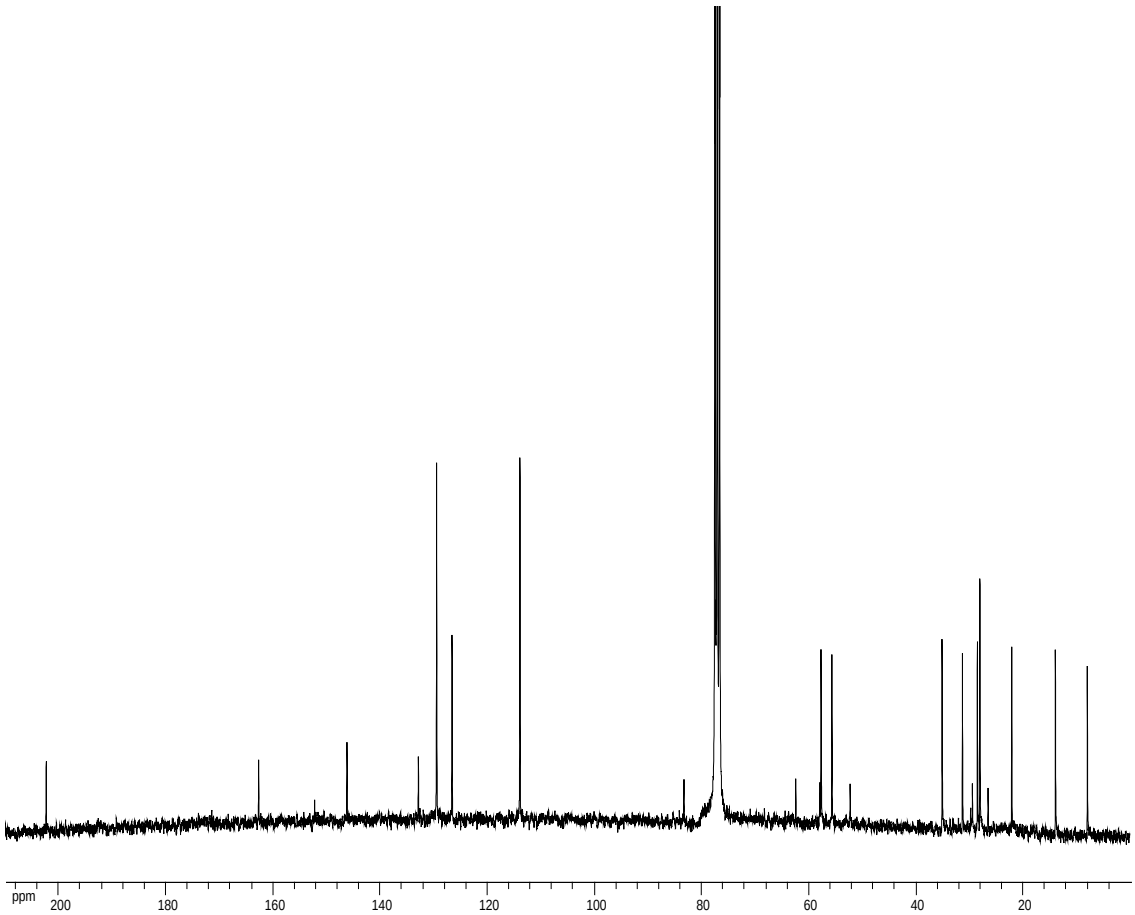
Compound 5q





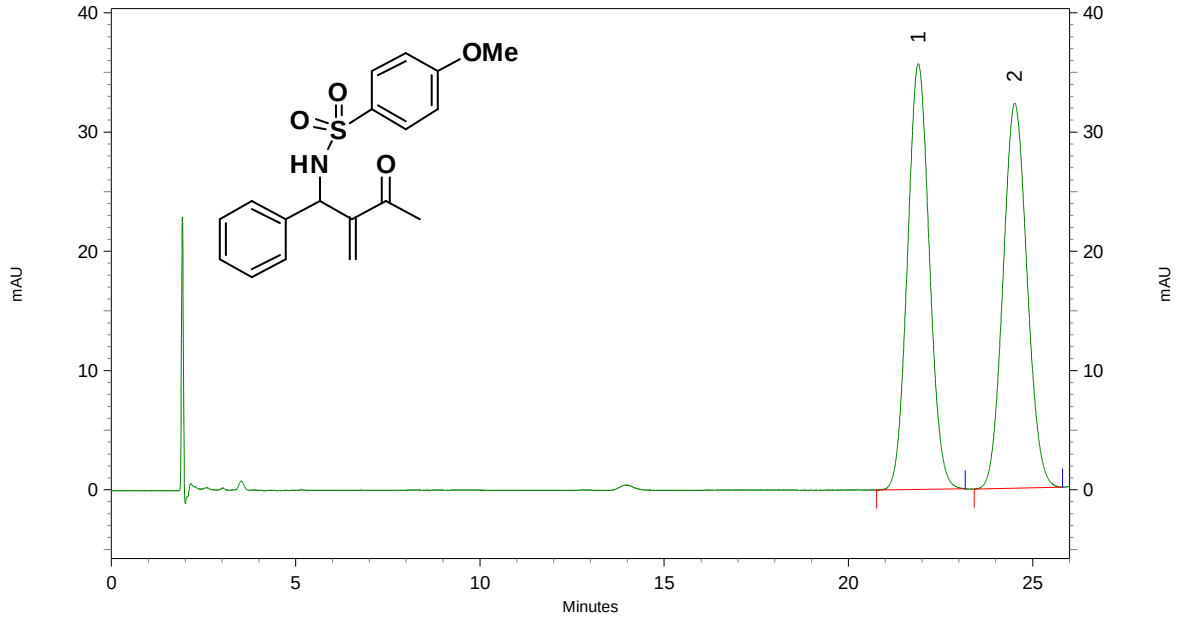
Compound 5r





VII] HPLC data of compounds 5(a) to 5(r)

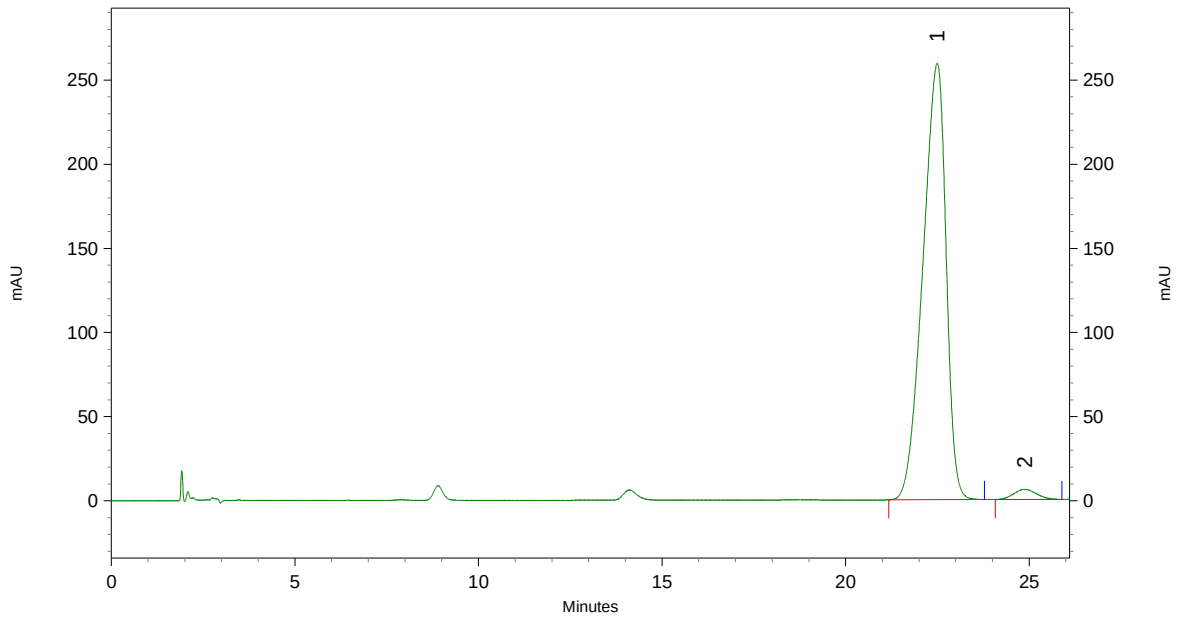
Compound 5a



DAD-CH1 254 nm

Results

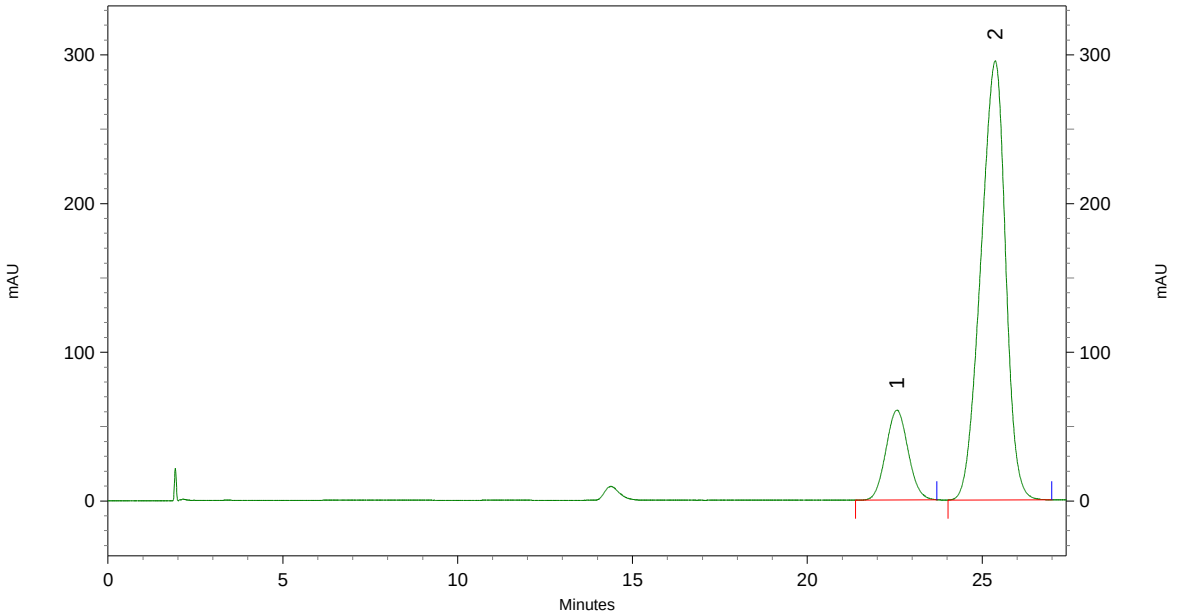
Pk #	Retention Time	Area	Area %
1	21.90	5903083	50.21
2	24.51	5852596	49.79



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	22.49	45383556	97.77
2	24.88	1035781	2.23

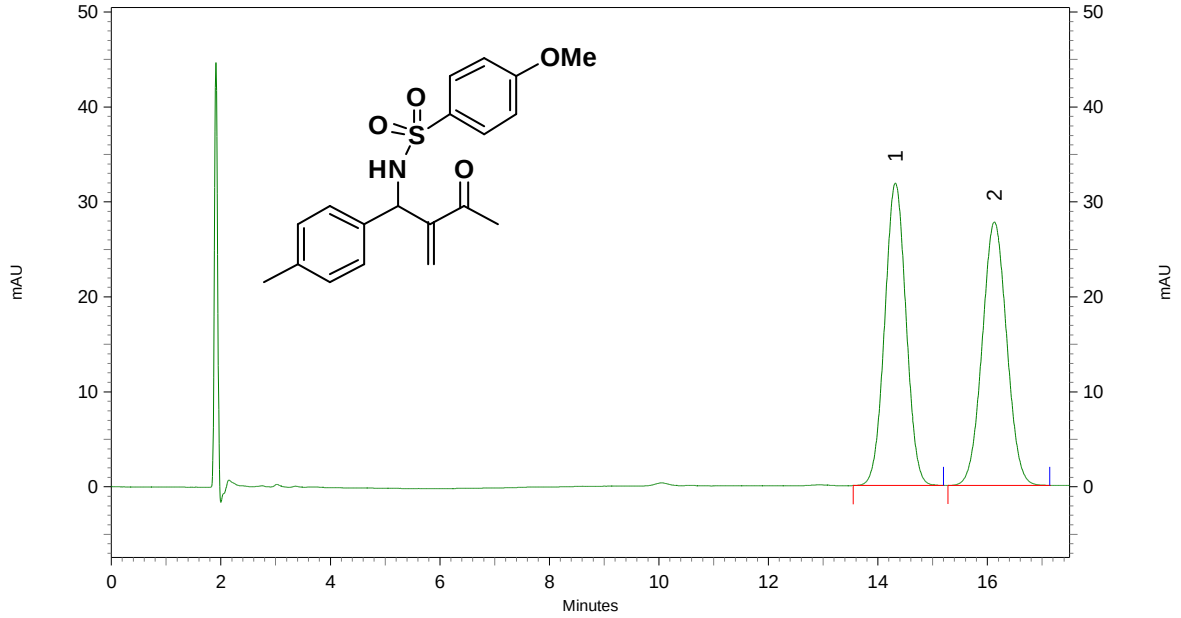


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	22.56	10679174	15.55
2	25.37	58011900	84.45

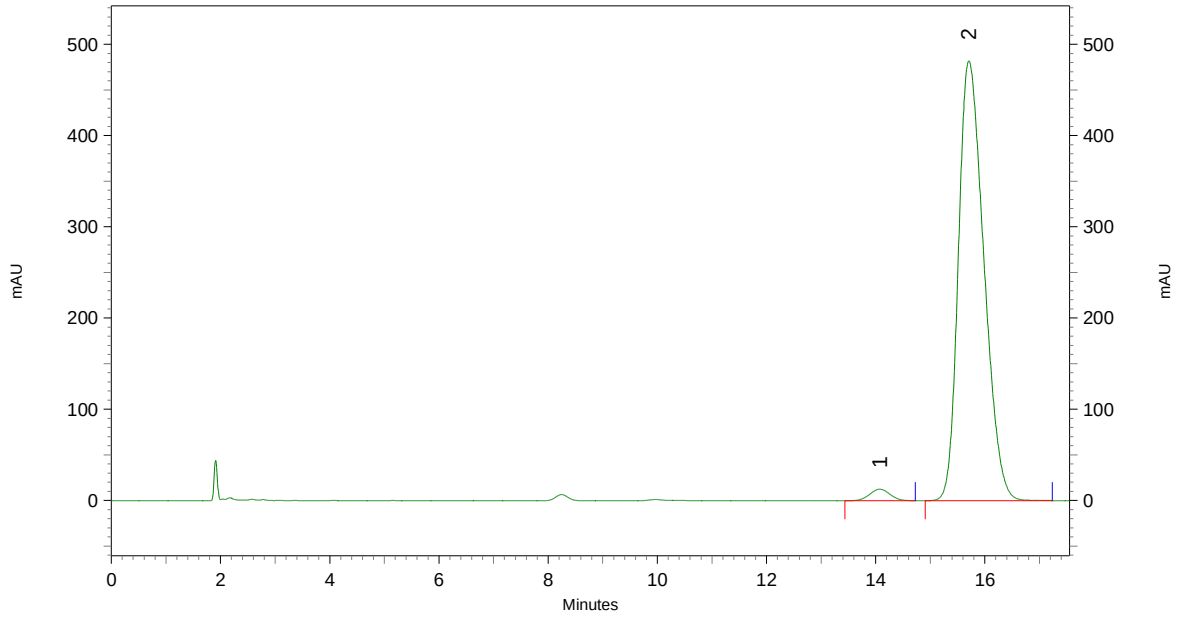
Compound 5b



DAD-CH1 254 nm

Results

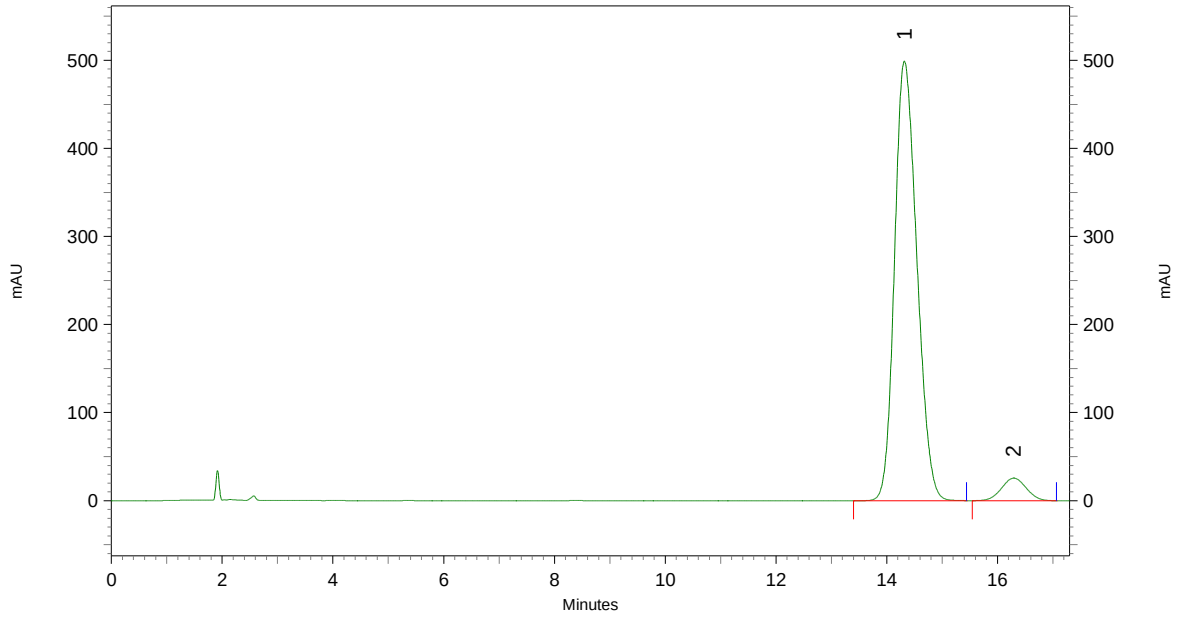
Pk #	Retention Time	Area	Area %
1	14.32	3450738	49.99
2	16.13	3452669	50.01



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	14.07	1317422	2.07
2	15.71	62379080	97.93

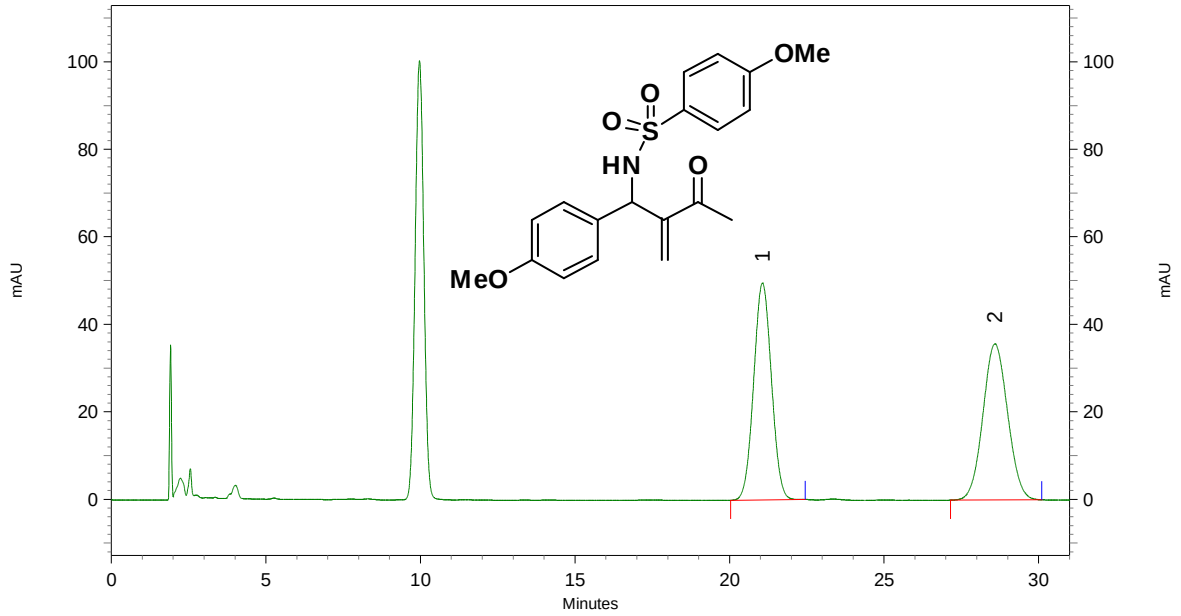


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	14.32	55839932	94.59
2	16.29	3196030	5.41

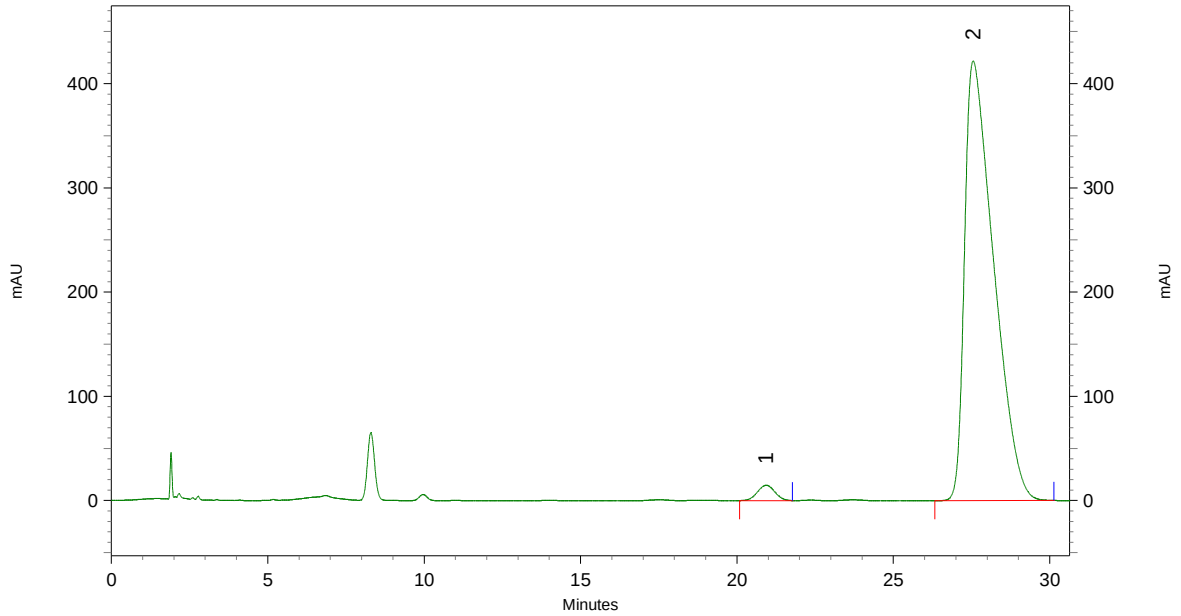
Compound 5c



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	21.07	7921017	49.94
2	28.59	7940030	50.06

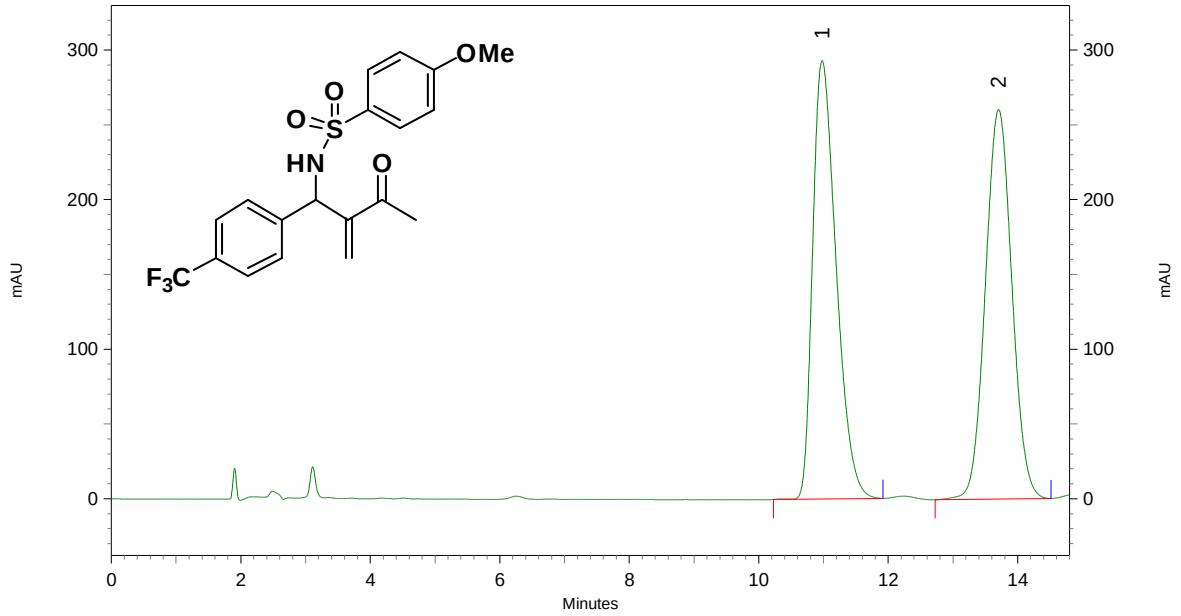


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	20.93	2279918	2.05
2	27.55	108889092	97.95

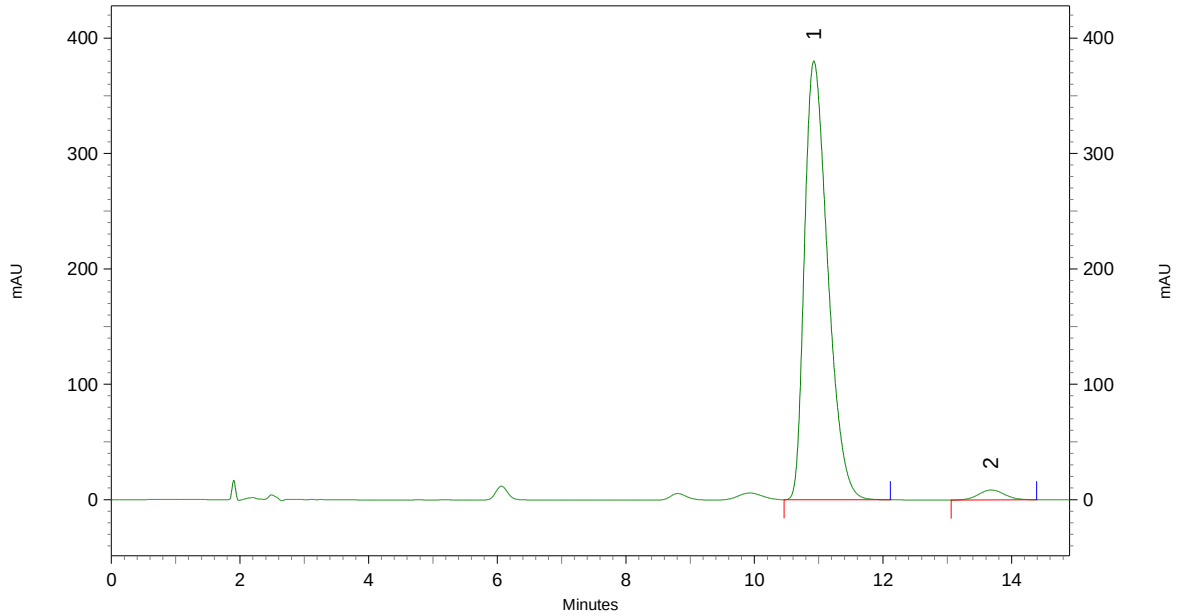
Compound 5d



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	10.98	29531420	49.94
2	13.71	29600991	50.06

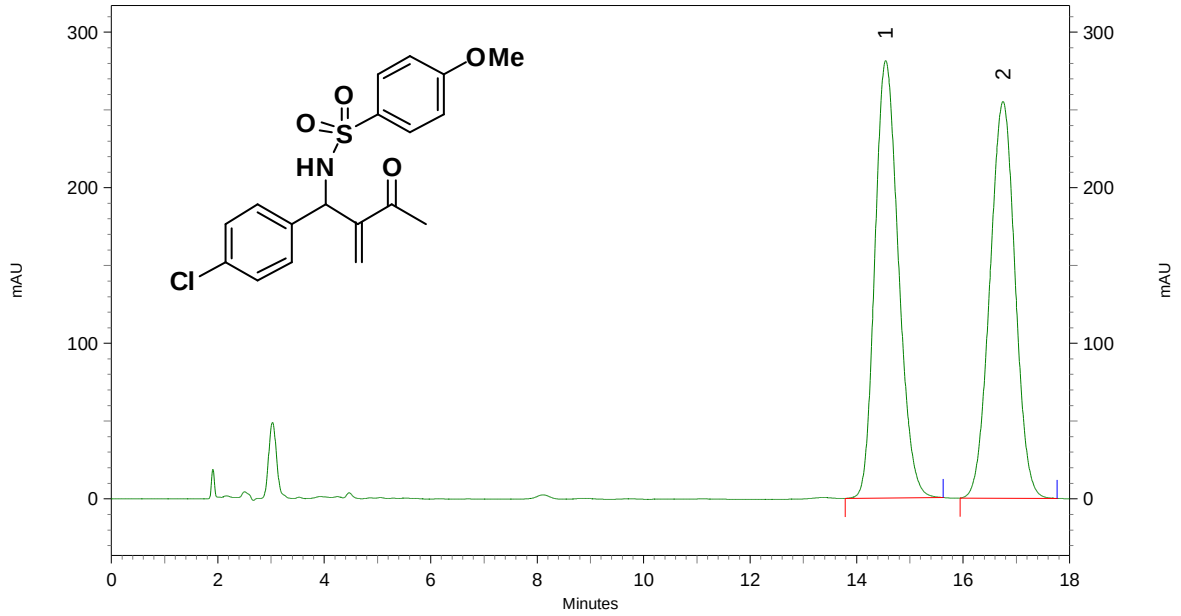


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	10.93	38249381	97.58
2	13.68	950270	2.42

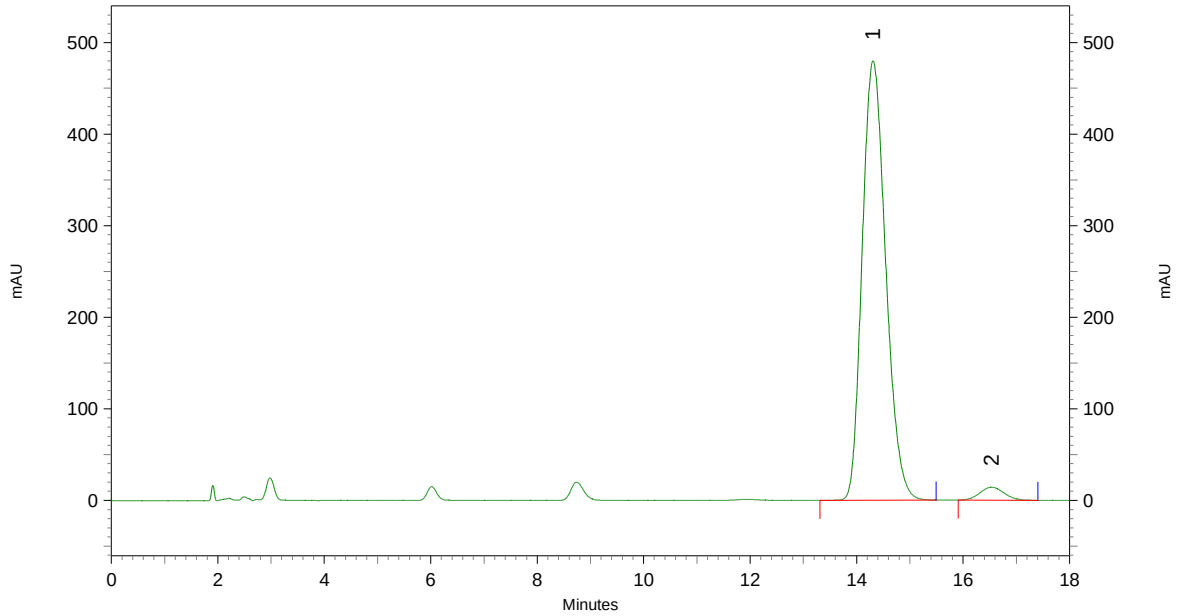
Compound 5e



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	14.55	34482998	50.66
2	16.75	33590856	49.34

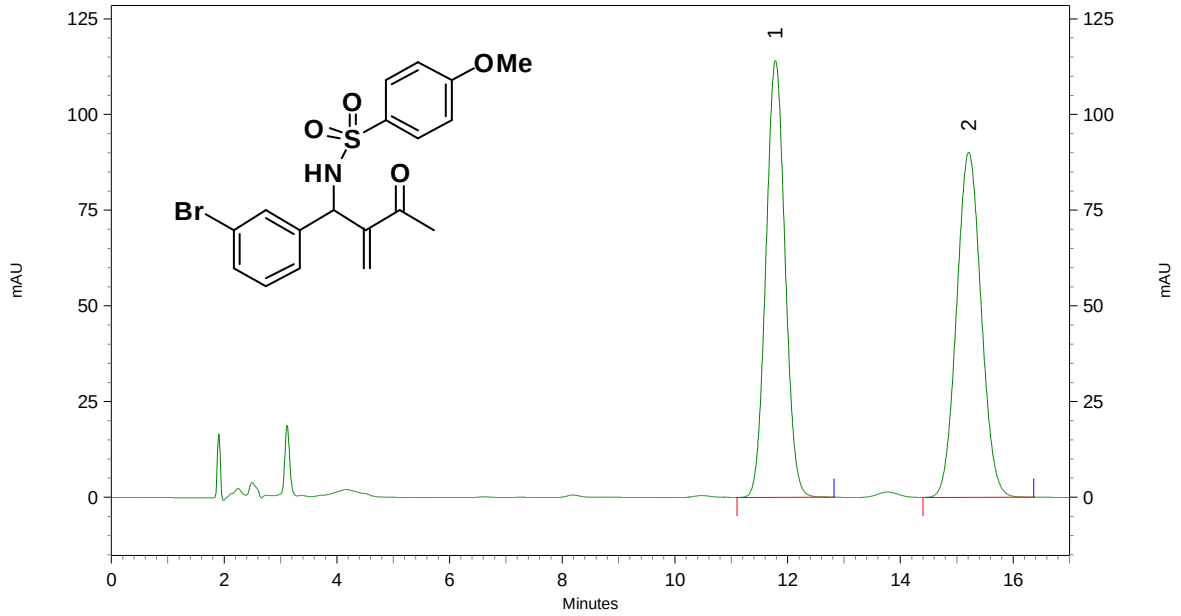


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	14.31	58863492	97.03
2	16.53	1802363	2.97

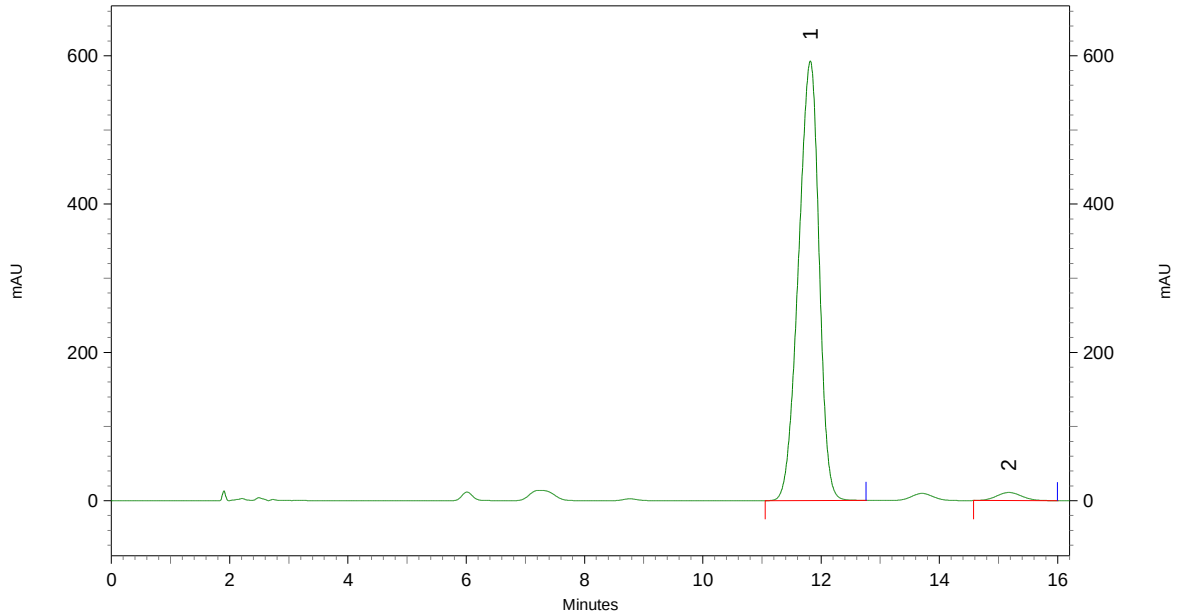
Compound 5f



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11.78	10776028	49.65
2	15.21	10925777	50.35

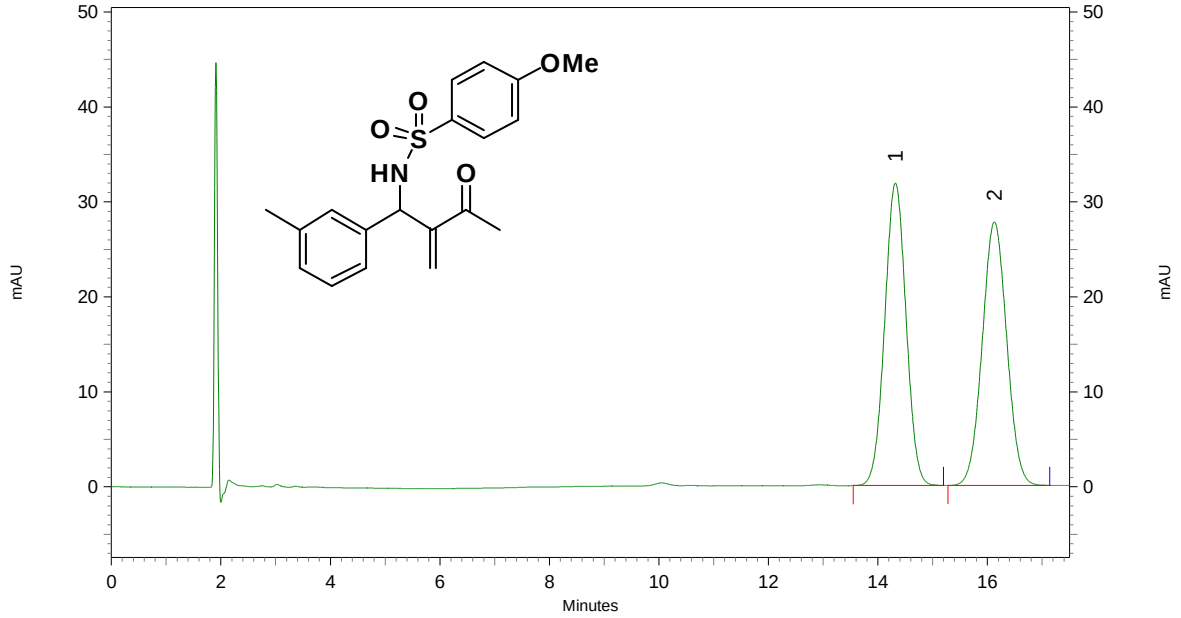


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11.82	57254266	97.79
2	15.17	1291217	2.21

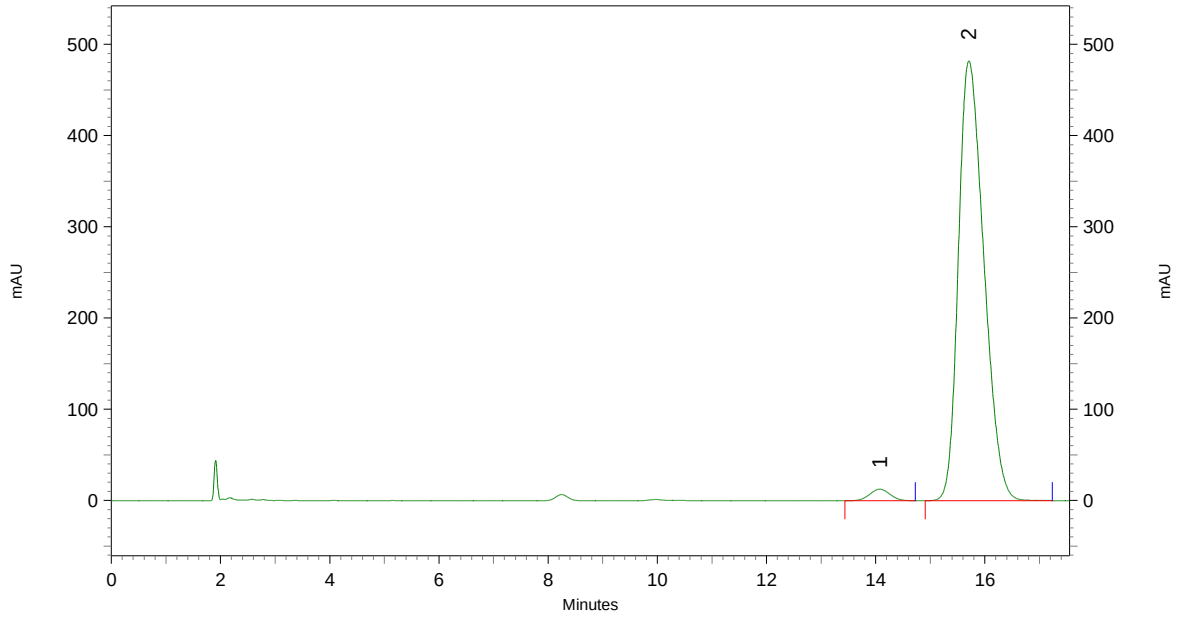
Compound 5g



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	14.32	3450738	49.99
2	16.13	3452669	50.01

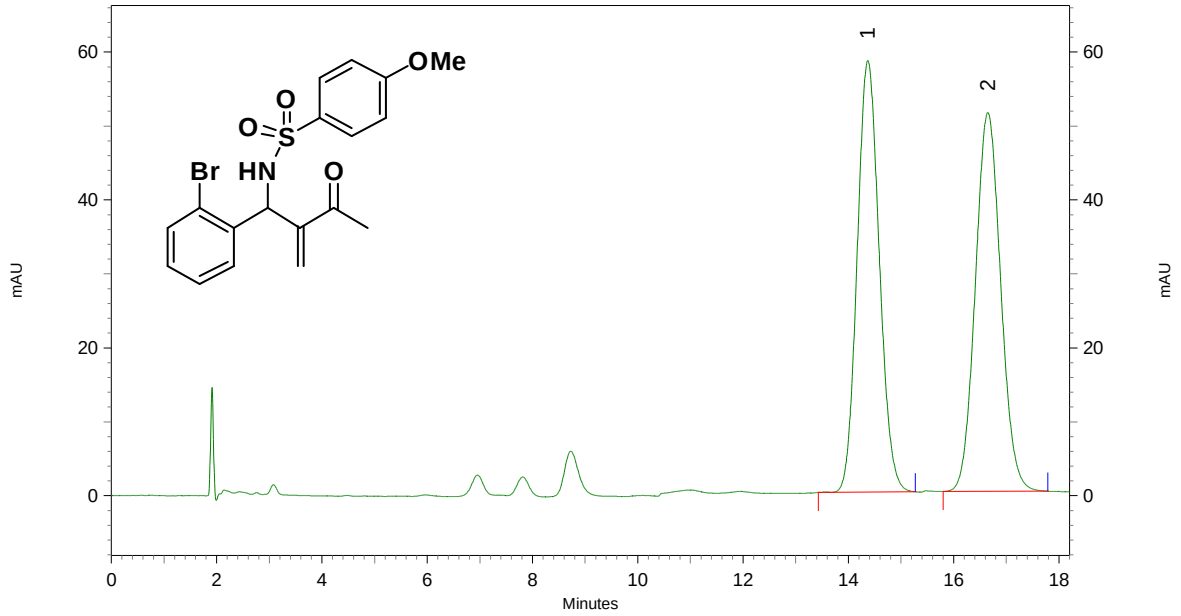


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	14.07	1317422	2.07
2	15.71	62379080	97.93

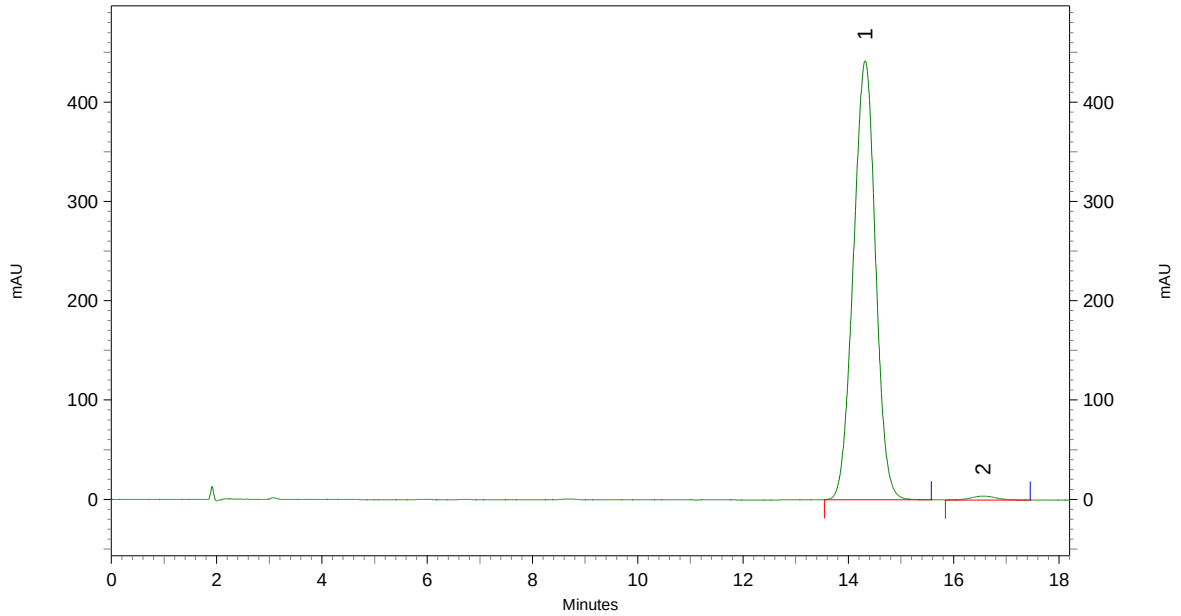
Compound 5h



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	14.37	6797984	49.78
2	16.65	6857379	50.22

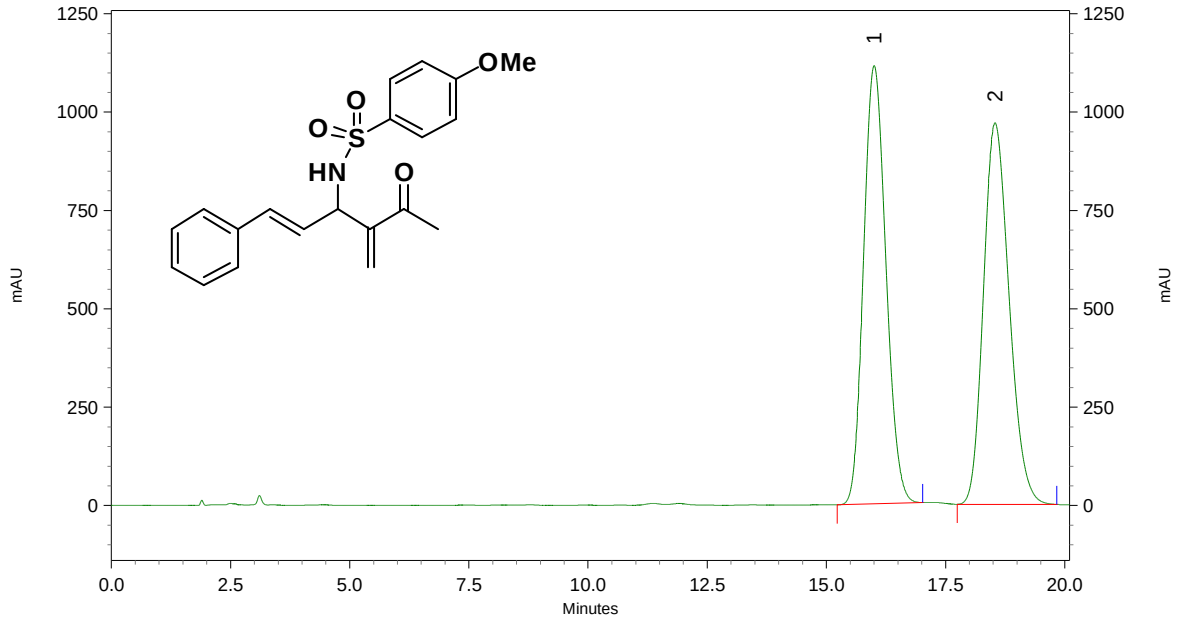


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	14.32	51682668	99.04
2	16.56	501180	0.96

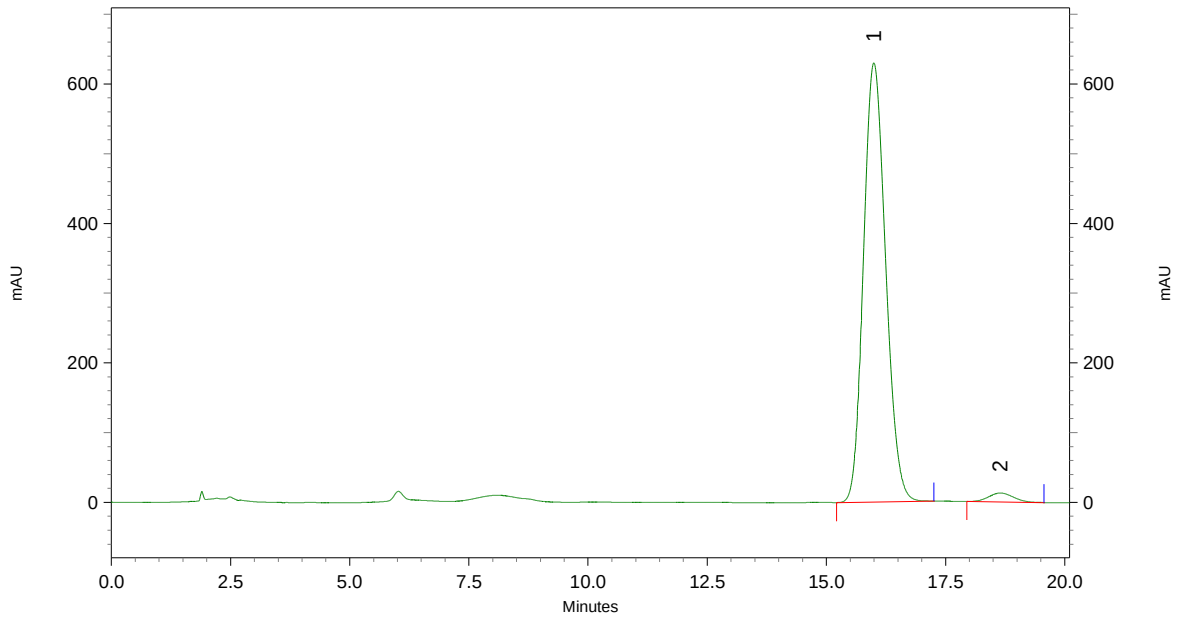
Compound 5i



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	16.00	144491407	49.79
2	18.54	145689861	50.21

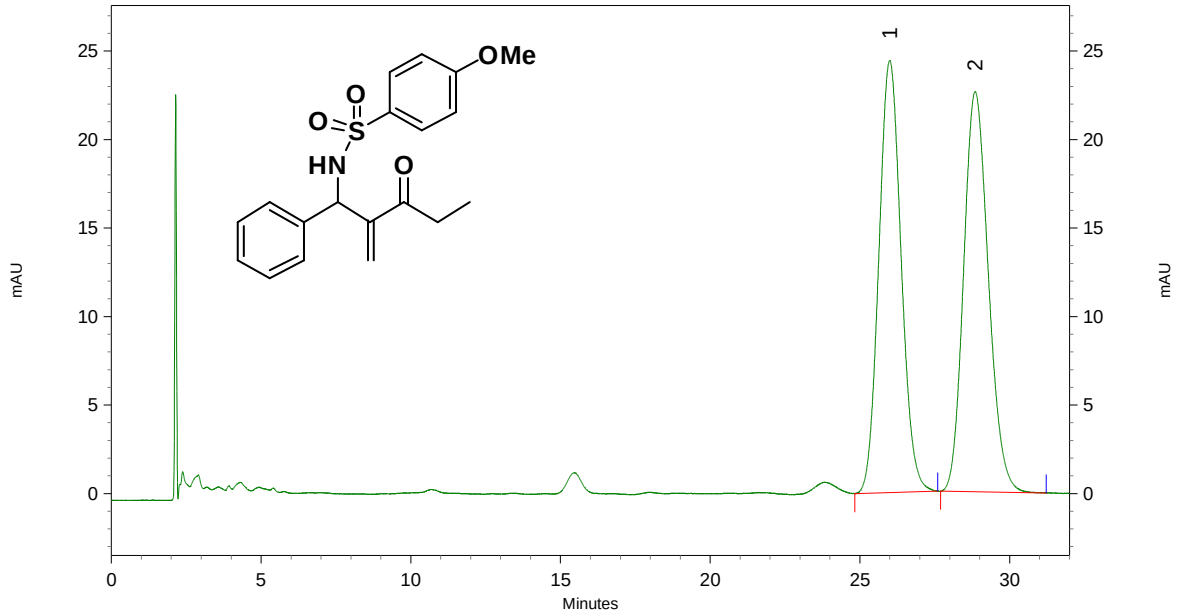


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	15.99	80969028	97.76
2	18.65	1851747	2.24

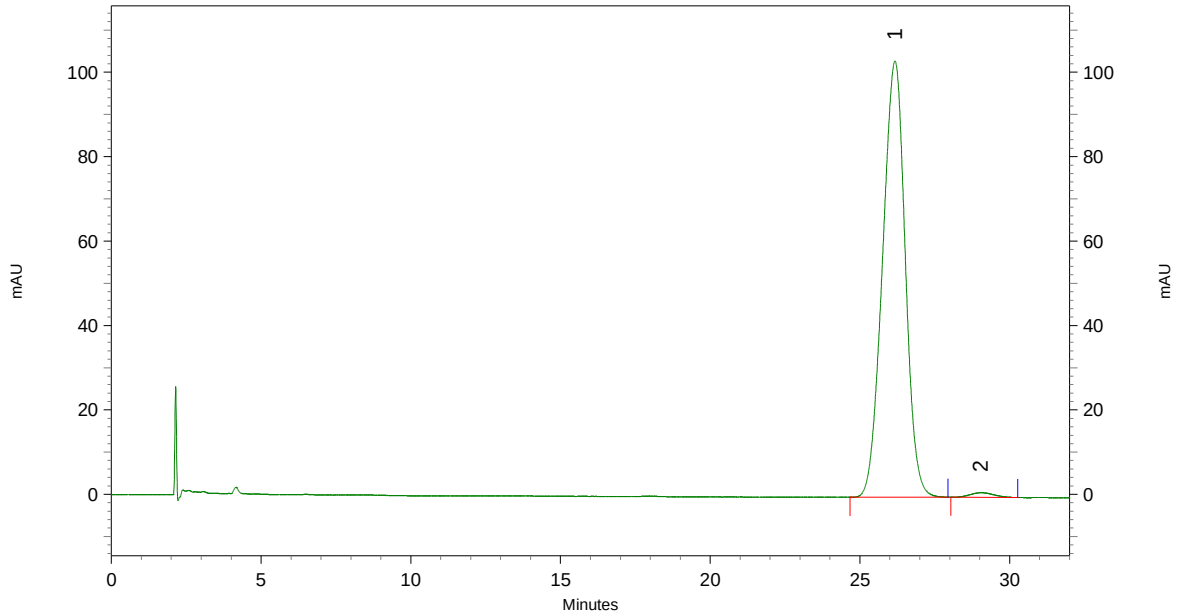
Compound 5j



DAD-CH1 254 nm

Results

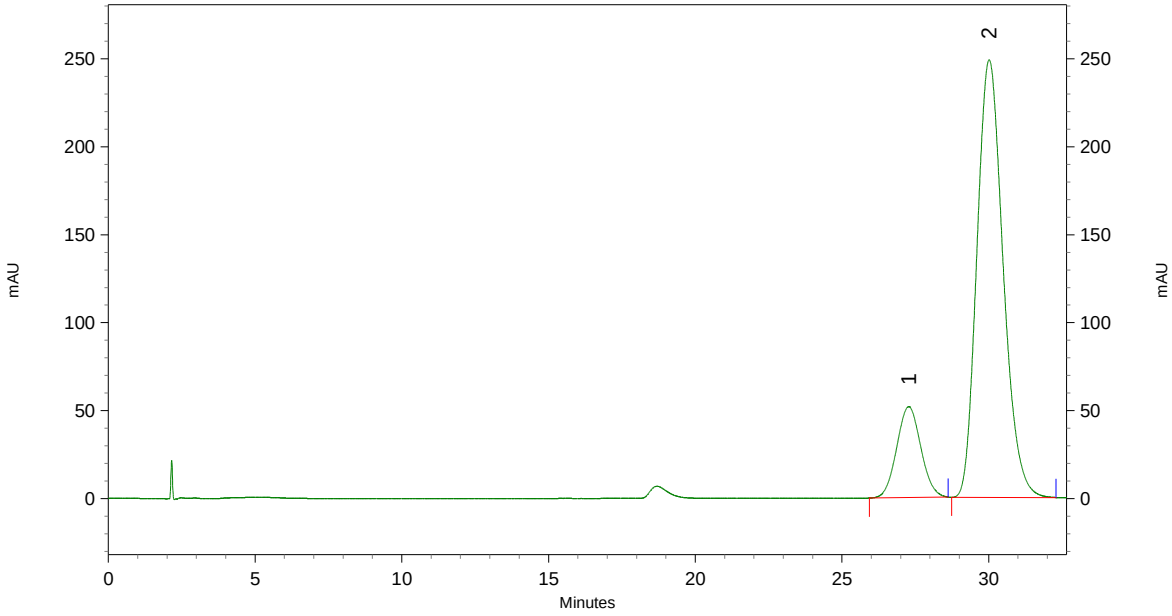
Pk #	Retention Time	Area	Area %
1	25.99	5038749	49.32
2	28.85	5176852	50.68



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	26.17	21770196	98.88
2	29.03	245964	1.12

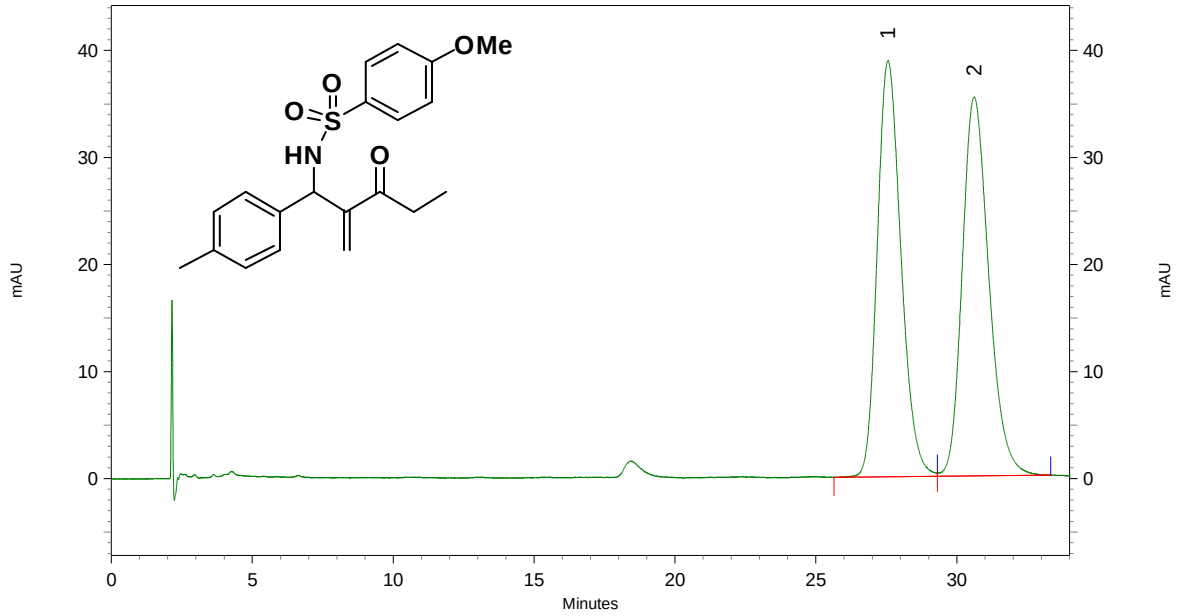


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	27.27	11818455	16.08
2	30.01	61684681	83.92

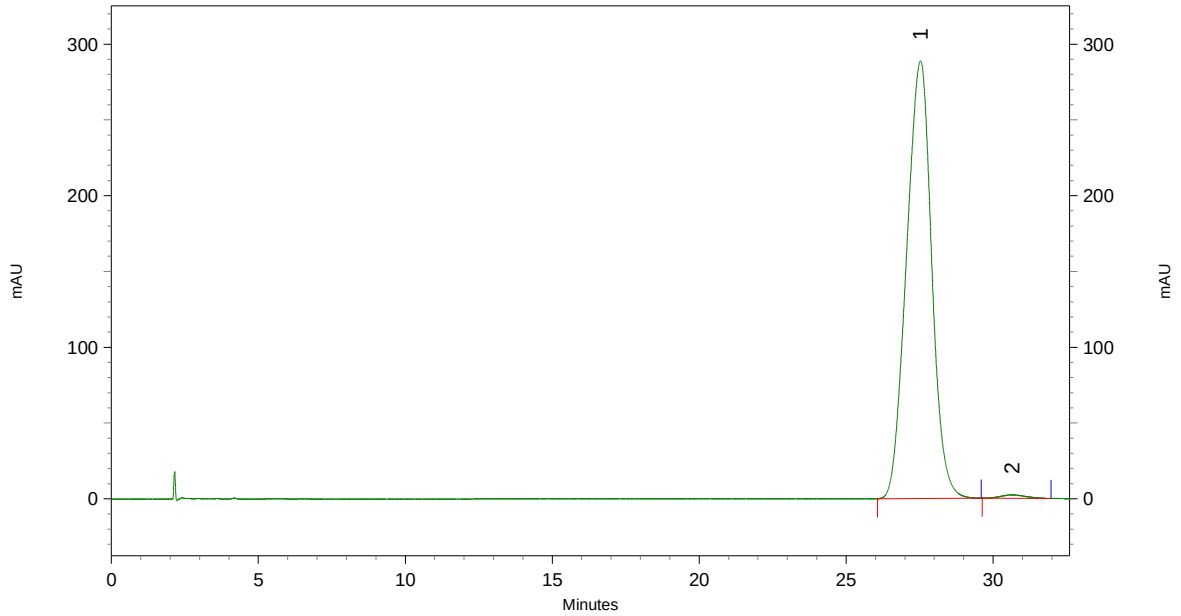
Compound 5k



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	27.56	9095617	49.43
2	30.62	9305777	50.57

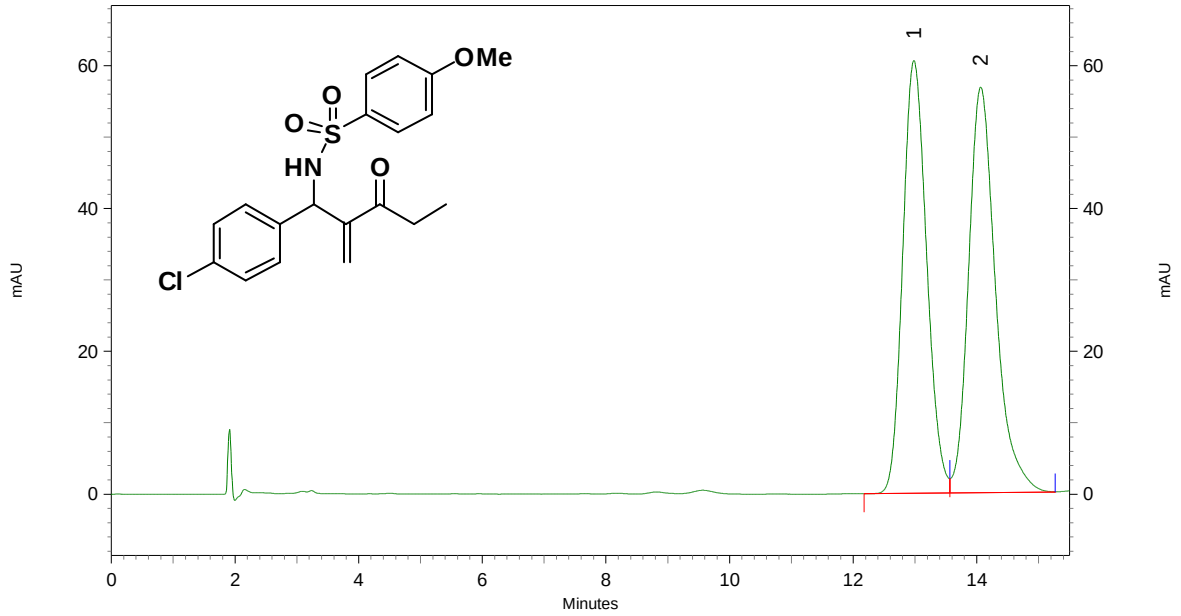


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	27.53	68565187	99.23
2	30.65	535178	0.77

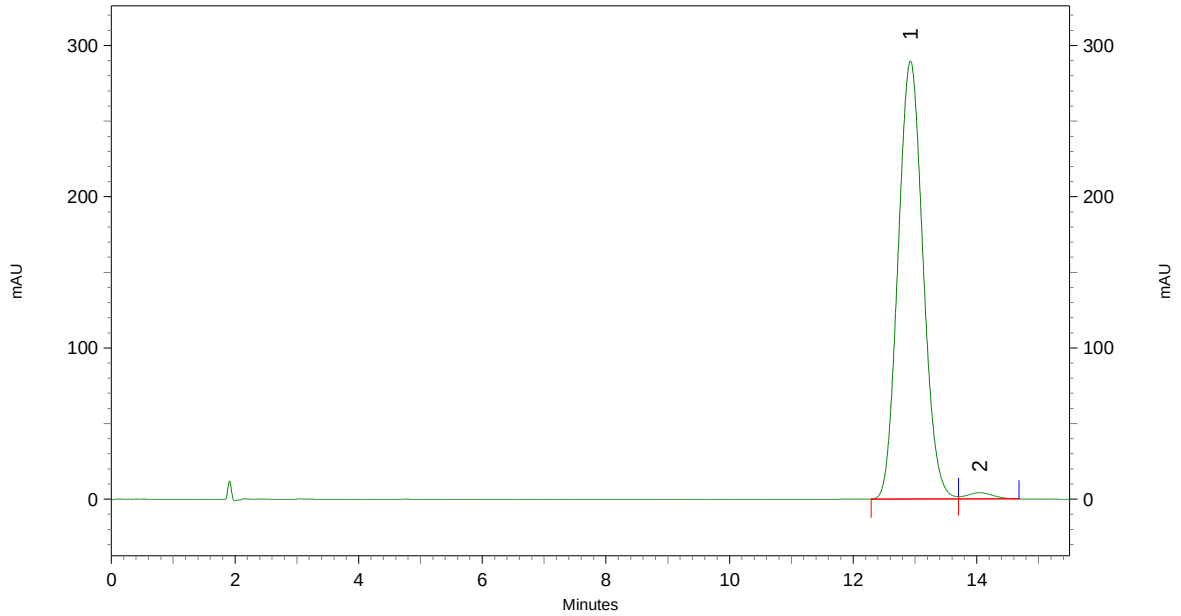
Compound 5l



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	12.98	6513423	48.64
2	14.06	6877741	51.36

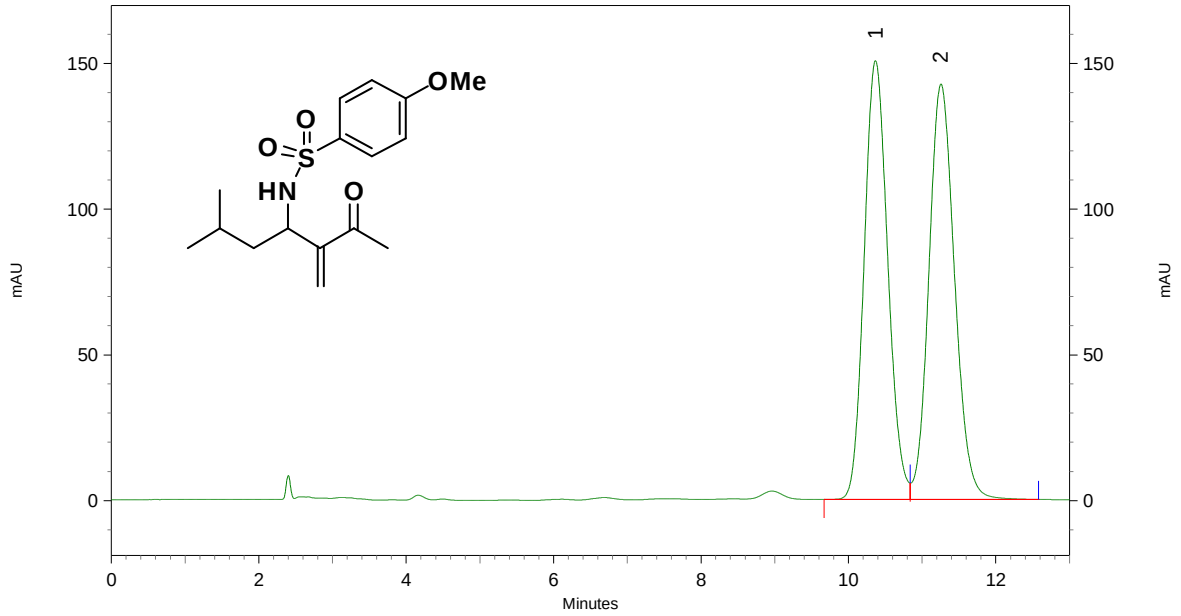


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	12.93	32420686	98.53
2	14.05	485007	1.47

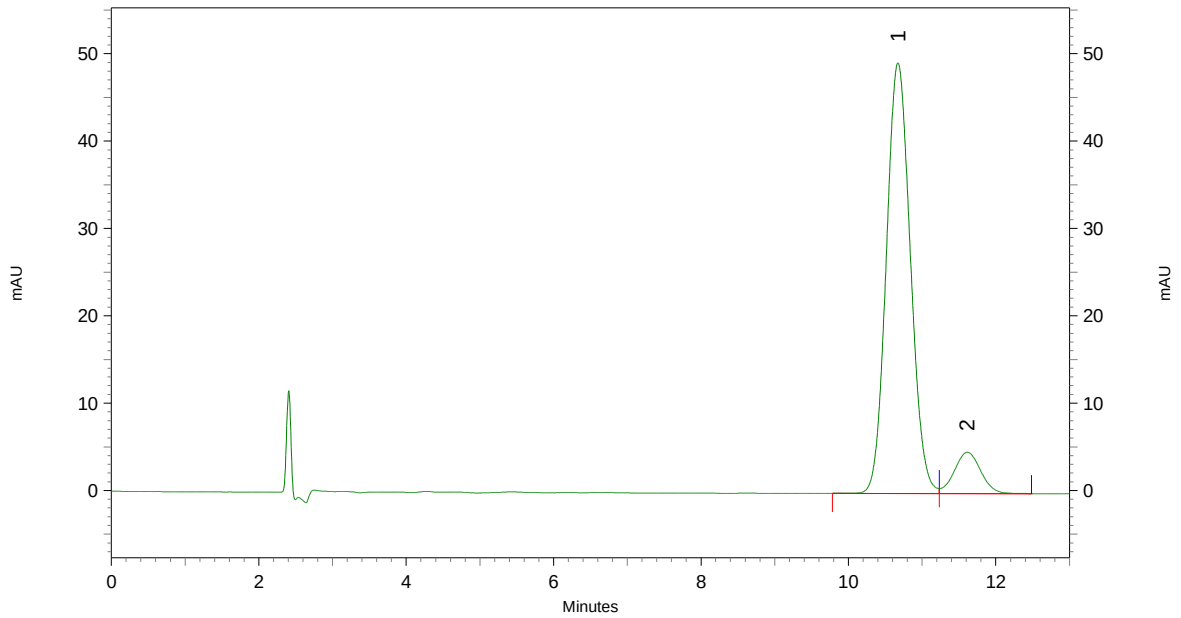
Compound 5m



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	10.37	13383976	49.21
2	11.25	13813787	50.79

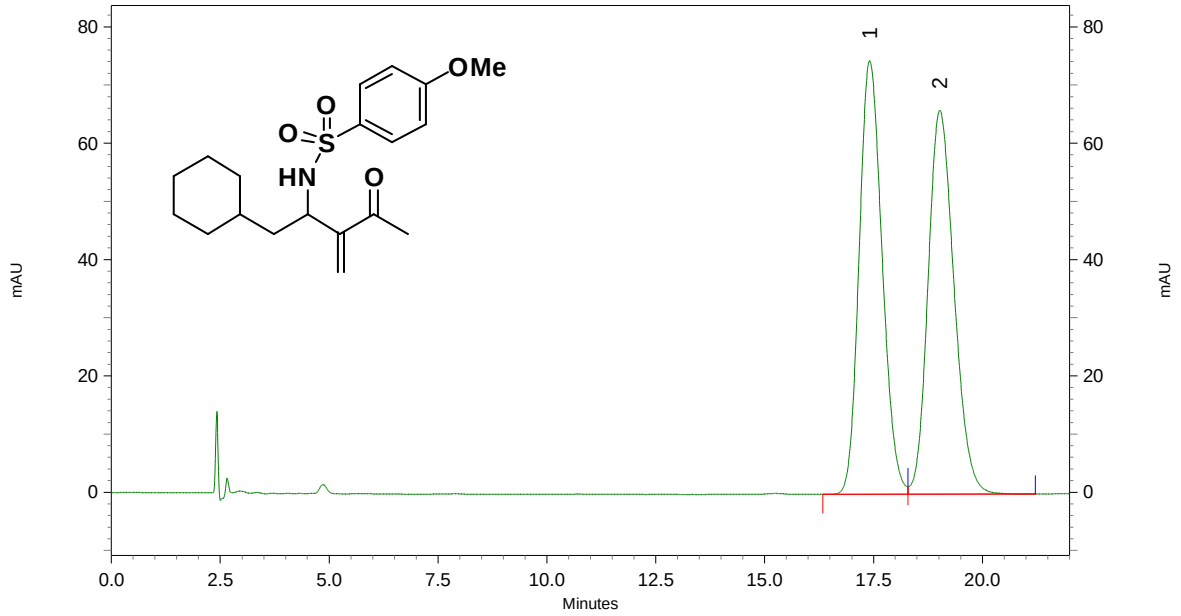


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	10.67	4466274	90.48
2	11.61	470188	9.52

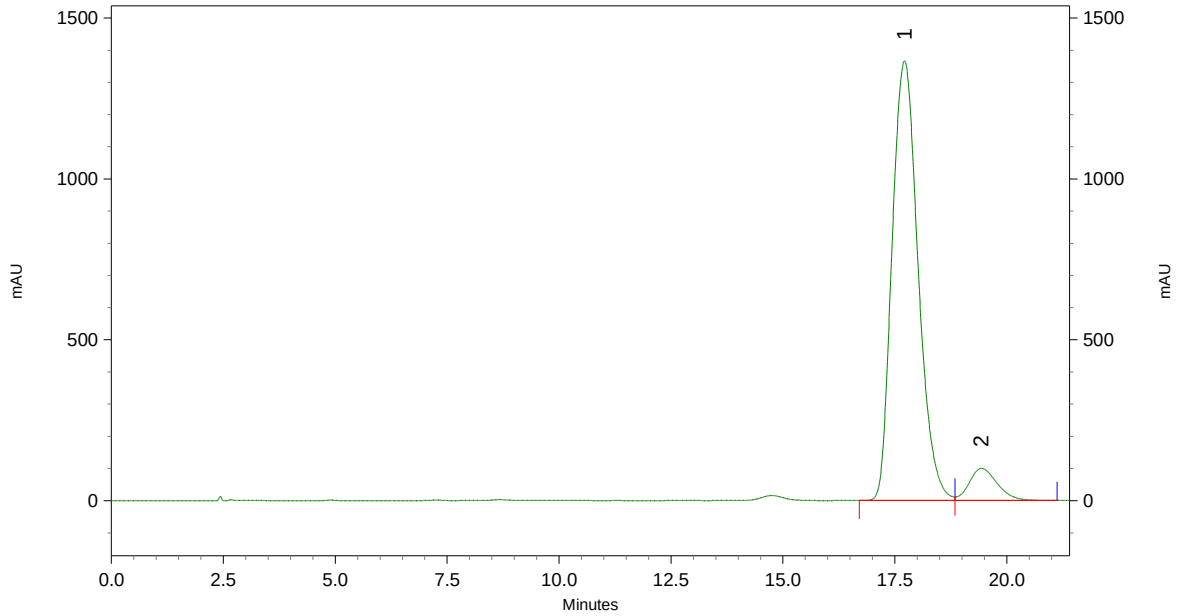
Compound 5n



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	17.41	10930075	49.95
2	19.02	10950860	50.05

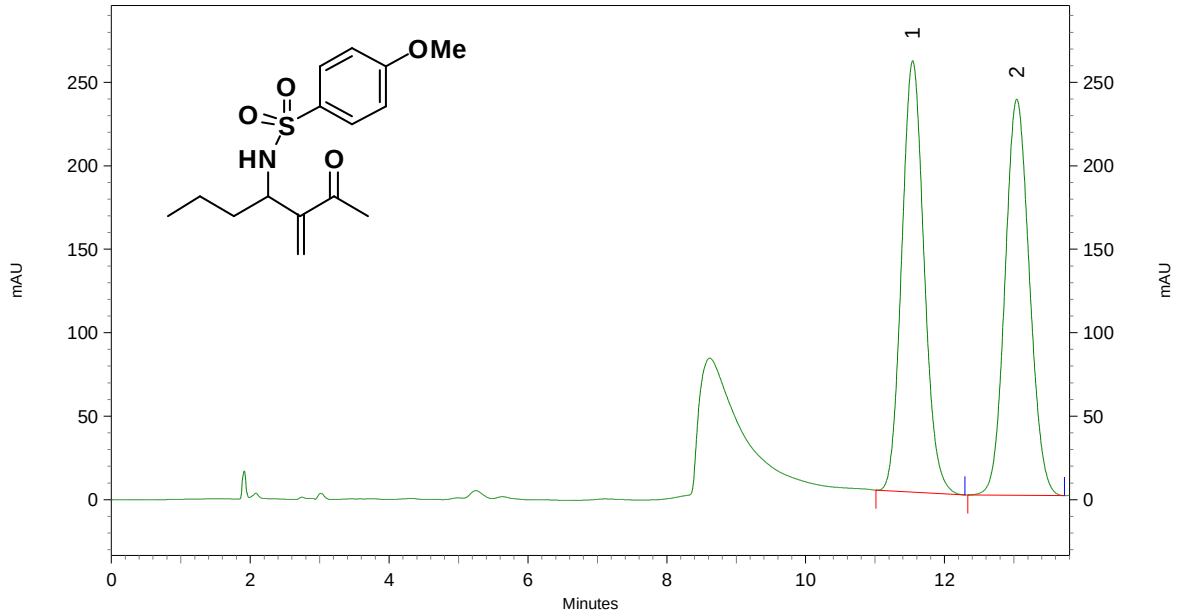


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	17.71	220448858	92.73
2	19.43	17281017	7.27

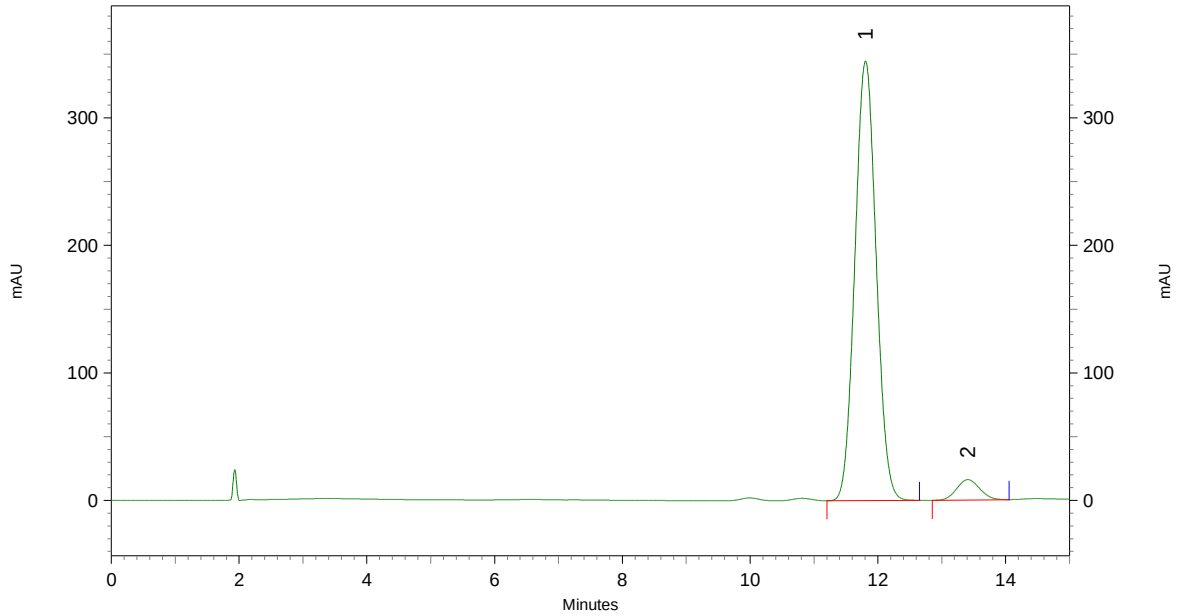
Compound 5o



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11.54	23058076	49.86
2	13.04	23184636	50.14

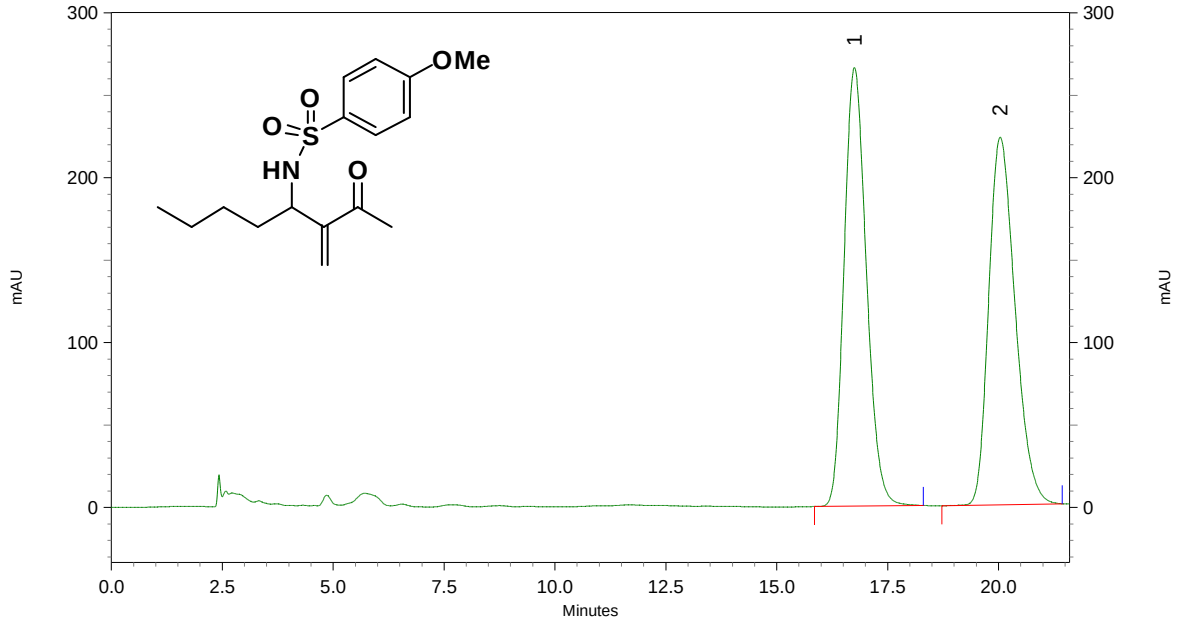


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11.81	31885410	95.21
2	13.41	1603048	4.79

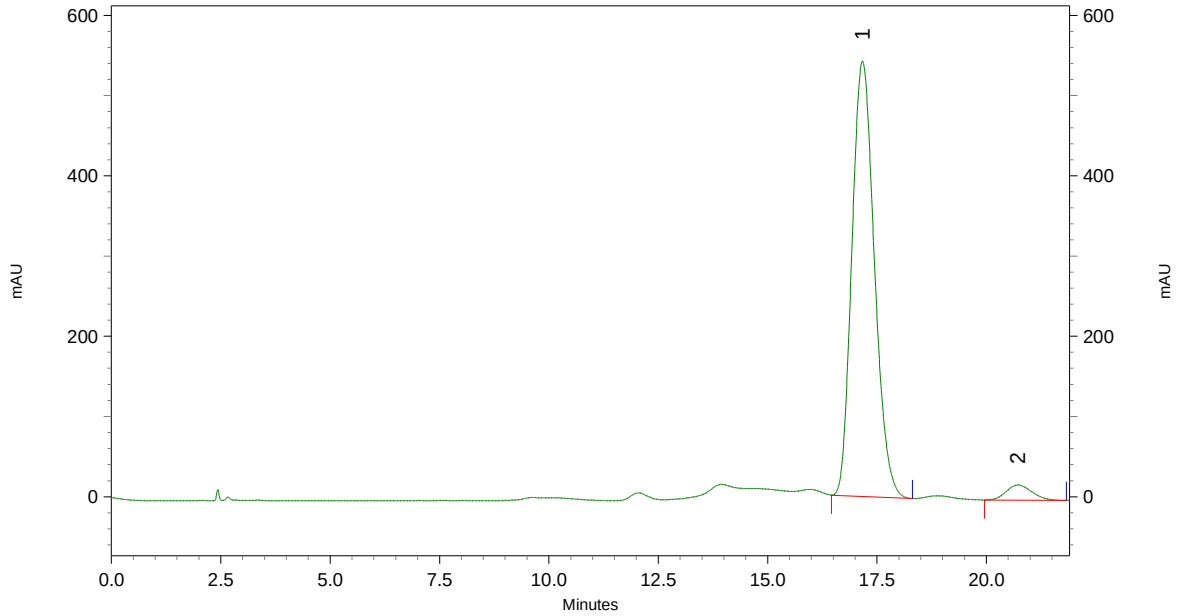
Compound 5p



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	16.75	37102379	50.23
2	20.04	36765131	49.77

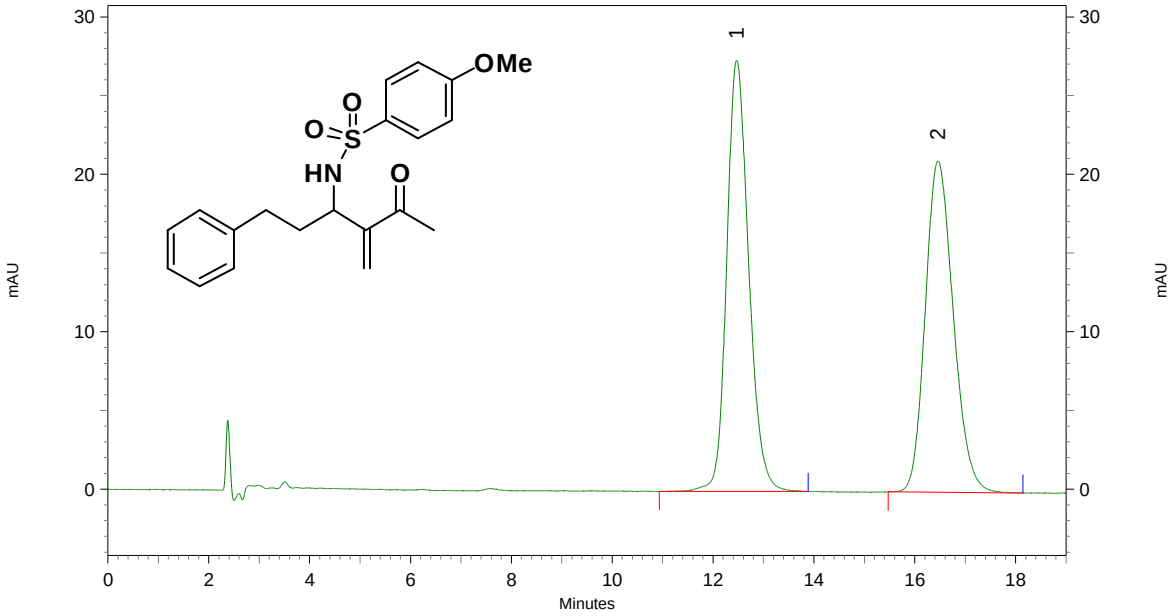


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	17.17	77423184	96.17
2	20.72	3087467	3.83

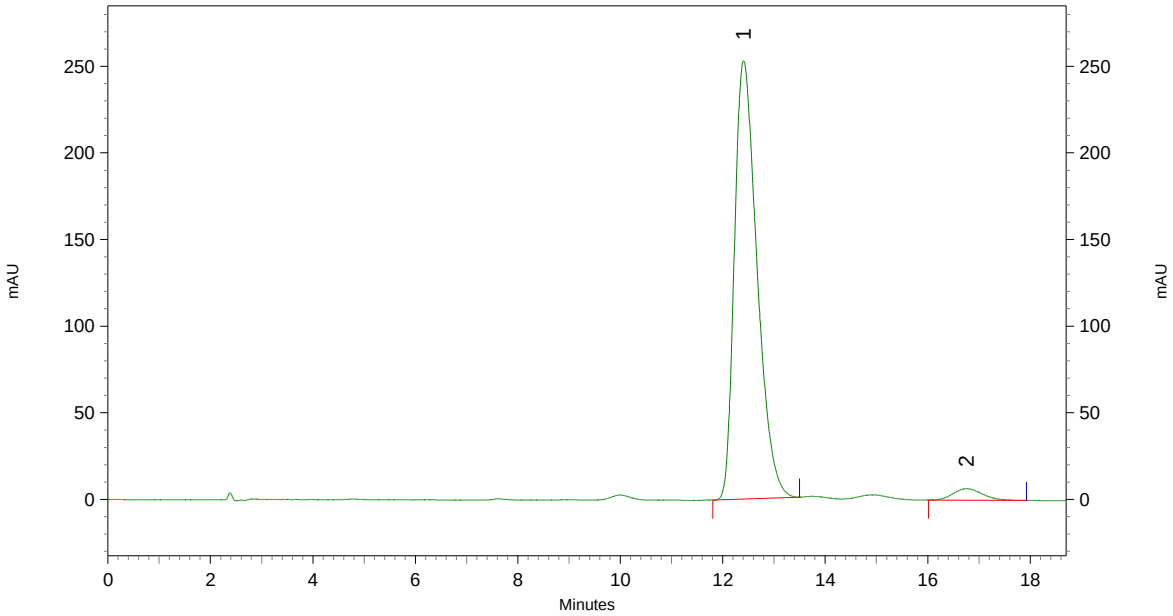
Compound 5q



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	12.47	3316796	50.53
2	16.46	3247126	49.47

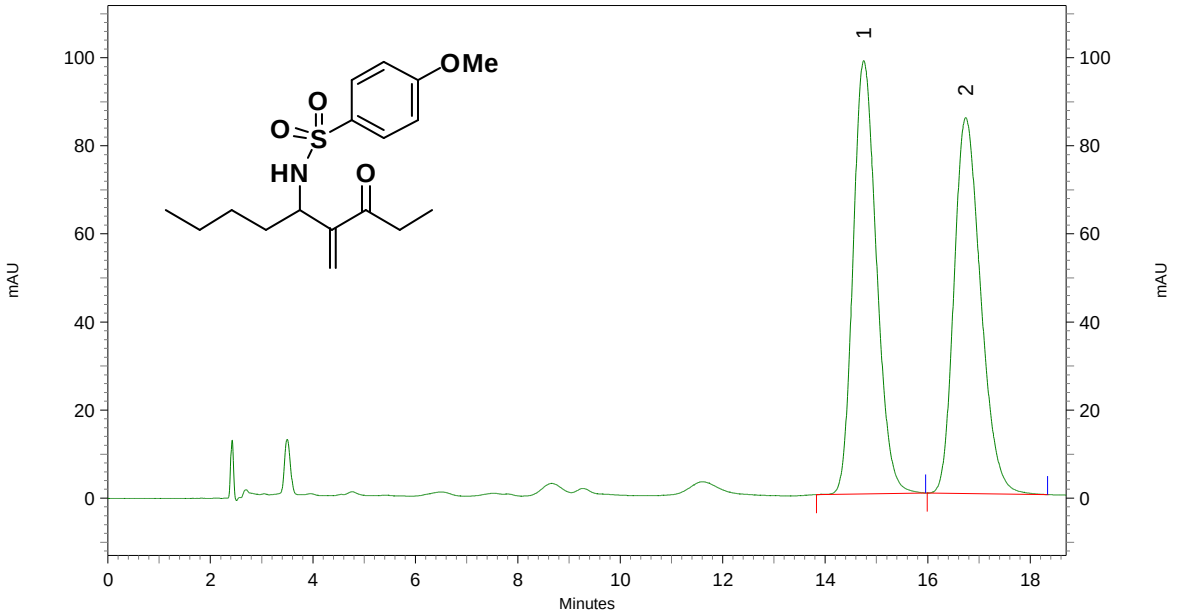


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	12.41	31008978	96.67
2	16.76	1068345	3.33

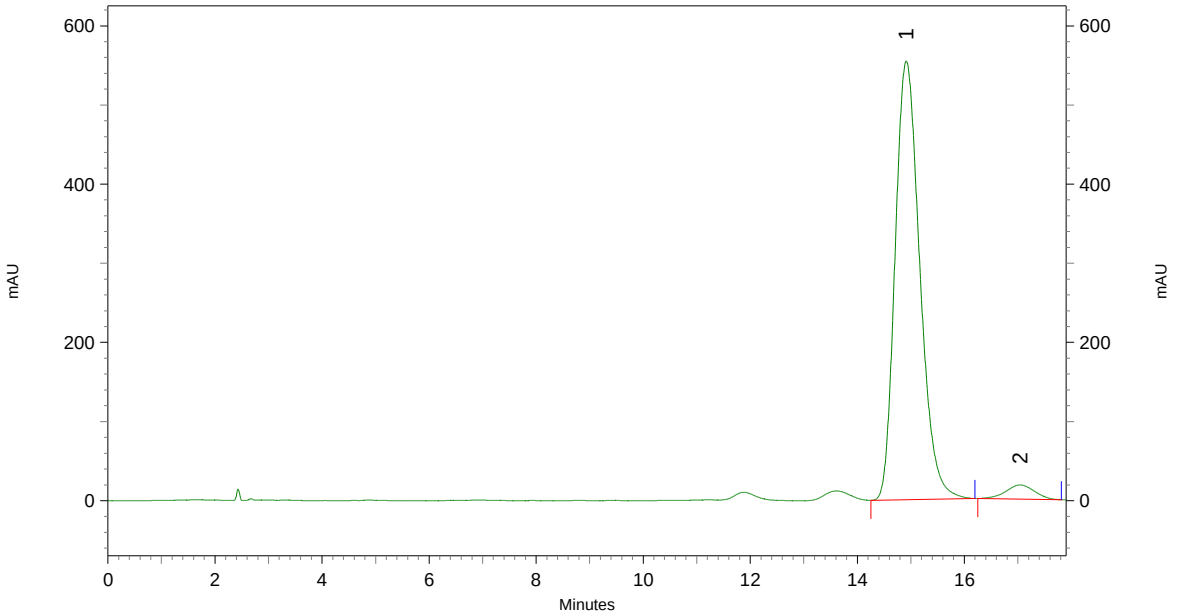
Compound 5r



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	14.75	12435601	50.20
2	16.74	12335787	49.80



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	14.91	70955215	96.38
2	17.04	2666144	3.62