Intramolecular aryl transfer to thionium ions in an approach to α-arylacetamides

Caroline Ovens[a], *Johannes Vogel*[a], *Nathaniel G. Martin*[b] *and David J. Procter*[a*]

[a]*The University of Manchester, Oxford Road, Manchester, M13 9PL, UK*

[b]*AstraZeneca, Mereside, Alderley Park, Macclesfield, Cheshire, SK10 4TG, UK*

[*]*E-mail: david.j.procter@manchester.ac.uk*

Fax: (+0044) 0161 275 4939

General Experimental

All reactions were carried out under an inert nitrogen atmosphere unless otherwise stated. Tetrahydrofuran was dried over sodium wire and benzophenone. Dichloromethane was dried over calcium hydride. Triethylamine was distilled from calcium hydride and stored over KOH. DMSO was distilled from calcium hydride, under reduced pressure, and stored over molecular sieves. All other solvents and reagents were purchased from commercial sources and used as supplied.

NMR spectra were recorded on 300, 400 and 500 MHz spectrometers. All chemical shift values are reported in ppm, with coupling constants in Hz. NMR assignments were performed with the aid of COSY, HMQC, HMBC, DEPT 135 and DEPT 90 experiments. The notation of signals is: -

δ_H: *chemical shift in ppm (multiplicity, J value(s), number of protons, rotamer/diasteromer assignment [if relevant], proton assignment)*
δ_C: *chemical shift in ppm (carbon assignment)*

For fluorine-containing compounds, carbon-fluorine couplings are reported with the carbon assignment. If assignment is ambiguous, for example in the case of overlapping aromatic signals, a range of shifts is reported.

$R^F = -CH_2CH_2C_8F_{17}$

Routine TLC analysis was carried out on aluminium sheets coated with silica gel 60 F254, 0.2 mm thickness. Solvent systems were either 40-60^o petroleum ether/EtOAc mixtures or methanol/dichloromethane mixtures. Plates were viewed with a 254 nm ultraviolet lamp and stained with aqueous potassium permanganate, anisaldehyde or DNP.

Flash column chromatography was carried out on 35 – 70 μ, 60A silica gel. Fluorous solid phase extraction (FSPE) was performed using fluorous silica gel packed in a glass column or with FSPE pre-packed cartridges.

Low-resolution mass spectra were obtained using electron impact ionisation (EI) and chemical ionisation (CI) techniques, or positive electrospray ionisation (ES^+).

Melting points were measured on a variable heater apparatus and are uncorrected.

IR spectra were recorded on an FTIR spectrometer as evaporated films (from dichloromethane) or neat, using sodium chloride windows.

Preparation of samarium (II) iodide[1]

Samarium metal (1.00 g, 6.62 mmol, 1.2 eq) was added to a dry 100 mL flask under a nitrogen atmosphere. THF (55 mL) was added and the mixture was degassed with N_2 for 5 minutes. I_2 (1.41 g, 5.52 mmol, 1 eq) was added, the flask was wrapped in aluminium foil and the mixture was degassed with N_2 for a further 5 minutes. The mixture was heated at 60 ºC for 18 hours to give a dark blue-black solution of SmI_2.

Fluorous solid phase extraction (FSPE)

A glass column was packed with fluorous silica gel using 80% aqueous MeCN. The mixture to be purified was dry loaded onto silica gel and transferred onto the fluorous silica gel. Elution with 80% aqueous MeCN (2-3 column volumes) separated the non-fluorous components of the mixture. Elution with 100% MeCN (2-3 column volumes) provided the fluorous components of the mixture. The fluorous column could be recycled by rinsing with 3 column volumes of Et_2O and drying with compressed air. The mixture could also be loaded onto the column in 80% aqueous MeCN, although sonication was usually necessary to aid dissolution.

[1] Imamoto, T.; Ono, M. *Chem. Lett.* **1987**, 501-2.

General procedure A: Preparation of α-Hydroxy amides

To the secondary benzylamine (1 eq) in CH_2Cl_2 (5 mL/mmol) was added acetoxyacetic acid (1.2 eq), 1-hydroxybenzotriazole hydrate (0.2 eq) and EDCI (1.2 eq) and the mixture stirred at room temperature for 6-20 hours. The reaction mixture was washed with 1M HCl (×3) and the organic layer dried (Na_2SO_4) and concentrated *in vacuo* to give the crude amide. To the resulting acetoxyacetamide (1 eq) in 2:1 MeOH/H_2O (6 mL/mmol) was added K_2CO_3 (4 eq) and the resulting mixture stirred at room temperature for 2-20 hours. MeOH was removed *in vacuo* and the residue taken up in H_2O and extracted with EtOAc (×3). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo* to afford the α-hydroxyamide.

General procedure B: Intramolecular aryl migration to give α-aryl acetamides

To oxalyl chloride (1.1 eq) in CH_2Cl_2 (4 mL/mmol) was added DMSO (2 eq) in CH_2Cl_2 (1 mL/mmol) *via* cannula at -78 ^oC. The mixture was stirred for 30 minutes at -78 ^oC. α-Hydroxyamide (1 eq) in CH_2Cl_2 (4 mL/mmol) was added *via* cannula at -78 ^oC and the mixture was stirred at this temperature for 1 hour. Triethylamine (5 eq) was added and the mixture allowed to warm to room temperature. The resulting yellow solution was stirred at room temperature for 3-15 hours. The organic layer was washed with aqueous saturated $NaHCO_3$ (×3), dried (Na_2SO_4) and concentrated *in vacuo* to yield the crude glyoxamide, usually as a yellow foam. To the crude glyoxamide (1 eq) in CH_2Cl_2 (12 mL/mmol) was added 1H,1H,2H,2H-perfluorodecane-1-thiol (0.7 eq) and the mixture was stirred at room temperature for 12-15 hours. Trifluoroacetic anhydride (9 eq) was added and the mixture was stirred at room temperature for 1 hour before the addition of $BF_3{\cdot}OEt_2$ (5 eq). After 3-8 hours stirring at room temperature, during which time the solution adopted an intense colour, aqueous saturated $NaHCO_3$ was added resulting in vigorous effervescence. The aqueous layer was extracted with CH_2Cl_2 (×3). The combined organic layers were washed with aqueous saturated $NaHCO_3$ (×3), dried (Na_2SO_4) and concentrated *in vacuo* to yield crude α-arylacetamide. Purification was achieved by FPSE or column chromatography on silica gel.

General procedure C: Alkylation of tagged α-aryl acetamides

Alkyl bromide (5 eq) was added to a solution of α-aryl amide (1 eq) in THF (0.03 mL/mmol). Sodium hydride (5 eq) was added and the reaction mixture was heated at reflux for 3-48 hours. EtOAc and H_2O were added and the layers separated. The aqueous layer was extracted with EtOAc (×2). The combined organic layers were dried (Na_2SO_4) and concentred *in vacuo*. Purification by FSPE or column chromatography on silica gel afforded the alkylated α-aryl acetamide.

General procedure D: Reductive cleavage of the fluorous tag from α-aryl acetamides

To a degassed solution of fluorous-tagged α-aryl acetamide (1 eq) in THF (0.5 mL/mmol) was added SmI_2 (0.1 M solution in THF, 2.2 – 4.0 eq). The dark blue coloured reaction mixture was stirred for 12-24 hours at room temperature until a colour change to yellow indicated consumption of SmI_2. TLC analysis was used to determine if a further addition of SmI_2 was required (2.2 – 4.0 eq). Saturated aqueous $NaHCO_3$ was added and the solution was extracted with Et_2O (×3). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by FSPE or flash column chromatography on silica gel afforded the detagged α-aryl acetamide.

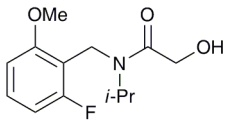
General procedure E: Palladium-catalysed Suzuki couplings of α-aryl acetamides

To a solution of fluorous-tagged α-aryl acetamide (1 eq), boronic acid (4 eq) and aqueous Na_2CO_3 (2 M, 7 eq) in a toluene:ethanol mix (2:1, 0.01 mL/mmol relative to Pd) was added $Pd(PPh_3)_4$ (20 mol%). The reaction was stirred at 90 °C for 18 hours and subsequently purified using FSPE to afford the cross-coupled product.

General procedure F: Reductive cleavage of the fluorous tag from modified α-aryl acetamides

To a degassed solution of the fluorous-tagged α-aryl acetamide (1 eq) in THF (0.05 mL/mmol) was added SmI_2 (0.1 M solution in THF, 4.0 eq). The dark blue coloured reaction mixture was stirred for 24 hours at room temperature. Saturated aqueous $Na_2S_2O_3$ was added and the solution was extracted with Et_2O (×3). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by FSPE afforded the detagged α-aryl acetamide.

N-(2-Fluoro-6-methoxy-benzyl)-2-hydroxy-*N*-*iso*-propylacetamide

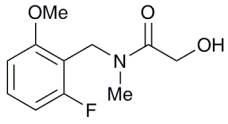


Following general procedure A: (2-Fluoro-6-methoxy-benzyl)-*iso*-propyl-amine (1.03 g, 5.24 mmol, 1 eq) was stirred with acetoxyacetic acid (0.742 g, 6.29 mmol, 1.2 eq), HOBt (0.142 g, 1.05 mmol, 0.2 eq) and EDCI (1.21 g, 6.29 mmol, 1.2 eq). The resulting crude amide (1.45 g, 4.88 mmol, 1 eq) was stirred with K_2CO_3 (2.70 g, 19.5 mmol, 4 eq). Work-up afforded *N*-(2-fluoro-6-methoxy-benzyl)-2-hydroxy-*N*-*iso*-propyl-acetamide as a yellow oil (0.990 g, 3.88 mmol, 74% over two steps). No further purification was required.

δ_H (400 MHz, $CDCl_3$, rotamer ratio 3:1) 1.10 (d, J = 6.8 Hz, major, 6H, 2 × C$\underline{H}_3$CH and minor, 6H, 2 × C$\underline{H}_3$CH), 3.68 (septet, J = 6.8 Hz, minor, 1H, C$\underline{H}$(CH$_3$)$_2$), 3.82 (s, major, 3H, C$\underline{H}_3$O and minor, 3H, C$\underline{H}_3$O), 4.03 (septet, J = 6.8 Hz, major, 1H, C$\underline{H}$(CH$_3$)$_2$), 4.20 (s, minor, 2H, C$\underline{H}_2$OH), 4.29 (s, major, 2H, C$\underline{H}_2$N), 4.33 (s, major, 2H, C$\underline{H}_2$OH), 4.77 (s, minor, 2H, C$\underline{H}_2$N), 6.61-6.71 (m, major, 2H, 2 × Ar$\underline{H}$ and minor, 2H, 2 × Ar$\underline{H}$), 7.17 (apparent q, J = 7.5 Hz, minor, 1H, Ar$\underline{H}$), 7.25 (apparent q, J = 7.8 Hz, 1H, Ar$\underline{H}$); δ_C (100 MHz, $CDCl_3$, major rotamer only) 19.4 (2 × $\underline{C}$H$_3$CH), 36.9 (d, J = 5 Hz, $\underline{C}$H$_2$N), 49.3 ($\underline{C}$H(CH$_3$)$_2$), 55.9 ($\underline{C}$H$_3$O), 60.5 ($\underline{C}$H$_2$OH), 106.4 (d, J = 3 Hz, Ar$\underline{C}$H), 108.2 (d, J = 23 Hz, Ar$\underline{C}$H), 112.1 (d, J = 16 Hz, Ar$\underline{C}$), 129.9 (d, J =

11 Hz, Ar<u>C</u>H), 159.1 (d, *J* = 7 Hz, Ar<u>C</u>OCH$_3$), 161.7 (d, *J* = 246 Hz, Ar<u>C</u>F), 171.7 (N<u>C</u>O); IR (neat/cm^{-1}) 3408 (broad, O-H), 2972, 2940 and 2843 (C-H), 1644 (C=O), 1615 and 1587 (Ar C=C); *m/z* (ES$^+$) 278 (MNa$^+$, 100%), 256 (MH$^+$, 73%); HRMS for $C_{13}H_{19}NO_3F$ (MH$^+$) found 256.1343, expected 256.1343.

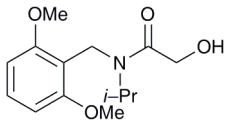
_N_-(2-Fluoro-6-methoxy-benzyl)-2-hydroxy-_N_-methylacetamide



Following general procedure A: *N*-(2-Fluoro-6-methoxy-benzyl)-*N*-methyl-amine (0.875 g, 5.18 mmol, 1 eq) was stirred with acetoxyacetic acid (0.734 g, 6.21 mmol, 1.2 eq), HOBt (0.140 g, 1.04 mmol, 0.2 eq) and EDCI (1.19 g, 6.21 mmol, 1.2 eq). The resulting crude amide (1.39 g, 5.18 mmol, 1 eq) was stirred with K_2CO_3 (2.86 g, 20.7 mmol, 4 eq). The crude acetamide was purifed by column chromatography om silica gel (50% EtOAc/petroleum ether) to afford *N*-(2-fluoro-6-methoxy-benzyl)-2-hydroxy-*N*-methyl- acetamide as a white solid (0.745 g, 3.28 mmol, 63% over two steps).

δ_H (400 MHz, $CDCl_3$, rotamer ratio 3:2) 2.72 (s, minor, 3H, C<u>H</u>$_3$N), 2.87 (s, major, 3H, C<u>H</u>$_3$N), 3.71 (t, *J* = 4.3 Hz, major, 1H, CH$_2$O<u>H</u>), 3.73 (t, *J* = 4.3 Hz, minor, 1H, CH$_2$O<u>H</u>), 3.84 (s, minor, 3H, C<u>H</u>$_3$O), 3.85 (s, major, 3H, C<u>H</u>$_3$O), 4.12 (d, *J* = 4.3 Hz, minor, 2H, C<u>H</u>$_2$OH), 4.35 (d, *J* = 1.3 Hz, major, 2H, C<u>H</u>$_2$N), 4.44 (d, *J* = 4.3 Hz, major, 2H, C<u>H</u>$_2$OH), 4.77 (d, *J* = 1.3 Hz, minor, 2H, C<u>H</u>$_2$N), 6.68-6.76 (m, major, 2H, 2 × Ar<u>H</u> and minor, 2H, 2 × Ar<u>H</u>) 7.23-7.32 (m, major, 1H, Ar<u>H</u> and minor, 1H, Ar<u>H</u>); δ_C (100 MHz, $CDCl_3$, major rotamer only) 32.2 (<u>C</u>H$_3$N), 39.3 (d, *J* = 5 Hz, <u>C</u>H$_2$N), 56.0 (<u>C</u>H$_3$O), 60.0 (<u>C</u>H$_2$OH), 106.4 (d, *J* = 3 Hz, Ar<u>C</u>H), 107.9 (d, *J* = 3 Hz, Ar<u>C</u>H), 110.7 (d, *J* = 17 Hz, Ar<u>C</u>), 130.3 (d, *J* = 11 Hz, Ar<u>C</u>H), 159.0 (d, *J* = 7 Hz, Ar<u>C</u>OCH$_3$), 162.2 (d, *J* = 247 Hz, Ar<u>C</u>F), 171.8 (N<u>C</u>O); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3409 (broad, O-H), 2939 and 2843 (C-H), 1650 (C=O), 1616 and 1587 (Ar C=C); *m/z* (ES$^+$) 250 (MNa$^+$, 100%), 228 (MH$^+$, 51%); HRMS for $C_{11}H_{15}NO_3F$ (MH$^+$) found 228.1040, expected 228.1030; anal. calcd. for $C_{11}H_{14}NO_3F$: C (58.14%), H (6.21%), N (6.16%), found C (58.07%), H (6.07%), N (5.94%); mp ($CHCl_3$) 68.7-72.3 °C.

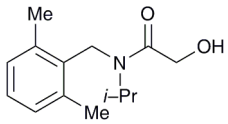
2-Hydroxy-*N*-*iso*-propyl-*N*-(2,6-dimethoxy-benzyl)acetamide



Following general procedure A: *N*-*iso*-Propyl-*N*-(2,6-dimethoxy-benzyl)-amine (1.36 g, 6.51 mmol, 1 eq) was stirred with acetoxyacetic acid (0.920 g, 7.81 mmol, 1.2 eq), HOBt (0.176 g, 1.30 mmol, 0.2 eq) and EDCI (1.50 g, 7.81 mmol, 1.2 eq). The resulting crude amide (1.81 g, 5.86 mmol, 1 eq) was stirred with K_2CO_3 (3.24 g, 23.4 mmol, 4 eq) to afford 2-hydroxy-*N*-*iso*-propyl-*N*-(2,6-dimethoxy-benzyl)-acetamide as a cream solid (2.57 g, 3.75 mmol, 85% over two steps). No further purification was required.

δ_H (500 MHz, $CDCl_3$, rotamer ratio 8:1) 1.03 (d, *J* = 6.6 Hz, minor, 6H, 2 × C$\underline{H}_3$CH), 1.09 (d, *J* = 6.9 Hz, major, 6H, 2 × C$\underline{H}_3$CH), 3.61 (septet, *J* = 6.6 Hz, minor, 1H, C$\underline{H}$(CH$_3$)$_2$), 3.80 (s, minor, 6H, 2 × C$\underline{H}_3$O), 3.81 (s, major, 6H, 2 × C$\underline{H}_3$O), 3.90 (septet, *J* = 6.9 Hz, major, 1H, C$\underline{H}$(CH$_3$)$_2$), 3.92 (t, *J* = 4.1 Hz, major, 1H, CH$_2$O$\underline{H}$), 4.18 (d, *J* = 5.8 Hz, minor, C$\underline{H}_2$OH), 4.32 (s, major, 2H, C$\underline{H}_2$N), 4.35 (d, *J* = 4.1 Hz, major, 2H, C$\underline{H}_2$OH), 4.87 (s, minor, 2H, C$\underline{H}_2$N), 6.53 (d, *J* = 8.5 Hz, minor, 2H, 2 × Ar$\underline{H}$) 6.55 (d, *J* = 8.5 Hz, major, 2H, 2 × Ar$\underline{H}$) 7.20 (t, *J* = 8.5 Hz, minor, 1H, Ar$\underline{H}$), 7.24 (t, *J* = 8.5 Hz, major, 1H, Ar$\underline{H}$); δ_C (125 MHz, $CDCl_3$, major rotamer only) 19.5 (2 × $\underline{C}$H$_3$CH), 37.4 ($\underline{C}$H$_2$N), 49.4 ($\underline{C}$H(CH$_3$)$_2$), 55.6 (2 × $\underline{C}$H$_3$O), 60.6 ($\underline{C}$H$_2$OH), 103.7 (2 × Ar$\underline{C}$H), 112.2 (Ar$\underline{C}$), 129.6 (Ar$\underline{C}$H), 159.0 (2 × Ar$\underline{C}$OCH$_3$), 171.6 (N$\underline{C}$O); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3400 (broad, O-H), 3103, 2992, 2967 and 2842 (C-H), 1643 (C=O), 1595 (Ar C=C); *m/z* (ES$^+$) 290 (MNa$^+$, 14%), 210 (8%); HRMS for $C_{14}H_{22}NO_4$ (MH$^+$) found 268.1546, expected 268.1543; anal. calcd. for $C_{14}H_{21}NO_4$: found C (63.22%), H (8.29%), N (5.24%); expected C (62.90%), H (7.92%), N (5.24%); mp (*iso*-propanol) 64.1-65.2 °C.

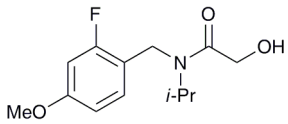
2-Hydroxy-*N*-(2,6-dimethyl-benzyl)-*N*-*iso*-propylacetamide



Following general procedure A: (2,4-Dimethyl-benzyl)-*iso*-propyl-amine (1.77 g, 10.0 mmol, 1 eq) was stirred with acetoxyacetic acid (1.42 g, 12.0 mmol, 1.2 eq), HOBt (0.270 g, 2.00 mmol, 0.2 eq) and EDCI (2.30 g, 12.0 mmol, 1.2 eq). The resulting crude amide (2.05 g, 7.40 mmol, 1 eq) was stirred with K_2CO_3 (4.09 g, 29.6 mmol, 4 eq). Purification by column chromatography on silica gel afforded 2-hydroxy-*N*-(2,4-dimethyl-benzyl)-*N*-*iso*-propyl-acetamide as a cream solid (0.968 g, 4.12 mmol, 41% over two steps).

δ_H (400 MHz, d_6-DMSO, 100 ºC) 1.12 (d, J = 6.8 Hz, 6H, 2 × C$\underline{H}_3$CH), 2.33 (s, 6H, 2 × ArC$\underline{H}_3$), 3.00 (br s, 1H, O$\underline{H}$), 3.45 (septet, J = 6.8 Hz, 1H, C$\underline{H}$(CH$_3$)$_2$), 4.19 (s, 2H, C$\underline{H}_2$OH), 4.56 (s, 2H, C$\underline{H}_2$N), 7.03-7.05 (m, 2H, 2 × Ar$\underline{H}$), 7.10 (dd, J = 8.5 Hz, 6.3 Hz, 1H, Ar$\underline{H}$); δ_C (100 MHz, d_6-DMSO, 100 ºC) 19.5 (2 × Ar$\underline{C}$H$_3$), 19.7 (2 × $\underline{C}$H$_3$CH), 42.4 ($\underline{C}$H$_2$N), 48.0 ($\underline{C}$H(CH$_3$)$_2$), 60.8 ($\underline{C}$H$_2$OH), 127.3 (Ar$\underline{C}$H), 128.5 (2 × Ar$\underline{C}$H), 133.4 (Ar$\underline{C}$), 137.3 (2 × Ar$\underline{C}$), 171.8 (N$\underline{C}$O); IR (neat/cm^{-1}) 3399 (broad, O-H), 3066, 2967 and 2935 (C-H), 1641 (C=O), 1595 (Ar C=C); *m/z* (ES$^+$) 258 (MNa$^+$, 100%), 236 (MH$^+$, 28%); HRMS for $C_{14}H_{21}NO_2Na$ (MNa$^+$) found 258.1465, expected 258.1465; anal. calcd. for $C_{14}H_{21}NO_2$: C (71.46%), H (8.99%), N (5.95%), found C (71.81%), H (9.04%), N (5.86%), mp ($CHCl_3$) 96.6-97.4 ºC.

_N_-(2-Fluoro-4-methoxy-benzyl)-2-hydroxy-_N_-_iso_-propylacetamide

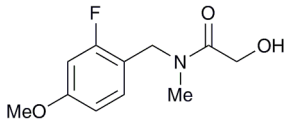


Following general procedure A: *N*-(2-Fluoro-4-methoxy-benzyl)-*N*-*iso*-propylamine (2.00 g, 10.2 mmol, 1 eq) was stirred with acetoxyacetic acid (1.44 g, 12.2 mmol, 1.2 eq), HOBt (0.274 g, 2.03 mmol, 0.2 eq) and EDCI (2.34 g, 12.2 mmol, 1.2 eq). The resulting crude amide (3.27 g, 11.0 mmol, 1 eq) was stirred with K_2CO_3 (6.09 g, 44.0 mmol, 4 eq). Purification by column chromatography on silica gel (3:3:1 petroleum ether/CH_2Cl_2/EtOAc) afforded *N*-(2-fluoro-4-methoxy-benzyl)-2-hydroxy-*N*-*iso*-propylacetamide as an orange oil (1.99 g, 7.80 mmol, 76% over two steps).

δ_H (500 MHz, $CDCl_3$, rotamer ratio 4:3) 1.08 (d, J = 6.9 Hz, minor, 6H, C$\underline{H}_3$CH), 1.09 (d, J = 6.6 Hz, major, 6H, C$\underline{H}_3$CH), 2.65-3.05 (br s, major, 1H, O$\underline{H}$ and minor, 1H, O$\underline{H}$), 3.67-3.75 (m, minor, 1H, C$\underline{H}$(CH$_3$)$_2$), 3.71 (s, major, 3H, C$\underline{H}_3$O), 3.73 (s,

minor, 3H, C<u>H</u>$_3$O), 4.04 (s, minor, 2H, C<u>H</u>$_2$OH), 4.22 (s, major, 2H, C<u>H</u>$_2$OH and minor, 2H, C<u>H</u>$_2$N), 4.52 (s, major, 2H, C<u>H</u>$_2$N), 4.61 (septet, J = 6.6 Hz, major, 1H, C<u>H</u>(CH$_3$)$_2$), 6.47-6.64 (m, major, 2H, 2 × Ar<u>H</u> and minor, 2H, 2 × Ar<u>H</u>), 6.98 (apparent t, J = 8.8 Hz, minor, 1H, Ar<u>H</u>), 7.12 (apparent t, J = 8.8 Hz, major, 1H, Ar<u>H</u>); δ_C (125 MHz, $CDCl_3$, major rotamer only) 20.8 (2 × <u>C</u>H$_3$CH), 36.8 (<u>C</u>H$_2$N), 47.5 (<u>C</u>H(CH$_3$)$_2$), 55.5 (<u>C</u>H$_3$O), 60.1 (<u>C</u>H$_2$OH), 101.3 (d, J = 25 Hz, Ar<u>C</u>H), 110.1 (d, J = 3 Hz, Ar<u>C</u>H), 117.4 (d, J = 14 Hz, Ar<u>C</u>), 129.9 (d, J = 6 Hz, Ar<u>C</u>H), 159.9 (d, J = 11 Hz, Ar<u>C</u>OCH$_3$), 160.3 (d, J = 245 Hz, Ar<u>C</u>F), 172.0 (N<u>C</u>O); IR (neat/cm^{-1}) 3412 (broad, O-H), 2975 and 2938 (C-H), 1642 (C=O), 1588 (Ar C=C); *m/z* (ES$^+$) 278 (MNa$^+$, 100%), 256 (MH$^+$, 4%), 211 (26%), 139 (11%); HRMS for $C_{13}H_{18}NO_3FNa$ (MNa$^+$) found 278.1174, expected 278.1163.

_N_-(2-Fluoro-4-methoxy-benzyl)-2-hydroxy-_N_-methylacetamide

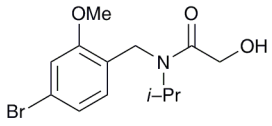


Following general procedure A: (2-Fluoro-4-methoxy-benzyl)-methylamine (0.959 g, 5.67 mmol, 1 eq) was stirred with acetoxyacetic acid (0.804 g, 6.81 mmol, 1.2 eq), HOBt (153 mg, 1.13 mmol, 0.2 eq) and EDCI (1.31 g, 6.81 mmol, 1.2 eq). The resulting crude amide (1.52 g, 5.65 mmol, 1 eq) was stirred with K_2CO_3 (3.12 g, 22.6 mmol, 4 eq). The crude acetamide was purifed by column chromatography on silica gel (50% EtOAc/petroleum ether) to afford *N*-(2-fluoro-4-methoxy-benzyl)-2-hydroxy-*N*-methylacetamide as an orange oil (1.02 g, 4.49 mmol, 79% over two steps).

δ_H (400 MHz, $CDCl_3$, rotamer ratio 2:1) 2.69 (s, major, 3H, C<u>H</u>$_3$N), 2.81 (s, minor, 3H, C<u>H</u>$_3$N), 3.64 (s, major, 3H, C<u>H</u>$_3$O), 3.65 (s, minor, 3H, C<u>H</u>$_3$O), 3.64-3.70 (m, major, 1H, O<u>H</u> and minor, 1H, O<u>H</u>), 4.03 (d, J = 2.8 Hz, major, 2H, C<u>H</u>$_2$OH), 4.16 (d, J = 2.8 Hz, minor, 2H, C<u>H</u>$_2$OH), 4.17 (s, minor, 2H, C<u>H</u>$_2$N), 4.47 (s, major, 2H, C<u>H</u>$_2$N), 6.46-6.58 (m, major, 2H, 2 × Ar<u>H</u> and minor, 2H, 2 × Ar<u>H</u>), 6.93 (t, J = 8.6 Hz, minor, 1H, Ar<u>H</u>) 7.10 (t, J = 8.6 Hz, major, 1H, Ar<u>H</u>); δ_C (75 MHz, $CDCl_3$, major rotamer) 32.3 (d, J = 2 Hz, <u>C</u>H$_3$N), 44.3 (d, J = 3 Hz, <u>C</u>H$_2$N), 55.4 (<u>C</u>H$_3$O), 59.8 (<u>C</u>H$_2$OH), 101.3 (d, J = 26 Hz, Ar<u>C</u>H), 110.1 (d, J = 3 Hz, Ar<u>C</u>H), 114.9 (d, J = 16

Hz, Ar<u>C</u>), 131.3 (d, *J* = 6 Hz, Ar<u>C</u>H), 160.4 (d, *J* = 11 Hz, Ar<u>C</u>OCH$_3$), 161.5 (d, *J* = 246 Hz, Ar<u>C</u>F), 171.6 (N<u>C</u>O); IR (neat/cm^{-1}) 3419 (broad, O-H), 3075, 2938 and 2840 (C-H), 1652 (C=O), 1626, 1587 and 1511 (Ar C=C); *m/z* (ES$^+$) 477 (dimer+Na, 98%), 335 (56%), 250 (MNa$^+$, 100%), 228 (MH$^+$, 71%); HRMS for $C_{11}H_{15}NO_3F$ (MH$^+$) found 228.1039, expected 228.1030.

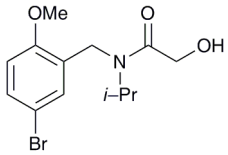
_N_-(4-Bromo-2-methoxy-benzyl)-2-hydroxy-_N_-_iso_-propylacetamide



Following general procedure A: *N*-(4-Bromo-2-methoxy-benzyl)-*N*-*iso*-propylamine (0.942 g, 3.65 mmol, 1 eq) was stirred with acetoxyacetic acid (0.517 g, 4.38 mmol, 1.2 eq), HOBt (99 mg, 0.730 mmol, 0.2 eq) and EDCI (0.840 g, 4.38 mmol, 1.2 eq). The resulting crude amide (1.16 g, 3.24 mmol, 1 eq) was stirred with K_2CO_3 (1.79 g, 13.0 mmol, 4 eq) to afford *N*-(4-bromo-2-methoxy-benzyl)-2-hydroxy-*N*-*iso*-propyl-acetamide as a colourless oil (0.877 g, 2.78 mmol, 76% over two steps). No further purification was required.

δ_H (400 MHz, $CDCl_3$, rotamer ratio 1.1:1), 1.14 (apparent t, *J* = 6.4 Hz, major, 6H, 2 × C<u>H</u>$_3$CH and minor, 6H, 2 × C<u>H</u>$_3$CH), 3.81 (septet, *J* = 6.6 Hz, minor, C<u>H</u>(CH$_3$)$_2$), 3.86 (s, major, 3H, C<u>H</u>$_3$O and minor, 3H, C<u>H</u>$_3$O), 4.04 (s, major, 2H, C<u>H</u>$_2$OH), 4.22 (s, major, 2H, C<u>H</u>$_2$N), 4.33 (s, minor, 2H, C<u>H</u>$_2$OH), 4.51 (s, minor, 2H, C<u>H</u>$_2$N), 4.76 (septet, *J* = 6.8 Hz, major, 1H, C<u>H</u>(CH$_3$)$_2$), 6.92-7.10 (m, major, 3H, 3 × Ar<u>H</u> and minor, 3H, 3 × Ar<u>H</u>); δ_C (100 MHz, $CDCl_3$) 19.9 (major, 2 × <u>C</u>H$_3$CH), 20.8 (minor, 2 × <u>C</u>H$_3$CH), 38.6 (minor, <u>C</u>H$_2$N), 40.1 (major, <u>C</u>H$_2$N), 47.1 (minor, <u>C</u>H(CH$_3$)$_2$), 47.3 (major, <u>C</u>H(CH$_3$)$_2$), 55.6 (major, <u>C</u>H$_3$O and minor <u>C</u>H$_3$O), 60.1 (minor, <u>C</u>H$_2$OH), 60.3 (major, <u>C</u>H$_2$OH), 113.7 (minor, Ar<u>C</u>H), 113.9 (major, Ar<u>C</u>H), 121.0 (minor, Ar<u>C</u>), 121.8 (major, Ar<u>C</u>), 123.5 (minor, Ar<u>C</u>H), 123.6 (major, Ar<u>C</u>H), 124.3 (major, Ar<u>C</u>), 125.5 (minor, Ar<u>C</u>), 127.6 (major, Ar<u>C</u>H), 128.6 (minor, Ar<u>C</u>H), 156.8 (minor, Ar<u>C</u>OCH$_3$), 157.0 (major, Ar<u>C</u>OCH$_3$), 171.9 (minor, N<u>C</u>O), 172.5 (major, N<u>C</u>O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3413 (broad, O-H), 2974 *m/z* (ES$^+$) 340 (^{81}Br, MNa$^+$, 32%), 338 (^{79}Br, MNa$^+$, 31%), 318 (^{81}Br, MH$^+$, 94%), 316 (^{79}Br, MH$^+$, 100%); HRMS for $C_{13}H_{19}NO_3{}^{79}Br$ (MH$^+$) found 316.0545, expected 316.0543.

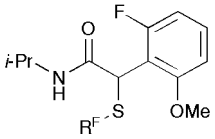
_N_-(5-Bromo-2-methoxy-benzyl)-2-hydroxy-_N_-_iso_-propyl-acetamide



Following general procedure A: (5-Bromo-2-methoxy-benzyl)-*iso*-propylamine (2.59 g, 10.0 mmol, 1 eq) was stirred with acetoxyacetic acid (1.42 g, 12.0 mmol, 1.2 eq), HOBt (0.271 g, 2.01 mmol, 0.2 eq) and EDCI (2.31 g, 12.0 mmol, 1.2 eq). The resulting crude amide (3.58 g, 10.0 mmol, 1 eq) was stirred with K_2CO_3 (5.53 g, 40.0 mmol, 4 eq). Purification by column chromatography on silica gel (gradient elution 10-50% EtOAc/petroleum ether) afforded *N*-(5-bromo-2-methoxy-benzyl)-2-hydroxy-*N*-*iso*-propylacetamide as a colourless oil (1.85 g, 5.85 mmol, 59% over two steps).
δ_H (400 MHz, $CDCl_3$, 1:1 rotamer ratio) 1.13-1.15 (m, one rotamer, 6H, 2 × C$\underline{H}_3$CH and one rotamer, 6H, 2 × C$\underline{H}_3$CH), 3.65 (t, *J* = 4.3 Hz, one rotamer, 1H, O$\underline{H}$), 3.78-3.85 (m, one rotamer, 1H, O$\underline{H}$ and one rotamer, 1H, C$\underline{H}$(CH_3)$_2$), 3.83 (s, one rotamer, 3H, C$\underline{H}_3$O and one rotamer, 3H, C$\underline{H}_3$O), 4.03 (d, *J* = 3.5 Hz, one rotamer, 2H, C$\underline{H}_2$OH), 4.24 (s, one rotamer, 2H, C$\underline{H}_2$N), 4.33 (d, *J* = 3.3 Hz, one rotamer, 2H, C$\underline{H}_2$OH), 4.54 (s, one rotamer, 2H, C$\underline{H}_2$N), 4.74 (septet, *J* = 6.8 Hz, one rotamer, 1H, C$\underline{H}$(CH_3)$_2$), 6.71 (d, *J* = 8.6 Hz, one rotamer, 1H, Ar$\underline{H}$), 6.74 (d, *J* = 8.6 Hz, one rotamer, 1H, Ar$\underline{H}$), 7.12 (s, one rotamer, 1H, Ar$\underline{H}$), 7.17 (s, one rotamer, 1H, Ar$\underline{H}$), 7.29 (d, *J* = 8.6 Hz, one rotamer, 1H, Ar$\underline{H}$), 7.35 (d, *J* = 8.6 Hz, one rotamer, 1H, Ar$\underline{H}$); δ_C (100 MHz, $CDCl_3$) 19.9 (one rotamer, 2 × $\underline{C}H_3$CH), 20.8 (one rotamer, 2 × $\underline{C}H_3$CH), 38.5 (one rotamer, $\underline{C}H_2$N), 40.1 (one rotamer, $\underline{C}H_2$N), 47.1 (one rotamer, $\underline{C}$H(CH_3)$_2$), 47.3 (one rotamer, $\underline{C}$H(CH_3)$_2$), 55.5 (both rotamers, $\underline{C}H_3$O), 60,1 (one rotamer, $\underline{C}H_2$OH), 60.3 ($\underline{C}H_2$OH), 111.7 (one rotamer, Ar$\underline{C}$H), 111.8 (one rotamer, Ar$\underline{C}$H), 112.9 (one rotamer, Ar$\underline{C}$), 113.0 (one rotamer, Ar$\underline{C}$), 127.4 (one rotamer, Ar$\underline{C}$), 128.7 (one rotamer, Ar$\underline{C}$), 129.0 (one rotamer, Ar$\underline{C}$H), 129.9 (one rotamer, Ar$\underline{C}$H), 130.5 (one rotamer, Ar$\underline{C}$H), 131.2 (one rotamer, Ar$\underline{C}$H), 155.2 (one rotamer, Ar$\underline{C}$OCH_3), 155.5 (one rotamer, Ar$\underline{C}$OCH_3), 171.9 (one rotamer, N$\underline{C}$O), 172.4 (one rotamer, N$\underline{C}$O); IR (neat/cm^{-1}) 3411 (broad, O-H), 3072, 2971, 2937 and 2838 (C-H), 1645 (C=O), 1593 (Ar C=C); m/z (ES^+) 340 (^{81}Br, MNa^+, 28%), 338 (^{79}Br, MNa^+,

29%), 318 (^{81}Br, MH^+, 79%), 316 (^{79}Br, MH^+, 77%), 259 (75%), 174 (100%); HRMS for $C_{13}H_{19}NO_3{}^{79}Br$ (MH^+) found 316.0540, expected 316.0543.

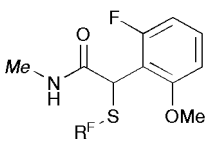
***rac*-2-(2-Fluoro-6-methoxy-phenyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-*N*-*iso*-propylacetamide 8**



Following general procedure B: Treatment of the crude glyoxamide **5** (0.1337 g, 0.487 mmol, 1 eq) with 1H,1H,2H,2H-perfluorodecane-1-thiol (0.10 mL, 0.341 mmol, 0.7 eq), TFAA (0.62 mL, 4.38 mmol, 9 eq) and $BF_3{\cdot}OEt_2$ (0.30 mL, 0.244 mmol, 5 eq) gave a colourless oil and purification by FSPE afforded acetamide **8** as a yellow oil (0.153 g, 0.218 mmol, 64% over two steps).

δ_H (400 MHz, $CDCl_3$) 1.19 (d, *J* = 6.6 Hz, 6H, 2 × C$\underline{H}_3$CH), 2.33-2.50 (m, 2H, $CH_2C\underline{H}_2C_8F_{17}$), 2.78-2.83 (m, 2H, C$\underline{H}_2CH_2C_8F_{17}$), 3.84 (s, 3H, C$\underline{H}_3$O), 4.06-4.18 (m, 1H, C$\underline{H}(CH_3)_2$), 4.94 (s, 1H, C$\underline{H}$S), 6.68-6.74 (m, 2H, 2 × Ar$\underline{H}$), 6.85 (d, *J* = 8.1 Hz, 1H, N$\underline{H}$), 7.23 (td, *J* = 8.4 Hz, 6.7 Hz, 1H, Ar$\underline{H}$); δ_C (100 MHz, $CDCl_3$) 22.4 (2 × $\underline{C}H_3$CH), 23.9 ($\underline{C}H_2CH_2C_8F_{17}$), 32.0 (t, *J* = 22 Hz, $CH_2\underline{C}H_2C_8F_{17}$), 42.0 ($\underline{C}H(CH_3)_2$), 44.1 ($\underline{C}$HS), 55.9 ($\underline{C}H_3$O), 106.8 (d, *J* = 3 Hz, Ar$\underline{C}$H), 108.5 (d, *J* = 23 Hz, Ar$\underline{C}$H), 114.8 (d, *J* = 17 Hz, Ar$\underline{C}$), 129.6 (d, *J* = 11 Hz, Ar$\underline{C}$H), 157.8 (d, *J* = 7 Hz, Ar$\underline{C}OCH_3$), 161.0 (d, *J* = 246 Hz, Ar$\underline{C}$F), 167.4 (N$\underline{C}$O); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3370 (N-H), 3318, 2879, 2941 and 2972 (C-H), 1667 (C=O) 1584 and 1613 (Ar C=C); *m/z* (ES^+) 726 (MNa^+, 100%), 278 (17%); HRMS for $C_{22}H_{19}NO_2F_{18}SNa$ (MNa^+) found 726.0732, expected 726.0741.

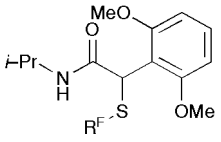
***rac*-2-(2-Fluoro-6-methoxy-phenyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-*N*-methylacetamide 16**



Following general procedure B: Treatment of the crude glyoxamide **9** (0.117 g, 0.521 mmol, 1 eq) with 1H,1H,2H,2H-perfluorodecane-1-thiol (0.11 mL, 0.365 mmol, 0.7 eq), TFAA (0.66 mL, 4.69 mmol, 9 eq) and $BF_3 \cdot OEt_2$ (0.32 mL, 2.61 mmol, 5 eq) and purification by FSPE afforded acetamide **16** as a cream amorphous solid (0.126g, 0.187 mmol, 51% over two steps).

δ_H (400 MHz, $CDCl_3$) 2.34-2.49 (m, 2H, $C\underline{H}_2C_8F_{17}$), 2.81-2.85 (m, 2H, $C\underline{H}_2CH_2C_8F_{17}$), 2.90 (d, *J* = 5.0 Hz, 3H, $C\underline{H}_3NH$), 3.86 (s, 3H, $C\underline{H}_3O$), 4.98 (s, 1H, C<u>H</u>S), 6.71-6.76 (m, 2H, 2 × Ar<u>H</u>), 6.95-7.01 (br q, 1H, N<u>H</u>), 7.25 (dt, *J* = 8.3, 6.8 Hz, 1H, Ar<u>H</u>); δ_C (75 MHz, $CDCl_3$) 24.0 ($\underline{C}H_2CH_2C_8F_{17}$), 27.0 ($\underline{C}H_3N$), 32.0 (t, *J* = 22 Hz, $CH_2\underline{C}H_2C_8F_{17}$), 43.9 (d, *J* = 2 Hz, <u>C</u>HS), 56.0 ($\underline{C}H_3O$), 107.0 (d, *J* = 3 Hz, Ar<u>C</u>H), 108.6 (d, *J* = 23 Hz, Ar<u>C</u>H), 114.8 (d, *J* = 16 Hz, Ar<u>C</u>), 129.7 (d, *J* = 11 Hz, Ar<u>C</u>H), 157.8 (d, *J* = 8 Hz, Ar<u>C</u>OCH_3), 161.0 (d, *J* = 247 Hz, Ar<u>C</u>F), 169.1 (N<u>C</u>O); IR (evaporated film/cm^{-1}) 3334 (N-H), 3048, 2844 and 2846 (C-H), 1660 (C=O), 1615, 1588 and 1531 (Ar C=C); *m/z* (ES^+) 698 (MNa^+, 49%), 693 (MNH_4^+ 42%), 676 (MH^+, 100%); HRMS for $C_{20}H_{16}NO_2F_{18}S$ (MH^+) found 676.0609, expected 676.0609.

rac-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfanyl)-2-(2,6-dimethoxy-phenyl)-_N_-_iso_-propylacetamide 17

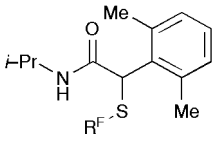


Following general procedure B: Treatment of crude glyoxamide **10** (0.190 g, 0.720 mmol, 1 eq) with 1H,1H,2H,2H-perfluorodecane-1-thiol (0.15 mL, 0.504 mmol, 0.7 eq), TFAA (0.91 mL, 6.45 mmol, 9 eq) and $BF_3 \cdot OEt_2$ (0.45 mL, 3.58 mmol, 5 eq) and purification by column chromatography on silica gel (35% EtOAc/petroleum ether) afforded acetamide **17** as a yellow solid (0.171 g, 0.239 mmol, 48% over two steps).

δ_H (500 MHz, $CDCl_3$) 1.18 (d, *J* = 6.6 Hz, 6H, 2 × $C\underline{H}_3CH$), 2.33-2.56 (m, 2H, $CH_2C\underline{H}_2C_8F_{17}$), 2.78 (t, *J* = 8.2 Hz, 2H, $C\underline{H}_2CH_2C_8F_{17}$), 3.82 (s, 6H, 2 × $C\underline{H}_3O$), 4.10 (m, 1H, $C\underline{H}(CH_3)_2$), 5.05 (s, 1H, C<u>H</u>S), 5.56 (d, *J* = 8.2 Hz, 2H, 2 × Ar<u>H</u>), 6.74 (d, *J* = 7.9 Hz, 1H, N<u>H</u>), 7.23 (t, *J* = 8.2 Hz, 1H, Ar<u>H</u>); δ_C (125 MHz, $CDCl_3$) 22.7 (2 × $\underline{C}H_3CH$), 23.9 ($\underline{C}H_2CH_2C_8F_{17}$), 32.3 (t, *J* = 23 Hz, $CH_2\underline{C}H_2C_8F_{17}$), 41.8 ($\underline{C}H(CH_3)_2$),

44.7 (CHS), 55.7 (2 × CH_3O), 104.2 (2 × ArCH), 115.3 (ArC), 129.4 (ArCH), 157.6 (2 × $ArCOCH_3$), 168.8 (NCO); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3369 (N-H), 2970, 2936 and 2841 (C-H), 1665 (C=O), 1594 and 1516 (Ar C=C); *m/z* (ES^+) 738 (MNa^+, 100%), 426 (42%); HRMS for $C_{23}H_{22}NO_3SNa$ (MNa^+) found 738.0942, expected 738.0941; mp (CH_2Cl_2) 90.8-93.0 °C.

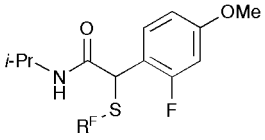
rac-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-decylsulfanyl)-2-(2,6-dimethyl-phenyl)-_N_-_iso_-propylacetamide 18



Following general procedure B: Treatment of the crude glyoxamide **11** (0.340 g, 1.46 mmol, 1 eq) with 1H,1H,2H,2H-perfluorodecane-1-thiol (0.30 mL, 1.02 mmol, 0.7 eq), TFAA (1.85 mL, 13.1 mmol, 9 eq) and $BF_3 \cdot OEt_2$ (0.90 mL, 7.30 mmol, 5 eq) and purification by column chromatography on silica gel (5% EtOAc/petroleum ether) afforded acetamide **18** as a yellow amorphous solid (0.526 g, 0.770 mmol, 75% over two steps).

δ_H (400 MHz, $CDCl_3$) 1.13 (d, *J* = 6.6 Hz, 6H, 2 × CH_3CH), 2.18-2.49 (m, 2H, $CH_2C_8F_{17}$), 2.38 (s, 6H, 2 × CH_3Ar), 2.78-2.95 (m, 2H, $CH_2CH_2C_8F_{17}$), 4.12 (m, 1H, $CH(CH_3)_2$), 4.97 (s, 1H, CHS), 5.94 (d, *J* = 7.6 Hz, 1H, NH), 7.05-7.07 (m, 2H, 2 × ArH), 7.11-7.15 (m, 1H, ArH); δ_C (100 MHz, $CDCl_3$) 20.6 (2 × CH_3Ar), 22.4 (2 × CH_3CH), 24.1 (t, *J* = 4 Hz, $CH_2CH_2C_8F_{17}$), 31.9 (t, *J* = 22 Hz, $CH_2C_8F_{17}$), 42.1 ($CH(CH_3)_2$), 50.8 (CHS), 128.2 (2 × ArCH), 129.4 (ArCH), 134.3 (2 × ArC), 137.1 (ArC), 168.4 (NCO); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3294 (N-H), 3036, 2973, 2937 and 2877 (C-H), 1652 (C=O), 1520 (Ar C=C); *m/z* (ES^+) 706 (MNa^+, 100%), 684 (MH^+, 25%), 402 (13%); HRMS for $C_{23}H_{23}NOF_{17}S$ (MH^+) found 684.1231, expected 684.1223.

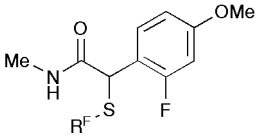
rac-2-(2-Fluoro-4-methoxyphenyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-_N_-_iso_-propylacetamide 19



Following general procedure B: Treatment of crude glyoxamide **12** (0.550 g, 2.17 mmol, 1 eq) with 1H,1H,2H,2H-perfluorodecane-1-thiol (0.45 mL, 1.52 mmol, 0.7 eq), TFAA (2.76 mL, 19.6 mmol, 9 eq) and $BF_3{\cdot}OEt_2$ (1.43 mL, 10.9 mmol, 5 eq) and purification by FSPE afforded acetamide **19** as a yellow foam (0.650 g, 0.925 mmol, 61% over two steps).

δ_H (500 MHz, $CDCl_3$) 1.15 (d, J = 6.6 Hz, 3H, C$\underline{H}_3$CH), 1.18 (d, J = 6.6 Hz, 3H, C$\underline{H}_3$CH), 2.28-2.45 (m, 2H, $CH_2C\underline{H}_2C_8F_{17}$), 2.72-2.82 (m, 2H, C$\underline{H}_2CH_2C_8F_{17}$), 3.79 (s, 3H, C$\underline{H}_3$O), 4.10 (m, 1H, C$\underline{H}(CH_3)_2$), 4.77 (s, 1H, C$\underline{H}$S), 6.36 (d, J = 7.9 Hz, 1H, N$\underline{H}$), 6.63 (dd, J = 11.7 Hz, 2.5 Hz, 1H, Ar$\underline{H}$), 6.70 (dd, J = 8.5 Hz, 2.5 Hz, 1H, Ar$\underline{H}$), 7.36 (t, J = 8.5 Hz, 1H, Ar$\underline{H}$); δ_C (125 MHz, $CDCl_3$) 22.5 (2 × ($\underline{C}H_3)_2$CH), 23.0 ($\underline{C}H_2CH_2C_8F_{17}$), 31.5 (t, J = 21 Hz, $CH_2\underline{C}H_2C_8F_{17}$), 42.1 ($\underline{C}H(CH_3)_2$), 47.0 ($\underline{C}$HS), 55.6 ($\underline{C}H_3$O), 101.9 (d, J = 26 Hz, Ar$\underline{C}$H), 110.6 (d, J = 3 Hz, Ar$\underline{C}$H), 115.7 (d, J = 5 Hz, Ar$\underline{C}$), 129.8 (Ar$\underline{C}$H), 159.9 (d, J = 11 Hz, Ar$\underline{C}$OCH$_3$, 161.8 (d, J = 246 Hz, Ar$\underline{C}$F), 167.6 (N$\underline{C}$O); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3306 (N-H), 3063, 2977, 2940 and 2840 (C-H), 1651 (C=O), 1634, 1585 and 1538 (Ar C=C); _m/z_ (ES^+) 726 (MNa^+, 100%), 704 (MH^+, 22%); HRMS for $C_{22}H_{20}NO_2F_{18}S$ (MH^+) found 704.0919, expected 704.0922.

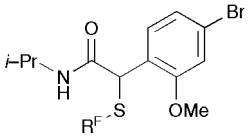
rac-2-(2-Fluoro-4-methoxy-phenyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-_N_-methylacetamide 20



Following general procedure B: Treatment of the crude glyoxamide **20** (0.130 g, 0.455 mmol, 1 eq) with 1H,1H,2H,2H-perfluorodecane-1-thiol (0.09 mL, 0.319 mmol, 0.7 eq), TFAA (0.58 mL, 4.10 mmol, 9 eq) and $BF_3 \cdot OEt_2$ (0.28 mL, 2.28 mmol, 5 eq) and purification by FSPE removed all non-fluorous impurities. Subsequent column chromatography of the fluorous fraction on silica gel (10% EtOAc/petroleum ether) afforded acetamide **20** as white needles (0.084 g, 0.124 mmol, 39% over two steps).

δ_H (300 MHz, $CDCl_3$) 2.26-2.45 (m, 2H, $C\underline{H}_2C_8F_{17}$), 2.74-2.81 (m, 2H, $C\underline{H}_2CH_2C_8F_{17}$), 2.88 (d, *J* = 4.9 Hz, 3H, $NC\underline{H}_3$), 3.81 (s, 3H, $C\underline{H}_3O$), 4.82 (s, 1H, C<u>H</u>S), 6.43-6.51 (br s, 1H, N<u>H</u>), 6.64 (dd, *J* = 12.0 Hz, 2.5 Hz, Ar<u>H</u>), 6.73 (ddd, *J* = 8.7 Hz, 2.6 Hz, 0.8 Hz, Ar<u>H</u>), 7.40 (t, *J* = 8.7 Hz, 1H, Ar<u>H</u>); δ_C (75 MHz, $CDCl_3$) 23.0 ($\underline{C}H_2CH_2C_8F_{17}$), 26.8 ($\underline{C}H_3N$), 31.6 (t, *J* = 22 Hz, $\underline{C}H_2C_8F_{17}$), 46.8 (d, *J* = 2 Hz, <u>C</u>HS), 55.6 ($\underline{C}H_3O$), 101.7 (d, *J* = 26 Hz, Ar<u>C</u>H), 110.7 (d, *J* = 3 Hz, Ar<u>C</u>H), 115.7 (d, *J* = 16 Hz, Ar<u>C</u>), 130.0 (d, *J* = 4 Hz, Ar<u>C</u>H), 159.6 (Ar<u>C</u>OCH_3), 160.7 (d, *J* = 246 Hz, Ar<u>C</u>F), 169.2 (N<u>C</u>O); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3253 (N-H), 3055 and 2988 (C-H), 1644 (C=O), 1557 and 1506 (Ar C=C); *m/z* (ES^+) 698 (MNa^+, 100%), 693 (M+18, 93%), 676 (MH^+, 43%); HRMS for $C_{20}H_{16}NO_2F_{18}S$ (MH^+) found 676.0603, expected 676.0609; anal. calcd. for $C_{20}H_{15}NO_2F_{18}$: C (35.57%), H (2.24%), N (2.07%), found C (36.00%), H (2.26%), N (2.02%); mp ($CHCl_3$) 100.1-102.4 °C.

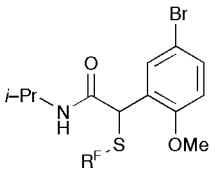
rac-2-(4-Bromo-2-methoxy-phenyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-_N-iso_-propylacetamide 21



Following general procedure B: Treatment of the crude glyoxamide **14** (0.609 g, 1.94 mmol, 1 eq) with 1H,1H,2H,2H-perfluorodecane-1-thiol (0.40 mL, 1.36 mmol, 0.7 eq), TFAA (2.47 mL, 17.5 mmol, 9 eq) and $BF_3 \cdot OEt_2$ (1.20 mL, 9.70 mmol, 5 eq) and purification by column chromatography on silica gel (20% EtOAc/petroleum ether) afforded acetamide **21** as a white amorphous solid (0.683 g, 0.894 mmol, 66% over two steps).

δ_H (400 MHz, $CDCl_3$) 1.14 (d, *J* = 6.6 Hz, 3H, C$\underline{H}_3$CH), 1.17 (d, *J* = 6.6 Hz, 3H, C$\underline{H}_3$CH), 2.31-2.47 (m, 2H, C$\underline{H}_2C_8F_{17}$), 2.66-2.82 (m, 2H, C$\underline{H}_2CH_2C_8F_{17}$), 3.85 (s, 3H, C$\underline{H}_3$O), 4.02-4.14 (m, 1H, C$\underline{H}(CH_3)_2$), 4.86 (s, 1H, C$\underline{H}$S), 6.31 (d, *J* = 8.1 Hz, 1H, N$\underline{H}$), 7.03 (d, *J* = 1.8 Hz, 1H, Ar$\underline{H}$), 7.11 (dd, *J* = 8.1 Hz, 1.8 Hz, 1H, Ar$\underline{H}$), 7.27 (d, *J* = 8.1 Hz, 1H, Ar$\underline{H}$); δ_C (100 MHz, $CDCl_3$) 22.4 (C$\underline{H}_3$CH), 22.6 (C$\underline{H}_3$CH), 23.1 (C$\underline{H}_2CH_2C_8F_{17}$), 31.7 (t, *J* = 22 Hz, C$\underline{H}_2C_8F_{17}$), 42.0 (C$\underline{H}$N), 47.6 (C$\underline{H}$S), 55.8 (C$\underline{H}_3$O), 114.5 (ArC$\underline{H}$), 122.8 (Ar$\underline{C}$), 124.3 (ArC$\underline{H}$), 124.5 (Ar$\underline{C}$), 129.9 (ArC$\underline{H}$), 157.1 (Ar$\underline{C}$OCH$_3$), 167.9 (N$\underline{C}$O); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3297 (N-H), 2930 and 2972 (C-H), 1651 (C=O), 1587 and 16828 (Ar C=C); *m/z* (ES^+) 788 (MNa^+, 58%), 786 (MNa^+, 51%), 766 (MH^+, 23%), 764 (MH^+, 21%), 627 (57%), 625 (100%); HRMS for $C_{22}H_{19}NO_2F_{17}SBrNa$ (MNa^+) found 785.9941, expected 785.9941.

rac-2-(5-Bromo-2-methoxyphenyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-*N*-*iso*-propylacetamide 22

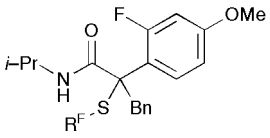


Following general procedure B: Treatment of the crude glyoxamide **15** (0.428 g, 1.36 mmol, 1 eq) with 1H,1H,2H,2H-perfluorodecane-1-thiol (0.28 mL, 0.954 mmol, 0.7 eq), TFAA (1.73 mL, 12.3 mmol, 9 eq) and $BF_3 \cdot OEt_2$ (0.84 mL, 6.82 mmol, 5 eq) and purification by column chromatography on silica gel (10% EtOAc/petroleum ether) afforded acetamide **22** as a white amorphous solid (0.464 g, 0.607 mmol, 64% over two steps).

δ_H (400 MHz, $CDCl_3$) 1.16 (d, *J* = 6.6 Hz, 3H, C$\underline{H}_3$CH), 1.20 (d, *J* = 6.6 Hz, 3H, C$\underline{H}_3$CH), 2.34-2.47 (m, 2H, C$\underline{H}_2C_8F_{17}$), 2.70-2.83 (m, 2H, C$\underline{H}_2CH_2C_8F_{17}$), 3.85 (s, 3H, C$\underline{H}_3$O), 4.04-4.16 (m, 1H, C$\underline{H}(CH_3)_2$), 4.86 (s, 1H, C$\underline{H}$S), 6.35 (br d, *J* = 7.8 Hz, 1H, N$\underline{H}$), 6.78 (d, *J* = 8.8 Hz, 1H, Ar$\underline{H}$), 7.39 (dd, *J* = 8.8 Hz, 2.5 Hz, 1H, Ar$\underline{H}$), 7.50 (d, *J* = 2.5 Hz, 1H, Ar$\underline{H}$); δ_C (75 MHz, $CDCl_3$) 22.5 (C$\underline{H}_3$CH), 22.7 (C$\underline{H}_3$CH), 23.2 (C$\underline{H}_2CH_2C_8F_{17}$), 31.7 (t, *J* = 22 Hz, C$\underline{H}_2C_8F_{17}$), 42.1 (C$\underline{H}(CH_3)_2$), 47.8 (C$\underline{H}$S), 55.8

(CH_3O), 112.6 (ArCH), 113.4 (ArC), 127.5 (ArC), 131.5 (ArCH), 132.2 (ArCH), 157.7 (ArCOCH_3), 167.7 (NCO); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3290 (N-H), 3073, 2970, 2930, 2874 and 2849 (C-H), 1644 (C=O), 1617, 1589 and 1552 (Ar C=C); *m/z* (ES$^+$) 788 (^{81}Br, MNa$^+$, 53%), 786 (^{79}Br, MNa$^+$, 51%), 766 (^{81}Br, MH$^+$, 100%), 764 (^{79}Br, MH$^+$, 99%); HRMS for $C_{22}H_{20}NO_2F_{17}S^{79}Br$ (MH$^+$) found 764.0150, expected 764.0121; anal. calcd. for $C_{22}H_{19}NO_2F_{17}SBr$: C (34.57%), H (2.51%), N (1.83%), found C (34.52%), H (2.34%), N (1.76%).

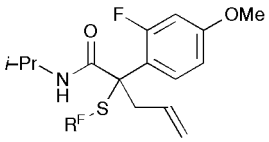
rac-2-Benzyl-2-(2-fluoro-4-methoxy-phenyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-_N_-_iso_-propyl-acetamide 23



Following general procedure C: Benzyl bromide (0.04 mL, 0.341 mmol, 5 eq) and sodium hydride (8 mg, 0.341 mmol, 5 eq) were heated at reflux with α-aryl acetamide **19** (48 mg, 0.068 mmol, 1 eq) for 18 hours. Purification of the crude product by column chromatography on silica gel (10% EtOAc/petroleum ether) gave **23** as a yellow oil (39 mg, 0.042 mmol, 71%).

δ_H (400 MHz, $CDCl_3$) 0.98 (d, *J* = 6.6 Hz, 3H, CH$_3$CH), 1.11 (d, *J* = 6.6 Hz, 3H, CH$_3$CH), 2.09-2.35 (m, 2H, CH$_2$C$_8$F$_{17}$), 2.63-2.80 (m, 2H, CH$_2$CH$_2$C$_8$F$_{17}$), 3.56 (s, 2H,CH$_2$Ph), 3.81 (s, 3H, CH$_3$O), 4.02-4.10 (m, 1H, CH(CH$_3$)$_2$), 5.97 (d, *J* = 8.1 Hz, 1H, NH), 6.61-6.69 (m, 2H, 2 × ArH), 6.95-6.98 (m, 2H, 2 × ArH), 7.14-7.20 (m, 4H, 4 × ArH); δ_C (75 MHz, $CDCl_3$) 20.6 (CH$_2$CH$_2$C$_8$F$_{17}$), 22.2 (CH$_3$CH), 22.5 (CH$_3$CH), 31.1 (t, *J* = 22 Hz, CH$_2$C$_8$F$_{17}$), 41.9 (CH(CH$_3$)$_2$), 42.3 (CHN), 55.6 (CH$_3$O), 59.4 (d, *J* = 3 Hz, CS), 102.4 (d, *J* = 27 Hz, ArCH), 109.7 (d, *J* = 3 Hz, ArCH), 119.1 (d, *J* = 11 Hz, ArC), 126.9 (ArCH), 127.6 (2 × ArCH), 130.0 (d, *J* = 5 Hz, ArCH), 130.9 (2 × ArCH), 135.7 (ArC), 160.8 (d, *J* = 11 Hz, ArCOCH$_3$), 160.7 (d, *J* = 249 Hz, ArCF), 169.7 (NCO); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3367 (N-H), 3064, 3032, 2974, 2939, 2877 and 2843 (C-H), 1668 (C=O), 1622, 1580 and 1505 (Ar C=C); *m/z* (ES$^+$) 991 (49%), 816 (MNa$^+$, 100%); HRMS for $C_{29}H_{26}NO_2F_{18}S$ (MH$^+$) found 794.1393, expected 794.1391.

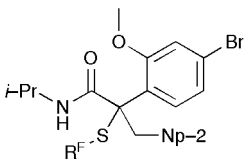
2-(2-Fluoro-4-methoxy-phenyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-pent-4-enoic acid isopropylamide 24



Following general procedure C: Allyl bromide (0.11 mL, 1.21 mmol, 5 eq) and sodium hydride (48 mg, 1.21 mmol, 5 eq) were heated at reflux with α-aryl acetamide **19** (0.17 g, 0.242 mmol, 1 eq) for 18 hours. Purification of the crude product by FSPE gave **24** as a yellow oil (0.1526 g, 0.177 mmol, 73 %).

δ_H (400 MHz, $CDCl_3$) 1.15 (d, *J* = 2.3 Hz, 3H, $CHC\underline{H}_3$), 1.14 (d, *J* = 2.3 Hz, 3H, $CHC\underline{H}_3$), 2.16 - 2.34 (m, 2H, $C\underline{H}_2CF_2$), 2.65 - 2.79 (m, 2H, $SC\underline{H}_2$), 3.01 (t, *J* = 6.4 Hz, 2H, $C\underline{H}_2CH=CH_2$), 3.83 (s, 3H, $OC\underline{H}_3$), 4.06 - 4.20 (m, 1H, $C\underline{H}(CH_3)_2$), 5.03 - 5.11 (m, 2H, $C\underline{H}_2=CH$), 5.59 - 5.72 (m, 1H, $CH_2=C\underline{H}$), 5.92 (d, *J* = 8.1 Hz, 1H, NH), 6.65 (dd, *J* = 13.4, 2.5 Hz, 1H, ArCH), 6.73 (dd, *J* = 8.7, 2.6 Hz, 1H, ArCH), 7.41 (t, *J* = 9.0 Hz, 1H, ArCH); δ_C (101 MHz, $CDCl_3$) 20.2 (SCH_2), 22.4 ($CH\underline{C}H_3$), 22.5 ($CH\underline{C}H_3$), 31.1 (t, *J* = 22 Hz, $\underline{C}H_2CF_2$), 40.7 ($\underline{C}H_2CH=CH_2$), 42.0 ($\underline{C}H(CH_3)_2$), 55.6 (OCH_3), 57.8 ($S\underline{C}$), 102.7 (ArCH), 109.6 (ArCH), 118.8 (ArC), 119.0 ($CH=\underline{C}H_2$), 129.5 (ArCH), 132.6 ($\underline{C}H=CH_2$), 157.6 (t, *J* = 249 Hz, ArCF), 160.8 (ArC), 170.1 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3306 (NH), 2928 (C-H), 1669 (C=O), 1623 (-C=C-), 1507 (-C-C-); *m/z* (ES^+) 766 (MNa^+, 100%), 264 (80%); HRMS for $C_{25}H_{23}NO_2F_{18}S$ (MNa^+) found 766.1066, expected 766.1054.

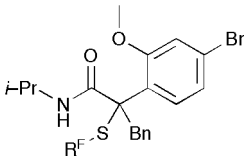
***rac*-2-(4-Bromo-2-methoxy-phenyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-2-(2-naphthylmethyl)-*N*-*iso*-propylacetamide 25**



Following general procedure C: 2-Naphthyl bromide (9 mg, 0.406 mmol, 5 eq) and sodium hydride (10 mg, 0.406 mmol, 5 eq) were heated at reflux with α-aryl acetamide **21** (62 mg, 0.812 mmol, 1 eq) for 48 hours. FSPE removed non-fluorous impurities then purification by column chromatography on silica gel (15% EtOAc/petroleum ether) gave **25** as a yellow oil (33 mg, 0.037 mmol, 44%).

δ_H (400 MHz, $CDCl_3$) 0.98 (d, *J* = 6.6 Hz, 3H, C$\underline{H}_3$CH), 1.09 (d, *J* = 6.6 Hz, 3H, C$\underline{H}_3$CH), 2.23-2.42 (m, 2H, C$\underline{H}_2C_8F_{17}$), 2.75-2.82 (m, 1H, C$\underline{H}$HCH$_2C_8F_{17}$), 2.85-2.92 (m, 1H, CH$\underline{H}$CH$_2C_8F_{17}$), 3.60 (d, *J* = 14.0 Hz, 1H, C$\underline{H}$HNp), 3.79 (d, *J* = 14.0 Hz, 1H, CH$\underline{H}$Np), 3.84 (s, 3H, C$\underline{H}_3$O), 4.02-4.09 (m, 1H, C$\underline{H}$(CH$_3$)$_2$), 5.48 (d, *J* = 7.8 Hz, 1H, N$\underline{H}$), 6.84 (dd, *J* = 8.6 Hz, 1.8 Hz, 1H, Ar$\underline{H}$), 6.97 (dd, *J* = 8.3 Hz, 1.8 Hz, 1H, Ar$\underline{H}$), 7.02 (d, *J* = 8.3 Hz, 1H, Ar$\underline{H}$), 7.10 (d, *J* = 1.8 Hz, 1H, Ar$\underline{H}$), 7.28 (s, 1H, Ar$\underline{H}$), 7.39-7.44 (m, 2H, 2 × Ar$\underline{H}$), 7.56 (d, *J* = 8.6 Hz, 1H, Ar$\underline{H}$), 7.64-7.68 (m, 1H, Ar$\underline{H}$), 7.73-7.76 (m, 1H, Ar$\underline{H}$); δ_C (75 MHz, $CDCl_3$) 20.6 (C$\underline{H}_2$CH$_2C_8F_{17}$), 22.3 (C$\underline{H}_3$CH), 22.6 (C$\underline{H}_3$CH), 31.1 (t, *J* = 21 Hz, C$\underline{H}_2C_8F_{17}$), 40.5 (C$\underline{H}_2$Np), 41.8 (C$\underline{H}$(CH$_3$)$_2$), 55.6 (C$\underline{H}_3$O), 59.8 (C$\underline{C}$H$_2$Np), 114.9 (Ar$\underline{C}$H), 123.0 (Ar$\underline{C}$), 123.7 (Ar$\underline{C}$H), 125.5 (Ar$\underline{C}$H), 125.7 (Ar$\underline{C}$H), 126.7 (Ar$\underline{C}$H and Ar$\underline{C}$), 127.5 (Ar$\underline{C}$H), 127.7 (Ar$\underline{C}$H), 129.0 (Ar$\underline{C}$H), 129.7 (Ar$\underline{C}$H), 130.8 (Ar$\underline{C}$H), 132.2 (Ar$\underline{C}$), 132.8 (Ar$\underline{C}$), 133.7 (Ar$\underline{C}$), 157.2 (Ar$\underline{C}$OCH$_3$), 170.3 (N$\underline{C}$O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3399 (NH), 1667 (C=O), 1651 (C=C); *m/z* (ES$^+$) 906 (^{81}Br, MH$^+$, 63%), 904 (^{79}Br, MH$^+$, 100%), 516 (21%); HRMS for $C_{33}H_{28}NO_2F_{17}S^{79}Br$ (MH$^+$) found 904.0749, expected 904.0747.

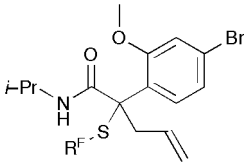
2-Benzyl-2-(4-Bromo-2-methoxy-phenyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-pent-4-enoic acid isopropylacetamide 26



Following general procedure C: Allyl bromide (0.09 mL, 0.78 mmol, 5 eq) and sodium hydride (30 mg, 0.78 mmol, 5 eq) were heated at reflux with α-aryl acetamide **21** (0.109 g, 0.156 mmol, 1 eq) for 18 hours. Purification of the crude product by FSPE gave **26** as a yellow oil (67 mg, 0.056 mmol, 51%).

δ_H (400 MHz, $CDCl_3$) 0.94 (d, *J* = 6.8 Hz, 3H, CHC<u>H</u>$_3$), 1.01 (d, *J* = 6.6 Hz, 3H, CHC<u>H</u>$_3$), 2.13 - 2.32 (m, 2H, C<u>H</u>$_2$CF$_2$), 2.62 - 2.82 (m, 2 H, SC<u>H</u>$_2$), 3.35 (d, *J* = 13.9 Hz, 1H, C<u>H</u>HPh), 3.55 (d, *J* = 13.9 Hz, 1H, CH<u>H</u>Ph), 3.75 (s, 3 H, OCH$_3$), 3.91 - 4.02 (m, 1H, C<u>H</u>(CH$_3$)$_2$), 5.38 (d, *J* = 7.8 Hz, 1H, NH), 6.68 - 6.73 (m, 2H, 2 × ArCH), 6.89 - 6.97 (m, 2H, 2 × ArCH), 6.99 (d, *J* = 1.5 Hz, 1H, ArCH), 7.00 - 7.10 (m, 3H, 3 × ArCH); δ_C (101 MHz, $CDCl_3$) 20.5 (S<u>C</u>H$_2$), 22.3 (CH<u>C</u>H$_3$), 22.7 (CH<u>C</u>H$_3$), 31.0 (t, *J* = 22 Hz, <u>C</u>H$_2$CF$_2$), 40.2 (<u>C</u>H$_2$Ph), 41.8 (<u>C</u>H(CH$_3$)$_2$), 55.6 (O<u>C</u>H$_3$), 59.6 (S<u>C</u>), 114.9 (Ar<u>C</u>H), 123.0 (Ar<u>C</u>H), 123.7 (Ar<u>C</u>), 126.6 (Ar<u>C</u>), 126.6 (Ar<u>C</u>H), 127.4 (Ar<u>C</u>H), 130.7 (Ar<u>C</u>H), 130.8 (Ar<u>C</u>H), 136.1 (Ar<u>C</u>), 157.1 (Ar<u>C</u>H), 170.3 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3377 (NH), 2971 (C-H), 1667 (C=O); *m/z* (ES$^+$) 878 (^{81}Br, 60%), 876 (^{79}Br, MNa$^+$, 100%), 856 (^{81}Br, MH$^+$, 18%), 854 (^{79}Br, MH$^+$, 20%); HRMS for $C_{29}H_{25}NO_2F_{17}S^{79}Br$ (MNa$^+$) found 876.0416, expected 876.0402.

2-(4-Bromo-2-methoxy-phenyl)-pent-4-enoic acid isopropylamide 27

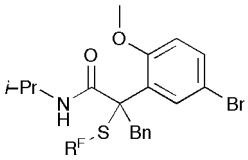


Following general procedure C: Allyl bromide (0.04 mL, 0.454 mmol, 5 eq) and sodium hydride (18 mg, 0.454 mmol, 5 eq) were heated at reflux with α-aryl acetamide **21** (68 mg, 0.091 mmol, 1 eq) for 18 hours and purification of the crude product by FSPE gave **27** as a yellow oil (37 mg, 0.046 mmol, 51%).

δ_H (400 MHz, $CDCl_3$) 1.00 (d, *J* = 6.6 Hz, 3H, CHC<u>H</u>$_3$), 1.02 (d, *J* = 6.6 Hz, 3H, CHC<u>H</u>$_3$), 2.11 - 2.30 (m, 2H, C<u>H</u>$_2$CF$_2$), 2.63 - 2.71 (m, 2H, SCH$_2$), 2.81 - 2.90 (m, 1H, C<u>H</u>HCH=CH$_2$), 2.92 - 3.02 (m, 1H, CCH<u>H</u>CH=CH$_2$), 3.71 (s, 3H, OCH$_3$), 3.94 - 4.01 (m, 1H, C<u>H</u>(CH$_3$)$_2$), 4.88 - 4.92 (m, 2H, CH=C<u>H</u>$_2$), 5.35 (d, *J* = 8.1 Hz, 1H, NH), 5.38 - 5.51 (m, 1H, C<u>H</u>=CHH), 6.95 (d, *J* = 2.0 Hz, 1H, ArCH), 7.07 (dd, *J* = 8.3, 2.0 Hz, 1H, ArCH), 7.30 (d, *J* = 8.3 Hz, 1H, ArCH); δ_C (101 MHz, $CDCl_3$) 21.1 (SCH$_2$), 22.5 (CH<u>C</u>H$_3$), 22.6 (CH<u>C</u>H$_3$), 31.1 (<u>C</u>H$_2$CF$_2$), 38.6 (<u>C</u>H$_2$CH=CH$_2$), 41.8 (<u>C</u>H(CH$_3$)$_2$), 55.6 (OCH$_3$), 58.2 (S<u>C</u>), 115.1 (ArCH), 118.3 (CH=<u>C</u>H$_2$), 123.0 (ArC), 123.7 (ArCH), 126.8 (ArC), 130.2 (ArCH), 133.1 (<u>C</u>H=CH$_2$), 157.1 (ArC), 170.5 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3378 (NH), 2971 (C-H), 1671 (C=O); *m/z* (ES$^+$) 828

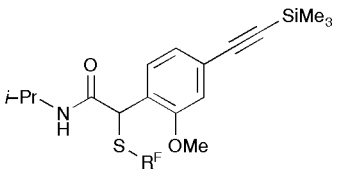
(^{81}Br, MNa^+, 62%), 826 (^{79}Br, MNa^+, 100%) HRMS for $C_{25}H_{24}NO_2S^{79}BrF_{17}$ (MH^+) found 804.0435, expected 804.0440.

rac-2-Benzyl-2-(3-bromo-6-methoxy-phenyl)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-_N_-_iso_-propylacetamide 28



Following general procedure C: Benzyl bromide (0.04 mL, 0.332 mmol, 5 eq) and sodium hydride (13 mg, 0.332 mmol, 5 eq) were heated at reflux with α-aryl acetamide **22** (0.05 g, 0.0067 mmol, 1 eq) for 18 hours. Purification of the crude product by FSPE gave **28** as a yellow oil (34.4 mg, 0.0041 mmol, 61 %).
δ_H (400 MHz, $CDCl_3$) 0.99 (d, J = 6.6 Hz, 3H, C$\underline{H}_3$CH), 1.08 (d, J = 6.6 Hz, 3H, C$\underline{H}_3$CH), 2.20-2.37 (m, 2H, C$\underline{H}_2C_8F_{17}$), 2.73-2.86 (m, 2H, C$\underline{H}_2CH_2C_8F_{17}$), 3.44 (d, J = 13.9 Hz, 1H, C$\underline{H}$HPh), 3.63 (d, J = 13.9 Hz, 1H, CH$\underline{H}$Ph), 3.79 (s, 3H, C$\underline{H}_3$O), 3.97-4.06 (m, 1H, C$\underline{H}(CH_3)_2$), 5.58 (d, J = 7.8 Hz, 1H, N$\underline{H}$), 6.80-6.85 (m, 3H, 3 × Ar$\underline{H}$), 7.11-7.20 (m, 3H, 3 × Ar$\underline{H}$), 7.31 (d, J = 2.5 Hz, 1H, Ar$\underline{H}$), 7.42 (dd, J = 8.6 Hz, 2.5 Hz, 1H, Ar$\underline{H}$); δ_C (75 MHz, $CDCl_3$) 20.6 ($\underline{C}H_2CH_2C_8F_{17}$), 22.3 ($\underline{C}H_3CH$), 22.6 ($\underline{C}H_3CH$), 31.2 (t, J = 22 Hz, $\underline{C}H_2C_8F_{17}$), 40.9 (Ph$\underline{C}H_2$), 41.7 ($\underline{C}H(CH_3)_2$), 55.5 ($\underline{C}H_3O$), 59.5 ($\underline{C}S$) 113.1 (2 × Ar$\underline{C}$H), 113.2 (Ar$\underline{C}$), 126.8 (Ar$\underline{C}$H), 127.4 (2 × Ar$\underline{C}$H), 130.0 (Ar$\underline{C}$), 130.8 (Ar$\underline{C}$H), 132.2 (2 × Ar$\underline{C}$H), 135.9 (Ar$\underline{C}$), 155.8 (Ar$\underline{C}OCH_3$), 170.0 (N$\underline{C}$O); IR ($CH_2Cl_2$ evaporated film/cm^{-1}) 3376 (N-H), 3064, 3032, 2973, 2939 and 2845 (C-H), 1653 (C=O), 1591, 1515 and 1505 (Ar C=C); _m/z_ (ES^+) 878 (^{81}Br, MNa^+, 100%), 876 (^{79}Br, MNa^+, 50%), 487 (13%); HRMS for $C_{29}H_{24}NO_2{}^{79}BrF_{17}S$ (MH^+) found 852.0556, expected 852.0445.

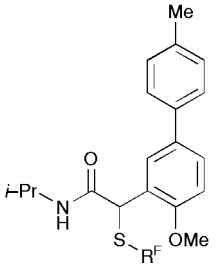
2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-decylsulfanyl)-_N_-isopropyl-2-(2-methoxy-4-trimethylsilanylethynyl-phenyl)acetamide 29



To a solution of α-aryl acetamide **21** (0.104 g, 0.138 mmol, 1 eq), trimethylsilylacetylene (0.19 mL, 1.38 mmol, 10 eq) and copper iodide (0.011 g, 0.055, 0.4 eq) in toluene:NEt_3 (0.3 mL, 2:1) was added $Pd(PPh_3)_4$ (0.032 g, 0.028 mmol, 0.2 eq) and the reaction mixture stirred at 110 °C for 18 h. The resulting reaction mixture was purified using FSPE to give **29** as brown solid (0.107 g, 1.38 mmol, 100%).

δ_H (400 MHz, $CDCl_3$) 0.16 (s, 9 H, 3 × $SiCH_3$), 1.03 (d, *J* = 6.6 Hz, 3H, $CHC\underline{H}_3$), 1.07 (d, *J* = 6.6 Hz, 3H, $CHC\underline{H}_3$), 2.31 (m, 3H, $C\underline{H}_2CF_2$), 2.53 - 2.74 (m, 3H, SCH_2), 3.77 (s, 3H, OCH_3), 3.94 – 4.03 (m, 1H, $C\underline{H}(CH_3)_2$), 4.82 (s, 1H, SCH), 6.07 (d, *J* = 7.8 Hz, 1H, NH), 6.89 (d, *J* = 1.5 Hz, 1H, ArCH), 7.00 (dd, *J* = 7.8, 1.5 Hz, 1H, ArCH), 7.17 (d, *J* = 7.8 Hz, 1H, ArCH); δ_C (75 MHz, $CDCl_3$) 22.6 ($CH\underline{C}H_3$), 22.7 ($CH\underline{C}H_3$), 23.1 (SCH_2), 31.9 (t, 22 Hz, $\underline{C}H_2CF_2$), 42.1 ($\underline{C}H(CH_3)_2$), 48.0 (SCH), 55.8 (OCH_3), 95.1 ($C\equiv\underline{C}Si(CH_3)_3$), 104.6 ($Ar\underline{C}\equiv C$), 114.2 (ArCH), 124.3 (ArC), 125.2 (ArCH), 128.8 (ArCH), 129.9 (ArC), 156.3 (ArC), 168.2 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3297 (NH), 2970 (C-H), 2159 (-C≡C-), 1653 (C=O); *m/z* (ES^+) 804 (MNa^+, 40%), 782 (MH^+, 10%), 462 (10%), 353 (55%), 293 (100%) HRMS for $C_{27}H_{29}NO_2F_{17}SSi$ (MH^+) found 782.1417, expected 782.1411; mp ($CHCl_3$) 65.2-66.0 °C.

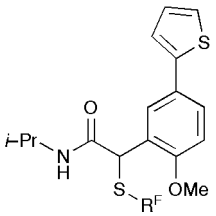
2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-decylsulfanyl)-*N*-isopropyl-2-(2-methoxyl-5-(4-methylphenyl)phenyl)acetamide 30



Following general procedure E: *p*-Tolyl boronic acid (0.09 g, 0.66 mmol, 4 eq), α-aryl acetamide **22** (0.125 g, 0.166 mmol, 1 eq), aqueous Na_2CO_3 (0.58 mL, 2 M, 1.16 mmol, 7 eq) and $Pd(PPh_3)_4$ (38 mg, 0.033 mmol, 0.2 eq) were stirred in toluene (2 mL) and ethanol (1 mL) at 90 °C for 18 hours. The resulting reaction mixture was purified using FSPE to give **30** as a white solid (0.057 g, 0.101 mmol, 61%).

δ_H (500 MHz, $CDCl_3$) 1.08 (d, *J* = 6.6 Hz, 3H, $C\underline{H}_3CH$), 1.12 (d, *J* = 6.6 Hz, 3H, $C\underline{H}_3CH$), 2.27 - 2.42 (m, 5H, SCH_2 and $ArCH_3$), 2.64 - 2.78 (m, 2H, $C_8F_{17}CH_2$), 4.00 - 4.09 (m, 1H, $C\underline{H}(CH_3)_2$), 4.91 (s, 3H, $ArOCH_3$), 6.29 (d, *J* = 8.2 Hz, 1H, NH), 6.89 (d, *J* = 8.5 Hz, 1H, ArH), 7.15 (d, *J* = 7.9 Hz, 2H, 2 × ArH), 7.35 (d, *J* = 7.9 Hz, 2H, 2 × ArH), 7.43 (dd, *J* = 8.5, 1.9 Hz, 1H, ArH), 7.53 (d, *J* = 1.9 Hz, 1H, ArH); δ_C (125 MHz, $CDCl_3$) 21.1 ($Ar\underline{C}H_3$), 22.5 ($CH\underline{C}H_3$), 22.7 ($CH\underline{C}H_3$), 23.3 ($S\underline{C}H_2$), 31.8 (t, *J* = 22 Hz, $\underline{C}H_2CF_2$), 42.0 ($\underline{C}H(CH_3)_2$), 48.4 ($S\underline{C}H$), 56.6 (OCH_3), 111.3 (ArCH), 125.5 (ArC), 126.6 (2 × ArCH), 127.4 (ArCH), 127.8 (ArCH), 129.5 (2 × ArCH), 134.3 (ArC), 136.7 (ArC), 137.4 (ArC), 155.9 (ArC), 168.5 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3322 (NH), 2932 (C-H), 1653 (C=O), 1647 (C=C); *m/z* (ES^+) 798 (MNa^+, 100%), 797 (80%), 774 (10%); HRMS for $C_{29}H_{25}NO_2F_{17}S$ (M - H) found 774.1334, expected 774.1340; mp (Hexane) 107.8-109.1 °C

2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-decylsulfanyl)-*N*-isopropyl-2-(2-methoxy-5-thiophen-2'-yl-phenyl)acetamide 31

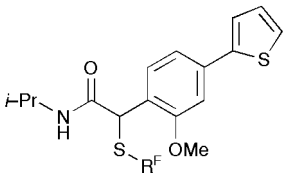


Following general procedure E: 2-Thienylboronic acid (0.051 g, 0.4 mmol, 4 eq), α-aryl amide **22** (0.075 g, 0.1 mmol, 1 eq), aqueous Na_2CO_3 (0.14 mL, 2 M, 0.7 mmol, 7 eq) and $Pd(PPh_3)_4$ (23 mg, 0.02 mmol, 0.2 eq) were stirred in toluene (2 mL) and ethanol (1 mL) at 90 °C for 18 hours. The resulting reaction mixture was purified using FSPE to give **31** as a yellow solid (0.051 g, 0.068 mmol, 68%).

δ_H (500 MHz, $CDCl_3$) 1.19 (d, *J* = 6.6 Hz, 3H, $CHC\underline{H}_3$), 1.24 (d, *J* = 6.6 Hz, 3H, $CHC\underline{H}_3$), 2.37 - 2.53 (m, 2H, SCH_2), 2.74 - 2.89 (m, 2H, CH_2CF_2), 3.92 (s, 3H,

OCH_3), 4.05 - 4.29 (m, 1H, C<u>H</u>$(CH_3)_2$), 4.97 (s, 1H, C(O)CH), 6.44 (d, *J* = 7.9 Hz, 1H, NH), 6.94 (d, *J* = 8.5 Hz, 1H, ArCH), 7.07 (dd, *J* = 5.0, 3.5 Hz, 1H, ArCH), 7.22 (d, *J* = 3.5 Hz, 1H, ArCH), 7.25 (d, *J* = 5.5 Hz, 1H, ArCH), 7.55 (dd, *J* = 8.5, 2.5 Hz, 1H, ArCH), 7.63 (d, *J* = 2.5 Hz, 1H, ArCH); δ_C (125 MHz, $CDCl_3$) 22.5 (CH<u>C</u>H_3), 22.8 (CH<u>C</u>H_3), 23.6 (S<u>C</u>H_2), 31.5 (t, *J* = 22 Hz, <u>C</u>H_2CF_2), 42.0 (<u>C</u>HCH_3), 48.3 (S<u>C</u>H), 55.8 (OCH_3), 111.4 (ArCH), 122.6 (ArCH), 124.3 (ArCH), 125.8 (ArC), 126.5 (ArCH), 127.1 (ArCH), 127.9 (ArC), 128.0 (ArCH), 143.7 (ArC), 156.1 (ArC), 168.3 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3311 (NH), 2929 (C-H), 1653 (C=O), 1212 (C-N); *m/z* (ES^+) 790 (MNa^+, 30%), 768 (MH^+, 100%), 443 (10%); HRMS for $C_{26}H_{23}NO_2F_{17}S_2$ (MH^+) found 768.0882, expected 768.0893; mp ($CHCl_3$) 116.4-118.9 °C.

2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-decylsulfanyl)-*N*-isopropyl-2-(2-methoxy-4-thiophen-2'-yl-phenyl)acetamide 32

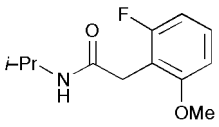


Following general procedure E: 2-Thienylboronic acid (0.15 g, 1.19 mmol, 4 eq), α-aryl acetamide **21** (0.224 g, 0.3 mmol, 1 eq), aqueous Na_2CO_3 (1.04 mL, 2 M, 2.09 mmol, 7 eq) and $Pd(PPh_3)_4$ (69 mg, 0.06 mmol, 0.2 eq) were stirred in toluene (4 mL) and ethanol (2 mL) at 90 °C for 18 hours. The resulting reaction mixture was purified using FSPE to give **32** as a yellow solid (0.145 g, 0.75 mmol, 63%).

δ_H (400 MHz, $CDCl_3$) 1.08 (d, *J* = 6.6 Hz, 3H, CHC<u>H</u>$_3$), 1.11 (d, *J* = 6.6 Hz, 3H, CHC<u>H</u>$_3$), 2.22 - 2.45 (m, 2H, S<u>C</u>H_2), 2.61 - 2.81 (m, 2H, CH_2CF_2), 3.85 (s, 3H, OCH_3), 3.95 - 4.11 (m, 1H, C<u>H</u>$(CH_3)_2$), 4.87 (s, 1H, SCH), 6.22 (d, *J* = 8.1 Hz, 1H, NH), 7.00 - 7.04 (m, 2H, 2 × ArCH), 7.15 (dd, *J* = 8.1, 1.8 Hz, 1H, ArCH), 7.21 - 7.25 (m, 2H, 2 × ArCH), 7.32 (d, *J* = 8.1 Hz, 1H, ArCH); δ_C (101 MHz, $CDCl_3$) 22.5 (CH<u>C</u>H_3), 22.7 (CH<u>C</u>H_3), 23.1 (S<u>C</u>H_2), 31.8 (<u>C</u>H_2CF_2), 42.0 (C<u>H</u>$(CH_3)_2$), 47.9 (S<u>C</u>H), 55.6 (OCH_3), 108.5 (ArCH), 119.0 (ArCH), 123.6 (ArCH), 124.4 (ArC), 125.3 (ArCH), 128.1 (ArCH), 129.2 (ArCH), 135.8 (ArC), 143.8 (ArC), 156.8 (ArC), 168.3 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3292 (NH), 2973 (C-H), 1682 (C=O); *m/z*

(ES^+) 806 (100%), 790 (MNa^+, 20%) HRMS for $C_{26}H_{22}NO_2NaS_2F_{17}$ (MNa^+) found 790.0710, expected 790.0718; mp ($CHCl_3$) 117.4-118.3 °C.

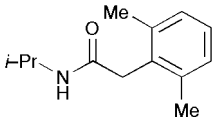
2-(2-Fluoro-6-methoxy-phenyl)-*N-iso*-propylacetamide 33



Following general procedure D: Acetamide **8** (0.153 g, 0.218 mmol, 1 eq) and SmI_2 (4.79 mL, 0.479 mmol, 2.2 eq) were stirred at room temperature for 48 hours. Purification by FSPE afforded **33** as a brown oil (30 mg, 0.133 mmol, 61%). Starting material (6%) was also recovered.

δ_H (400 MHz, $CDCl_3$) 1.08 (d, J = 6.6 Hz, 6H, 2 × C$\underline{H}_3$CH), 3.56 (d, J = 1.5 Hz, 2H, ArC$\underline{H}_2$), 3.86 (s, 3H, C$\underline{H}_3$O), 4.00-4.11 (m, 1H, C$\underline{H}$(CH_3)$_2$), 5.30-5.37 (br s, 1H, N$\underline{H}$), 6.70-6.76 (m, 2H, 2 × Ar$\underline{H}$), 7.23 (td, J = 8.3 Hz, 6.8 Hz, 1H, Ar$\underline{H}$); δ_C (100 MHz, $CDCl_3$) 22.6 (2 × $\underline{C}H_3CH$), 30.9 (6, J = 3 Hz, Ar$\underline{C}H_2$), 41.3 ($\underline{C}H(CH_3)_2$), 55.9 ($\underline{C}H_3O$), 106.3 (d, J = 3 Hz, Ar$\underline{C}$H), 108.0 (Ar$\underline{C}$H), 111.4 (Ar$\underline{C}$), 128.8 (d, J = 11 Hz, Ar$\underline{C}$H), 158.6 (Ar$\underline{C}$), 161.6 (d, J = 244 Hz), 169.2 (N$\underline{C}$O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3292 (N-H), 2969 and 2932 (C-H), 1651 (C=O), 1617, 1587 and 1545 (Ar C=C); *m/z* (ES^+) 248 (MNa^+, 62%), 226 (MH^+, 100%), 173 (19%); HRMS for $C_{12}H_{17}NO_2F$ (MH^+) found 226.1232, expected 226.1238.

2-(2,6-Dimethyl-phenyl)-*N-iso*-propylacetamide 34

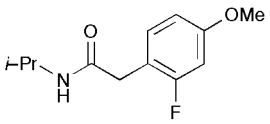


Following general procedure D: Acetamide **18** (150 mg, 0.220 mmol, 1 eq) and SmI_2 (4.83 mL, 0.483 mmol, 2.2 eq) were stirred at room temperature for 30 hours. Purification by FSPE afforded **34** as a yellow amorphous solid (39 mg, 0.190 mmol, 87%).

δ_H (400 MHz, $CDCl_3$) 1.02 (d, J = 6.6 Hz, 6H, 2 × C$\underline{H}_3$CH), 2.28 (s, 6H, 2 × ArC$\underline{H}_3$), 3.60 (s, 2H, ArC$\underline{H}_2$), 4.03-4.12 (m, 1H, C$\underline{H}$(CH_3)$_2$), 5.01-5.11 (br s, 1H, N$\underline{H}$), 7.06-7.15 (m, 3H, 3 × Ar$\underline{H}$); δ_C (100 MHz, $CDCl_3$) 20.1 (2 × Ar$\underline{C}H_3$), 22.5 (2 × $\underline{C}H_3CH$),

37.9 (Ar<u>C</u>H$_2$), 41.2 (<u>C</u>H(CH$_3$)$_2$), 127.5 (Ar<u>C</u>H), 128.5 (2 × Ar<u>C</u>H), 131.9 (Ar<u>C</u>), 137.4 (2 × Ar<u>C</u>), 169.4 (N<u>C</u>O); IR (CH$_2$Cl$_2$ evaporated film/cm^{-1}) 3299 (N-H), 3062, 2969, 2922 and 2863 (C-H), 1639 (C=O), 1543 (Ar C=C); *m/z* (ES$^+$) 228 (MNa$^+$, 100%), 211 (5%), 151 (10%) HRMS for $C_{13}H_{20}NO$ (MH$^+$) found 206.1538, expected 206.1545.

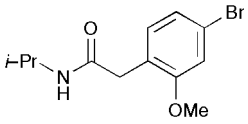
2-(2-Fluoro-4-methoxy-phenyl)-*N*-*iso*-propylacetamide 35



Following general procedure D: Acetamide **19** (40 mg, 0.057 mmol, 1 eq) and SmI_2 (1.25 mL, 0.125 mmol, 2.2 eq) were stirred at room temperature for 24 hours. SmI_2 (0.57 mL, 0.057 mmol, 1 eq) was added and the reaction mixture stirred at room temperature for 6 hours. Purification using FSPE afforded **35** as a yellow waxy solid (8 mg, 0.036 mmol, 63%, 77% based on recovered starting material).

δ_H (400 MHz, $CDCl_3$, 3:2 rotamer ratio) 1.06 (d, *J* = 6.6 Hz, minor, 3H, C<u>H</u>$_3$CH), 1.10 (d, *J* = 6.6 Hz, major, 6H, 2 × C<u>H</u>$_3$CH), 1.18 (d, *J* = 6.6 Hz, minor, 3H, C<u>H</u>$_3$CH), 3.48 (s, major, 2H, ArC<u>H</u>$_2$ and minor, 2H, ArC<u>H</u>$_2$), 3.79 (s, minor, 3H, C<u>H</u>$_3$O), 3.80 (s, major, 3H, C<u>H</u>$_3$O), 4.02-4.11 (m, major, 1H, C<u>H</u>(CH$_3$)$_2$ and minor, 1H, C<u>H</u>(CH$_3$)$_2$), 5.20-5.29 (br s, major, 1H, N<u>H</u>), 5.47 (br d, minor, 1H, N<u>H</u>), 6.61-6.71 (m, major, 2H, 2 × Ar<u>H</u> and m, minor, 2H, 2 × Ar<u>H</u>), 7.19 (apparent t, *J* = 8.8 Hz, major, 1H, Ar<u>H</u>), 7.19 (apparent t, *J* = 8.8 Hz, minor, 1H, Ar<u>H</u>); δ_C (100 MHz, $CDCl_3$, major rotamer only) 22.2 (<u>C</u>H$_3$CH), 22.7 (<u>C</u>H$_3$CH), 36.5 (Ar<u>C</u>H$_2$), 41.5 (<u>C</u>H(CH$_3$)$_2$), 55.6 (<u>C</u>H$_3$O), 101.08 (Ar<u>C</u>H), 110.3 (Ar<u>C</u>H), 114.0 (Ar<u>C</u>), 131.9 (Ar<u>C</u>H), 160.1 (Ar<u>C</u>OCH$_3$), 161.5 (d, *J* = 230 Hz, Ar<u>C</u>F), 173.1 (N<u>C</u>O); IR (CH$_2$Cl$_2$ evaporated film/cm^{-1}) 3289 (N-H), 3080, 2973 and 2935 (C-H), 1627 (C=O), 1586, 1549 and 1510 (Ar C=C); *m/z* (ES$^+$) 248 (MNa$^+$, 62%), 226 (MH$^+$, 100%), 173 (19%); HRMS for $C_{12}H_{17}NO_2F$ (MH$^+$) found 226.1232, expected 226.1238.

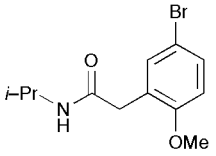
(4-Bromo-2-methoxy-phenyl)-*N*-*iso*-propylacetamide 36



Following general procedure D: Acetamide **21** (80 mg, 0.105 mmol, 1 eq) and SmI_2 (2.30 mL, 0.230 mmol, 2.2 eq) were stirred at room temperature for 20 hours. Purification by FSPE afforded **36** as a white amorphous solid (23 mg, 0.080 mmol, 77%).

δ_H (400 MHz, $CDCl_3$) 1.07 (d, J = 6.6 Hz, 6H, 2 × C$\underline{H}_3$CH), 3.45 (s, 2H, C$\underline{H}_2$Ar), 3.84 (s, 3H, C$\underline{H}_3$O), 4.03 (m, 1H, C$\underline{H}$(CH$_3$)$_2$), 5.31-5.44 (br s, 1H, N$\underline{H}$), 7.03 (s, 1H, Ar$\underline{H}$), 7.09-7.11 (m, 2H, 2 × Ar$\underline{H}$); δ_C (100 MHz, $CDCl_3$), 22.7 (2 × $\underline{C}$H$_3$CH), 38.5 ($\underline{C}$H$_2$Ar), 55.7 ($\underline{C}$H$_3$O), 114.3 (Ar$\underline{C}$H), 121.8 (Ar$\underline{C}$), 123.0 (Ar$\underline{C}$), 124.0 (Ar$\underline{C}$H), 132.3 (Ar$\underline{C}$H), 157.8 (Ar$\underline{C}$OCH$_3$), 169.6 (N$\underline{C}$O); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3306 (N-H), 2973 and 2931 (C-H), 1644 (C=O), 1595 and 1579 (Ar C=C); *m/z* (ES$^+$) 310 (^{81}Br, MNa$^+$, 49%), 308 (^{79}Br, MNa$^+$, 53%), 288 (^{81}Br, MH$^+$, 71%), 286 (^{79}Br, MH$^+$, 76%); HRMS for $C_{12}H_{17}NO_2{}^{79}Br$ (MH$^+$) found 286.0445, expected 286.0437.

2-(5-Bromo-2-methoxy-phenyl)-*N*-*iso*-propylacetamide 37

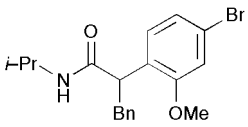


Following general procedure F: Acetamide **28** (0.150 g, 0.196 mmol, 1 eq) and SmI_2 (4.32 mL, 0.432 mmol, 2.2 eq) were stirred at room temperature for 24 hours. SmI_2 (0.78 mL, 0.078 mmol, 0.4 eq) was added and the reaction mixture stirred at room temperature for 24 hours. Purification by FSPE afforded **37** as a cream amorphous solid (39 mg, 0.136 mmol, 69%). Starting material (10%) was also recovered.

δ_H (400 MHz, $CDCl_3$, 12:1 rotamer ratio) 1.03 (d, J = 6.6 Hz, minor, 3H, C$\underline{H}_3$CH), 1.08 (d, J = 6.6 Hz, major, 6H, 2 × C$\underline{H}_3$CH), 1.16 (d, J = 6.6 Hz, minor, 3H, C$\underline{H}_3$CH), 3.45 (s, major, 2H, ArC$\underline{H}_2$ and minor, 2H, ArC$\underline{H}_2$), 3.82 (s, major, 3H, C$\underline{H}_3$O), 3.83 (s, minor, 3H, C$\underline{H}_3$O), 3.97-4.09 (m, major, 1H, C$\underline{H}$(CH$_3$)$_2$ and minor, 1H, C$\underline{H}$(CH$_3$)$_2$), 5.42-5.51 (br s, major, 1H, N$\underline{H}$), 5.59-5.64 (br d, J = 7.6 Hz, minor, 1H, N$\underline{H}$), 6.75-6.78 (m, major, 1H, Ar$\underline{H}$ and minor, 1H, Ar$\underline{H}$), 7.33-7.38 (m, major, 2H, 2

× ArH and minor, 2H, 2 × ArH); δ_C (100 MHz, $CDCl_3$, major rotamer only) 22.7 (2 × CH_3CH), 38.7 (ArCH_2), 41.4 ($CH(CH_3)_2$), 55.6 (CH_3O), 112.3 (ArCH), 113.1 (ArC), 126.2 (ArC), 131.3 (ArCH), 133.8 (ArCH), 156.4 ($ArCOCH_3$), 169.5 (NCO); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3287 (N-H), 2972 and 2936 (C-H), 1644 (C=O), 1593 and 1551 (Ar C=C); *m/z* (ES^+) 310 (^{81}Br, MNa^+, 89%), 308 (^{79}Br, MNa^+, 91%), 288 (^{81}Br, MH^+, 98%), 286 (^{79}Br, MH^+, 100%), 179 (11%), 101 (20%); HRMS for $C_{12}H_{17}NO_2{}^{79}Br$ (MH^+) found 286.0425, expected 286.0437.

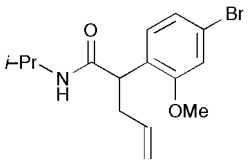
rac-2-Benzyl-2-(4-bromo-2-methoxy-phenyl)-_N-iso_-propylacetamide 38



Following general procedure F: Acetamide **26** (0.150 g, 0.196 mmol, 1 eq) and SmI_2 (7.2 mL, 0.712 mmol, 4 eq) were stirred at room temperature for 24 hours. Purification by FSPE afforded **38** as a cream solid (48 mg, 0.133 mmol, 68%).

δ_H (400 MHz, $CDCl_3$) 0.98 (d, *J* = 4.3 Hz, 3H, $CHCH_3$), 1.00 (d, *J* = 4.3 Hz, 3H, $CHCH_3$), 2.91 (dd, *J* = 13.6, 6.3 Hz, 1H, C(O)CH), 3.44 - 3.53 (m, 1H, PhCHH), 3.80 (s, 3H, OCH_3), 3.91 - 4.03 (m, 2H, $CH(CH_3)_2$ and PhCHH), 5.27 (d, *J* = 7.8 Hz, 1H, NH), 6.99 (d, *J* = 1.8 Hz, 1H, ArCH), 7.11 (dd, *J* = 8.2, 1.9 Hz, 1H, ArCH), 7.15 - 7.21 (m, 3H, 3 × ArCH), 7.22 - 7.28 (m, 2H, 2 × ArCH), 7.31 (d, *J* = 8.3 Hz, 1H, ArCH); δ_C (125 MHz, $CDCl_3$) 22.5 ($CHCH_3$), 22.7 ($CHCH_3$), 37.8 (CH_2Ph), 41.3 ($CH(CH_3)_2$), 47.2 (C(O)CH), 55.7 (OCH_3), 114.2 (ArCH), 124.1 (ArCH), 126.1 (ArCH), 127.5 (ArC), 128.2 (ArCH), 129.0 (ArCH), 129.8 (ArCH) 134.6 (ArC), 139.9 (ArC), 159.5 (ArC), 171.3 (C=O); IR (CH_2Cl_2 evaporated film/cm^{-1}) 3317 (NH), 2968 (C-H), 1643 (C=O); *m/z* (ES^+) 400 (^{81}Br, MNa^+, 43%), 398 (^{79}Br, MNa^+, 45%), 377 (^{81}Br, MH^+, 32%), 375 (^{79}Br, MH^+, 30%), 320 (30%), 293 (30%), 257 (25%) HRMS for $C_{19}H_{23}NO_2{}^{79}Br$ (MH^+) found 376.0893, expected 376.0907, mp ($CHCl_3$) 143.9-144.5 °C.

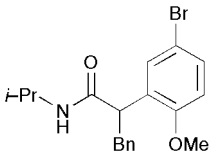
2-(4-Bromo-2-methoxy-phenyl)-pent-4-enoic acid _N-iso_propylamide 39



Following general procedure F: Acetamide **27** (0.124 g, 0.156 mmol, 1 eq) and SmI_2 (6.3 mL, 0.626 mmol, 4 eq) were stirred at room temperature for 24 hours. Purification by FSPE afforded **39** as a white solid (38 mg, 0.121 mmol, 78%).

δ_H (500 MHz, $CDCl_3$) 0.94 (d, *J* = 6.3 Hz, 3H, $CHC\underline{H}_3$), 1.03 (d, *J* = 6.3 Hz, 3H, $CHC\underline{H}_3$), 2.37 (dt, *J* = 14.3, 7.2 Hz, 1H, CH_2=$CHC\underline{H}H$), 2.75 - 2.85 (m, 1H, CH_2=$CHCH\underline{H}$), 3.69 (t, *J* = 7.6 Hz, 1H, C(O)C$\underline{H}$), 3.78 (s, 3H, OCH_3), 3.89 - 4.00 (m, 1H, C$\underline{H}(CH_3)_2$), 4.89 (d, *J* = 10.4 Hz, 1H, C$\underline{H}$H=CH), 4.97 (dd, *J* = 17.0, 1.6 Hz, 1H, CH$\underline{H}$=CH), 5.32 (d, *J* = 6.9 Hz, 1H, NH), 5.65 (m, *J* = 17.0, 10.4, 6.9, 6.9 Hz, 1H, CH_2=C$\underline{H}$), 6.93 (d, *J* = 1.9 Hz, 1H, ArCH), 7.02 (dd, *J* = 8.2, 1.9 Hz, 1H, ArCH), 7.13 (d, *J* = 8.2 Hz, 1H, ArCH); δ_C (75 MHz, $CDCl_3$) 22.6 ($CH\underline{C}H_3$), 22.9 ($CH\underline{C}H_3$), 35.4 (CH_2=$CH\underline{C}H_2$), 41.3 ($\underline{C}H(CH_3)_2$), 44.8 (S$\underline{C}$H), 55.7 (OCH_3), 114.2 (ArCH), 116.5 ($\underline{C}H_2$=CH), 121.3 (ArC), 124.2 (ArCH), 127.2 (ArC), 129.7 (ArCH), 136.1 (CH_2=$\underline{C}$H), 157.2 (ArC), 171.5 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3303 (NH), 2969 (C-H), 1636 (C=O); *m/z* (ES^-) 362 (^{81}Br, M + Cl^-, 100%), 360 (^{79}Br, M + Cl^-, 70%), 349 (25%), 258 (15%), 239 (35%), 183 (20%) HMRS for $C_{15}H_{20}NO_2{}^{79}BrCl$ found 360.0357, expected 360.0366; mp ($CHCl_3$) 108.4-110.2 °C.

rac-2-Benzyl-2-(5-bromo-2-methoxy-phenyl)-_N_-_iso_-propylacetamide 40

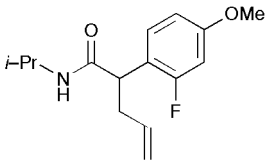


Following general procedure F: Acetamide **28** (0.097 g, 0.114 mmol, 1 eq) and SmI_2 (4.54 mL, 0.454 mmol, 4 eq) were stirred at room temperature for 24 hours. Purification by FSPE afforded **40** as a cream amorphous solid (33 mg, 0.088 mmol, 77%).

δ_H (400 MHz, $CDCl_3$) 0.98 (apparent t, *J* = 6.5 Hz, 6H, 2 × $C\underline{H}_3$CH), 2.90 (dd, *J* = 13.3 Hz, 5.6 Hz, 1H, C$\underline{H}$HPh), 3.48 (dd, *J* = 13.3 Hz, 9.0 Hz, 1H, CH$\underline{H}$Ph), 3.78 (s, 3H, $C\underline{H}_3O$), 3.92 - 4.00 (m, 2H, C$\underline{H}(CH_3)_2$ and C$\underline{H}$C(O)Ph), 5.26 (d, *J* = 7.3 Hz, 1H,

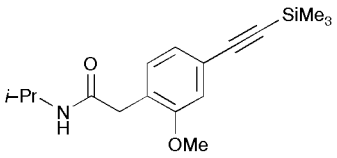
NH), 6.73 (d, *J* = 8.8 Hz, 1H, ArH), 7.17-7.19 (m, 3H, 3 × ArH), 7.22-7.24 (m, 2H, 2 × ArH), 7.32 (dd, *J* = 8.5 Hz, 2.5 Hz, 1H, ArH), 7.56 (d, *J* = 2.5 Hz, 1H, ArH); δ_C (100 MHz, $CDCl_3$) 22.5 ($\underline{C}H_3CH$), 22.7 ($\underline{C}H_3CH$), 37.8 ($\underline{C}H_2Ph$), 41.2 ($\underline{C}H(CH_3)_2$), 47.3 ($\underline{C}H(O)Ph$), 55.6 ($\underline{C}H_3O$), 112.1 (Ar$\underline{C}$H), 113.5 (Ar$\underline{C}$), 126.2 (Ar$\underline{C}$H), 128.2 (2 × Ar$\underline{C}$H), 129.0 (2× Ar$\underline{C}$H), 130.6 (Ar$\underline{C}$), 130.7 (Ar$\underline{C}$H), 131.2 (Ar$\underline{C}$H), 139.9 (Ar$\underline{C}$), 155.5 (Ar$\underline{C}OCH_3$), 171.1 (N$\underline{C}$O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3318 (NH), 1648 (C=O); *m/*z (ES^+) 400 (^{81}Br, MNa^+, 90%) 398 (^{79}Br, MNa^+, 100%), 377 (^{81}Br, M, 12%) 375 (^{79}Br, M, 10%), 183 (20%); HRMS for $C_{19}H_{23}NO_2{}^{79}Br$ (MH^+) found 376.0912, expected 376.0909.

2-(2-Fluoro-4-methoxy-phenyl)-pent-4-enoic acid *N-iso*propylamide 41



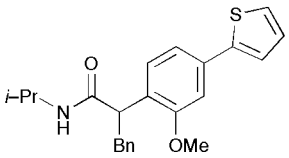
Following general procedure F: Acetamide **24** (0.14 g, 0.188 mmol, 1 eq) and SmI_2 (7.54 mL, 0.754 mmol, 4 eq) were stirred at room temperature for 24 hours. Purification by FSPE afforded **42** as a brown oil (35.4 mg, 0.133 mmol, 71%).
δ_H (500 MHz, $CDCl_3$) 1.06 (d, *J* = 6.6 Hz, 3H, CHC$\underline{H}_3$), 1.14 (d, *J* = 6.3 Hz, 3H, CHC$\underline{H}_3$), 2.41 - 2.57 (m, 1H, CH_2=CHC$\underline{H}$H), 2.82 - 2.96 (m, 1H, CH_2=CHCH$\underline{H}$), 3.64 (t, *J* = 7.6 Hz, 1H, C(O)C$\underline{H}$), 3.81 (s, 3H, OCH_3), 4.06 (m, 1H, C$\underline{H}(CH_3)_2$), 5.00 (d, *J* = 10.4 Hz, 1H, C$\underline{H}$H=CH), 5.07 (dd, *J* = 16.9, 1.4 Hz, 1H, CH$\underline{H}$=CH), 5.31 (d, *J* = 7.06 Hz, 1H, NH), 5.74 (m, 1H, CHH=C$\underline{H}$), 6.63 (dd, *J* = 12.1, 2.7 Hz, 1H, ArCH), 6.72 (dd, *J* = 8.2, 2.8 Hz, 1H, ArCH), 7.34 (t, *J* = 8.2 Hz, 1H, ArCH); δ_C (100 MHz, $CDCl_3$) 22.5 (CH$\underline{C}H_3$), 22.8 (CH$\underline{C}H_3$), 36.3 ($\underline{C}H_2CH=CH_2$), 41.5 ($\underline{C}H(CH_3)_2$), 44.3 (S$\underline{C}$H), 55.6 (OCH_3), 101.5 (ArCH), 110.3 (ArCH), 116.9 (ArC), 118.4 (CH=$\underline{C}H_2$), 129.5 (ArCH), 135.7 ($\underline{C}H=CH_2$), 159.8 (ArC), 160.1 (d, *J* = 223 Hz, ArC-F), 171.4 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3313 (NH), 2967 (C-H), 1647 (C=O)**;** *m/z* (ES^+) 288 (MNa^+, 50%), 287 (80%), 266 (MH^+, 100%), 238 (10%); HRMS for $C_{15}H_{21}NO_2F$ found 266.1561, expected 266.1556.

***N-iso*propyl-2-(2-methoxy-4-trimethylsilanylethynyl-phenyl)acetamide 42**



Following general procedure F: Acetamide **31** (0.08 g, 0.104 mmol, 1 eq) and SmI_2 (4.16 mL, 0.416 mmol, 4 eq) were stirred at room temperature for 24 hours. Purification by FSPE afforded **41** as a white solid (27.5 mg, 0.090 mmol, 87%).
δ_H (500 MHz, $CDCl_3$) 0.19 (s, 9 H, $Si(C\underline{H}_3)_3$), 0.97 (d, *J* = 6.6 Hz, 6H, $CH(C\underline{H}_3)_2$), 3.43 (s, 2H, $C(O)C\underline{H}_2$), 3.78 (s, 3H, OCH_3), 3.90 - 3.99 (m, 1H, $C\underline{H}(CH_3)_2$), 5.29 (br. s., 1H, NH), 6.92 (d, *J* = 1.3 Hz, 1H, ArCH), 7.01 (dd, *J* = 7.6, 1.6 Hz, 1H, ArCH), 7.08 (d, *J* = 7.9 Hz, 1H, ArCH); δ_C (75 MHz, $CDCl_3$) 0.0 ($Si(CH_3)_3$), 22.7 ($CH(\underline{C}H_3)_2$), 39.0 ($\underline{C}H(CH_3)_2$), 41.3 ($C(O)\underline{C}H_2$), 55.5 (OCH_3), 94.4 ($C\equiv\underline{C}Si(CH_3)_3$), 104.8 ($Ar\underline{C}\equiv C$), 114.0 (ArCH), 123.4 (ArC), 125.0 (ArCH), 125.1 (ArCH), 131.1 (ArC), 156.8 (ArC), 169.8 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3267 (NH), 2969), 1640 (C=O); *m/z* (ES^+) 326 (MNa^+, 100%), 304 (MH^+, 45%), 220 (10%) HRMS for $C_{17}H_{26}NO_2Si$ found 304.1720, expected 304.1727; mp (Hexane) 141.7-142.9 °C.

***N-iso*propyl-2-(2-methoxy-5-thiophen-2'-yl-phenyl)-3-phenyl-propionamide 43**

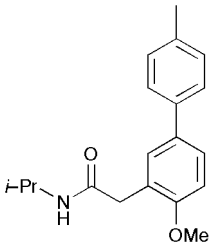


To a suspension of propionamide **32** (0.10 g, 0.130 mmol, 1 eq) and NaH (60% in mineral dispersion, 0.026 g, 0.652 mmol, 5 eq) in dry THF (4 ml), benzyl bromide (0.08mL, 0.652 mmol, 5 eq) was added dropwise at room temperature, heated at reflux and stirred for 18 hours. The reaction was quenched with water (5 mL) and the organic layer extracted with Et_2O (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by FSPE and subsequently by column chromatography afforded an inseparable mixture of benzyl propionamide and **43** (49 mg).

The mixture was dissolved in dry, degassed THF (2 mL) and SmI_2 (2.23 mL, 0.223 mmol, approx. 4 eq) was added. The reaction was stirred at room temperature for 24 hours. Saturated aqueous $Na_2S_2O_3$ (5 mL) was added and the organic layer extracted with Et_2O (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (15:85 ethyl acetate:petroleum ether 60/40) gave **43** (19 mg, 0.052 mmol, 38% over 2 steps, approx. 94% for SmI_2 reaction) as a white solid.

δ_H (400 MHz, $CDCl_3$) 0.90 (d, *J* = 6.6 Hz, 3H, CHC$\underline{H}_3$), 0.91 (d, *J* = 6.5 Hz, 3H, CHC$\underline{H}_3$), 2.88 (dd, *J* = 13.6, 6.3 Hz, 1H, C$\underline{H}$HPh), 3.47 (dd, *J* = 13.5, 8.7 Hz, 1H, C$\underline{H}$HPh), 3.78 (s, 3H, OCH_3), 3.86 - 3.97 (m, 2H, C$\underline{H}(CH_3)_2$ and C$\underline{H}$(O)), 5.27 (d, *J* = 7.8 Hz, 1H, NH), 6.98 - 7.03 (m, 2H, 2 × ArCH), 7.05 - 7.24 (m, 8H, 8 × ArCH), 7.32 (d, *J*=7.8 Hz, 1H, ArCH); δ_C (101 MHz, $CDCl_3$) 22.5 (CH$\underline{C}H_3$), 22.7 (CH$\underline{C}H_3$), 37.7 ($\underline{C}H_2$Ph), 41.3 ($\underline{C}H(CH_3)_2$), 47.5 ($\underline{C}$HC(O)), 55.5 (OCH_3), 108.3 (ArCH), 118.9 (ArCH), 123.2 (ArCH), 124.9 (ArCH), 126.1 (ArCH), 127.7 (ArC), 128.0 (ArCH), 128.2 (ArCH), 129.0 (ArCH), 129.1 (ArCH), 134.4 (ArC), 140.3 (ArC), 144.2 (ArC), 156.8 (ArC), 171.7 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3320 (NH), 2971 (C-H), 1640 (C=O); *m/z* (ES^+) 380 (MH^+, 100%), 210 (10%), 204 (12%), 173 (18%), 115 (14%) HRMS for $C_{23}H_{26}NO_2S$ (MH^+) found 380.1681, expected 380.1684; mp (Hexane) 141.7-142.9 °C.

***N-iso*propyl-2-(2-methoxy-5-(4'-methylphenyl)-phenyl)acetamide 44**



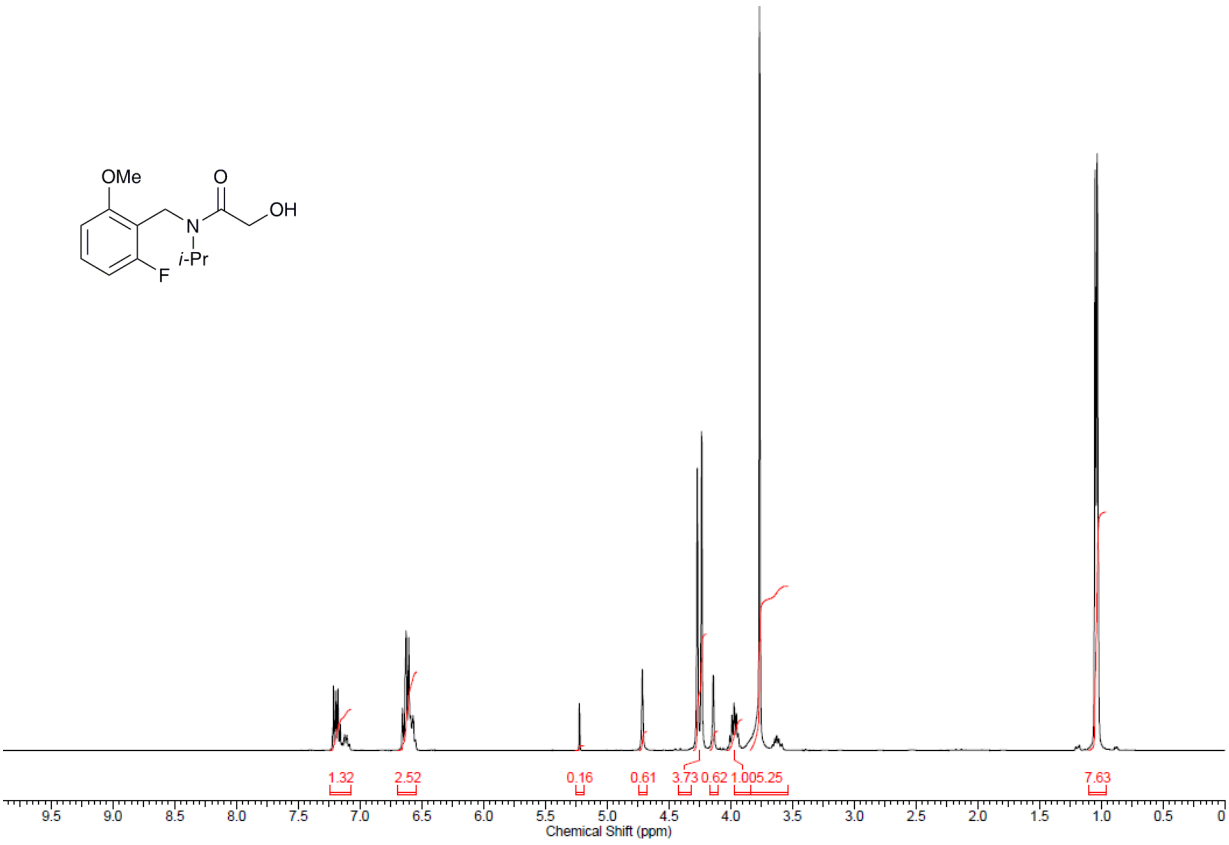
Following general procedure F: Acetamide **29** (0.057 g, 0.0735 mmol, 1 eq) and SmI_2 (2.94 mL, 0.294 mmol, 4 eq) were stirred at room temperature for 24 hours. Purification by FSPE afforded **43** as a cream solid (14.6 mg, 0.049 mmol, 67%).

δ_H (400 MHz, $CDCl_3$) 1.00 (d, *J* = 6.6 Hz, 6H, 2 × CHC$\underline{H}_3$), 2.32 (s, 3H, $ArCH_3$), 3.50 (s, 2H, $C(O)CH_2$), 3.82 (s, 3H, OC$\underline{H}_3$), 3.98 (m, 1H, C$\underline{H}(CH_3)_2$), 5.46 (d, *J* = 6.3 Hz, 1H, NH), 6.89 (d, *J* = 8.3 Hz, 1H, ArCH), 7.16 (d, *J* = 7.8 Hz, 2H, 2 × ArCH),

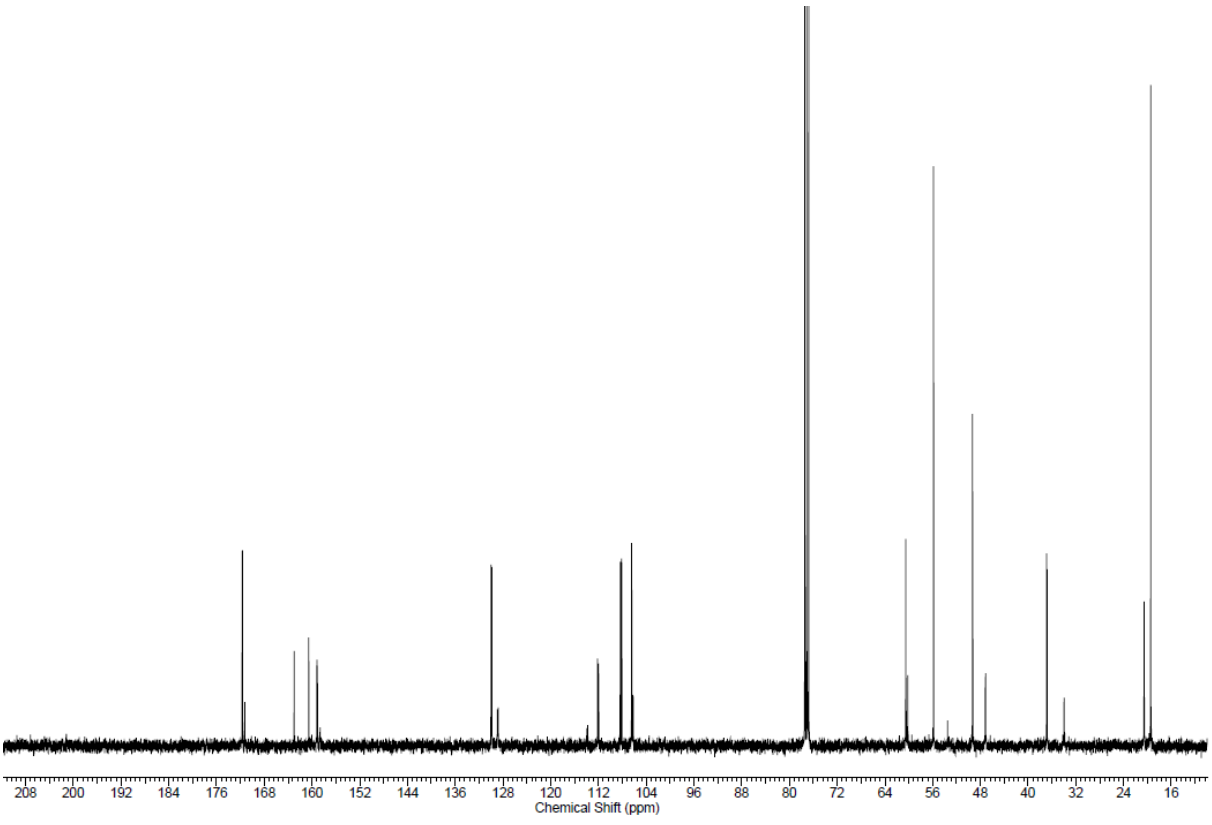
7.34 - 7.51 (m, 3H, 3 × ArCH), 7.57 - 7.70 (m, 1H, ArCH); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 21.1 ($ArCH_3$), 22.7 (2 × $CH\underline{C}H_3$), 39.3 (C(O)$\underline{C}$H), 41.3 ($\underline{C}H(CH_3)_2$), 55.5 (OCH_3), 111.0 (ArCH), 124.2 (ArC), 126.6 (ArCH), 128.5 (ArCH), 129.5 (ArCH), 129.9 (ArCH), 132.1 (ArC), 136.6 (ArC), 137.5 (ArC), 156.6 (ArC), 170.3 (C=O); IR ($CHCl_3$ evaporated film/cm^{-1}) 3269 (NH), 2970 (C-H), 1641 (C=O); *m/z* (ES^+) 320 (MNa^+, 100%), 298 (MH^+, 5%), 229 (7%) HRMS for $C_{19}H_{22}NO_2$ (MH^+) found 298.1796, expected 298.1807; mp (Hexane) 110.2-112.0 °C.

NMR spectra: α-hydroxyamides

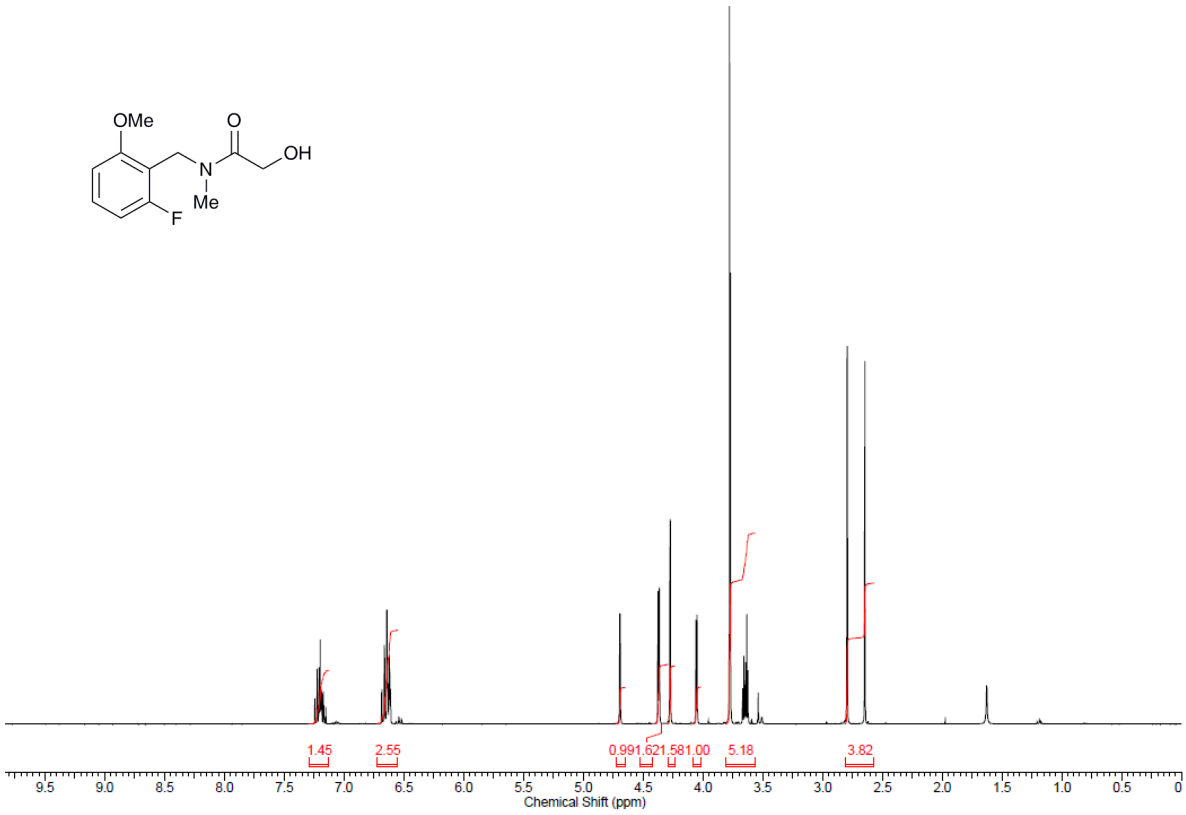
400 MHz ($CDCl_3$)



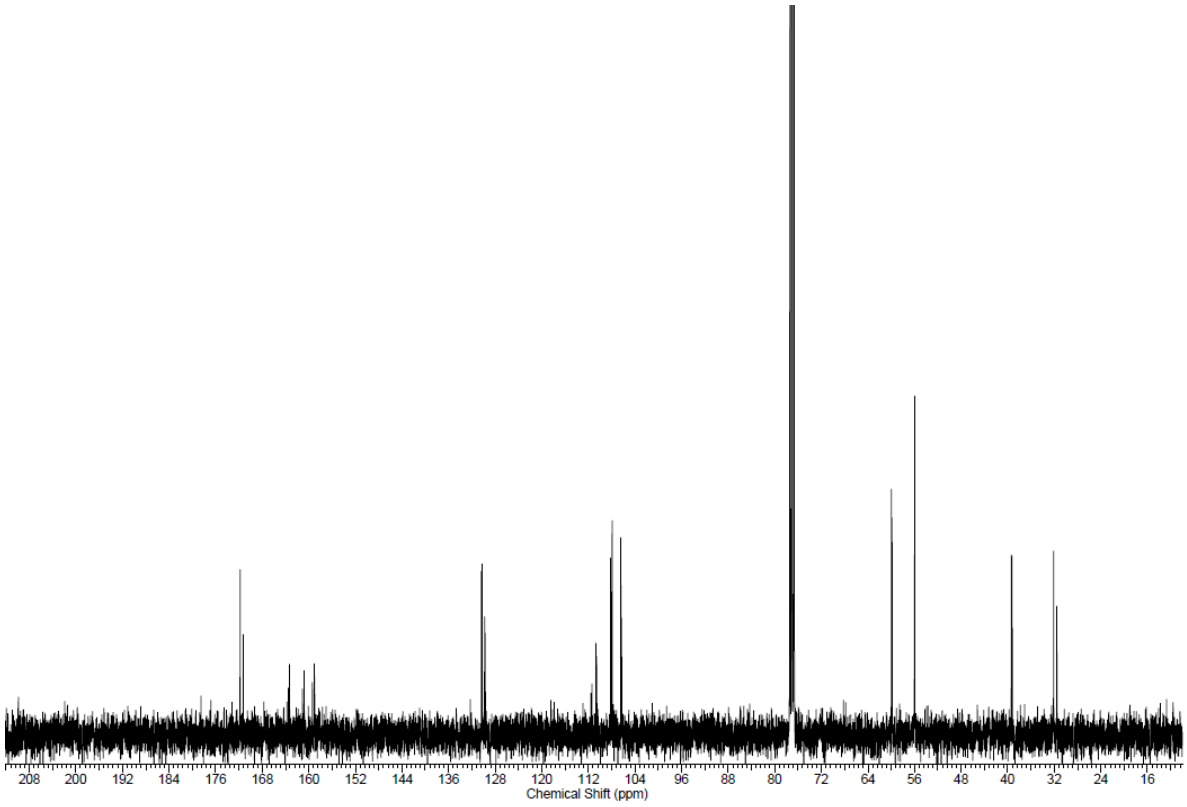
100 MHz ($CDCl_3$)



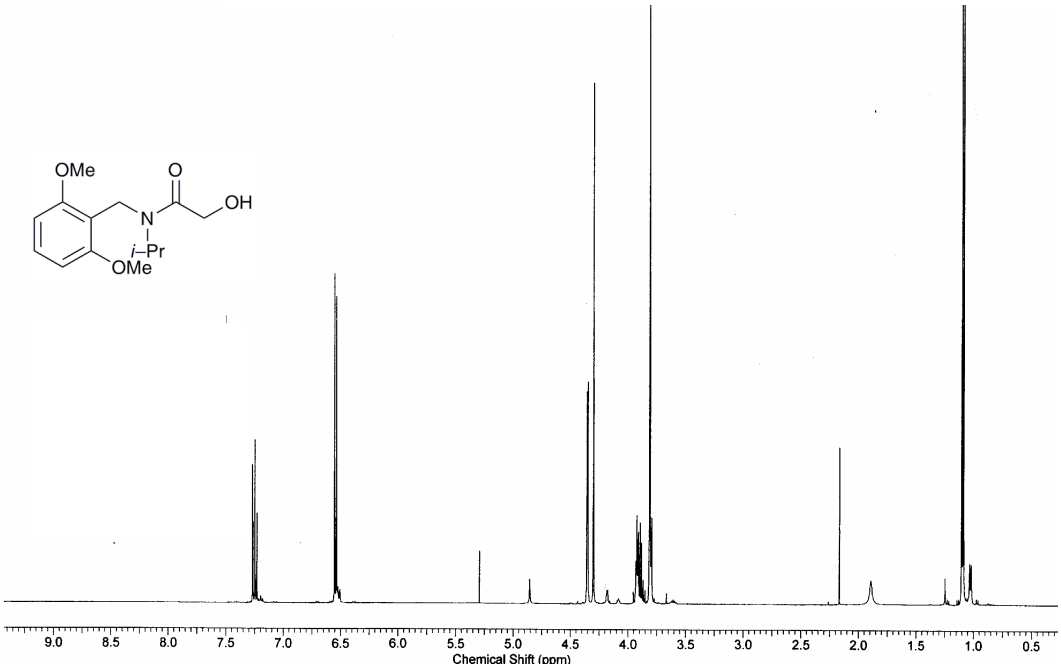
400 MHz ($CDCl_3$)



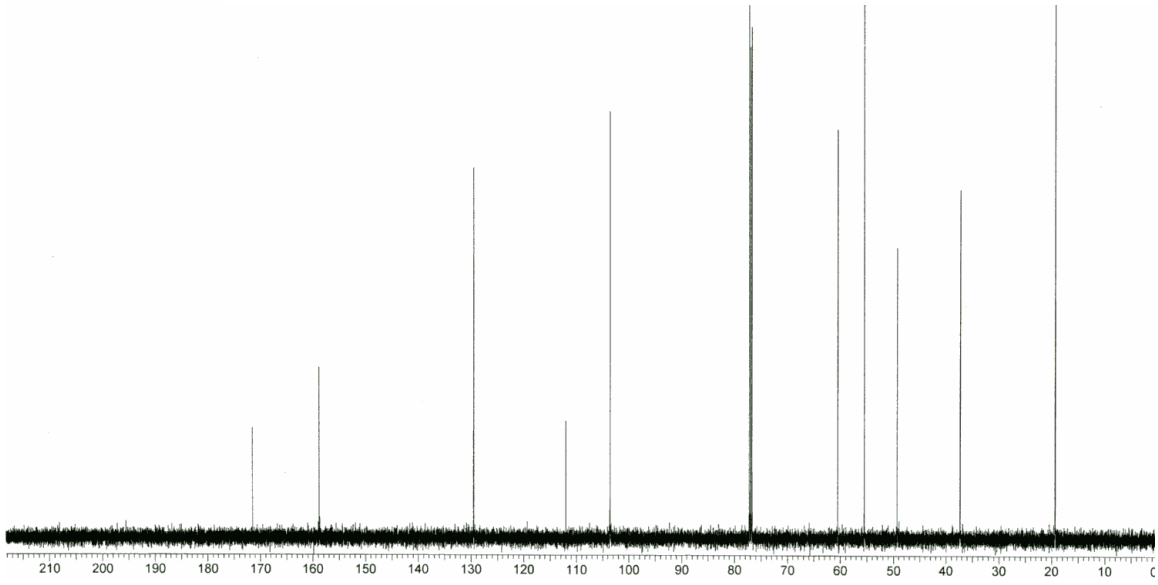
100 MHz ($CDCl_3$)



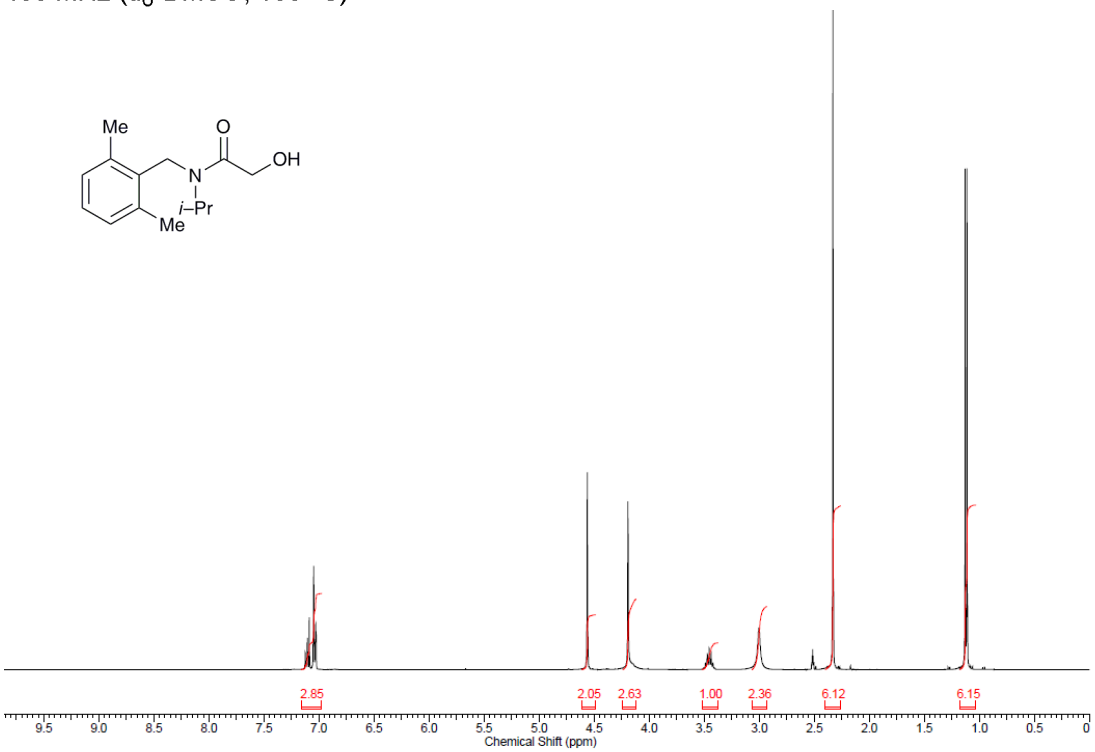
500 MHz ($CDCl_3$)



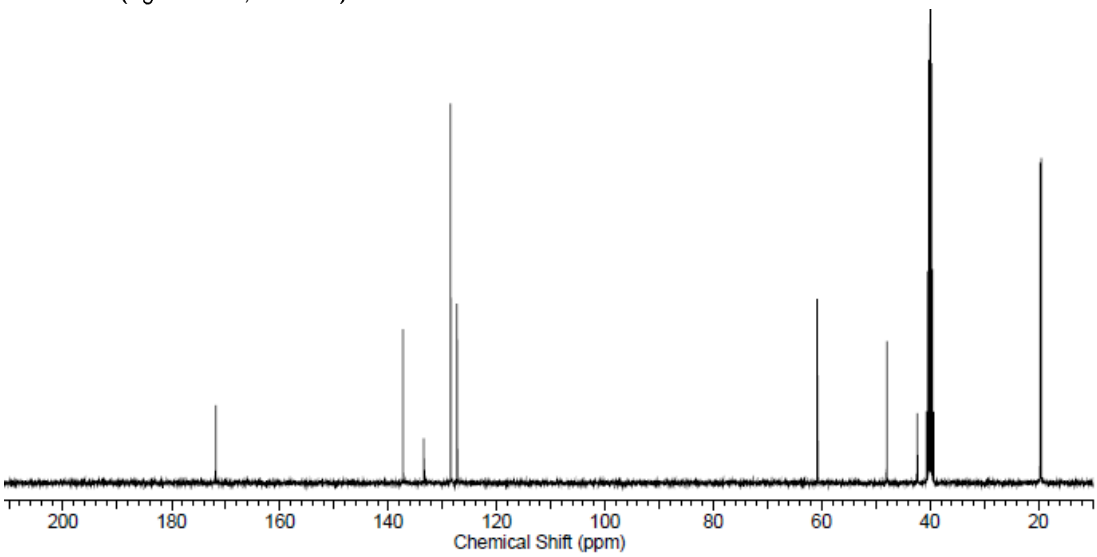
125 MHz ($CDCl_3$)



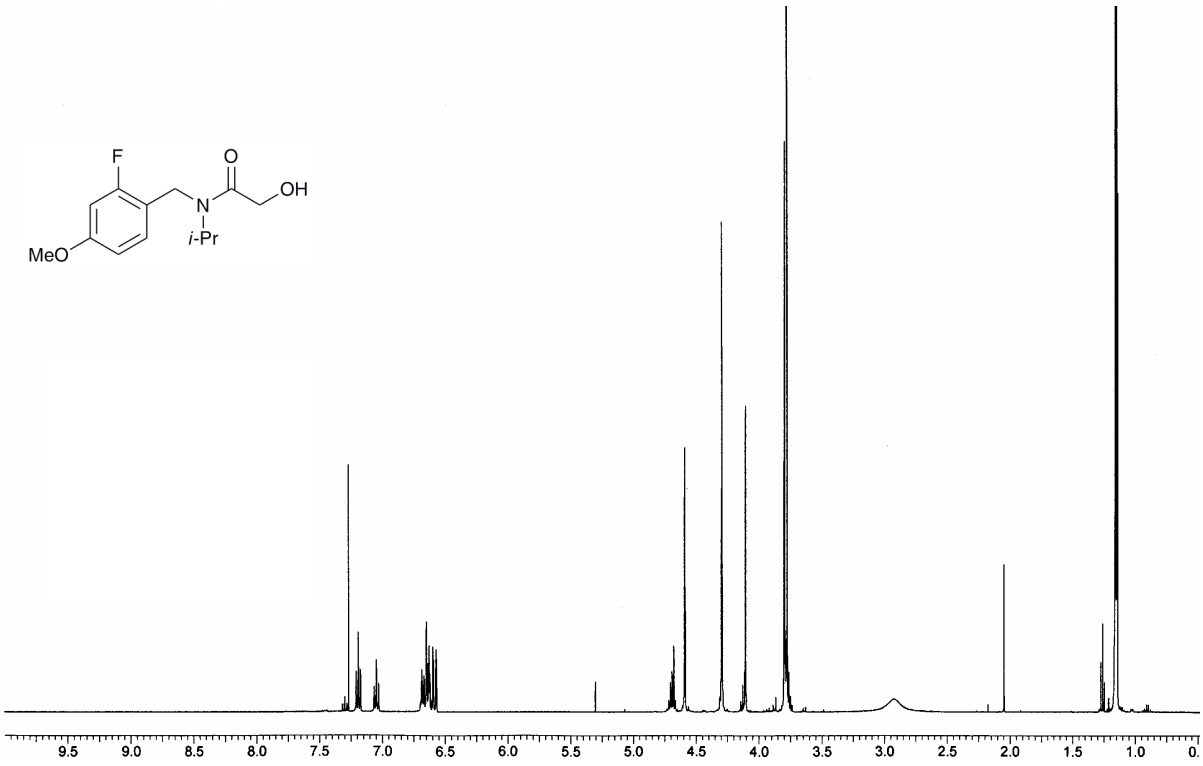
400 MHz (d_6-DMSO, 100 °C)



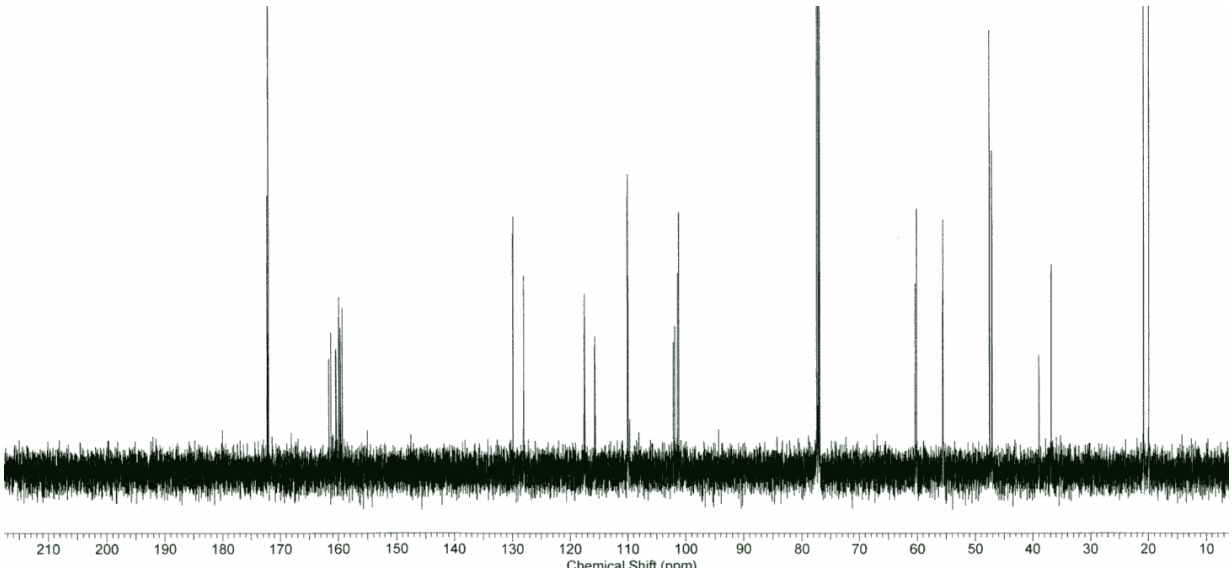
100 MHz (d_6-DMSO, 100 °C)



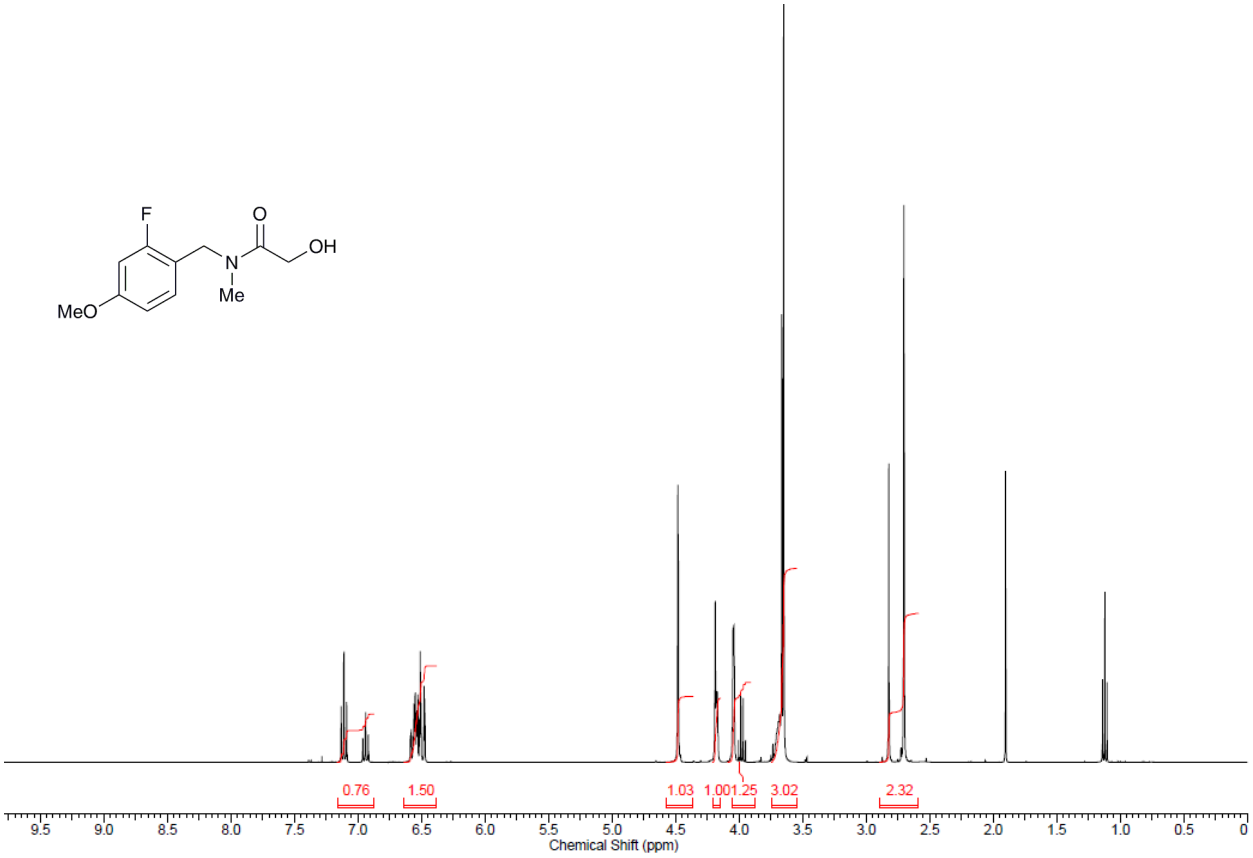
500 MHz ($CDCl_3$)



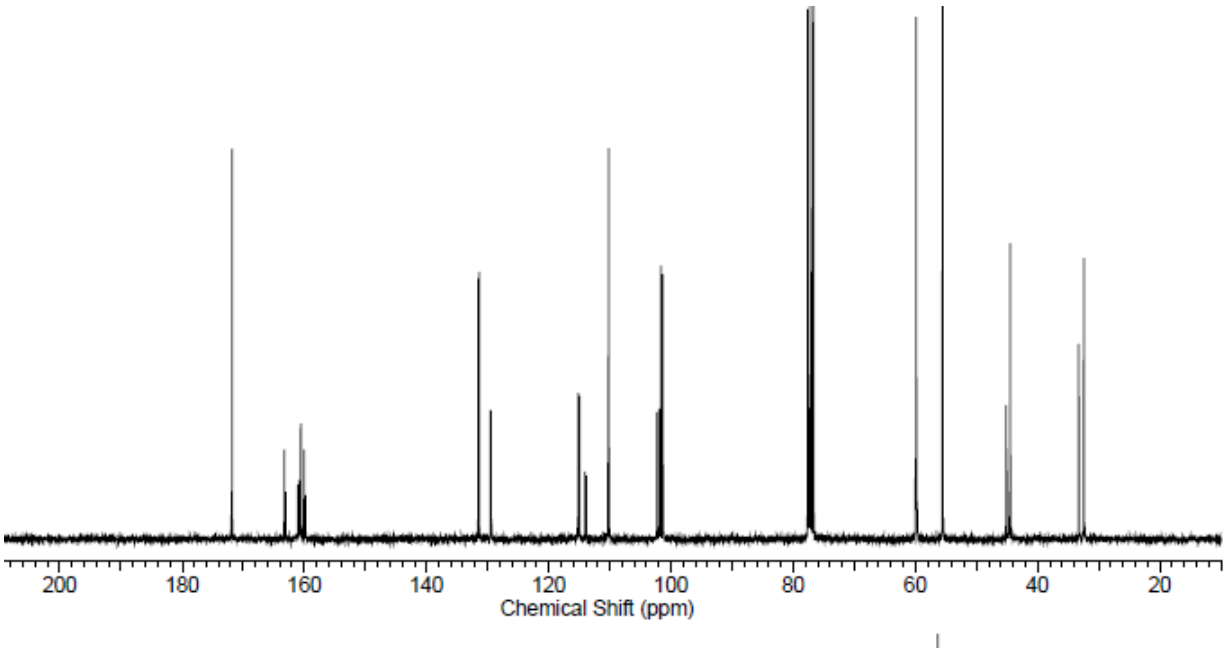
125 MHz ($CDCl_3$)



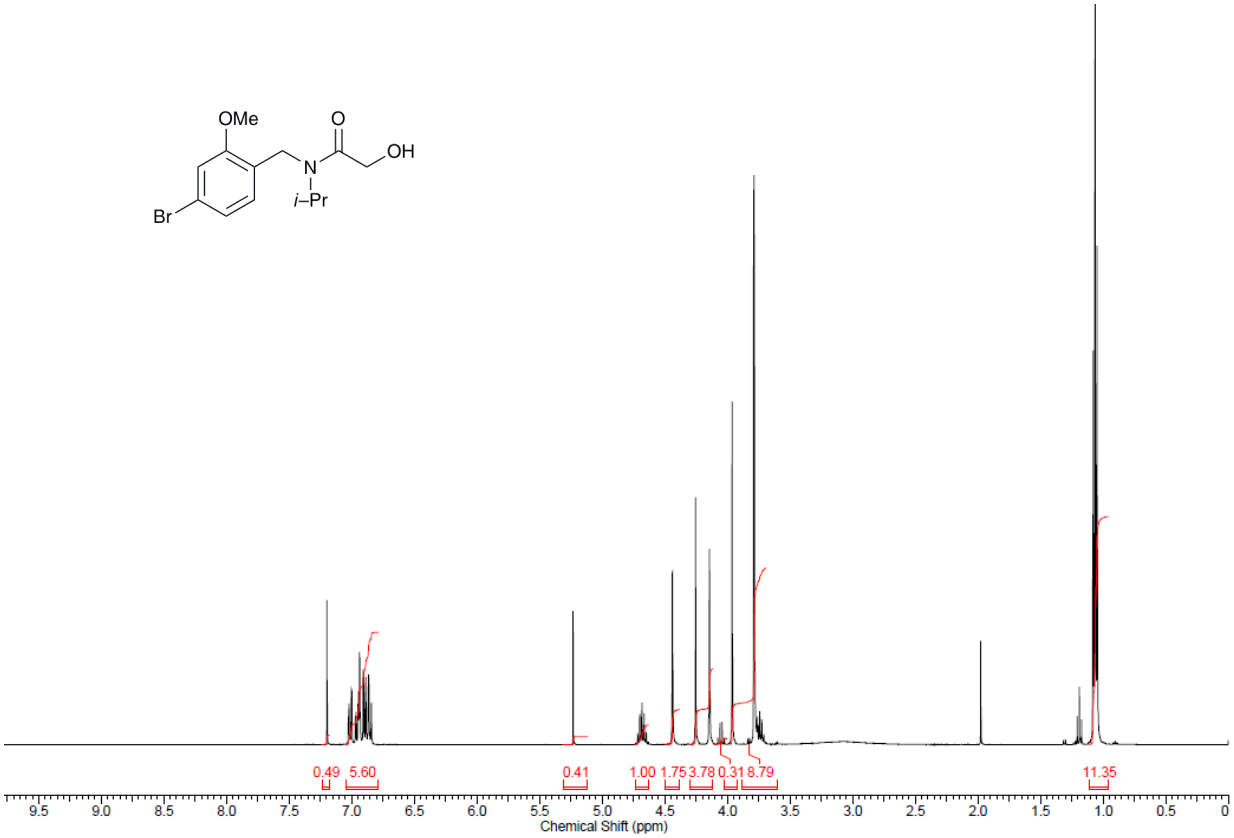
400 MHz ($CDCl_3$)



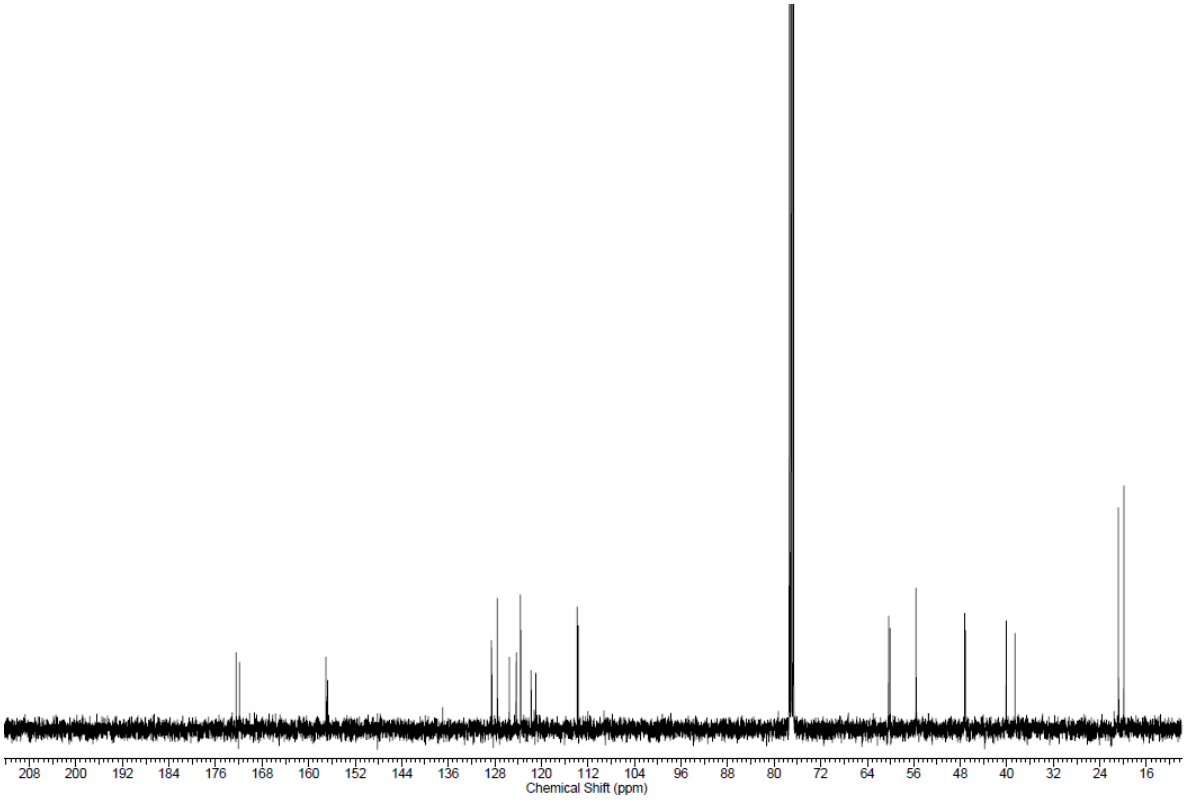
100 MHz ($CDCl_3$)



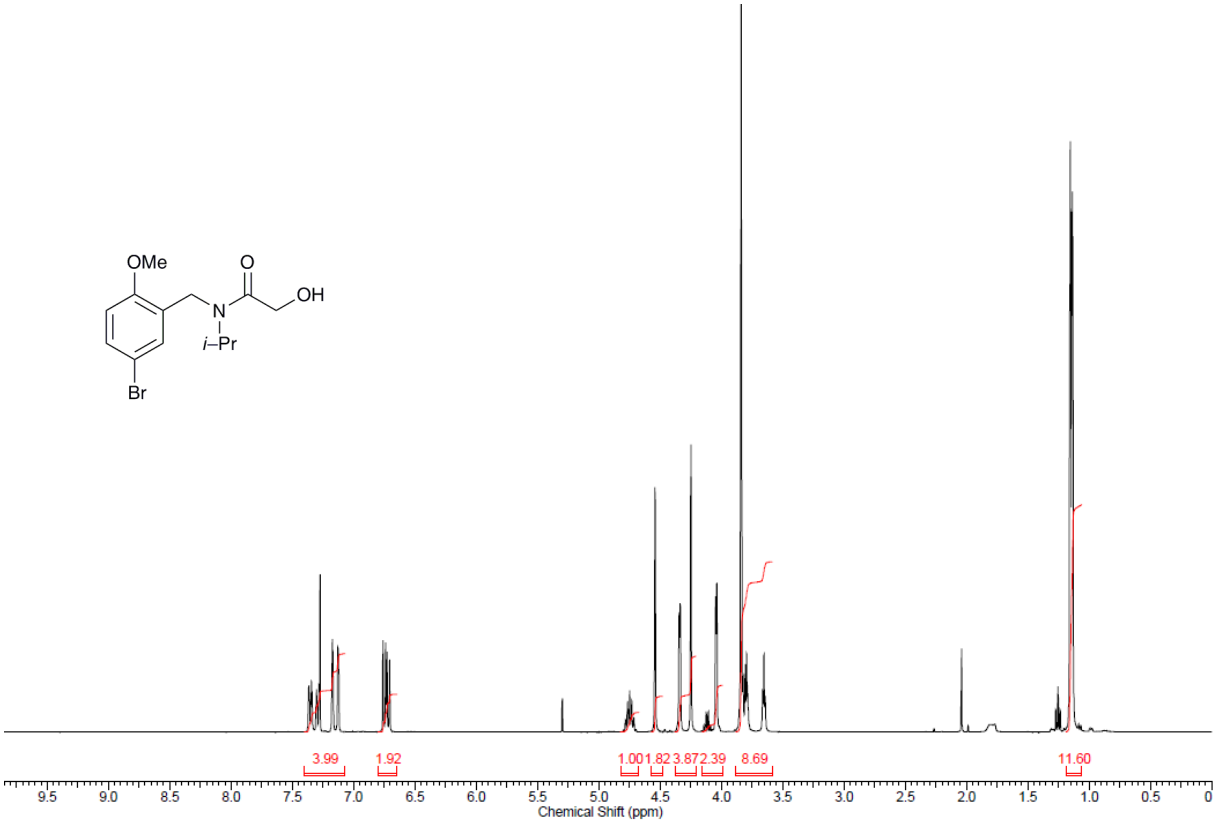
400 MHz ($CDCl_3$)



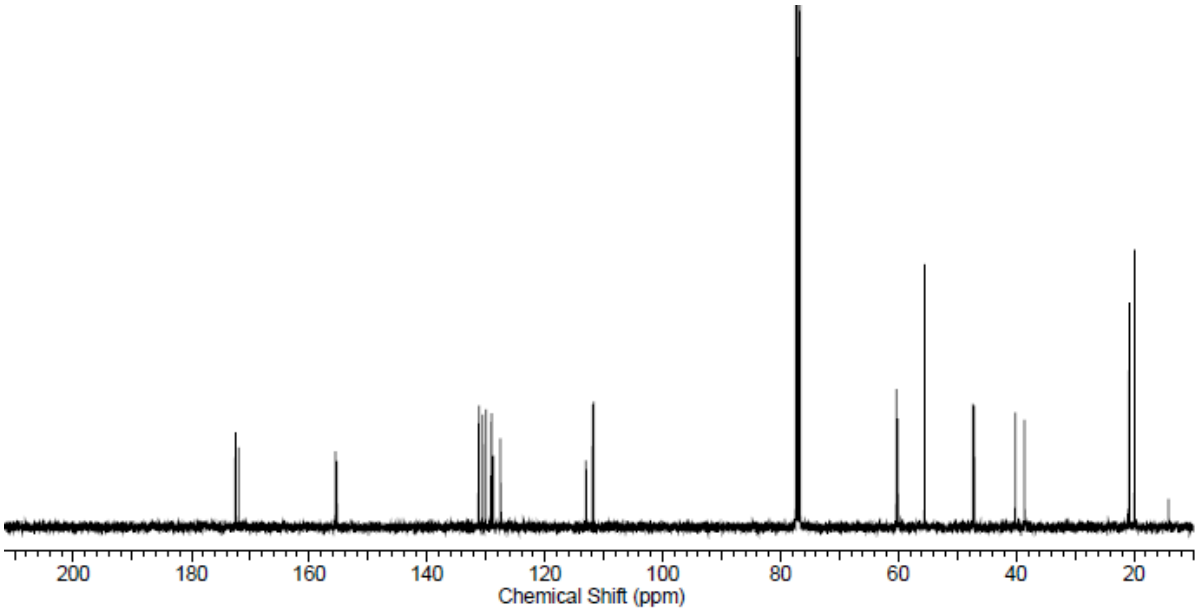
100 MHz ($CDCl_3$)



400 MHz ($CDCl_3$)

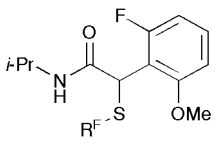


100 MHz ($CDCl_3$)



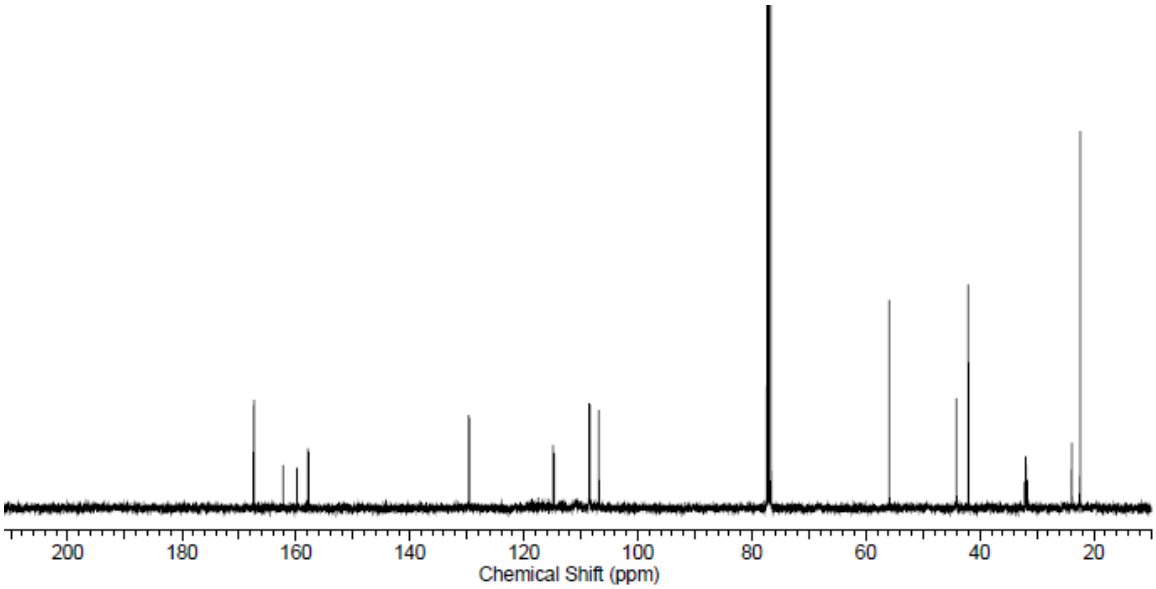
NMR data for aryl transfer products

400 MHz ($CDCl_3$)

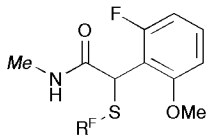


8

100 MHz ($CDCl_3$)

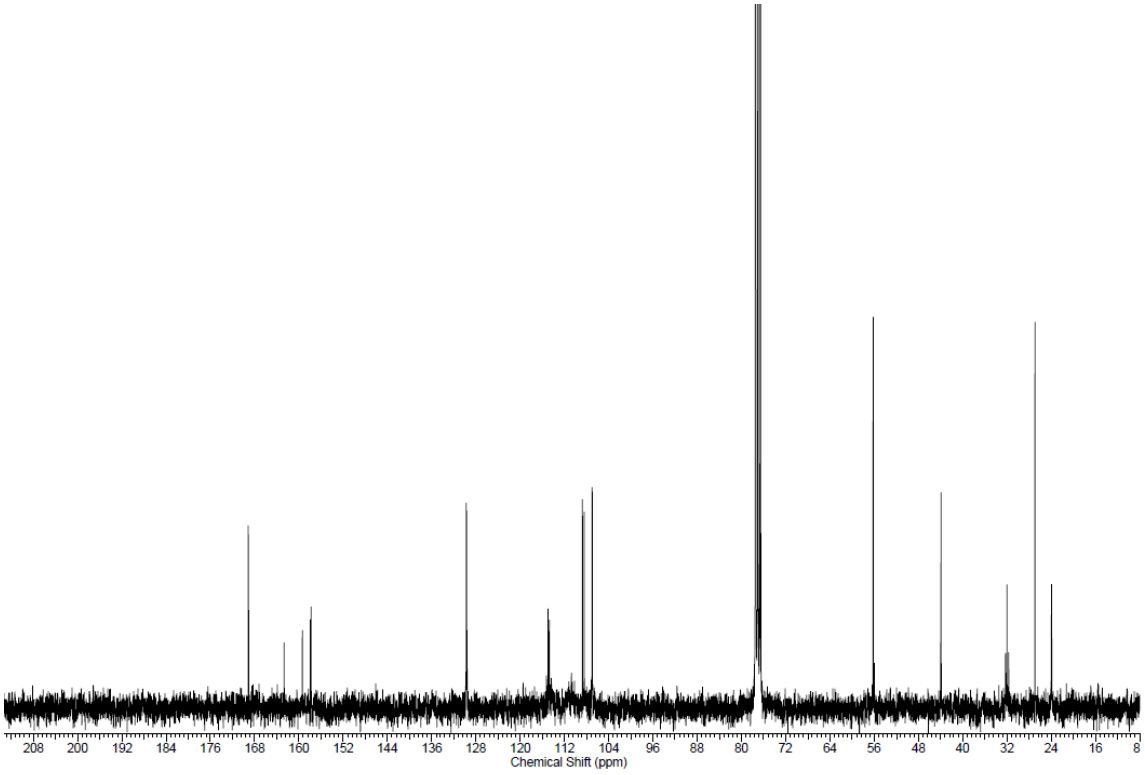


400 MHz ($CDCl_3$)

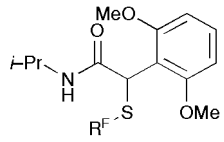


16

75 MHz ($CDCl_3$)

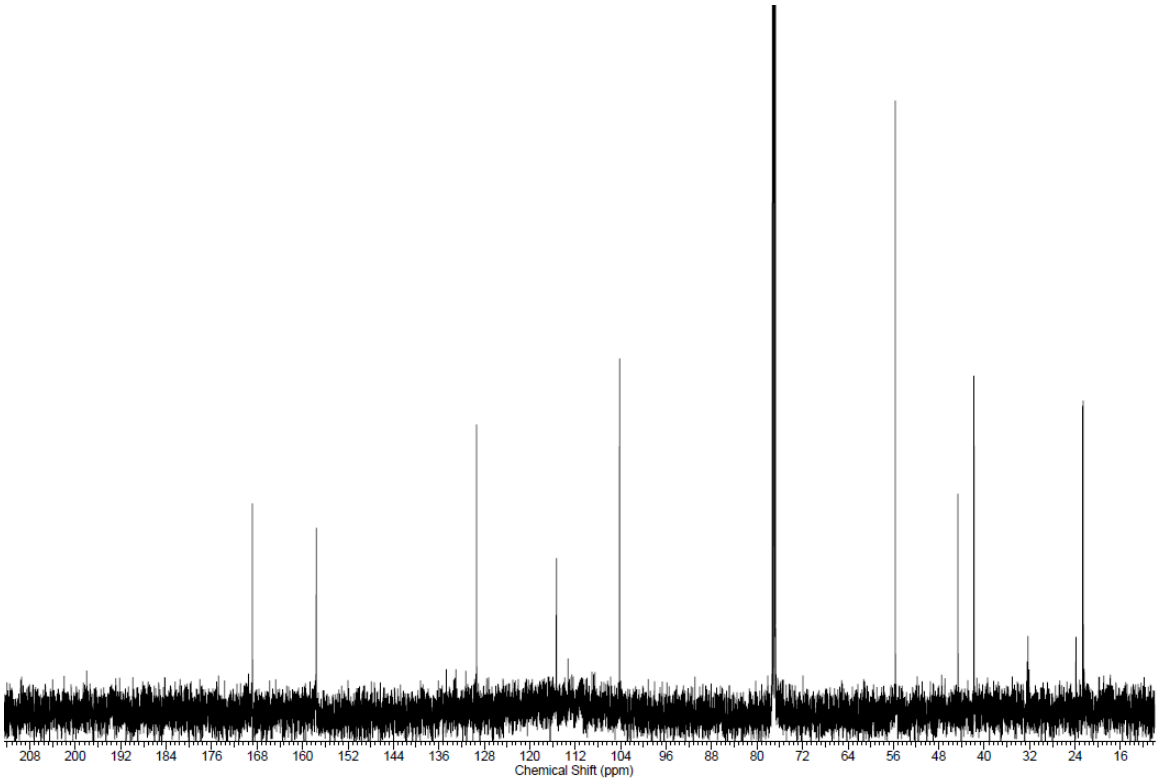


500 MHz ($CDCl_3$)

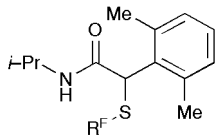


17

125 MHz ($CDCl_3$)

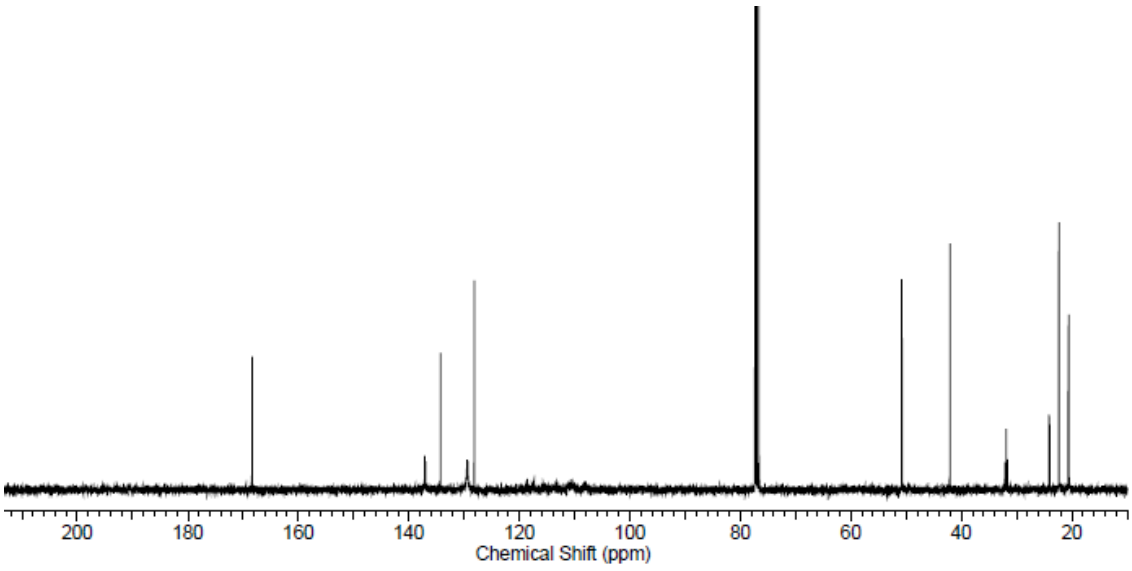


400 MHz ($CDCl_3$)

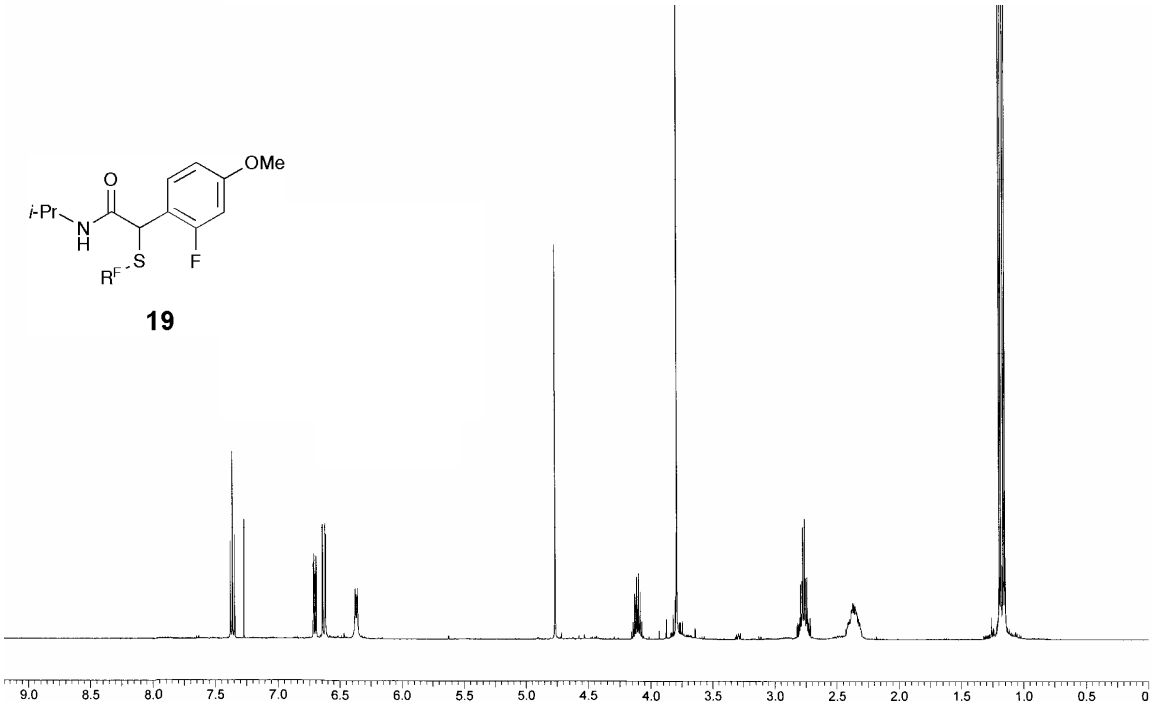


18

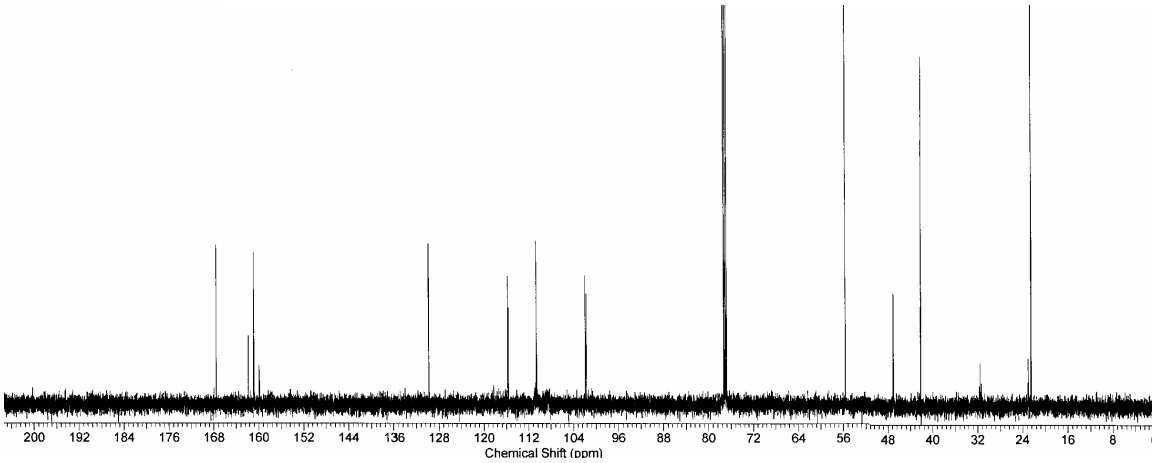
100 MHz ($CDCl_3$)



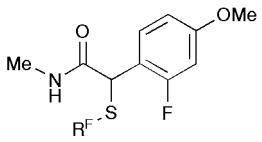
500 MHz ($CDCl_3$)



125 MHz ($CDCl_3$)

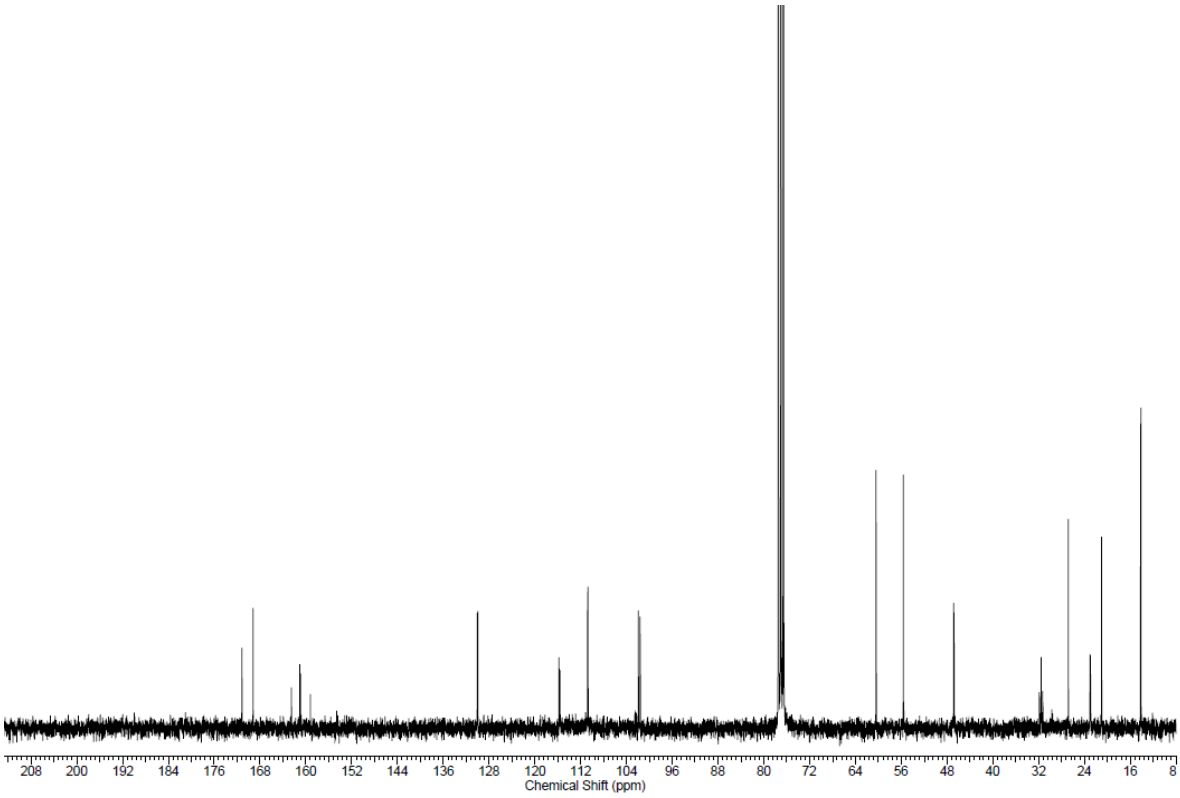


300 MHz ($CDCl_3$)

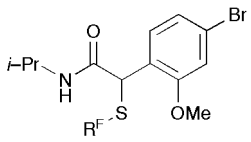


20

75 MHz ($CDCl_3$)

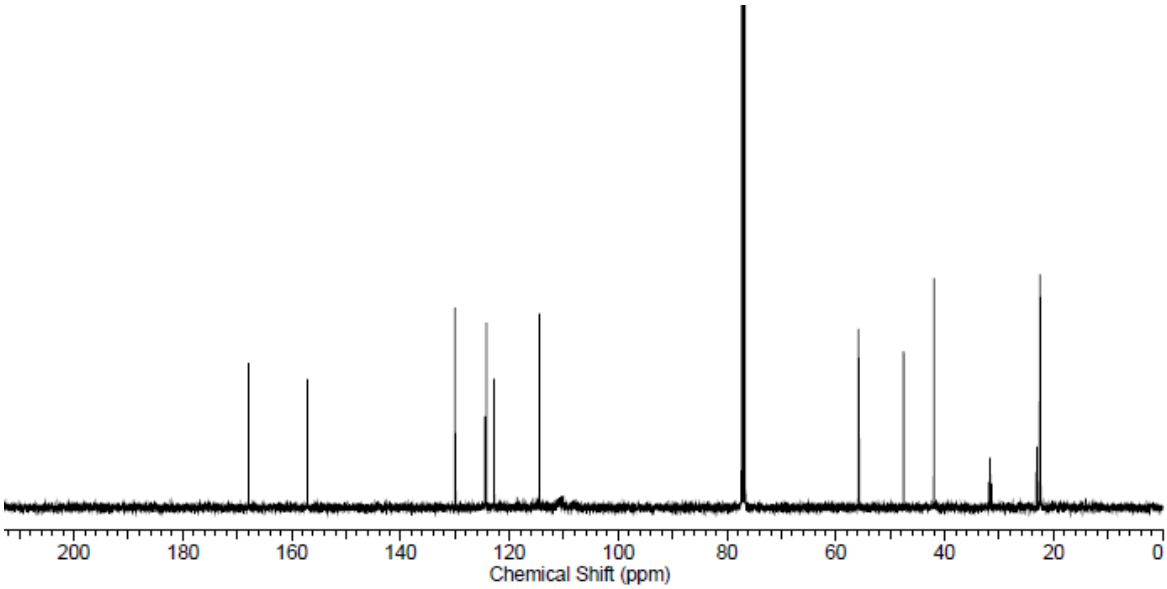


400 MHz ($CDCl_3$)

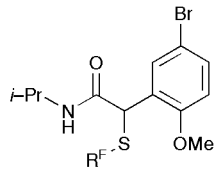


21

100 MHz ($CDCl_3$)

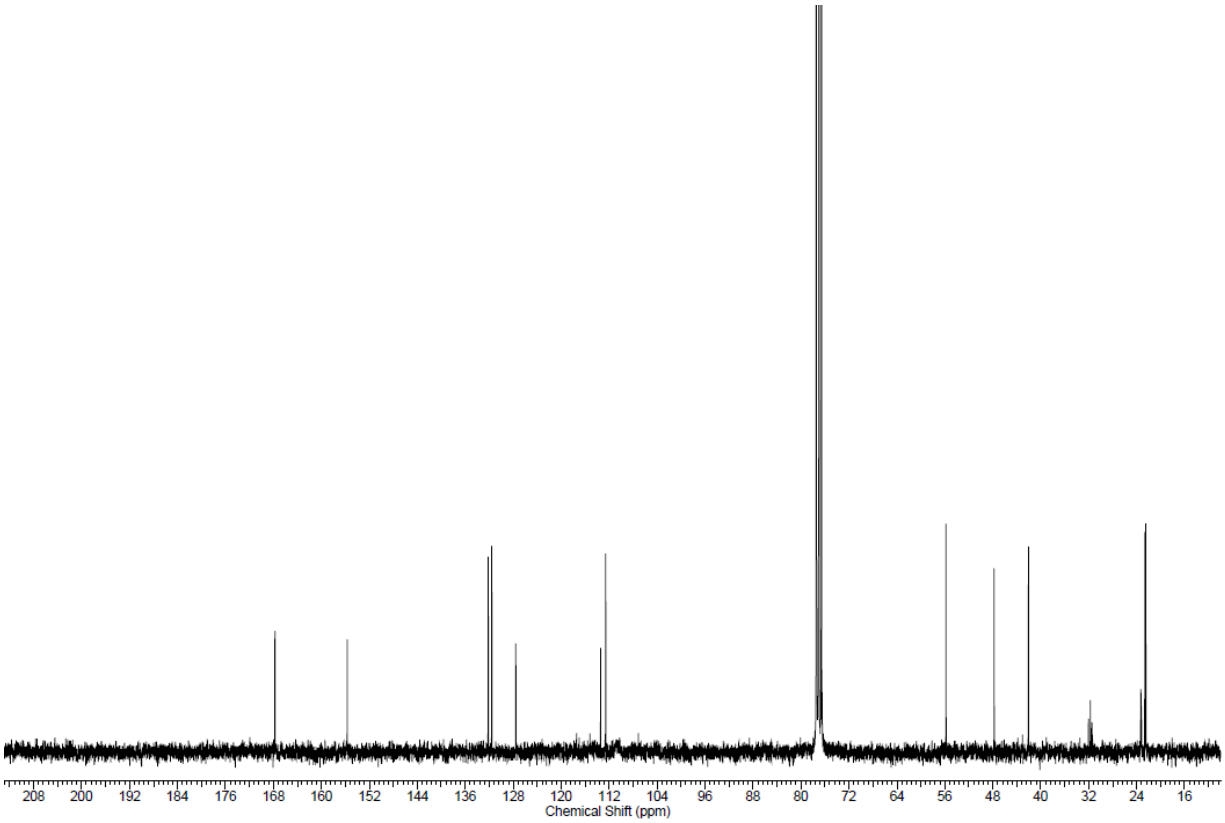


400 MHz ($CDCl_3$)



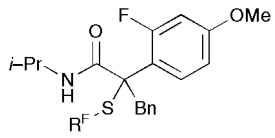
22

75 MHz ($CDCl_3$)



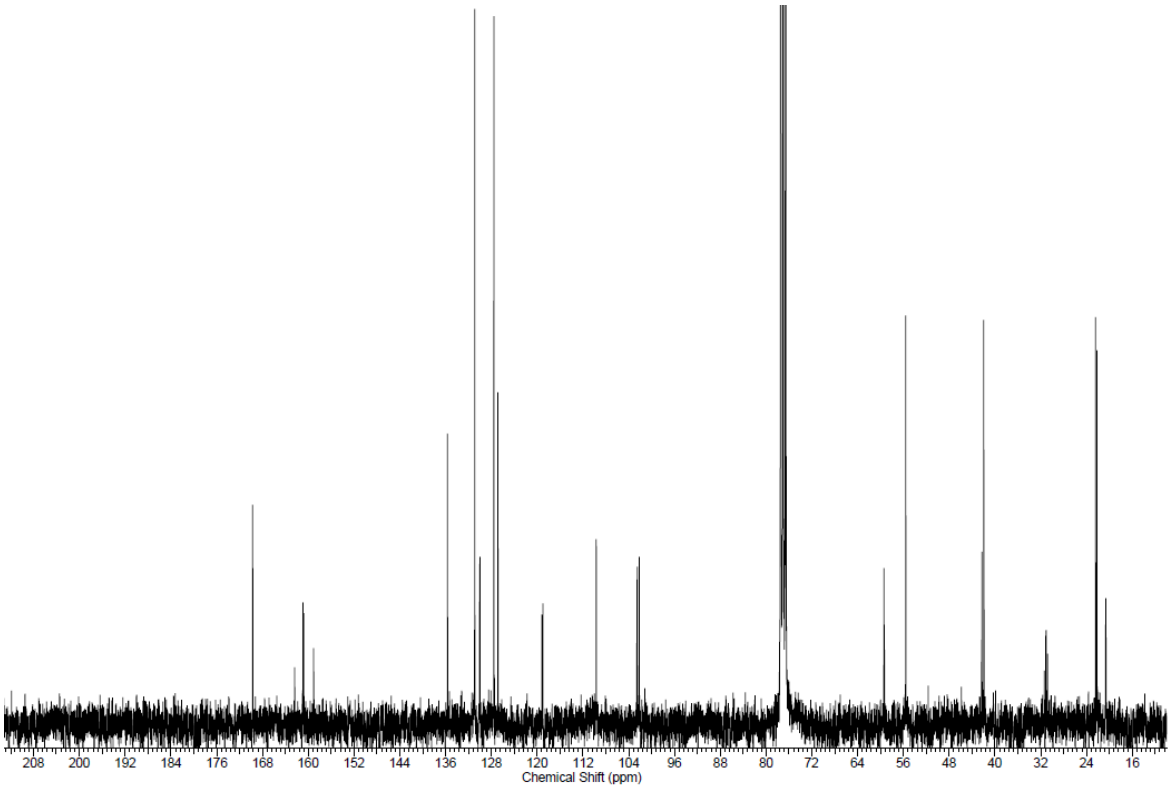
NMR data for modified aryl transfer products:

400 MHz ($CDCl_3$)

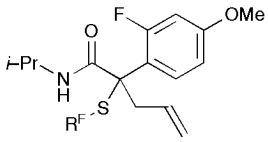


23

75 MHz ($CDCl_3$)

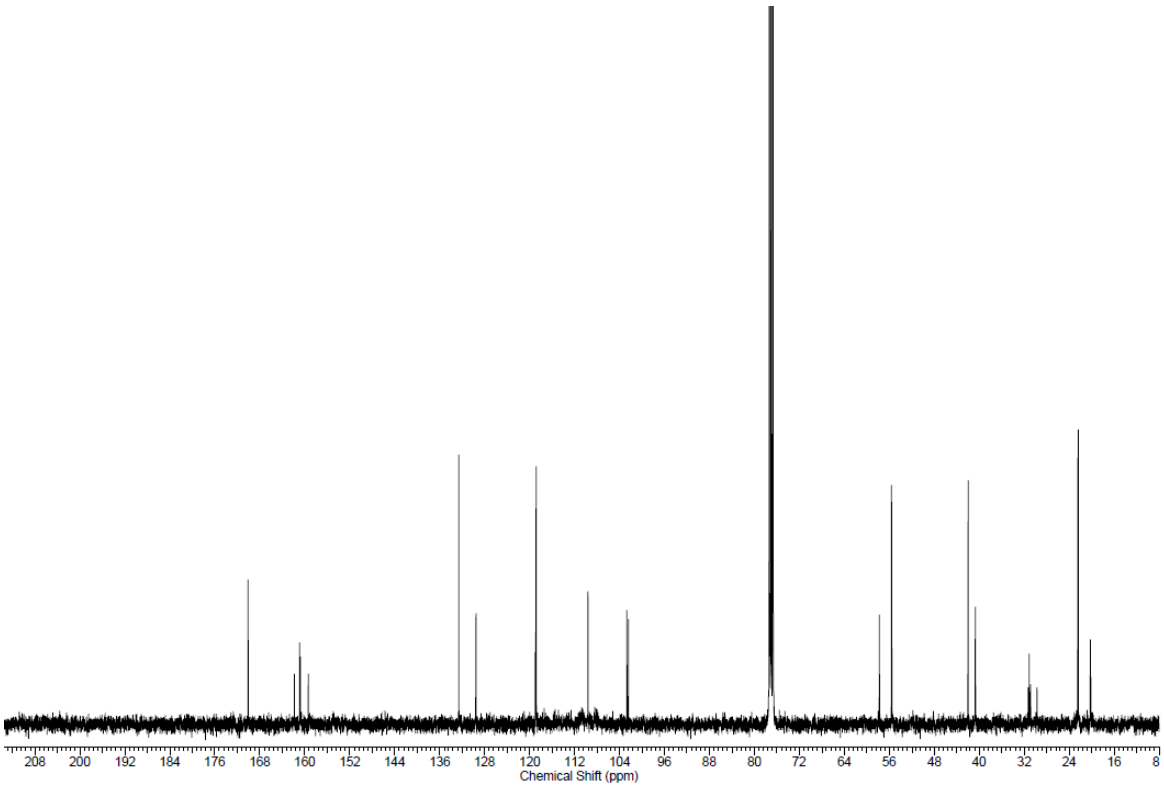


400 MHz ($CDCl_3$)

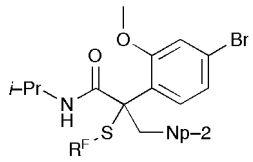


24

100 MHz ($CDCl_3$)

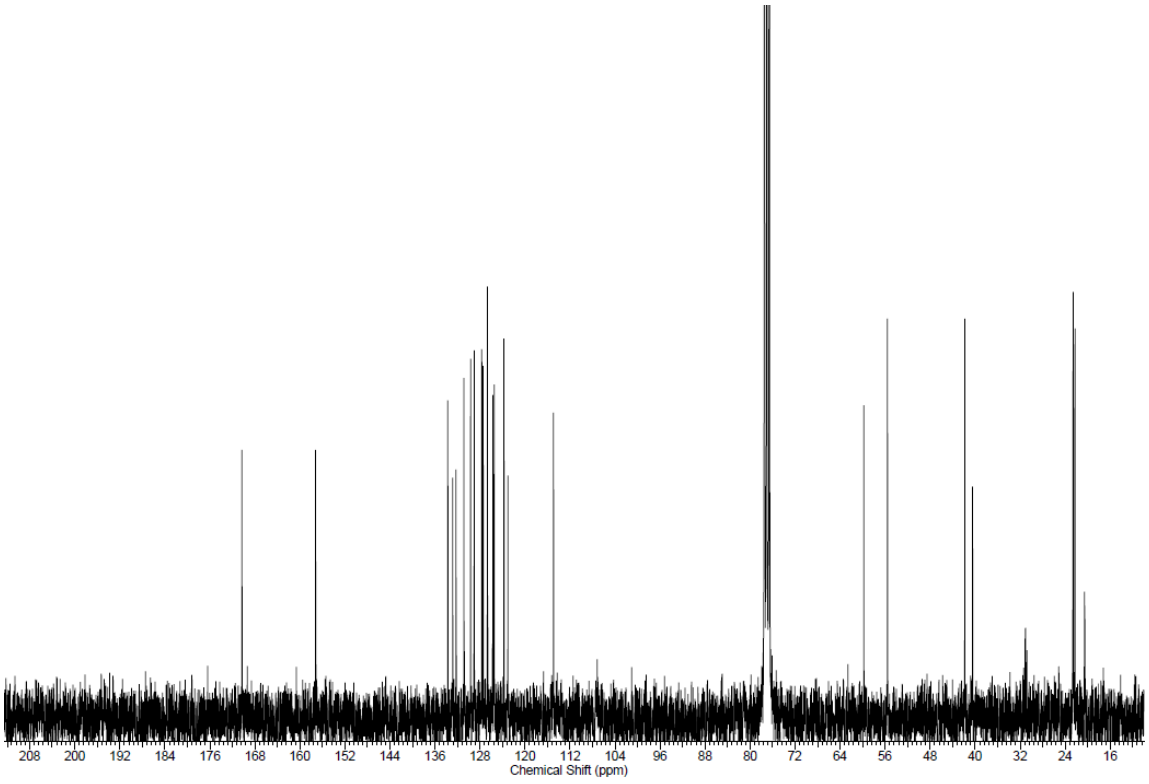


400 MHz ($CDCl_3$)

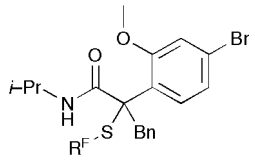


25

75 MHz ($CDCl_3$)

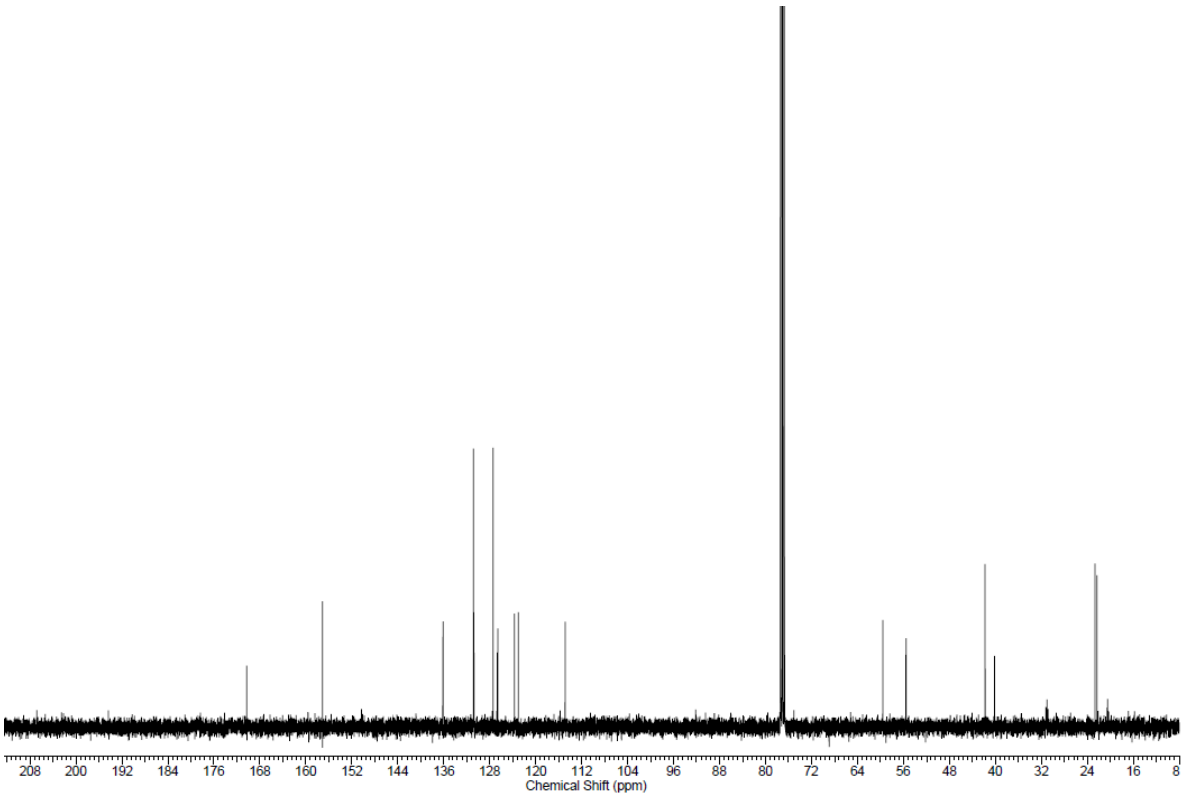


400 MHz ($CDCl_3$)

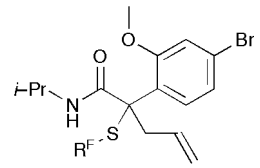


26

100 MHz ($CDCl_3$)

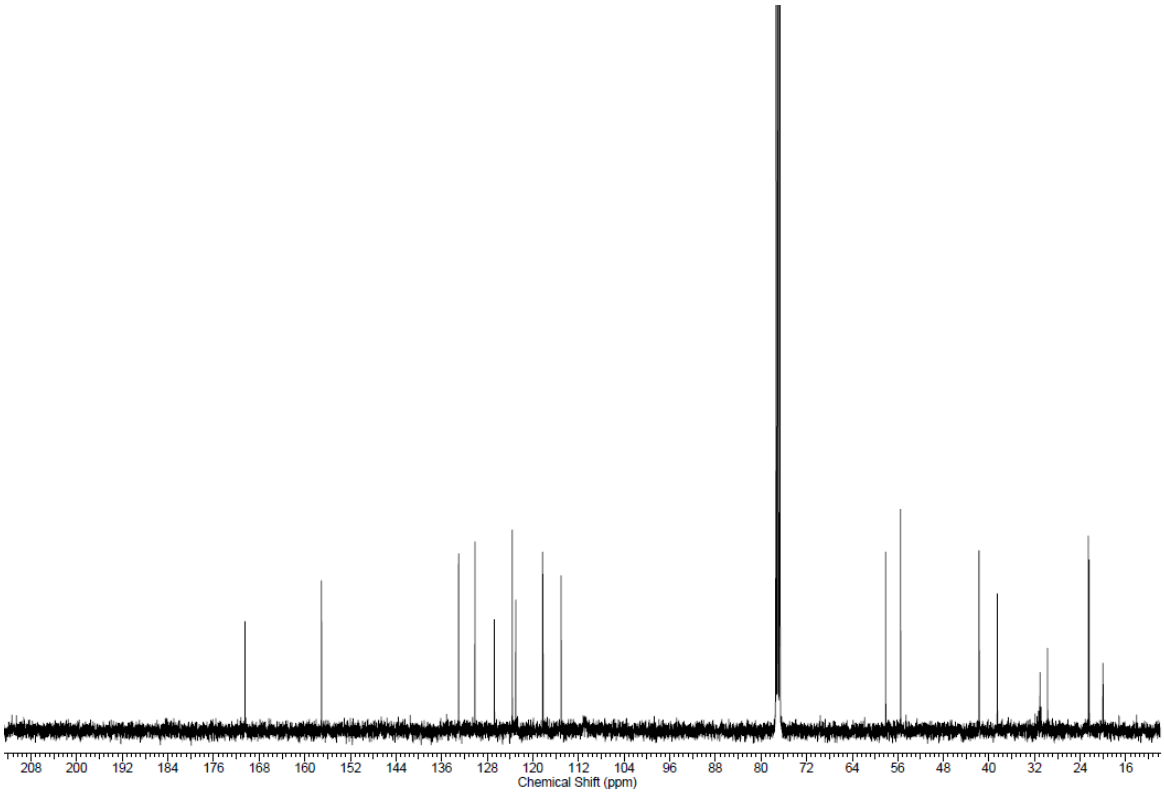


400 MHz ($CDCl_3$)

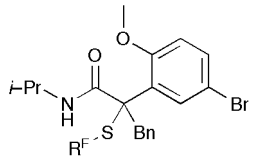


27

75 MHz ($CDCl_3$)

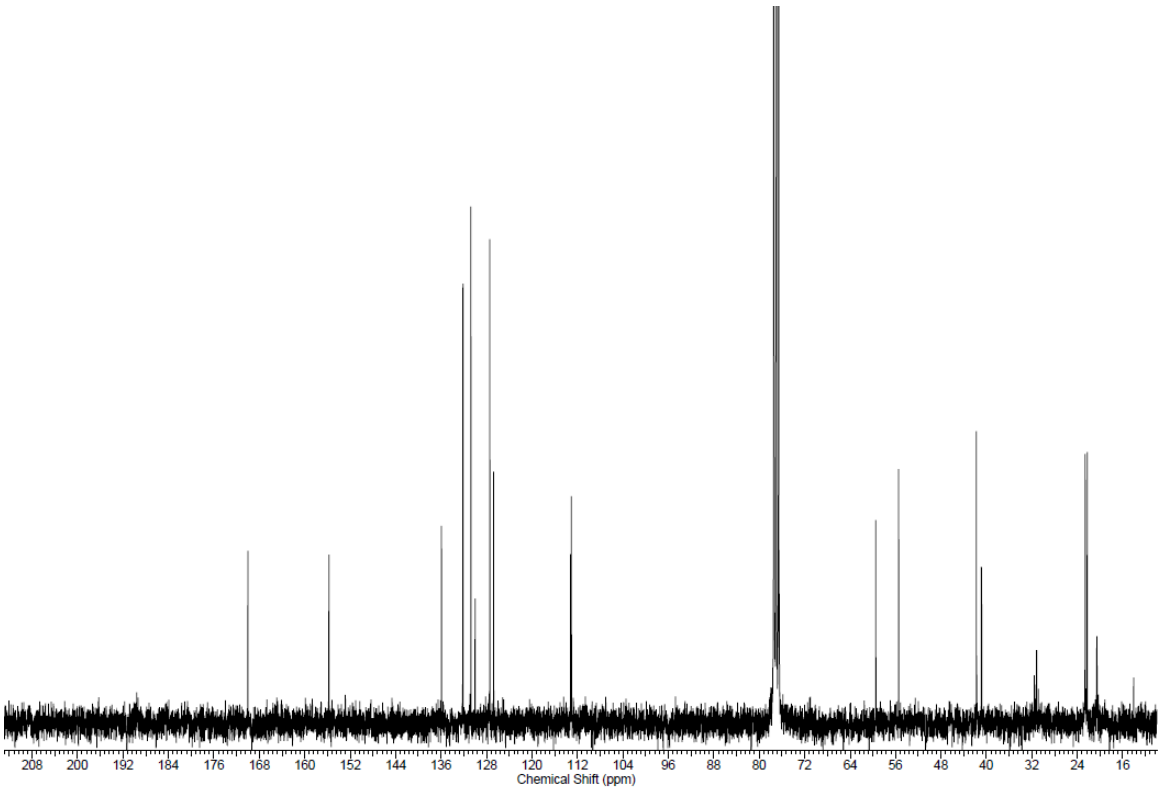


400 MHz ($CDCl_3$)

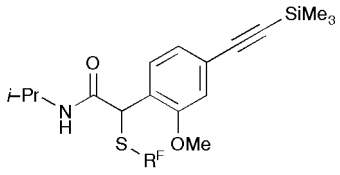


28

75 MHz ($CDCl_3$)

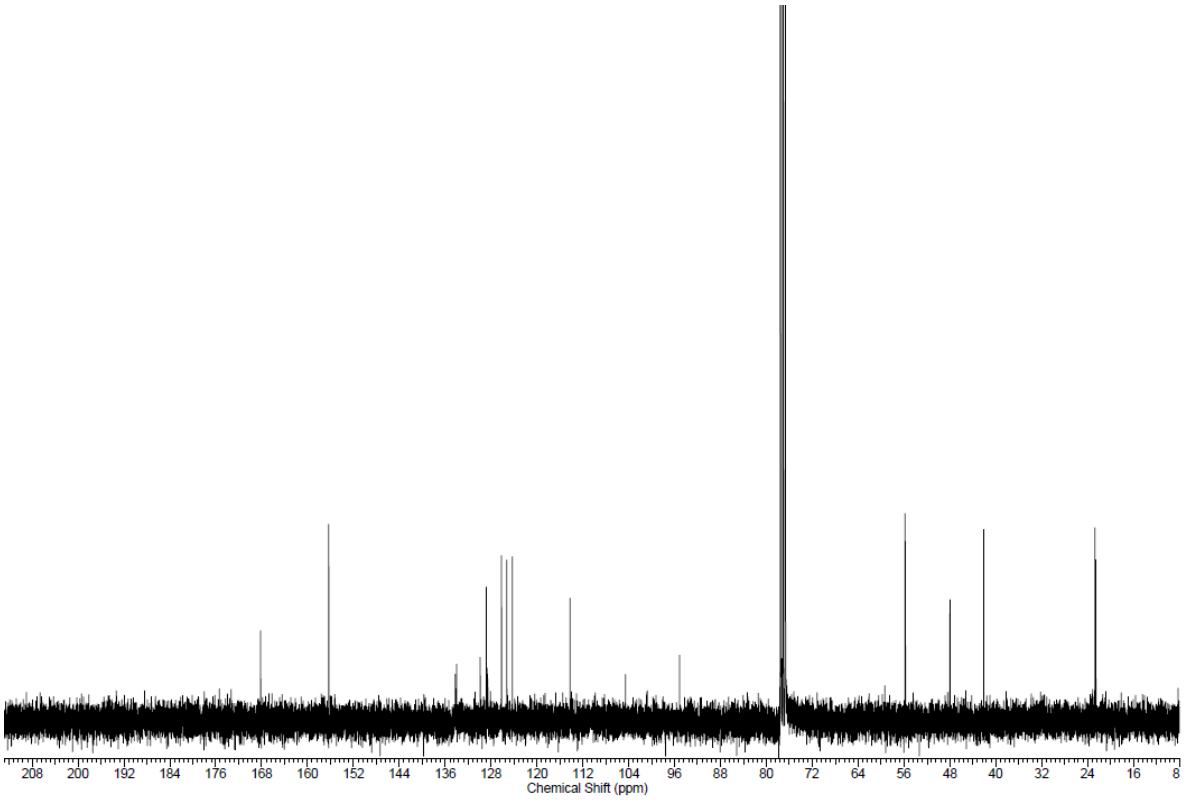


400 MHz ($CDCl_3$)

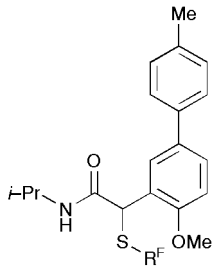


29

75 MHz ($CDCl_3$)

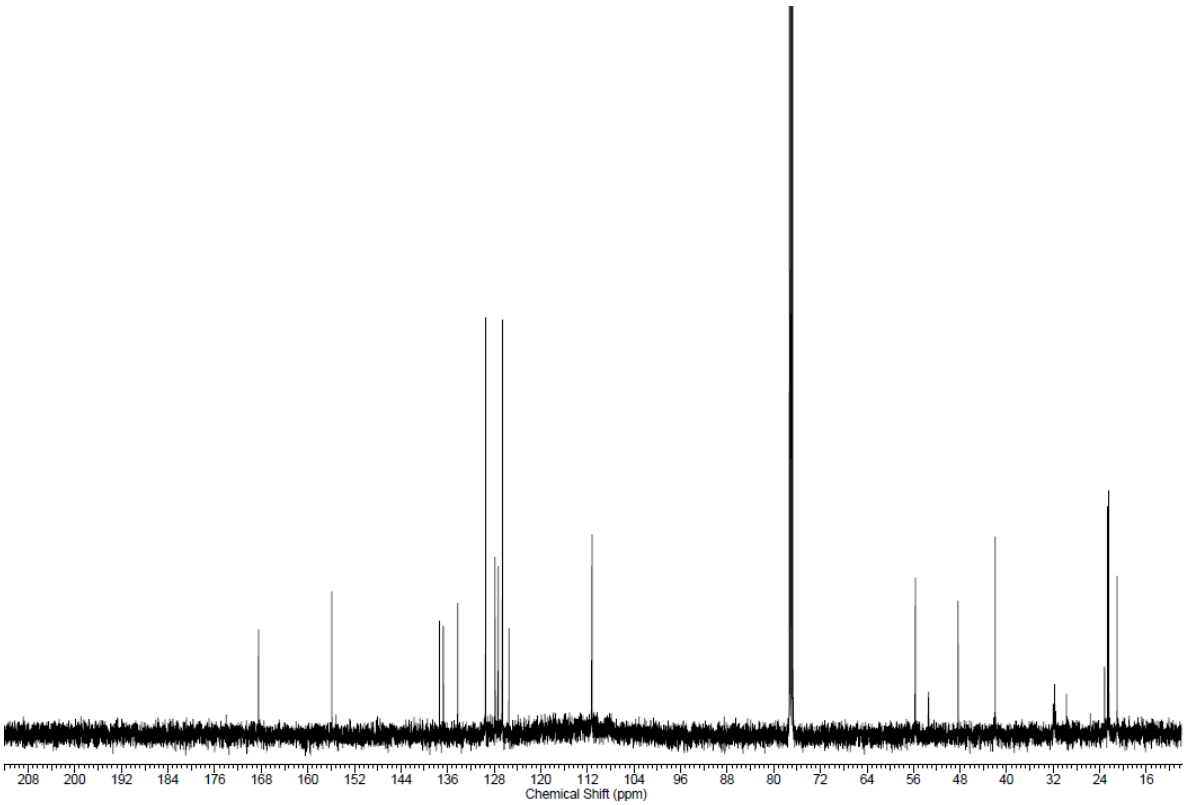


500 MHz ($CDCl_3$)

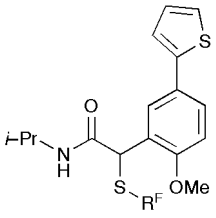


30

75 MHz ($CDCl_3$)

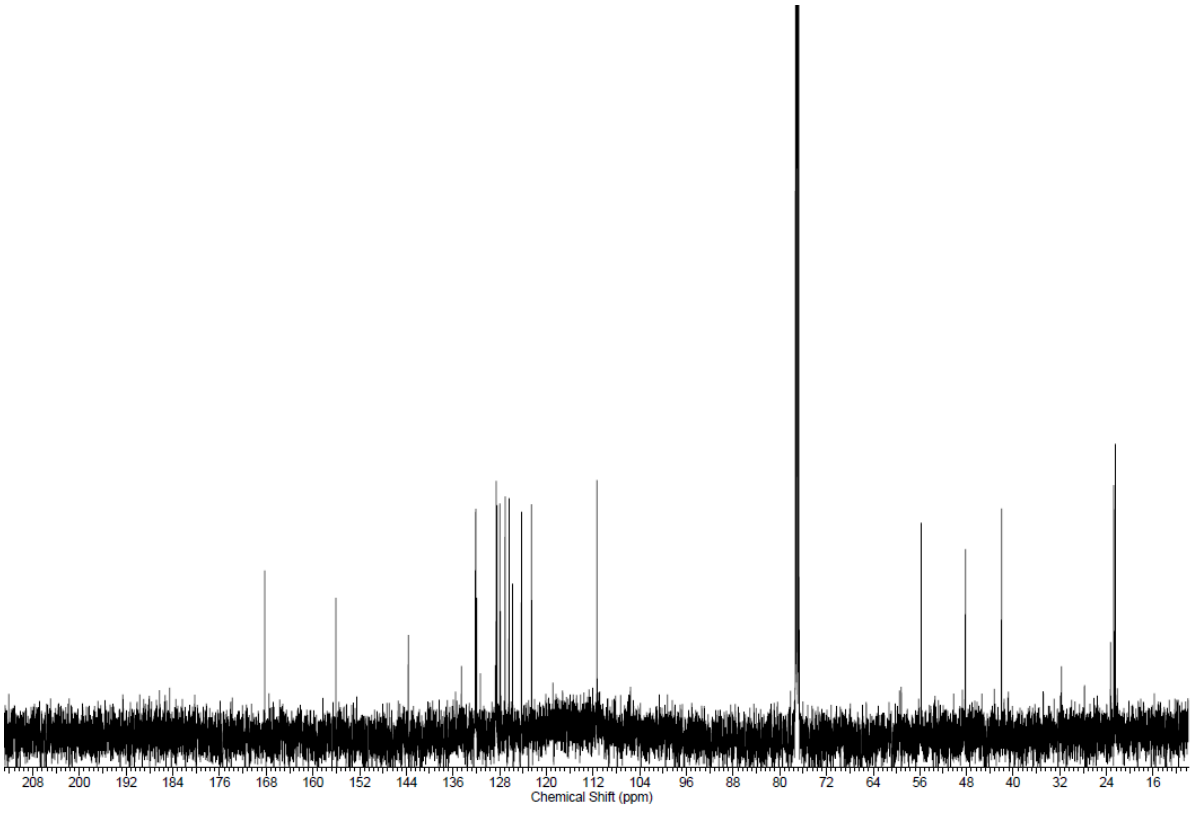


500 MHz ($CDCl_3$)

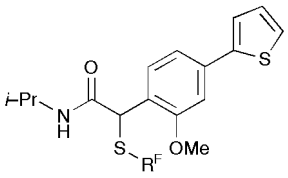


31

125 MHz ($CDCl_3$)

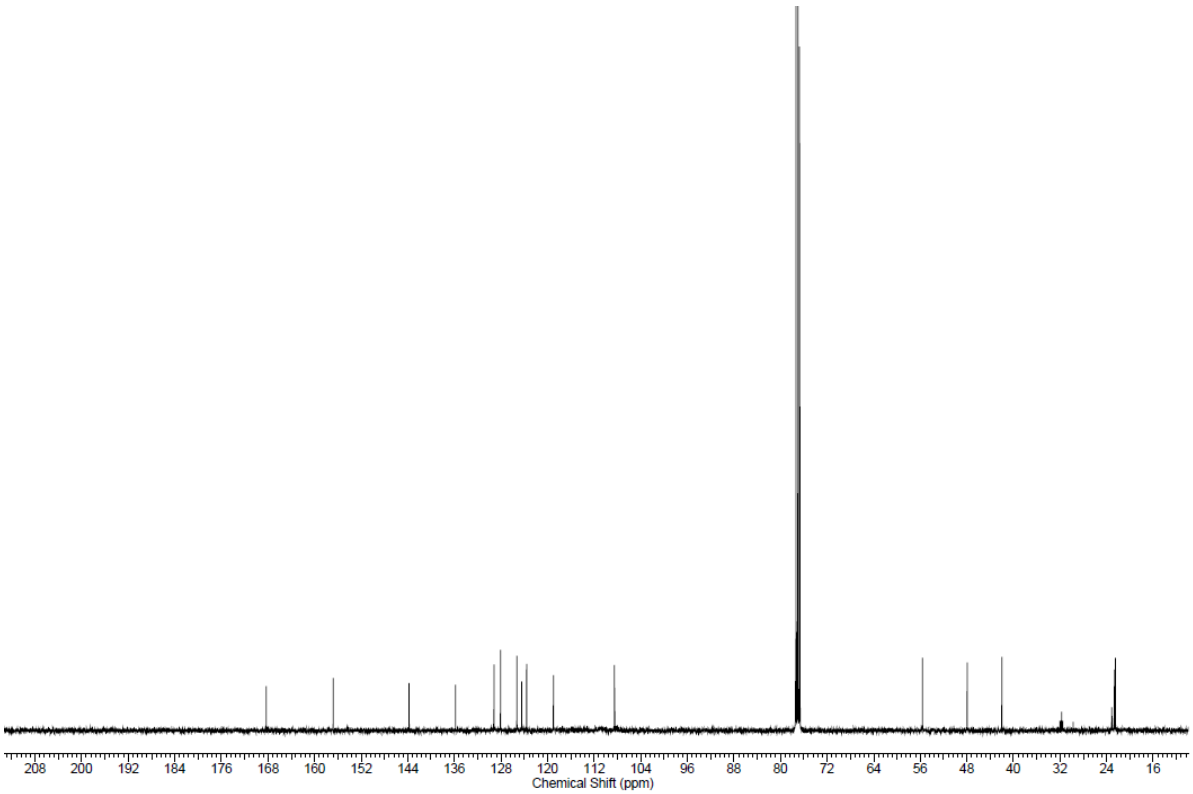


400 MHz ($CDCl_3$)



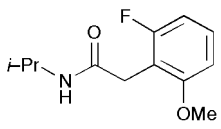
32

100 MHz ($CDCl_3$)



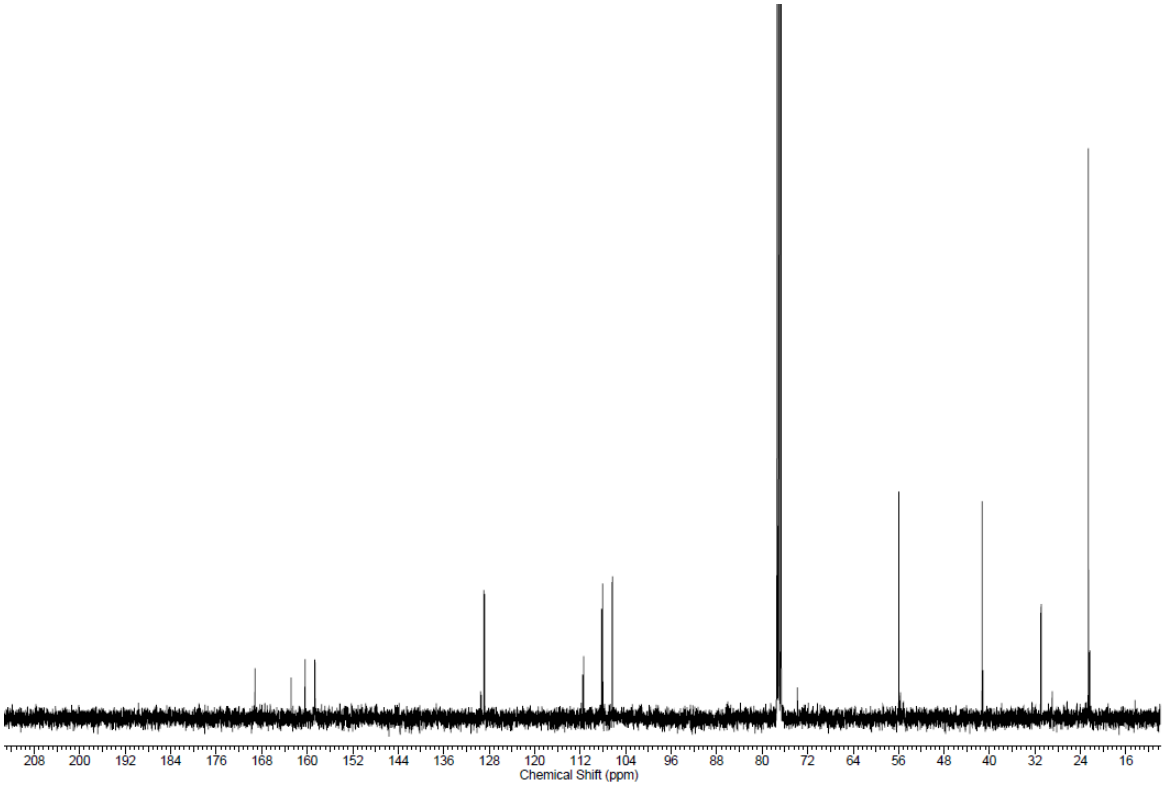
NMR spectra: Tag cleaved products

400 MHz ($CDCl_3$)

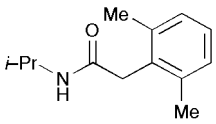


33

100 MHz ($CDCl_3$)

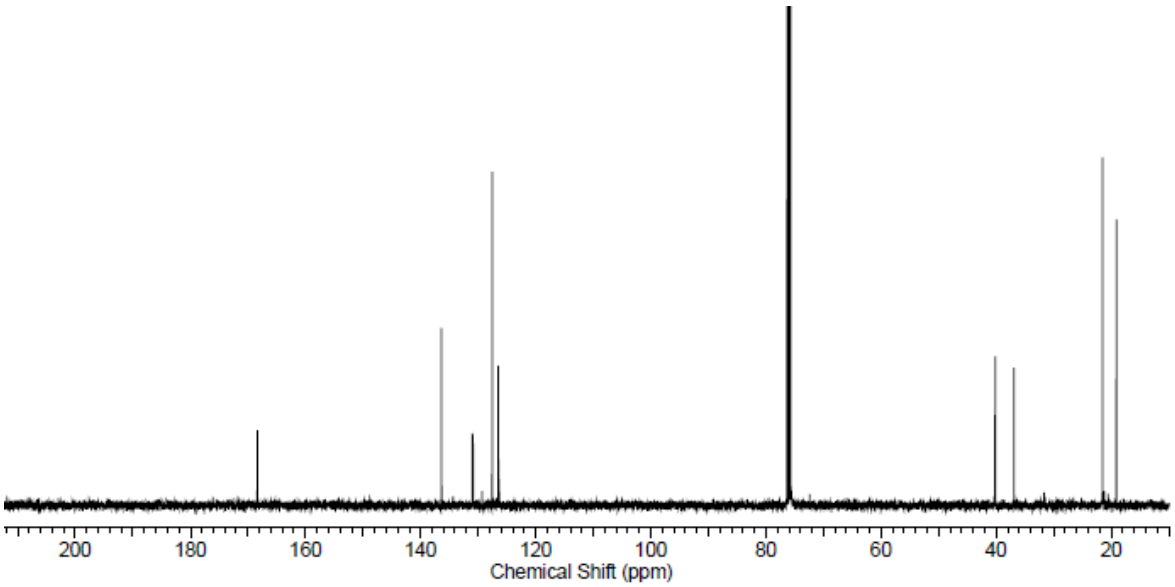


400 MHz ($CDCl_3$)

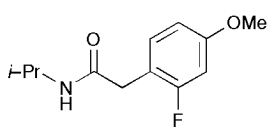


34

100 MHz ($CDCl_3$)

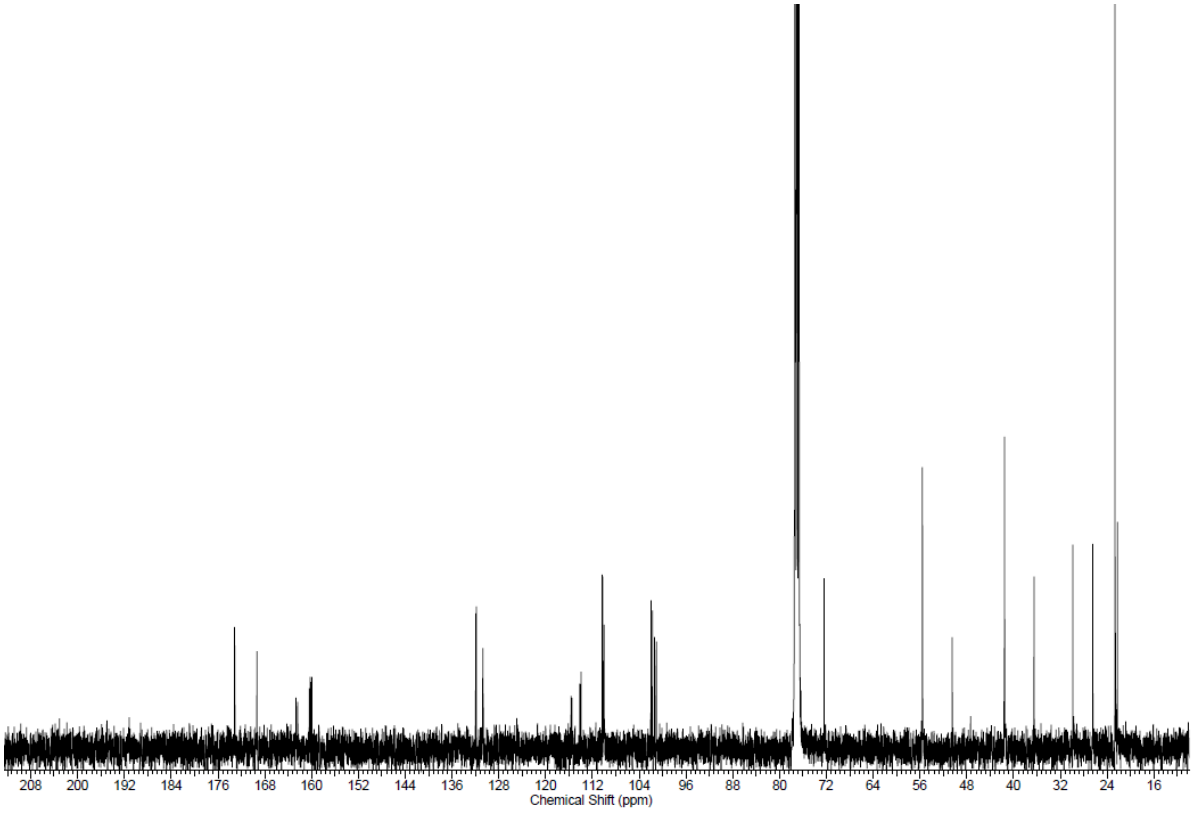


400 MHz ($CDCl_3$)

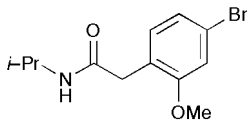


35

100 MHz ($CDCl_3$)

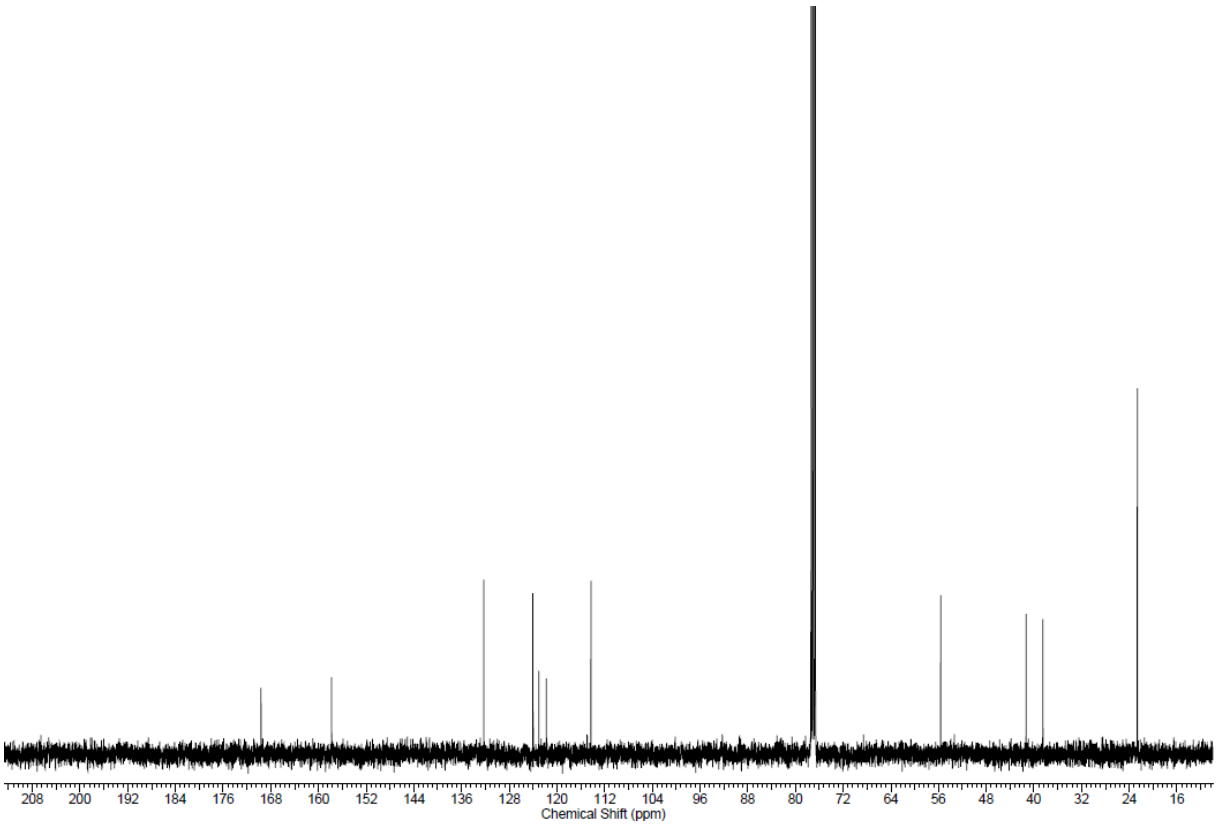


400 MHz ($CDCl_3$)

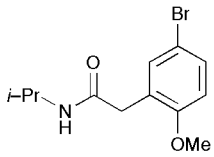


36

100 MHz ($CDCl_3$)

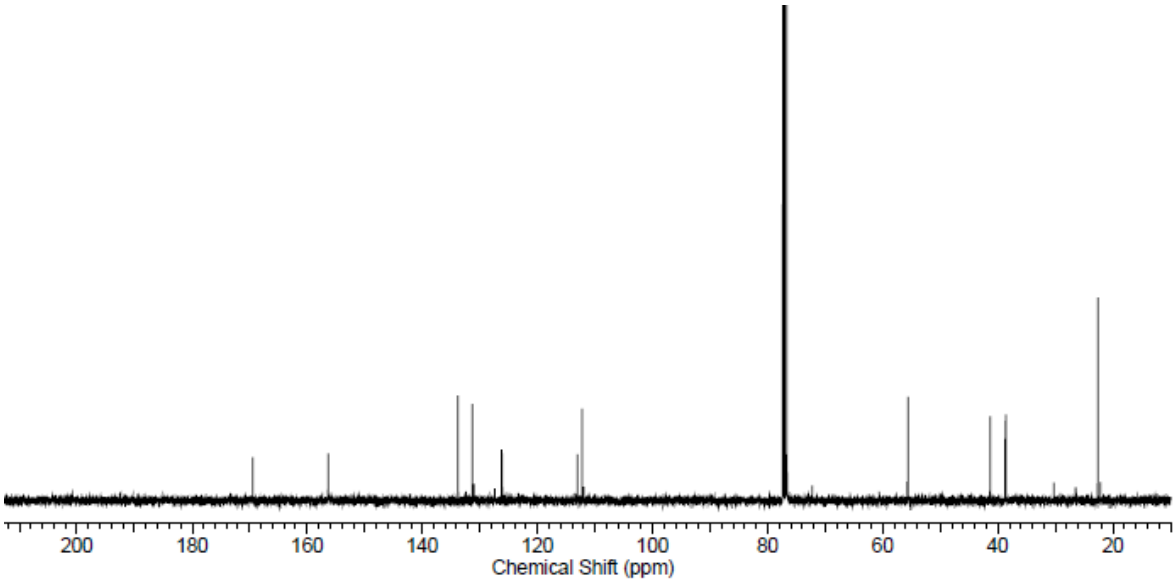


400 MHz ($CDCl_3$)

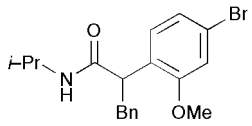


37

100 MHz ($CDCl_3$)

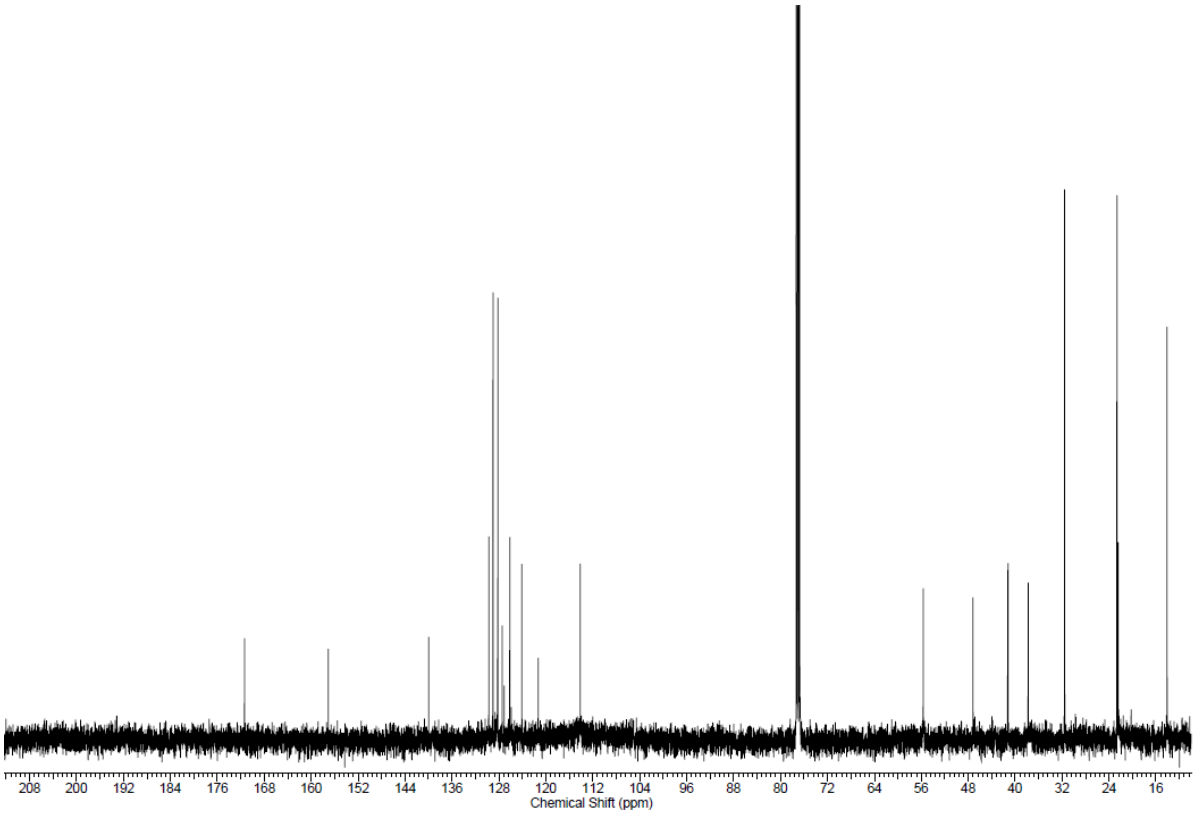


400 MHz ($CDCl_3$)

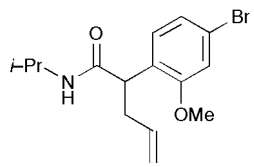


38

125 MHz ($CDCl_3$)

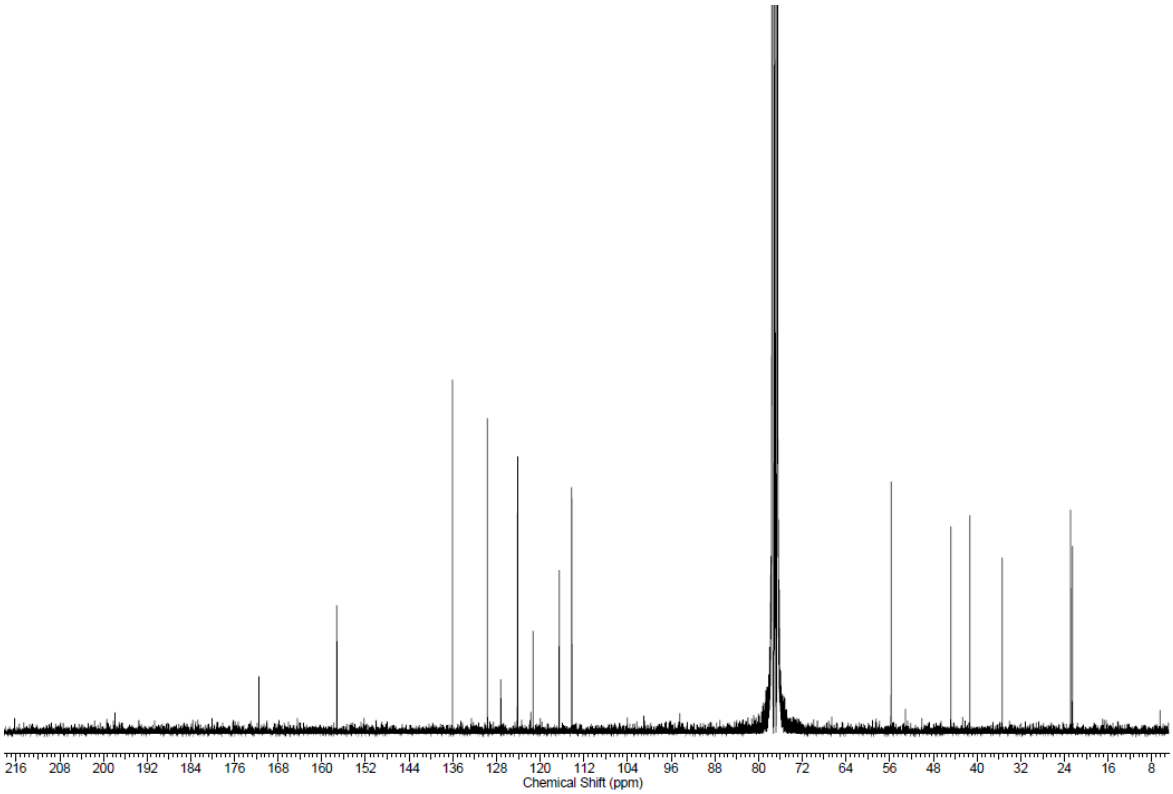


500 MHz ($CDCl_3$)

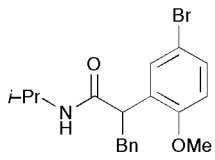


39

75 MHz ($CDCl_3$)

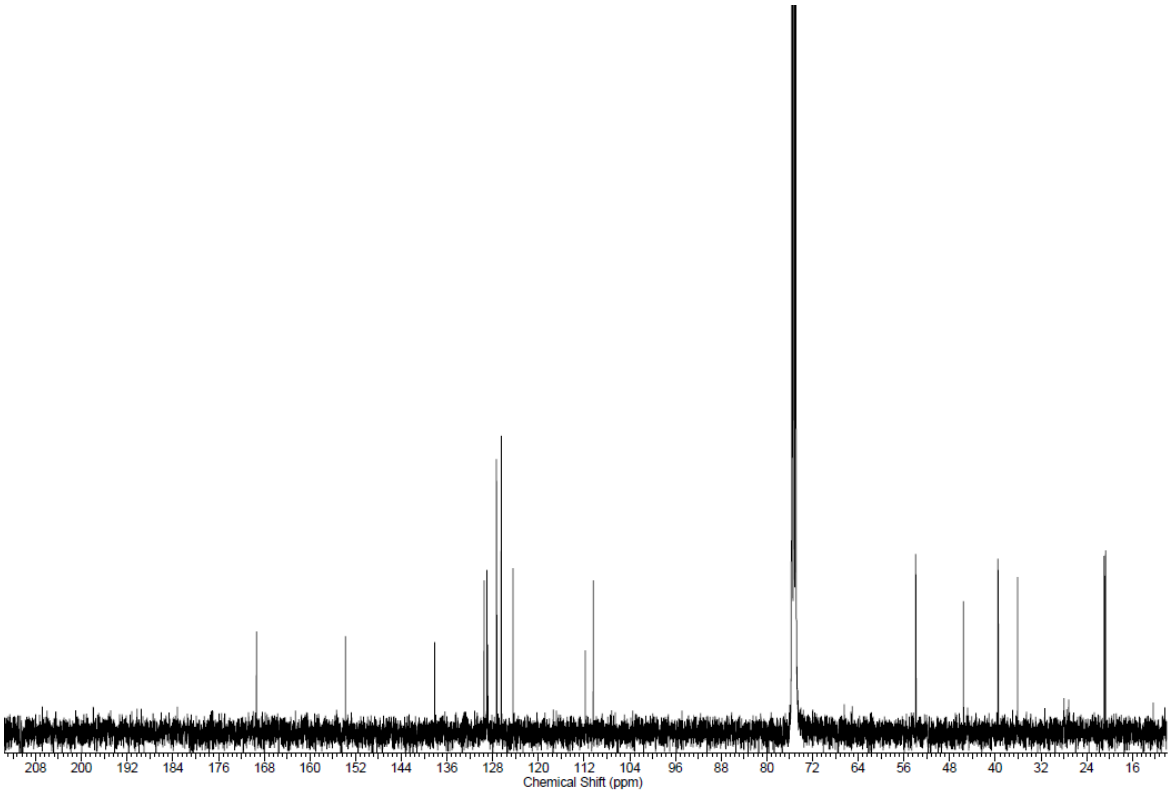


400 MHz ($CDCl_3$)

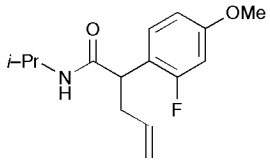


40

100 MHz ($CDCl_3$)

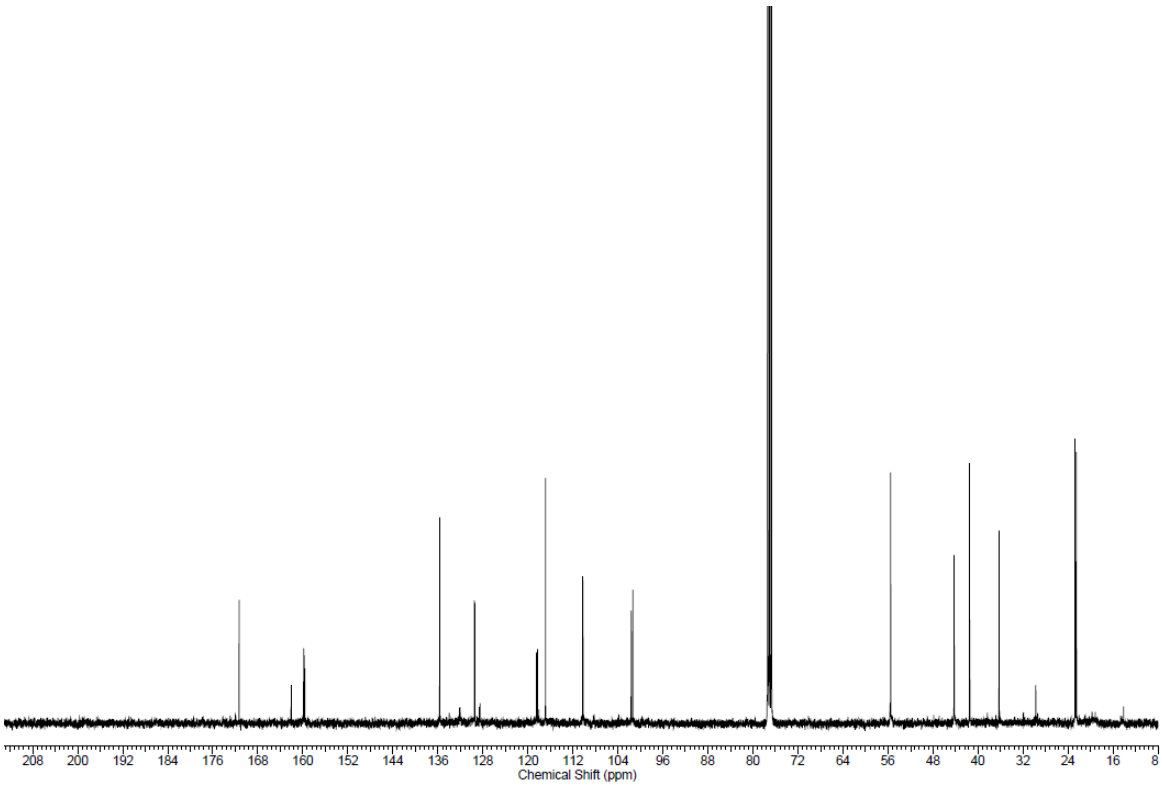


400 MHz ($CDCl_3$)

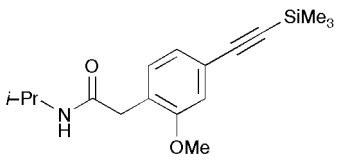


41

100 MHz ($CDCl_3$)

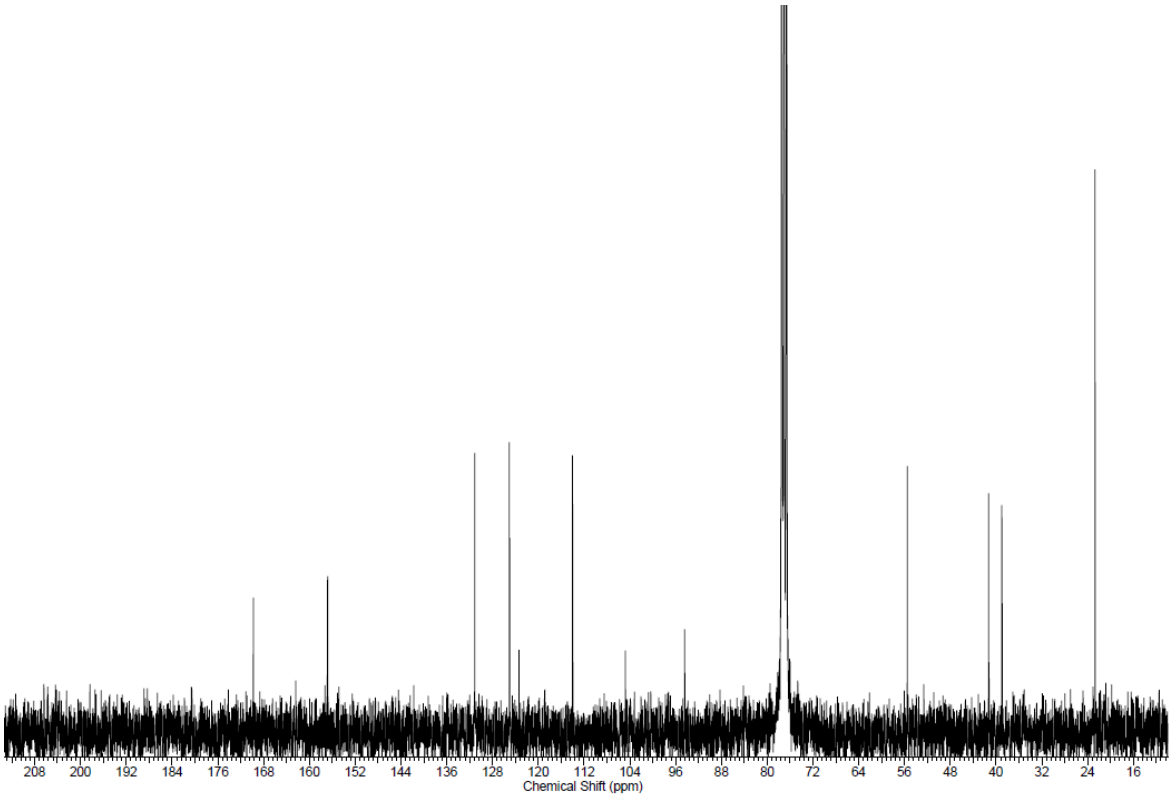


500 MHz ($CDCl_3$)

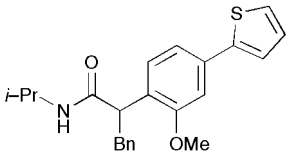


42

75 MHz ($CDCl_3$)

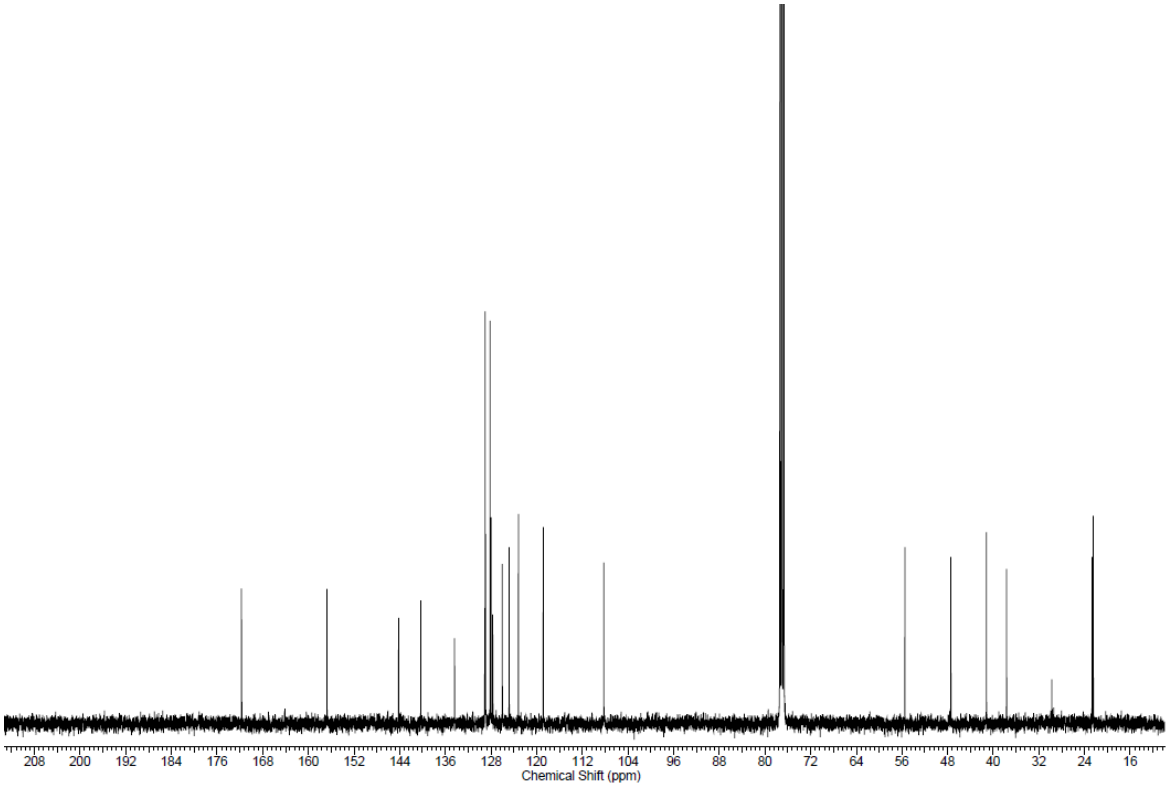


400 MHz ($CDCl_3$)

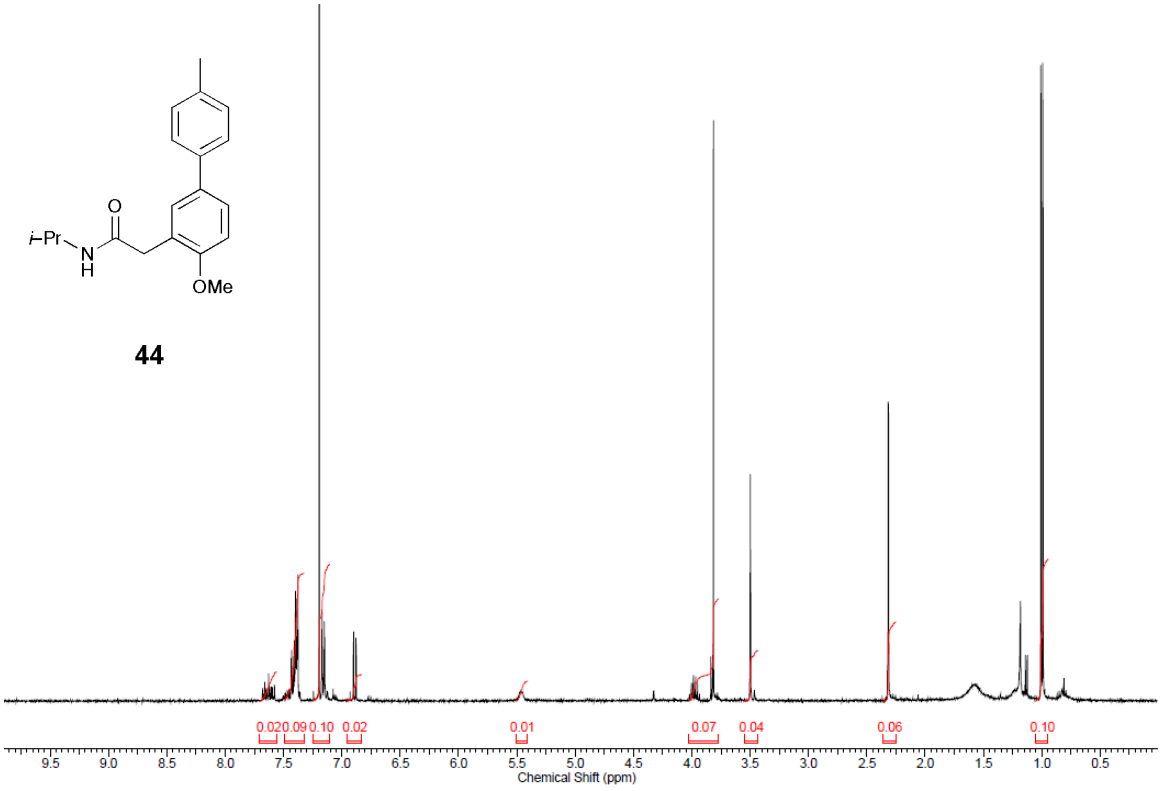


43

100 MHz ($CDCl_3$)



400 MHz ($CDCl_3$)



44

100 MHz ($CDCl_3$)