Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Generation of (*E*)-*β*-sulfonyl enamines from sulfur dioxide via a radical process

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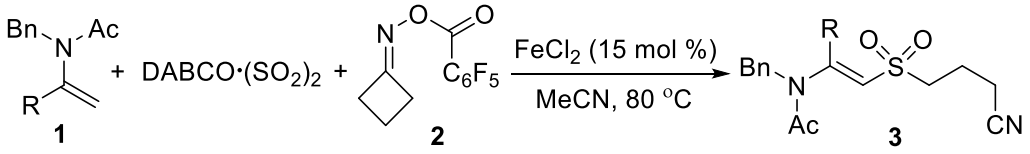
Supporting Information

General experimental methods:

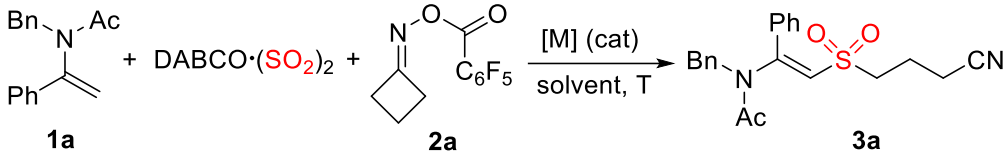
Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25-35 °C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

*General experimental procedure for the iron(II)-catalyzed reaction of N-vinylacetamides **1**, cyclobutanone O-perfluorobenzoyl oximes **2** and DABCO·(SO$_2$)$_2$.*



Cyclobutanone *O*-perfluorobenzoyl oxime **2** (0.45 mmol) was added to a mixture of DABCO·(SO$_2$)$_2$ (0.45 mmol), *N*-benzyl-*N*-(1-phenylvinyl)acetamide **1** (0.3 mmol) and $FeCl_2$ (15 mol %) in CH_3CN (1.5 mL) at 80 °Cunder N_2 atmosphere. The mixture was stirred for 12 hours. After completion of reaction as indicated by TLC, the solvent was evaporated and the residue was purified directly by flash column chromatography (*n*-hexane/ethyl acetate = 1:1) to give the corresponding product **3**.

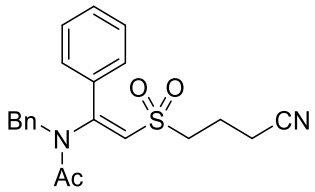
Table S1. Optimization of reaction conditions [a]



Entry	[M]	Solvent	T (°C)	Yield (%)[b]
1	CuCl (10 mol %)	DMF	50	Trace
2	$Fe(acac)_3$ (10 mol %)	DMF	50	16
3	$Fe(NO_3)_3$ (10 mol %)	DMF	50	10
4	$Fe(OTf)_3$ (10 mol %)	DMF	50	12
5	$FeCl_3$ (10 mol %)	DMF	50	37
6	$FeSO_4$ (10 mol %)	DMF	50	9
7	$FeBr_2$ (10 mol %)	DMF	50	trace
8	$FeCl_2$ (10 mol %)	DMF	50	45
9	$Fe(OAc)_2$ (10 mol %)	DMF	50	trace
10	$Fe(OTf)_2$ (10 mol %)	DMF	50	12
11	$FeCl_2$ (5 mol %)	DMF	50	23
12	$FeCl_2$ (15 mol %)	DMF	50	55
13	$FeCl_2$ (20 mol %)	DMF	50	51
14	$FeCl_2$ (15 mol %)	DMSO	50	14
15	$FeCl_2$ (15 mol %)	MeCN	50	75
16	$FeCl_2$ (15 mol %)	toluene	50	54
17	$FeCl_2$ (15 mol %)	DMA	50	20
18	$FeCl_2$ (15 mol %)	NMP	50	25
19	$FeCl_2$ (15 mol %)	dioxane	50	47
20	$FeCl_2$ (15 mol %)	MeCN	25	62
21	$FeCl_2$ (15 mol %)	MeCN	80	82 (78)
22	$FeCl_2$ (15 mol %)	MeCN	110	72

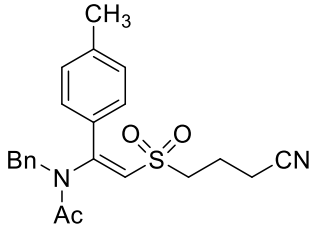
[a] Reaction conditions: *N*-benzyl-*N*-(1-phenylvinyl)acetamide **1a** (0.3 mmol), cyclobutanone *O*-perfluorobenzoyl oxime **2a** (0.45 mmol, 1.5 equiv), $DABCO{\cdot}(SO_2)_2$

(0.45 mmol, 1.5 equiv), catalyst (15 mol %), , solvent (1.5 mL), N_2, 80 °C, 12 h. [b] ^{1}H NMR yield using 1,3,5-trimethoxybenzene as internal standard (Isolated yield in parentheses).



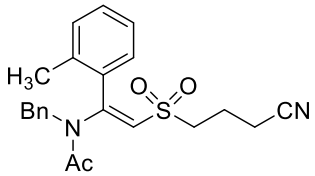
(*E*)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (**3a**)

Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3a**. Colorless oil; 89.4 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.57 (m, 1H), 7.43-7.50 (m, 4H), 7.27-7.38 (m, 3H), 7.14-7.20 (m, 2H), 6.18 (s, 1H), 4.65 (s, 2H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.19 (s, 3H), 1.91-2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 153.1, 136.2, 132.1, 131.8, 129.8, 128.9, 128.8, 128.1, 128.0, 125.0, 117.9, 53.1, 50.9, 23.5, 18.4, 16.1; HRMS (ESI) calcd for $C_{21}H_{22}N_2O_3SNa$ $[M+Na]^+$: 405.1243, found: 405.1245.



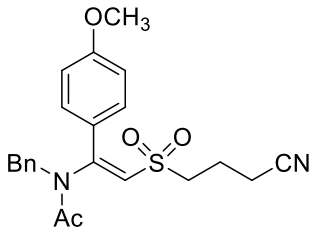
(*E*)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(p-tolyl)vinyl)acetamide (**3b**)

Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3b**. Colorless oil; 102.3 mg, 86% yield;1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.38 (m, 5H), 7.27-7.31 (m, 2H), 7.15-7.20 (m, 2H), 6.11 (s, 1H), 4.65 (s, 2H), 2.81 (t, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 5H), 2.17 (s, 3H), 1.92-2.01 (m, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 170.5, 153.3, 142.6, 136.3, 129.8, 129.5, 129.2, 128.9, 128.2, 128.0, 124.4, 118.0, 53.0, 50.9, 23.5, 21.6, 18.4, 16.1; HRMS (ESI) calcd for $C_{22}H_{24}N_2O_3SNa$ $[M+Na]^+$: 419.1400, found: 419.1409.



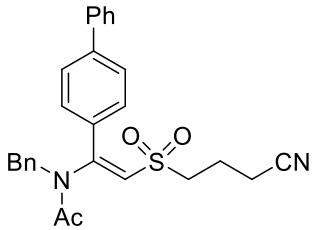
(*E*)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(o-tolyl)vinyl)acetamide (**3c**)

Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3c**. Colorless oil; 104.6 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.41 (m, 1H), 7.28-7.35 (m, 2H), 7.18-7.28 (m, 3H), 7.10-7.15 (m, 1H), 7.03-7.09 (m, 2H), 6.53 (s, 1H), 4.54 (s, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 2.24 (s, 3H), 1.99-2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 152.8, 136.9, 136.3, 131.1, 130.8, 130.8, 130.6, 128.8, 127.6, 126.7, 125.6, 122.8, 118.1, 53.6, 50.3, 23.7, 19.5, 18.5, 15.9; HRMS (ESI) calcd for $C_{22}H_{24}N_2O_3SNa$ $[M+Na]^+$: 419.1400, found: 419.1404.



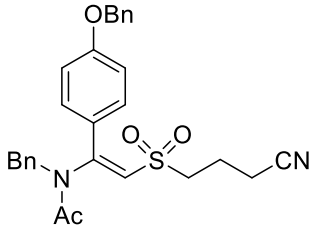
(*E*)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(4-methoxyphenyl)vinyl)acetamide (**3d**)

Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3d**. Colorless oil; 104.0 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.46 (m, 2H), 7.27-7.37 (m, 3H), 7.15-7.21 (m, 2H), 6.92-6.99 (m, 2H), 6.07 (s, 1H), 4.66 (s, 2H), 3.85 (s, 3H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.14 (s, 3H), 1.89-1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 162.3, 152.8, 136.3, 131.6, 128.7, 128.1, 127.8, 124.0, 123.4, 118.0, 114.1, 55.3, 52.8, 50.9, 23.3, 18.3, 15.9; HRMS (ESI) calcd for $C_{22}H_{24}N_2O_4SNa$ $[M+Na]^+$: 435.1349, found: 435.1353.



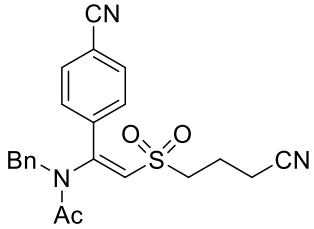
(*E*)-*N*-(1-([1,1'-biphenyl]-4-yl)-2-((3-cyanopropyl)sulfonyl)vinyl)-*N*-benzylacetamide (**3e**)

Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3e**. Colorless oil; 114.2 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.72 (m, 4H), 7.51-7.56 (m, 2H), 7.44-7.50 (m, 2H), 7.27-7.43 (m, 4H), 7.17-7.23 (m, 2H), 6.18 (s, 1H), 4.69 (s, 2H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.44 (t, *J* = 7.0 Hz, 2H), 2.21 (s, 3H), 1.94-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 152.8, 144.5, 139.3, 136.3, 130.7, 130.3, 128.9, 128.9, 128.3, 128.2, 128.0, 127.3, 127.2, 124.9, 118.0, 53.1, 51.0, 23.4, 18.5, 16.1; HRMS (ESI) calcd for $C_{27}H_{26}N_2O_3SNa$ $[M+Na]^+$: 481.1556, found: 481.1569.



(*E*)-*N*-benzyl-N-(1-(4-(benzyloxy)phenyl)-2-((3-cyanopropyl)sulfonyl)vinyl)acetamide (**3f**)

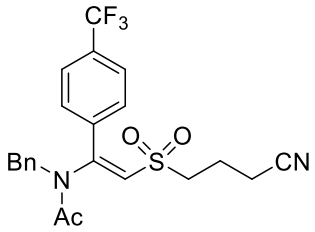
Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3f**. Colorless oil; 98.2 mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.46 (m, 6H), 7.26-7.37 (m, 4H), 7.14-7.20 (m, 2H), 7.01-7.06 (m, 2H), 6.06 (s, 1H), 5.10 (s, 2H), 4.66 (s, 2H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.40 (t, *J* = 7.0 Hz, 2H), 2.14 (s, 3H), 1.89-1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 161.5, 152.7, 136.3, 135.9, 131.6, 128.7, 128.6, 128.2, 128.2, 127.9, 127.5, 124.2, 123.6, 118.0, 114.9, 52.9, 50.9, 23.4, 18.3, 16.0; HRMS (ESI) calcd for $C_{28}H_{28}N_2O_4SNa$ $[M+Na]^+$: 511.1662, found: 511.1666.



(*E*)-*N*-benzyl-*N*-(1-(4-cyanophenyl)-2-((3-cyanopropyl)sulfonyl)vinyl)acetamide (**3g**)

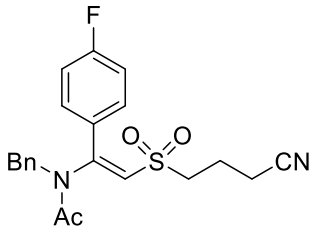
Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3g**. Colorless oil; 51.3 mg, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.75 (m, 2H), 7.48-7.53 (m, 2H), 7.31-7.39 (m, 3H), 7.09-7.15 (m, 2H), 6.36 (s, 1H), 4.61 (s, 2H), 2.97 (t, *J* = 7.4 Hz, 2H), 2.48 (t, *J* = 6.9 Hz, 2H), 2.25 (s, 3H), 1.98-2.08 (m, 2H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 170.4, 151.0, 136.5, 135.6, 132.0, 130.4, 129.1, 128.3, 127.6, 125.9, 117.9, 117.7, 114.9, 53.6, 51.2, 23.3, 18.3, 16.0; HRMS (ESI) calcd for $C_{22}H_{21}N_2O_3SNa$ $[M+Na]^+$: 430.1196, found: 430.1203.



(*E*)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(4-(trifluoromethyl)phenyl)vinyl)acetamide (**3h**)

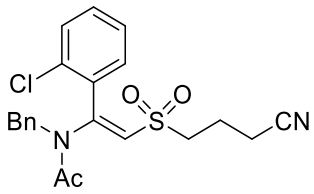
Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3h**. Colorless oil; 77.0 mg, 57% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz , 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.28-7.39 (m, 3H), 7.13 (d, *J* = 6.9 Hz , 2H), 6.33 (s, 1H), 4.61 (s, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.42-2.50 (m, 2H), 2.24 (s, 3H), 1.96-2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 151.5, 135.8, 135.6, 133.03 (q, *J* = 32.6 Hz), 130.2, 129.0, 128.1, 127.8, 125.9, 125.43 (q, *J* = 3.7 Hz), 123.41 (q, *J* = 271.0 Hz), 117.9, 53.5, 51.0, 23.3, 18.4, 16.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.96; HRMS (ESI) calcd for $C_{22}H_{21}F_3N_2O_3SNa$ $[M+Na]^+$: 473.1117, found: 473.1125.



(*E*)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(4-fluorophenyl)vinyl)acetamide (**3i**)

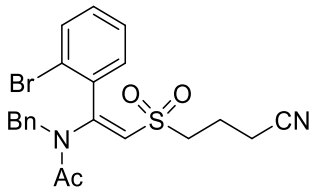
Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3i**. Colorless oil; 91.2 mg, 76% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.48 (m, 2H), 7.30-7.38 (m, 3H), 7.12-7.18(m, 4H), 6.18 (s, 1H), 4.64 (s, 2H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.47 (t, *J* = 7.0 Hz, 2H), 2.20 (s, 3H), 1.96-2.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 164.59 (d, *J* = 252.0 Hz), 152.1, 136.1, 132.10 (d, *J* = 8.9 Hz), 129.0, 128.1, 128.0, 124.9, 117.9, 116.06 (d, *J* = 22.0 Hz), 53.3, 51.0, 23.4, 18.4, 16.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.60-106.35 (m); HRMS (ESI) calcd for $C_{21}H_{21}FN_2O_3SNa$ $[M+Na]^+$: 423.1149, found:

423.1158.



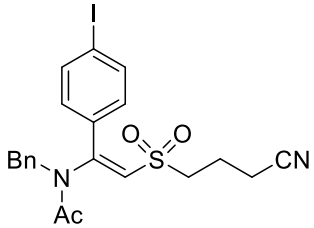
(*E*)-*N*-benzyl-*N*-(1-(2-chlorophenyl)-2-((3-cyanopropyl)sulfonyl)vinyl)acetamide (**3j**)

Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3j**. Colorless oil; 85.1 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.52 (m, 1H), 7.28-7.42 (m, 6H), 7.12-7.17 (m, 2H), 6.25 (s, 1H), 4.61 (s, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.22 (s, 3H), 1.97-2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 151.4, 136.0, 134.6, 133.7, 131.5, 129.8, 129.2, 128.8, 128.2, 128.0, 127.8, 125.6, 118.0, 53.3, 50.9, 23.3, 18.3, 16.0; HRMS (ESI) calcd for $C_{21}H_{21}ClN_2O_3SNa$ $[M+Na]^+$: 439.0854, found: 439.0857.



(*E*)-*N*-benzyl-*N*-(1-(2-bromophenyl)-2-((3-cyanopropyl)sulfonyl)vinyl)acetamide (**3k**)

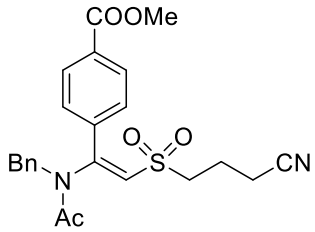
Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3k**. Colorless oil; 70.6 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.66 (m, 1H), 7.26-7.37 (m, 5H), 7.21-7.25 (m, 1H), 7.02-7.08 (m, 2H), 6.59 (s, 1H), 4.56 (s, 2H), 2.99 (t, *J* = 7.3 Hz, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.35 (s, 3H), 2.10-2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 151.8, 136.2, 134.3, 133.1, 132.1, 132.1, 128.9, 127.7, 126.9, 126.5, 122.9, 121.5, 118.1, 53.8, 50.9, 23.8, 18.7, 16.0; HRMS (ESI) calcd for $C_{21}H_{21}BrN_2O_3SNa$ $[M+Na]^+$: 483.0359, found: 483.0359.



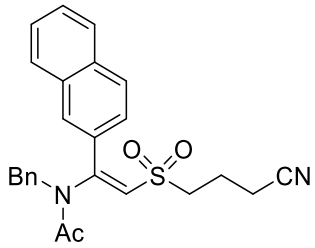
(*E*)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(4-iodophenyl)vinyl)acetamide (**3l**)

Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3l**.

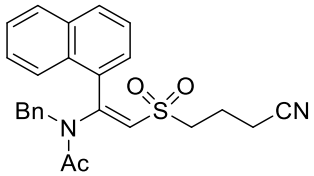
Colorless oil; 100.7 mg, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.82 (m, 2H), 7.28-7.37 (m, 3H), 7.10-7.17 (m, 4H), 6.22 (s, 1H), 4.60 (s, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.41-2.47 (m, 2H), 2.19 (s, 3H), 1.91-2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 152.1, 137.9, 136.0, 131.4, 131.2, 128.9, 128.1, 127.9, 125.1, 117.9, 98.7, 53.3, 51.0, 23.4, 18.4, 16.1; HRMS (ESI) calcd for $C_{21}H_{21}IN_2O_3SNa$ [M+Na]$^+$: 531.0210, found: 531.0217.



Methyl (*E*)-4-(1-(*N*-benzylacetamido)-2-((3-cyanopropyl)sulfonyl)vinyl)benzoate (**3m**) Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3m**. Colorless oil; 81.9 mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.28-7.40 (m, 3H), 7.11-7.17 (m, 2H), 6.29 (s, 1H), 4.61 (s, 2H), 3.95 (s, 3H),2.90 (t, *J* = 7.3 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.23 (s, 3H), 1.95-2.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 165.9, 152.0, 136.3, 135.9, 132.7, 129.8, 129.6, 129.0, 128.1, 127.9, 125.6, 117.9, 53.4, 52.4, 51.0, 23.4, 18.4, 16.0; HRMS (ESI) calcd for $C_{23}H_{24}N_2O_5SNa$ [M+Na]$^+$: 463.1298, found: 463.1302.

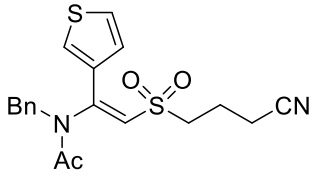


(*E*)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(naphthalen-2-yl)vinyl)acetamide (**3n**) Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3n**. Colorless oil; 111.6 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-8.01 (m, 4H), 7.53-7.63 (m, 2H), 7.44-7.50 (m, 1H), 7.28-7.38 (m, 3H), 7.15-7.21 (m, 2H), 6.27 (s, 1H), 4.67 (s, 2H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.37 (t, *J* = 7.0 Hz, 2H), 2.23 (s, 3H), 1.90-2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 153.1, 136.3, 134.4, 132.3, 131.0, 129.2, 128.9, 128.6, 128.2, 128.1, 128.0, 127.8, 127.2, 125.4, 125.2, 118.0, 53.2, 51.0, 23.5, 18.5, 16.0; HRMS (ESI) calcd for $C_{25}H_{24}N_2O_3SNa$ [M+Na]$^+$: 455.1400, found: 455.1408.



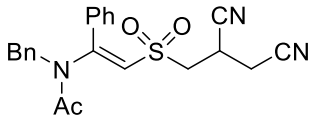
(*E*)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(naphthalen-1-yl)vinyl)acetamide (**3o**)

Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3o**. Colorless oil; 116.8 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-8.00 (m, 2H), 7.70-7.77 (m, 1H), 7.52-7.58 (m, 2H), 7.37-7.48 (m, 2H), 7.26-7.35 (m, 3H), 7.00-7.06 (m, 2H), 6.86 (s, 1H), 4.40 (d, *J* = 87.0 Hz, 2H), 2.77 (s, 2H), 2.33 (s, 3H), 2.26 (t, *J* = 7.1 Hz, 2H), 1.98-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 151.3, 136.3, 133.2, 131.4, 130.8, 130.8, 129.0, 128.9, 128.3, 127.8, 127.7, 126.7, 126.4, 125.3, 124.7, 123.5, 118.0, 53.4, 50.8, 23.9, 18.8, 15.8; HRMS (ESI) calcd for $C_{25}H_{24}N_2O_3SNa$ $[M+Na]^+$: 455.1400, found: 455.1410.



(*E*)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(thiophen-3-yl)vinyl)acetamide (**3p**)

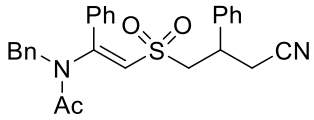
Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3p**. Colorless oil; 106.1 mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.84 (m, 1H), 7.41-7.45 (m, 1H), 7.28-7.38 (m, 3H), 7.21-7.24 (m, 3H), 6.10 (s, 1H), 4.73 (s, 2H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 2.10 (s, 3H), 1.89-1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 147.3, 136.2, 133.2, 131.5, 128.8, 128.3, 128.0, 127.8, 127.1, 124.9, 117.9, 52.5, 51.2, 23.1, 18.4, 16.0; HRMS (ESI) calcd for $C_{19}H_{20}N_2O_3SNa$ $[M+Na]^+$: 411.0808, found: 411.0809.



(*E*)-*N*-benzyl-*N*-(2-((2,3-dicyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (**3q**)

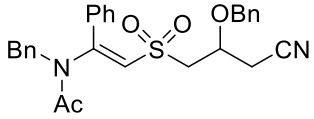
Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3q**. Colorless oil; 38.5 mg, 32% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.60 (m, 1H), 7.41-7.51 (m, 4H), 7.29-7.40 (m, 3H), 7.13-7.20 (m, 2H), 6.30 (s, 1H), 4.65-4.76 (m, 2H), 3.32-

3.41 (m, 1H), 2.94-3.08 (m, 2H), 2.75-2.83 (m, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 154.8, 136.0, 132.0, 131.8, 129.9, 129.0, 128.9, 128.1, 127.6, 122.6, 116.5, 114.7, 53.7, 51.6, 23.9, 23.2, 20.5; HRMS (ESI) calcd for $C_{22}H_{21}N_3O_3SNa$ $[M+Na]^+$: 430.1196, found: 430.1204.



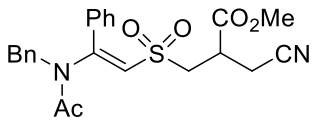
(*E*)-*N*-benzyl-*N*-(2-((3-cyano-2-phenylpropyl)sulfonyl)-1-phenylvinyl)acetamide (**3r**)

Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3r**. Colorless oil; 119.7 mg, 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.54 (m, 1H), 7.41 (d, *J* = 4.2 Hz, 4H), 7.26-7.35 (m, 6H), 7.05-7.15 (m, 4H), 6.10 (s, 1H), 4.60 (d, *J* = 15.4Hz, 1H), 4.53 (d, *J* = 15.4 Hz, 1H), 3.44-3.55 (m, 1H), 3.15-3.25 (m, 1H), 2.99-3.08 (m, 1H), 2.70-2.82 (m, 2H), 2.12 (d, J = 0.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 153.0, 139.0, 136.1, 132.0, 131.6, 129.7, 129.1, 128.7, 128.5, 128.3, 127.9, 127.8, 126.9, 124.9, 117.1, 58.3, 50.8, 35.7, 24.0, 23.3; HRMS (ESI) calcd for $C_{27}H_{26}N_2O_3SNa$ $[M+Na]^+$: 481.1556, found: 481.1566.



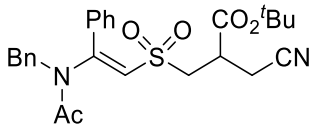
(*E*)-*N*-benzyl-*N*-(2-((2-(benzyloxy)-3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (**3s**)

Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3s**. Colorless oil; 123.1 mg, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.54 (m, 1H), 7.39-7.46 (m, 4H), 7.23-7.36 (m, 8H), 7.06-7.12 (m, 2H), 6.25 (s, 1H), 4.63 (d, *J* = 15.2 Hz, 1H), 4.51 (d, *J* = 11.2 Hz, 1H), 4.37-4.45 (m, 2H), 4.10-4.18 (m, 1H), 3.18-3.26 (m, 1H), 2.92-2.99 (m, 1H), 2.63-2.71 (m, 1H), 2.44-2.53 (m, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 152.6, 136.2, 136.0, 132.2, 131.5, 129.4, 128.6, 128.6, 128.5, 128.1, 128.0, 127.7, 125.7, 115.9, 72.4, 69.3, 58.6, 50.6, 23.2, 22.8; HRMS (ESI) calcd for $C_{28}H_{28}N_2O_4SNa$ $[M+Na]^+$: 511.1662, found: 511.1663.



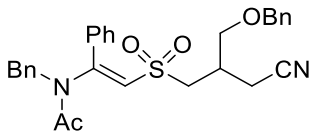
Methyl (*E*)-3-((2-(*N*-benzylacetamido)-2-phenylvinyl)sulfonyl)-2-(cyanomethyl)propanoate (**3t**)

Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3t**. Colorless oil; 69.4 mg, 35% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.58 (m, 1H), 7.43-7.50 (m, 4H), 7.28-7.37 (m, 3H), 7.14-7.18 (m, 2H), 6.26 (s, 1H), 4.59-4.70 (m, 2H), 3.72 (d, *J* = 0.8 Hz, 3H), 3.36 (dd, *J* = 14.2, 4.1 Hz, 1H), 3.14-3.22 (m, 1H), 2.97-3.05 (m, 1H), 2.75-2. 87 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.7, 153.8, 136.1, 131.9, 131.7, 129.8, 128.8, 128.6, 127.9, 127.9, 124.4, 116.4, 54.1, 53.2, 50.9, 35.8, 23.4, 19.0; HRMS (ESI) calcd for $C_{23}H_{24}N_2O_5SNa$ [M+Na]$^+$: 463.1298, found: 463.1303.



tert-butyl (*E*)-3-((2-(*N*-benzylacetamido)-2-phenylvinyl)sulfonyl)-2-(cyanomethyl)propanoate (**3u**)

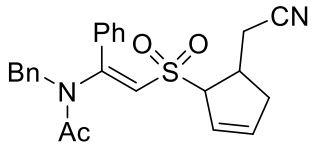
Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3u**. Colorless oil; 65.2 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.57 (m, 1H), 7.43-7.50 (m, 4H), 7.27-7.37 (m, 3H), 7.14-7.19 (m, 2H), 6.23 (s, 1H), 4.64 (s, 2H), 3.33 (dd, *J* = 14.1, 3.8 Hz, 1H), 3.02-3.10 (m, 1H), 2.91-2.99 (m, 1H), 2.71-2.83 (m, 2H), 2.20 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 168.2, 153.8, 136.3, 132.1, 131.8, 129.9, 128.9, 128.8, 128.1, 128.0, 124.9, 116.6, 83.8, 54.3, 51.0, 36.7, 27.8, 23.5, 19.4; HRMS (ESI) calcd for $C_{26}H_{30}N_2O_5SNa$ [M+Na]$^+$: 505.1768, found: 505.1772.



(*E*)-*N*-benzyl-*N*-(2-((3-(benzyloxy)-2-(cyanomethyl)propyl)sulfonyl)-1-phenylvinyl)acetamide (**3v**)

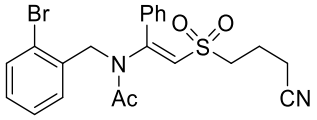
Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3v**. Colorless oil; 67.9 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.53 (m, 1H), 7.41-7.45 (m, 4H), 7.28-7.36 (m, 6H), 7.23-7.26 (m, 2H), 7.12-7.17(m, 2H), 6.18 (s, 1H), 4.61 (s, 2H), 4.44 (s, 2H), 3.38-3.47 (m, 2H), 2.96 (dd, *J* = 14.6, 5.2 Hz, 1H), 2.74-2.81 (m, 1H),

2.45-2.66 (m, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 153.1, 137.2, 136.2, 132.0, 131.7, 129.7, 128.8, 128.6, 128.4, 128.1, 128.0, 127.9, 127.7, 125.3, 117.2, 73.3, 69.8, 55.0, 50.8, 30.9, 23.4, 19.0; HRMS (ESI) calcd for $C_{29}H_{30}N_2O_4SNa$ $[M+Na]^+$: 525.1818, found: 525.1823.



(*E*)-*N*-benzyl-*N*-(2-((5-(cyanomethyl)cyclopent-2-en-1-yl)sulfonyl)-1-phenylvinyl)acetamide (**3w**)

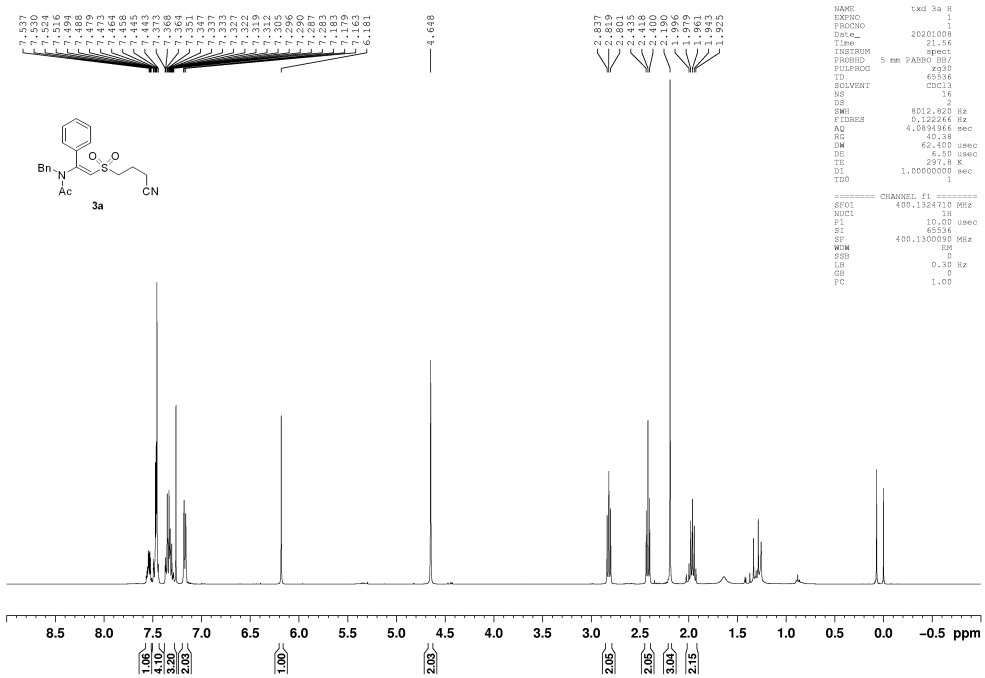
Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3w**. Colorless oil; 56.8 mg, 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.57 (m, 1H), 7.45-7.50 (m, 4H), 7.27-7.37 (m, 3H), 7.14-7.18 (m, 2H), 6.18 (s, 1H), 5.73-5.78 (m, 1H), 5.52-5.58 (m, 1H), 4.62 (s, 2H), 3.43-3.50 (m, 1H), 3.14-3.22 (m, 1H), 2.55-2.70 (m, 3H), 2.39-2.48 (m, 1H),2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 153.3, 136.2, 132.1, 131.6, 130.8, 129.6, 129.6, 128.8, 128.5, 127.9, 123.6, 117.0, 65.3, 50.8, 42.5, 34.4, 23.2, 23.0; HRMS (ESI) calcd for $C_{24}H_{24}N_2O_3SNa$ $[M+Na]^+$: 443.1400, found: 443.1402.

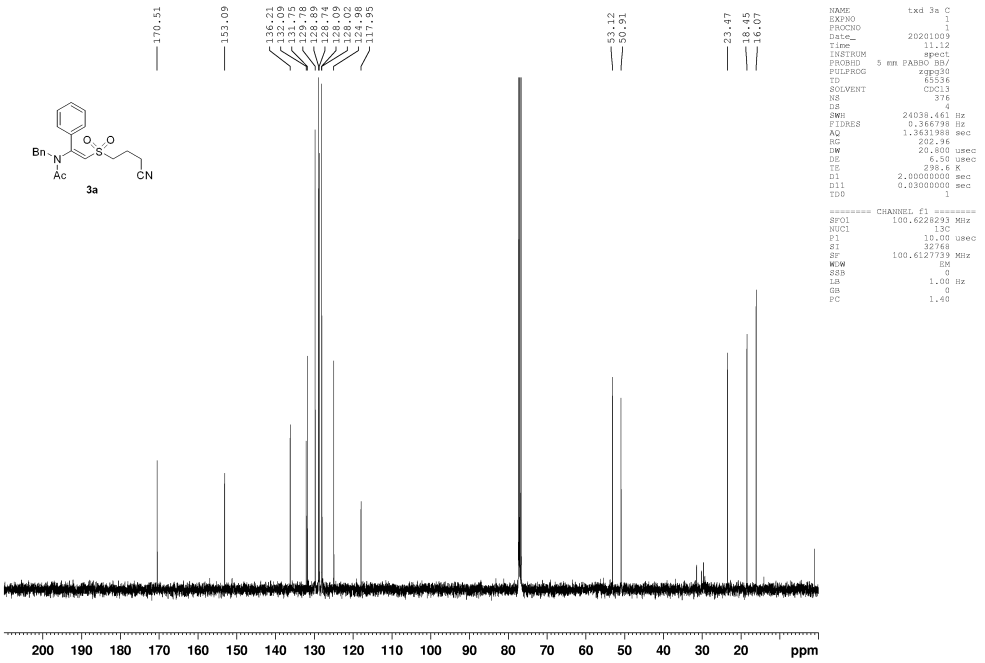


(*E*)-*N*-(2-bromobenzyl)-*N*-(2-((3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (**3x**)

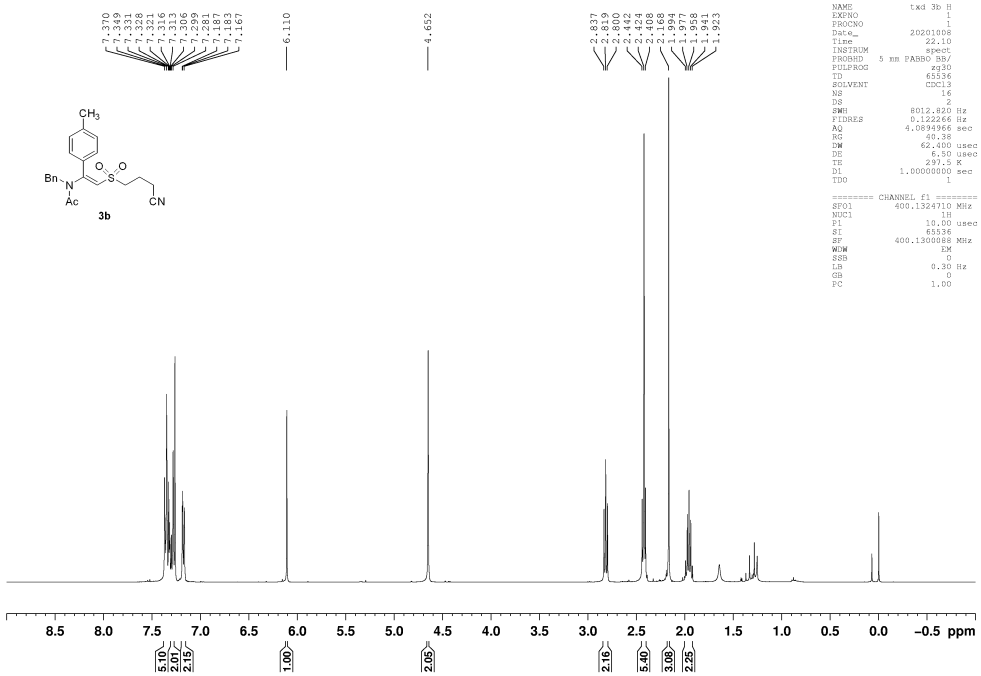
Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1) afforded **3x**. Colorless oil; 161.9 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.58 (m, 2H), 7.40-7.49 (m, 4H), 7.29-7.35 (m, 1H), 7.11-7.22 (m, 2H), 6.35 (s, 1H), 4.80 (s, 2H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.19 (s, 3H), 1.97-2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 153.1, 135.0, 133.2, 132.0, 131.8, 129.8, 129.6, 129.5, 128.7, 127.9, 124.7, 123.2, 118.0, 53.1, 51.5, 23.5, 18.5, 16.1; HRMS (ESI) calcd for $C_{21}H_{21}BrN_2O_3SNa$ $[M+Na]^+$: 483.0348, found: 483.0361.

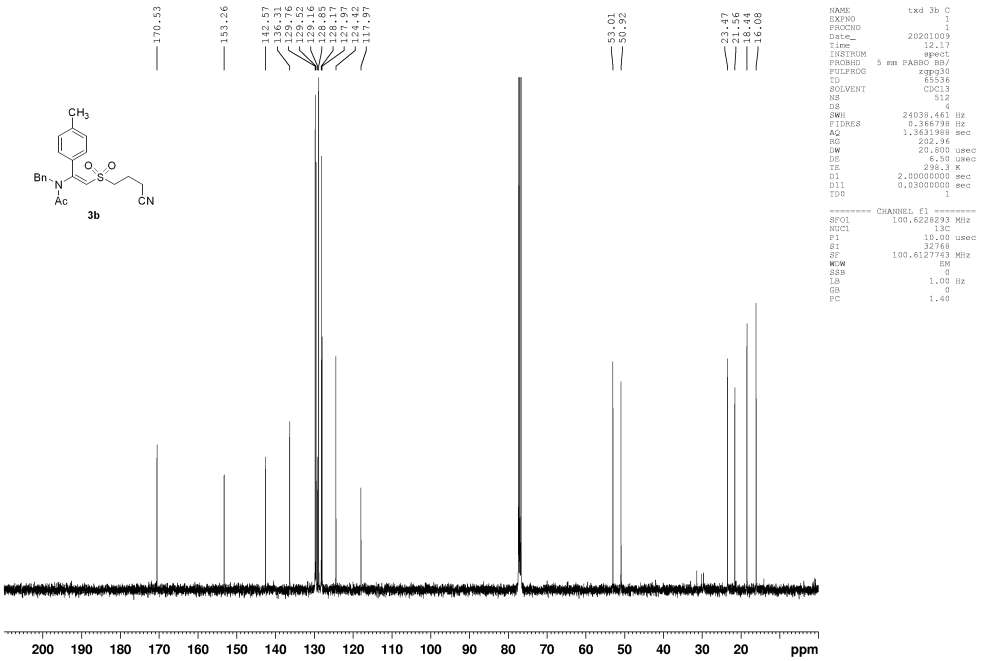
(E)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (**3a**)



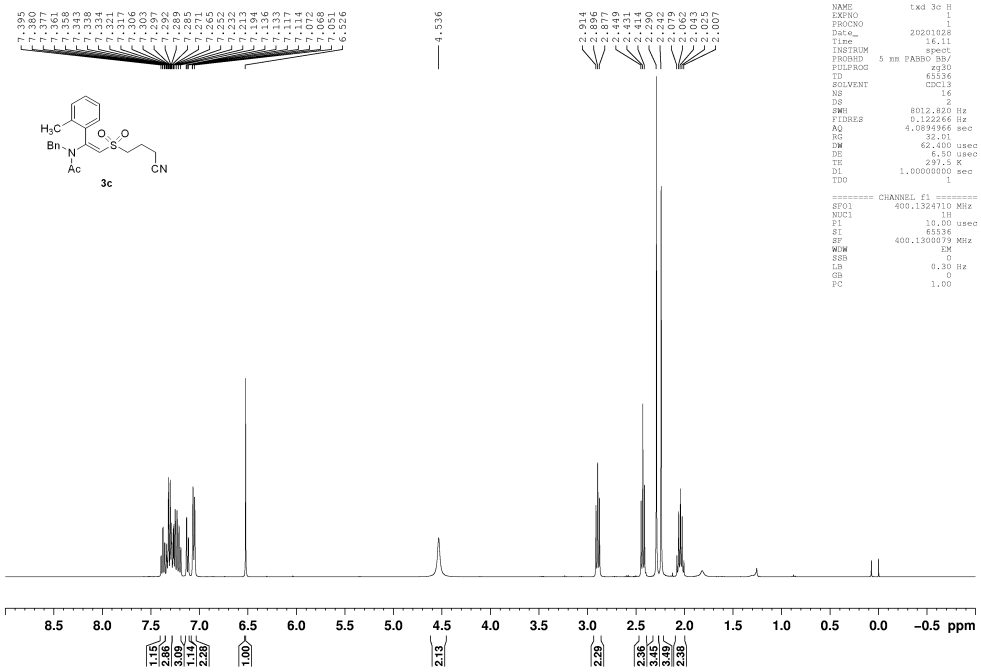


(E)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(p-tolyl)vinyl)acetamide (**3b**)





(E)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(o-tolyl)vinyl)acetamide (**3c**)

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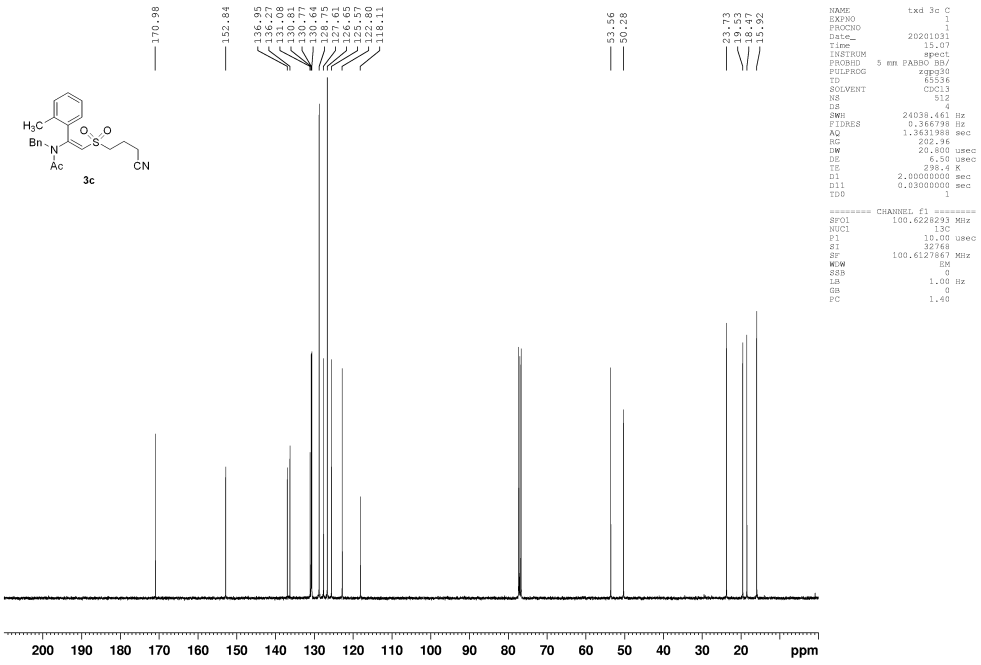


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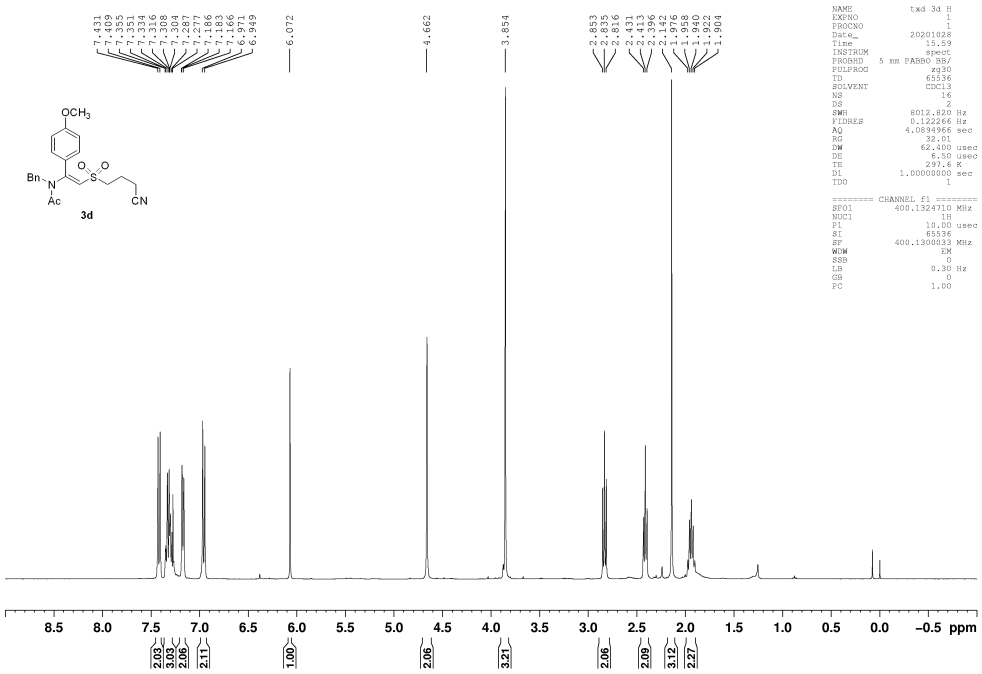
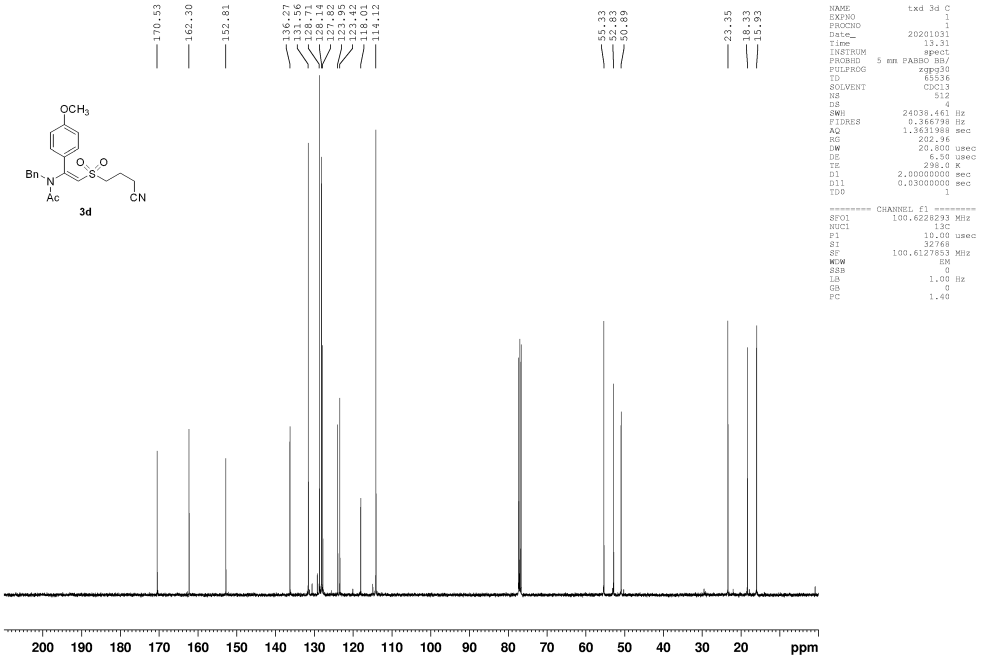
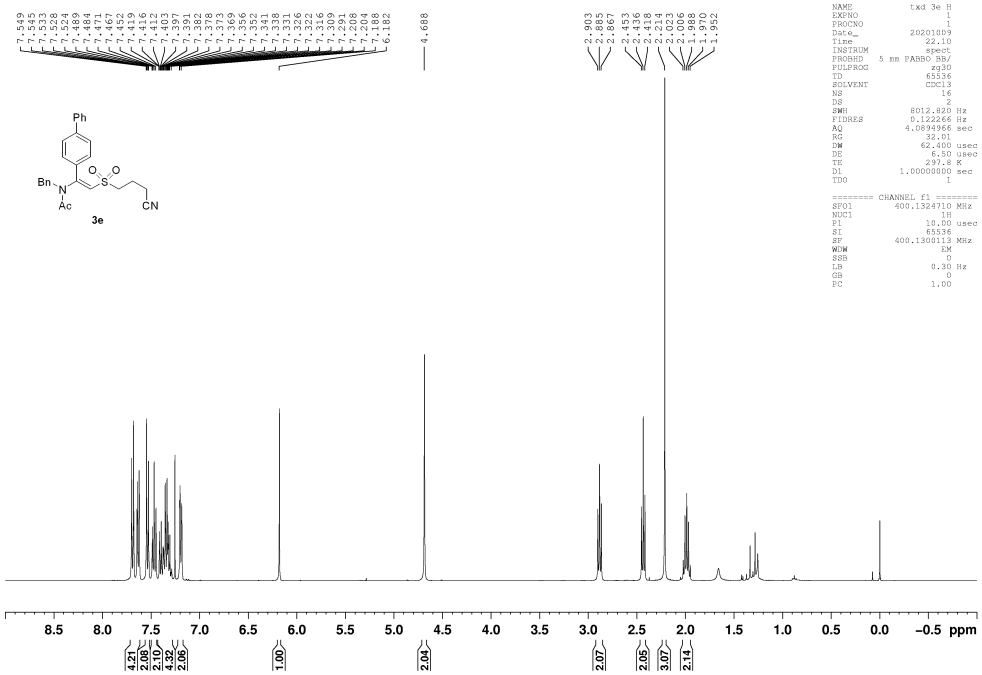
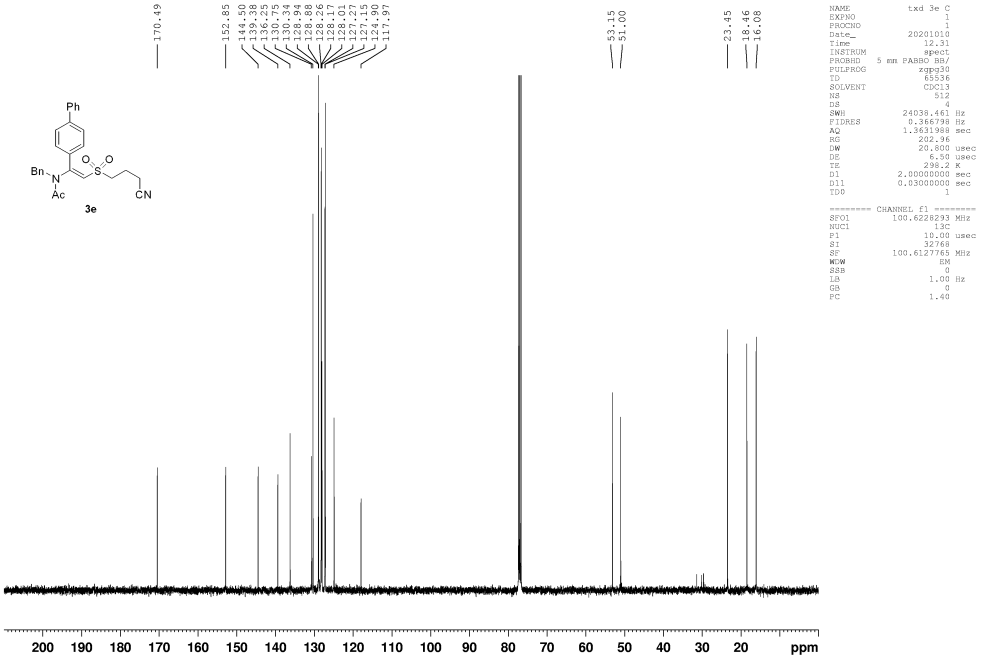
(E)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(4-methoxyphenyl)vinyl)acetamide (**3d**)



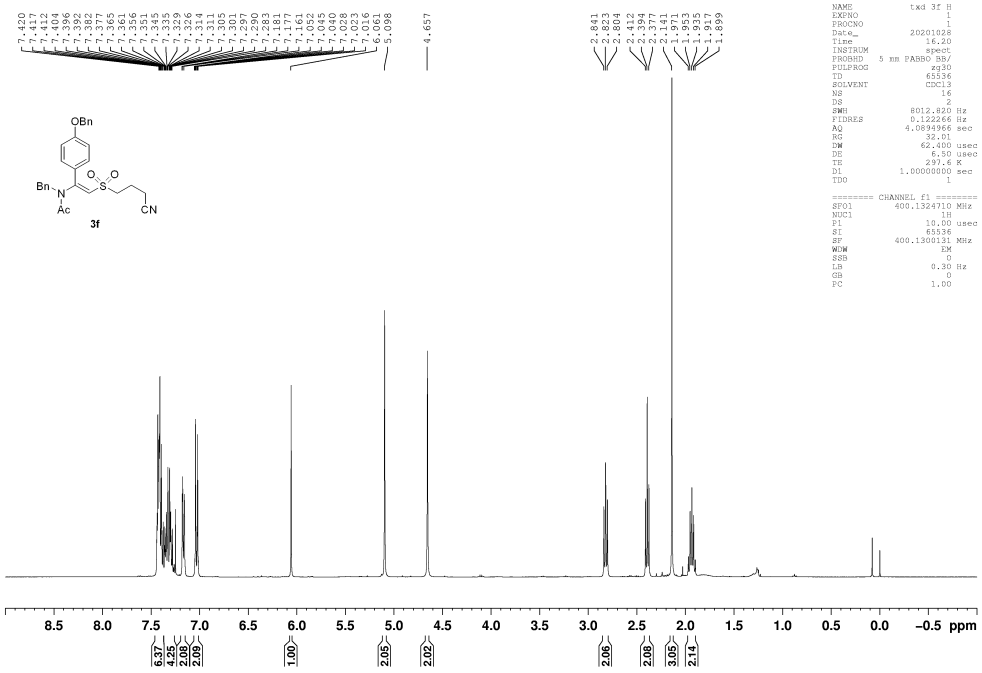


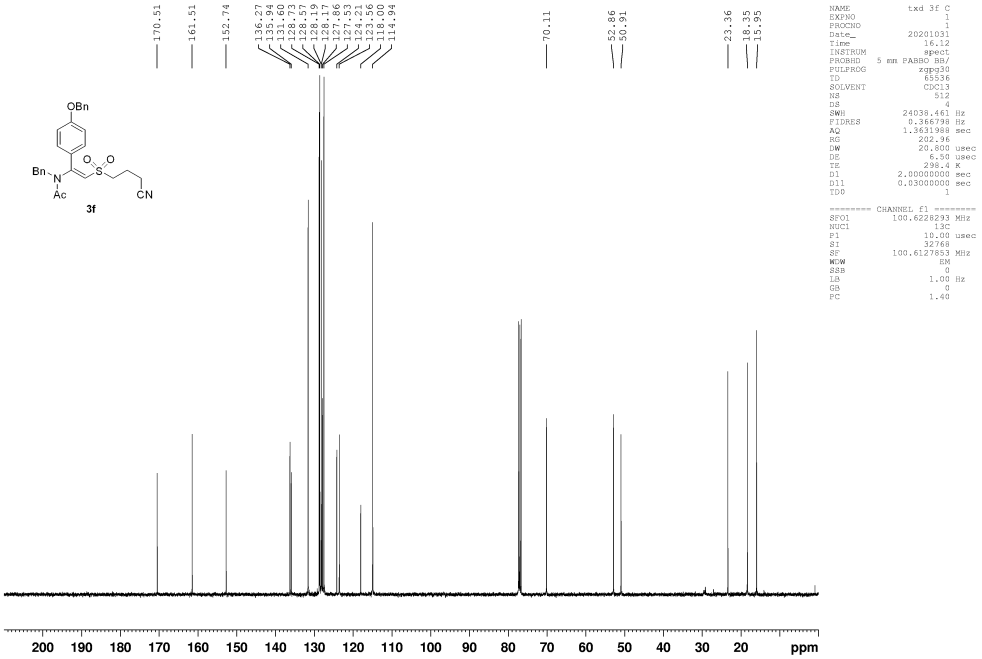
(E)-*N*-(1-([1,1'-biphenyl]-4-yl)-2-((3-cyanopropyl)sulfonyl)vinyl)-*N*-benzylacetamide (**3e**)



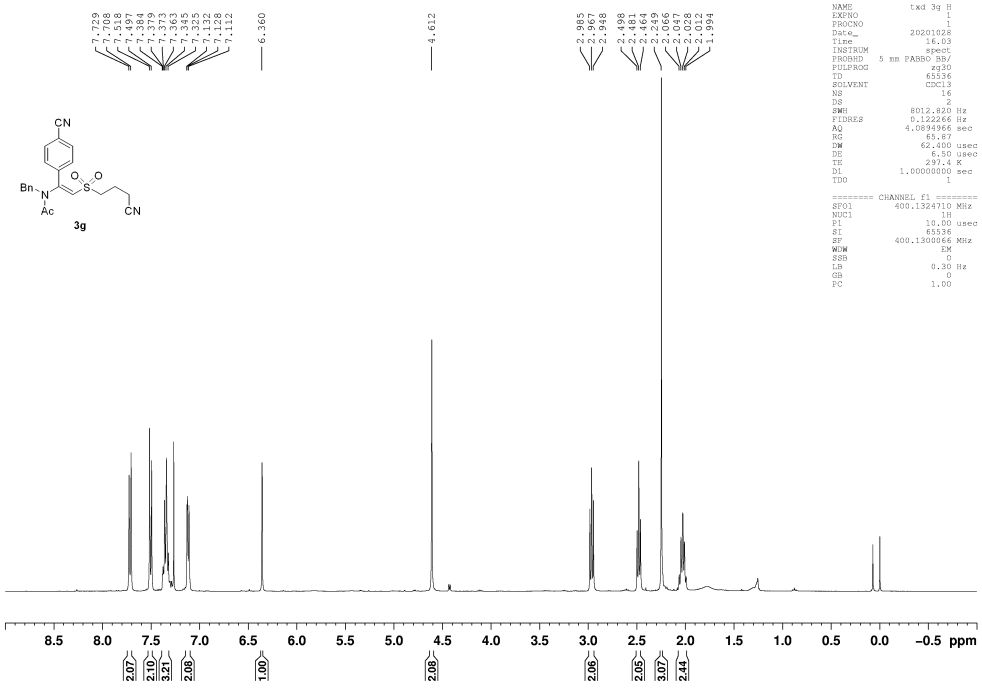


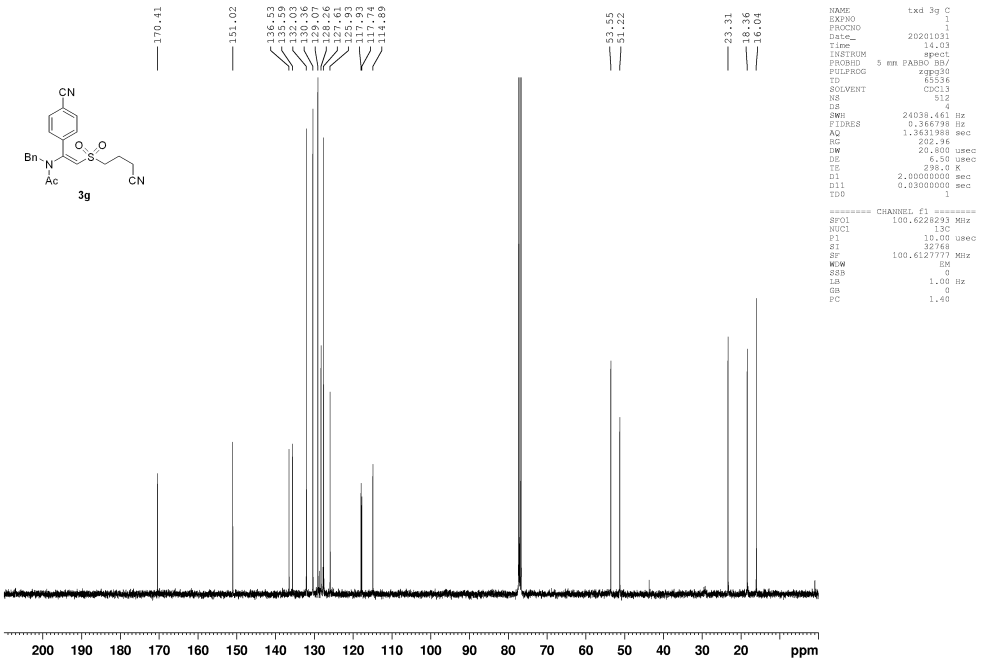
(E)-*N*-benzyl-*N*-(1-(4-(benzyloxy)phenyl)-2-((3-cyanopropyl)sulfonyl)vinyl)acetami-de (**3f**)



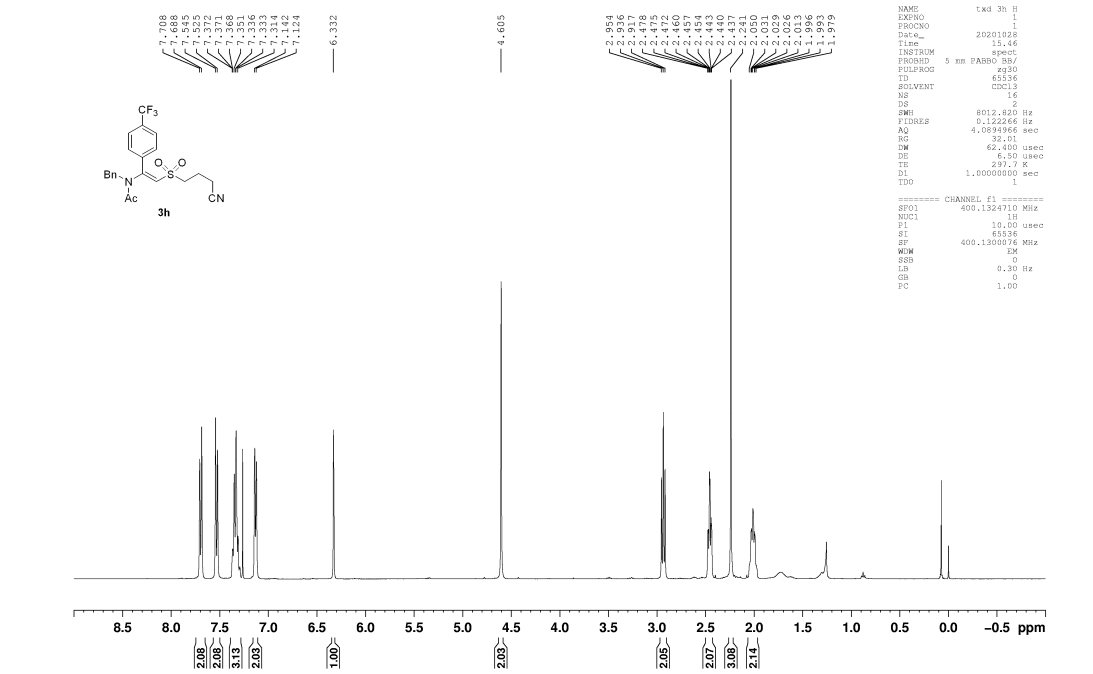


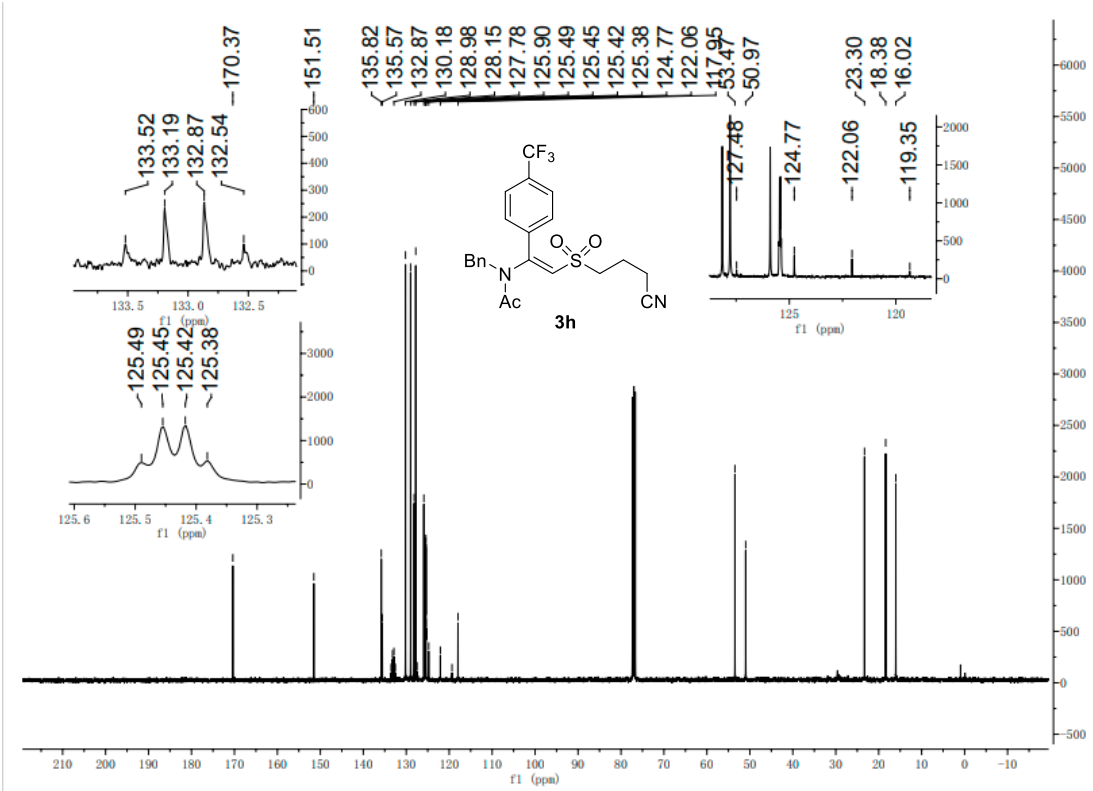
(E)-*N*-benzyl-*N*-(1-(4-cyanophenyl)-2-((3-cyanopropyl)sulfonyl)vinyl)acetamide (**3g**)

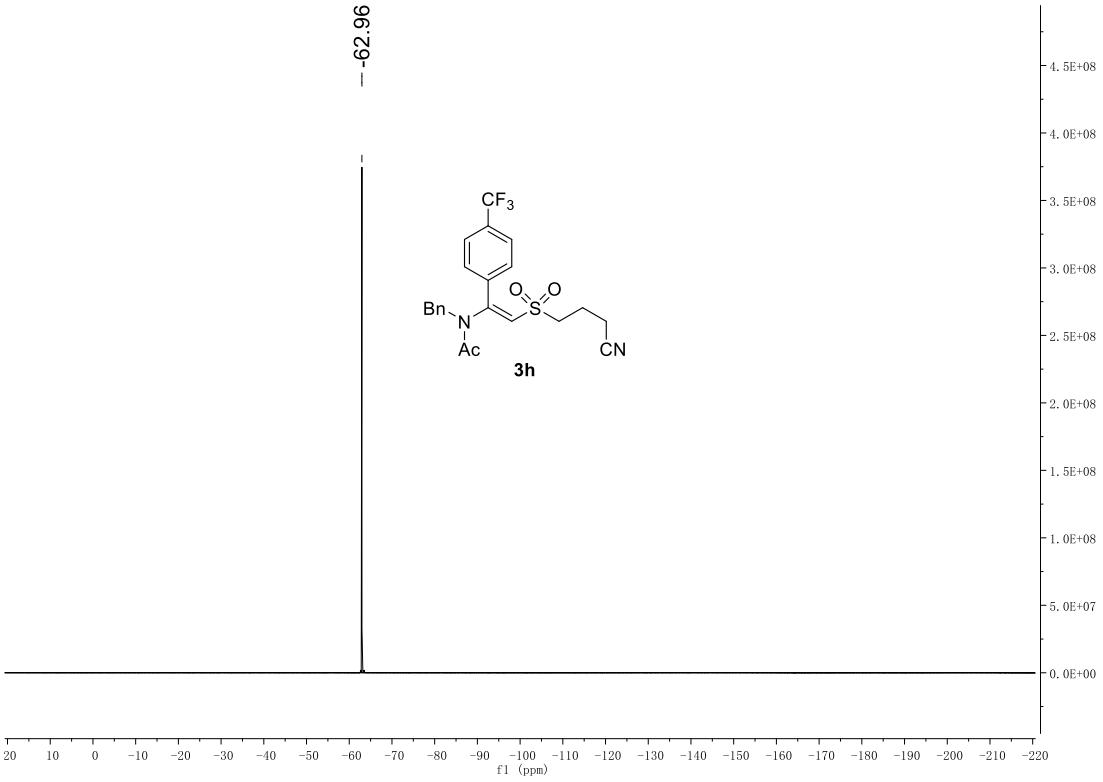




(E)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(4-(trifluoromethyl)phenyl)vinyl)aceta-mide (**3h**)



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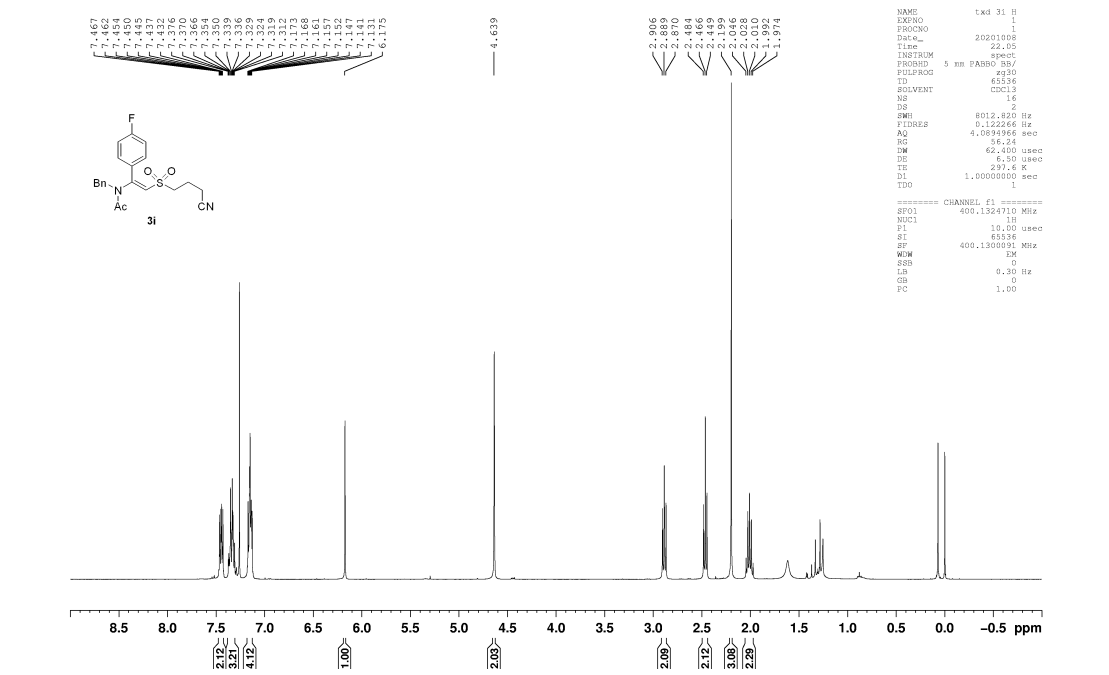
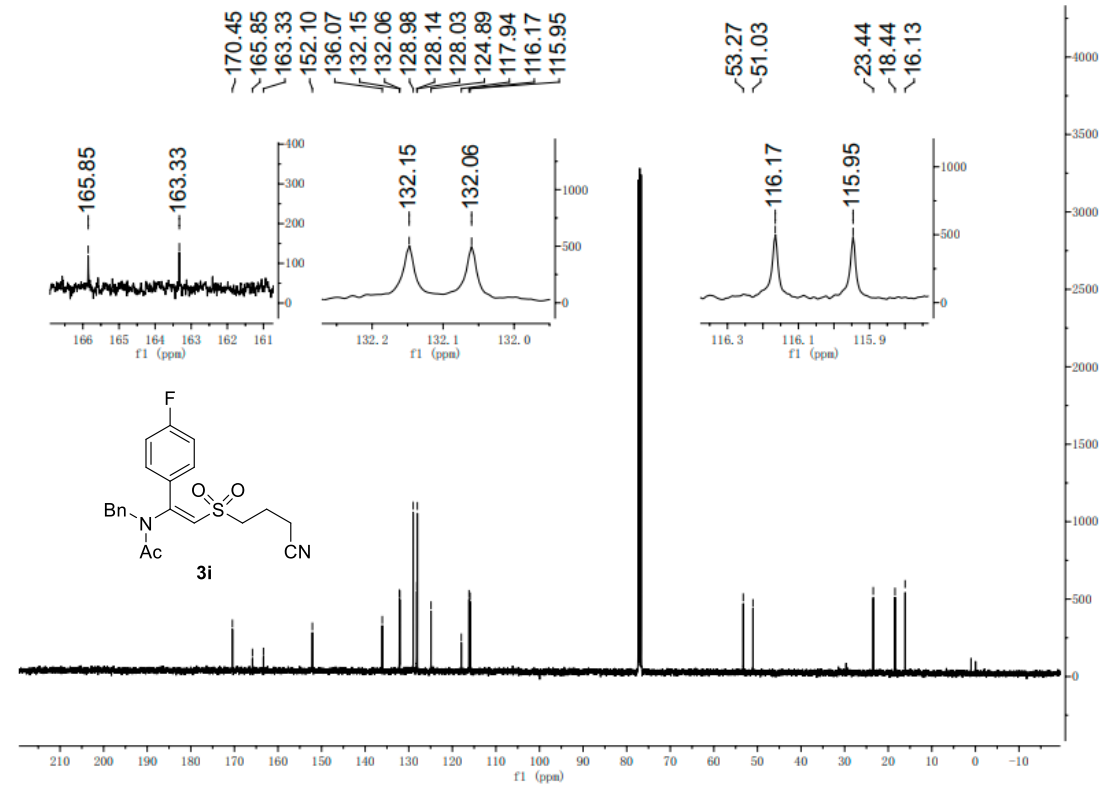
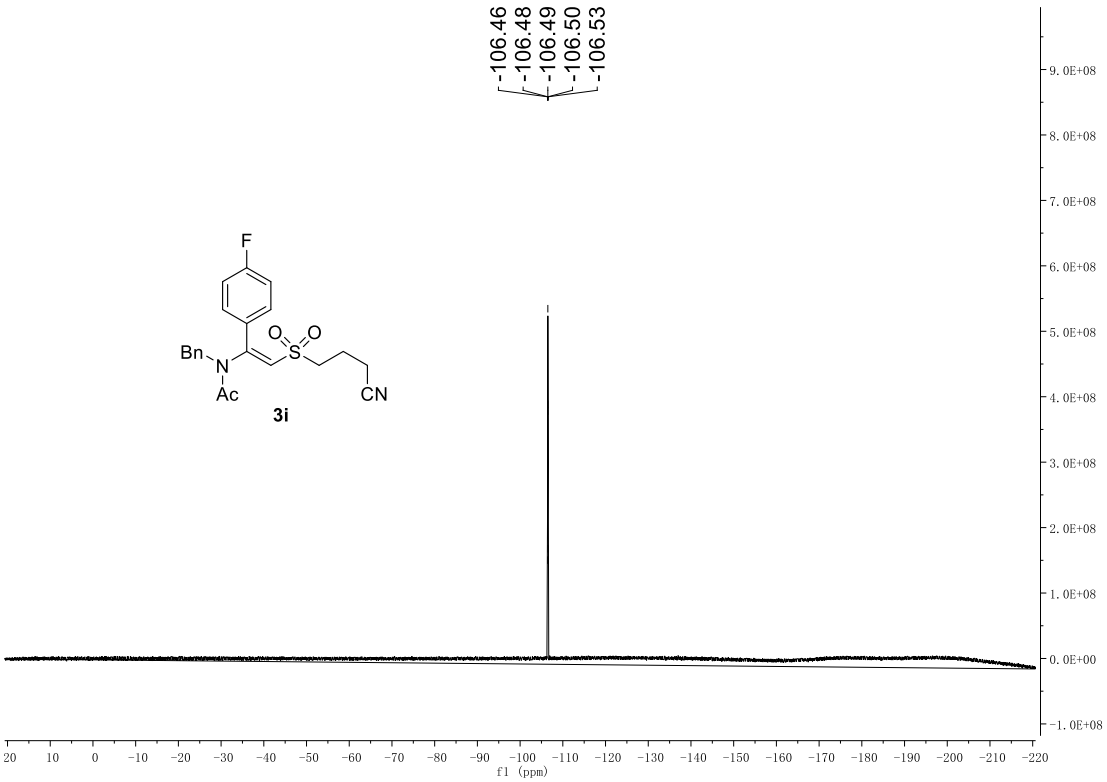
O
O
S
Bn
N
Ac
CN
3h
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

(E)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(4-fluorophenyl)vinyl)acetamide (**3i**)



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-106.49
-106.50
-106.53
F
O
O
S
Bn
N
Ac
CN
3i
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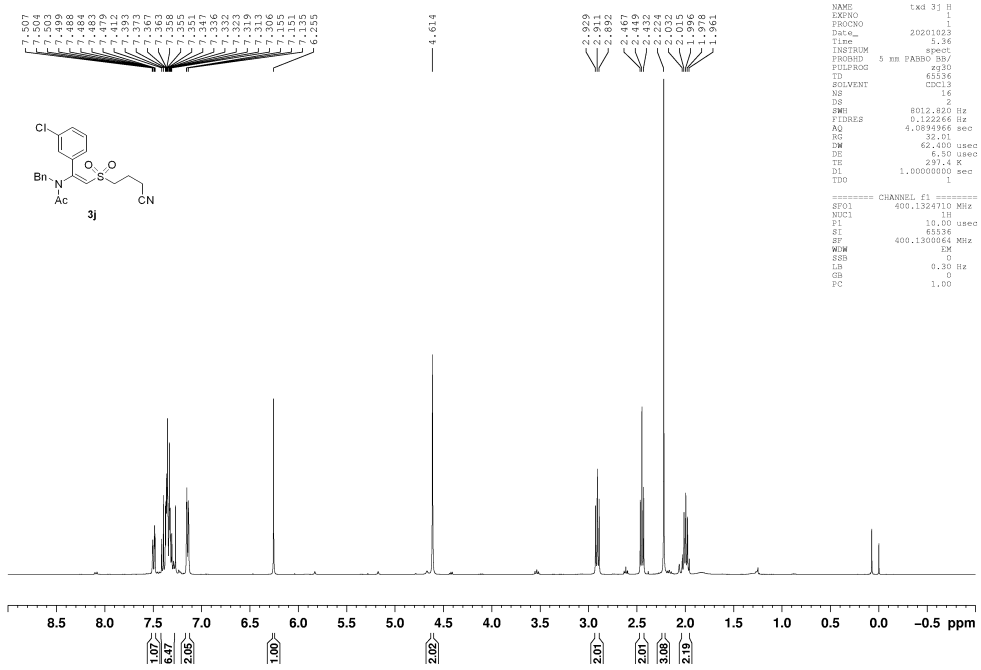
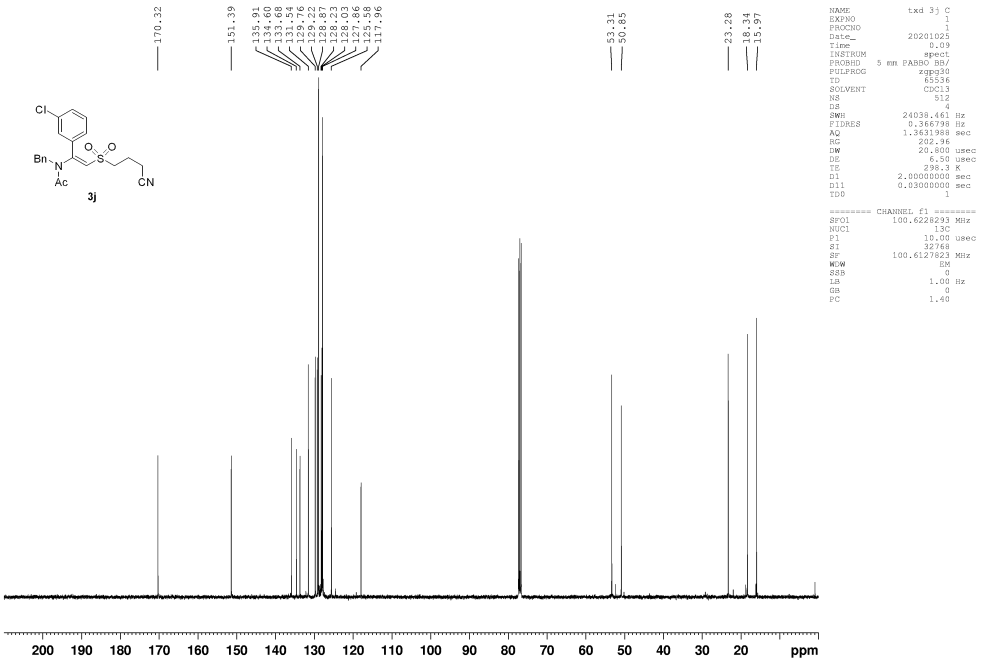
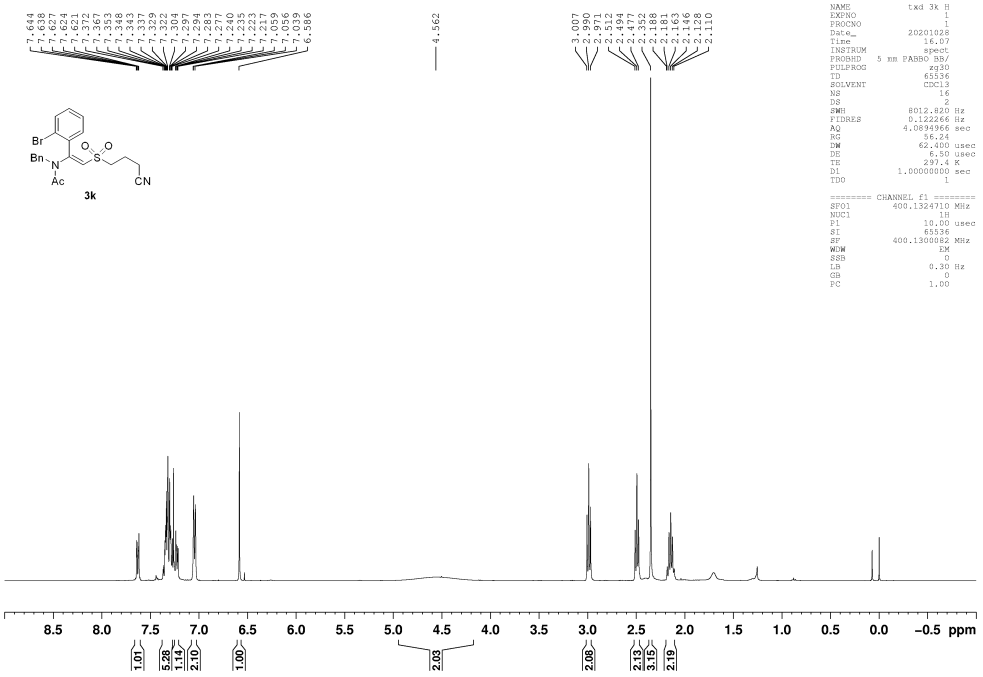
8.0E+08
7.0E+08
6.0E+08
5.0E+08
4.0E+08
3.0E+08
2.0E+08
1.0E+08
0.0E+00
-1.0E+08
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

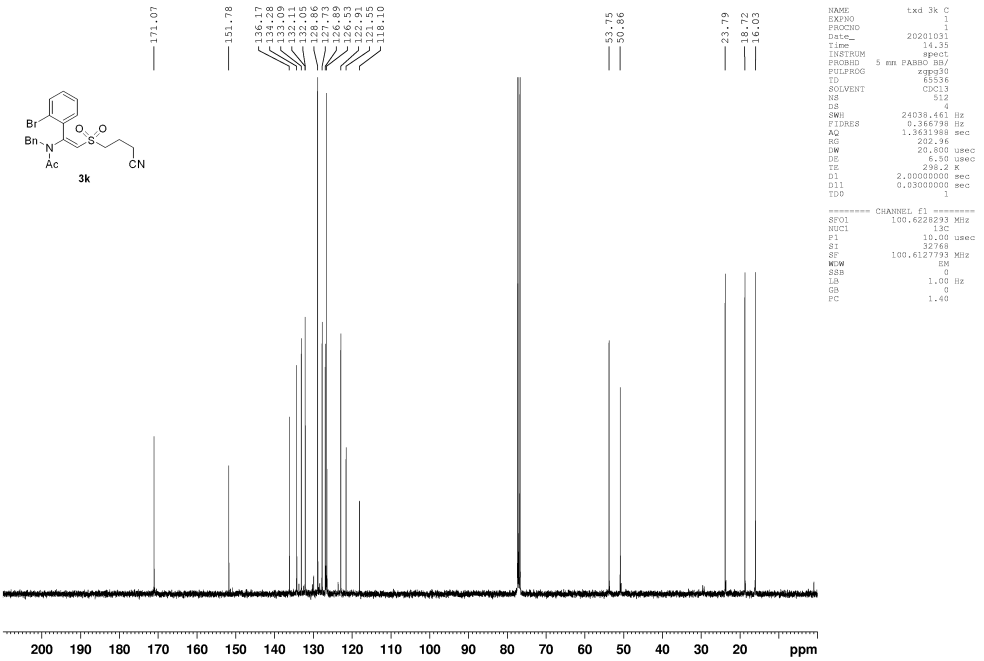
(E)-*N*-benzyl-*N*-(1-(2-chlorophenyl)-2-((3-cyanopropyl)sulfonyl)vinyl)acetamide (**3j**)



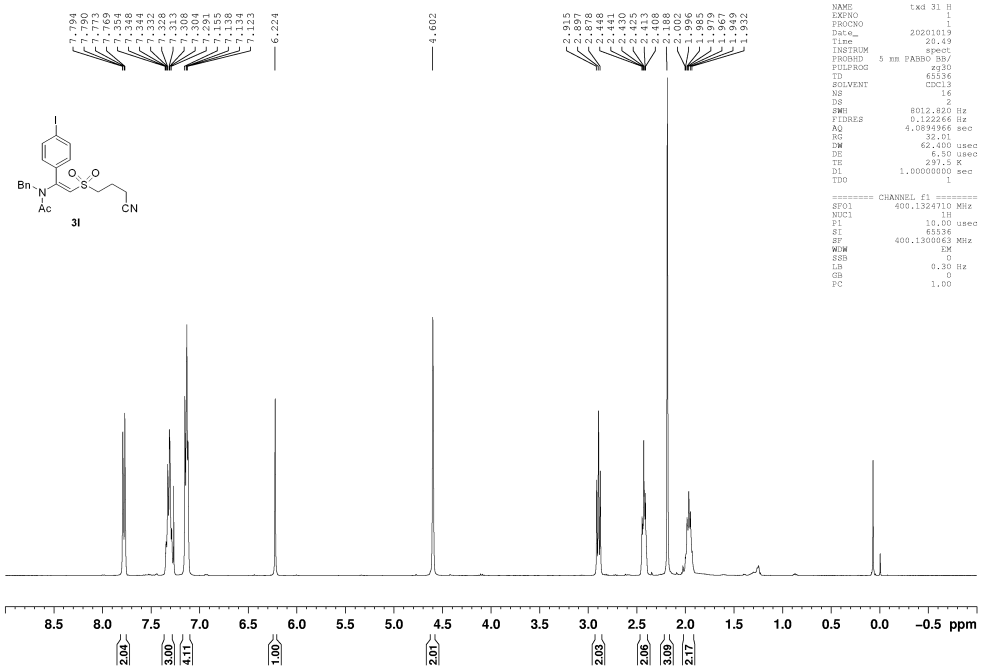


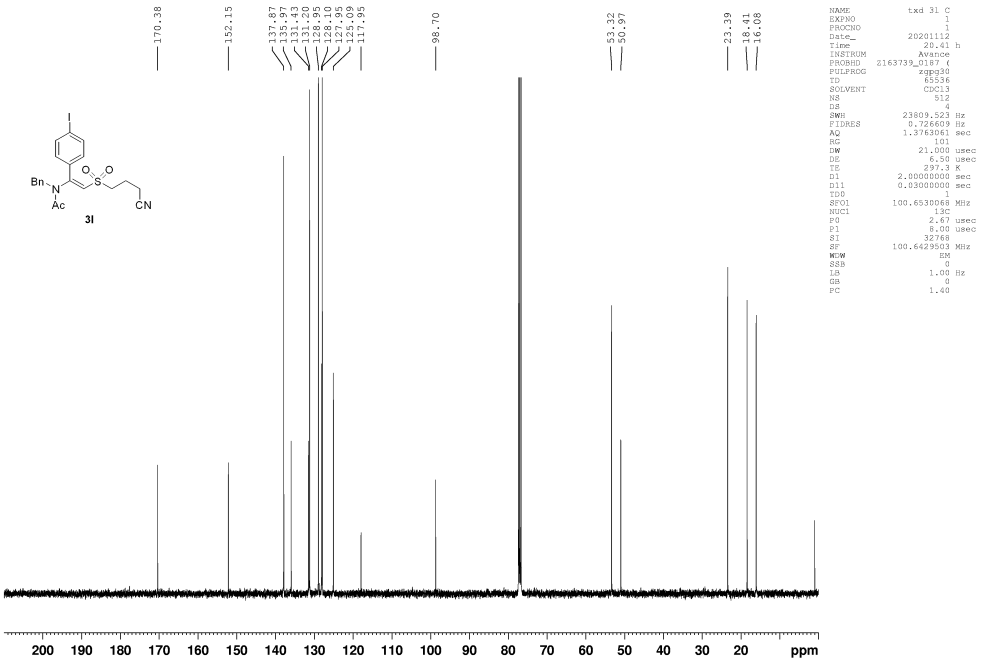
(E)-*N*-benzyl-*N*-(1-(2-bromophenyl)-2-((3-cyanopropyl)sulfonyl)vinyl)acetamide (**3k**)



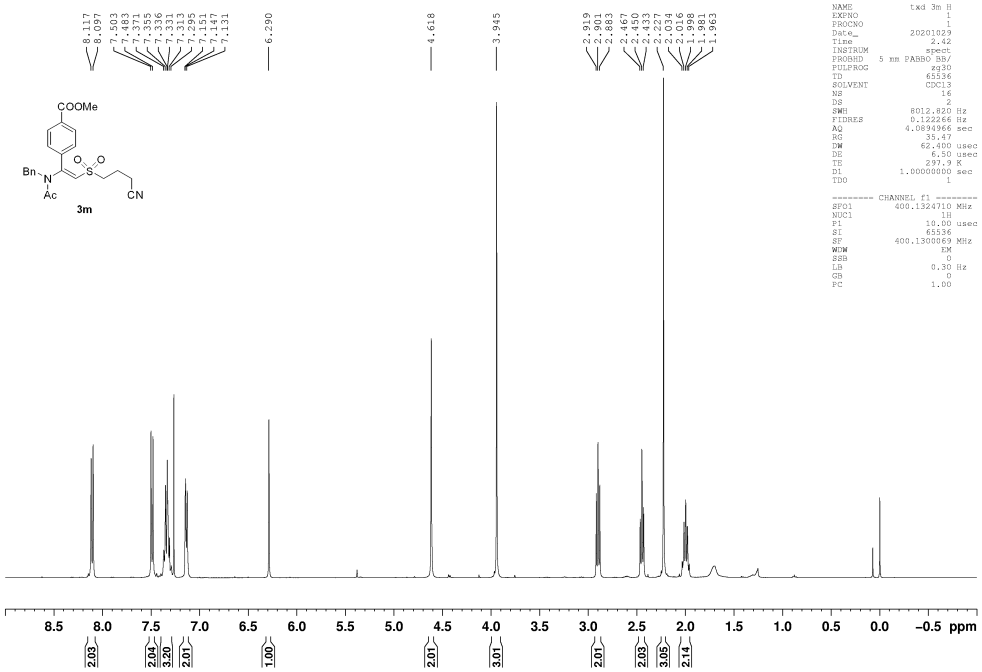


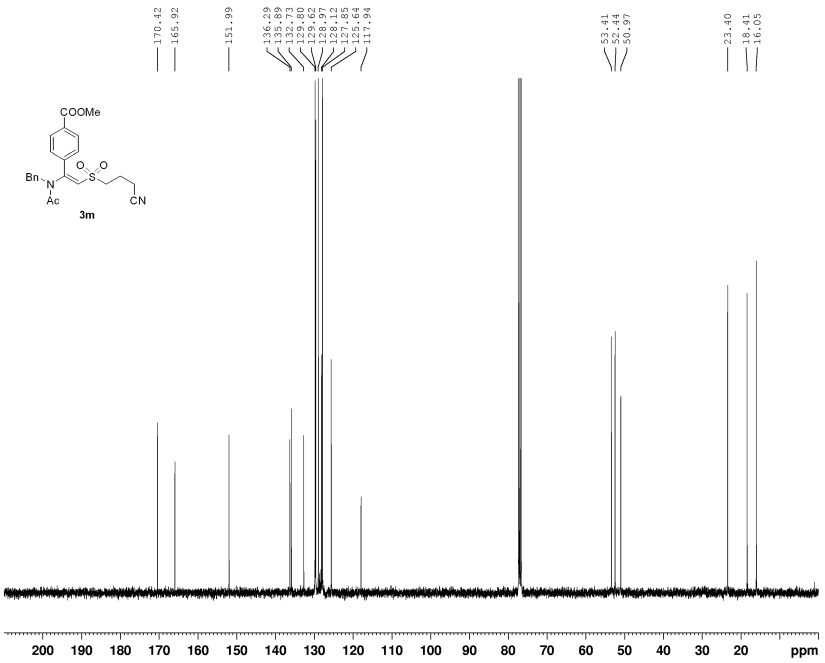
(E)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(4-iodophenyl)vinyl)acetamide (**3l**)



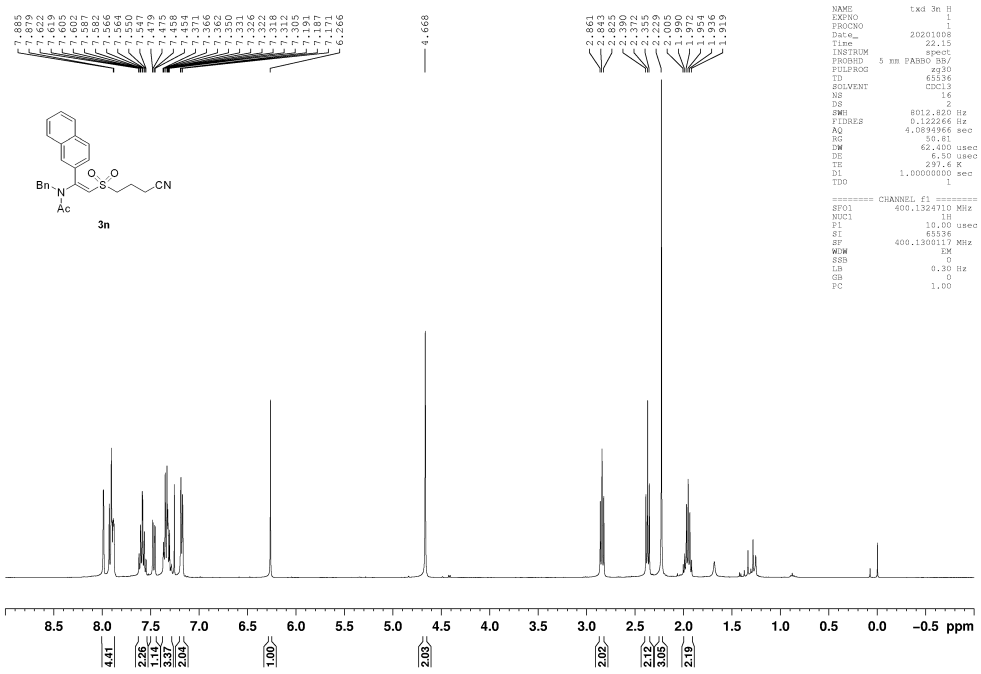


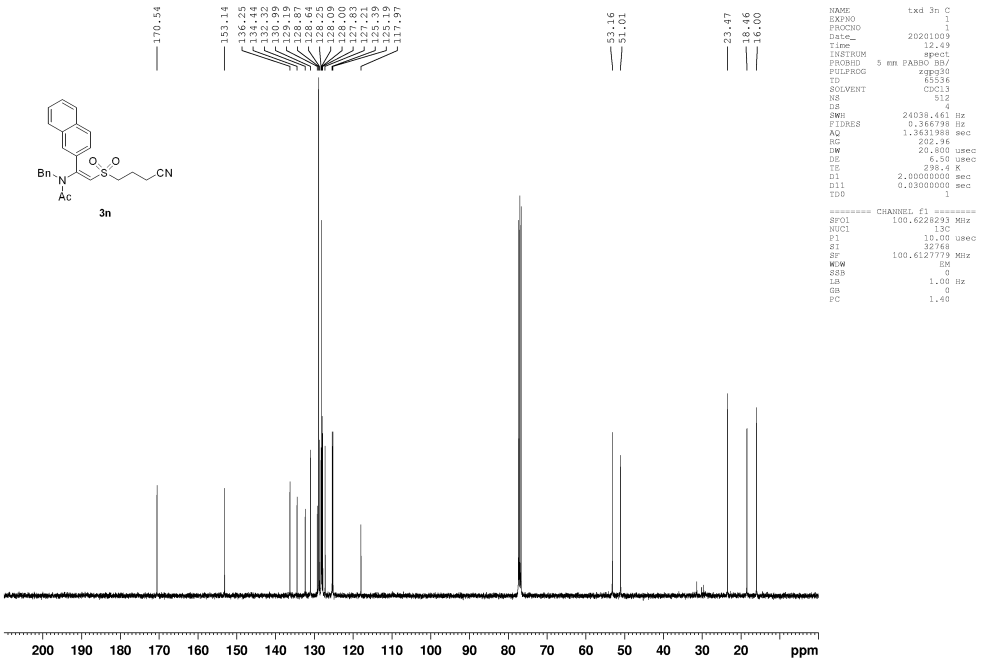
Methyl (E)-4-(1-(*N*-benzylacetamido)-2-((3-cyanopropyl)sulfonyl)vinyl)benzoate (**3m**)





(E)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(naphthalen-2-yl)vinyl)acetamide (**3n**)





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PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 50.81
DW 62.400 usec
DE 6.50 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1

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NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300117 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

NAME txd 3n C
EXPNO 1
PROCNO 1
Date_ 20201009
Time 12.49
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 202.96
DW 20.800 usec
DE 6.50 usec
TE 298.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
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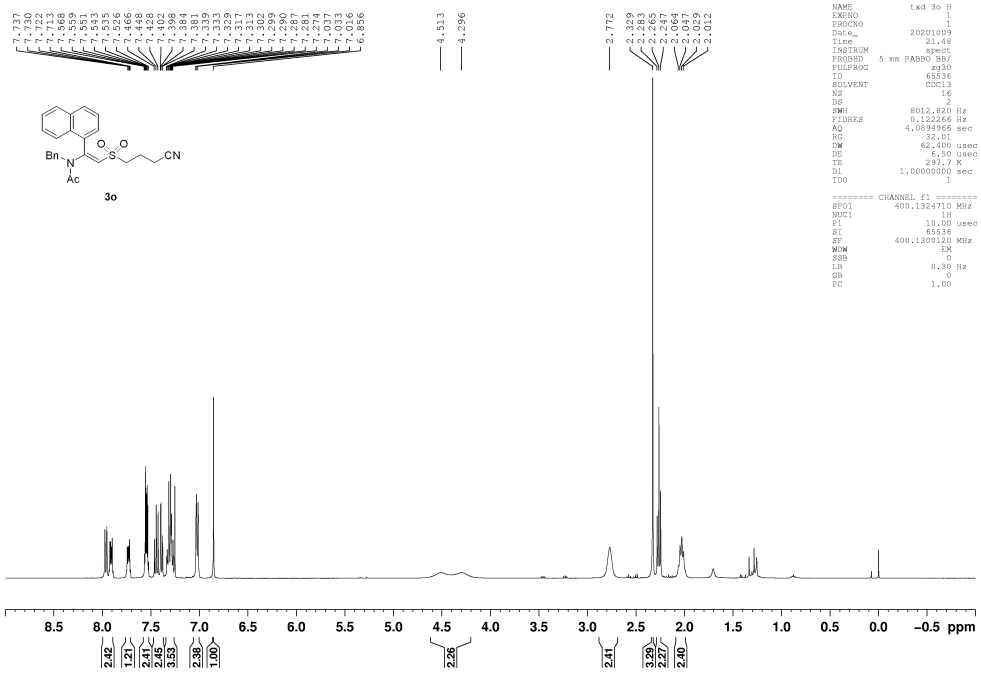
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127779 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

(E)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(naphthalen-1-yl)vinyl)acetamide (**3o**)

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PROCNO                   1
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Time                 21.48
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      16
DS                       2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894966 sec
RG                   32.01
DW                62.400 usec
DE                 6.50 usec
TE                 297.7 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
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NUC1                    1H
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WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
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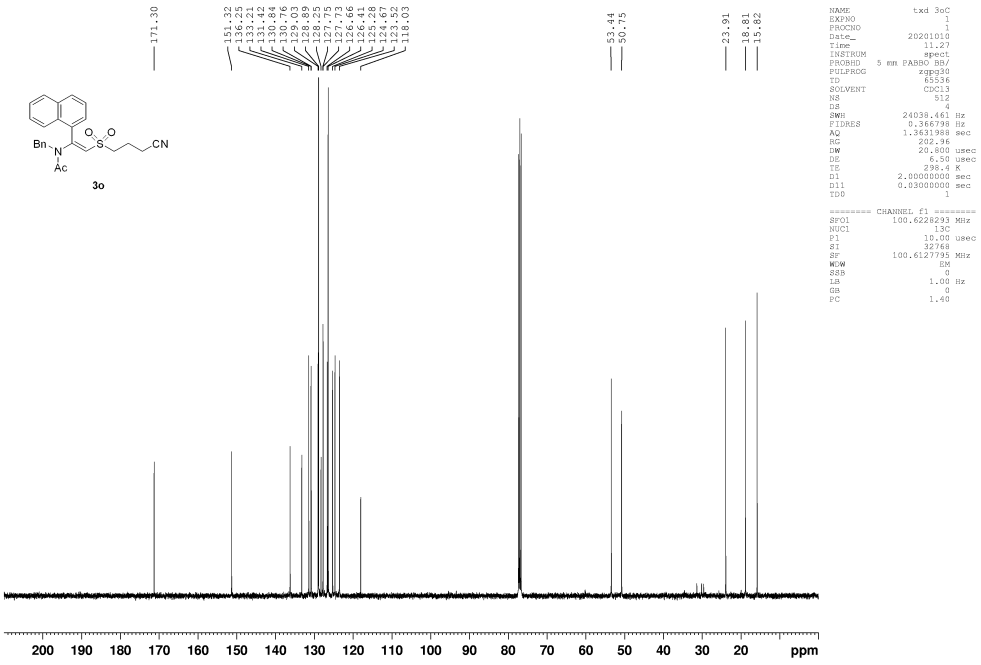


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PROCNO                   1
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Time                 11.27
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     512
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                  202.96
DW                20.800 usec
DE                 6.50 usec
TE                 298.4 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
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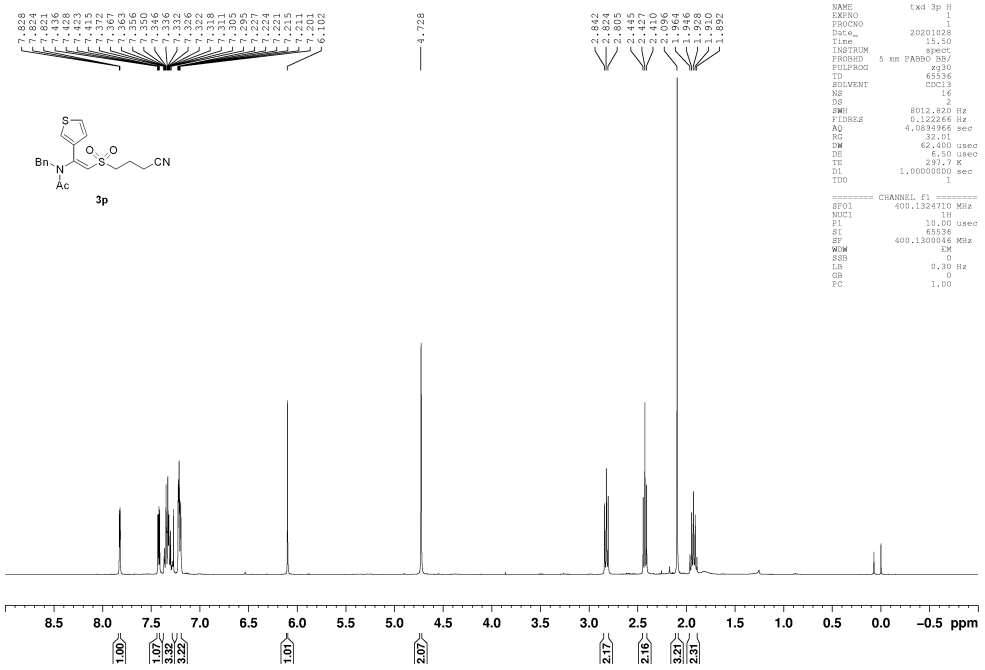
NUC1                    13C
P1                  10.00 usec
SI                   32768
SF            100.6127795 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```

(E)-*N*-benzyl-*N*-(2-((3-cyanopropyl)sulfonyl)-1-(thiophen-3-yl)vinyl)acetamide (**3p**)

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PROCNO                   1
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INSTRUM              spect
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      16
DS                       2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894966 sec
RG                   32.01
DW                62.400 usec
DE                 6.50 usec
TE                 297.7 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
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NUC1                    1H
P1                  10.00 usec
SI                   65536
SF            400.1300046 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
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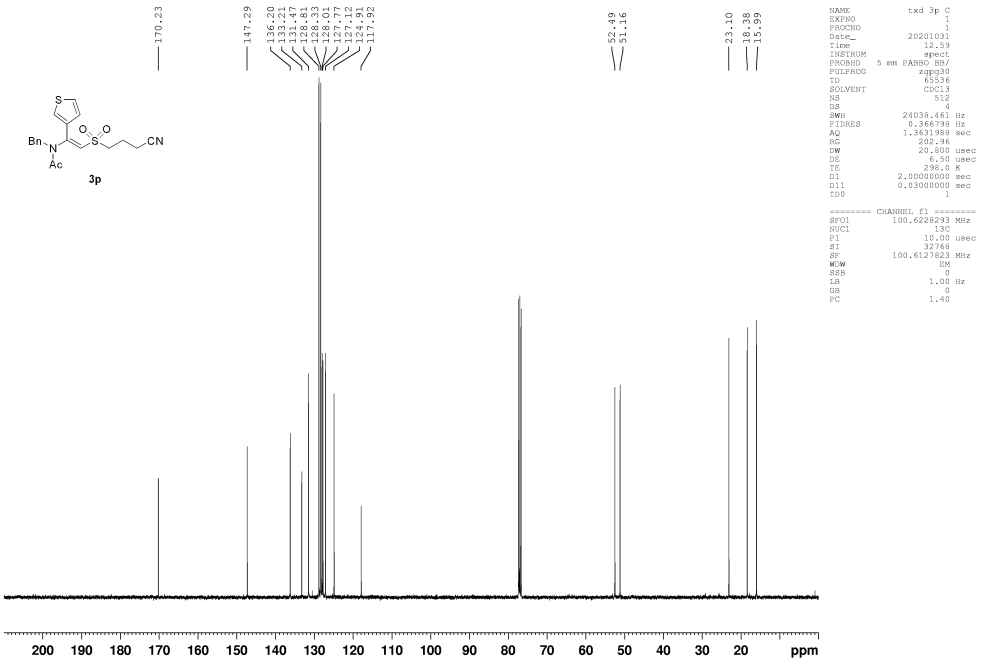


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PROCNO                   1
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INSTRUM              spect
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PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     512
DS                       4
SWH              24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                  202.96
DW                20.800 usec
DE                 6.50 usec
TE                 298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                    13C
P1                  10.00 usec
SI                   32768
SF            100.6127823 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```
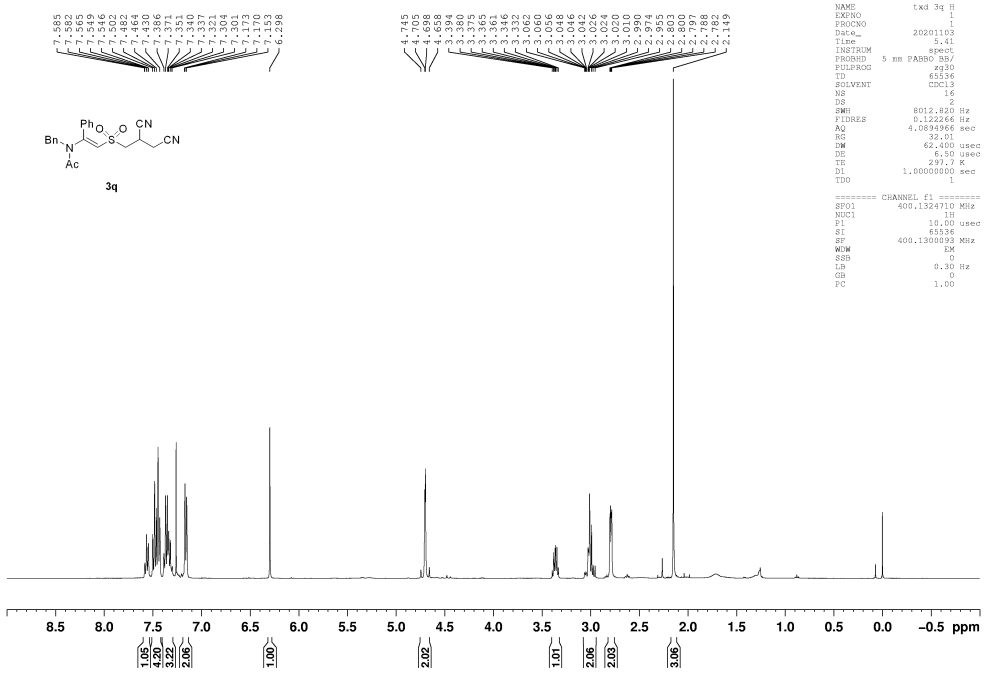
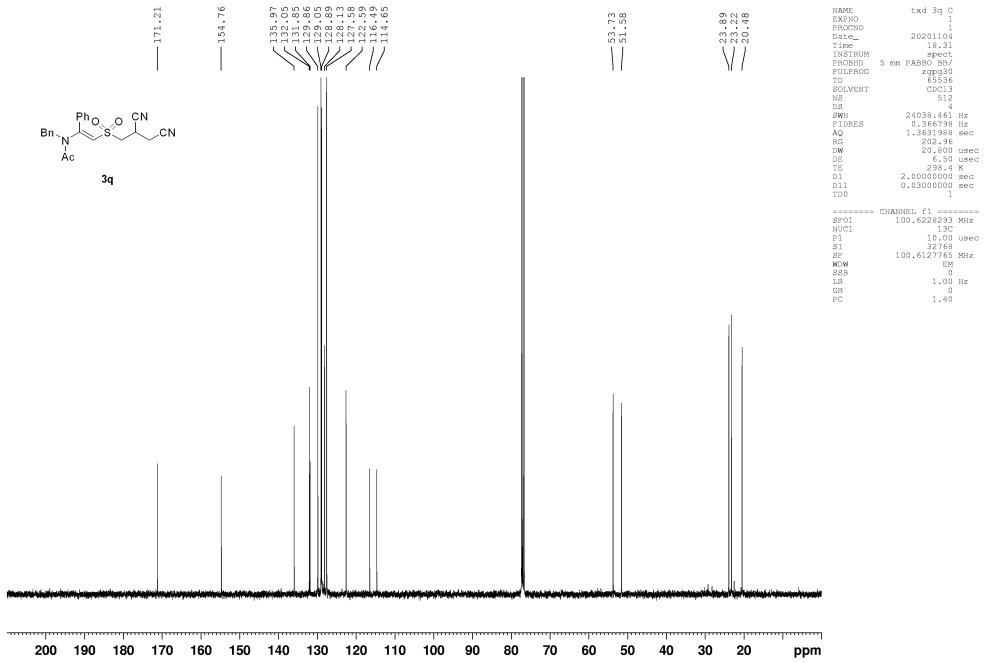
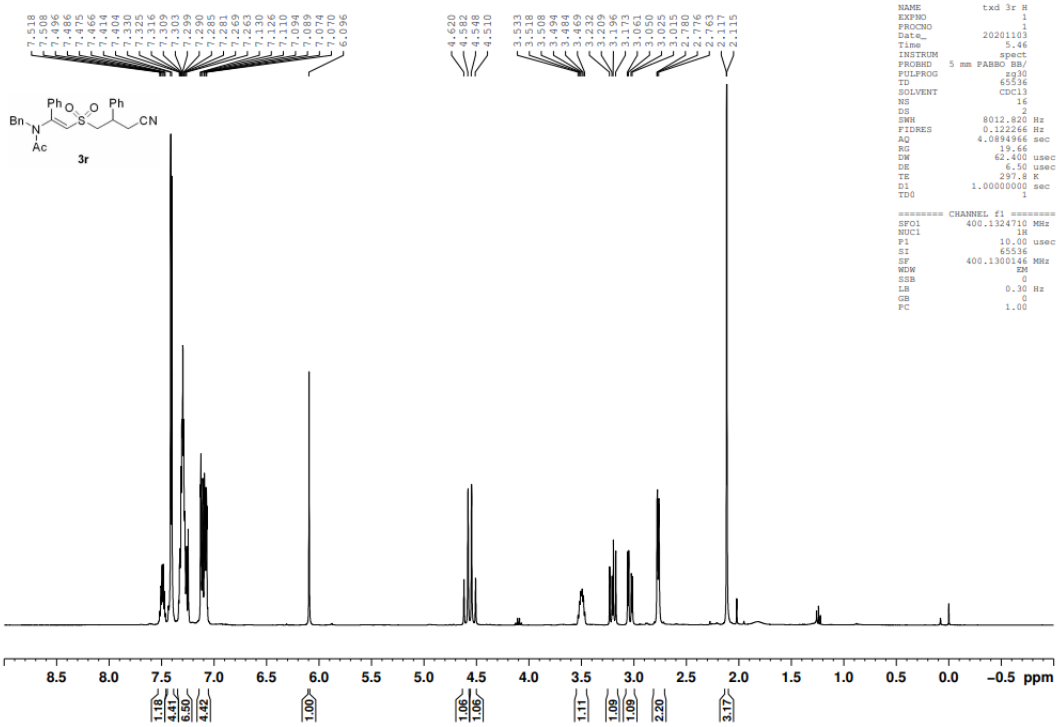
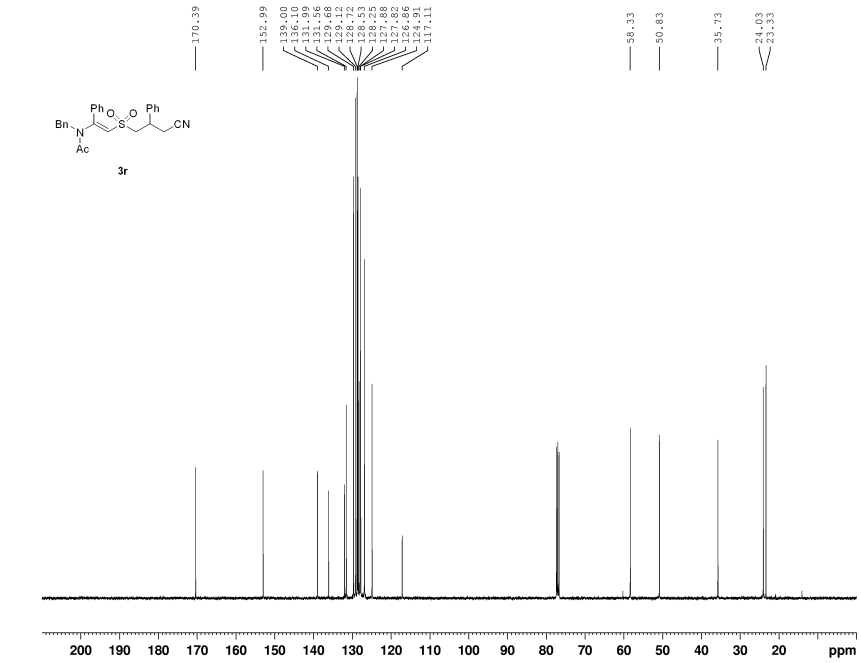

(E)-*N*-benzyl-*N*-(2-((2,3-dicyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (**3q**)



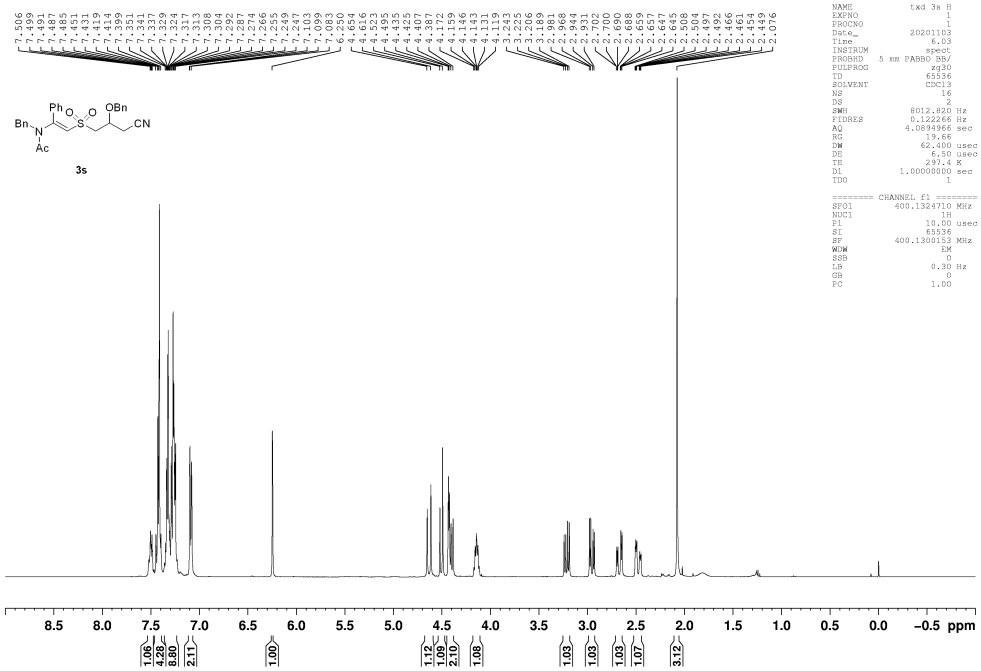


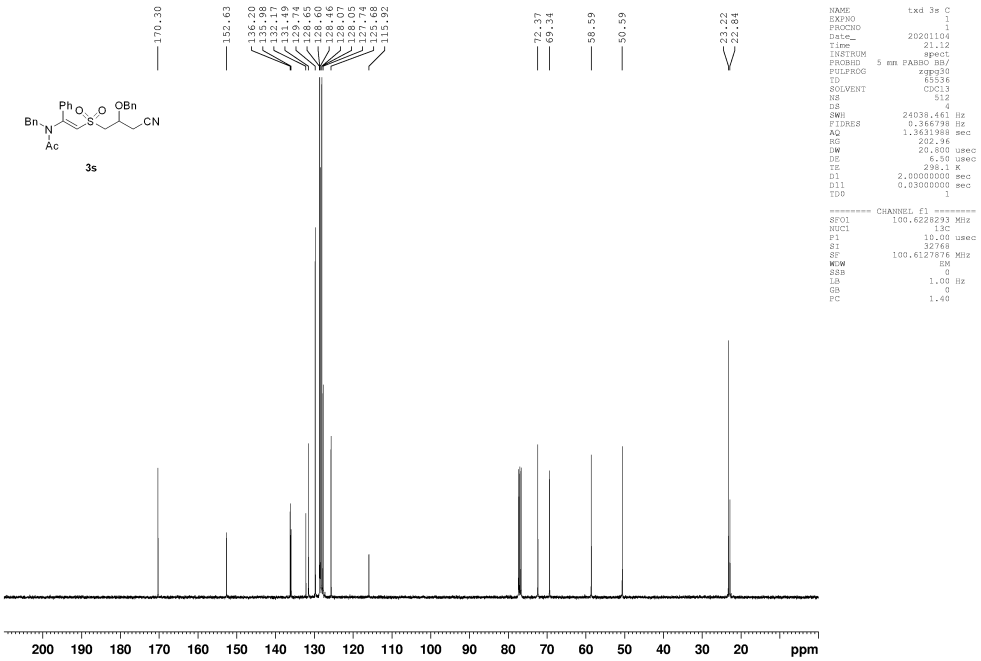
(E)-*N*-benzyl-*N*-(2-((3-cyano-2-phenylpropyl)sulfonyl)-1-phenylvinyl)acetamide (**3r**)



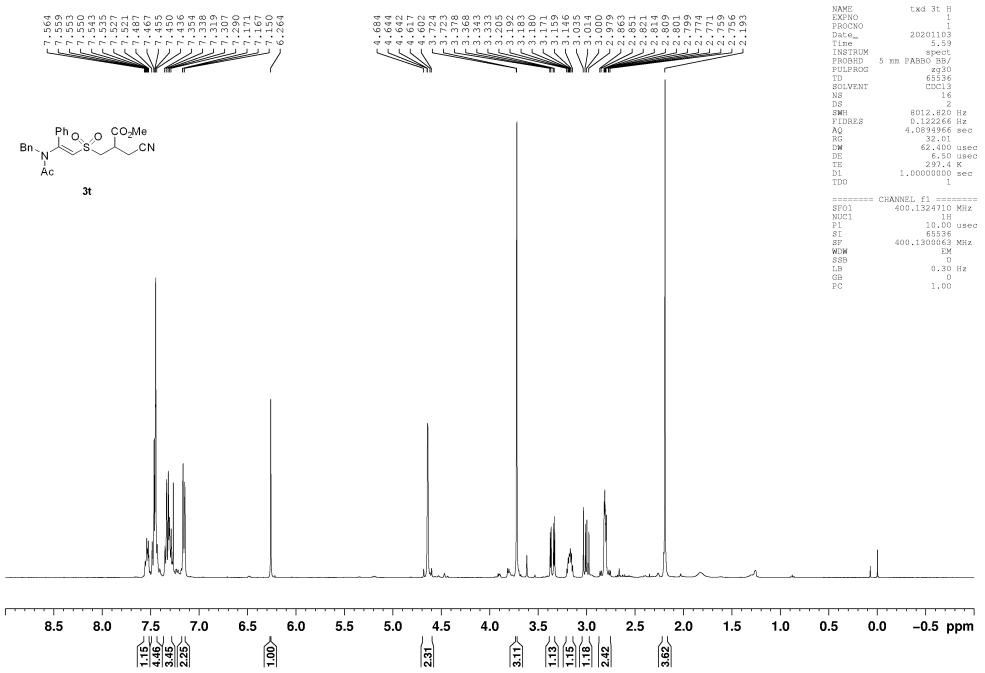


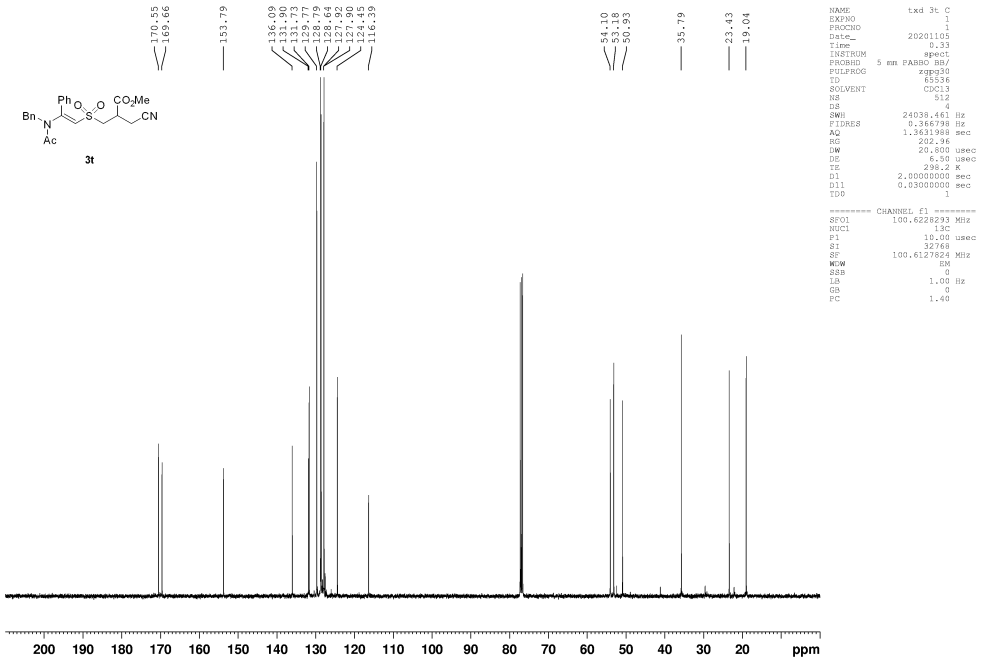
(E)-*N*-benzyl-*N*-(2-((2-(benzyloxy)-3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (**3s**)



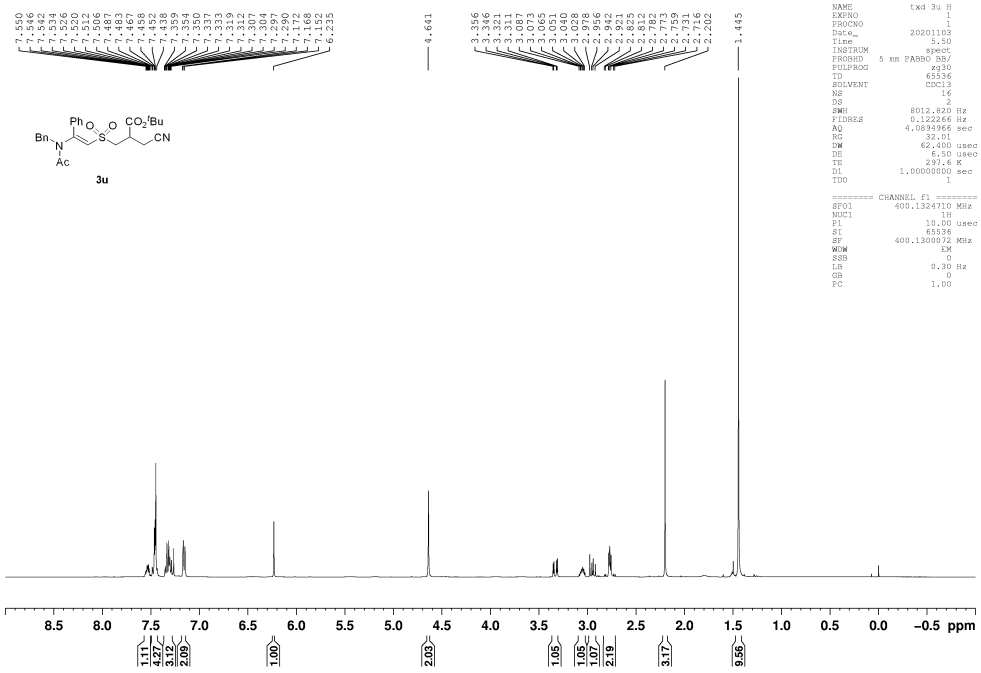


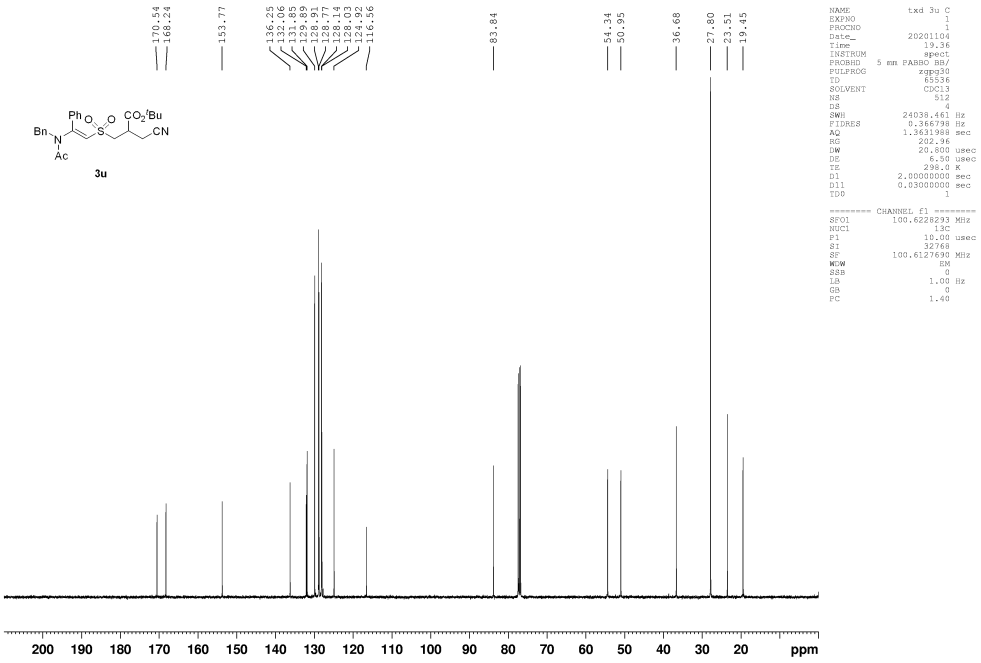
Methyl(E)-3-((2-(*N*-benzylacetamido)-2-phenylvinyl)sulfonyl)-2-(cyanomethyl)propanoate (**3t**)



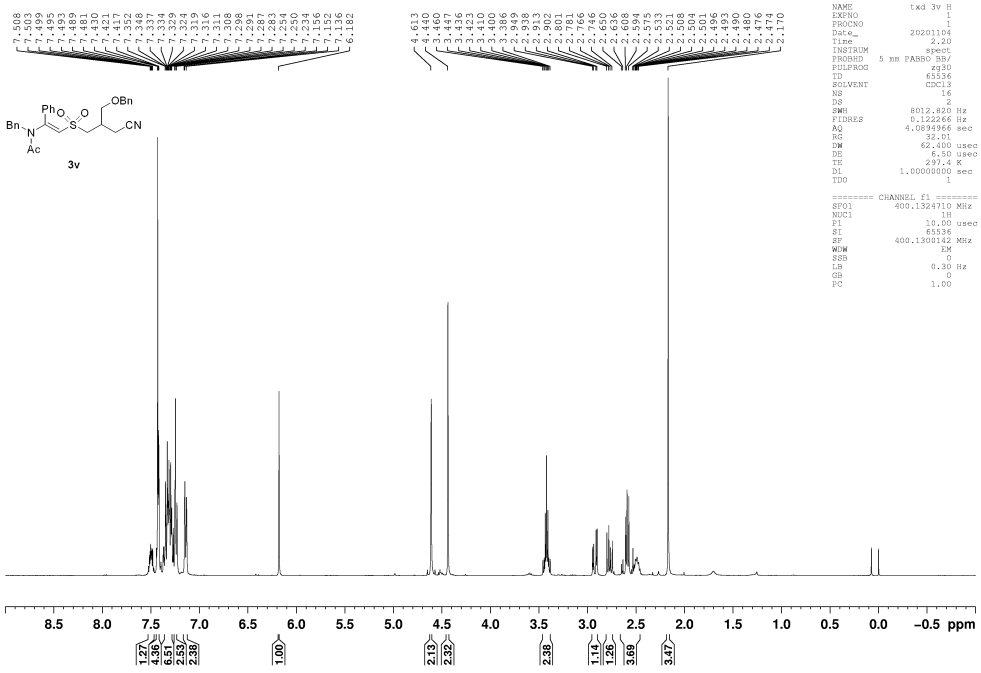


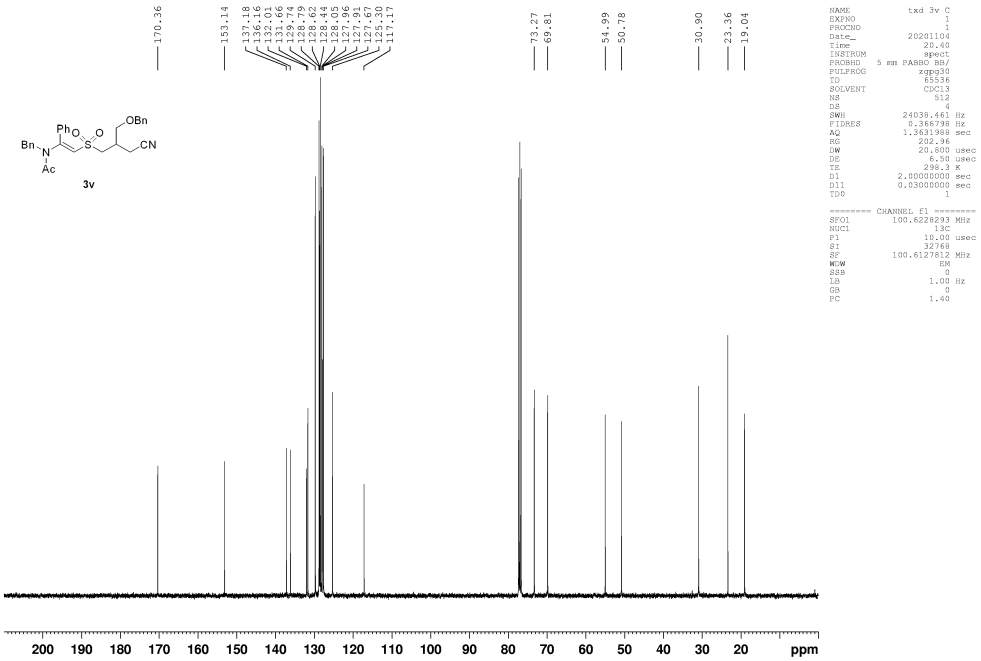
tert-butyl(E)-3-((2-(*N*-benzylacetamido)-2-phenylvinyl)sulfonyl)-2-(cyanomethyl)propanoate (**3u**)



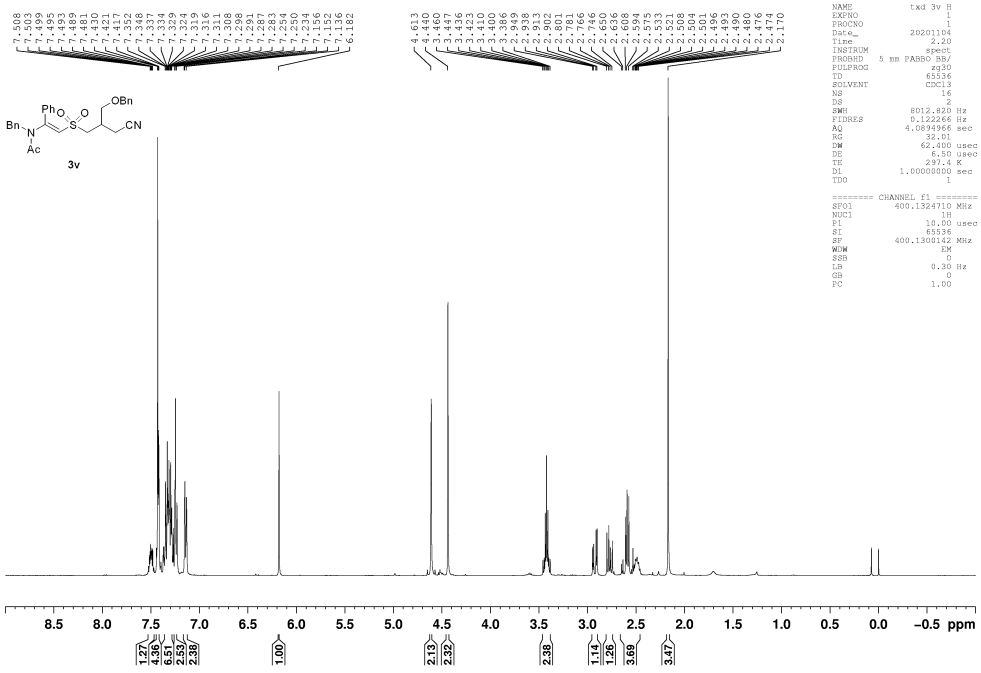


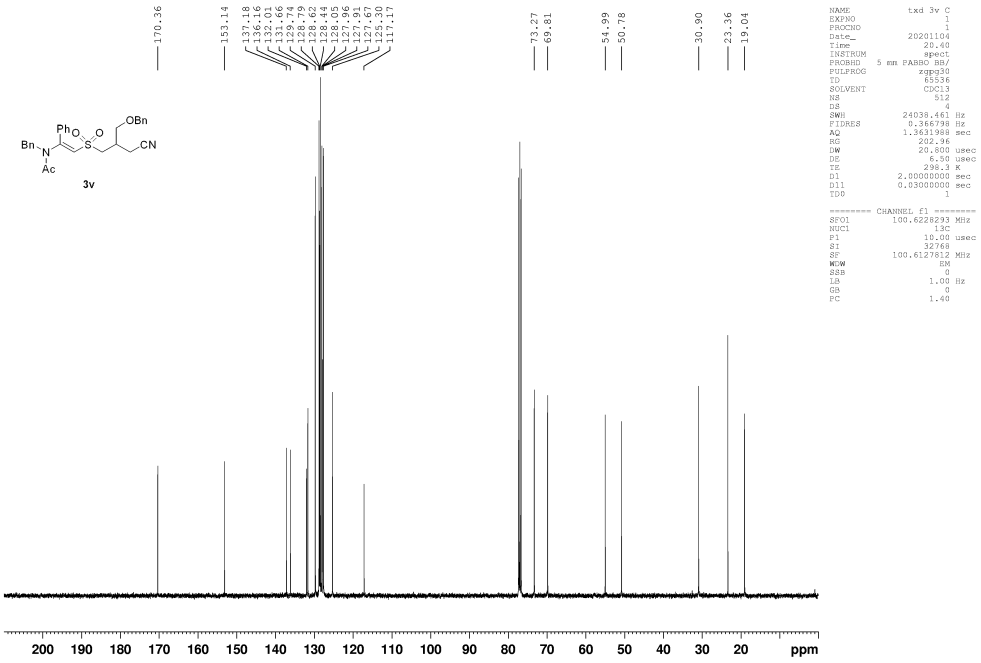
(E)-*N*-benzyl-*N*-(2-((3-(benzyloxy)-2-(cyanomethyl)propyl)sulfonyl)-1-phenylvinyl)acetamide (**3v**)





(E)-*N*-benzyl-*N*-(2-((5-(cyanomethyl)cyclopent-2-en-1-yl)sulfonyl)-1-phenylvinyl)acetamide (**3w**)





(E)-*N*-(2-bromobenzyl)-*N*-(2-((3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (**3x**)