

Access to distal *meta*-C–H functionalization of arylmethanesulfonic acid derivatives

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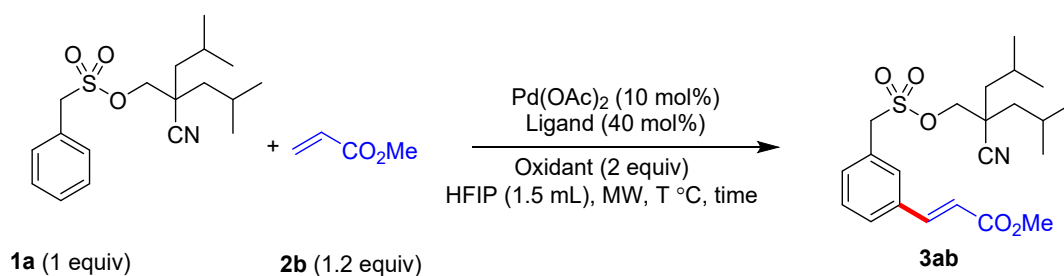
Supporting Information

Supporting Information

Experimental procedure and spectral data for all new compounds	S06-S49
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Experimental:

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^1H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in CDCl_3 ; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion concerning either internal standard tetramethylsilane (TMS) ($\delta_{\text{H}} = 0.00$ ppm) or CDCl_3 ($\delta_{\text{H}} = 7.25$ ppm). $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in CDCl_3 . Chemical shifts (δ ppm) are reported relative to CDCl_3 [$\delta_{\text{C}} = 77.00$ ppm (central line of the triplet)]. In ^1H -NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet. In $^{13}\text{C}\{^1\text{H}\}$ NMR, the nature of carbons (C, CH, CH_2 , and CH_3) was determined by recording the DEPT-135 spectra. The assignment of signals was confirmed by ^1H , $^{13}\text{C}\{^1\text{H}\}$ CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. Melting points are recorded using Tempo and Mettler FP1 melting point apparatus in capillary tubes and are uncorrected. A single crystal of **3jb** was selected and mounted on an Oxford SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 298 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using direct methods, and refined with the olex2.refinement package using Gauss–Newton minimization. All small-scale reactions were carried out by using a Schlenk tube. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; petroleum ether the boiling range of 60–80 °C was used. $\text{Pd}(\text{OAc})_2$, Ac-Gly-OH, AgOAc and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were purchased from Sigma-Aldrich and used as received. Olefin coupling partners, NCS, DMF, DCM, ACN, K_2CO_3 , NaOH and NEt_3 were purchased from Sigma-Aldrich/TCI/local sources and used as received. Acme’s silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

Table S1. Optimization conditions for *meta*-C–H olefination of arylmethanesulfonate **1a**.

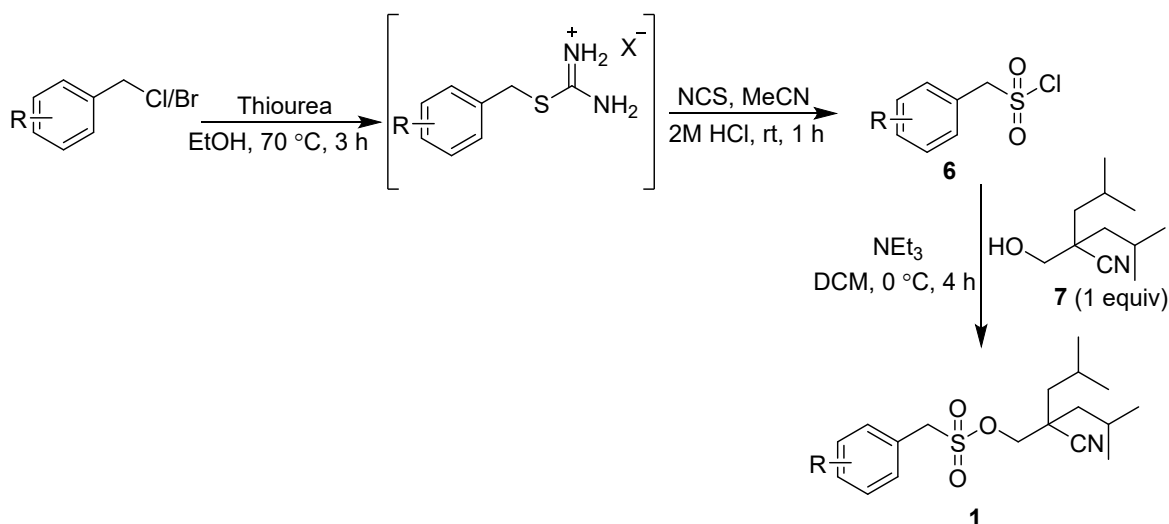
Entry	Oxidant	Ligand	Time (min)	Irradiation temp (°C)	Yield of 3ab (<i>m:o</i>) ^a
1	Ag ₂ CO ₃	Ac-Gly-OH	15	60	37% (96:04)
2	AgOAc	Ac-Gly-OH	15	60	59% (99:01)
3	AgO	Ac-Gly-OH	15	60	9% (96:04)
4	Cu(OAc) ₂	Ac-Gly-OH	15	60	Trace
7	AgOAc	<i>N</i> -Boc-Gly-OH	15	60	Trace
8	AgOAc	<i>N</i> -Boc-L-valine	15	60	Trace
9	AgOAc	Ac-Gly-OH	20	60	67% (99:01)
10	AgOAc	Ac-Gly-OH	25	75	75% (99:01)
11 ^b	AgOAc	Ac-Gly-OH	25	90	83% (100:0)
12	AgOAc	Ac-Gly-OH	35	90	72% (99:01) ^c
13 ^{d,e}	AgOAc	Ac-Gly-OH	25	90	No product
14 ^{f,g,h}	AgOAc	Ac-Gly-OH	25	90	No product

Reaction conditions: ^aYields of isolated product **3ab**. Regioselectivity was determined by ¹H-NMR analysis. ^b1.5 equiv of **2b** was used. ^cBis-olefination product was observed. ^dTFE as the solvent. ^eAcetic acid as the solvent. ^fPdCl₂ was used as the catalyst. ^gPdCl₂(PPh₃)₂ was used as the catalyst. ^hPd(PPh₃)₄ was used as the catalyst.

Only 37% of the product **3ab** was observed when the reaction was carried out for 15 minutes at 60 °C by using Ag₂CO₃ as the oxidant (Entry 1, Table S1). Notably, when the oxidant was changed from Ag₂CO₃ to AgOAc, the product **3ab** yield was improved to 59% with “*meta*:others = 99:01”. When AgO was used as the oxidant, the yield decreased drastically to 9% (Entry 3, Table S1). Unfortunately, only a trace amount of the product was observed when Cu(OAc)₂ was used as an oxidant. Later, the ligands were changed, such as *N*-Boc-Gly-OH (Entry 7, Table S1) and *N*-Boc-L-valine (Entry 8, Table S1) failed to provide the product **3ab**. Notably, the yield of **3ab** was improved to 67% when the time was increased to 20 min (Entry 9, Table S1). Later, the time is increased to 25 min, and the temperature rose to 75 °C. Then, it was observed that yield of **3ab** improved to 75% (Entry 10, Table S1). Significantly, it was observed that the increase in the concentration of olefin (1.5 equiv) resulted in improving the mono-olefination product **3ab** in 83% of the yield with exclusive *meta*-selectivity along with trace amount of bis-olefination product (Entry 11, table S1). Encouraged by the above observation, we intended to increase the time further to 35 minutes, but it observed that the product **3ab** had been started converting to the bis-olefination product was formed in just 10% yield (entry 12, Table S1). Unfortunately, the reaction not shown any

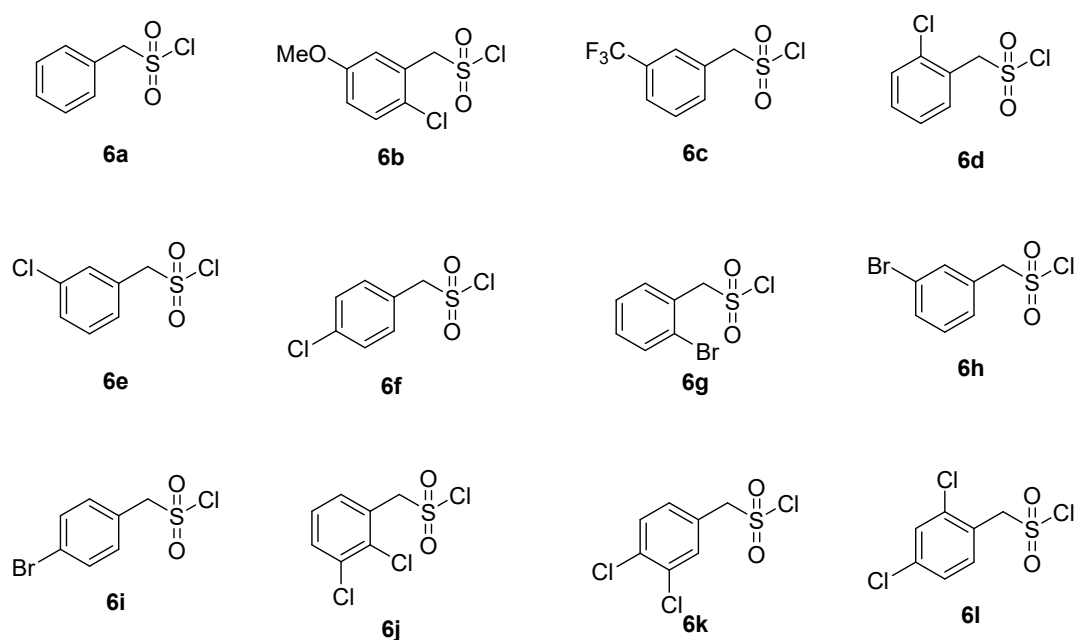
progress when the reaction was carried out in TFE and AcOH as the solvent (Entry 13, Table S1). In contrast, the reactions did not furnish any product using other palladium catalysts, such as with PdCl₂, PdCl₂(PPh₃)₂, and Pd(PPh₃)₄ (Entry 14, Table S1).

The required template bearing synthetic precursor **1** have been synthesized in two steps, as depicted in Scheme S1.



Scheme S1. Synthetic sequence for the preparation of arylmethanesulfonate ester template **1**.

Table S2. Reported sulfonyl chloride starting materials.¹



General Procedure-1 (GP-1) Preparation of arylmethanesulfonyl chlorides (6):

To an oven dried 50 mL round bottom flask charged with a magnetic stirring bar, were added bezyl halide **7** (1 equiv) and thiourea (1 equiv) were refluxed together in EtOH (5 mL) at 70 °C for 3 h. The reaction progress was monitored by TLC, then EtOH was removed under reduced pressure, the obtained solid or sticky oil was slowly added to a mixture of *N*-chlorosuccinimide (5 equiv), 2 M HCl (2.5 mL), and MeCN (8 mL) in a 10 °C water bath to maintain the internal temperature between 10 and 20 °C and allowed the mixture to stir for 1 h. After completion of the reaction, the mixture was quenched by the addition of an aqueous NH₄Cl solution and extracted with ethyl acetate (3×20 mL). The organic phase was separated, dried (Na₂SO₄), and concentrated under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the arylmethanesulfonyl chlorides **6** in quantitative yield, as a white or brown solid/liquid.

General Procedure-2 (GP-2) for the Preparation of Arylmethanesulfonate Esters (1):

To an oven dried 25 mL round bottom flask charged with a magnetic stirring bar, were added arylmethanesulfonyl chloride **6** (1 equiv), nitrile alcohol template **7** (1 equiv), in Dichloromethane (15 mL) as solvent then triethyl amine (1.5 equiv) was added dropwise to the reaction mixture. The reaction mixture was stirred at room temperature for 4 h. The conversion was monitored by TLC. Then, the mixture was quenched by the addition of an aqueous NH₄Cl solution and extracted with dichloromethane (3×15 mL). The organic layers were washed with saturated NaCl solution, dried (Na₂SO₄), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the arylmethanesulfonate esters **1** in quantitative yields.

General Procedure-3 (GP-3) for Microwave Assisted *meta*-Selective C–H Olefination (3):

An oven-dried 10 mL glass vial equipped with a magnetic stirring bar, was charged with arylmethanesulfonate ester **1** (0.2 mmol), olefin **2** (0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol%), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (67 mg, 0.4 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL). The resulting reaction mixture was subjected to microwave irradiation 90 °C for 25 minutes. The reaction mixture was cooled to room temperature. The progress of the reaction was monitored by TLC. The reaction mixture diluted with ethyl acetate (15 mL) and

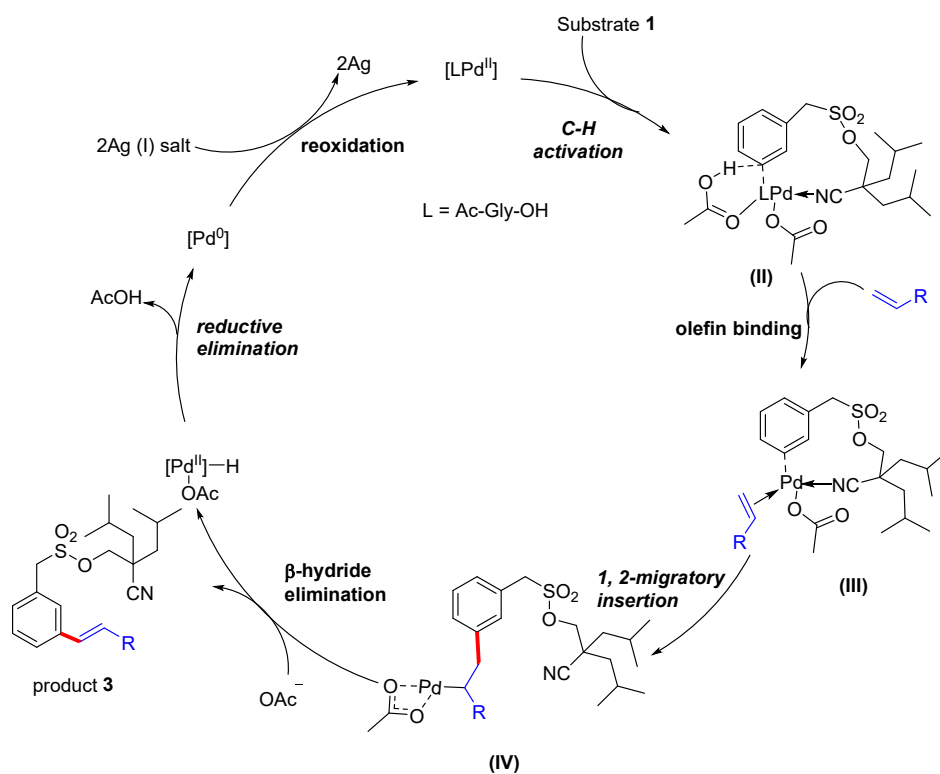
filtered through a short pad of celite with an additional amount of ethyl acetate (15 mL). Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the desired *meta*-olefinated product **3** in 52% to 83% yields, as viscous colourless/pale-yellow/brown liquid or solid.

General Procedure-4 (GP-4) for Microwave Assisted One-pot Homo-Bis-*meta*-Selective C–H Olefination (4):

An oven-dried 10 mL glass vial equipped with a magnetic stirring bar, was charged with arylmethanesulfonate ester **1** (0.2 mmol), olefin **2** (0.72 mmol), Pd(OAc)₂ (5 mg, 10 mol%), *N*-Ac-Gly-OH (10 mg, 40 mol%), AgOAc (134 mg, 0.8 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL). The resulting reaction mixture was subjected to microwave irradiation at 100 °C for 35 minutes. The reaction mixture was cooled to room temperature. The progress of the reaction was monitored by TLC. The reaction mixture diluted with ethyl acetate (15 mL) and filtered through a short pad of celite with an additional amount of ethyl acetate (15 mL). Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the desired homo-bis-*meta*-olefinated product **4a-e** in 60% to 70% yields, as viscous colourless/pale-yellow/brown liquid or solid.

Plausible catalytic cycle for the formation of mono-*meta* olefination product **3:**

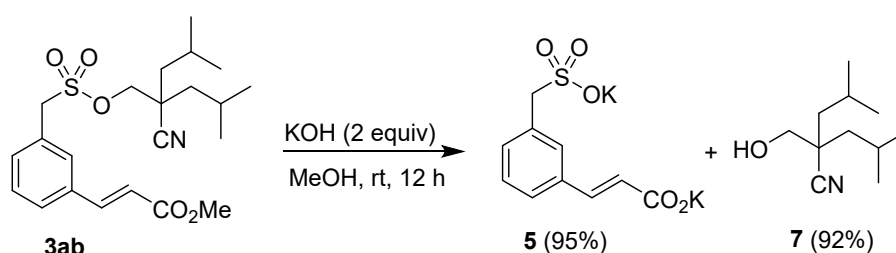
The plausible catalytic cycle for the coupling has been proposed based on the previous reports^{2,3} as described in Scheme S2. Essentially, the weak coordination of nitrile group with palladium leads the metal-center to the close vicinity of the *meta*-C–H bond and to facilitate to form 11 membered palladacycle **II** by cleaving the *meta*-C–H bond. Then olefin binding with Pd-centre of **II** takes place resulted in forming intermediate **III**. Subsequently, 1,2-migratory insertion leads to the formation of **IV** followed by β-hydride elimination occasioned the *meta*-olefination product **3**. Sequentially, the reductive elimination of acetate and hydrogen (as AcOH) from H-Pd-OAc, resulted in forming zero oxidation state palladium. The reoxidation of the Pd(0) to Pd (II) can be done by the silver(I) salt.



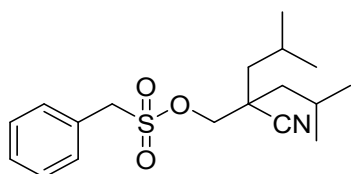
Scheme S2. Proposed mechanistic cycle.

Removal of the directing template:

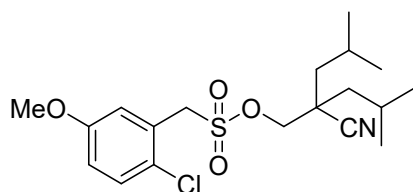
Thus, base hydrolysis of arylmethanesulfonate ester-derived olefin product **3ab** using potassium hydroxide in methanol at room temperature afforded the potassium salt product **5** in 95% yield along with 92% of recovery of nitrile alcohol template **7**, which has been reused further (Scheme S3).



Scheme S3. Removal of the directing template.

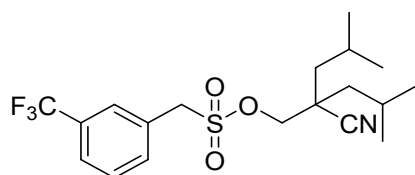


2-Cyano-2-isobutyl-4-methylpentyl phenylmethanesulfonate (1a): GP-2 was carried out with arylmethanesulfonyl chloride **6a** (114 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 95/5), furnished the product **1a** (186 mg, 92%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 95:5, $R_f(\mathbf{6a}) = 0.50$, $R_f(\mathbf{1a}) = 0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2959, 2355, 1741, 1461, 980, 653 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.32 (m, 5H), 4.45 (s, 2H), 3.96 (s, 2H), 1.76 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.51 – 1.38 (m, 4H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 130.7, 129.3, 129.0, 127.2, 121.2, 71.1, 57.2, 43.0 (2C), 39.3, 24.6 (2C), 23.8 (2C), 23.7 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{NH}_4)]^+$ Calcd for $\text{C}_{18}\text{H}_{31}\text{N}_2\text{O}_3\text{S}^+$ 355.2050; Found 355.2063.



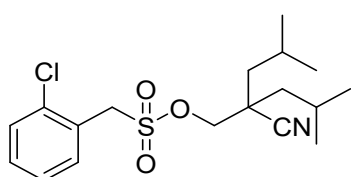
2-Cyano-2-isobutyl-4-methylpentyl (2-chloro-5-methoxyphenyl)methanesulfonate (1b): GP-2 was carried out with arylmethanesulfonyl chloride **6b** (153 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **1b** (214 mg, 89%) as a colourless solid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6b}) = 0.60$, $R_f(\mathbf{1b}) = 0.50$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2958, 2353, 1595, 1471, 1175, 754 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 8.9$ Hz, 1H), 7.09 (d, $J = 3.0$ Hz, 1H), 6.90 (dd, $J = 8.9, 3.0$ Hz, 1H), 4.63 (s, 2H), 4.12 (s, 2H), 3.82 (s, 3H), 1.79 (dd, $J = 13.1, 6.5$ Hz, 2H), 1.50 – 1.45 (m, 4H), 1.0 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 158.4, 130.6, 126.3, 126.2, 121.3, 117.6, 116.8, 70.5, 55.7,

53.9, 43.0 (2C), 39.2, 24.7 (2C), 23.8 (2C), 23.7 (2C) ppm. HRMS (ESI) m/z : $[(M+K)]^+$
Calcd for $C_{19}H_{28}ClKNO_4S^+$ 440.1059; Found 440.1075.



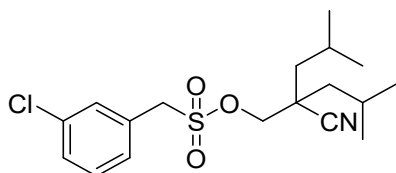
2-Cyano-2-isobutyl-4-methylpentyl (3-(trifluoromethyl)phenyl)methanesulfonate (1c):

GP-2 was carried out with arylmethanesulfonyl chloride **6c** (154 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 93/07), furnished the product **1c** (194 mg, 80%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6c}) = 0.60$, $R_f(\mathbf{1b}) = 0.50$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2961, 2239, 1460, 1329, 1128, 745 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.63 (m, 3H), 7.57 (t, $J = 7.7$ Hz, 1H), 4.51 (s, 2H), 4.07 (s, 2H), 1.77 (dp, $J = 13.0, 6.5$ Hz, 2H), 1.51 – 1.40 (m, 4H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H)ppm. ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 134.2, 131.6, 131.3, 129.6, 128.4, 127.4, 127.4, 126.1, 126.1, 124.9, 122.2, 121.2, 71.0, 56.5, 43.0 (2C), 39.4, 24.7 (2C), 23.7 (2C), 23.7 (2C) ppm. HRMS (ESI) m/z : $[(M+K)]^+$ Calcd for $C_{19}H_{26}F_3KNO_3S^+$ 444.1217; Found 444.1238.

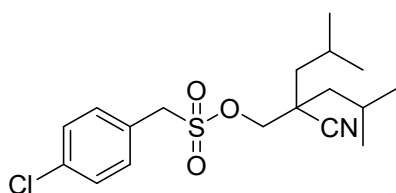


2-Cyano-2-isobutyl-4-methylpentyl (2-chlorophenyl)methanesulfonate (1d): GP-2 was carried out with arylmethanesulfonyl chloride **6d** (133 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **1d** (193 mg, 87%) as a colourless solid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6d}) = 0.70$, $R_f(\mathbf{1d}) = 0.60$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2959, 1461, 1331, 1170, 1130, 738 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, $J = 7.0, 2.3$ Hz, 1H), 7.47 (dd, $J = 7.5, 1.7$ Hz, 1H), 7.39 – 7.30 (m, 2H), 4.68 (s, 2H), 4.10 (s, 2H), 1.79 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.48 (d, J

= 6.3 Hz, 4H), 1.0 (d, $J = 6.6$ Hz, 6H), 0.95 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 135.0, 132.7, 130.7, 130.0, 127.3, 125.6, 121.1, 70.4, 53.7, 43.0 (2C), 39.2, 24.6 (2C), 23.8 (2C), 23.7 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{Na})]^+$ Calcd for $\text{C}_{18}\text{H}_{26}\text{ClNNaO}_3\text{S}^+$ 394.1214; Found 394.1206.

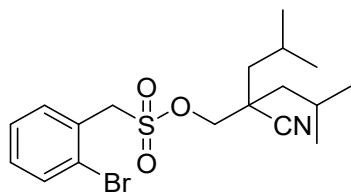


2-Cyano-2-isobutyl-4-methylpentyl (3-chlorophenyl)methanesulfonate (1e): GP-2 was carried out with arylmethanesulfonyl chloride **6e** (133 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **1e** (200 mg, 90%) as a colourless solid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6e}) = 0.70$, $R_f(\mathbf{1e}) = 0.60$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2958, 1467, 1358, 1209, 980, 740 cm^{-1} . ^1H NMR (600 MHz, CDCl_3) δ 7.45 (s, 1H), 7.39 (ddd, $J = 13.5, 6.6, 4.7$ Hz, 1H), 7.37 – 7.30 (m, 2H), 4.42 (s, 2H), 4.05 (s, 2H), 1.78 (dt, $J = 13.1, 6.5$ Hz, 2H), 1.52 – 1.41 (m, 4H), 1.01 (d, $J = 6.7$ Hz, 6H), 0.98 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 134.8, 130.7, 130.2, 129.5, 129.1, 129.0, 121.2, 71.0, 56.4, 43.0 (2C), 39.3, 24.7 (2C), 23.8 (2C), 23.8 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{H})]^+$ Calcd for $\text{C}_{18}\text{H}_{27}\text{ClNO}_3\text{S}^+$ 372.1395; Found 372.1395.

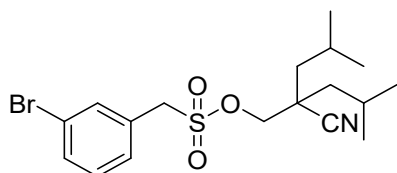


2-Cyano-2-isobutyl-4-methylpentyl (4-chlorophenyl)methanesulfonate (1f): GP-2 was carried out with arylmethanesulfonyl chloride **6f** (133 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **1f** (204 mg, 92%) as a colourless solid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6f}) = 0.70$, $R_f(\mathbf{1f}) =$

0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2956, 1464, 1360, 1169, 978, 750 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.40 (s, 4H), 4.42 (s, 2H), 4.02 (s, 2H), 1.77 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.46 (m, $J = 6.2, 4.5$ Hz, 4H), 1.0 (d, $J = 6.6$ Hz, 6H), 0.97 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 135.7, 132.2, 129.3, 125.8, 121.3, 71.3, 56.6, 43.2 (2C), 39.5, 24.8 (2C), 23.9 (2C), 23.9 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{H})]^+$ Calcd for $\text{C}_{18}\text{H}_{27}\text{ClNO}_3\text{S}^+$ 372.1395; Found 372.1401.

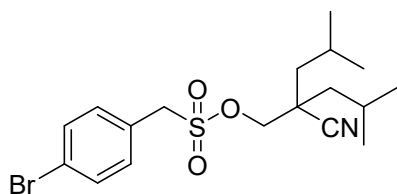


2-Cyano-2-isobutyl-4-methylpentyl (2-bromophenyl)methanesulfonate (1g): GP-2 was carried out with arylmethanesulfonyl chloride **6g** (269 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **1g** (202 mg, 81%) as a colourless solid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6g}) = 0.70$, $R_f(\mathbf{1g}) = 0.60$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2956, 1465, 1360, 1175, 981, 754 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.65 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.59 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.38 (td, $J = 7.6, 1.3$ Hz, 1H), 7.27 (ddd, $J = 7.7, 6.3, 1.7$ Hz, 1H), 4.72 (s, 2H), 4.10 (s, 2H), 1.78 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.48 (m, $J = 6.2$ Hz, 4H), 1.0 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 133.5, 132.8, 131.0, 128.1, 127.6, 125.6, 121.2, 70.6, 56.4, 43.0 (2C), 39.3, 24.0 (2C), 23.9 (2C), 23.8 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{H})]^+$ Calcd for $\text{C}_{18}\text{H}_{27}^{79}\text{BrNO}_3\text{S}^+$ 416.0890; Found 416.0895; Calcd for $\text{C}_{26}\text{H}_{23}^{81}\text{BrNO}_3\text{S}^+$ 418.0869; Found 418.0880.

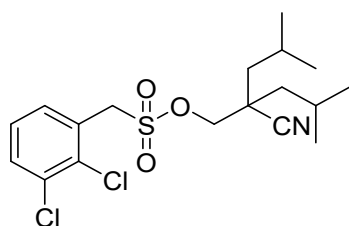


2-Cyano-2-isobutyl-4-methylpentyl (3-bromophenyl)methanesulfonate (1h): GP-2 was carried out with arylmethanesulfonyl chloride **6h** (269 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column

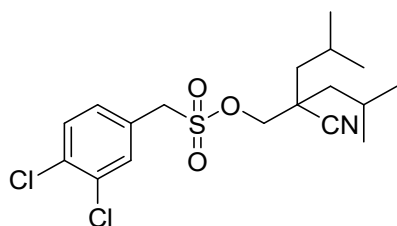
chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **1h** (199 mg, 80%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6h}) = 0.70$, $R_f(\mathbf{1h}) = 0.60$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2958, 1466, 1357, 1171, 979, 818, 688 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.60 (t, $J = 1.7$ Hz, 1H), 7.58 – 7.52 (m, 1H), 7.40 (d, $J = 7.9$ Hz, 1H), 7.30 (t, $J = 7.8$ Hz, 1H), 4.41 (s, 2H), 4.05 (s, 2H), 1.78 (dt, $J = 13.0$, 6.5 Hz, 2H), 1.52 – 1.41 (m, 4H), 1.01 (d, $J = 6.6$ Hz, 6H), 0.98 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 133.6, 132.5, 130.5, 129.4, 129.4, 122.9, 121.2, 71.1, 56.5, 43.1 (2C), 39.4, 24.8 (2C), 23.9 (2C), 23.8 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{H})]^+$ Calcd for $\text{C}_{18}\text{H}_{27}^{79}\text{BrNO}_3\text{S}^+$ 416.0890; Found 416.0896; Calcd for $\text{C}_{18}\text{H}_{27}^{81}\text{BrNO}_3\text{S}^+$ 418.0869; Found 418.0877.



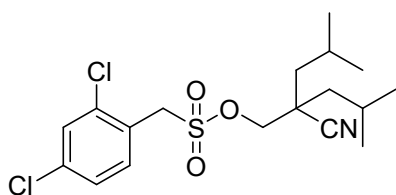
2-Cyano-2-isobutyl-4-methylpentyl (4-bromophenyl)methanesulfonate (1i): GP-2 was carried out with arylmethanesulfonyl chloride **6i** (269 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **1i** (207 mg, 83%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6i}) = 0.70$, $R_f(\mathbf{1i}) = 0.60$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2959, 1473, 1358, 979, 644 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 4.39 (s, 2H), 4.00 (s, 2H), 1.75 (dt, $J = 13.0$, 6.5 Hz, 2H), 1.52 – 1.37 (m, 4H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 132.3, 132.1, 126.2, 123.7, 121.2, 71.2, 56.4, 43.0 (2C), 39.3, 24.7 (2C), 23.8 (2C), 23.7 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{NH}_4)]^+$ Calcd for $\text{C}_{18}\text{H}_{30}^{79}\text{BrNO}_3\text{S}^+$ 433.1155; Found 433.1164; Calcd for $\text{C}_{18}\text{H}_{30}^{81}\text{BrN}_2\text{O}_3\text{S}^+$ 435.1135; Found 435.1143.



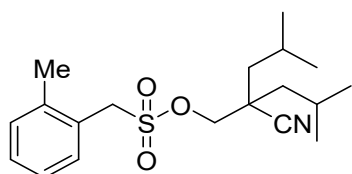
2-Cyano-2-isobutyl-4-methylpentyl (2,3-dichlorophenyl)methanesulfonate (1j): GP-2 was carried out with arylmethanesulfonyl chloride **6j** (154 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **1j** (190 mg, 78%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6j}) = 0.60$, $R_f(\mathbf{1j}) = 0.50$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2958, 1458, 1362, 1177, 980, 752 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.52 (ddd, $J = 13.3, 7.9, 1.5$ Hz, 2H), 7.29 (t, $J = 7.9$ Hz, 1H), 4.73 (s, 2H), 4.13 (s, 2H), 1.80 (dt, $J = 13.1, 6.5$ Hz, 2H), 1.48 (m, $J = 6.2, 2.7$ Hz, 4H), 1.01 (d, $J = 6.6$ Hz, 6H), 0.97 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 134.1, 133.7, 131.6, 130.9, 128.0, 127.7, 121.1, 70.7, 54.5, 43.1 (2C), 39.3, 24.8 (2C), 23.9 (2C), 23.8 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{NH}_4)]^+$ Calcd for $\text{C}_{18}\text{H}_{29}\text{Cl}_2\text{N}_2\text{O}_3\text{S}^+$ 423.1270; Found 423.1280.



2-Cyano-2-isobutyl-4-methylpentyl (3,4-dichlorophenyl)methanesulfonate (1k): GP-2 was carried out with arylmethanesulfonyl chloride **6k** (154 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **1k** (192 mg, 79%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6k}) = 0.60$, $R_f(\mathbf{1k}) = 0.50$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2958, 1563, 1360, 1173, 979, 821 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 2.1$ Hz, 1H), 7.51 (d, $J = 8.3$ Hz, 1H), 7.34 – 7.29 (m, 1H), 4.40 (s, 2H), 4.09 (s, 2H), 1.91 – 1.69 (m, 2H), 1.48 (t, $J = 6.0$ Hz, 4H), 1.01 (d, $J = 6.6$ Hz, 6H), 0.98 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 134.0, 133.3, 132.7, 132.6, 131.2, 131.0, 130.1, 130.0, 127.4, 121.3, 71.3, 56.0, 43.2 (2C), 39.5, 24.8 (2C), 23.9 (2C), 22.7 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{K})]^+$ Calcd for $\text{C}_{18}\text{H}_{25}\text{Cl}_2\text{KNO}_3\text{S}^+$ 444.0564; Found 444.0585.

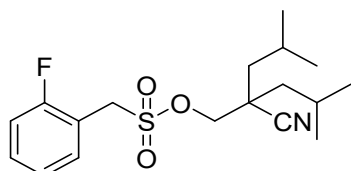


2-Cyano-2-isobutyl-4-methylpentyl (2,4-dichlorophenyl)methanesulfonate (11): GP-2 was carried out with arylmethanesulfonyl chloride **6l** (154 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **11** (211 mg, 87%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6l}) = 0.60$, $R_f(\mathbf{11}) = 0.50$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2958, 1468, 1359, 1170, 977, 825, 741 cm^{-1} . ^1H NMR (600 MHz, CDCl_3) δ 7.51 (d, $J = 8.3$ Hz, 1H), 7.48 (d, $J = 2.1$ Hz, 1H), 7.32 (dd, $J = 8.3, 2.1$ Hz, 1H), 4.63 (s, 2H), 4.12 (s, 2H), 1.79 (dt, $J = 13.1, 6.5$ Hz, 2H), 1.52 – 1.41 (m, 4H), 1.01 (d, $J = 6.7$ Hz, 6H), 0.97 (d, $J = 6.7$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 136.2, 135.8, 133.5, 129.8, 127.8, 124.3, 121.1, 70.6, 53.1, 43.0 (2C), 39.2, 24.7 (2C), 23.8 (2C), 23.7 (2C) ppm. HRMS (ESI) m/z : $[(M)]^+$ Calcd for $\text{C}_{18}\text{H}_{25}\text{Cl}_2\text{NO}_3\text{S}^+$ 405.0932; Found 405.0936.

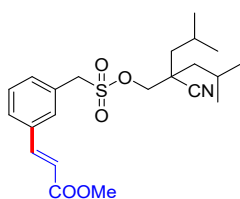


2-cyano-2-isobutyl-4-methylpentyl *o*-tolylmethanesulfonate (1m): GP-2 was carried out with arylmethanesulfonyl chloride **6m** (122 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **1m** (170 mg, 81%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6m}) = 0.60$, $R_f(\mathbf{1m}) = 0.50$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2958, 2036, 1361, 1172, 984, 821, 738 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, $J = 7.9$ Hz, 1H), 7.25 – 7.22 (m, 1H), 7.19 (d, $J = 8.4$ Hz, 2H), 4.45 (s, 2H), 3.91 (s, 2H), 2.41 (s, 3H), 1.71 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.42 – 1.37 (m, 4H), 0.94 (d, $J = 6.6$ Hz, 6H), 0.91 (d, $J = 6.6$ Hz, 6H). ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 138.3, 131.9, 131.1, 129.6, 126.5, 125.7, 121.3, 71.0, 54.7, 43.1 (2C),

39.4, 24.8 (2C), 23.9 (2C), 23.8 (2C), 19.7. HRMS (ESI) m/z : $[(M+NH_4)]^+$ Calcd for $C_{19}H_{33}N_2O_3S^+$ 369.2206; Found 369.2207.

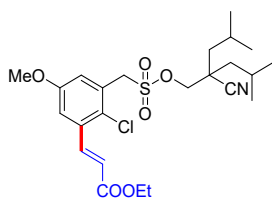


2-cyano-2-isobutyl-4-methylpentyl (2-fluorophenyl)methanesulfonate (1n): GP-2 was carried out with arylmethanesulfonyl chloride **6n** (124 mg, 0.6 mmol), triethyl amine (90 mg, 0.9 mmol), nitrile alcohol (110 mg, 0.6 mmol) in dichloromethane (DCM) (15 mL) solvent at room temperature for 4 h. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/10), furnished the product **1n** (166 mg, 78%) as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{6n}) = 0.60$, $R_f(\mathbf{1n}) = 0.50$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2958, 2036, 1361, 1172, 984, 821, 738 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.49 (td, $J = 7.5, 1.6$ Hz, 1H), 7.40 (d, $J = 12.1$ Hz, 1H), 7.20 (dd, $J = 11.0, 4.2$ Hz, 1H), 7.13 (t, $J = 9.1$ Hz, 1H), 4.51 (s, 2H), 4.10 (s, 2H), 1.89 – 1.67 (m, 2H), 1.47 (dd, $J = 6.2, 1.1$ Hz, 4H), 1.00 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H). ^{13}C { 1H } NMR (101 MHz, $CDCl_3$) δ 161.0 (d, $J_{C-F} = 249.9$ Hz), 132.6 (d, $J_{C-F} = 2.4$ Hz), 131.4 (d, $J_{C-F} = 8.4$ Hz), 124.7 (d, $J_{C-F} = 3.8$ Hz), 121.0, 115.8 (d, $J_{C-F} = 21.5$ Hz), 114.9 (d, $J_{C-F} = 14.5$ Hz), 70.6, 49.8 (d, $J_{C-F} = 3.4$ Hz), 42.9 (2C), 39.2, 24.6 (2C), 23.8 (2C), 23.7 (2C). HRMS (ESI) m/z : $[(M+NH_4)]^+$ Calcd for $C_{18}H_{30}FN_2O_3S^+$ 373.1956; Found 373.1960.

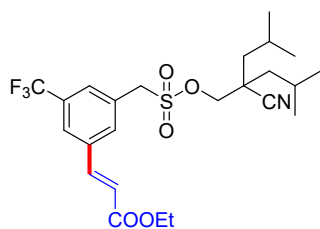


Methyl (E)-3-(3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ab): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2b** (26 mg, 0.3 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 $^\circ C$ for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate,

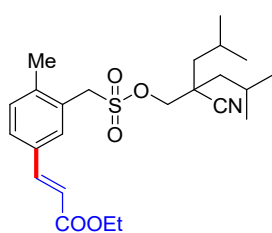
100/0 to 90/15), furnished the product **3ab** (70 mg, 83%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1a}) = 0.60$, $R_f(\mathbf{3ab}) = 0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2918, 2856, 1717, 1457, 754 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 16.1$ Hz, 1H), 7.62 – 7.53 (m, 2H), 7.50 – 7.40 (m, 2H), 6.48 (d, $J = 16.1$ Hz, 1H), 4.46 (s, 2H), 4.02 (s, 2H), 3.81 (s, 3H), 1.75 (td, $J = 13.0, 6.5$ Hz, 2H), 1.50 – 1.39 (m, 4H), 0.98 (d, $J = 6.6$ Hz, 6H), 0.95 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 167.0, 143.5, 135.3, 132.4, 130.2, 129.6, 128.7, 128.2, 121.2, 119.2, 71.2, 56.9, 51.8, 43.1 (2C), 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C) ppm. HRMS (ESI) m/z : $[(M+K)]^+$ Calcd for $\text{C}_{22}\text{H}_{31}\text{KNO}_5\text{S}^+$ 460.1555; Found 460.1551.



Ethyl (E)-3-(2-chloro-3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)-5-methoxyphenyl)acrylate (3ba): GP-3 was carried out by using arylmethanesulfonate ester **1b** (80 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ba** (71 mg, 71%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1b}) = 0.60$, $R_f(\mathbf{3ba}) = 0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2958, 1714, 1456, 1174, 980 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 15.9$ Hz, 1H), 7.26 (s, 1H), 7.15 (dd, $J = 10.1, 3.0$ Hz, 2H), 6.39 (d, $J = 15.9$ Hz, 1H), 4.69 (s, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 4.14 (s, 2H), 3.85 (s, 3H), 1.79 (dt, $J = 13.1, 6.5$ Hz, 2H), 1.48 (dd, $J = 6.2, 2.1$ Hz, 4H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.0 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.1, 158.0, 140.3, 135.0, 127.7, 126.9, 122.3, 121.1, 119.6, 114.0, 70.6, 60.9, 55.8, 54.2, 43.1 (2C), 39.3, 24.8 (2C), 23.8 (2C), 23.8 (2C), 14.3 ppm. HRMS (ESI) m/z : $[(M+K)]^+$ Calcd for $\text{C}_{24}\text{H}_{34}\text{ClKNO}_6\text{S}^+$ 538.1427; Found 538.1447.

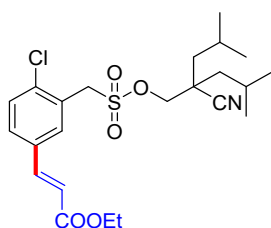


Ethyl (E)-3-(3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)-5-(trifluoromethyl)phenyl)acrylate (3ca): GP-3 was carried out by using arylmethanesulfonate ester **1c** (81 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ca** (75 mg, 75%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1c**) = 0.60, *R_f*(**3ca**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2962, 1712, 1358, 1169, 1134, 979, 821 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 7.1 Hz, 2H), 7.73 – 7.63 (m, 2H), 6.55 (d, *J* = 16.1 Hz, 1H), 4.52 (s, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.12 (s, 2H), 1.77 (dq, *J* = 13.0, 6.5 Hz, 2H), 1.52 – 1.42 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.0 (d, *J* = 6.6 Hz, 6H), 0.97 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 166.0, 141.5, 136.4, 133.3, 132.3 (d, *J*_{C-F} = 33 Hz), 129.4, 128.5 (d, *J*_{C-F} = 33 Hz), 125.2 (d, *J*_{C-F} = 3 Hz), 123.2 (d, *J*_{C-P} = 271 Hz), 121.6, 121.2, 71.2, 60.9, 56.4, 43.1 (2C), 39.5, 24.8 (2C), 23.8 (2C), 23.8 (2C), 14.2 ppm. HRMS (ESI) *m/z*: [(M+H)]⁺ Calcd for C₂₄H₃₃F₃NO₅S⁺ 504.2026; Found 504.2050.

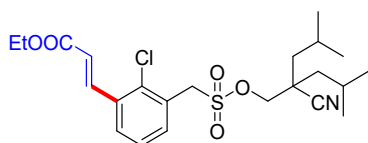


Ethyl (E)-3-(3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)-4-methylphenyl)acrylate (3ma): GP-3 was carried out by using arylmethanesulfonate ester **1m** (70 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ma** (68 mg, 76%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1m**) = 0.60, *R_f*(**3ma**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2948, 2252,

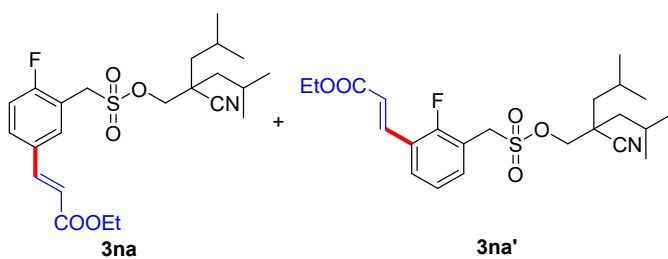
1711, 1267, 1171, 985, 732 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 16.0$ Hz, 1H), 7.54 (d, $J = 1.6$ Hz, 1H), 7.46 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 1H), 6.43 (d, $J = 16.0$ Hz, 1H), 4.51 (s, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 2.48 (s, 3H), 1.77 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.45 (dd, $J = 6.2, 4.3$ Hz, 4H), 1.32 (t, $J = 7.1$ Hz, 3H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.7, 143.2, 140.6, 132.9, 131.7, 131.4, 128.7, 126.5, 121.2, 118.6, 70.9, 60.5, 54.4, 43.1 (2C), 39.4, 24.7 (2C), 23.82 (2C), 23.77 (2C), 19.7, 14.2. HRMS (ESI) m/z : $[(\text{M}+\text{H})]^+$ Calcd for $\text{C}_{24}\text{H}_{36}\text{NO}_5\text{S}^+$ 449.2236; Found 450.2311.



Ethyl (E)-3-(4-chloro-3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3da): GP-3 was carried out by using arylmethanesulfonate ester **1d** (74 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3da** (73 mg, 78%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1d}) = 0.60$, $R_f(\mathbf{3da}) = 0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2958, 2237, 1711, 1360, 1171, 978, 819 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 1.6$ Hz, 1H), 7.63 (d, $J = 16.0$ Hz, 1H), 7.53 – 7.46 (m, 2H), 6.46 (d, $J = 16.1$ Hz, 1H), 1.79 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.48 (dd, $J = 6.2, 2.1$ Hz, 4H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.0 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{Na})]^+$ Calcd for $\text{C}_{23}\text{H}_{32}\text{ClNNaO}_5\text{S}^+$ 492.1582; Found 492.1593.

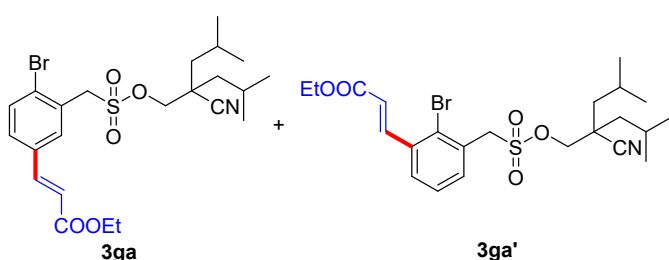


Ethyl (E)-3-(2-chloro-3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3da'): GP-3 was carried out by using arylmethanesulfonate ester **1d** (74 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3da'** (73 mg, 78%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1d**) = 0.60, *R_f*(**3da'**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2959, 2245, 1712, 1365, 1176, 982 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 16.0 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.61 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 4.74 (s, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.13 (s, 2H), 1.79 (dt, *J* = 13.1, 6.5 Hz, 2H), 1.48 (dd, *J* = 6.2, 2.0 Hz, 4H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.0 (d, *J* = 6.6 Hz, 6H), 0.96 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 166.1, 140.1, 135.4, 134.4, 133.9, 128.7, 127.3, 127.0, 122.3, 121.1, 70.5, 60.8, 54.1, 43.1 (2C), 39.4, 24.7 (2C), 23.9 (2C), 23.8 (2C), 14.2 ppm. HRMS (ESI) *m/z*: [(M+K)]⁺ Calcd for C₂₃H₃₂ClKNO₅S⁺ 508.1321; Found 508.1337.



Ethyl (E)-3-(3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)-4-fluorophenyl)acrylate (3na) & Ethyl (E)-3-(3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)-2-fluorophenyl)acrylate (3na'): GP-3 was carried out by using arylmethanesulfonate ester **1n** (71 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the isomeric mixture of products **3na+3na'** (62 mg, 69%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1n**) = 0.60,

$R_f(\mathbf{3na}+\mathbf{3na}') = 0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2923, 1714, 1461, 1175, 1034, 984, 817 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 16.2$ Hz, 1H), 7.67 – 7.49 (m, 2H), 7.36 – 7.07 (m, 1H), 6.89 – 6.23 (m, 1H), 4.52 (d, $J = 8.7$ Hz, 2H), 4.32 – 4.21 (m, 2H), 4.14 (d, $J = 2.7$ Hz, 2H), 1.85 – 1.74 (m, 2H), 1.47 (dd, $J = 6.2, 2.4$ Hz, 4H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.00 (dd, $J = 6.6, 1.2$ Hz, 6H), 0.98 – 0.95 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.3, 164.6, 160.7, 142.1, 136.0, 136.0, 134.0, 134.0, 132.2, 132.2, 130.9, 130.8, 130.2, 124.8, 123.2, 121.9, 121.0, 119.4, 116.7, 116.5, 116.1, 115.9, 70.7, 60.7, 60.6, 49.8, 43.0, 39.3, 24.7, 23.8, 23.7, 14.2. HRMS (ESI) m/z : $[(M+H)]^+$ Calcd for $\text{C}_{23}\text{H}_{33}\text{FNO}_5\text{S}^+$ 454.2058 ; Found 454.2064.



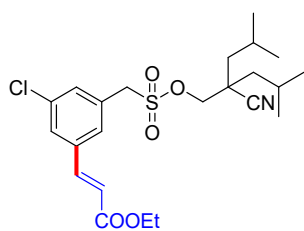
Ethyl

(E)-3-(4-bromo-3-(((2-cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ga) & Ethyl (E)-3-(2-bromo-3-(((2-

cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ga')

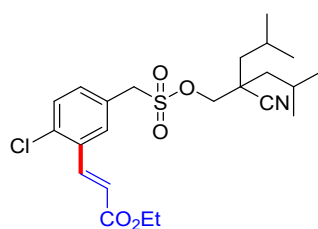
GP-3 was carried out by using arylmethanesulfonate ester **1g** (83 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the isomeric mixture of products **3ga+3ga'** (72 mg, 71%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1g}) = 0.60$, $R_f(\mathbf{3ga}+\mathbf{3ga}') = 0.40$, UV detection]. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 15.9$ Hz, 1H), 7.73 – 7.55 (m, 3H), 7.40 (dd, $J = 8.2, 2.5$ Hz, 1H), 6.35 (d, $J = 15.8$ Hz, 1H), 4.75 (d, $J = 33.3$ Hz, 3H), 4.35 – 4.19 (m, 3H), 4.12 (d, $J = 7.1$ Hz, 3H), 1.78 (ddd, $J = 15.3, 7.7, 5.4$ Hz, 4H), 1.47 (dd, $J = 6.2, 1.2$ Hz, 6H), 1.33 (dd, $J = 10.1, 4.1$ Hz, 6H), 1.02 – 0.92 (m, 17H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.3, 166.0, 143.1, 142.0, 136.6, 134.6, 134.0, 133.7, 132.0, 129.6, 128.9, 128.9, 128.3, 128.0, 127.9, 127.0, 123.3, 122.4, 121.1, 120.3, 70.6, 70.5, 66.4, 60.8, 60.7, 56.8, 56.1, 43.0, 42.9, 39.3, 24.8, 24.7, 24.0, 24.0, 23.8, 23.7, 14.2 ppm. HRMS (ESI) m/z : $[(M+\text{Na})]^+$ Calcd for $\text{C}_{23}\text{H}_{32}^{79}\text{BrNaNO}_5\text{S}^+$ 536.1077; Found 536.1061: Calcd for $\text{C}_{23}\text{H}_{32}^{81}\text{BrNNaO}_5\text{S}^+$ 538.1056; Found 536.1057.



Ethyl

(E)-3-(3-chloro-5-(((2-cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ea): GP-3 was carried out by using arylmethanesulfonate ester **1e** (74 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ea** (77 mg, 82%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1e**) = 0.60, *R_f*(**3ea**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2961, 1710, 1360, 978, 853 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 16.0 Hz, 1H), 7.55 (t, *J* = 1.5 Hz, 1H), 7.46 (dd, *J* = 6.9, 5.2 Hz, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.43 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 2H), 1.78 (dt, *J* = 13.1, 6.5 Hz, 2H), 1.52 – 1.44 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.0 (d, *J* = 6.6 Hz, 6H), 0.98 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 166.2, 141.7, 137.0, 135.5, 131.9, 129.8, 128.5, 128.5, 121.2, 121.1, 71.2, 60.8, 56.3, 43.1 (2C), 39.5, 24.8 (2C), 23.8 (2C), 23.8 (2C), 14.2 ppm. HRMS (ESI) *m/z*: [(M+H)]⁺ Calcd for C₂₃H₃₃ClNO₅S⁺ 470.1762; Found 470.1774.

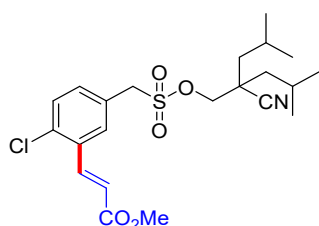


Ethyl

(E)-3-(2-chloro-5-(((2-cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3fa): GP-3 was carried out by using arylmethanesulfonate ester **1f** (74 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3fa** (73 mg, 78%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1d**) = 0.60, *R_f*(**3fa**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2956, 1715, 1365, 1176, 980, 754 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ

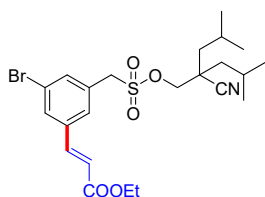
8.05 (d, $J = 16.1$ Hz, 1H), 7.70 (d, $J = 2.1$ Hz, 1H), 7.48 (d, $J = 8.3$ Hz, 1H), 7.46 – 7.35 (m, 1H), 6.50 (d, $J = 16.0$ Hz, 1H), 4.44 (s, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 4.08 (s, 2H), 1.77 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.47 (t, $J = 6.0$ Hz, 4H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.0 (d, $J = 6.6$ Hz, 6H), 0.97 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.2, 139.2, 136.0, 133.6, 133.0, 130.9, 129.9, 126.6, 122.2, 121.3, 71.3, 60.8, 56.4, 43.2 (2C), 39.5, 24.8 (2C), 23.9 (2C), 23.8 (2C), 14.3 ppm. HRMS (ESI) m/z : $[(\text{M}+\text{K})]^+$ Calcd for $\text{C}_{23}\text{H}_{32}\text{ClKNO}_5\text{S}^+$ 508.1321; Found 508.1342.



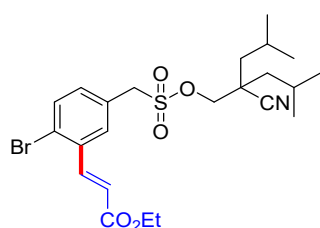
Methyl

(*E*)-3-(2-chloro-5-(((2-cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3fb**):** GP-3 was carried out by using arylmethanesulfonate ester **1f** (74 mg, 0.2 mmol), olefin **2b** (26 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3fb** (73 mg, 80%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1f}) = 0.60$, $R_f(\mathbf{3fb}) = 0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2956, 1717, 1361, 1175, 978, 754 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 16.1$ Hz, 1H), 7.63 (d, $J = 2.1$ Hz, 1H), 7.42 (d, $J = 8.3$ Hz, 1H), 7.35 (dd, $J = 8.3, 2.2$ Hz, 1H), 6.42 (t, $J = 13.0$ Hz, 1H), 4.38 (s, 2H), 4.00 (s, 2H), 3.76 (s, 3H), 1.70 (dt, $J = 13.1, 6.5$ Hz, 2H), 1.40 (t, $J = 6.1$ Hz, 4H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.6, 139.5, 136.1, 133.5, 133.0, 130.9, 129.9, 126.6, 125.7, 121.8, 121.3, 71.4, 56.4, 52.0, 43.2 (2C), 39.6, 29.7, 24.8 (2C), 23.9 (2C), 23.9 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{Na})]^+$ Calcd for $\text{C}_{22}\text{H}_{30}\text{ClNaO}_5\text{S}^+$ 478.1425; Found 478.1411.

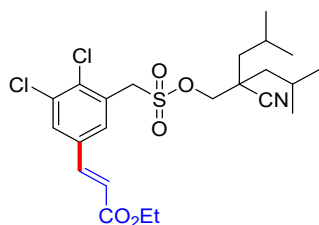


Ethyl **(E)-3-(3-bromo-5-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ha)**: GP-3 was carried out by using arylmethanesulfonate ester **1h** (83 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ha** (81 mg, 79%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1h**) = 0.60, *R_f*(**3ha**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2961, 1710, 1360, 1172, 734 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 1H), 7.61 – 7.55 (m, 2H), 7.52 (s, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.42 (s, 2H), 4.29 – 4.23 (m, 2H), 4.09 (d, *J* = 3.6 Hz, 2H), 1.77 (dd, *J* = 13.1, 6.5 Hz, 2H), 1.48 – 1.44 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.0 (d, *J* = 6.6 Hz, 6H), 0.97 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 166.1, 141.6, 137.2, 134.7, 131.4, 130.0, 129.0, 123.3, 121.2, 121.0, 71.2, 60.8, 56.2, 43.1 (2C), 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C), 14.2 ppm. HRMS (ESI) *m/z*: [(M+K)⁺ Calcd for C₂₃H₃₂⁷⁹BrKNO₅S⁺ 552.0816; Found 552.0817; Calcd for C₂₃H₃₂⁸¹BrKNO₅S⁺ 554.0796; Found 554.0800.



Ethyl **(E)-3-(2-bromo-5-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ia)**: GP-3 was carried out by using arylmethanesulfonate ester **1i** (83 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ia** (81 mg, 79%), as a pale yellow solid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1i**) = 0.60, *R_f*(**3ia**) = 0.40, UV detection]. Melting

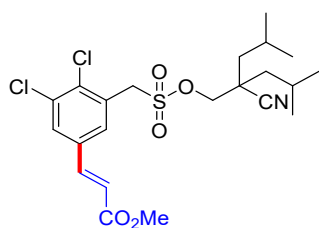
point: 72-74 °C. IR (MIR-ATR, 4000–600 cm⁻¹): 2960, 1710, 1359, 1172, 977, 827 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 16.0 Hz, 1H), 7.66 (dd, *J* = 5.2, 3.0 Hz, 2H), 7.32 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 4.42 (s, 2H), 4.27 (t, *J* = 7.1 Hz, 2H), 4.06 (s, 2H), 1.76 (dt, *J* = 13.0, 6.5 Hz, 2H), 1.47 (dd, *J* = 13.1, 7.1 Hz, 4H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 6H), 0.96 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 166.0, 141.7, 135.4, 134.1, 133.0, 129.9, 127.2, 126.3, 122.3, 121.3, 71.3, 60.8, 56.3, 43.1 (2C), 39.5, 24.8 (2C), 23.8 (2C), 23.8 (2C), 14.2 ppm. HRMS (ESI) *m/z*: [(M+H)]⁺ Calcd for C₂₃H₃₃⁷⁹BrNO₅S⁺ 514.1257; Found 514.1261; Calcd for C₂₃H₃₃⁸¹BrNO₅S⁺ 516.1237; Found 516.1247.



Ethyl

(*E*)-3-(3,4-dichloro-5-(((2-cyano-2-isobutyl-4-

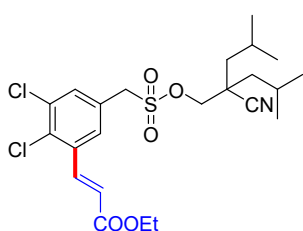
methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ja): GP-3 was carried out by using arylmethanesulfonate ester **1j** (81 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ja** (77 mg, 76%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1j**) = 0.60, *R_f*(**3ja**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2956, 1721, 1362, 1177, 980, 754 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 16.0 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.73 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.17 (s, 2H), 1.79 (td, *J* = 13.0, 6.5 Hz, 2H), 1.49 (dd, *J* = 6.2, 3.8 Hz, 4H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 6H), 0.98 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 166.0, 140.8, 134.9, 134.8, 134.5, 130.2, 130.1, 128.6, 121.5, 121.1, 70.7, 60.9, 54.4, 43.1 (2C), 39.4, 24.8 (2C), 23.9 (2C), 23.8 (2C), 14.3 ppm. HRMS (ESI) *m/z*: [(M+H)]⁺ Calcd for C₂₃H₃₂Cl₂NO₅S⁺ 504.1373; Found 504.1358.



Methyl

(*E*)-3-(3,4-dichloro-5-(((2-cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3jb): GP-3 was carried out by using arylmethanesulfonate ester **1j** (81 mg, 0.2 mmol), olefin **2b** (26 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3jb** (78 mg, 77%), as a colourless crystallin solid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1j**) = 0.60, *R_f*(**3jb**) = 0.40, UV detection]. Melting point: 95-97 °C. IR (MIR-ATR, 4000–600 cm⁻¹): 2924, 1716, 1456, 1266, 1175, 751 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.51 (d, *J* = 16.0 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.66 (s, 2H), 4.10 (s, 2H), 3.75 (s, 3H), 1.73 (dt, *J* = 13.1, 6.5 Hz, 2H), 1.42 (dd, *J* = 6.2, 3.9 Hz, 4H), 1.01 (d, *J* = 6.6 Hz, 6H), 0.97 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 166.5, 141.1, 135.0, 134.8, 134.4, 130.2, 130.1, 128.6, 121.1, 121.0, 70.8, 54.4, 52.1, 43.1 (2C), 39.4, 24.8 (2C), 23.9 (2C), 23.8 (2C) ppm. HRMS (ESI) *m/z*: [(M+H)]⁺ Calcd for C₂₂H₃₀Cl₂NO₅S⁺ 490.1216; Found 490.1211.

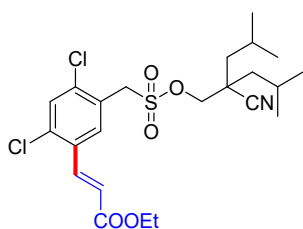


Ethyl

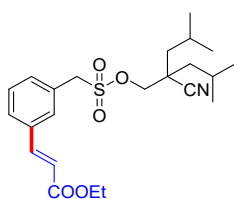
(*E*)-3-(2,3-dichloro-5-(((2-cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ka): GP-3 was carried out by using arylmethanesulfonate ester **1k** (81 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ka** (72 mg, 72%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1k**) = 0.60, *R_f*(**3ka**) = 0.40, UV detection]. IR (MIR-

ATR, 4000–600 cm^{-1}): 2957, 1714, 1464, 1176, 981, 755 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 16.0$ Hz, 1H), 7.27 (s, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 4.42 (s, 2H), 4.29 (d, $J = 7.1$ Hz, 2H), 4.14 (s, 2H), 1.78 (dd, $J = 13.1, 6.5$ Hz, 2H), 1.49 (t, $J = 6.5$ Hz, 4H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.01 (d, $J = 6.6$ Hz, 6H), 0.98 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 139.4, 135.8, 134.7, 134.2, 133.2, 128.1, 127.4, 123.5, 121.4, 71.5, 61.1, 56.0, 43.3 (2C), 39.7, 24.9 (2C), 23.9 (4C), 14.4 ppm. HRMS (ESI) m/z : $[(M+K)]^+$ Calcd for $\text{C}_{23}\text{H}_{31}\text{Cl}_2\text{KNO}_5\text{S}^+$ 542.0932; Found 542.0949.



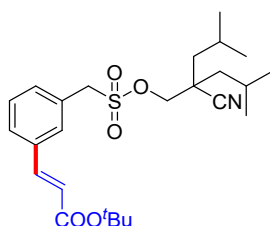
Ethyl (E)-3-(2,4-dichloro-5-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (31a): GP-3 was carried out by using arylmethanesulfonate ester **11** (81 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 $^\circ\text{C}$ for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **31a** (75 mg, 74%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{11}) = 0.60$, $R_f(\mathbf{31a}) = 0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2959, 1714, 1465, 1365, 1176, 979, 754 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 16.0$ Hz, 1H), 7.80 (s, 1H), 7.57 (s, 1H), 6.49 (d, $J = 16.0$ Hz, 1H), 4.64 (s, 2H), 4.31 – 4.25 (m, 2H), 4.17 (s, 2H), 1.83 – 1.77 (m, 2H), 1.49 (dd, $J = 6.2, 3.3$ Hz, 4H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.01 (d, $J = 6.6$ Hz, 6H), 0.97 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 165.9, 138.1, 136.6, 136.3, 132.4, 131.2, 131.2, 125.1, 122.7, 121.1, 70.8, 60.9, 53.1, 43.1 (2C), 39.4, 24.8 (2C), 23.8 (2C), 23.8 (2C), 14.2 ppm. HRMS (ESI) m/z : $[(M+H)]^+$ Calcd for $\text{C}_{23}\text{H}_{32}\text{Cl}_2\text{NO}_5\text{S}^+$ 504.1373; Found 504.1380.



Ethyl

(E)-3-(3-(((2-cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonylmethyl)phenyl)acrylate (3aa): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2a** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3aa** (70 mg, 81%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3aa**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2958, 1693, 1635, 1357, 1169, 979, 752 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 16.1 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.50 – 7.39 (m, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.46 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 2H), 1.76 (dp, *J* = 13.0, 6.5 Hz, 2H), 1.52 – 1.39 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 6H), 0.96 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 166.6, 143.2, 135.4, 132.3, 130.2, 129.6, 128.7, 128.1, 121.2, 119.6, 71.1, 60.6, 56.9, 43.1 (2C), 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C), 14.2 ppm. HRMS (ESI) *m/z*: [(M+K)]⁺ Calcd for C₂₃H₃₃KNO₅S⁺ 474.1711; Found 474.1721.

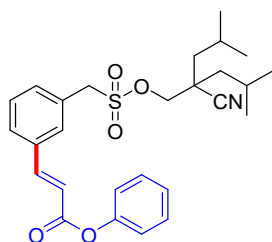


tert-Butyl

(E)-3-(3-(((2-cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonylmethyl)phenyl)acrylate (3ac): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2c** (38 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ac** (69 mg, 75%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3ac**) = 0.45, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2960, 1705, 1391, 1150, 983, 822 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.61 – 7.51 (m, 3H), 7.47 – 7.39 (m, 3H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.45 (s, 2H), 4.02 (s, 2H), 1.78 – 1.73 (m, 2H), 1.53 (s, 9H), 1.47 – 1.44 (m, 4H), 0.99 (d, *J* = 6.6 Hz, 6H), 0.96 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 165.9, 142.1, 135.6, 132.1, 130.8, 130.1, 129.6, 128.7, 128.1, 121.6, 80.8, 71.2, 57.0, 43.1 (2C), 39.4, 28.1 (3C), 24.8 (2C), 23.9

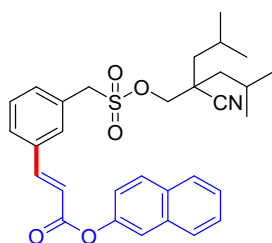
(2C), 23.8 (2C) ppm. HRMS (ESI) m/z: [(M+K)]⁺ Calcd for C₂₅H₃₇KNO₅S⁺ 502.2024; Found 502.2043.



Phenyl

(E)-3-(3-(((2-cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ad): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2d** (44 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ad** (70 mg, 72%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3ad**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2958, 1728, 1358, 1137, 979, 748 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 16.0 Hz, 1H), 7.66 (dd, *J* = 13.3, 3.6 Hz, 2H), 7.60 – 7.45 (m, 2H), 7.41 (dd, *J* = 8.3, 7.6 Hz, 2H), 7.26 (tt, *J* = 8.5, 1.1 Hz, 1H), 7.22 – 7.13 (m, 2H), 6.69 (d, *J* = 16.0 Hz, 1H), 4.49 (s, 2H), 4.05 (s, 2H), 1.78 (dt, *J* = 13.1, 6.5 Hz, 2H), 1.47 (dd, *J* = 6.2, 3.5 Hz, 4H), 1.0 (d, *J* = 6.6 Hz, 6H), 0.97 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 165.1, 150.7, 145.2, 135.1, 132.8, 130.5, 129.8, 129.5 (2C), 129.0, 128.4, 126.0, 121.6 (2C), 121.4, 118.7, 71.3, 56.9, 43.2 (2C), 39.5, 24.8 (2C), 23.9 (2C), 23.9 (2C) ppm. HRMS (ESI) m/z: [(M+K)]⁺ Calcd for C₂₇H₃₃KNO₅S⁺ 522.1711; Found 522.1718.

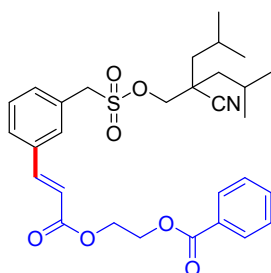


Naphthalen-2-yl

(E)-3-(3-(((2-cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ae): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2e** (59 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and

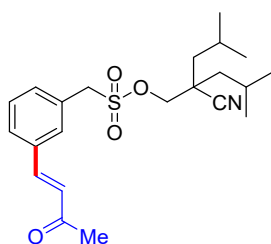
hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ae** (75 mg, 70%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1a}) = 0.60$, $R_f(\mathbf{3ae}) = 0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2926, 1732, 1363, 1137, 982, 759 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 16.0$ Hz, 1H), 7.89 (d, $J = 9.4$ Hz, 2H), 7.78 (d, $J = 8.3$ Hz, 1H), 7.73 (s, 1H), 7.68 (s, 1H), 7.55 – 7.48 (m, 5H), 7.33 (dd, $J = 7.5, 0.9$ Hz, 1H), 6.86 (d, $J = 16.0$ Hz, 1H), 4.51 (s, 2H), 4.07 (s, 2H), 1.79 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.48 (dd, $J = 6.2, 3.4$ Hz, 4H), 1.01 (d, $J = 6.6$ Hz, 6H), 0.98 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 165.2, 146.6, 145.6, 135.1, 134.7, 133.0, 130.6, 129.8, 129.1, 128.4, 128.1, 126.9, 126.6, 126.1, 125.6, 121.4, 121.3, 118.5, 118.1, 71.3, 56.9, 43.1 (2C), 39.5, 24.8 (2C), 23.9 (2C), 23.9 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{K})]^+$ Calcd for $\text{C}_{31}\text{H}_{35}\text{KNO}_5\text{S}^+$ 572.1868; Found 572.1873.



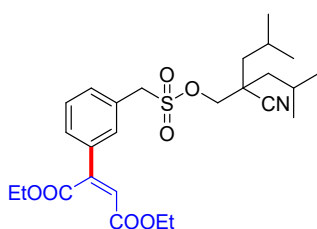
(E)-2-((3-(3-(((2-Cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonyl)methyl)phenyl)acryloyl)oxy)ethyl benzoate (3af**):** GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2f** (66 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3af** (81 mg, 73%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1a}) = 0.60$, $R_f(\mathbf{3af}) = 0.30$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2961, 1716, 1312, 1169, 981, 729 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.09 – 8.02 (m, 2H), 7.71 (d, $J = 16.1$ Hz, 1H), 7.59 (s, 1H), 7.58 – 7.53 (m, 2H), 7.49 – 7.41 (m, 4H), 6.51 (d, $J = 16.0$ Hz, 1H), 4.57 (dq, $J = 7.7, 4.0, 1.6$ Hz, 4H), 4.45 (s, 2H), 4.02 (s, 2H), 1.74 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.48 – 1.39 (m, 4H), 0.97 (d, $J = 6.6$ Hz, 6H), 0.94 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 166.4, 166.4, 144.2, 135.2, 133.2, 132.6, 130.3, 129.8, 129.8, 129.7 (2C), 128.9, 128.4, 128.3

(2C), 121.3, 119.0, 71.2, 62.8, 62.4, 56.9, 43.1 (2C), 39.4, 24.8 (2C), 23.9 (2C), 23.8 (2C) ppm. HRMS (ESI) m/z: [(M+NH₄)⁺] Calcd for C₃₀H₄₁N₂O₇S⁺ 573.2629; Found 573.2646.

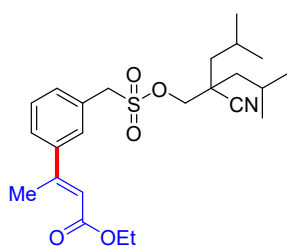


2-Cyano-2-isobutyl-4-methylpentyl (E)-(3-(3-oxobut-1-en-1-yl)phenyl)methanesulfonate (3ag): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2g** (21 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ag** (64 mg, 79%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3ag**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2922, 1671, 1614, 1357, 1172, 979, 818, 696 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.60 (dt, *J* = 6.8, 1.8 Hz, 1H), 7.52 (d, *J* = 16.4 Hz, 1H), 7.47 (dd, *J* = 12.0, 4.6 Hz, 2H), 6.76 (d, *J* = 16.3 Hz, 1H), 4.48 (s, 2H), 4.02 (s, 2H), 2.39 (s, 3H), 1.76 (dt, *J* = 13.0, 6.5 Hz, 2H), 1.50 – 1.41 (m, 4H), 0.99 (d, *J* = 6.6 Hz, 6H), 0.96 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 198.1, 142.0, 135.4, 132.6, 130.6, 129.7, 128.8, 128.2, 128.1, 121.3, 71.3, 56.9, 43.1 (2C), 39.4, 27.6, 24.7 (2C), 23.8 (2C), 23.8 (2C) ppm. HRMS (ESI) m/z: [(M+K)⁺] Calcd for C₂₂H₃₁KNO₄S⁺ 444.1605; Found 444.1633.

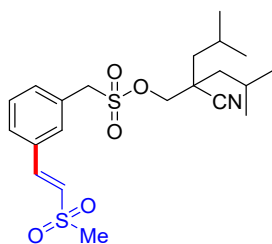


Diethyl 2-(3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)maleate (3ah): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2h** (52 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave

irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ah** (74 mg, 73%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1a}) = 0.60$, $R_f(\mathbf{3ah}) = 0.20$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2962, 1720, 1356, 1169, 980, 817 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 1.5$ Hz, 1H), 7.54 – 7.50 (m, 2H), 7.46 (dd, $J = 8.8, 6.5$ Hz, 1H), 6.33 (s, 1H), 4.46 (s, 2H), 4.42 (d, $J = 7.1$ Hz, 2H), 4.24 (q, $J = 7.1$ Hz, 2H), 4.04 (s, 2H), 1.77 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.46 (dd, $J = 6.2, 3.4$ Hz, 4H), 1.38 (d, $J = 7.1$ Hz, 3H), 1.31 (s, 2H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 167.4, 164.6, 147.4, 134.4, 132.6, 129.7, 128.8, 128.3, 127.7, 121.2, 118.8, 71.2, 62.0, 61.1, 56.8, 43.1 (2C), 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C), 14.1, 14.0 ppm. HRMS (ESI) m/z : $[(\text{M}+\text{H})]^+$ Calcd for $\text{C}_{26}\text{H}_{38}\text{NO}_7\text{S}^+$ 508.2363; Found 508.2372.



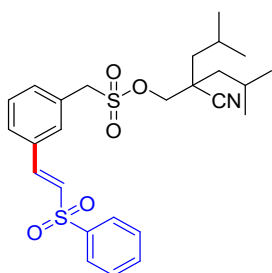
Ethyl (*E*)-3-(3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)but-2-enoate (3ai**):** GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2i** (34 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ai** (63 mg, 70%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1a}) = 0.60$, $R_f(\mathbf{3ai}) = 0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2960, 1709, 1359, 1167, 984, 755 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.55 – 7.49 (m, 2H), 7.44 (dd, $J = 5.4, 4.2$ Hz, 2H), 6.14 (dd, $J = 2.4, 1.1$ Hz, 1H), 4.47 (s, 2H), 4.22 (q, $J = 7.1$ Hz, 2H), 4.03 (s, 2H), 2.58 (d, $J = 1.3$ Hz, 3H), 1.77 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.46 (dd, $J = 6.2, 3.4$ Hz, 4H), 1.32 (t, $J = 7.1$ Hz, 3H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.5, 154.1, 143.1, 131.2, 129.2, 128.6, 127.6, 127.2, 121.2, 118.1, 71.1, 60.0, 57.1, 43.1 (2C), 39.4, 24.7 (2C), 23.9 (2C), 23.8 (2C), 17.9, 14.3 ppm. HRMS (ESI) m/z : $[(\text{M}+\text{H})]^+$ Calcd for $\text{C}_{24}\text{H}_{36}\text{NO}_5\text{S}^+$ 450.2309; Found 450.2315.



2-Cyano-2-isobutyl-4-methylpentyl

(E)-3-(2-

(methylsulfonyl)vinyl)phenyl)methanesulfonate (3aj): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2j** (32 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 65/35), furnished the product **3aj** (67 mg, 76%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3aj**) = 0.10, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2921, 2855, 1734, 1458, 1184, 900 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (s, 1H), 7.60 (d, *J* = 15.5 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.48 (dd, *J* = 8.8, 6.3 Hz, 1H), 7.03 (d, *J* = 15.5 Hz, 1H), 4.48 (s, 2H), 4.04 (s, 2H), 3.02 (s, 3H), 1.74 (dd, *J* = 13.0, 6.5 Hz, 2H), 1.50 – 1.41 (m, 4H), 0.98 (d, *J* = 6.6 Hz, 6H), 0.95 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 142.4, 133.5, 133.1, 130.3, 129.9, 129.7, 128.6, 127.8, 121.4, 71.4, 56.7, 43.2, 43.1 (2C), 39.5, 24.8 (2C), 23.8 (4C) ppm. HRMS (ESI) *m/z*: [(M+K)]⁺ Calcd for C₂₁H₃₁KNO₅S₂⁺ 480.1275; Found 480.1271.

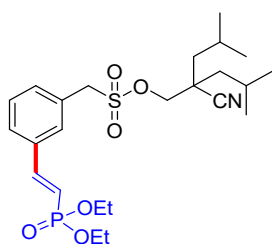


2-Cyano-2-isobutyl-4-methylpentyl

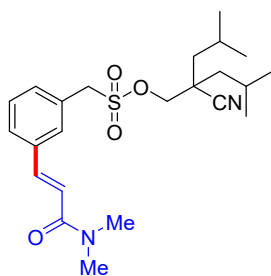
(E)-3-(2-

(phenylsulfonyl)vinyl)phenyl)methanesulfonate (3ak): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2k** (50 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 65/35), furnished the product **3ak** (77 mg, 77%), as a white solid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3ak**) = 0.10, UV detection]. Melting point: 85-87

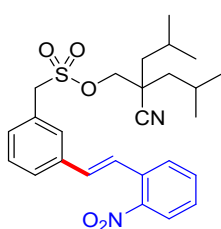
°C. IR (MIR-ATR, 4000–600 cm^{-1}): 2959, 1363, 1306, 1021, 770 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.94 (dd, $J = 5.3, 3.4$ Hz, 2H), 7.70 – 7.60 (m, 2H), 7.59 – 7.42 (m, 6H), 6.95 (d, $J = 15.4$ Hz, 1H), 4.45 (s, 2H), 4.03 (s, 2H), 1.74 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.48 – 1.39 (m, 4H), 0.96 (d, $J = 6.6$ Hz, 6H), 0.93 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 141.0, 140.3, 133.5, 133.3, 130.6, 129.8, 129.4, 129.3 (2C), 128.7, 128.4, 127.7 (2C), 121.3, 71.2, 56.7, 43.0 (2C), 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{Na})]^+$ Calcd for $\text{C}_{26}\text{H}_{33}\text{NNaO}_5\text{S}_2^+$ 526.1692; Found 526.1700.



2-Cyano-2-isobutyl-4-methylpentyl (E)-(3-(2-(diethoxyphosphoryl)vinyl)phenyl)methanesulfonate (3al): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2I** (49mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3al** (63 mg, 63%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1a}) = 0.60$, $R_f(\mathbf{3al}) = 0.20$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2963, 1465, 1359, 1171, 1026, 970, 736 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.58 (s, 1H), 7.55 – 7.52 (m, 1H), 7.49 (d, $J = 4.9$ Hz, 1H), 7.46 (d, $J = 2.0$ Hz, 1H), 7.45 – 7.40 (m, 1H), 6.32 (t, $J = 17.3$ Hz, 1H), 4.46 (s, 2H), 4.18 – 4.08 (m, 4H), 4.02 (s, 2H), 1.78 – 1.73 (m, 2H), 1.45 (dd, $J = 6.2, 4.1$ Hz, 4H), 1.35 (t, $J = 7.1$ Hz, 6H), 0.98 (d, $J = 6.6$ Hz, 6H), 0.95 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 147.2, 147.2, 135.7 (d, $J_{\text{C-P}} = 24$ Hz), 132.3, 129.7, 129.6, 128.6, 128.0, 121.2, 115.7 (d, $J_{\text{C-P}} = 24$ Hz), 71.2, 61.9, 61.9, 56.9, 43.1 (2C), 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C), 16.4, 16.3 ppm. HRMS (ESI) m/z : $[(\text{M}+\text{H})]^+$ Calcd for $\text{C}_{24}\text{H}_{39}\text{NO}_6\text{PS}^+$ 500.2230; Found 500.2248.

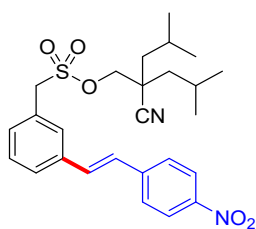


2-Cyano-2-isobutyl-4-methylpentyl (E)-3-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)phenylmethanesulfonate (3am): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2m** (30 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol%), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 65/35), furnished the product **3am** (64 mg, 74%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3am**) = 0.10, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2956, 1723, 1649, 1606, 1357, 979, 817, 691 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 15.3 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.46 – 7.39 (m, 2H), 6.96 (d, *J* = 15.5 Hz, 1H), 4.47 (s, 2H), 3.99 (s, 2H), 3.18 (s, 3H), 3.07 (s, 3H), 1.73 (dd, *J* = 13.1, 6.5 Hz, 2H), 1.48 – 1.38 (m, 4H), 0.97 (d, *J* = 6.6 Hz, 6H), 0.94 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 166.3, 141.0, 136.3, 131.6, 129.5, 129.4, 129.2, 127.9, 121.3, 118.7, 71.3, 57.0, 43.1 (2C), 39.4, 37.4, 36.0, 29.6, 24.7 (2C), 23.8 (2C), 23.8 (2C) ppm. HRMS (ESI) *m/z*: [(M+H)]⁺ Calcd for C₂₃H₃₅N₂O₄S⁺ 435.2312; Found 435.2321.



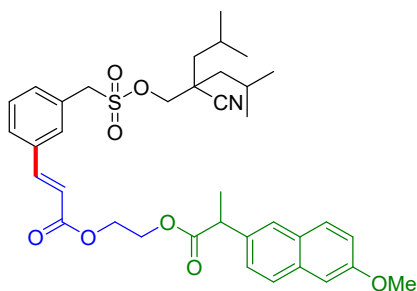
2-cyano-2-isobutyl-4-methylpentyl (E)-3-(2-nitrostyryl)phenylmethanesulfonate (3ax): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2x** (44 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol%), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 65/35), furnished the product **3ax** (75 mg, 78%), as a yellow coloured liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3ax**) = 0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2957, 1521, 1172, 978, 824, 741, 697 cm⁻¹.

^1H NMR (400 MHz, CDCl_3) δ 7.98 (dd, $J = 8.2, 1.1$ Hz, 1H), 7.75 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.62 (ddd, $J = 12.6, 4.5, 2.5$ Hz, 3H), 7.58 (s, 1H), 7.47 – 7.38 (m, 3H), 7.08 (d, $J = 16.2$ Hz, 1H), 4.48 (s, 2H), 4.01 (s, 2H), 1.76 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.46 (dd, $J = 6.2, 2.0$ Hz, 4H), 0.98 (d, $J = 6.6$ Hz, 6H), 0.95 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.9, 137.4, 133.2, 132.6, 132.6, 130.7, 129.8, 129.5, 128.3, 128.2, 127.9, 127.3, 124.8, 124.8, 121.3, 71.2, 57.0, 43.1 (2C), 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C). HRMS (ESI) m/z : $[(\text{M}+\text{NH}_4)]^+$ Calcd for $\text{C}_{26}\text{H}_{36}\text{N}_3\text{O}_5\text{S}^+$ 502.2370; Found 502.2373.

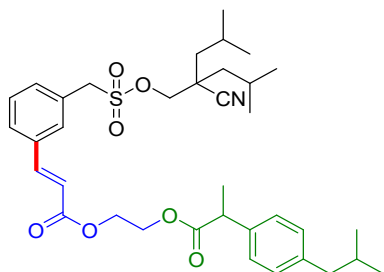


2-cyano-2-isobutyl-4-methylpentyl (E)-(3-(4-nitrostyryl)phenyl)methanesulfonate (3ay):

GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2y** (44 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol%), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 65/35), furnished the product **3ay** (73 mg, 75%), as a yellow coloured liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1a}) = 0.60$, $R_f(\mathbf{3ay}) = 0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2957, 1592, 1338, 1174, 1108, 979, 747 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, $J = 8.8$ Hz, 2H), 7.68 – 7.62 (m, 3H), 7.59 (dd, $J = 8.3, 2.6$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.41 (dd, $J = 6.2, 1.5$ Hz, 1H), 7.31 – 7.18 (m, 2H), 4.50 (s, 2H), 4.02 (s, 2H), 1.76 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.46 (dd, $J = 6.2, 3.2$ Hz, 4H), 0.98 (d, $J = 6.6$ Hz, 6H), 0.95 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.9, 143.3, 137.1, 132.0, 130.9, 129.6, 129.2, 128.0, 127.8, 127.5, 127.0 (2C), 124.2 (2C), 121.4, 71.4, 57.1, 43.1 (2C), 39.5, 24.7 (2C), 23.8 (2C), 23.8 (2C). HRMS (ESI) m/z : $[(\text{M}+\text{NH}_4)]^+$ Calcd for $\text{C}_{26}\text{H}_{36}\text{N}_3\text{O}_5\text{S}^+$ 502.2370; Found 502.2373.

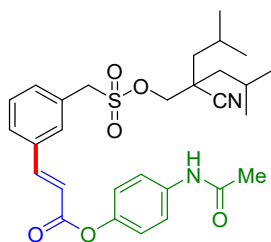


2-((2-(6-Methoxynaphthalen-2-yl)propanoyloxy)ethyl (E)-3-(3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3an): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2n** (98 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 65/35), furnished the product **3an** (100 mg, 76%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3an**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2958, 1720, 1637, 1359, 1160, 981, 816 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.64 (m, 3H), 7.53 (d, *J* = 16.1 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.44 (q, *J* = 3.5 Hz, 2H), 7.41 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.08 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.46 (s, 2H), 4.43 – 4.30 (m, 4H), 4.04 (s, 2H), 3.93 – 3.84 (m, 4H), 1.77 (dt, *J* = 13.0, 6.5 Hz, 2H), 1.59 (d, *J* = 7.2 Hz, 3H), 1.46 (dd, *J* = 6.2, 3.5 Hz, 4H), 0.99 (d, *J* = 6.6 Hz, 6H), 0.96 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 174.4, 166.1, 157.5, 143.8, 135.4, 135.1, 133.7, 132.4, 130.3, 129.6, 129.2, 128.8, 128.8, 128.1, 127.1, 126.2, 125.9, 121.3, 118.9, 118.7, 105.5, 71.2, 62.3, 62.2, 56.8, 55.2, 45.3, 43.1 (2C), 39.4, 24.8 (2C), 23.9 (2C), 23.8 (2C), 18.4 ppm. HRMS (ESI) *m/z*: [(M+K)]⁺ Calcd for C₃₇H₄₅KNO₈S⁺ 702.2497; Found 702.2515.



2-((2-(4-Isobutylphenyl)propanoyloxy)ethyl (E)-3-(3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ao): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2o** (91 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and

hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **3ao** (84 mg, 66%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1a}) = 0.60$, $R_f(\mathbf{3ao}) = 0.30$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2954, 1726, 1639, 1365, 1167, 985, 754 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 16.0$ Hz, 1H), 7.60 (s, 1H), 7.59 – 7.54 (m, 1H), 7.51 – 7.43 (m, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 7.06 (d, $J = 8.1$ Hz, 2H), 6.45 (d, $J = 16.1$ Hz, 1H), 4.47 (s, 2H), 4.41 – 4.29 (m, 4H), 4.05 (s, 2H), 3.74 (d, $J = 7.1$ Hz, 1H), 2.39 (d, $J = 7.2$ Hz, 2H), 1.50 (d, $J = 7.2$ Hz, 4H), 1.46 (dd, $J = 6.2, 3.4$ Hz, 4H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H), 0.86 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 174.5, 166.2, 143.9, 140.5, 137.4, 135.2, 132.5, 130.3, 129.6, 129.4, 129.3, 128.8 (2C), 128.2, 127.1, 127.0 (2C), 121.2, 118.8, 71.2, 62.3, 56.8, 44.9, 44.9, 43.1 (2C), 39.4, 30.1, 24.7 (2C), 23.8 (2C), 23.8 (2C), 22.3 (3C), 18.4 ppm. HRMS (ESI) m/z : $[(\text{M}+\text{K})]^+$ Calcd for $\text{C}_{36}\text{H}_{49}\text{KNO}_7\text{S}^+$ 678.2861; Found 678.2879.

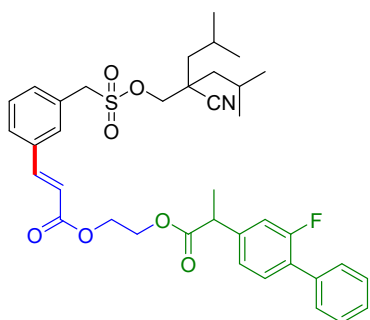


4-Acetamidophenyl

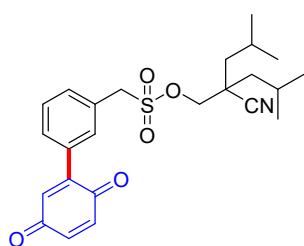
(*E*)-3-(3-(((2-cyano-2-isobutyl-4-

methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3ap**):** GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2p** (61 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 65/35), furnished the product **3ap** (70 mg, 65%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1a}) = 0.60$, $R_f(\mathbf{3ap}) = 0.10$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2922, 2859, 1726, 1678, 1510, 1182, 1142, 982 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 16.0$ Hz, 1H), 7.68 – 7.59 (m, 2H), 7.58 – 7.47 (m, 5H), 7.10 (d, $J = 8.8$ Hz, 2H), 6.66 (d, $J = 16.0$ Hz, 1H), 4.48 (s, 2H), 4.05 (s, 2H), 2.15 (s, 3H), 1.77 (dt, $J = 13.0, 6.5$ Hz, 3H), 1.47 (dd, $J = 6.2, 3.7$ Hz, 4H), 1.0 (d, $J = 6.6$ Hz, 6H), 0.97 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 168.4, 165.2, 146.8, 145.3, 135.7, 135.0, 132.8, 130.5, 129.7, 129.0, 128.3, 121.9, 121.3, 120.8, 118.5, 71.2, 56.8, 43.1 (2C), 39.5, 24.8

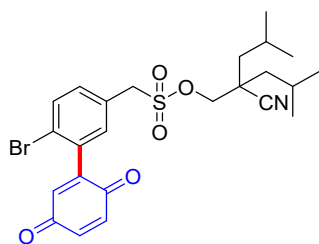
(2C), 24.4, 23.8 (2C), 23.8 (2C) ppm. HRMS (ESI) m/z : $[(M+H)]^+$ Calcd for $C_{29}H_{37}N_2O_6S^+$ 541.2367; Found 541.2384.



2-((2-(2-Fluoro-[1,1'-biphenyl]-4-yl)propanoyl)oxy)ethyl (*E*)-3-(3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)phenyl)acrylate (3aq): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2q** (102 mg, 0.3 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 80/20), furnished the product **3aq** (73 mg, 54%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1a}) = 0.60$, $R_f(\mathbf{3aq}) = 0.30$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2958, 1713, 1640, 1358, 1169, 980, 817, 734 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, $J = 16.1$ Hz, 1H), 7.54 – 7.43 (m, 5H), 7.43 – 7.30 (m, 5H), 7.15 (ddd, $J = 8.7, 5.4, 1.7$ Hz, 2H), 6.42 (d, $J = 16.0$ Hz, 1H), 4.39 (s, 6H), 4.02 (s, 2H), 3.83 – 3.78 (m, 1H), 1.75 (dd, $J = 13.1, 6.5$ Hz, 2H), 1.55 (d, $J = 7.2$ Hz, 3H), 1.45 (dd, $J = 6.2, 3.9$ Hz, 4H), 0.98 (d, $J = 6.6$ Hz, 6H), 0.95 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 166.1, 144.0, 141.0 ($J_{C-F} = 95$ Hz), 135.4, 135.1, 132.5, 130.8 ($J_{C-F} = 4$ Hz), 130.3, 129.6, 128.9, 128.9, 128.8, 128.4, 128.1, 127.6, 123.6 ($J_{C-F} = 3$ Hz), 121.2, 118.7, 115.3, 115.1, 71.1, 62.6, 62.1, 56.8, 44.9, 43.1 (2C), 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C), 18.2 ppm. HRMS (ESI) m/z : $[(M+NH_4)]^+$ Calcd for $C_{38}H_{48}FN_2O_7S^+$ 695.3161; Found 395.3141.

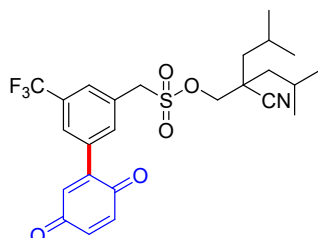


2-Cyano-2-isobutyl-4-methylpentyl (2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-3-yl)methanesulfonate (3ar): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), cyclicolefin **2r** (32 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ar** (57 mg, 65%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3ar**) = 0.30, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2957, 1657, 1593, 1355, 1274, 1170, 979, 823 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (dddd, *J* = 13.4, 11.9, 6.7, 4.4 Hz, 4H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.89 – 6.82 (m, 2H), 4.51 (s, 2H), 4.05 (s, 2H), 1.77 (dp, *J* = 13.0, 6.5 Hz, 2H), 1.48 (dd, *J* = 6.2, 1.4 Hz, 4H), 0.98 (d, *J* = 6.6 Hz, 6H), 0.95 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 187.3, 186.2, 144.9, 137.0, 136.3, 133.5, 133.1, 132.3, 131.7, 130.0, 129.3, 127.7, 121.3, 71.4, 56.9, 43.1 (2C), 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C) ppm. HRMS (ESI) *m/z*: [(M+K)]⁺ Calcd for C₂₄H₂₉KNO₅S⁺ 482.1398; Found 482.1406.

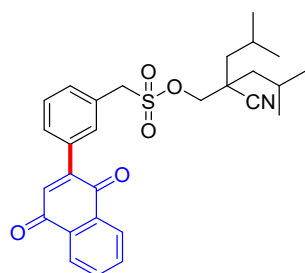


2-Cyano-2-isobutyl-4-methylpentyl (6-bromo-2',5'-dioxo-2',5'-dihydro-[1,1'-biphenyl]-3-yl)methanesulfonate (3ir): GP-3 was carried out by using arylmethanesulfonate ester **1i** (83 mg, 0.2 mmol), cyclicolefin **2r** (32 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3ir** (63 mg, 61%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1i**) = 0.60, *R_f*(**3ir**) = 0.30, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2957, 2927, 1660, 1463, 1358, 1174, 981, 828, 754 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.3 Hz, 1H), 7.40 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.32 (d, *J* = 2.2 Hz, 1H), 6.88 (d, *J* = 2.3 Hz, 2H), 6.81 (d, *J* = 1.6 Hz, 1H), 4.43 (s, 2H), 4.05 (s, 2H), 1.77 (dd, *J* = 13.0, 6.5 Hz, 2H), 1.48 (dd, *J* = 6.2, 1.9 Hz, 4H), 1.0 (d, *J* = 6.6 Hz, 6H), 0.98 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 187.0, 184.8, 146.4, 136.7, 136.6, 135.3, 135.2, 133.7, 133.0, 132.7,

126.9, 124.1, 121.4, 71.8, 56.3, 43.1 (2C), 39.5, 29.7, 24.8 (2C), 23.9 (2C), 23.9 (2C) ppm. HRMS (ESI) m/z : $[(M+Na)]^+$ Calcd for $C_{24}H_{28}^{79}BrNNaO_5S^+$ 546.0743; Found 546.0873: Calcd for $C_{24}H_{28}^{81}BrNNaO_5S^+$ 554.0796; Found 554.0800.

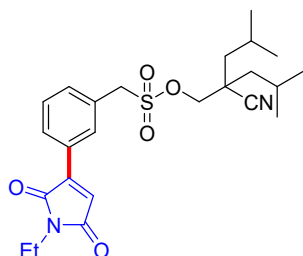


2-Cyano-2-isobutyl-4-methylpentyl (2',5'-dioxo-5-(trifluoromethyl)-2',5'-dihydro-[1,1'-biphenyl]-3-yl)methanesulfonate (3cr): GP-3 was carried out by using arylmethanesulfonate ester **1c** (81 mg, 0.2 mmol), cyclicolefin **2r** (32 mg, 0.3 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3cr** (61 mg, 60%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1c}) = 0.60$, $R_f(\mathbf{3cr}) = 0.30$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2959, 1659, 1601, 1358, 1170, 1130, 980, 754 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 3H), 6.94 (d, $J = 2.1$ Hz, 1H), 6.93 – 6.85 (m, 2H), 4.56 (s, 2H), 4.13 (s, 2H), 1.78 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.48 (dd, $J = 6.2, 4.0$ Hz, 4H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 186.8, 185.6, 143.6, 136.9, 136.5, 134.9, 134.4, 133.8, 132.5 (q, $J_{C-F} = 32$ Hz), 129.0, 128.7 (q, $J_{C-F} = 4$ Hz), 126.8 (q, $J_{C-F} = 4$ Hz), 123.2 (q, $J_{C-F} = 271$ Hz), 71.4, 56.4, 43.1 (2C), 39.5, 24.7(2C), 23.8(2C), 23.8(2C) ppm. HRMS (ESI) m/z : $[(M+K)]^+$ Calcd for $C_{25}H_{28}F_3KNO_5S^+$ 550.1272; Found 550.1275.



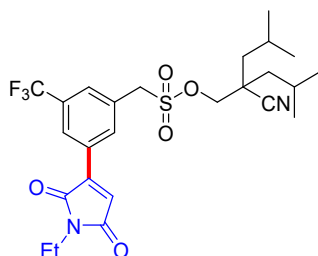
2-Cyano-2-isobutyl-4-methylpentyl (3-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)phenyl)methanesulfonate (3at): GP-3 was carried out by using arylmethanesulfonate

ester **1a** (67 mg, 0.2 mmol), cyclicolefin **2t** (47 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3at** (55 mg, 56%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3at**) = 0.30, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2958, 1661, 1594, 1356, 1255, 980, 821 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.17 (dd, *J* = 6.0, 3.0 Hz, 1H), 8.12 (dd, *J* = 6.1, 2.9 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.68 (d, *J* = 1.5 Hz, 1H), 7.64 – 7.50 (m, 3H), 7.16 – 7.01 (m, 3H), 4.52 (s, 2H), 4.08 (s, 2H), 2.26 (s, 3H), 1.78 (dt, *J* = 13.0, 6.5 Hz, 2H), 1.48 (d, *J* = 6.2 Hz, 4H), 0.97 0.99 (d, *J* = 6.6 Hz, 6H), 0.96 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 184.8, 184.0, 147.0, 136.4, 135.6, 134.2, 134.0, 134.0, 132.2, 132.0, 131.9, 130.1, 129.5, 129.21, 127.6, 127.0, 126.0, 125.7, 121.3, 71.4, 57.0, 43.1 (2C), 39.4, 24.7 (2C), 23.9 (2C), 23.8 (2C), 19.68 ppm. HRMS (ESI) *m/z*: [(M+H)]⁺ Calcd for C₂₈H₃₂NO₅S⁺ 494.1996; Found 494.1999.

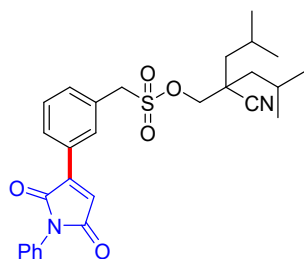


2-Cyano-2-isobutyl-4-methylpentyl (3-(1-ethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)phenyl)methanesulfonate (3au): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), cyclicolefin **2u** (37 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3au** (65 mg, 71%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3au**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2957, 1703, 1354, 1173, 982, 818 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 1.5 Hz, 1H), 7.95 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.57 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 6.79 (s, 1H), 4.50 (s, 2H), 4.06 (s, 2H), 3.64 (q, *J* = 7.2 Hz, 2H), 1.77 (dt, *J* = 13.0, 6.5 Hz, 2H), 1.52 – 1.43 (m, 4H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 6H), 0.96 (d, *J* = 6.6

Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.2, 169.9, 142.6, 133.1, 130.9, 129.7, 129.6, 129.3, 128.3, 125.0, 121.3, 71.3, 56.8, 43.1 (2C), 39.4, 33.0, 24.8 (2C), 23.9 (2C), 23.8 (2C), 13.9 ppm. HRMS (ESI) m/z : $[(\text{M}+\text{Na})]^+$ Calcd for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{NaO}_5\text{S}^+$ 483.1924; Found 483.1935.

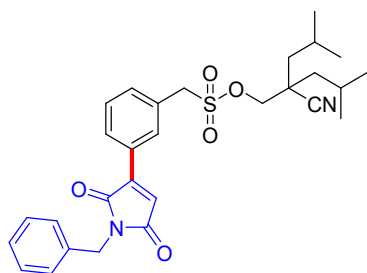


2-Cyano-2-isobutyl-4-methylpentyl (3-(1-ethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)-5-(trifluoromethyl)phenyl)methanesulfonate (3cu): GP-3 was carried out by using arylmethanesulfonate ester **1c** (81 mg, 0.2 mmol), cyclicolefin **2u** (37 mg, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3cu** (71 mg, 67%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1c}) = 0.60$, $R_f(\mathbf{3cu}) = 0.20$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2925, 1703, 1354, 1171, 1130, 978, 821 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.22 (s, 2H), 7.80 (s, 1H), 6.90 (s, 1H), 4.56 (s, 2H), 4.14 (s, 2H), 3.65 (q, $J = 7.2$ Hz, 2H), 1.78 (dp, $J = 13.0, 6.5$ Hz, 2H), 1.53 – 1.43 (m, 4H), 1.24 (t, $J = 7.2$ Hz, 3H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.97 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 169.8, 169.3, 141.2, 134.0, 132.3 (q, $J_{\text{C-F}} = 36$ Hz), 130.5, 129.5, 129.3 (q, $J_{\text{C-F}} = 4$ Hz), 126.4, 126.1 (q, $J_{\text{C-F}} = 4$ Hz), 123.1 (q, $J_{\text{C-F}} = 270$ Hz), 121.2, 71.4, 56.3, 43.0 (2C), 39.5, 33.2, 24.7 (2C), 23.8 (2C), 23.8 (2C), 13.8 ppm. HRMS (ESI) m/z : $[(\text{M}+\text{NH}_4)]^+$ Calcd for $\text{C}_{25}\text{H}_{35}\text{F}_3\text{N}_3\text{O}_5\text{S}^+$ 546.2244; Found 546.2258.



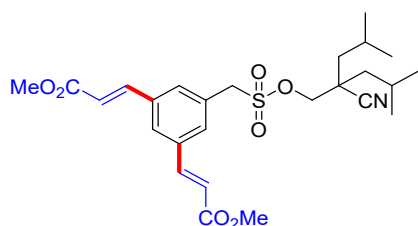
2-Cyano-2-isobutyl-4-methylpentyl (3-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)phenyl)methanesulfonate (3av): GP-3 was carried out by using arylmethanesulfonate

ester **1a** (67 mg, 0.2 mmol), cyclicolefin **2v** (52 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3av** (66 mg, 65%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3av**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2957, 1713, 1494, 1367, 1170, 978, 816, 736 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.58 (dt, *J* = 15.4, 7.7 Hz, 2H), 7.50 (dd, *J* = 10.8, 4.7 Hz, 2H), 7.44 – 7.33 (m, 3H), 6.96 (s, 1H), 4.52 (s, 2H), 4.08 (s, 2H), 1.78 (dp, *J* = 13.0, 6.5 Hz, 2H), 1.53 – 1.44 (m, 4H), 0.99 (d, *J* = 6.6 Hz, 6H), 0.96 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 169.2, 168.8, 142.6, 133.4, 131.3, 131.1, 129.7, 129.5, 129.4, 129.1, 128.4, 128.0, 126.2, 125.1, 121.3, 71.3, 56.8, 43.1 (2C), 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C) ppm. HRMS (ESI) *m/z*: [(M+K)]⁺ Calcd for C₂₈H₃₂KN₂O₅S⁺ 547.1664; Found 547.1677.

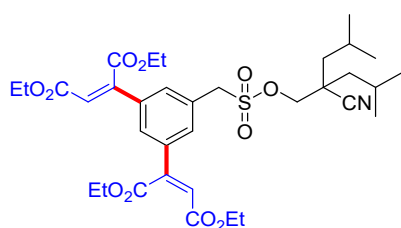


2-Cyano-2-isobutyl-4-methylpentyl (3-(1-benzyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)phenyl)methanesulfonate (3aw): GP-3 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), cyclicolefin **2w** (56 mg, 0.3 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (100 mg, 0.6 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 90 °C for 25 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **3aw** (62 mg, 60%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**) = 0.60, *R_f*(**3aw**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2958, 1710, 1355, 1173, 982, 703 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 1.5 Hz, 1H), 7.94 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.39 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.32 (ddd, *J* = 9.6, 4.4, 2.8 Hz, 3H), 6.82 (s, 1H), 4.74 (s, 2H), 4.49 (s, 2H), 4.06 (s, 2H), 1.77 (dd, *J* = 13.1, 6.5 Hz, 2H), 1.46 (dd, *J* = 6.2, 1.9 Hz, 4H), 0.97 (d, *J* = 6.6 Hz, 6H), 0.95 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 170.1, 169.6, 142.7, 136.2, 133.2, 130.9, 129.7, 129.6, 129.3, 128.7 (2C), 128.5 (2C), 128.3, 127.9, 125.0,

121.3, 71.2, 56.8, 43.1 (2C), 41.7, 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C) ppm. HRMS (ESI) m/z : $[(M+K)]^+$ Calcd for $C_{29}H_{34}KN_2O_5S^+$ 561.1820; Found 561.1833.

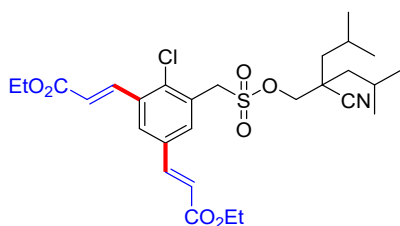


Dimethyl 3,3'-(5-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)-1,3-phenylene)(2E,2'E)-diacrylate (4a): GP-4 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2b** (21 mg, 0.48 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), $AgOAc$ (133 mg, 0.8 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 100 °C for 35 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **4a** (67 mg, 67%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1a}) = 0.60$, $R_f(\mathbf{4a}) = 0.20$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2954, 1713, 1639, 1445, 1276, 1170, 981, 821 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.58 (m, 5H), 6.51 (d, $J = 16.1$ Hz, 2H), 4.48 (s, 2H), 4.07 (s, 2H), 3.81 (s, 6H), 1.75 (dd, $J = 13.0, 6.5$ Hz, 2H), 1.45 (dt, $J = 13.5, 6.7$ Hz, 4H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 166.7 (2C), 142.6 (2C), 136.0 (2C), 131.3 (2C), 129.1, 128.1, 121.2, 120.1 (2C), 71.3, 56.6, 51.9, 43.1 (2C), 39.5, 24.7 (2C), 23.8 (2C), 23.8 (2C) ppm. HRMS (ESI) m/z : $[(M+H)]^+$ Calcd for $C_{26}H_{36}NO_7S^+$ 506.2207; Found 506.2218.

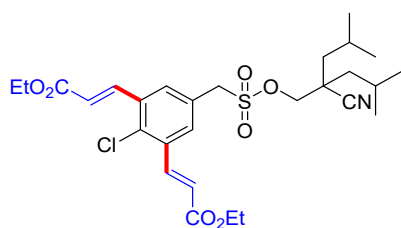


Tetraethyl 2,2'-(5-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)-1,3-phenylene)dimalate (4b): GP-4 was carried out by using arylmethanesulfonate ester **1a** (67 mg, 0.2 mmol), olefin **2h** (83 mg, 0.48 mmol), $Pd(OAc)_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), $AgOAc$ (133 mg, 0.8 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 100 °C for 35 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 75/25), furnished the product **4b** (81 mg, 60%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 85:15,

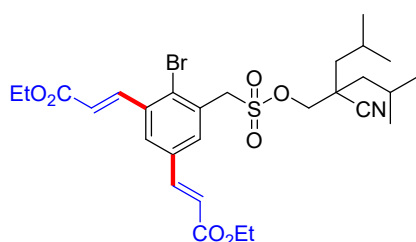
$R_f(\mathbf{1a}) = 0.70$, $R_f(\mathbf{4b}) = 0.20$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2964, 1722, 1361, 1173, 981, 753 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.62 (s, 3H), 6.33 (s, 2H), 4.46 (s, 2H), 4.41 (q, $J = 7.2$ Hz, 4H), 4.25 (d, $J = 7.1$ Hz, 4H), 4.12 (s, 2H), 1.81 – 1.77 (m, 2H), 1.48 (dd, $J = 6.2, 3.9$ Hz, 4H), 1.37 (t, $J = 7.2$ Hz, 6H), 1.33 (d, $J = 7.1$ Hz, 6H), 1.0 (d, $J = 6.6$ Hz, 6H), 0.97 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 167.0 (2C), 164.4 (2C), 146.4, 135.4, 130.3, 129.3, 125.9, 121.2, 120.2, 71.3, 62.2, 61.2, 56.5, 43.1, 39.5, 24.7 (2C), 23.9 (2C), 23.8 (2C), 14.1 (2C), 13.9 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{K})]^+$ Calcd for $\text{C}_{34}\text{H}_{47}\text{KNO}_{11}\text{S}^+$ 716.2501; Found 716.2508.



Diethyl 3,3'-(4-chloro-5-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)-1,3-phenylene)(2E,2'E)-diacrylate (4c**):** GP-4 was carried out by using arylmethanesulfonate ester **1d** (74 mg, 0.2 mmol), olefin **2a** (48 mg, 0.48 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (133 mg, 0.8 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 100 $^\circ\text{C}$ for 35 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **4c** (79 mg, 70%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{1d}) = 0.60$, $R_f(\mathbf{4c}) = 0.20$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2961, 1710, 1638, 1362, 1268, 1173, 1041, 976, 734 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 16.0$ Hz, 1H), 7.75 (dd, $J = 16.7, 2.0$ Hz, 2H), 7.63 (d, $J = 16.0$ Hz, 1H), 6.48 (dd, $J = 21.0, 16.0$ Hz, 2H), 4.74 (s, 2H), 4.28 (dq, $J = 8.6, 7.1$ Hz, 4H), 4.16 (s, 2H), 1.79 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.48 (dd, $J = 6.2, 3.0$ Hz, 4H), 1.34 (td, $J = 7.1, 5.6$ Hz, 6H), 1.0 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 166.1, 165.8, 141.4, 139.6, 136.5, 135.0, 133.8, 132.6, 127.8, 127.7, 123.0, 121.1, 121.0, 70.7, 60.9, 60.8, 54.0, 43.1 (2C), 39.4, 24.7 (2C), 23.8 (2C), 23.8 (2C), 14.2 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{H})]^+$ Calcd for $\text{C}_{28}\text{H}_{39}\text{ClNO}_7\text{S}^+$ 568.2130; Found 568.2134.

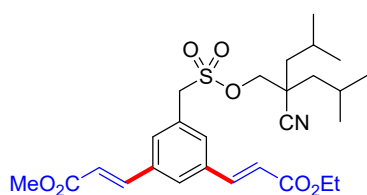


Diethyl 3,3'-(2-chloro-5-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)-1,3-phenylene)(2*E*,2'*E*)-diacrylate (4d**):** GP-4 was carried out by using arylmethanesulfonate ester **1f** (74 mg, 0.2 mmol), olefin **2a** (48 mg, 0.48 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (133 mg, 0.8 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 100 °C for 35 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **4d** (74 mg, 65%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1f**) = 0.60, *R_f*(**4d**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2929, 1716, 1637, 1366, 1263, 1176, 980, 823 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 16.0 Hz, 2H), 7.70 (s, 2H), 6.48 (d, *J* = 16.0 Hz, 2H), 4.46 (s, 2H), 4.29 (q, *J* = 7.1 Hz, 4H), 4.13 (s, 2H), 1.77 (dd, *J* = 13.0, 6.5 Hz, 2H), 1.48 (t, *J* = 6.5 Hz, 4H), 1.35 (t, *J* = 7.1 Hz, 6H), 1.0 (d, *J* = 6.6 Hz, 6H), 0.97 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 165.9 (2C), 139.3 (2C), 135.8, 135.0, 130.7 (2C), 126.6, 123.0 (2C), 121.3, 71.4, 60.9 (2C), 56.2, 43.1 (2C), 39.5, 24.8 (2C), 23.8 (4C), 14.2, 14.1. HRMS (ESI) *m/z*: [(M+K)]⁺ Calcd for C₂₈H₃₈ClNO₇S⁺ 606.1689; Found 606.1703.

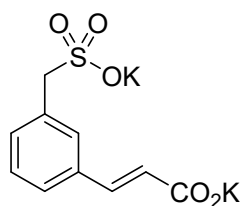


Diethyl 3,3'-(4-bromo-5-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)-1,3-phenylene)(2*E*,2'*E*)-diacrylate (4e**):** GP-4 was carried out by using arylmethanesulfonate ester **1g** (83 mg, 0.2 mmol), olefin **2a** (48 mg, 0.48 mmol), Pd(OAc)₂ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (133 mg, 0.8 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 100 °C for 35 minutes. Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **4e** (84 mg, 69%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, *R_f*(**1g**) = 0.60, *R_f*(**4e**) = 0.20, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): 2960, 1710,

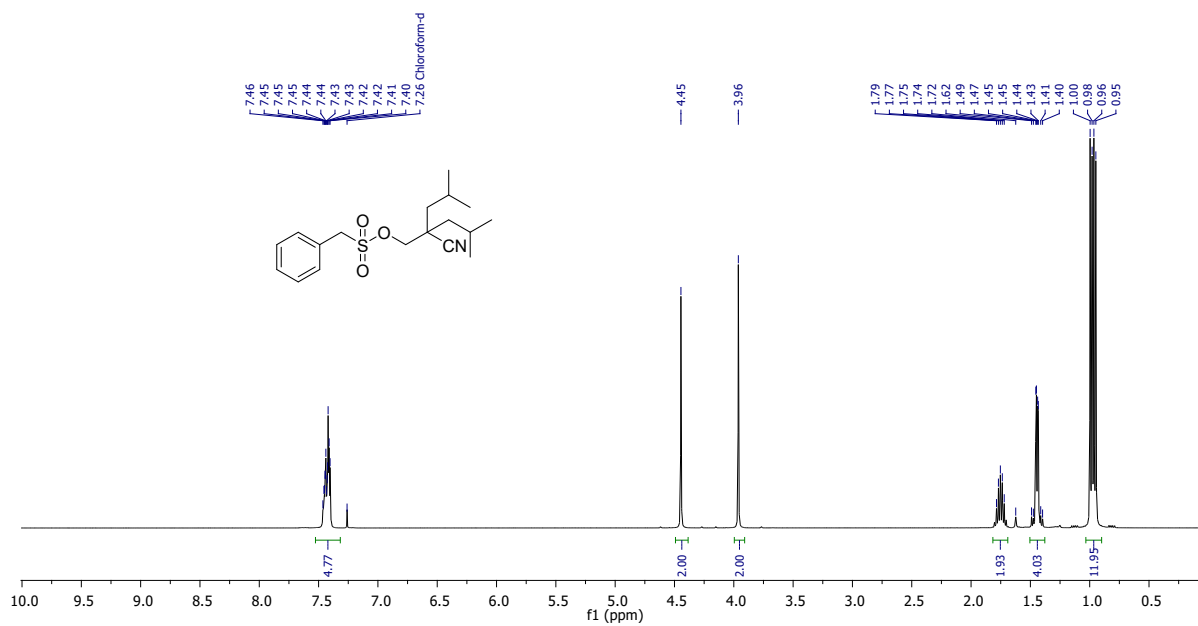
1637, 1267, 1172, 1033, 977 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 15.9$ Hz, 1H), 7.72 (d, $J = 1.5$ Hz, 2H), 7.63 (d, $J = 16.0$ Hz, 1H), 6.53 (d, $J = 16.0$ Hz, 1H), 6.40 (d, $J = 15.8$ Hz, 1H), 4.81 (s, 2H), 4.29 (dq, $J = 9.1, 7.1$ Hz, 4H), 4.17 (s, 2H), 1.80 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.49 (dd, $J = 6.2, 2.3$ Hz, 4H), 1.35 (td, $J = 7.1, 6.0$ Hz, 6H), 1.01 (d, $J = 6.6$ Hz, 6H), 0.97 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 166.2, 165.8, 142.6, 141.4, 137.3, 134.5, 132.4, 129.7, 129.2, 127.8, 123.2, 121.2, 70.8, 61.0, 60.9, 56.7, 43.2 (2C), 39.4, 36.6, 24.8 (2C), 23.9 (2C), 23.8 (2C), 14.3 (2C) ppm. HRMS (ESI) m/z : $[(\text{M}+\text{K})]^+$ Calcd for $\text{C}_{28}\text{H}_{38}^{79}\text{BrKNO}_7\text{S}^+$ 650.1184; Found 650.1200: Calcd for $\text{C}_{23}\text{H}_{33}^{81}\text{BrKNO}_7\text{S}^+$ 652.1163; Found 652.1181.



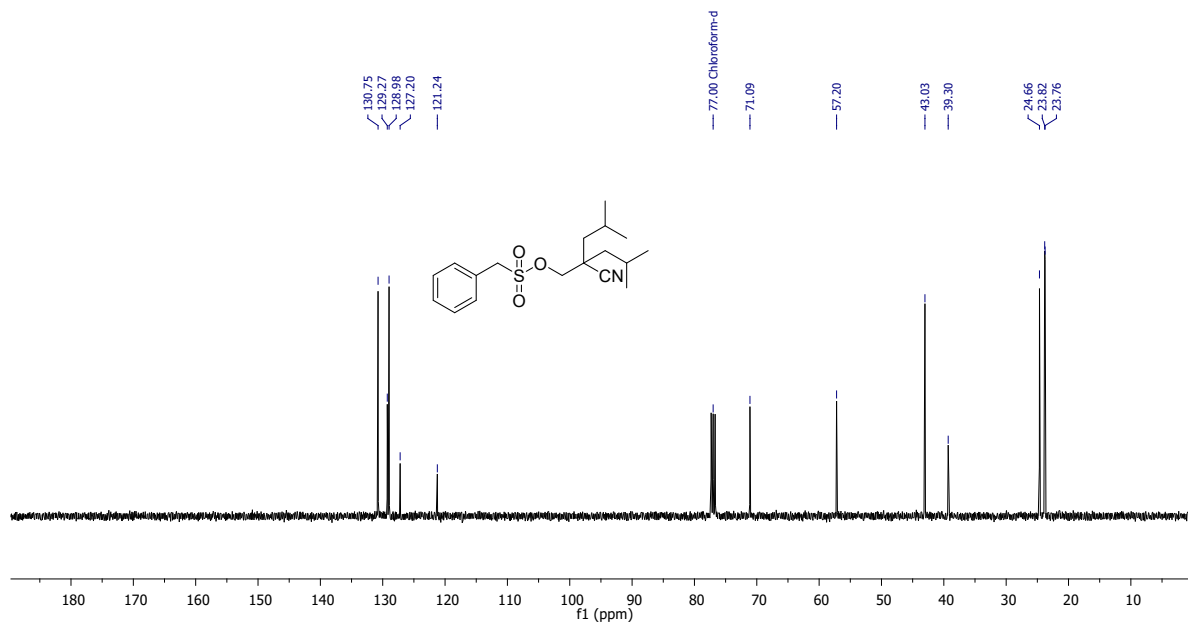
Ethyl (E)-3-(3-(((2-cyano-2-isobutyl-4-methylpentyl)oxy)sulfonyl)methyl)-5-((E)-3-methoxy-3-oxoprop-1-en-1-yl)phenyl)acrylate (4f): An oven-dried 10 mL glass vial equipped with a magnetic stirring bar, was charged with arylmethanesulfonate ester **3ab** (84 mg, 0.2 mmol), olefin **2a** (48 mg, 0.48 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 10 mol %), Ac-Gly-OH (10 mg, 40 mol%), AgOAc (133 mg, 0.8 mmol), and hexafluoroisopropanol (HFIP) (1.5 mL) under microwave irradiation at 100 $^\circ\text{C}$ for 35 minutes. The reaction mixture was cooled to room temperature. The progress of the reaction was monitored by TLC. The reaction mixture diluted with ethyl acetate (15 mL) and filtered through a short pad of celite with an additional amount of ethyl acetate (15 mL). Purification of crude product using silica gel column chromatography (hexane/ethyl acetate, 100/0 to 90/15), furnished the product **4f** (74 mg, 71%), as a colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10, $R_f(\mathbf{3ab}) = 0.60$, $R_f(\mathbf{4f}) = 0.20$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): 2959, 2873, 2235, 1576, 1363, 898, 749 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.73 – 7.63 (m, 3H), 7.61 (s, 2H), 6.51 (dd, $J = 16.1, 2.2$ Hz, 2H), 4.48 (s, 2H), 4.27 (q, $J = 7.1$ Hz, 2H), 4.08 (s, 2H), 3.82 (s, 3H), 1.77 (dt, $J = 13.0, 6.5$ Hz, 2H), 1.50 – 1.42 (m, 4H), 1.34 (t, $J = 7.1$ Hz, 3H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.96 (d, $J = 6.6$ Hz, 6H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.7, 166.3, 142.7, 142.3, 136.1, 136.0, 131.3, 131.3, 129.0, 128.1, 121.2, 120.6, 120.0, 71.2, 60.7, 56.6, 51.9, 43.1 (2C), 39.5, 24.7 (2C), 23.8 (2C), 23.8 (2C), 14.2 ppm. HRMS (ESI) m/z : $[(\text{M}+\text{H})]^+$ Calcd for $\text{C}_{28}\text{H}_{38}\text{NO}_7\text{S}^+$ 520.2363; Found 520.2355.



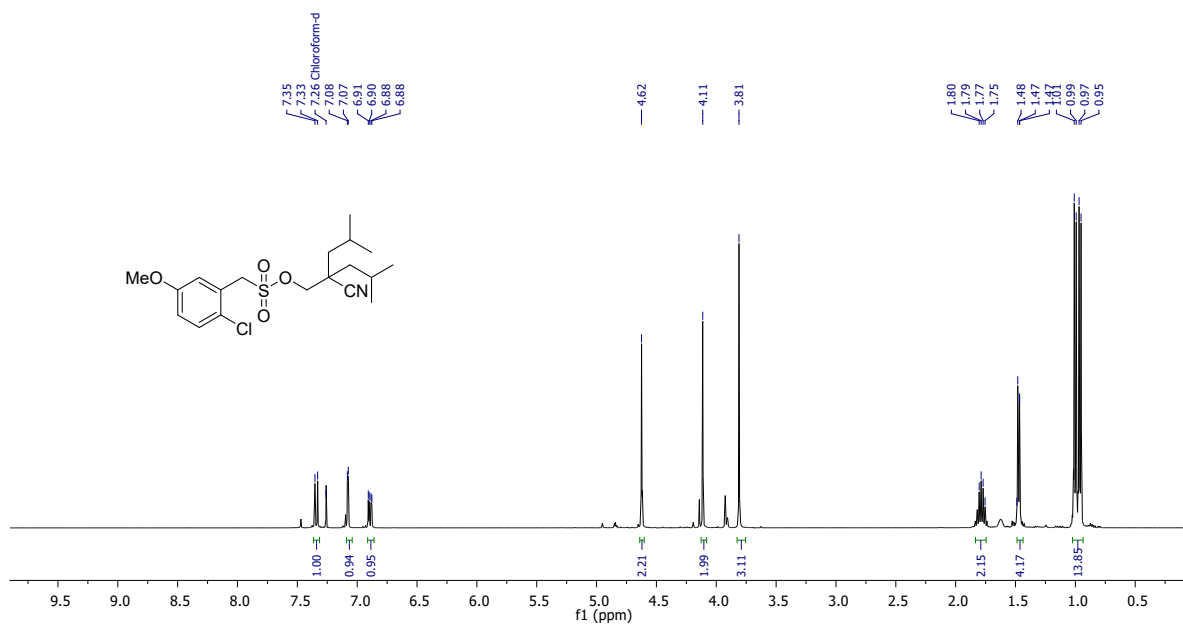
Potassium (*E*)-3-(3-(sulfonatomethyl)phenyl)acrylate (5**):** To an oven dried 25 mL round bottom flask charged with a magnetic stirring bar, were added substrate **3ab** (84 mg, 0.2 mmol) and MeOH (5 mL) followed by potassium hydroxide (2 equiv) at room temperature for 3 h. The reaction progress was monitored by TLC, then MeOH was removed under reduced pressure, resulted mixture was washed with ethyl acetate, the residue product **5** was obtained as white solid (60 mg, 95%). ¹H NMR (400 MHz, DMSO) δ 7.35 (s, 1H), 7.28 (d, *J* = 6.7 Hz, 1H), 7.19 (q, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 15.9 Hz, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 3.69 (s, 2H). HRMS (ESI) *m/z*: [(M+H)]⁺ Calcd for C₁₀H₉K₂O₅S⁺ 318.9439; Found 318.9434. ¹³C {¹H} NMR (101 MHz, DMSO) δ 170.63, 136.54, 136.14, 135.75, 130.71, 130.35, 129.24, 128.25, 125.30, 57.83, 39.90.



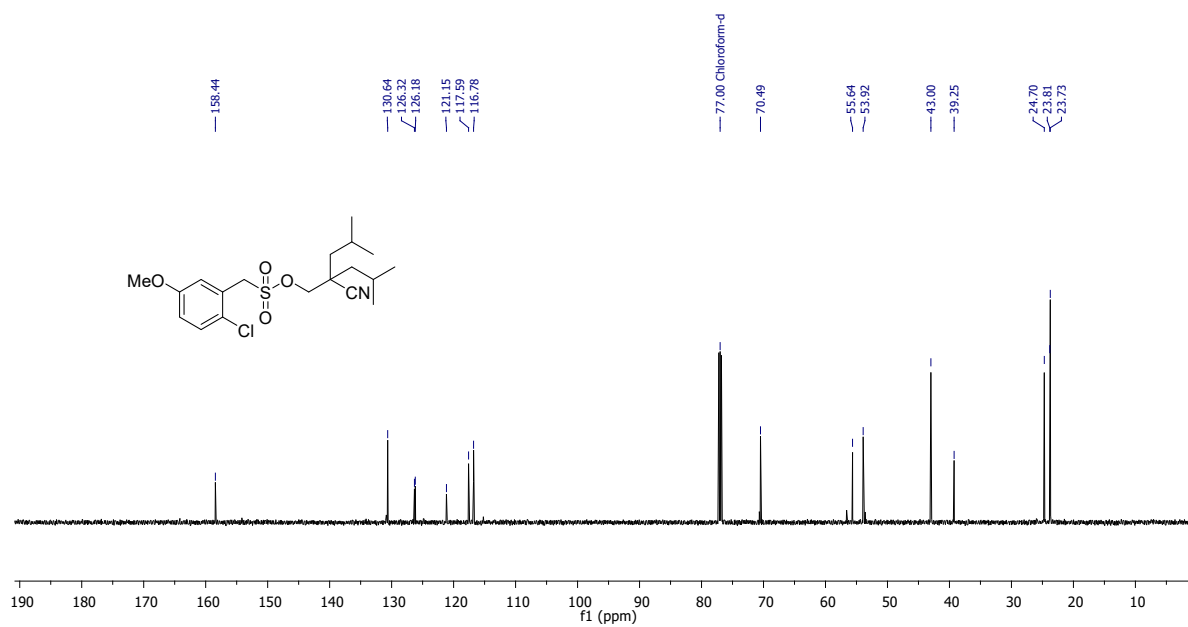
^1H NMR (400 MHz) spectrum of **1a** in CDCl_3



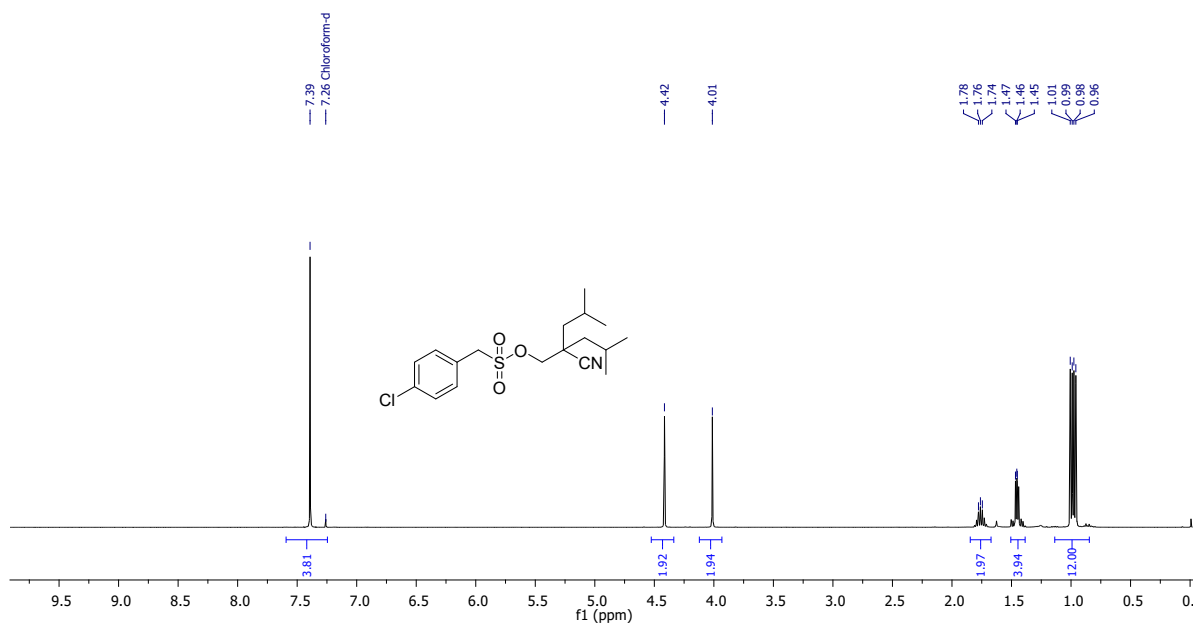
^{13}C $\{^1\text{H}\}$ NMR (100 MHz) spectrum of **1a** in CDCl_3



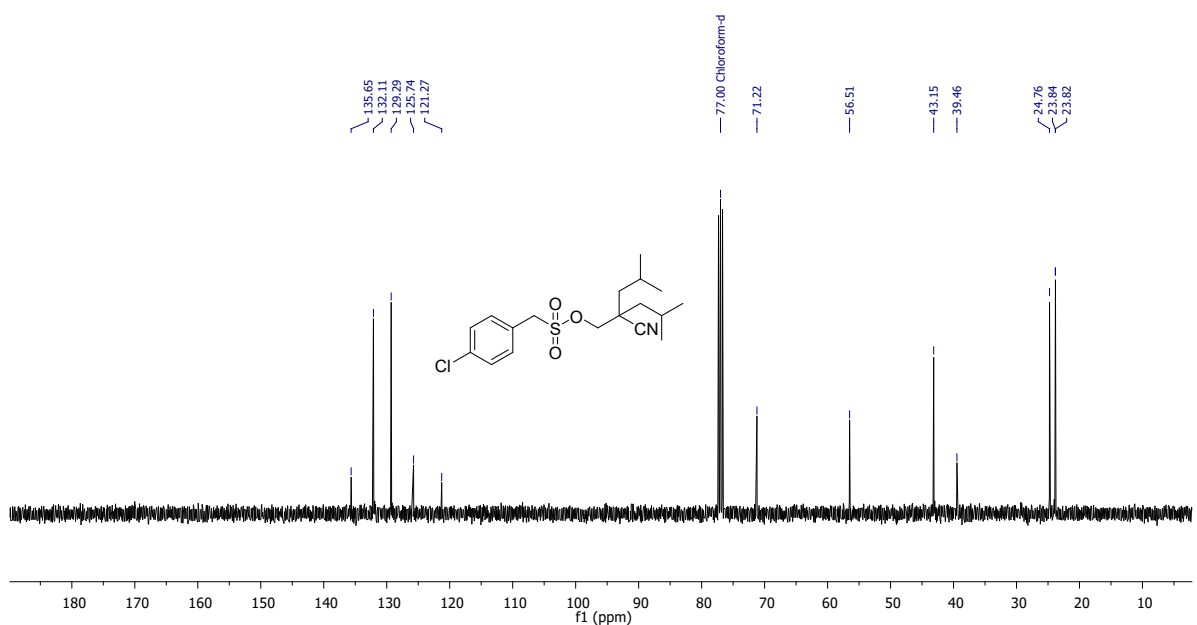
¹H NMR (400 MHz) spectrum of *1b* in CDCl₃



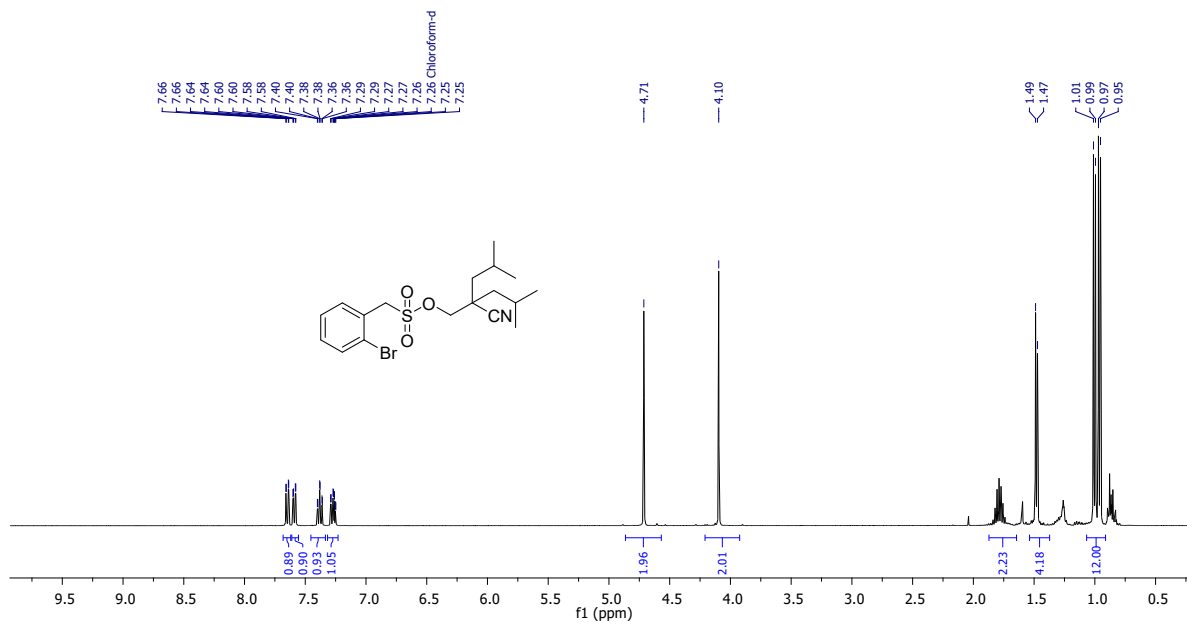
¹³C {¹H} NMR (151 MHz) spectrum of *1b* in CDCl₃



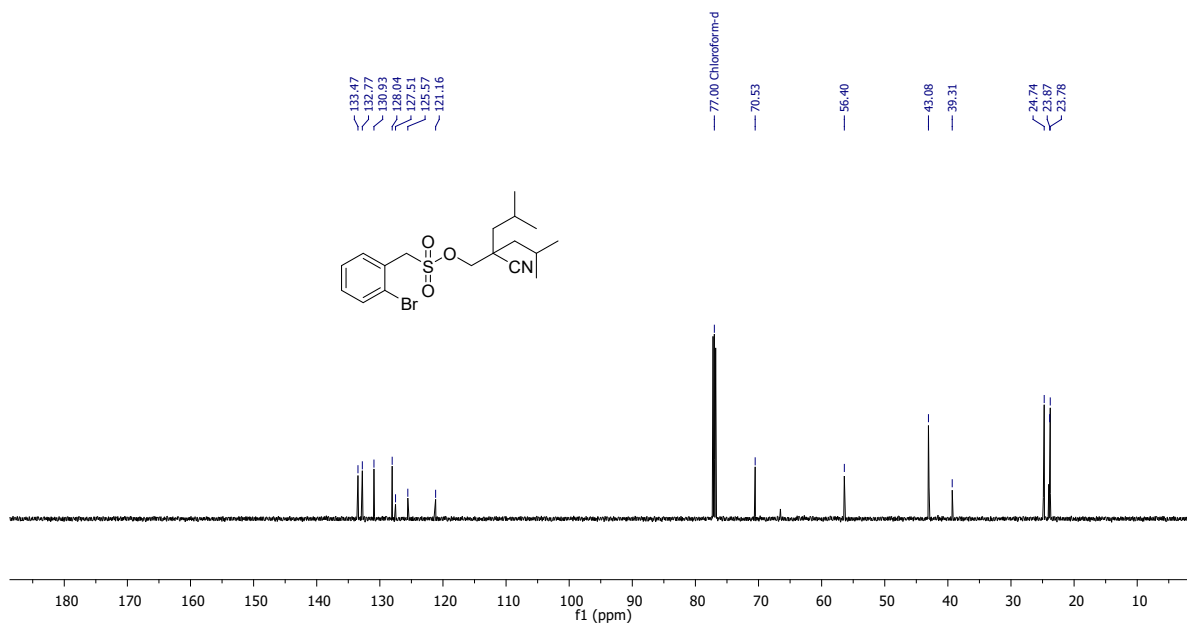
^1H NMR (400 MHz) spectrum of *If* in CDCl_3



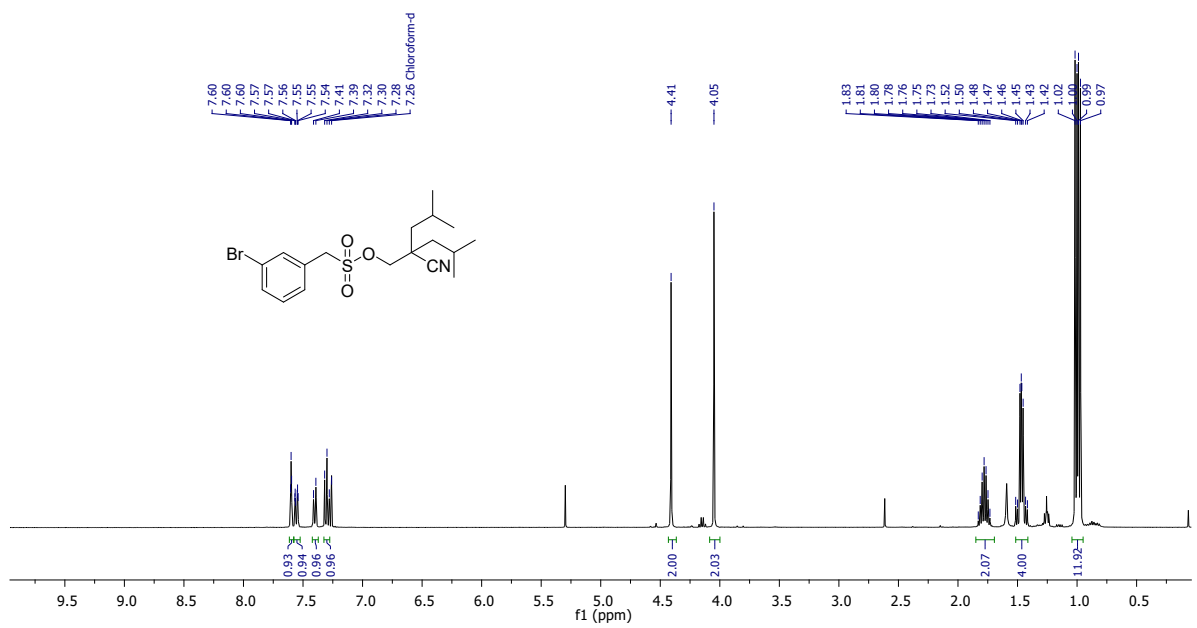
^{13}C $\{^1\text{H}\}$ NMR (100 MHz) spectrum of *If* in CDCl_3



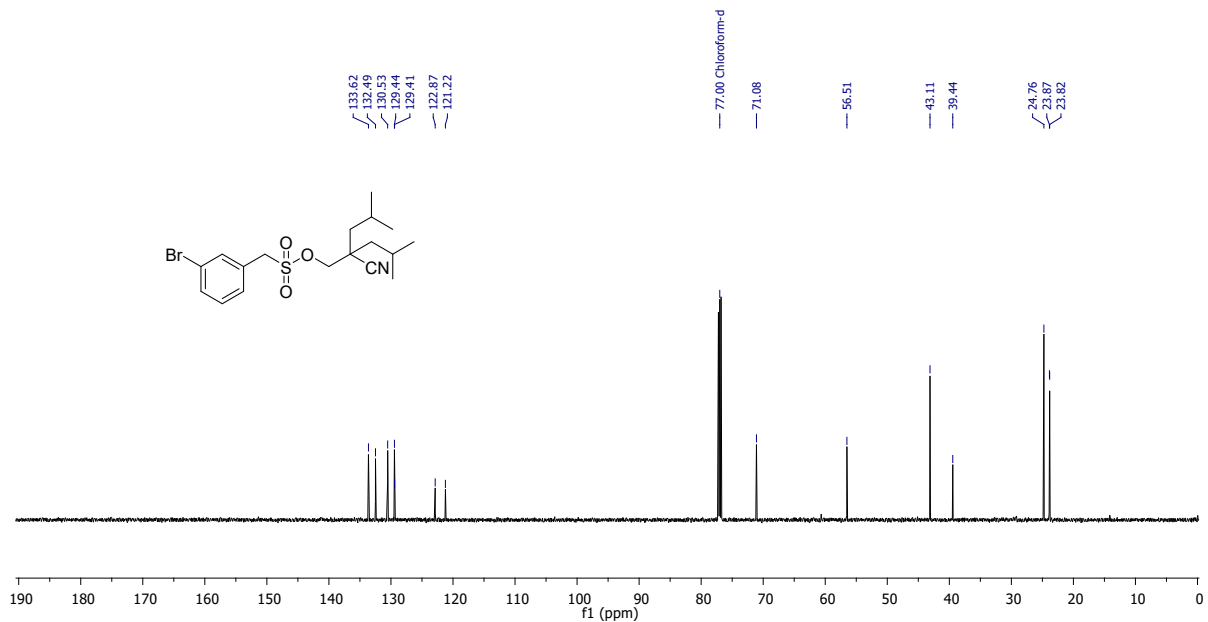
¹H NMR (400 MHz) spectrum of **1g** in CDCl₃



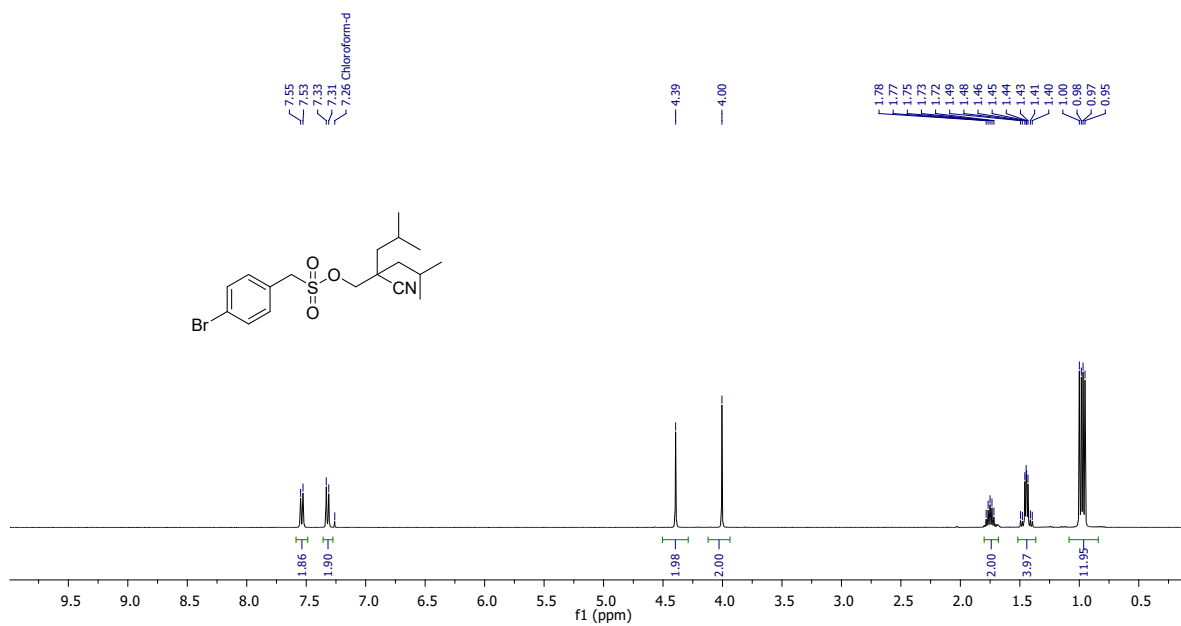
¹³C {¹H} NMR (151 MHz) spectrum of **1g** in CDCl₃



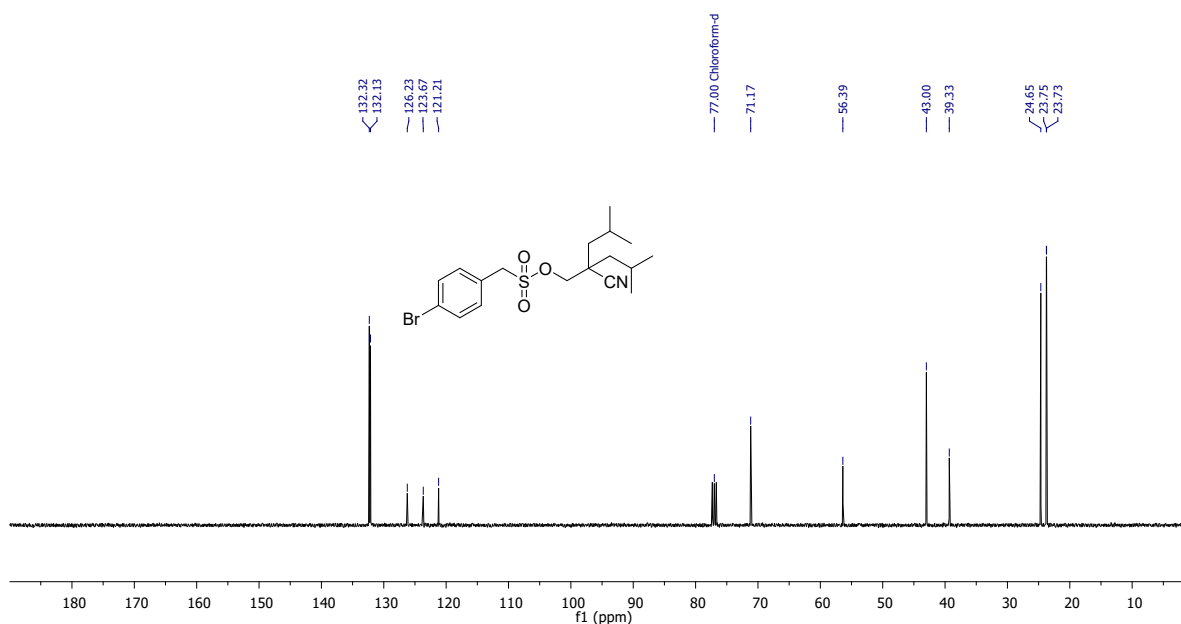
¹H NMR (400 MHz) spectrum of **1h** in CDCl₃



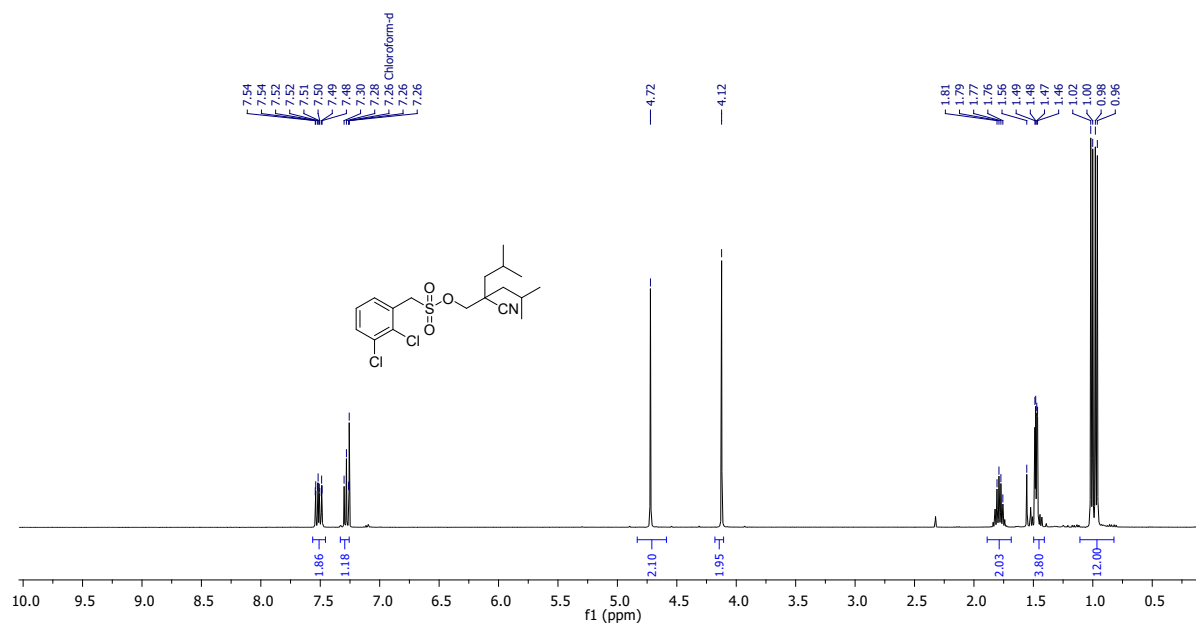
¹³C {¹H} NMR (151 MHz) spectrum of **1h** in CDCl₃



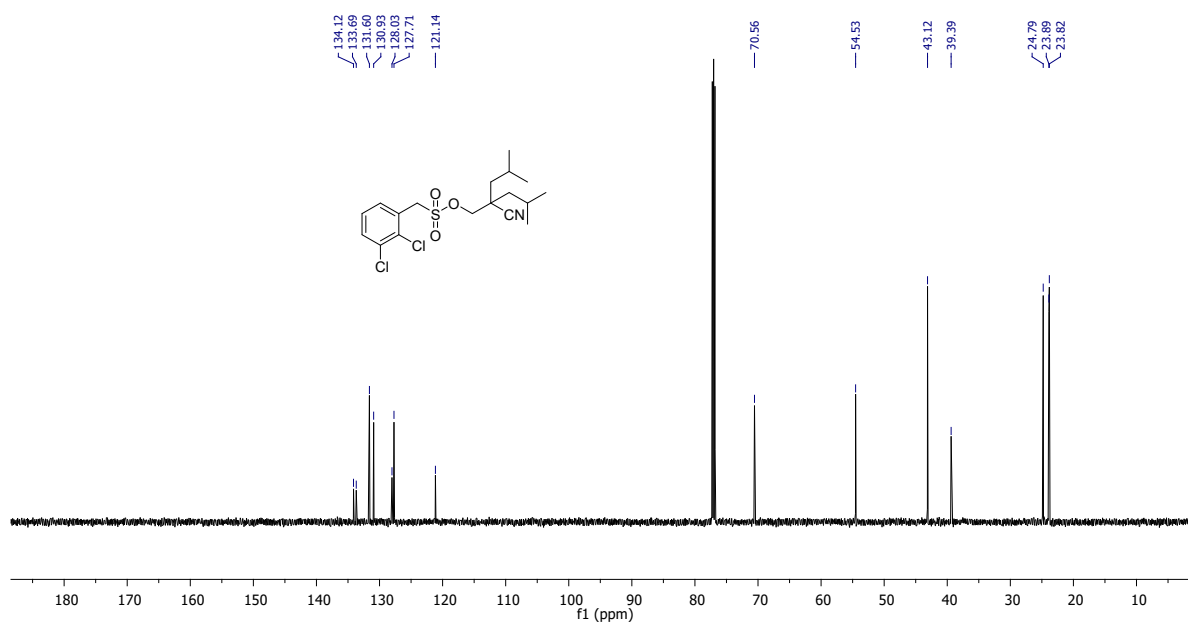
¹H NMR (400 MHz) spectrum of **1i** in CDCl₃



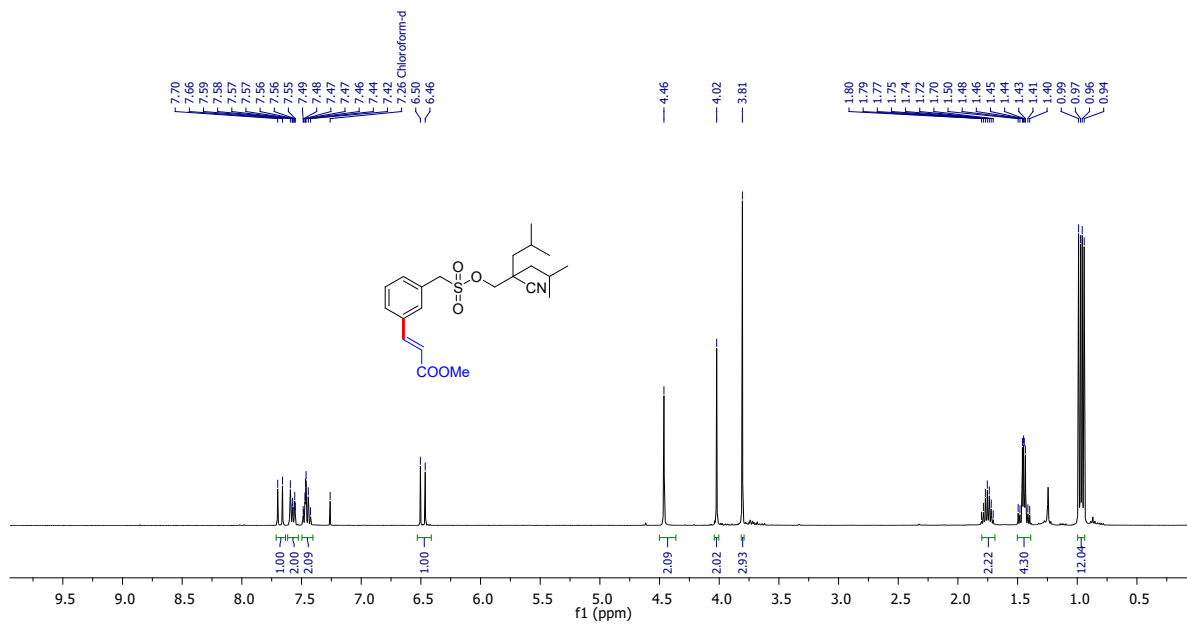
¹³C {¹H} NMR (100 MHz) spectrum of **1i** in CDCl₃



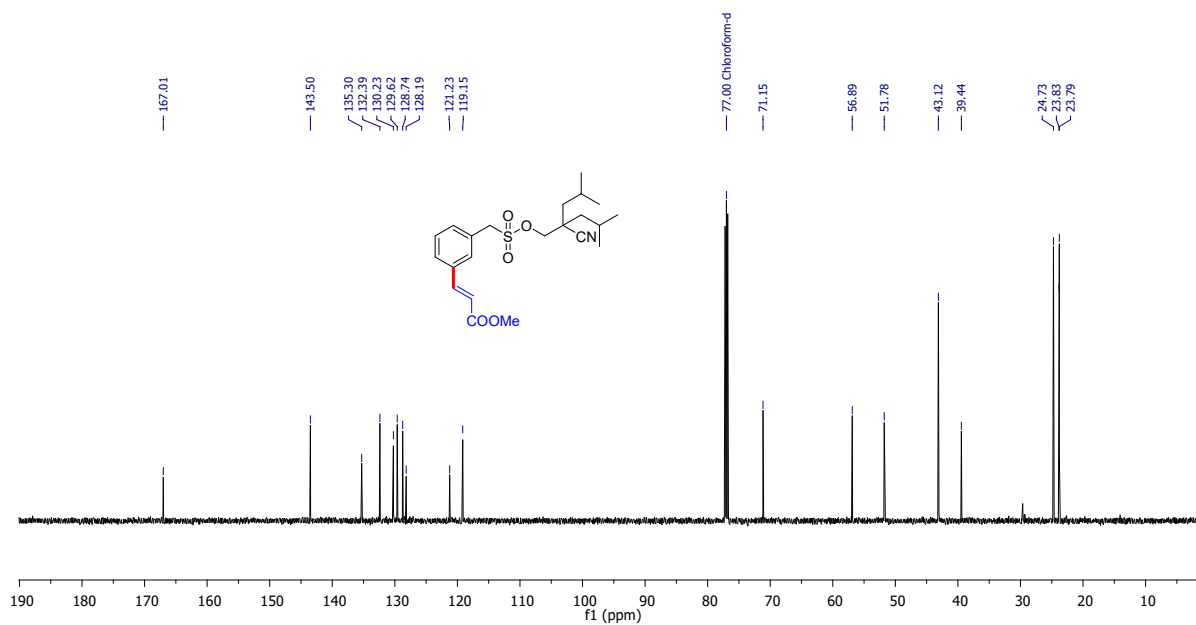
^1H NMR (400 MHz) spectrum of **1j** in CDCl_3



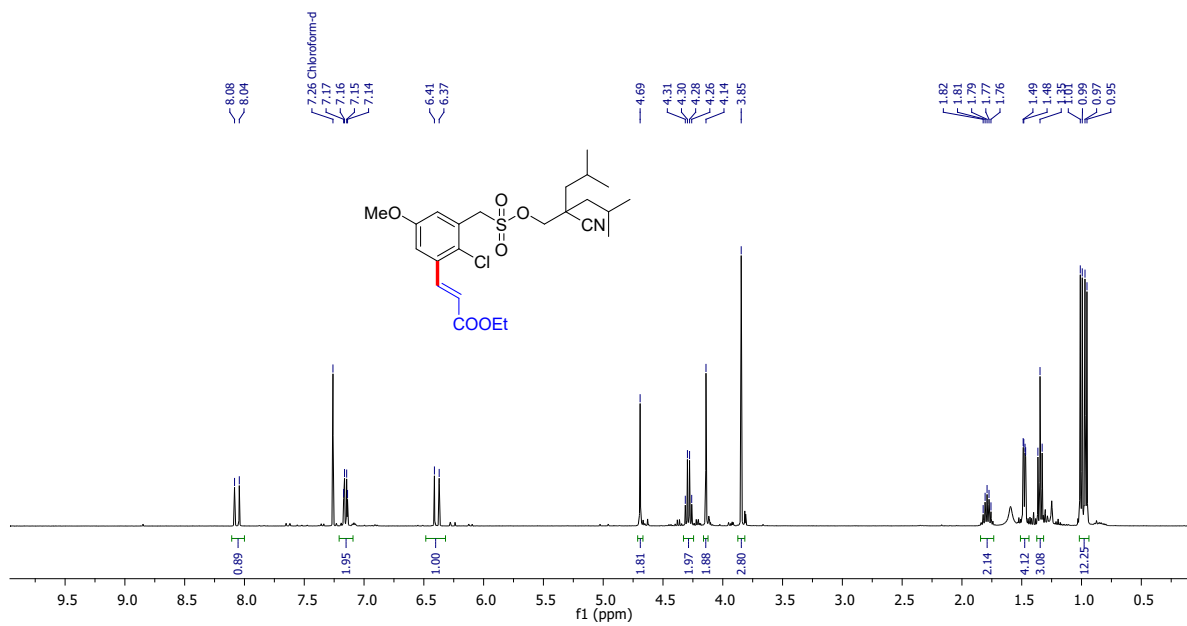
^{13}C $\{^1\text{H}\}$ NMR (151 MHz) spectrum of **1j** in CDCl_3



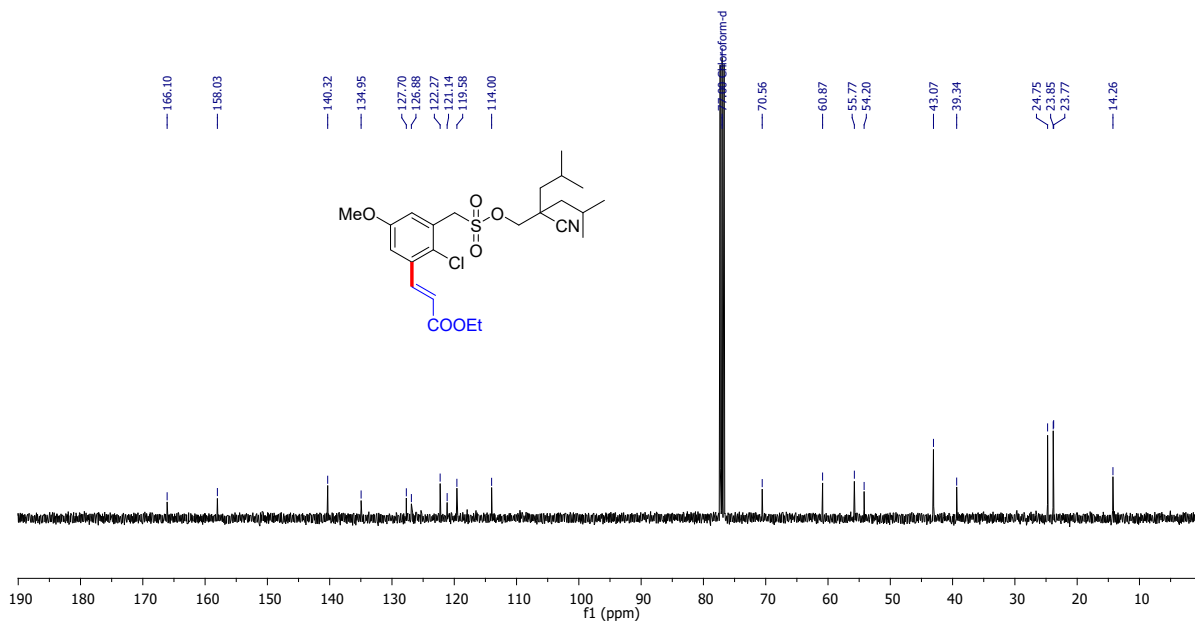
¹H NMR (400 MHz) spectrum of **3ab** in CDCl₃



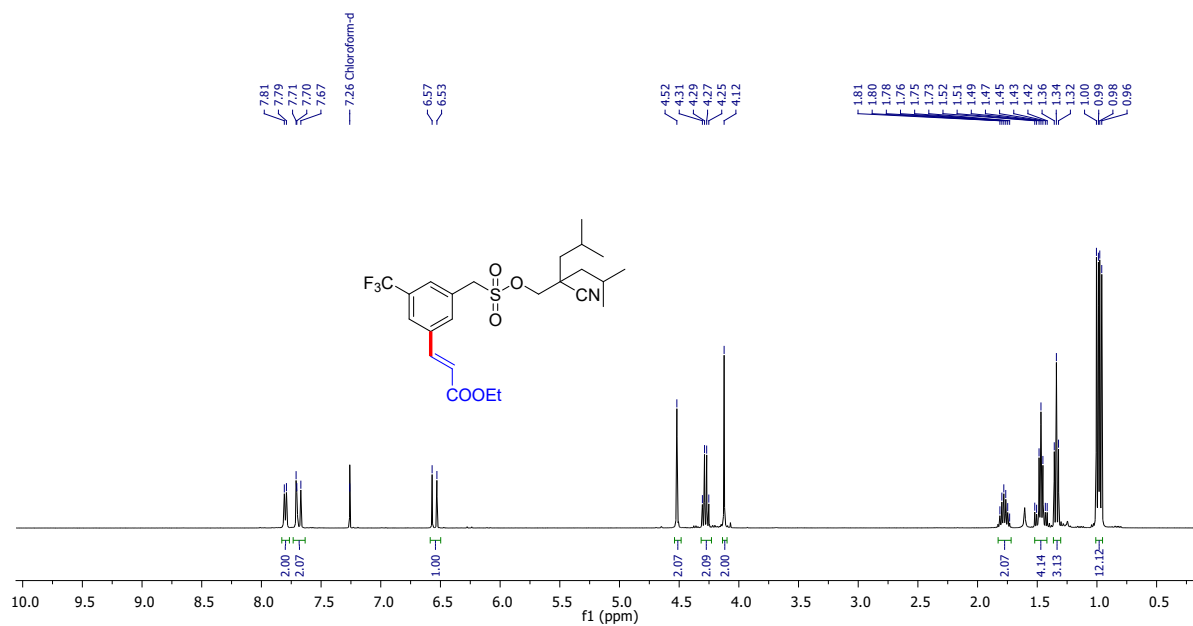
¹³C {¹H} NMR (151 MHz) spectrum of **3ab** in CDCl₃



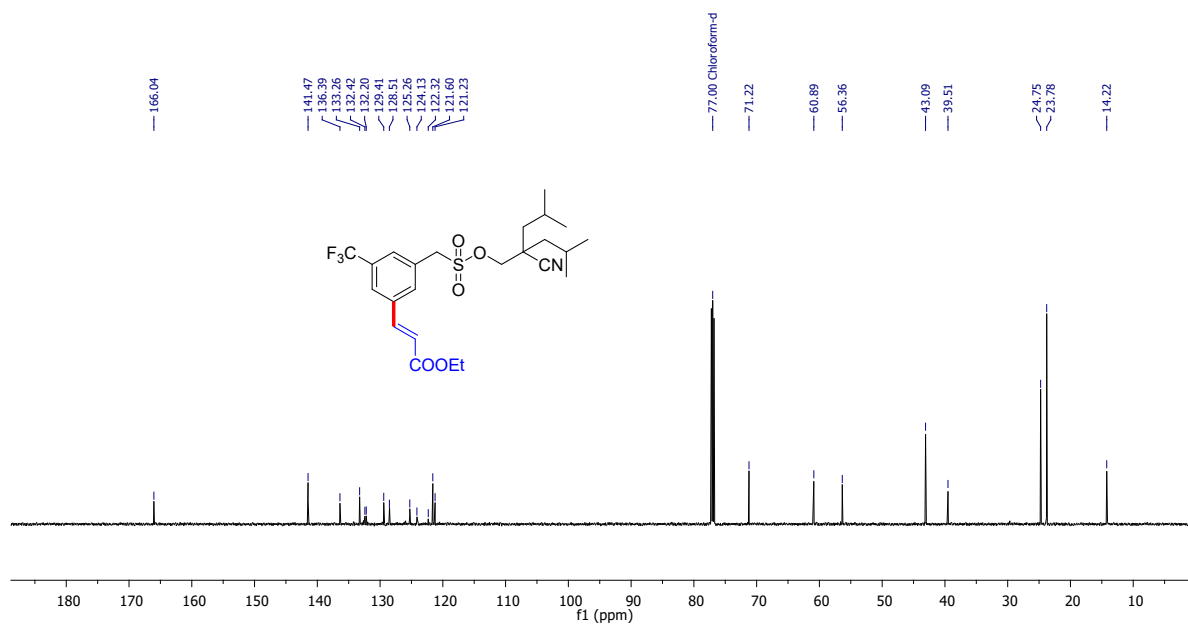
¹H NMR (400 MHz) spectrum of *3ba* in CDCl₃



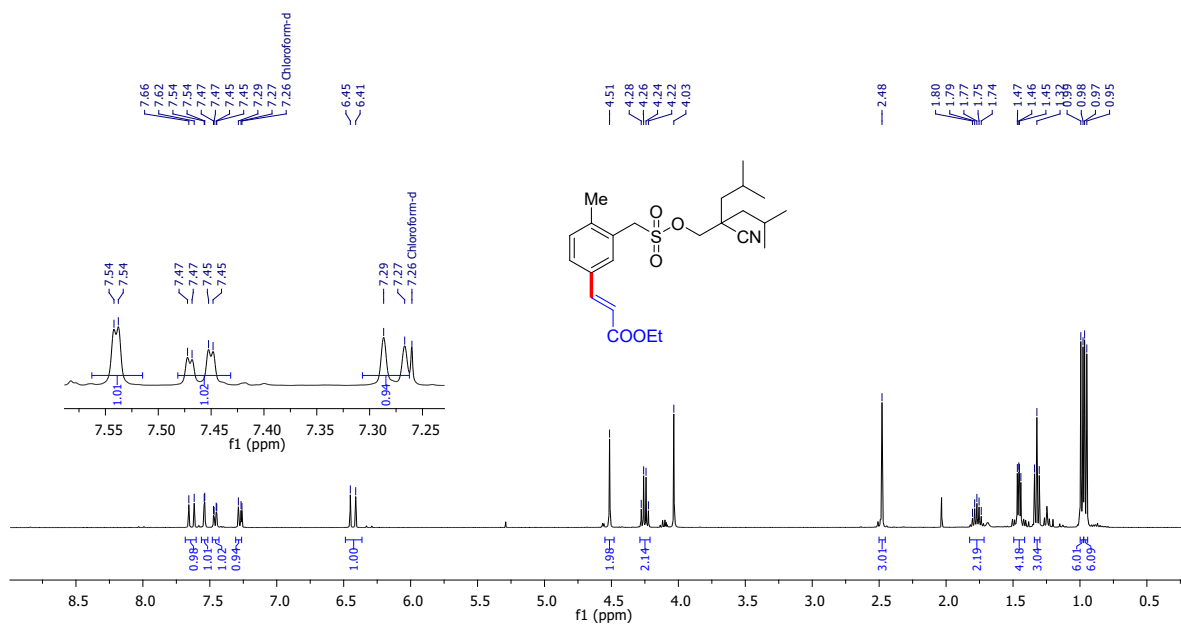
¹³C {¹H} NMR (100 MHz) spectrum of *3ba* in CDCl₃



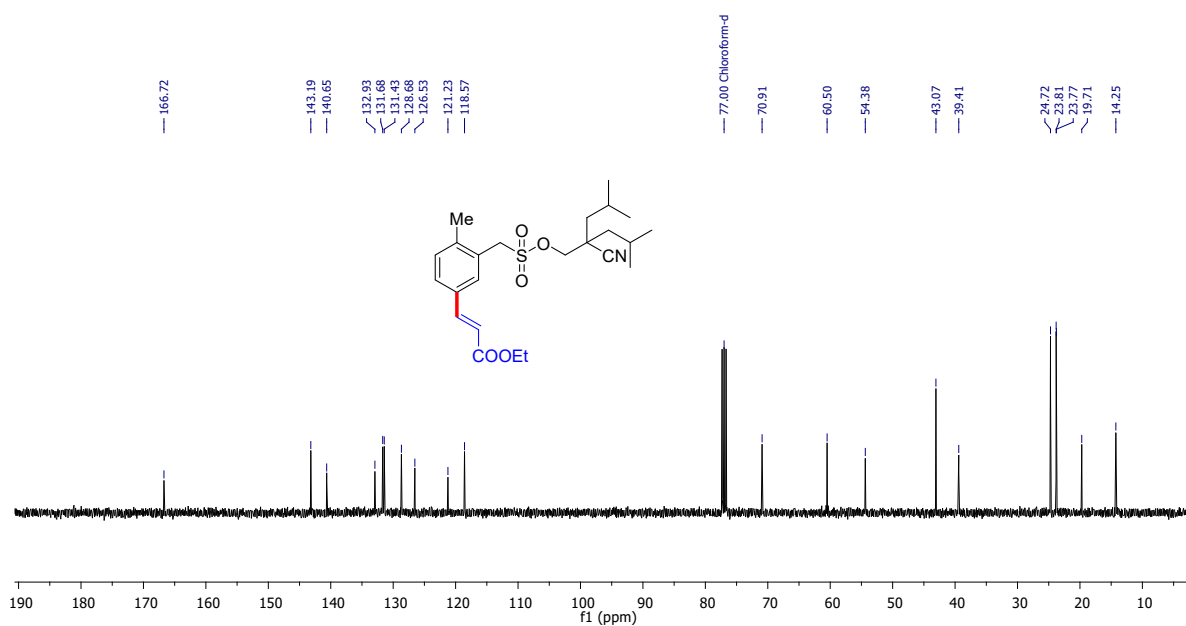
¹H NMR (400 MHz) spectrum of **3ca** in CDCl₃



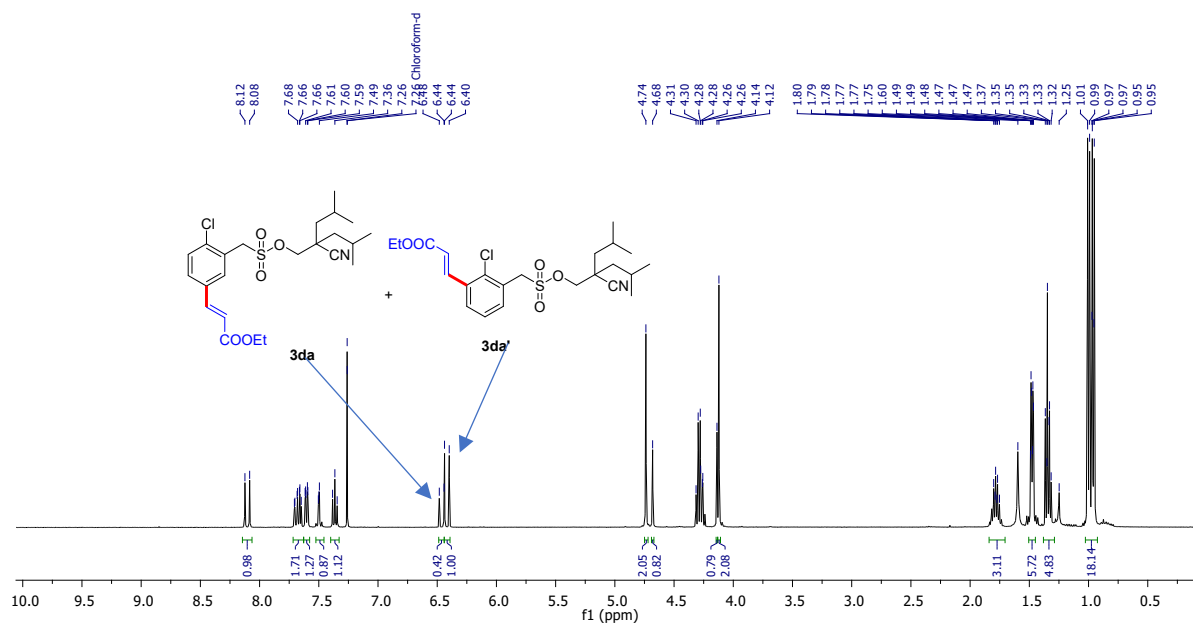
¹³C {¹H} NMR (151 MHz) spectrum of **3ca** in CDCl₃



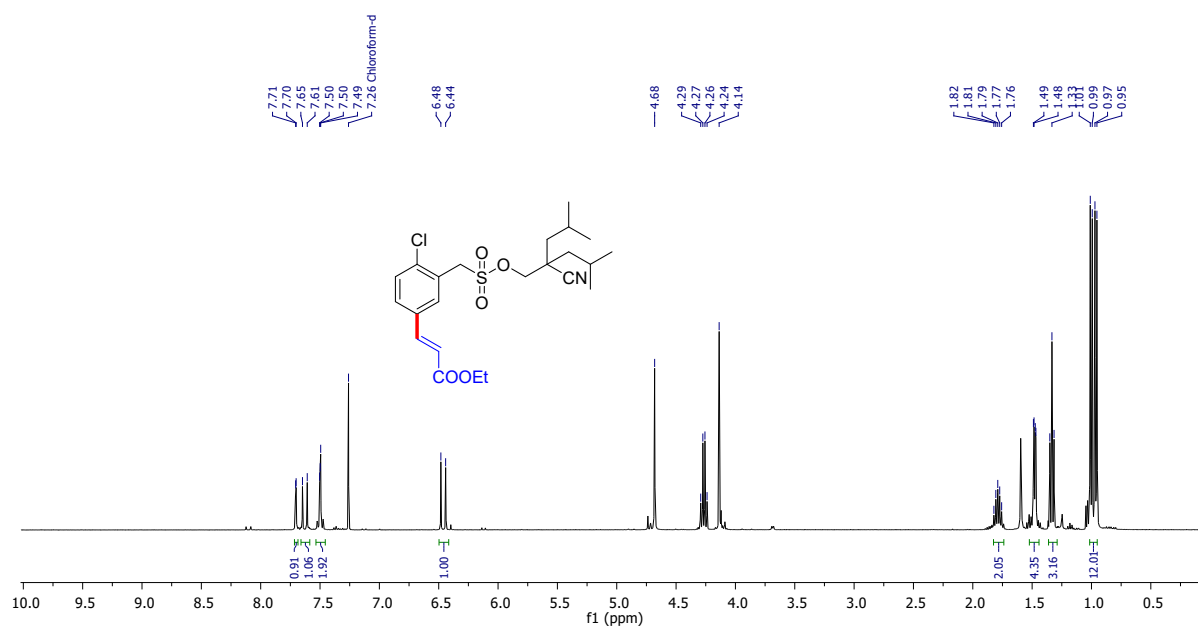
¹H NMR (400 MHz) spectrum of *3ma* in CDCl₃



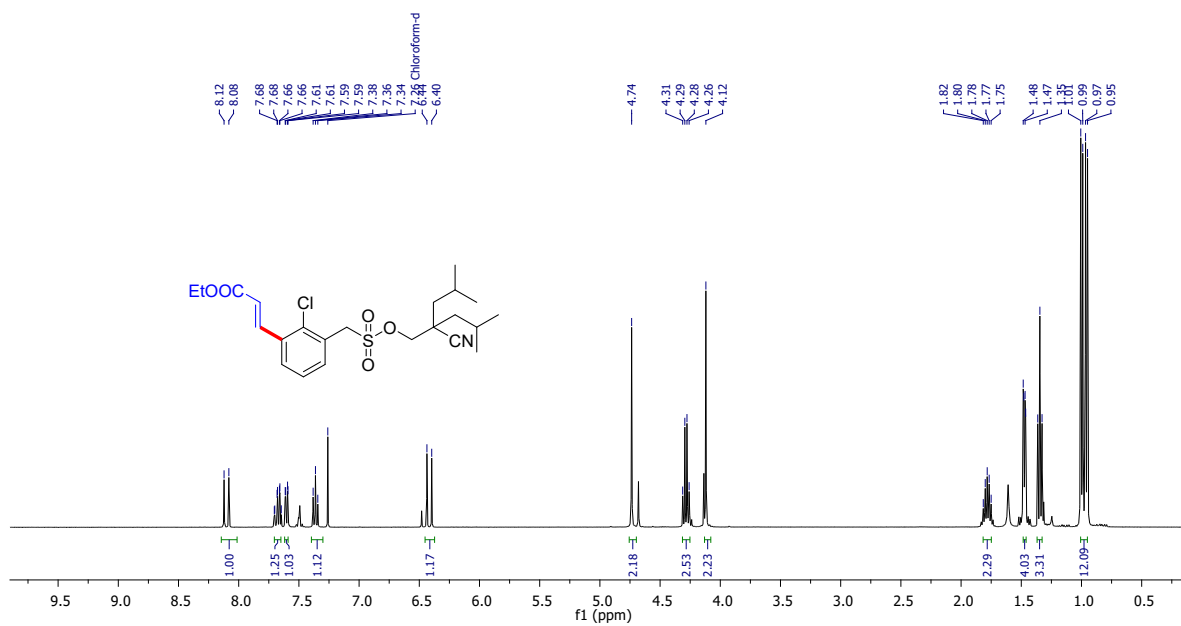
¹³C {¹H} NMR (100 MHz) spectrum of *3ma* in CDCl₃



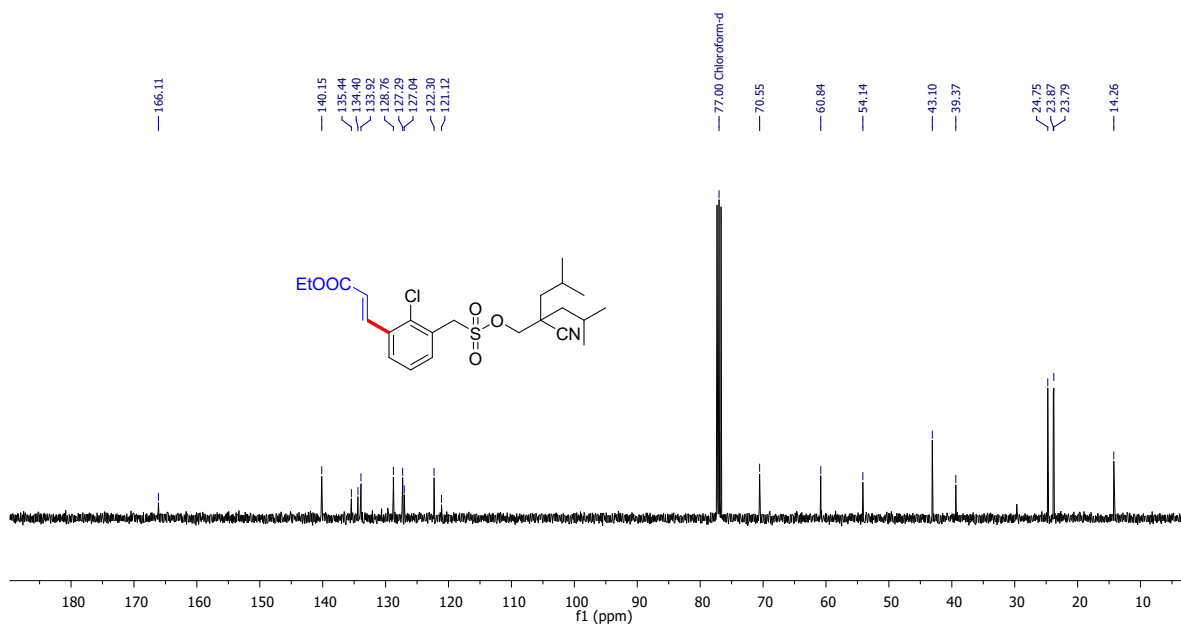
$^1\text{H NMR}$ (400 MHz) spectrum of mixture of **3da** and **3da'** in CDCl_3



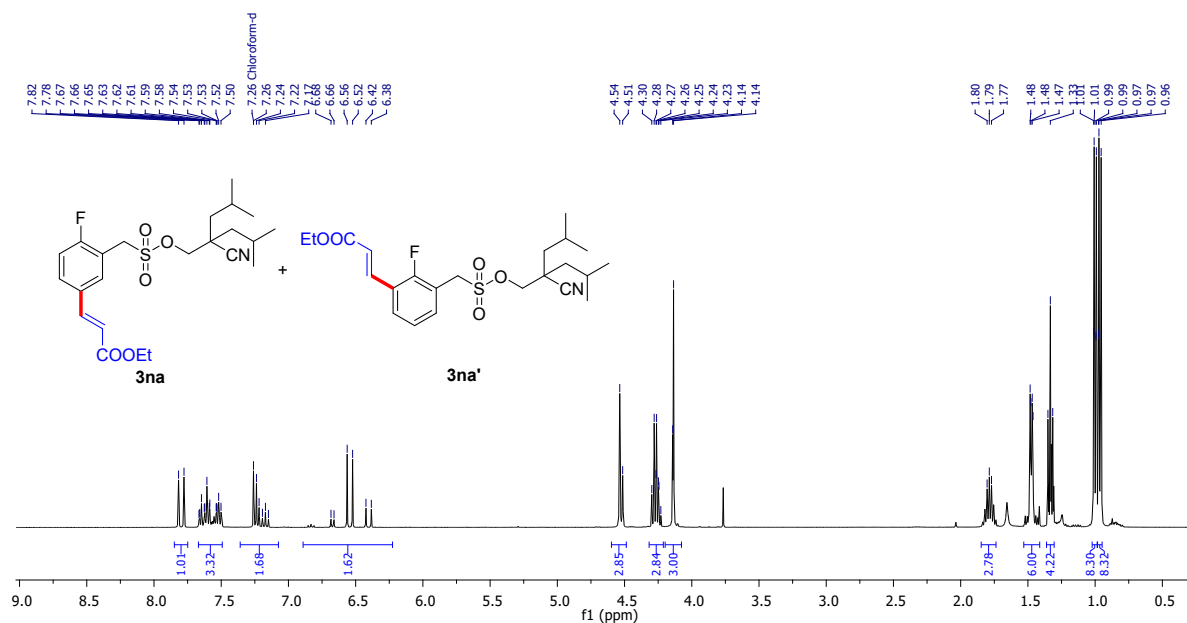
$^1\text{H NMR}$ (400 MHz) spectrum of **3da** in CDCl_3



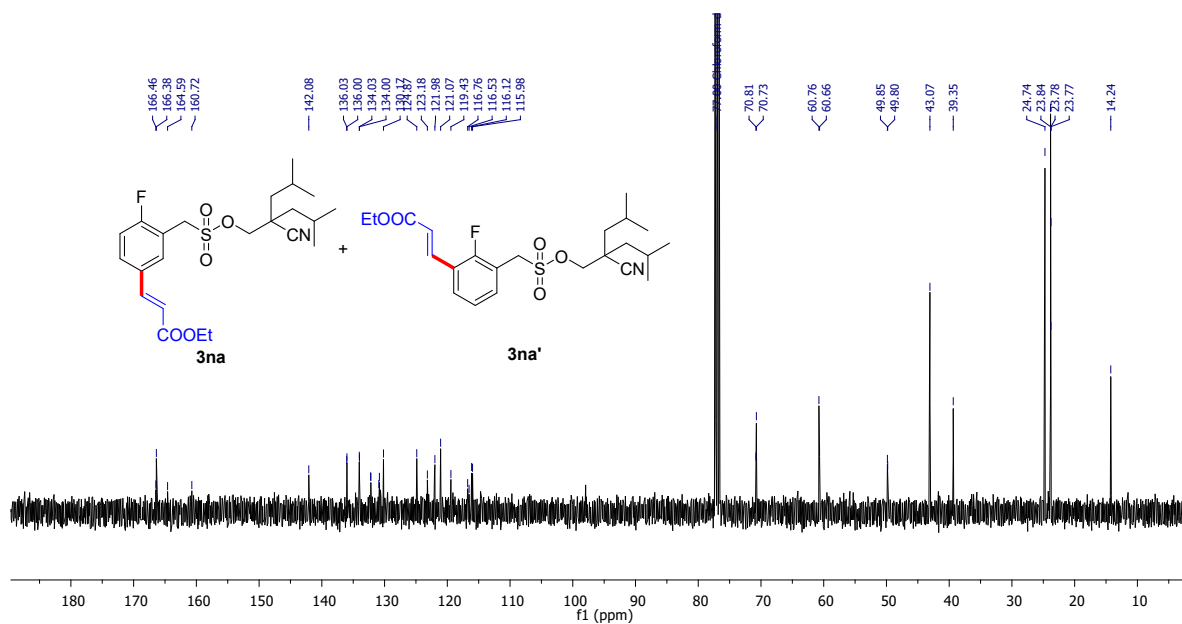
¹H NMR (400 MHz) spectrum of **3da'** in CDCl₃



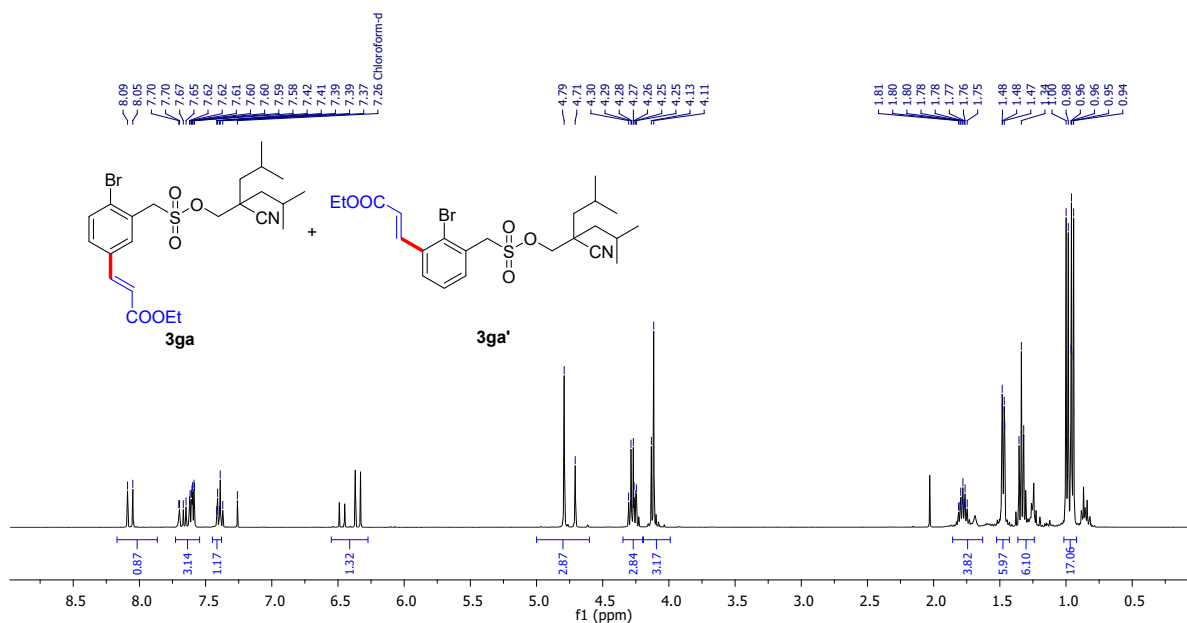
¹³C {¹H} NMR (100 MHz) spectrum of **3da'** in CDCl₃



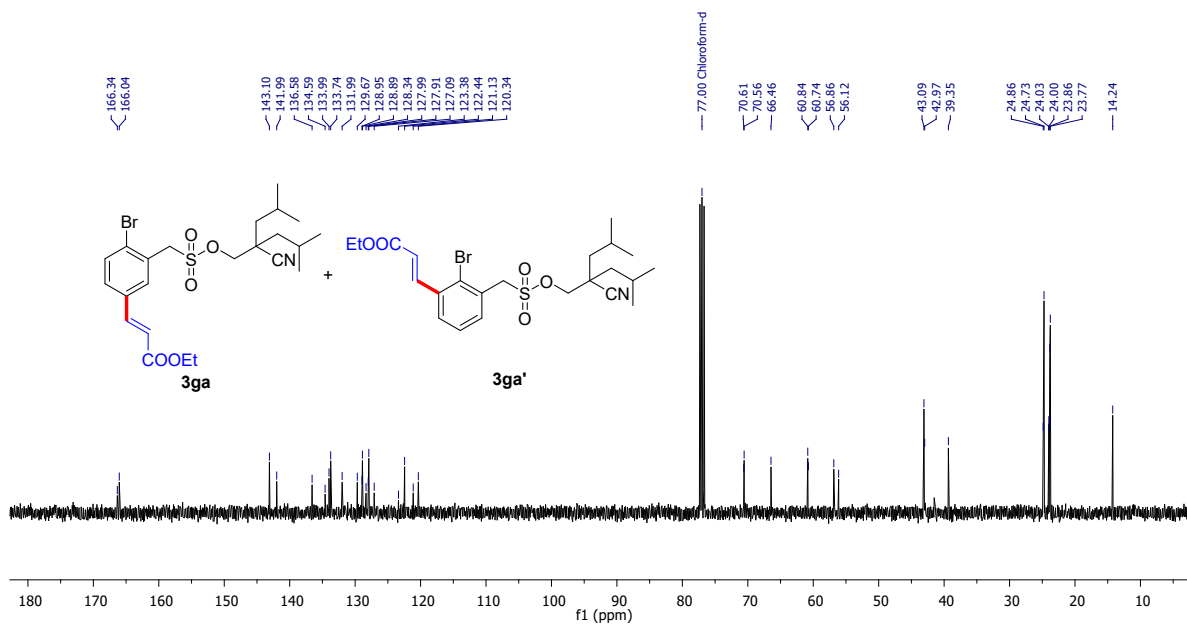
¹H NMR (400 MHz) spectrum of mixture of **3na** and **3na'** in CDCl₃



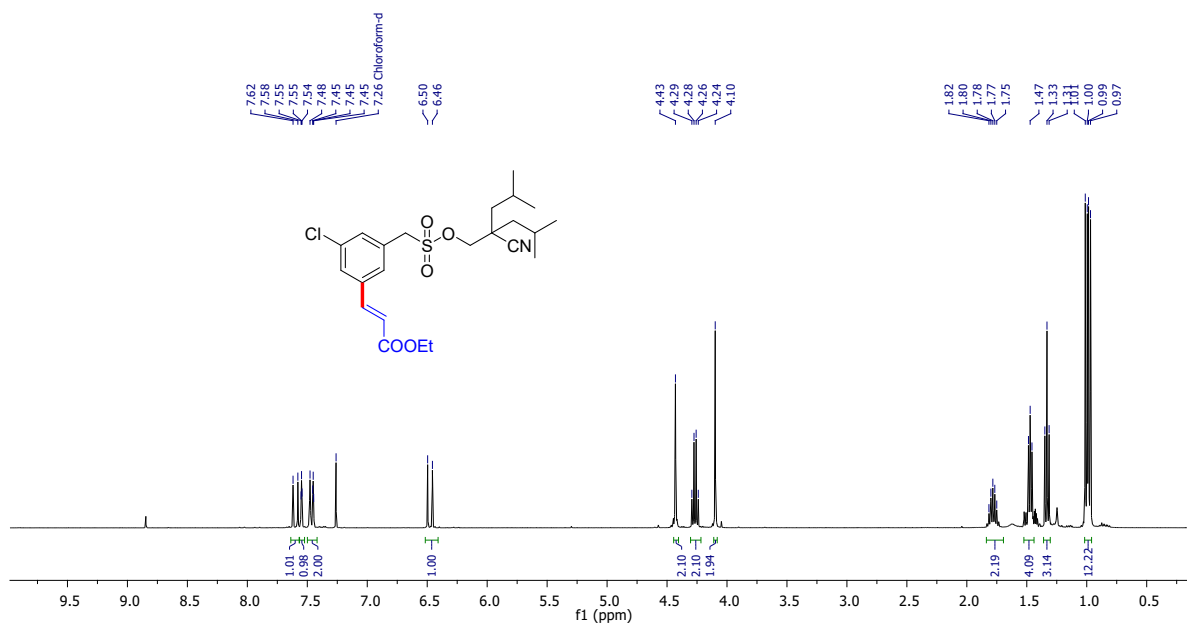
¹³C NMR (100 MHz) spectrum of mixture of **3na** and **3na'** in CDCl₃



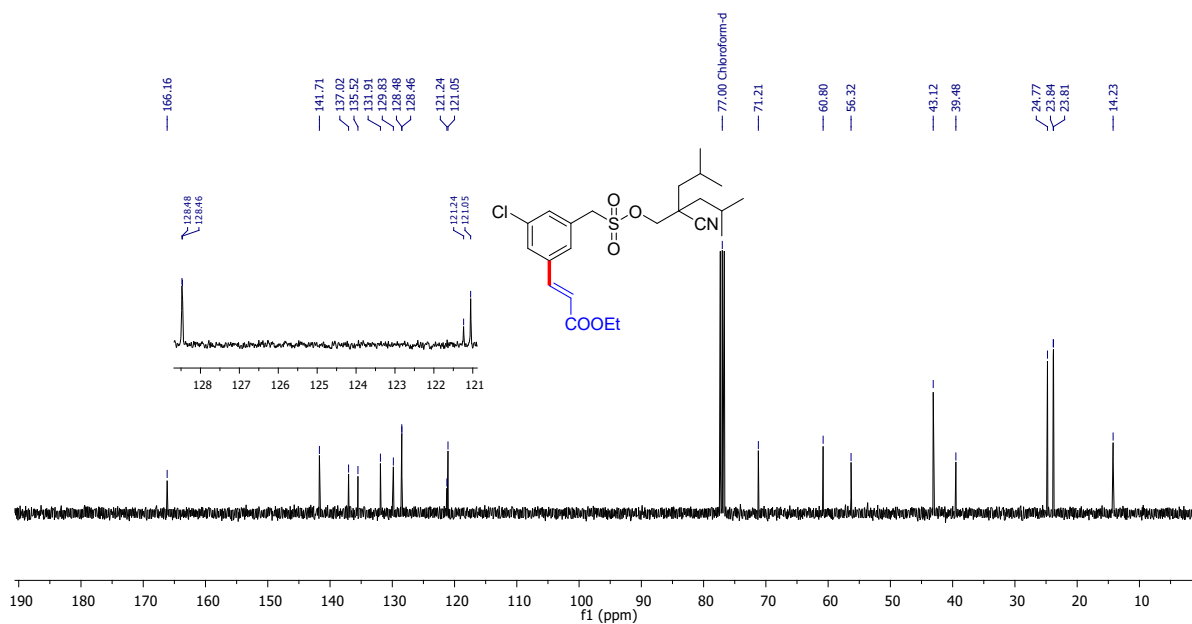
¹H NMR (400 MHz) spectrum of mixture of **3ga** and **3ga'** in CDCl₃



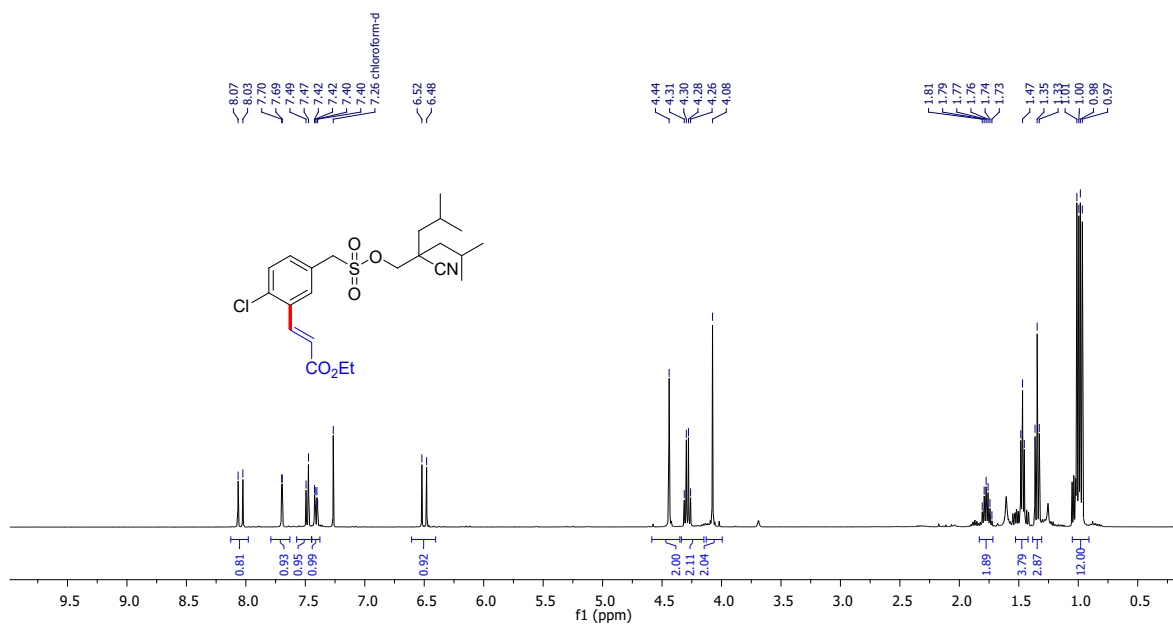
¹³C NMR (100 MHz) spectrum of mixture of **3ga** and **3ga'** in CDCl₃



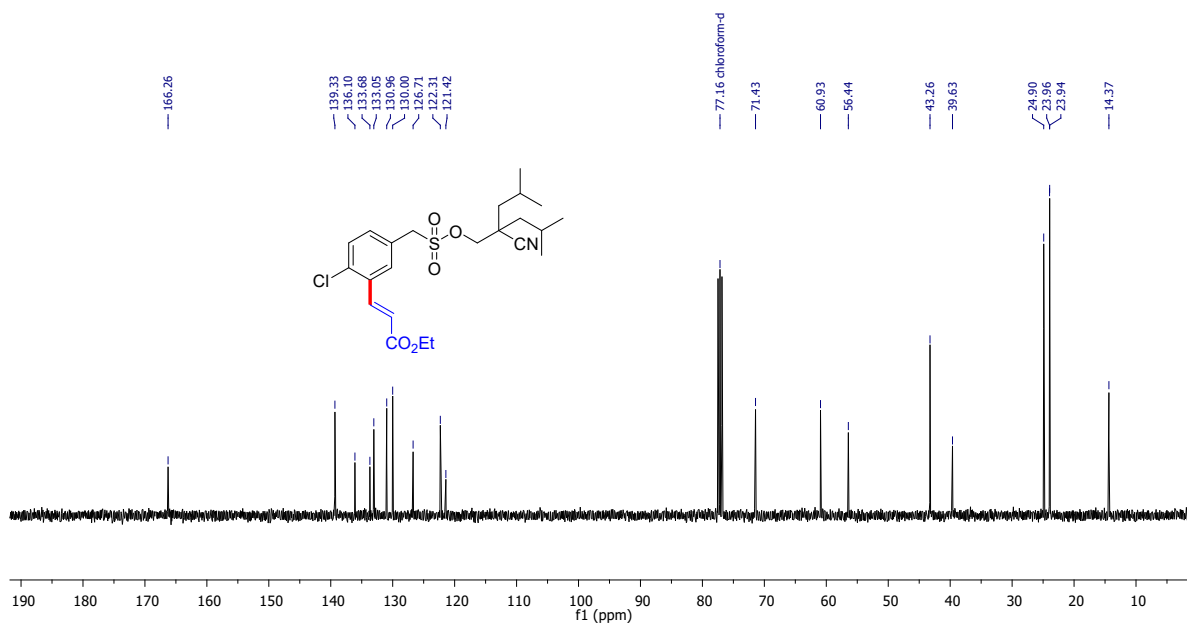
¹H NMR (400 MHz) spectrum of **3ea** in CDCl₃



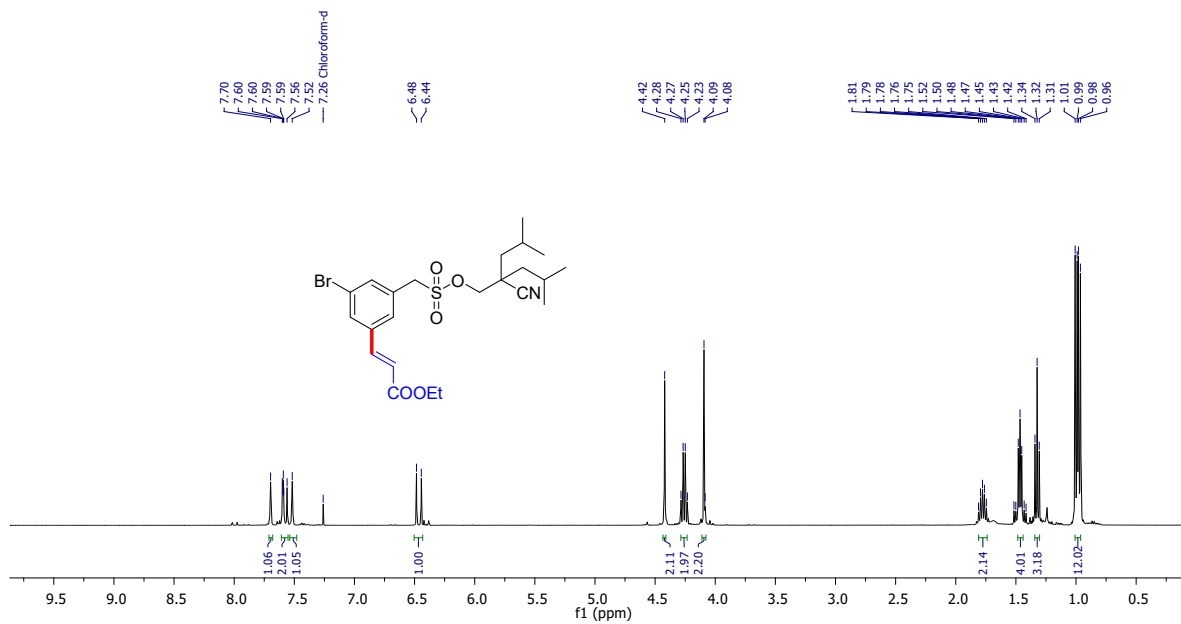
¹³C {¹H} NMR (100 MHz) spectrum of **3ea** in CDCl₃



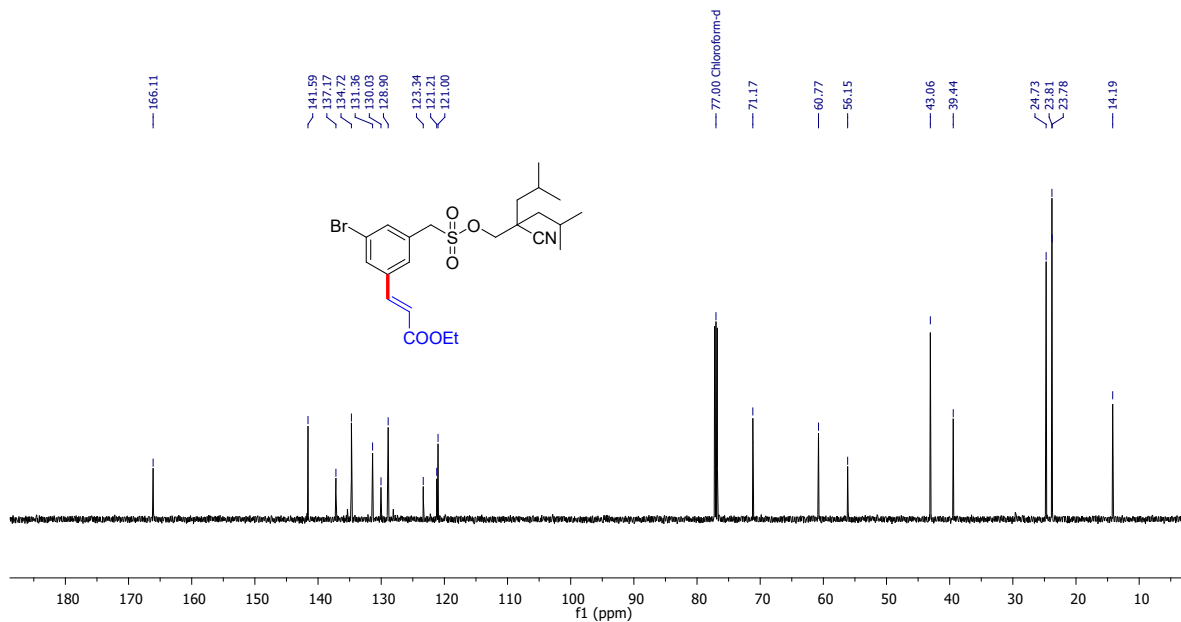
¹H NMR (400 MHz) spectrum of **3fa** in CDCl₃



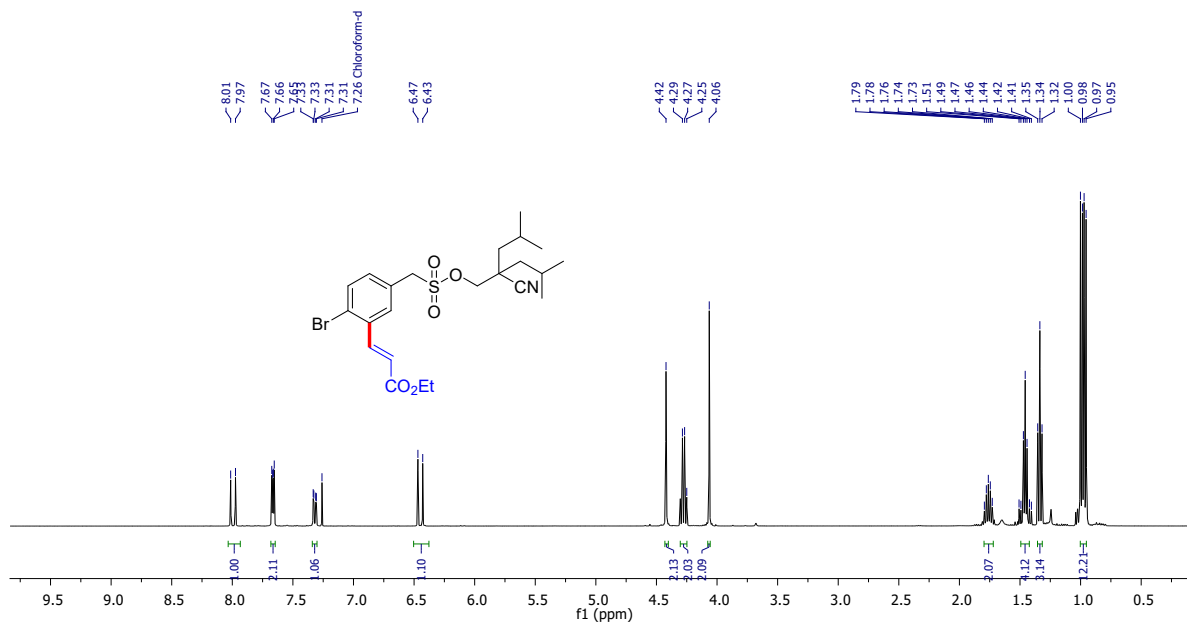
¹³C {¹H} NMR (100 MHz) spectrum of **3fa** in CDCl₃



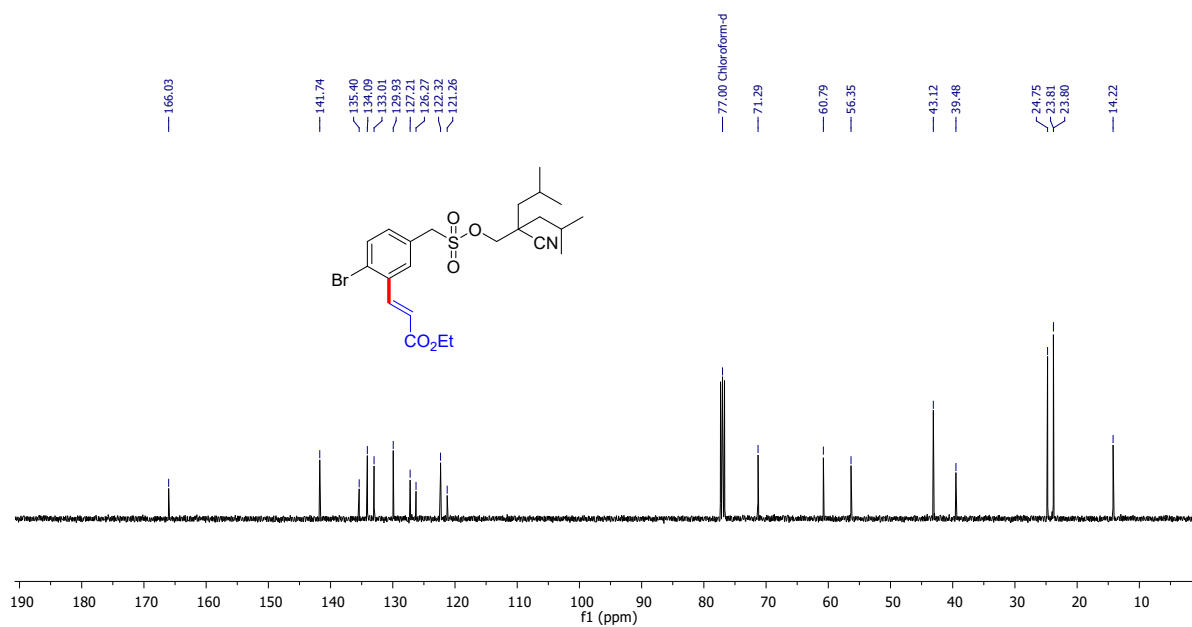
¹H NMR (400 MHz) spectrum of *3ha* in CDCl₃



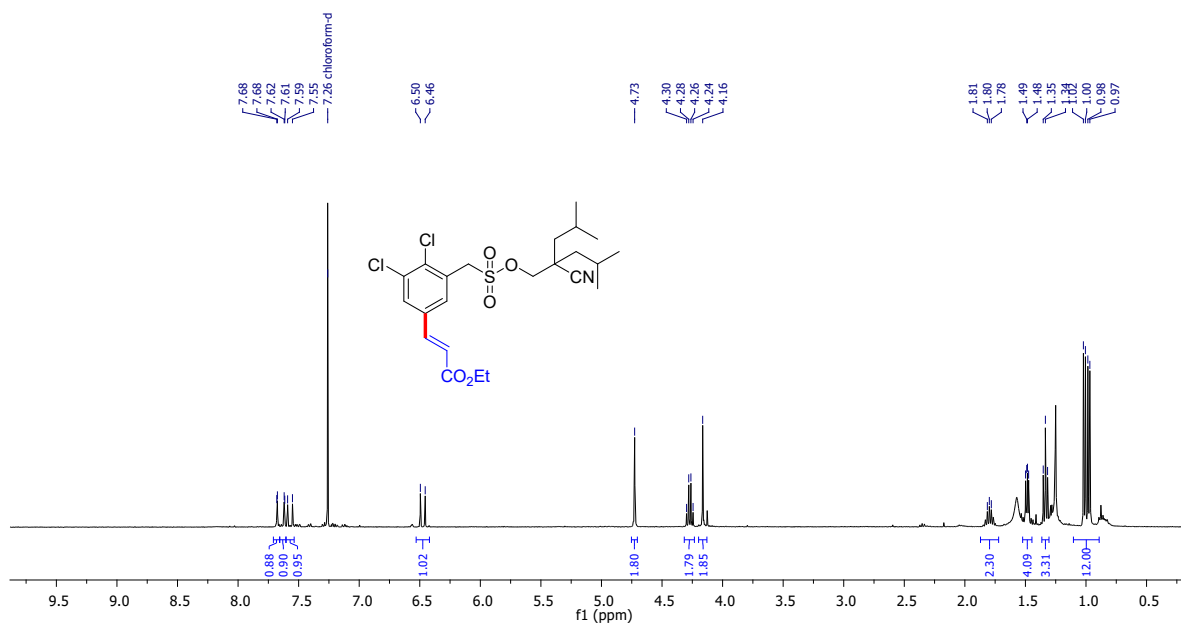
¹³C {¹H} NMR (151 MHz) spectrum of *3ha* in CDCl₃



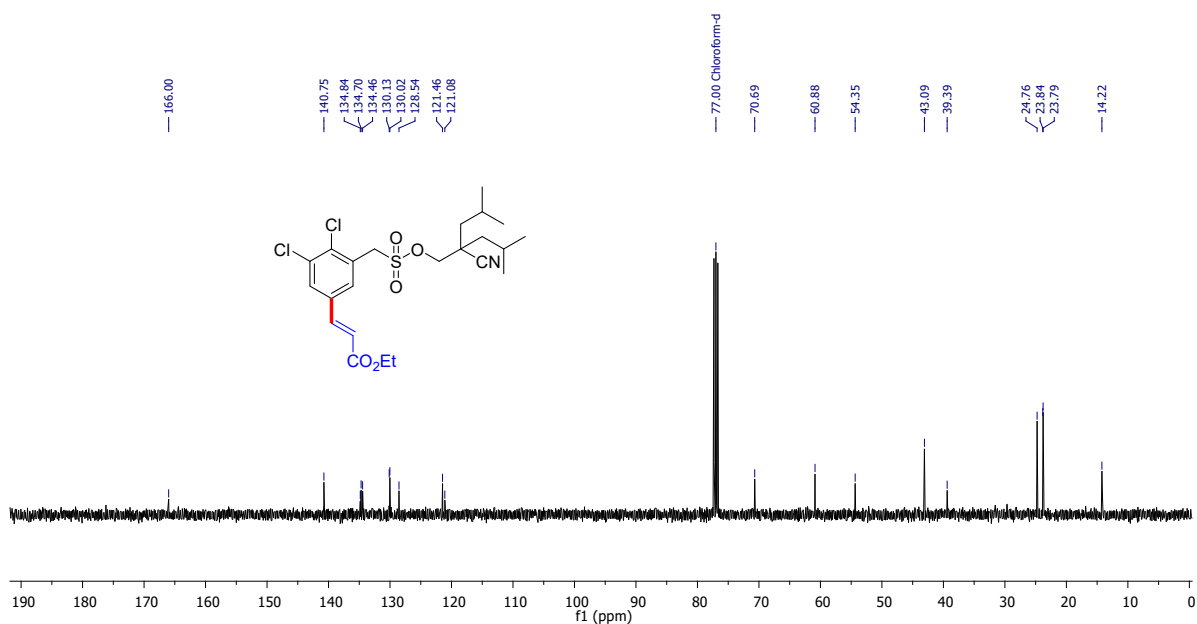
¹H NMR (400 MHz) spectrum of *3ia* in CDCl₃



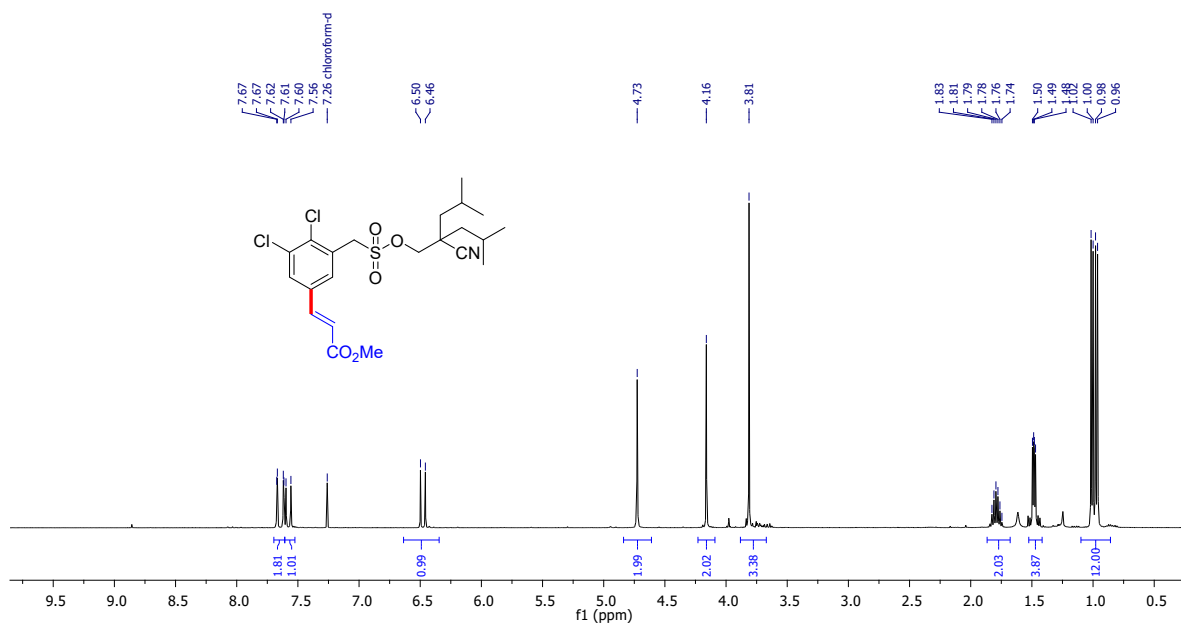
¹³C {¹H} NMR (100 MHz) spectrum of *3ia* in CDCl₃



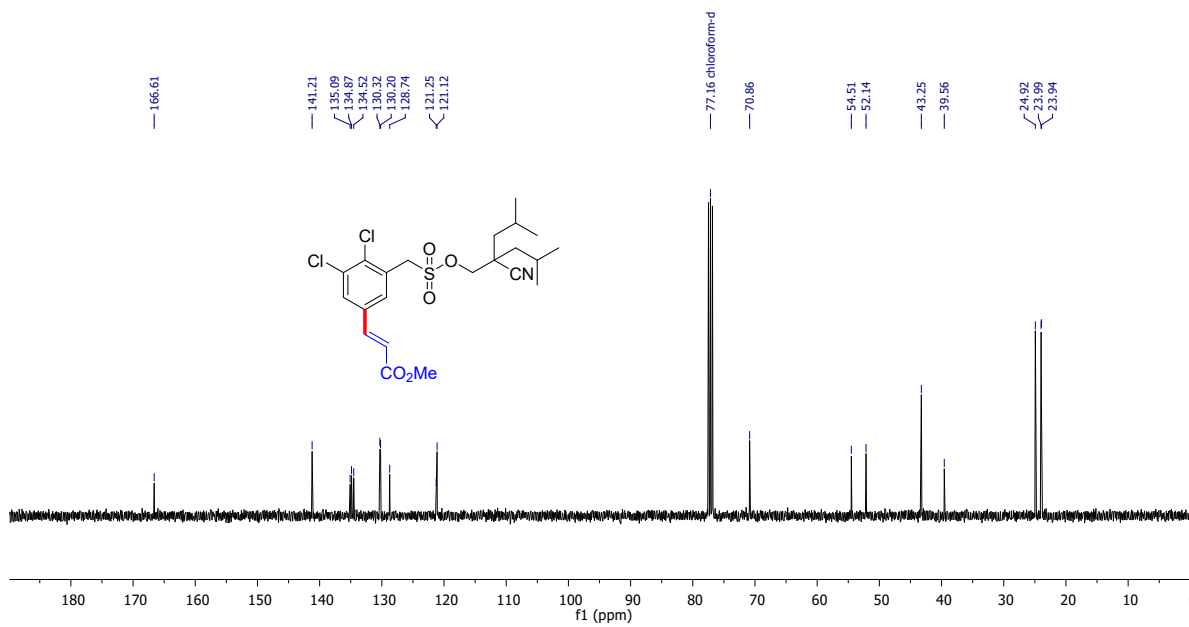
¹H NMR (400 MHz) spectrum of **3ja** in CDCl₃



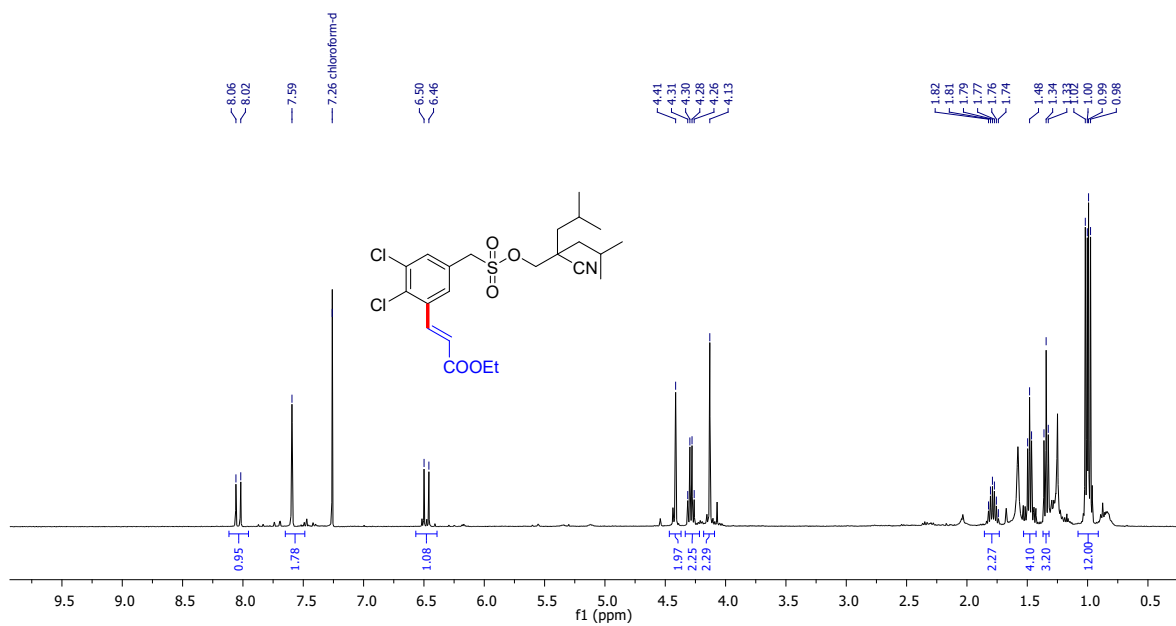
¹³C {¹H} NMR (100 MHz) spectrum of **3ja** in CDCl₃



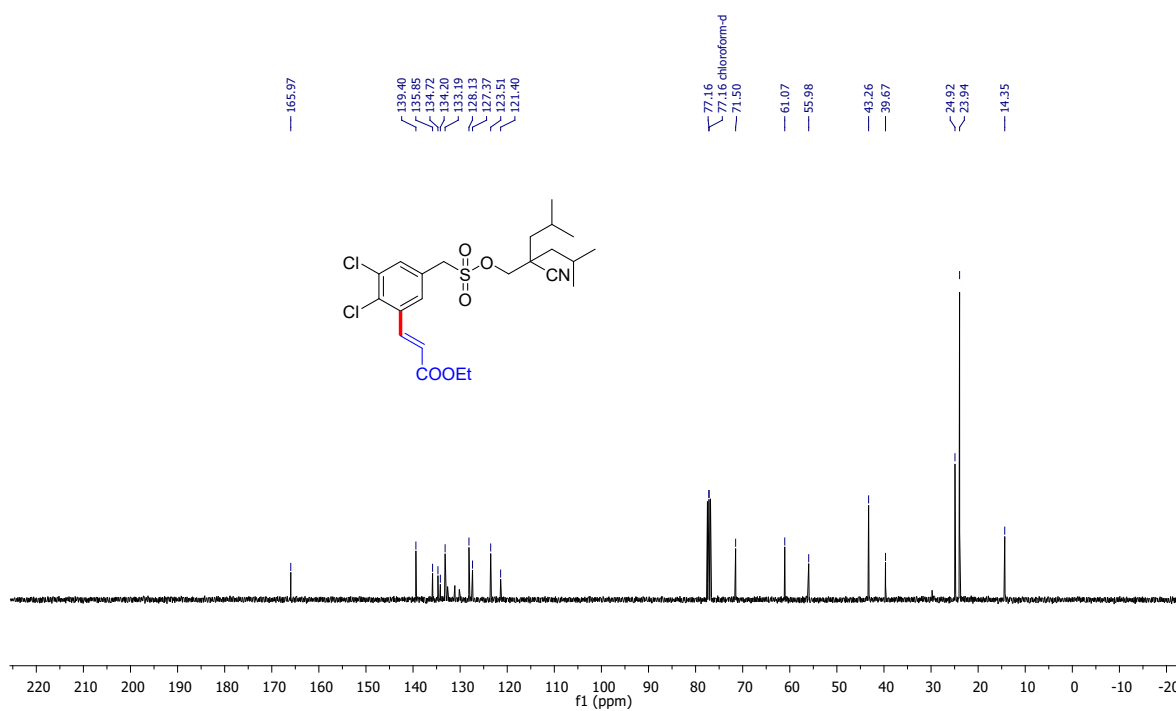
¹H NMR (400 MHz) spectrum of **3jb** in CDCl₃



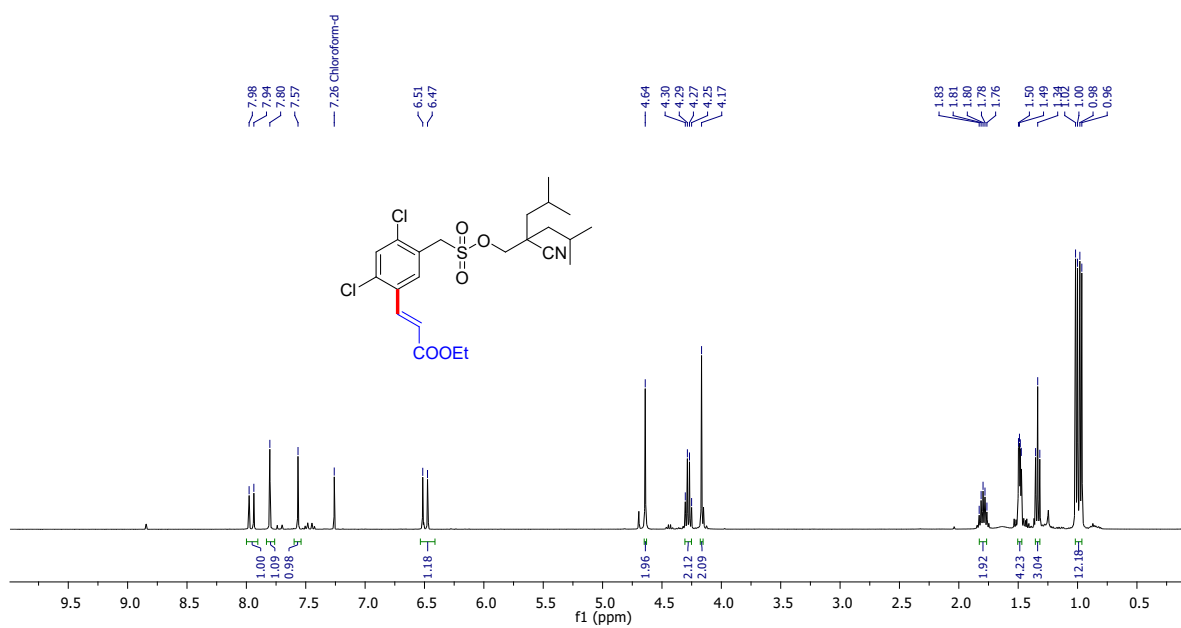
¹³C {¹H} NMR (100 MHz) spectrum of **3jb** in CDCl₃



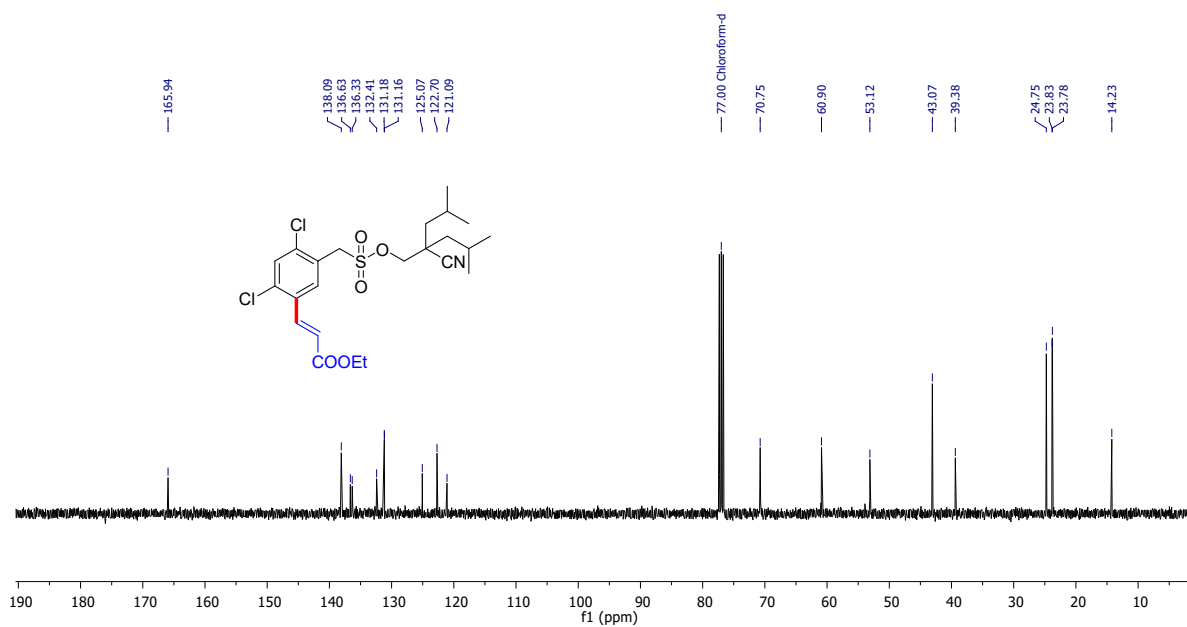
¹H NMR (400 MHz) spectrum of **3ka** in CDCl₃



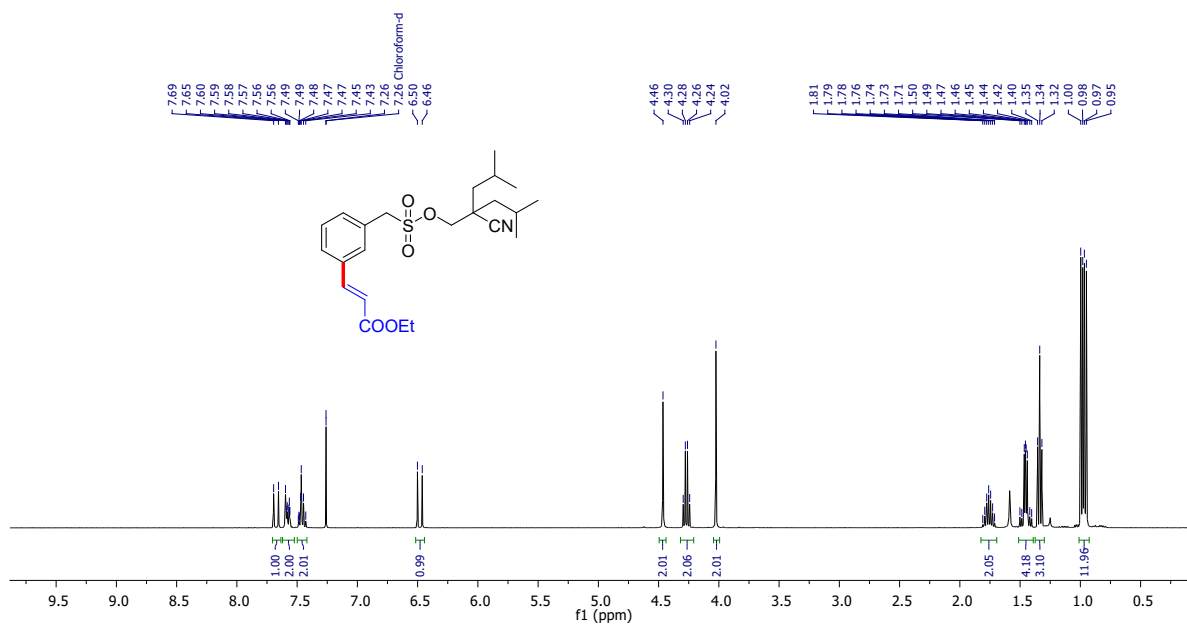
¹³C {¹H} NMR (100 MHz) spectrum of **3ka** in CDCl₃



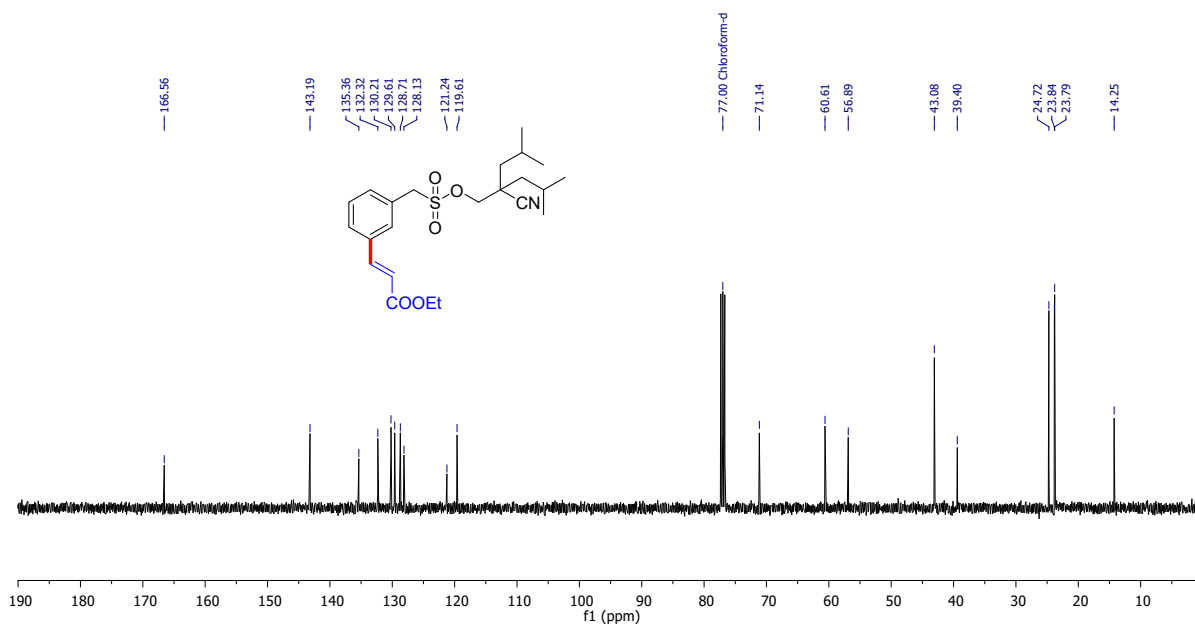
¹H NMR (400 MHz) spectrum of **3la** in CDCl₃



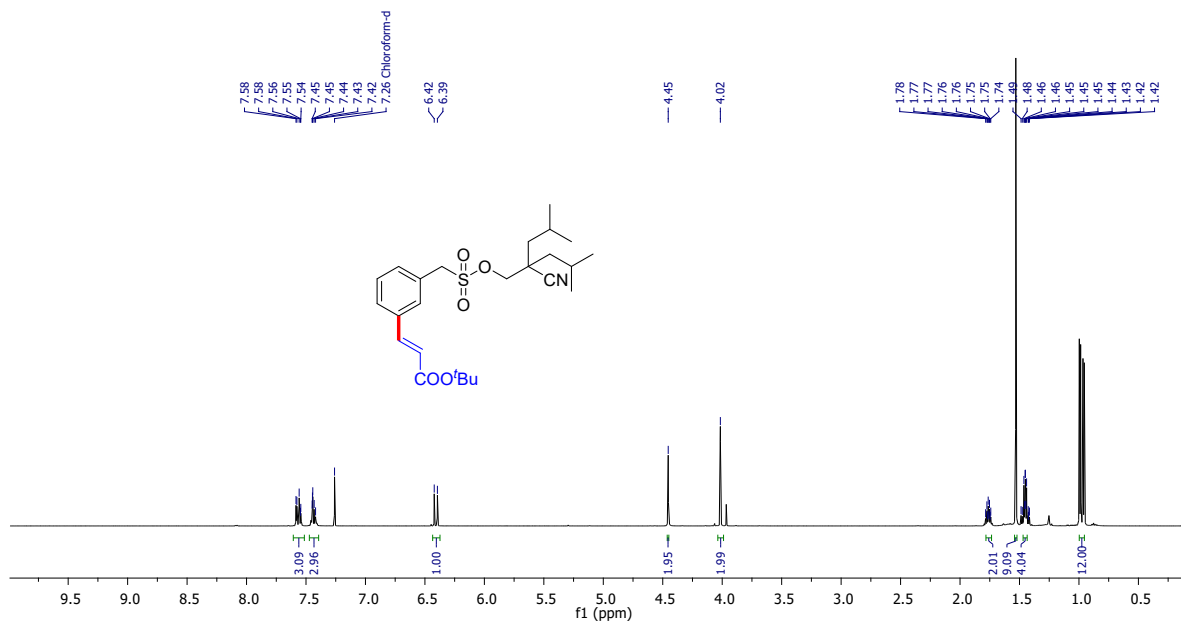
¹³C {¹H} NMR (100 MHz) spectrum of **3la** in CDCl₃



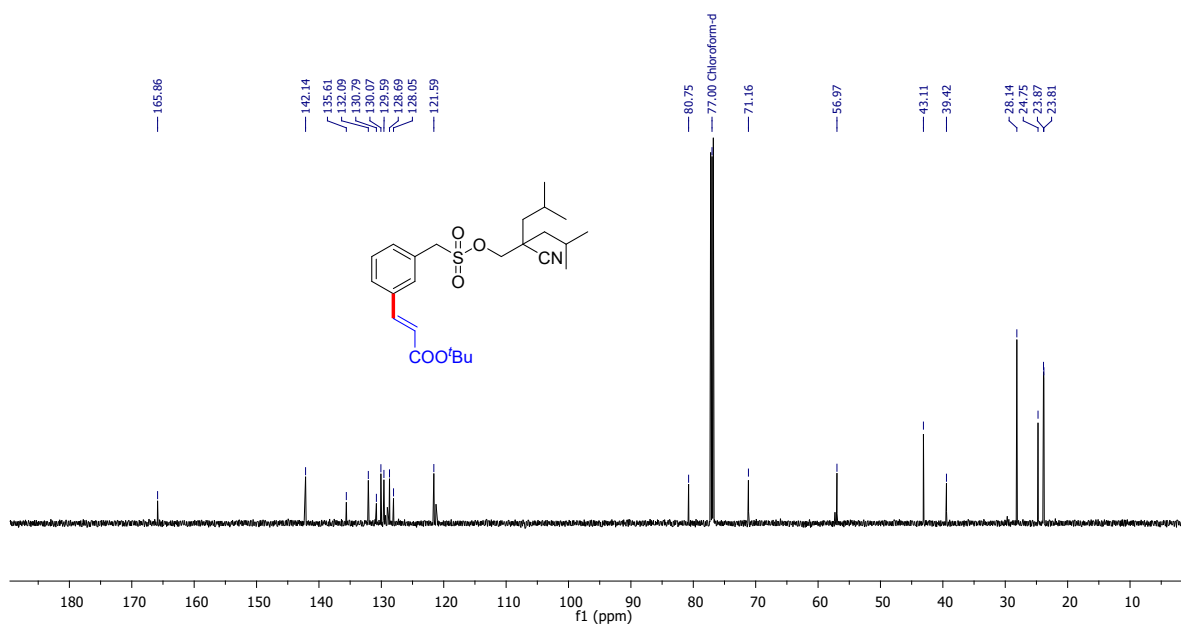
¹H NMR (400 MHz) spectrum of **3aa** in CDCl₃



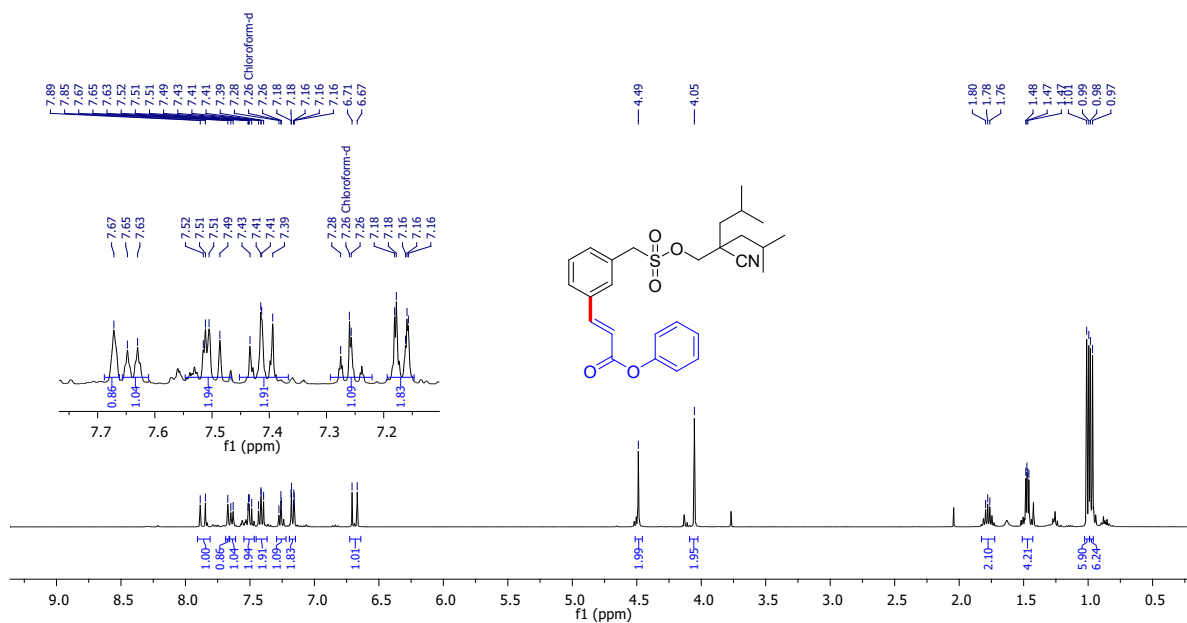
¹³C {¹H} NMR (100 MHz) spectrum of **3aa** in CDCl₃



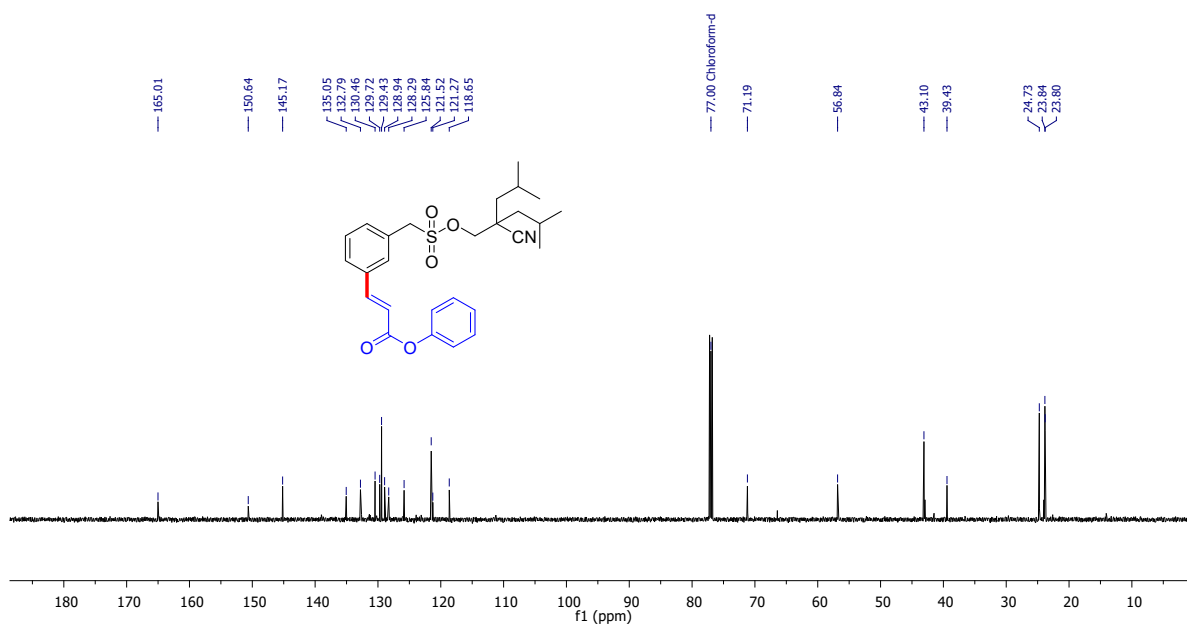
¹H NMR (600 MHz) spectrum of **3ac** in CDCl₃



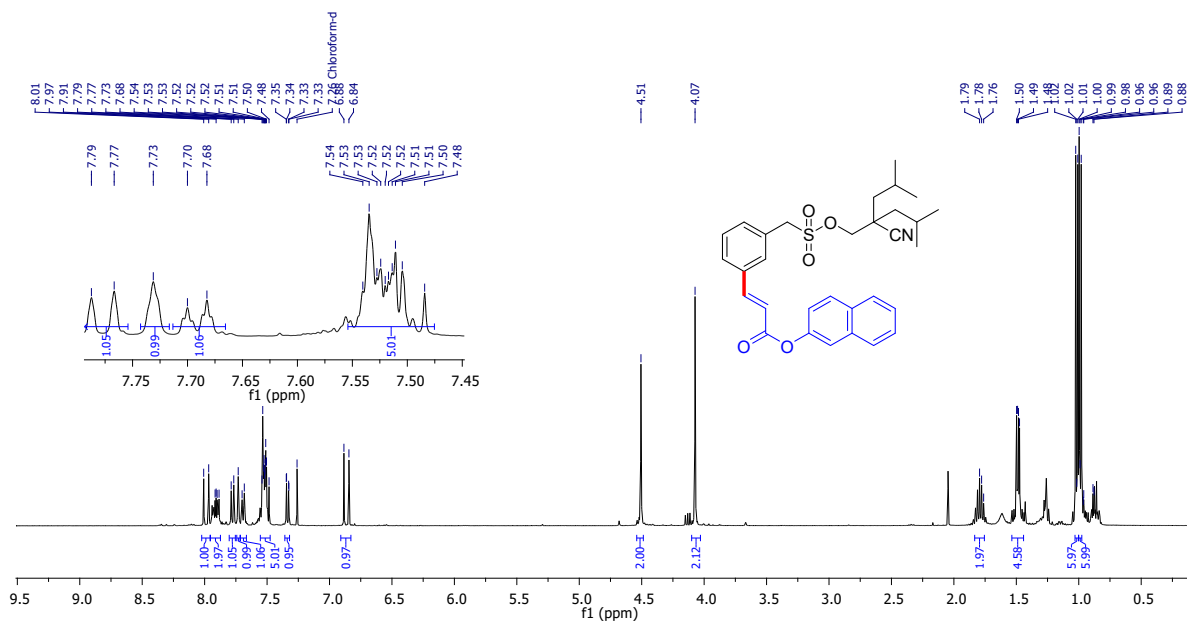
¹³C {¹H} NMR (151 MHz) spectrum of **3ac** in CDCl₃



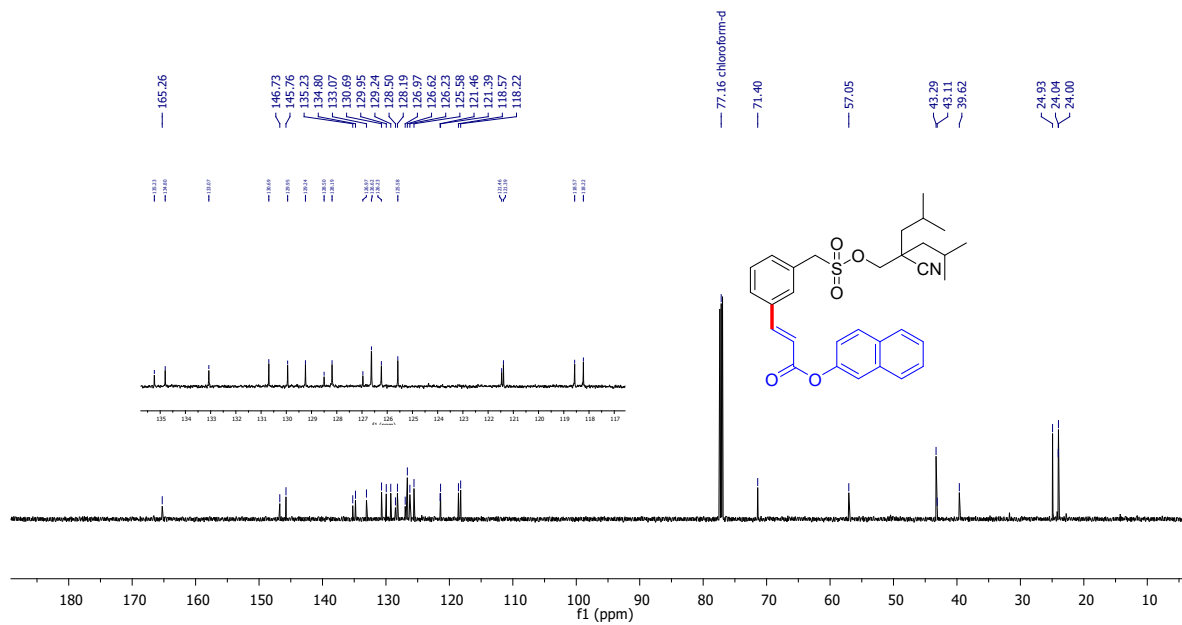
¹H NMR (400 MHz) spectrum of *3ad* in CDCl₃



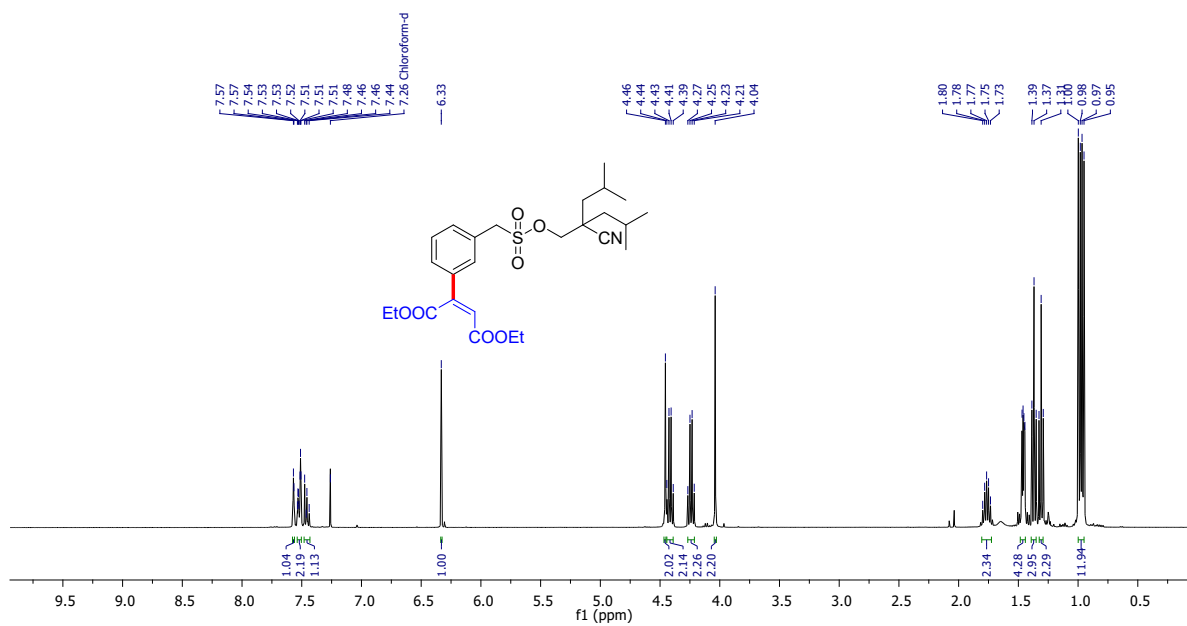
¹³C {¹H} NMR (151 MHz) spectrum of *3ad* in CDCl₃



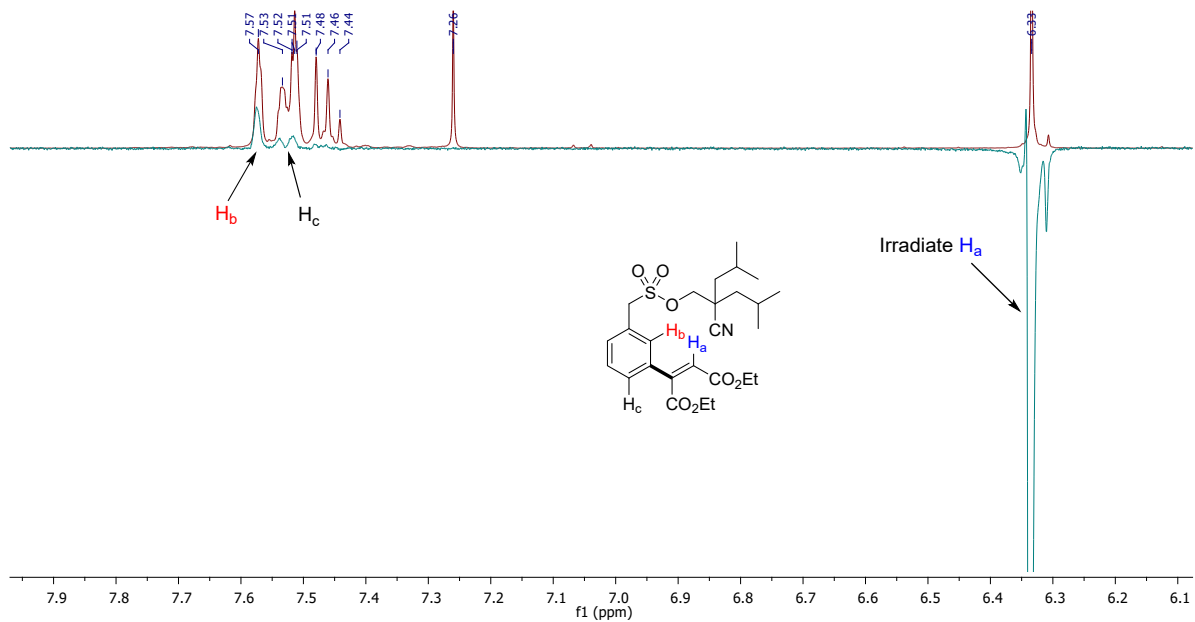
¹H NMR (400 MHz) spectrum of **3ae** in CDCl₃



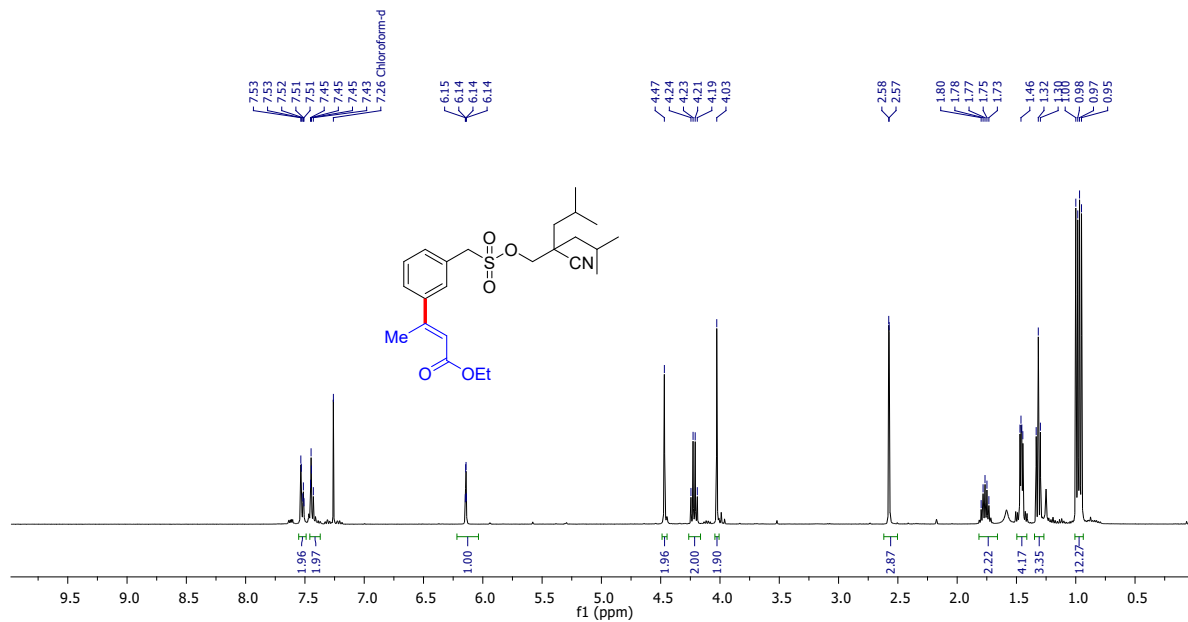
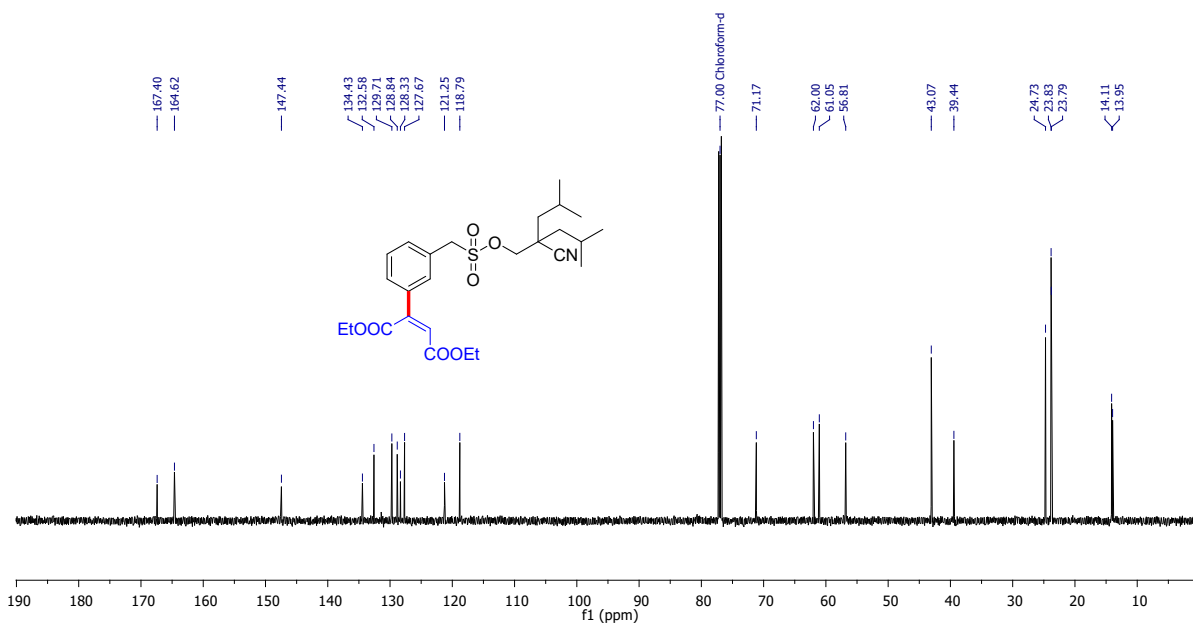
¹³C {¹H} NMR (151 MHz) spectrum of **3ae** in CDCl₃

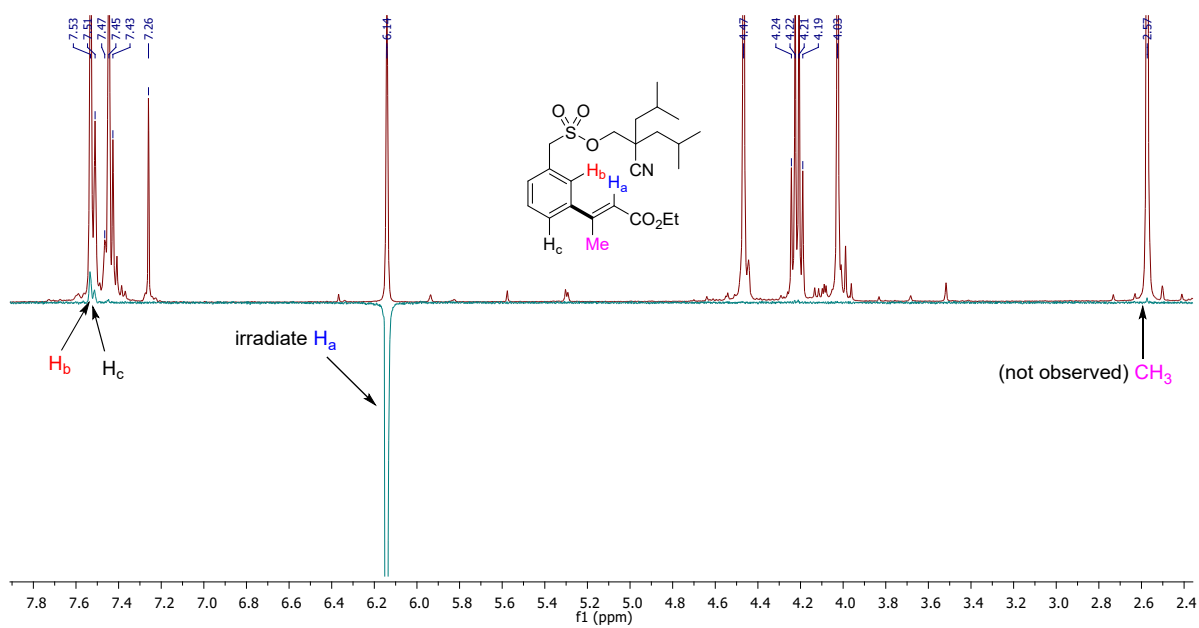


¹H NMR (400 MHz) spectrum of **3ah** in CDCl₃

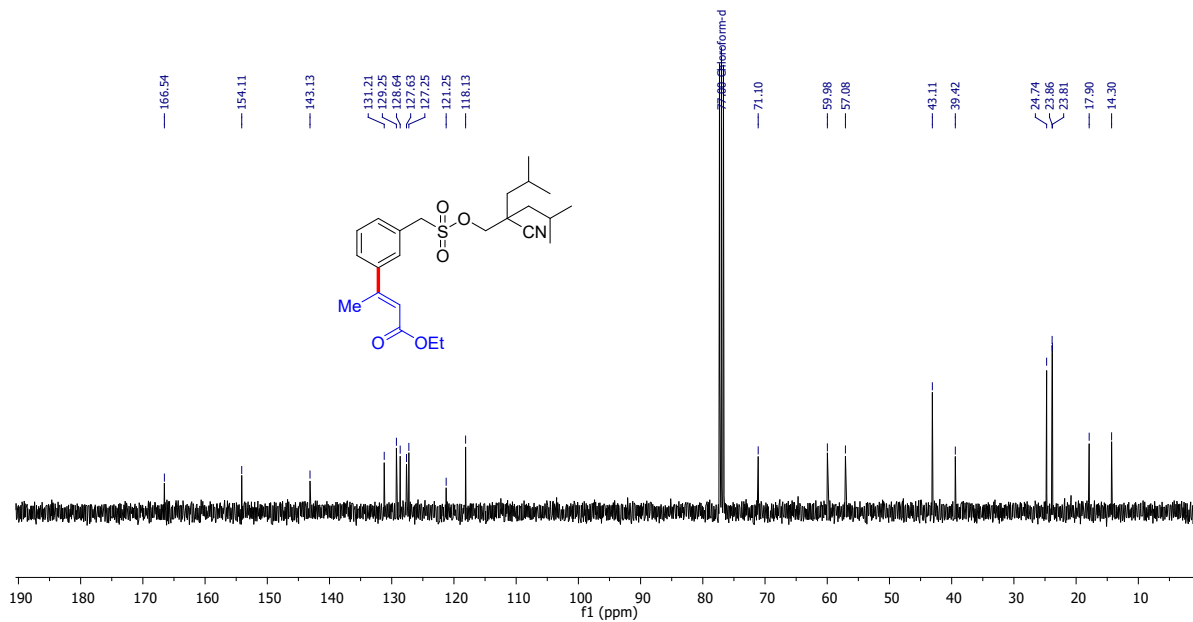


¹H NMR (400 MHz) spectrum vs NOE spectrum of **3ah** in CDCl₃

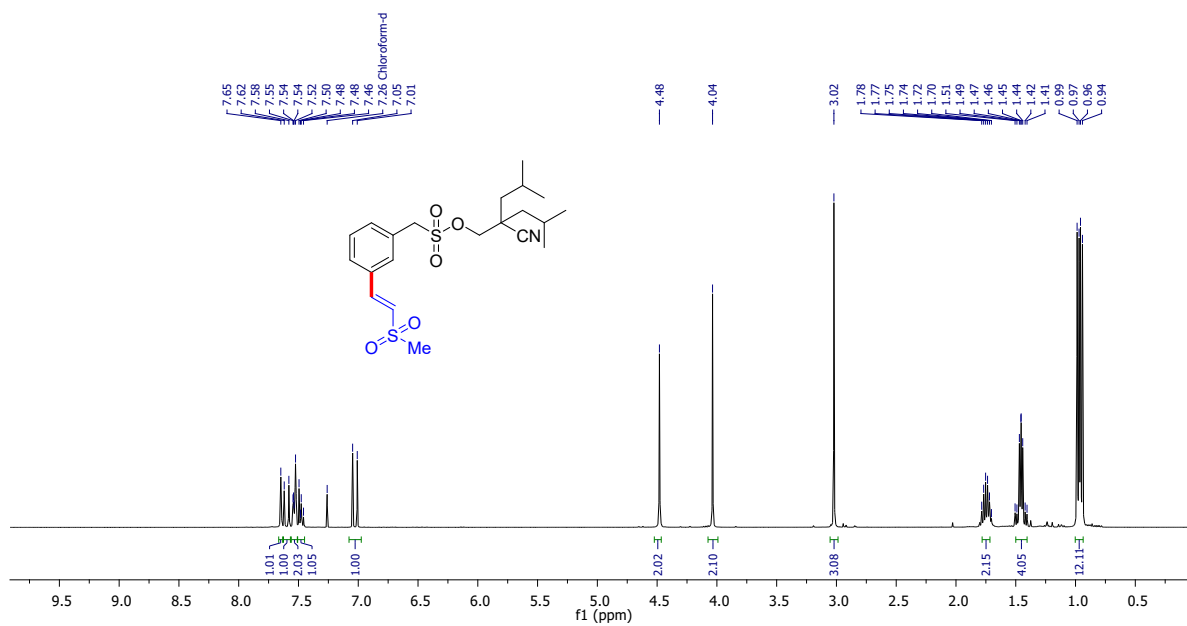




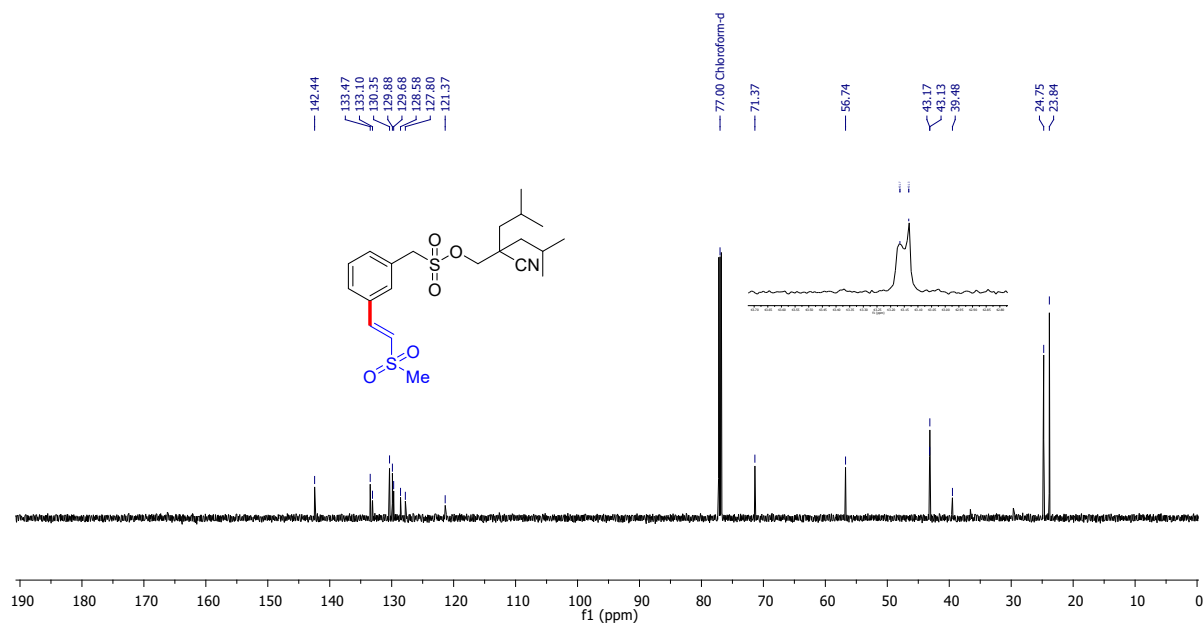
1H NMR (400 MHz) spectrum vs NOE spectrum of **3ai** in $CDCl_3$



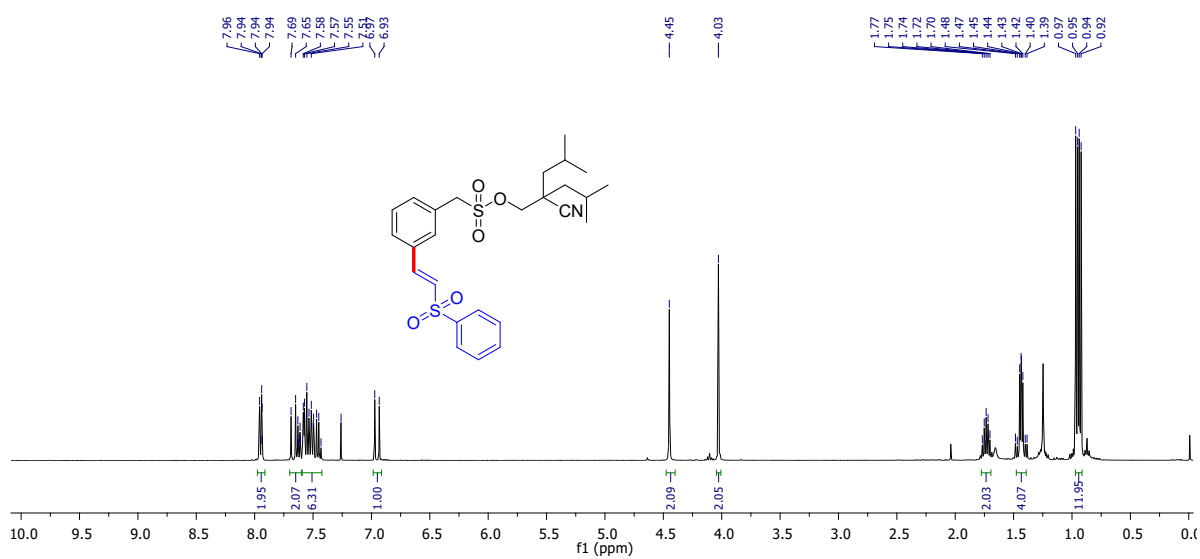
^{13}C $\{^1H\}$ NMR (100 MHz) spectrum of **3ai** in $CDCl_3$



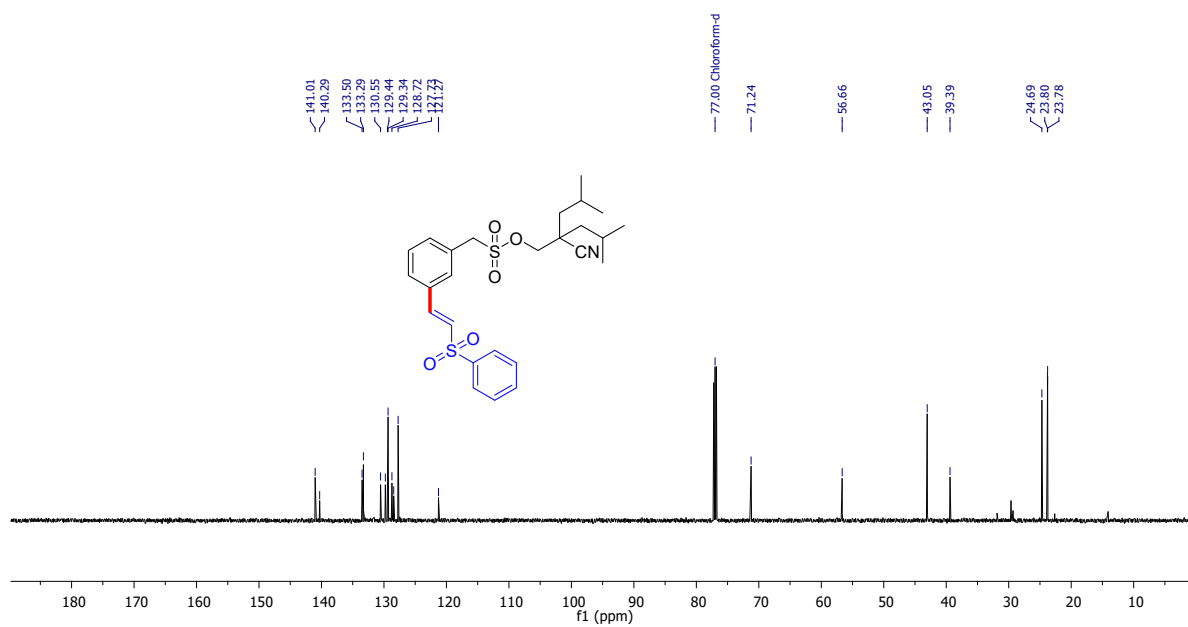
^1H NMR (400 MHz) spectrum of **3aj** in CDCl_3



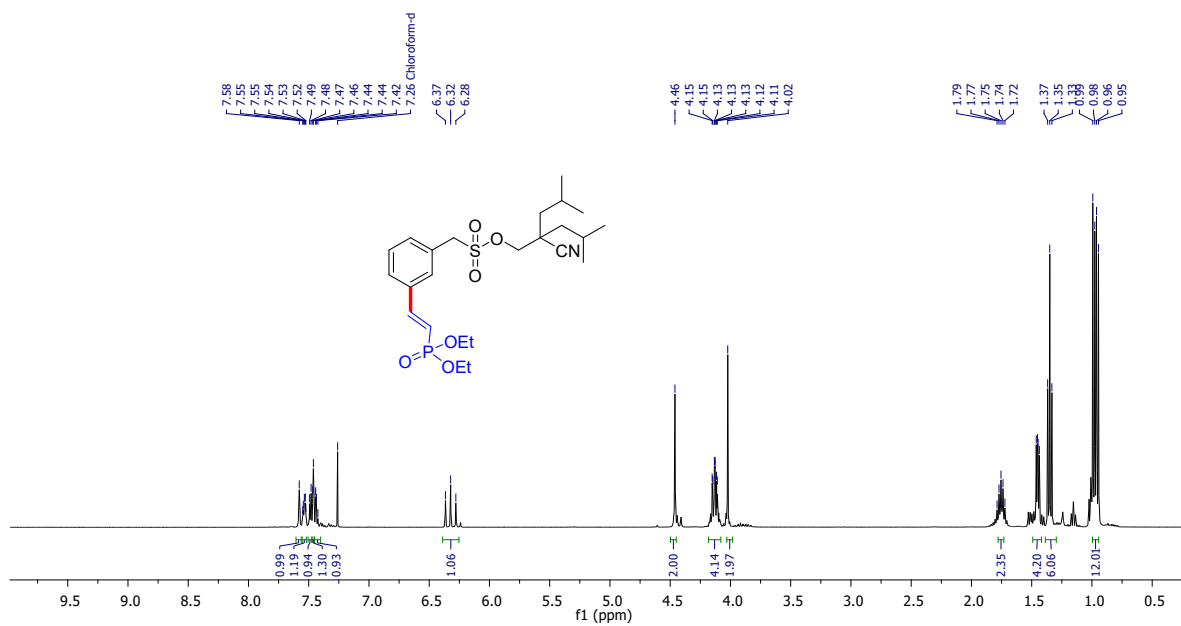
^{13}C $\{^1\text{H}\}$ NMR (151 MHz) spectrum of **3aj** in CDCl_3



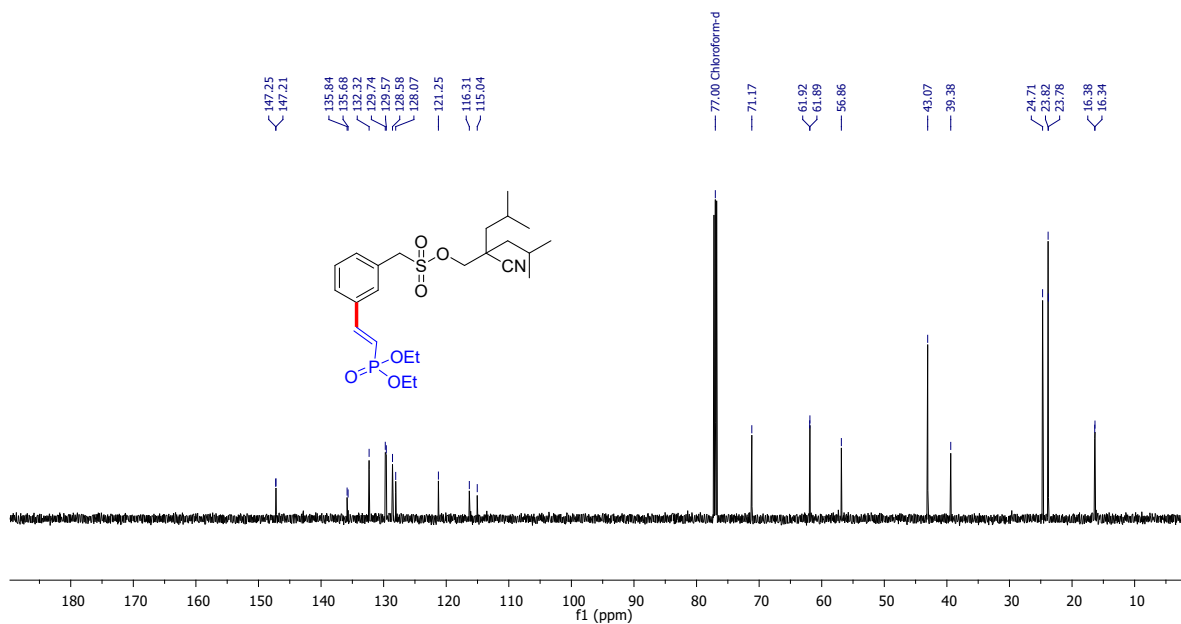
¹H NMR (400 MHz) spectrum of *3ak* in CDCl₃



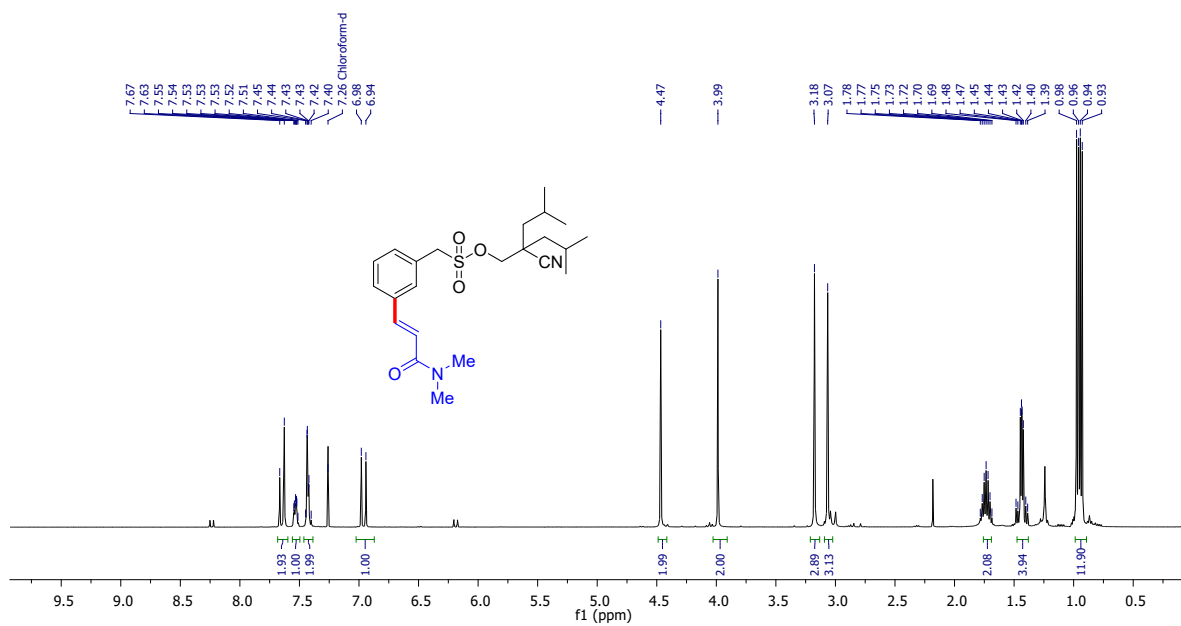
¹³C {¹H} NMR (151 MHz) spectrum of *3ak* in CDCl₃



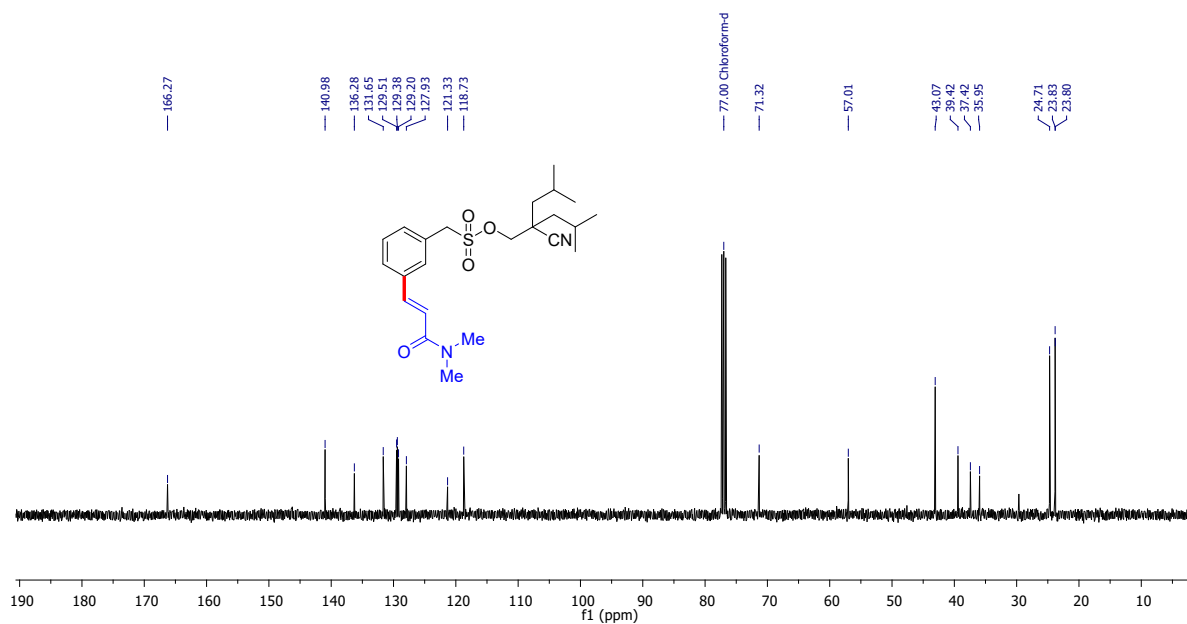
¹H NMR (400 MHz) spectrum of **3al** in CDCl₃



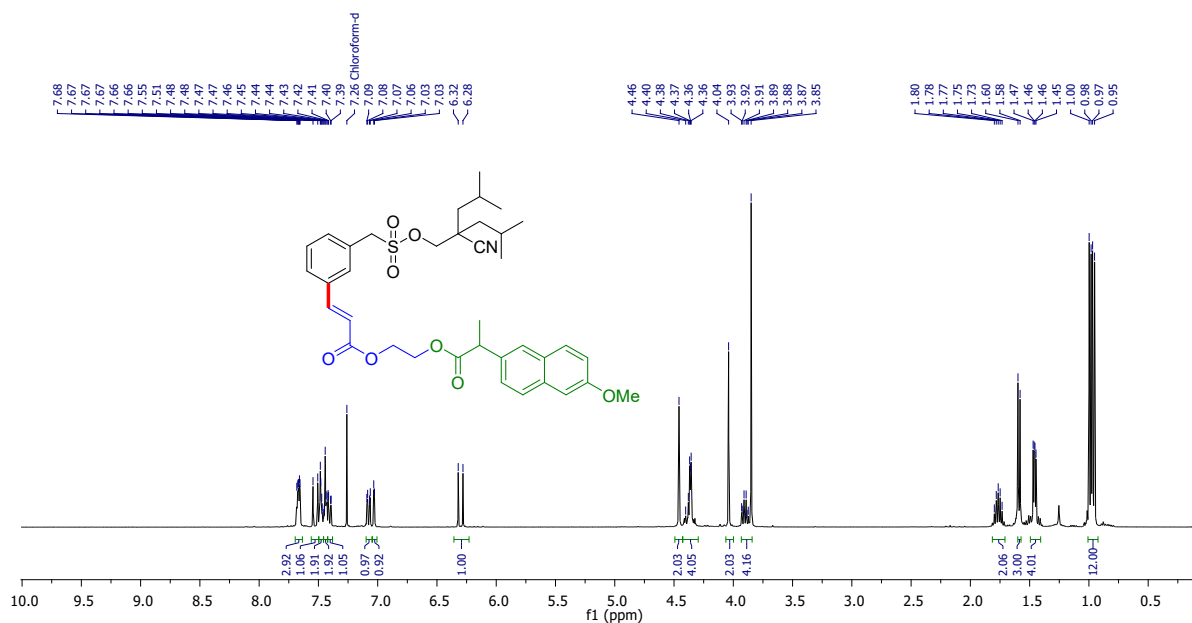
¹³C {¹H} NMR (151 MHz) spectrum of **3al** in CDCl₃



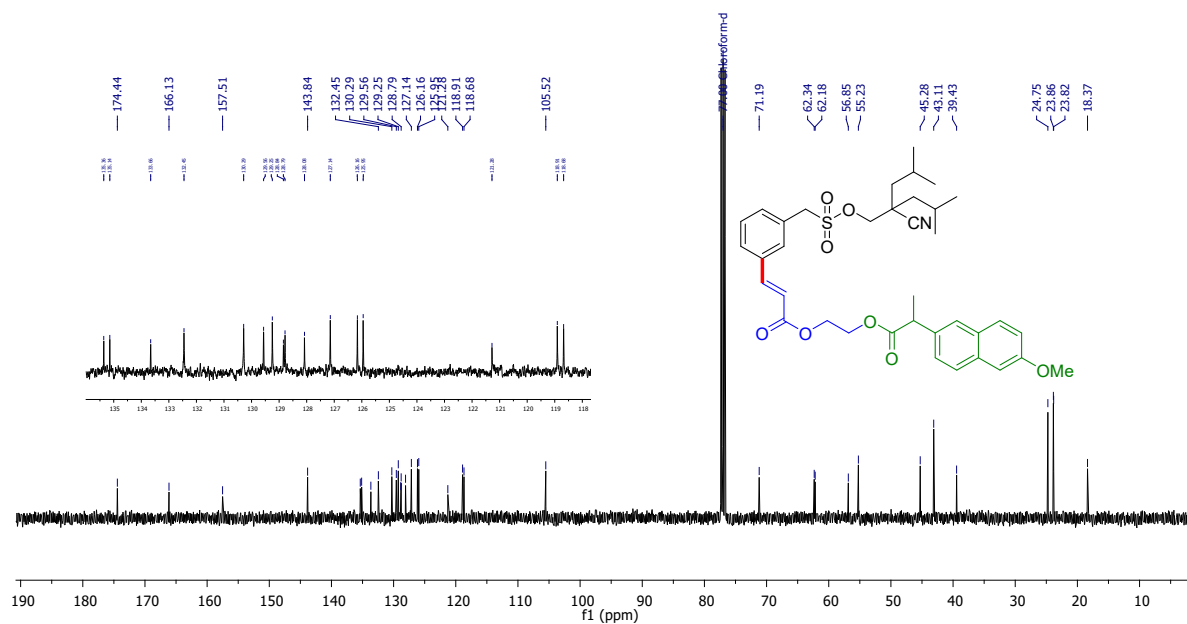
¹H NMR (400 MHz) spectrum of **3am** in CDCl₃



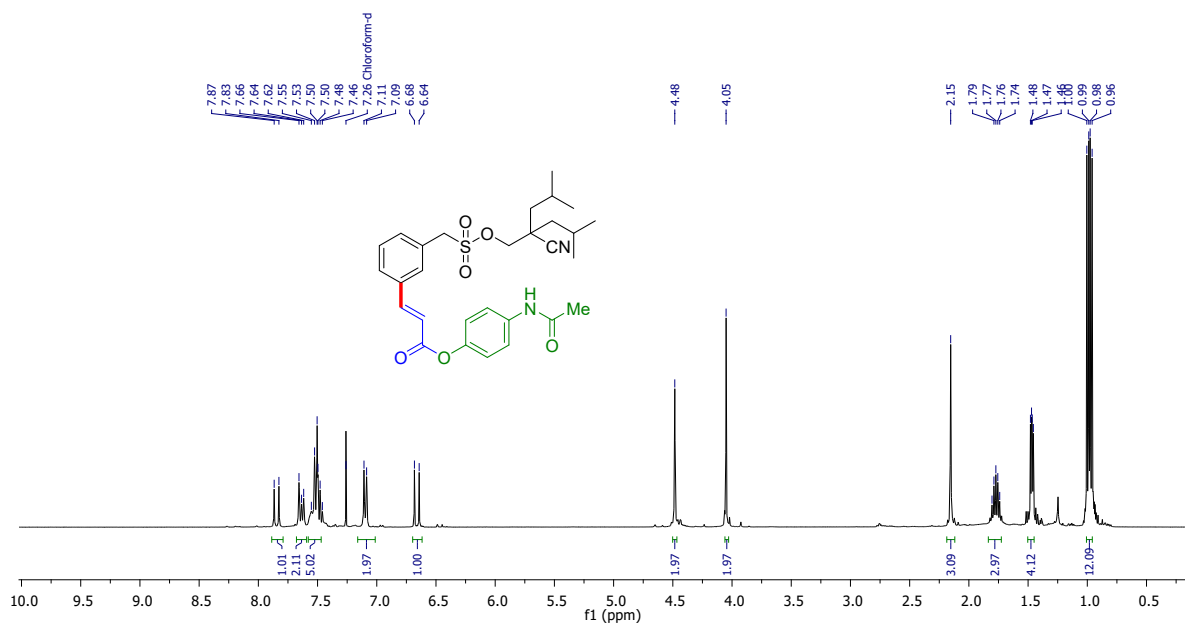
¹³C {¹H} NMR (100 MHz) spectrum of **3am** in CDCl₃



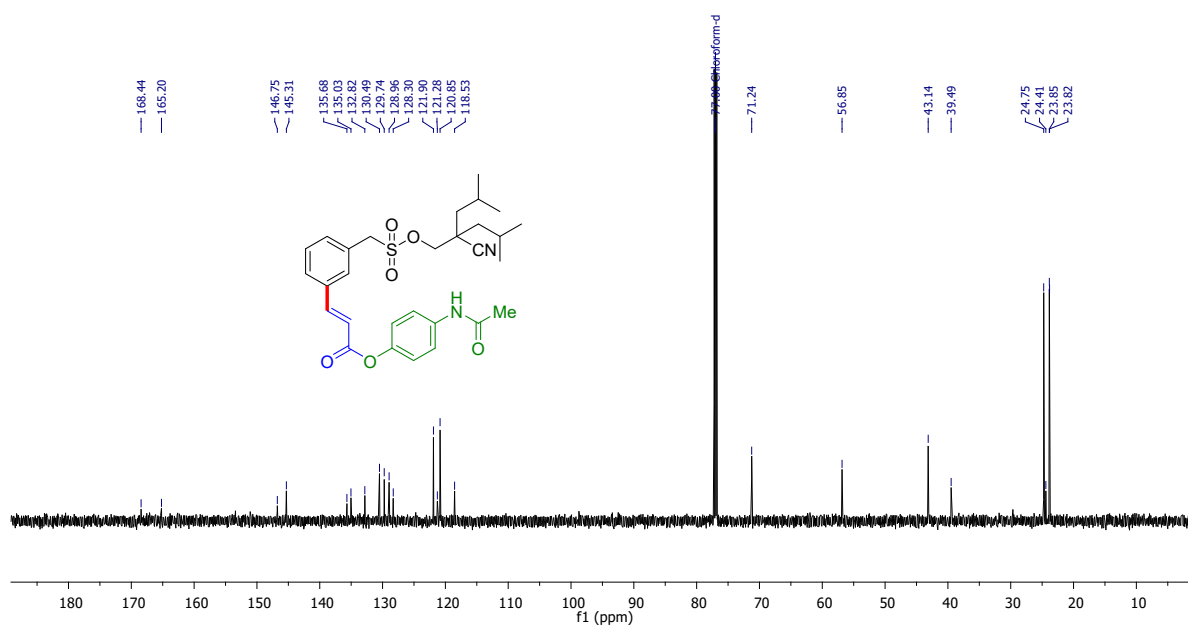
¹H NMR (400 MHz) spectrum of **3an** in CDCl₃



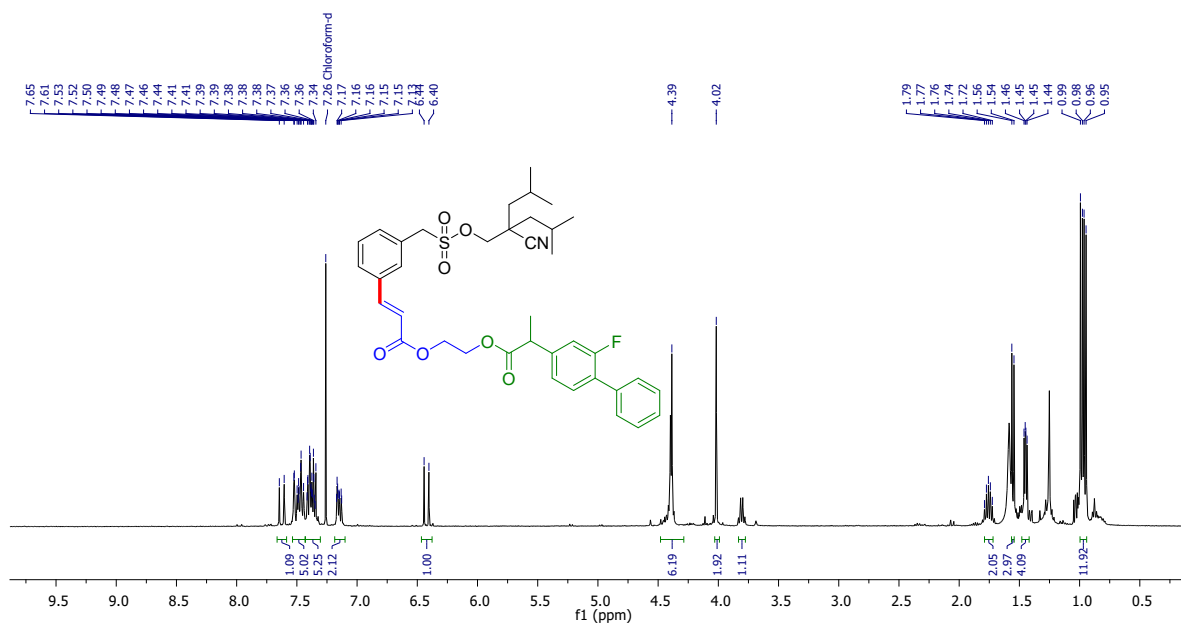
¹³C {¹H} NMR (100 MHz) spectrum of **3an** in CDCl₃



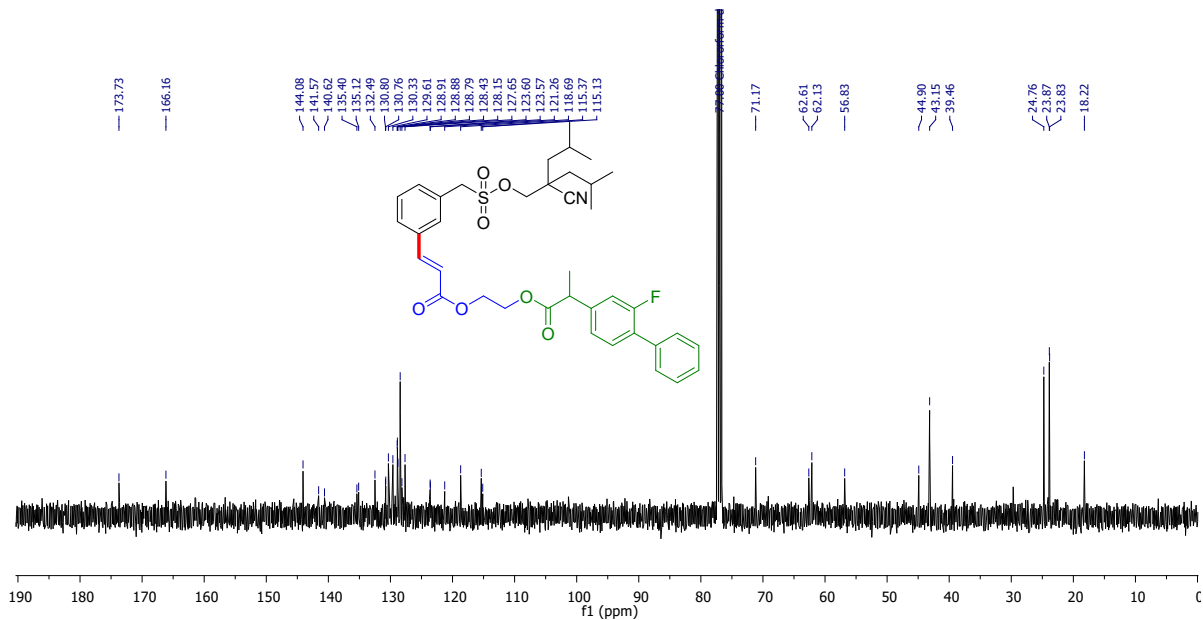
¹H NMR (400 MHz) spectrum of **3ap** in CDCl₃



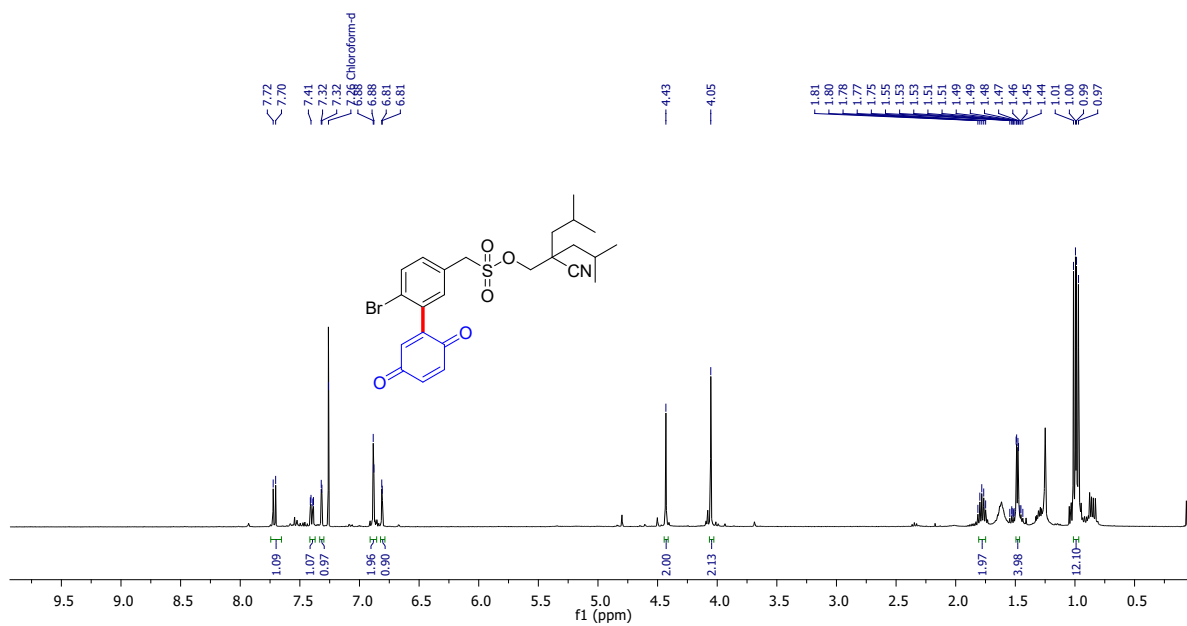
¹³C {¹H} NMR (151 MHz) spectrum of **3ap** in CDCl₃



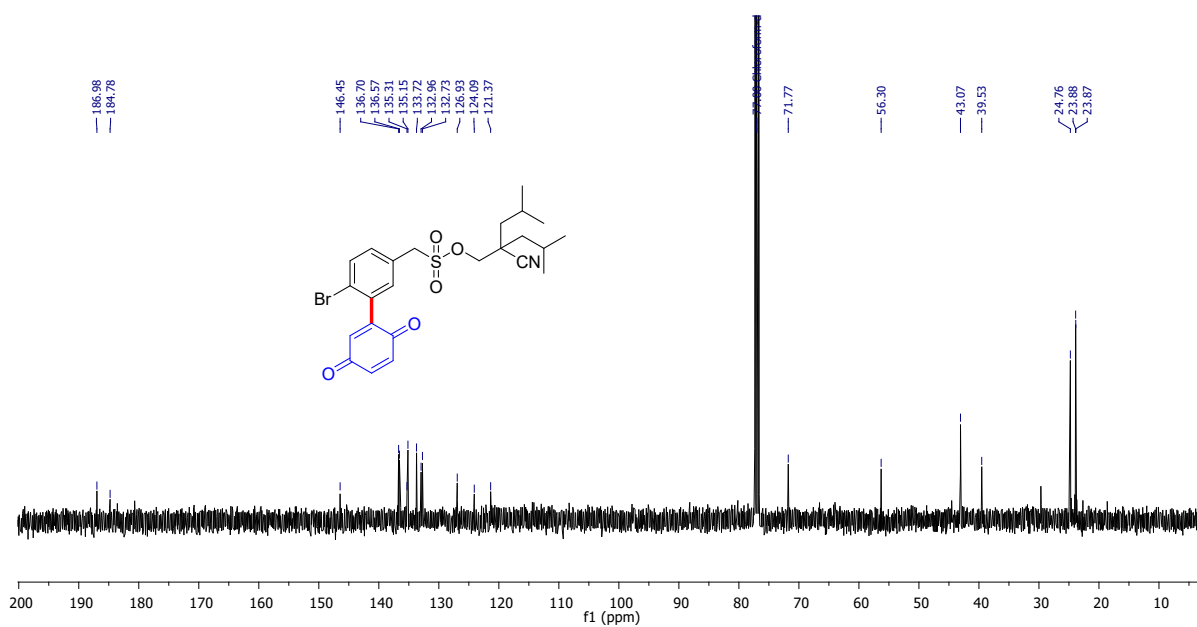
¹H NMR (400 MHz) spectrum of **3aq** in CDCl₃



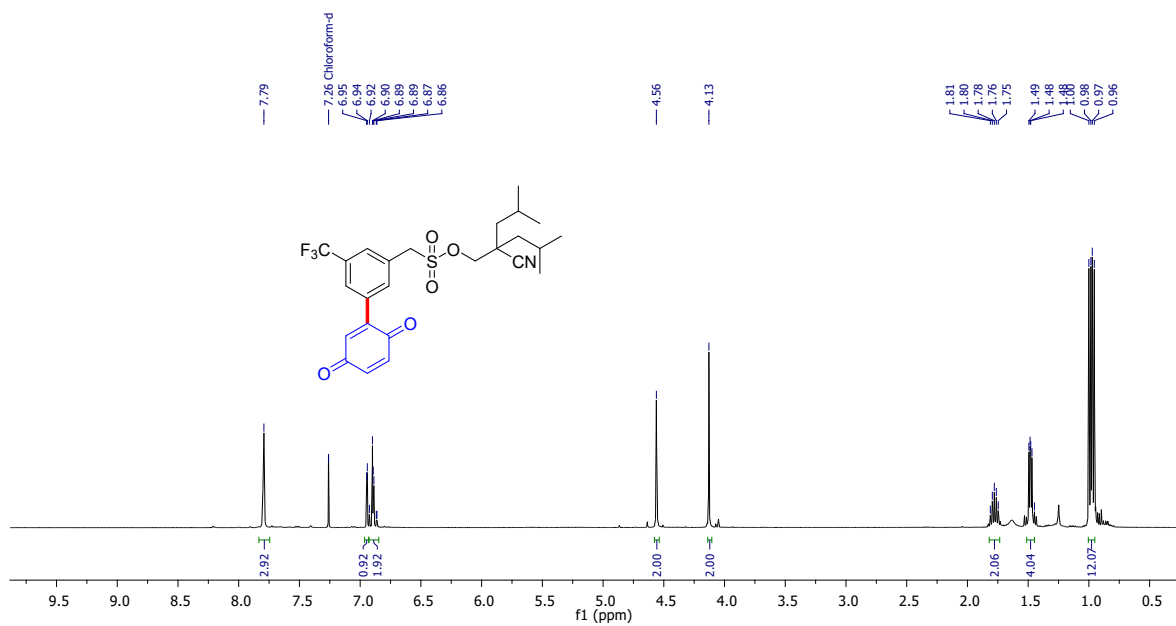
¹³C {¹H} NMR (100 MHz) spectrum of **3aq** in CDCl₃



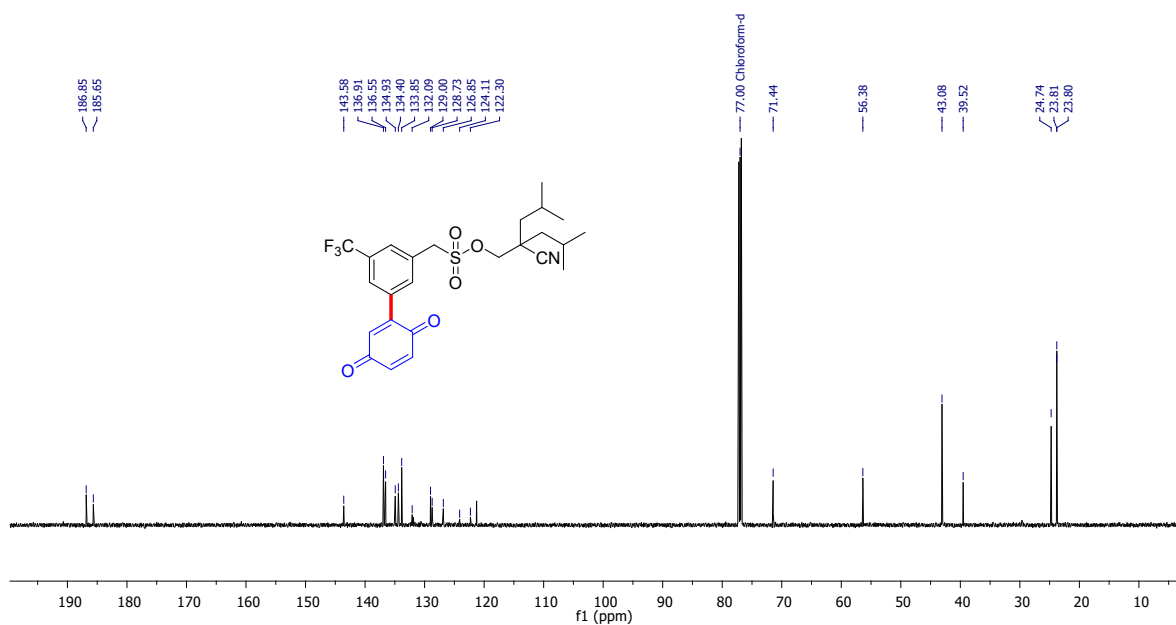
¹H NMR (400 MHz) spectrum of **3ir** in CDCl₃



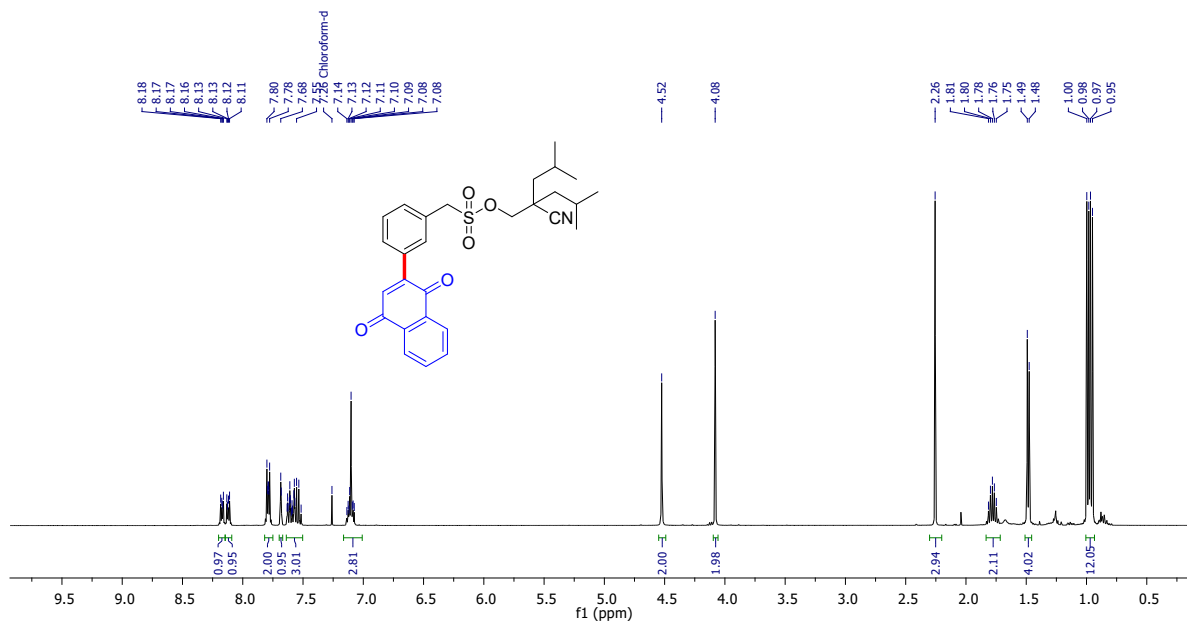
¹³C {¹H} NMR (100 MHz) spectrum of **3ir** in CDCl₃



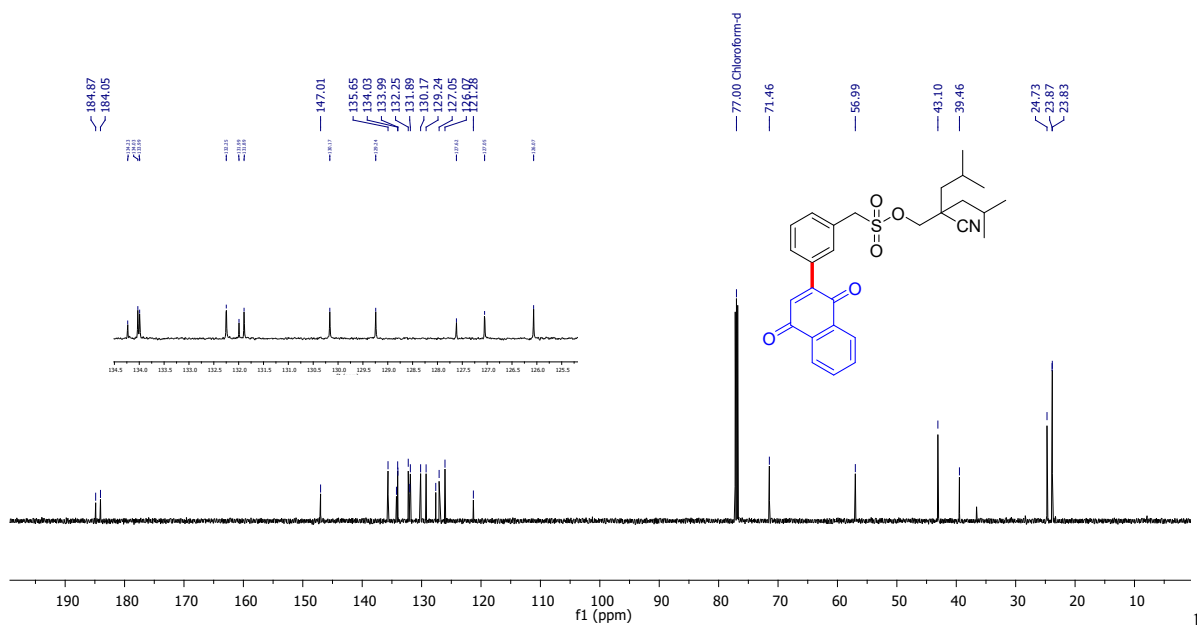
¹H NMR (400 MHz) spectrum of **3cr** in CDCl₃



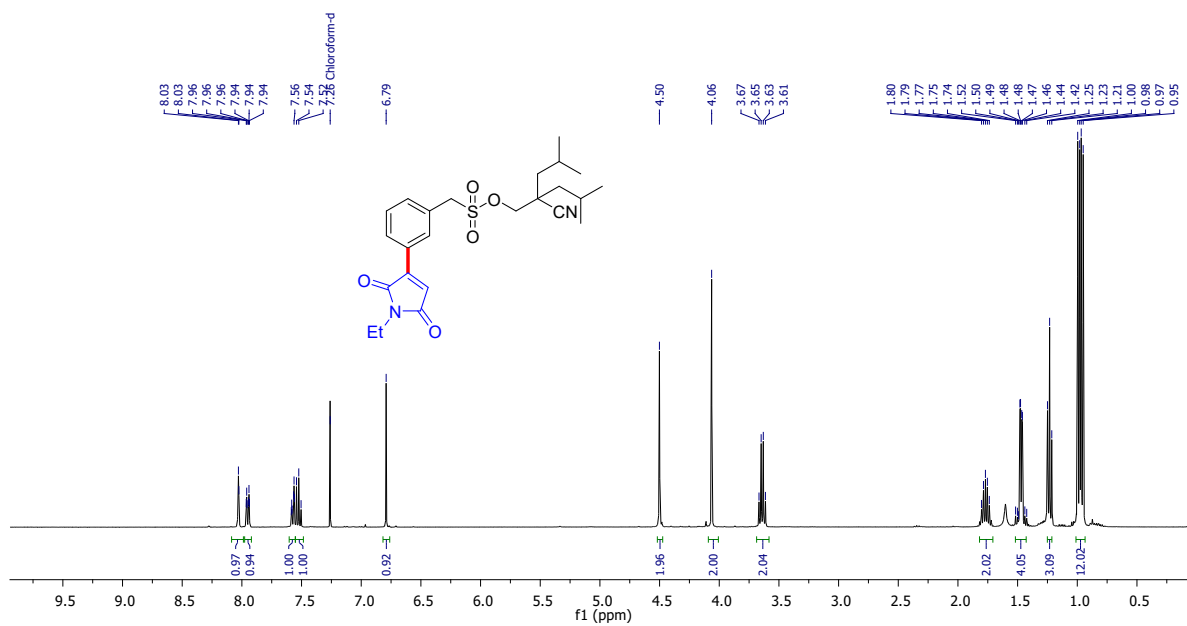
¹³C {¹H} NMR (151 MHz) spectrum of **3cr** in CDCl₃



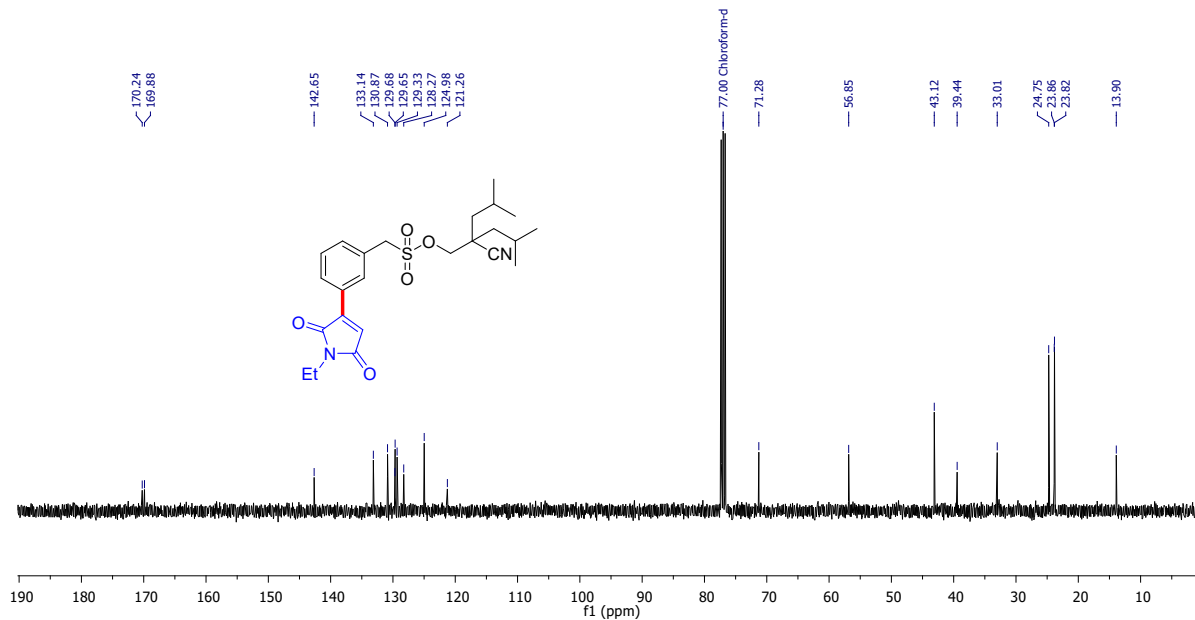
¹H NMR (400 MHz) spectrum of **3at** in CDCl₃



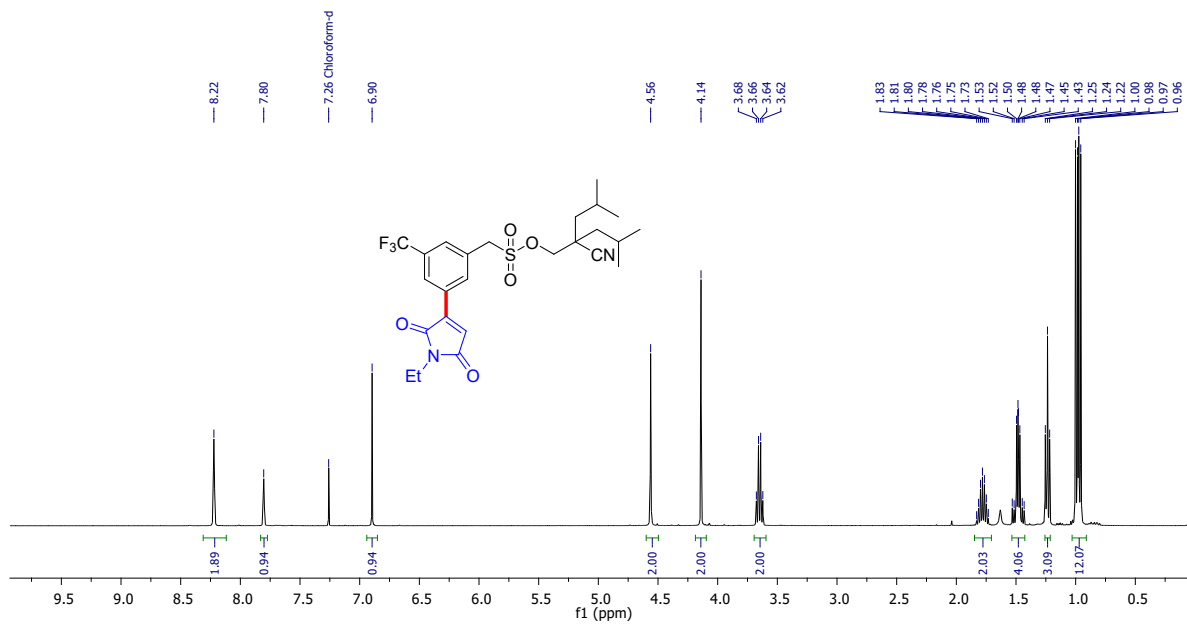
¹³C {¹H} NMR (100 MHz) spectrum of **3at** in CDCl₃



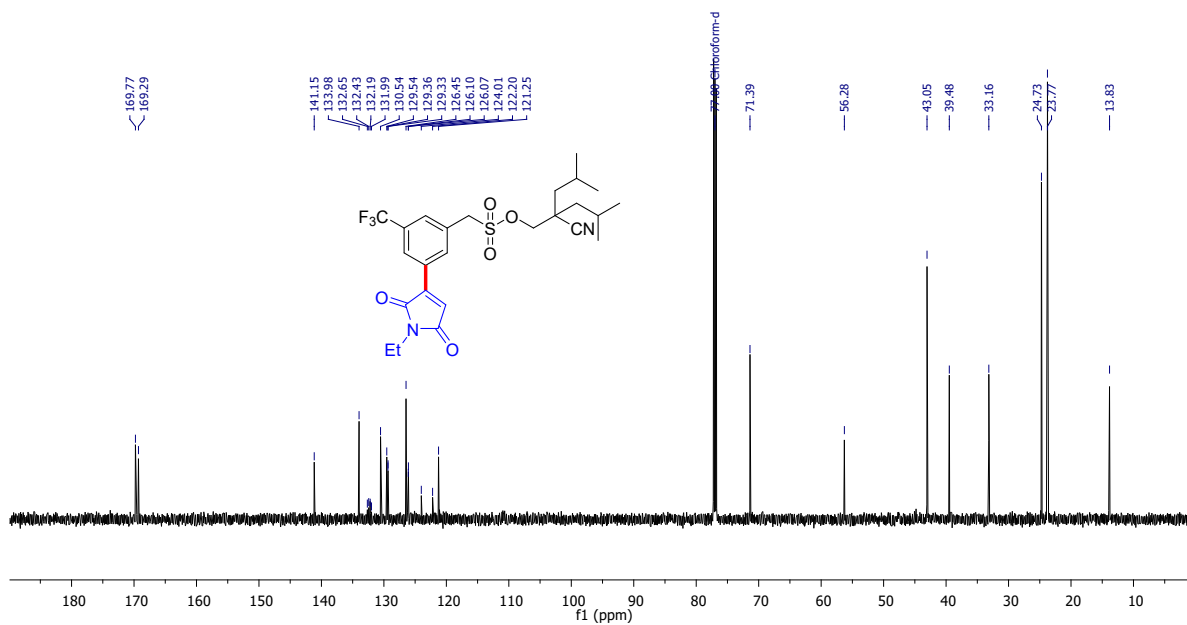
¹H NMR (400 MHz) spectrum of **3au** in CDCl₃



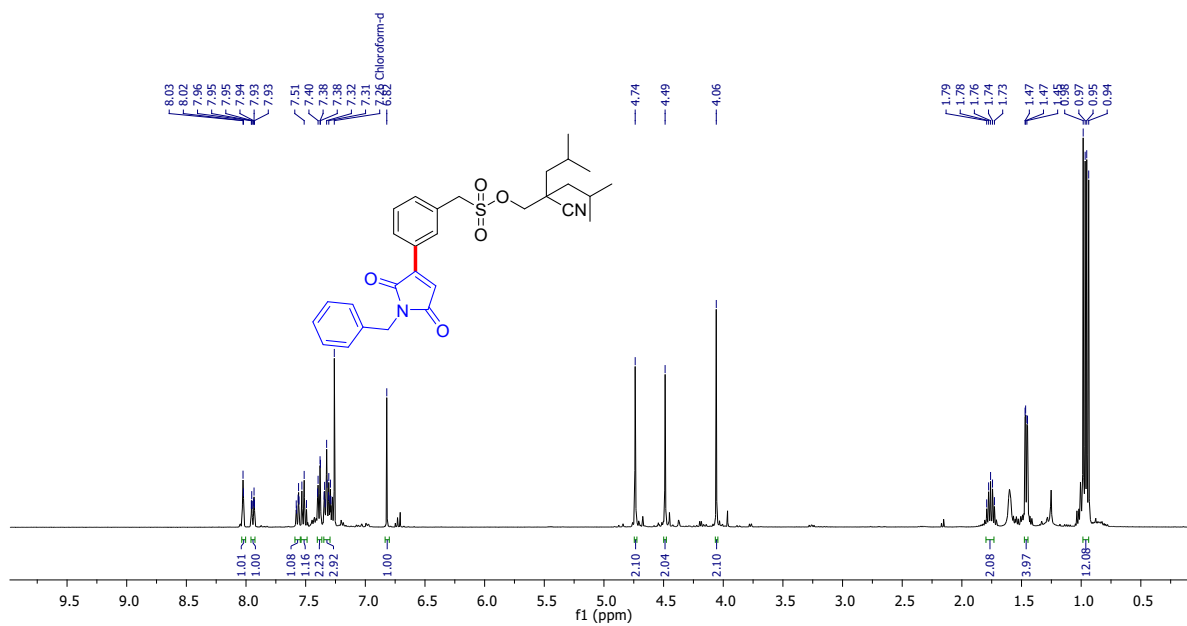
¹³C {¹H} NMR (100 MHz) spectrum of **3au** in CDCl₃



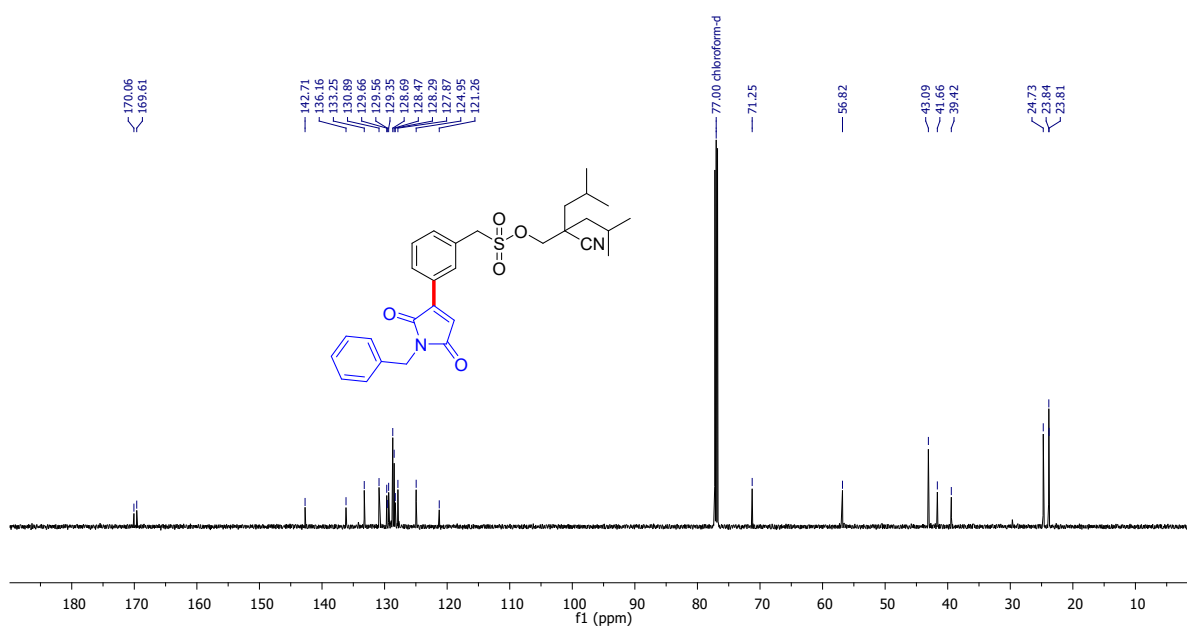
¹H NMR (400 MHz) spectrum of **3cu** in CDCl₃



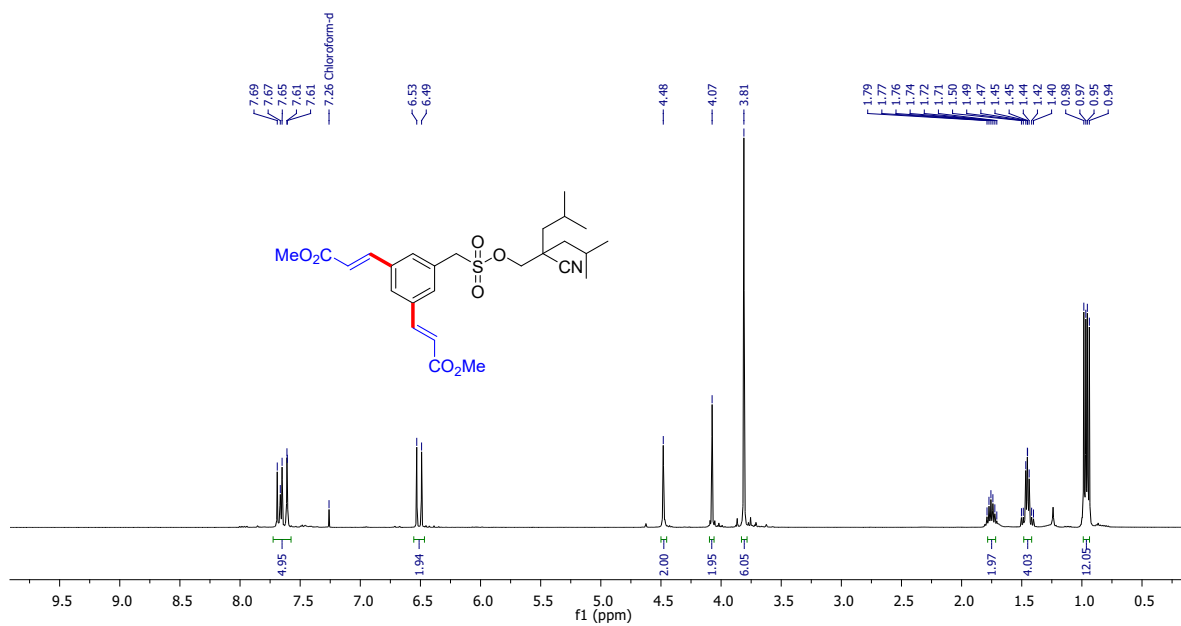
¹³C {¹H} NMR (151 MHz) spectrum of **3cu** in CDCl₃



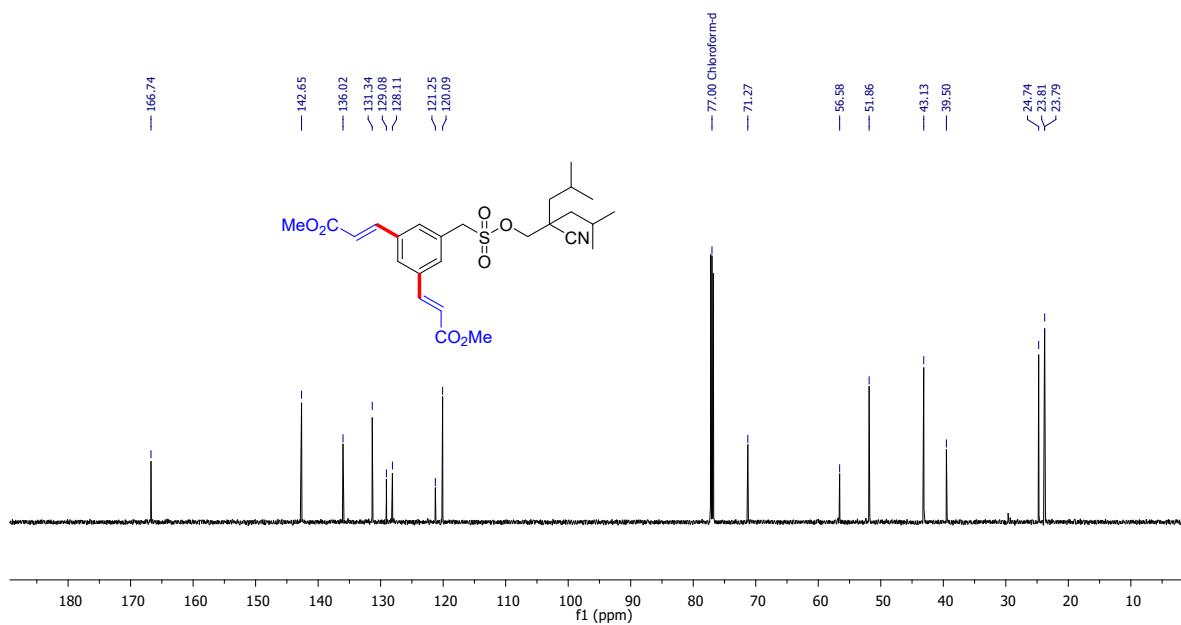
¹H NMR (400 MHz) spectrum of **3aw** in CDCl₃



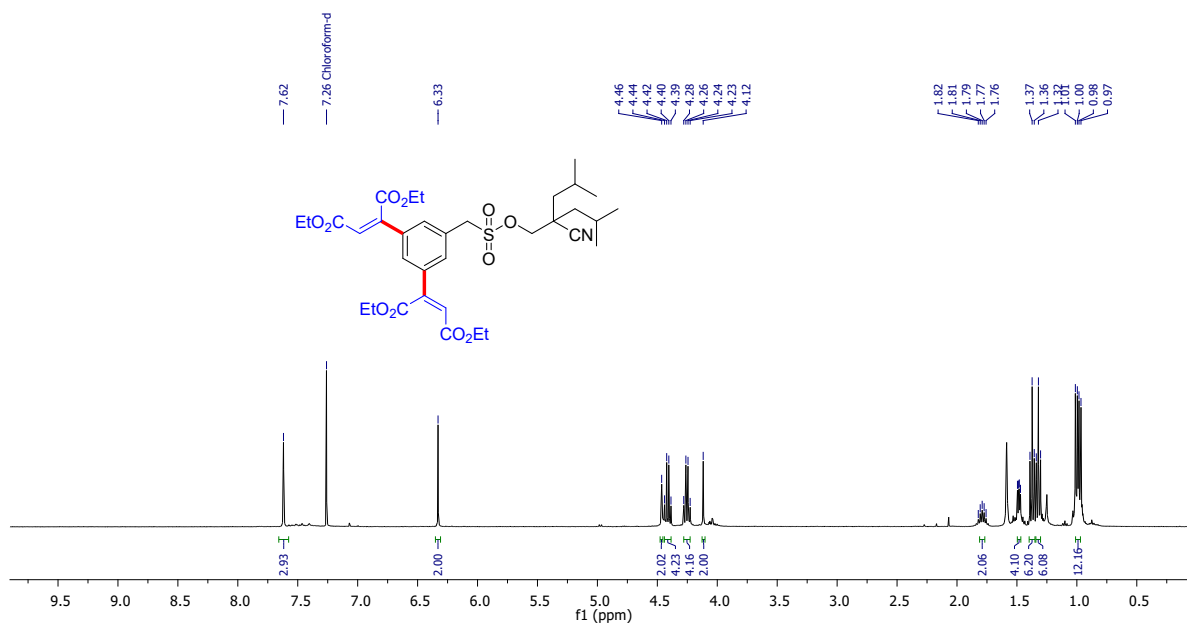
¹³C {¹H} NMR (151 MHz) spectrum of **3aw** in CDCl₃



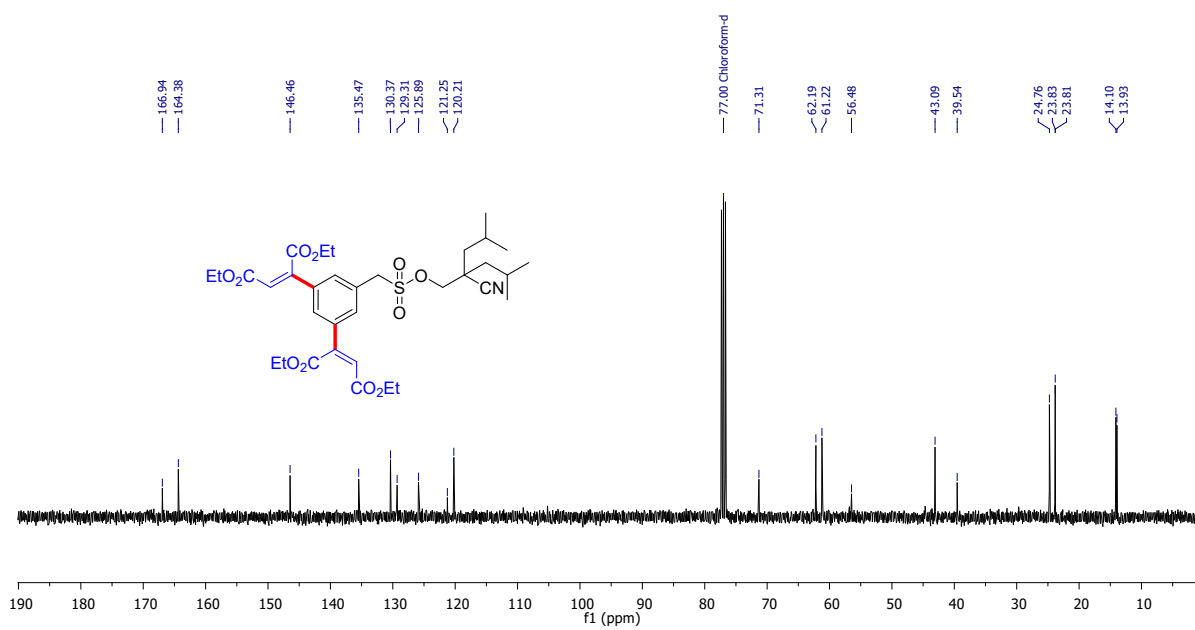
¹H NMR (400 MHz) spectrum of **4a** in CDCl₃



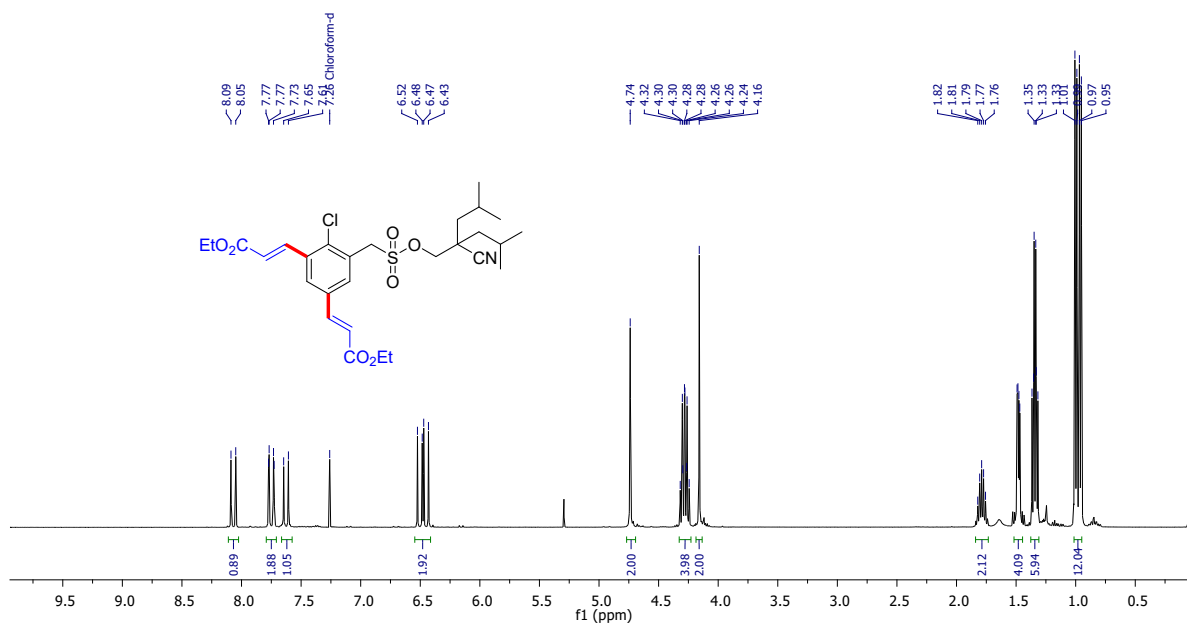
¹³C {¹H} NMR (151 MHz) spectrum of **4a** in CDCl₃



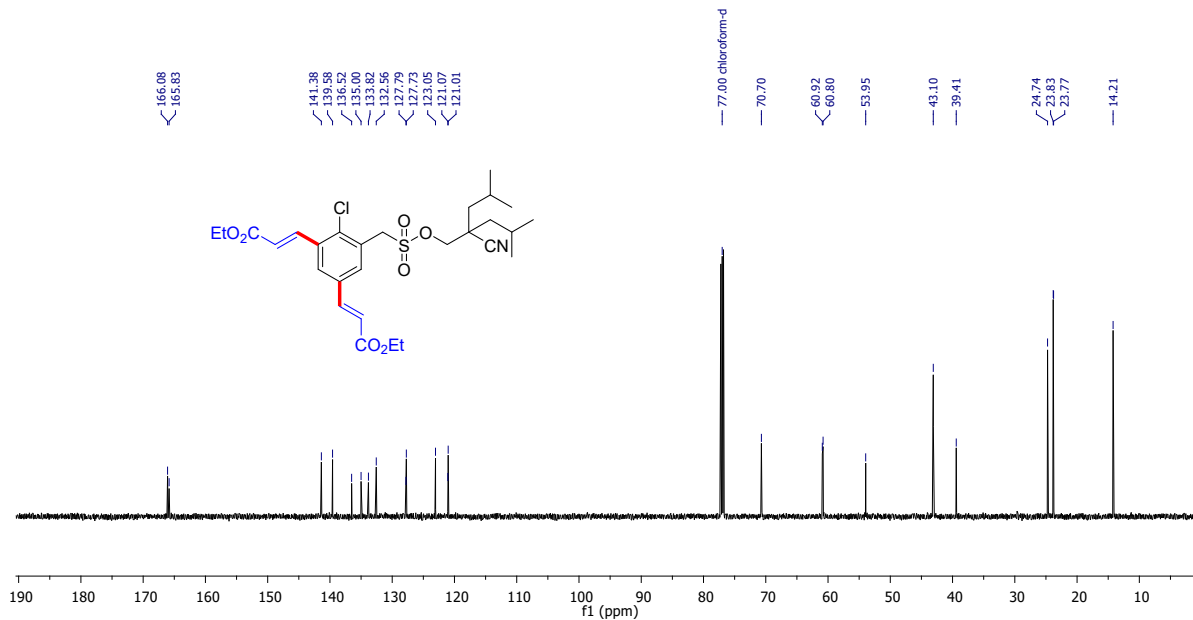
¹H NMR (400 MHz) spectrum of **4b** in CDCl₃



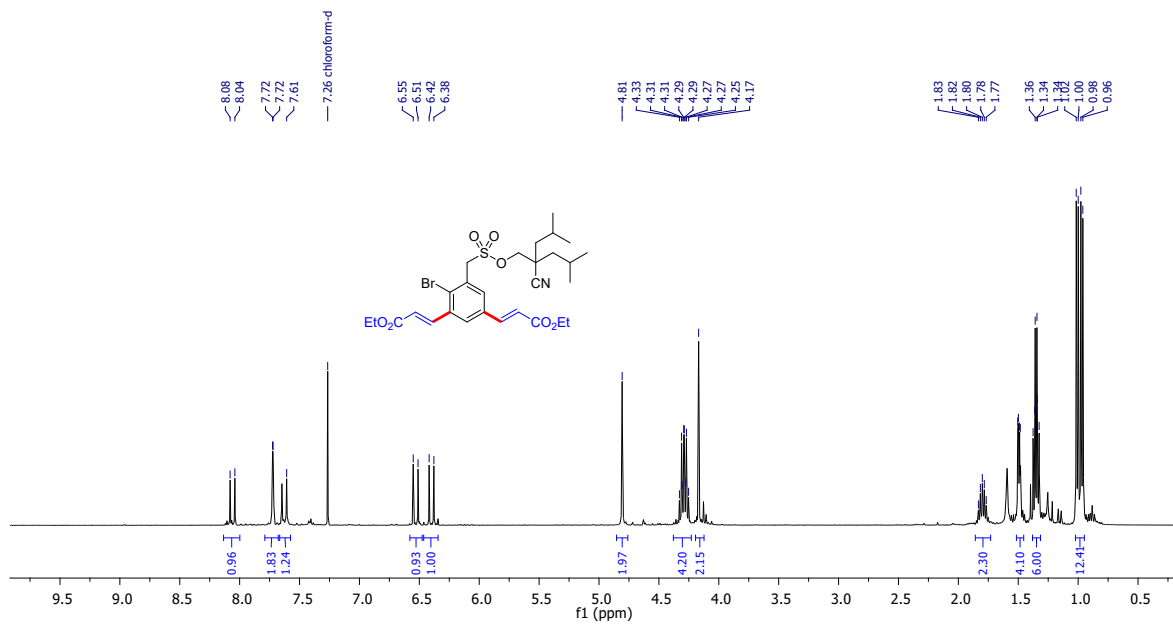
¹³C {¹H} NMR (151 MHz) spectrum of **4b** in CDCl₃



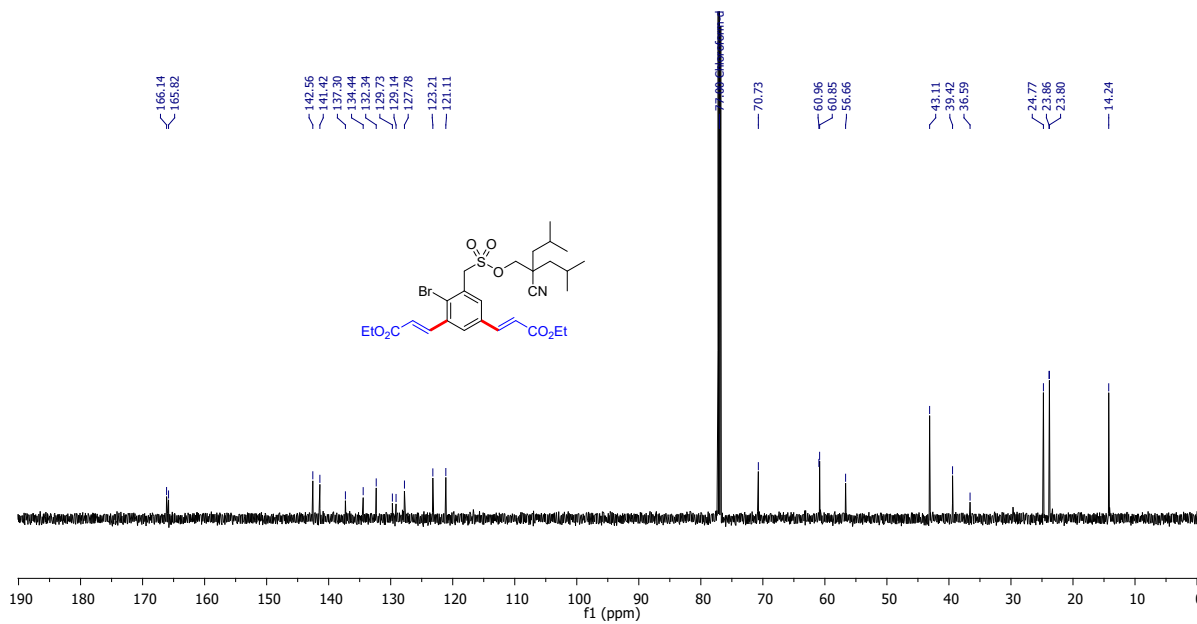
^1H NMR (400 MHz) spectrum of **4c** in CDCl_3



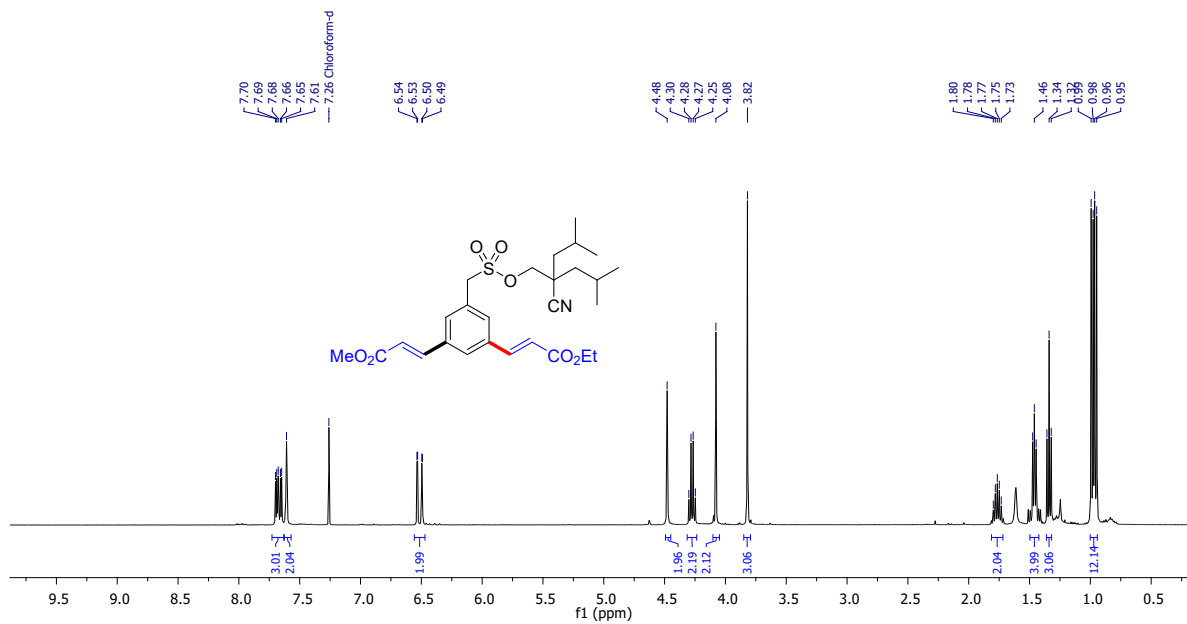
^{13}C $\{^1\text{H}\}$ NMR (151 MHz) spectrum of **4c** in CDCl_3



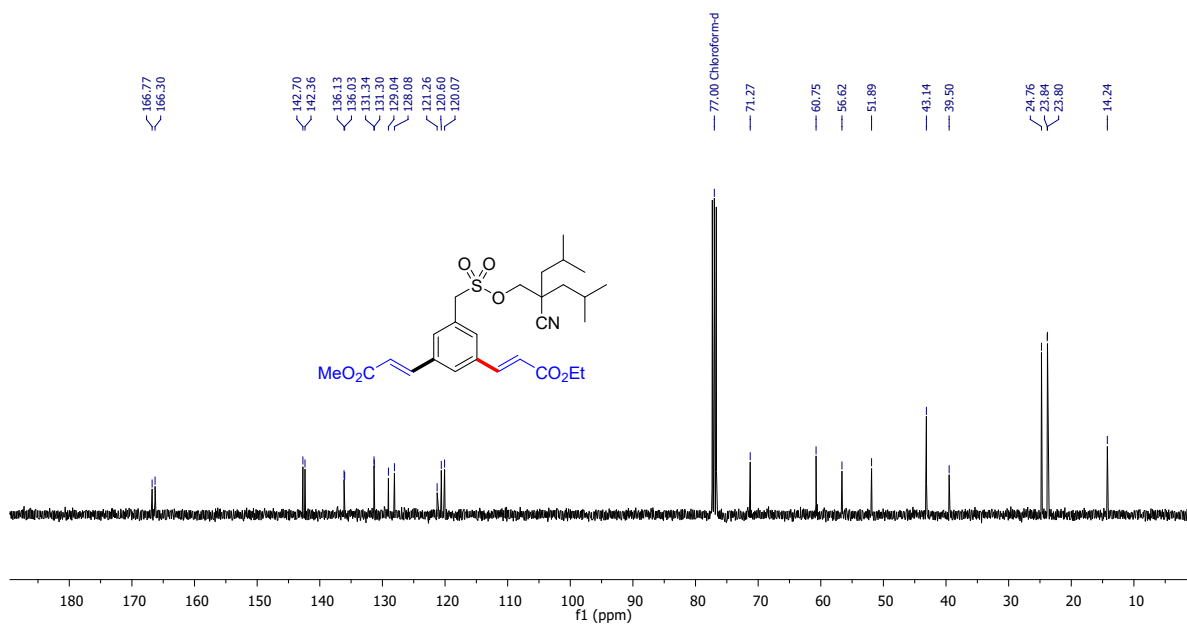
^1H NMR (400 MHz) spectrum of **4e** in CDCl_3



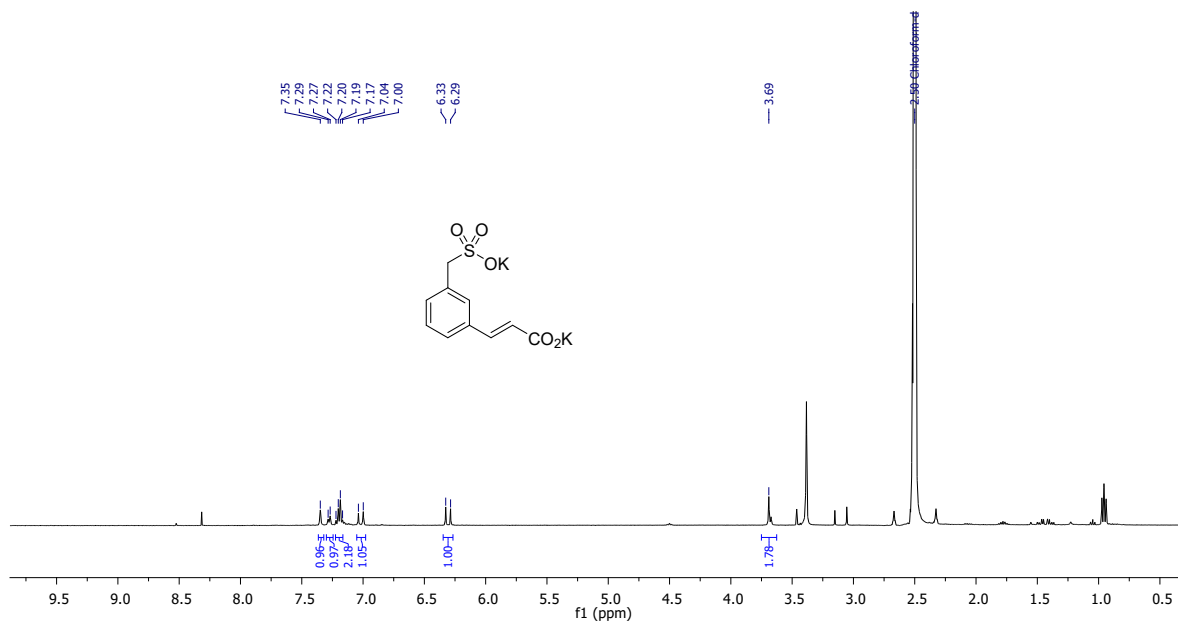
^{13}C $\{^1\text{H}\}$ NMR (151 MHz) spectrum of **4e** in CDCl_3



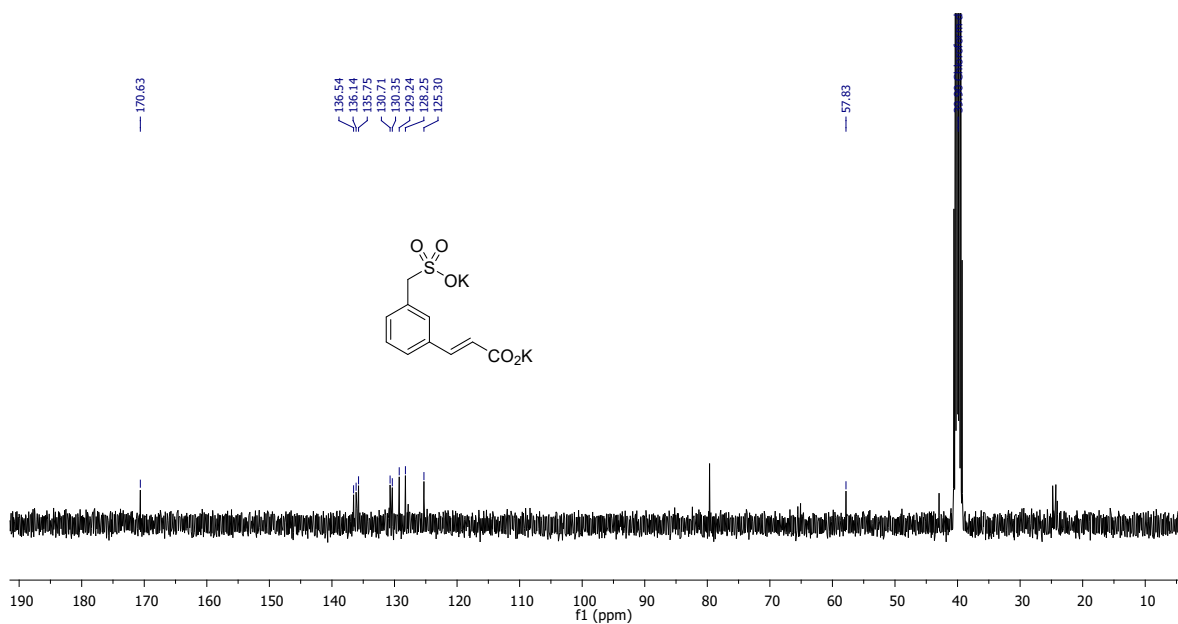
¹H NMR (400 MHz) spectrum of **4f in CDCl₃**



¹³C {¹H} NMR (100 MHz) spectrum of **4f in CDCl₃**



¹H NMR (400 MHz) spectrum of **5** in DMSO-d₆



¹³C {¹H} NMR (100 MHz) spectrum of **5** in DMSO-d₆

X-ray Diffraction Analysis of Compound 3jb:

Crystal of compound **3jb** was obtained by dissolving product in mixture of Acetonitrile and hexane in 3:1 ratio, allowing the solvent to slowly evaporate at room temperature. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. **CCDC No: 2255976** contains the crystal structure information of this compound and can be obtained free of charge via <http://www.ccdc.cam.ac.uk>

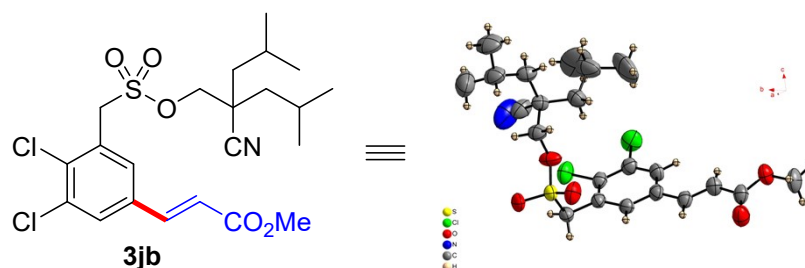


Figure S1. X-ray structure of the product **3jb** with the ellipsoids drawn at the 50% probability level.

Table 1 Crystal data and structure refinement for mo_GS_DS_1_KM_340_3_0m.

Identification code	mo_GS_DS_1_KM_340_3_0m
Empirical formula	C ₂₂ H ₂₉ Cl ₂ NO ₅ S
Formula weight	490.42
Temperature/K	299
Crystal system	triclinic
Space group	P-1
a/Å	6.3605(5)
b/Å	11.1325(10)
c/Å	18.2872(15)
α/°	83.955(3)
β/°	85.127(3)
γ/°	77.934(3)
Volume/Å ³	1256.60(18)
Z	2
ρ _{calc} /cm ³	1.296
μ/mm ⁻¹	0.373
F(000)	516.0
Crystal size/mm ³	0.056 × 0.056 × 0.023
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.756 to 54.298
Index ranges	-7 ≤ h ≤ 8, -14 ≤ k ≤ 14, -23 ≤ l ≤ 23
Reflections collected	24035
Independent reflections	5525 [R _{int} = 0.0765, R _{sigma} = 0.0763]
Data/restraints/parameters	5525/0/285
Goodness-of-fit on F ²	1.017
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0551, wR ₂ = 0.1187
Final R indexes [all data]	R ₁ = 0.1284, wR ₂ = 0.1484

Largest diff. peak/hole / e Å⁻³ 0.29/-0.28

References

- 1 Z. Yang and J. Xu, *Synthesis*, 2013, **45**, 1675–1682.
- 2 M. Bera, A. Maji, S. K. Sahoo and D. Maiti, *Angew. Chem. Int. Ed.*, 2015, **54**, 8515–8519.
- 3 Y.-F. Yang, G.-J. Cheng, P. Liu, D. Leow, T.-Y. Sun, P. Chen, X. Zhang, J.-Q. Yu, Y.-D. Wu and K. N. Houk, *J. Am. Chem. Soc.*, 2014, **136**, 344–355.