Supporting Information

Solid Phase Synthesis of S-N-substituted 2-mercaptobenzoimidazoles

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1. General methods and instruments

^{1}H NMR spectra were recorded on a BRUKER 250 (250 MHz), BRUKER 300 (300 MHz) and a BRUKER AM 400 (400 MHz) spectrometer. Chemical shifts are given in parts per million (δ/ppm), downfield from tetramethylsilane (TMS) are referenced to chloroform (7.26 ppm) as internal standards. All coupling constants are absolute values and *J* values are expressed in Hertz (Hz). The description of signals include: s = singlet, br. s = broad singlet, d = doublet, bd = broad doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, q = quartet, quin = quintet, sept = septet, m = multiplet. The spectra were analyzed according to first order.

^{13}C NMR spectra were recorded on BRUKER 250 (63 MHz), Bruker 300 (75 MHz) and Bruker AM 400 (100 MHz) spectrometers. Chemical shifts are expressed in parts per million (ppm,δ) downfield from tetramethylsilane (TMS) are referenced to $CDCl_3$ (77.4 ppm) as internal standard.

MS (EI) (electron impact mass spectrometry): Finnigan MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (m/z), the intensities as a percentage value relative to the intensity of the base signal (100%).

IR (infrared spectroscopy): ATR spectra were recorded by diamond crystal on Bruker ALPHA-IR.

Elemental Analysis (EA): ELEMENTAR, Model: vario Micro cube. Scale: SARTORIUS M2P. The values for carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) were given in percent. Calc. = calculated (theoretical) value, found = found value.

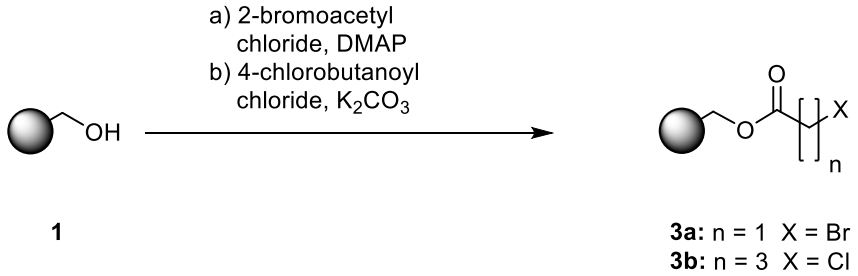
Routine monitoring of reactions were performed using silica gel coated aluminium plates (Merck, silica gel 60, F254) which were analyzed under UV-light at 254 nm and/or dipped into a solution of molybdato phosphate (5% phosphor molybdic acid in ethanol, dipping solution) and heated with a heat gun. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Solvents, reagents and chemicals were purchased from SigmaAldrich, Alfa Aesar, ABCR and VWR. Solvents, reagents and chemicals were used as purchased unless stated otherwise. Wang resin was purchased from Polymer Laboratories (PL-WANG resin 1.70 mmol/g, 100-200 µm, WANG 070).

The yields and the loadings after each solid supported reaction were calculated as followed:

For the yields, the difference between the mass of the linker after the reaction and the mass of the starting resin was taken. In order to calculate the loading of the resin, the amount of yield after the reaction (percentage) is multiplied with the available mmol amount according to the starting resin. The resulting value was divided by the amount of resin, which has been gained after the reaction and multiplied by 100.

2. Reactions on Solid Phases

2.1 Attachment of the linker units



Scheme 1. Attachment of linkers with different lengths on Wang resin.

*GP1A: Synthesis of linker unit **3a.***

Wang-resin was swollen in CH_2Cl_2 (7.50 mL of solvent per 1.00 g resin) for 15 min. After that 1.50 equiv. of DMAP were added and the mixture was shaken at room temperature for 30 min. Afterwards the resin mixture was cooled down to 0 °C and 1.20 equiv. of 2-bromoacetylchloride in CH_2Cl_2 were added dropwise. The mixture was shaken at room temperature for 3 h and the resin was washed according to GWP1 and was dried in an oven at 90 °C

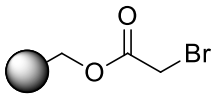
*GP1B: Synthesis of linker unit **3b.***

Wang-resin was swollen in CH_2Cl_2 (10 mL of solvent per 1.00 g resin) and 3.00 equiv. of 4-chlorobutyrylchlorid and 3.00 equiv. of K_2CO_3 were added to the mixture. The mixture was shaken at room temperature for 18 h. The resin was washed according to GWP1 and was dried in an oven at 90 °C.

*GWP1: Washing of the linker unit resin **3a and 3b**.*

Resin was washed successively three times with DMF, three times with dist. water, three times with MeOH and three times with CH_2Cl_2.

Polystyrene-2-bromoacetate **(3a)**

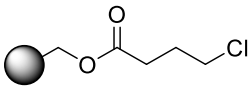


Wang-resin **1** (1.00 g, loading: 1.70 mmol/g, 1.70 mmol) was swollen in 7.50 mL of CH_2Cl_2 for 15 min. After that 316 mg of DMAP (1.50 equiv., 2.57 mmol) were added and the mixture was shaken at room temperature for 30 min. Afterwards the resin mixture was cooled down to 0 °C and 175 µL of 2-bromoacetylchloride (1.20 equiv., 2.10 mmol) in 2.50 mL of CH_2Cl_2 were added dropwise. The mixture was shaken at room temperature for 3 h and the resin was washed according to GWP1 and was dried in an oven at 90 °C. After the purification, 1.17 g of the target resin **3a** were obtained. Conversion and loading calculated according to mass difference for 1 step: see table below.

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 25.9 (CH_2Br), 167.1 (CO). FTIR (ATR): $\tilde{\nu}$ = 3024, 2918, 1736, 1610, 1512, 1492, 1451, 1374, 1220, 1160, 963, 822, 757, 697, 538, 431 cm^{-1}. EA ($C_{45}H_{45}BrO_3$): calc.: C 75.73, H 6.36, found: C 75.89, H 6.27.

No	start [g]	n [mmol]	diff. (theory)	conversion [%]	target (theory) [g]	loading [mmol/g]
1	1.00	1.70	0.2055	82	1.17 (1.208)	1.20
2	5.00	8.50	1.0275	87	5.89 (6.0275)	1.25

Polystyrene-4-chlorobutanoate **(3b)**

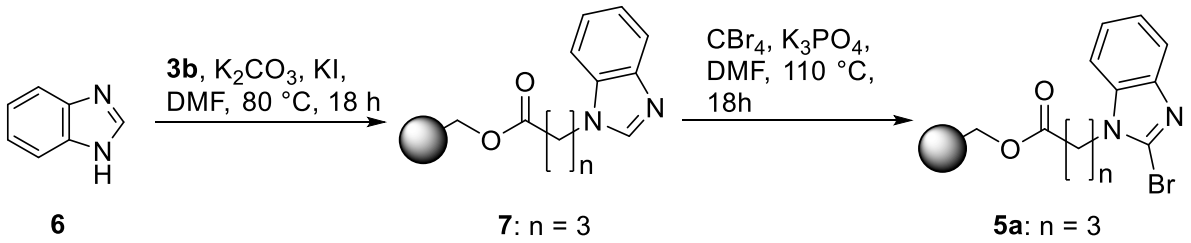


Wang-resin **1** (10.0 g, loading: 1.70 mmol/g, 17.0 mmol) was swollen in 100 mL of CH_2Cl_2 and 5.71 mL of 4-chlorobutyrylchlorid (7.19 g, 3.00 equiv., 51.0 mmol) and 7.05 g of K_2CO_3 (3.00 equiv., 51.0 mmol) were added to the mixture. The mixture was shaken at room temperature for 18 h. The resin was washed according to GWP1 and was dried in an oven at 90 °C. After the purification, 11.8 g of the target resin **3b** were obtained. [Conversion and loading calculated according to mass difference for 1 step: see table below.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 27.7, 31.4, 44.2 (CH_2Cl), 66.3, 172.6 (CO). FTIR (ATR): $\tilde{\nu}$ = 3023, 2917, 1730, 1602, 1510, 1491, 1450, 1217, 1171, 696 cm^{-1}. EA ($C_{47}H_{49}ClO_3$): calc.: C 80.95, H 7.08, found: C 80.95, H 6.96.

No	start [g]	n [mmol]	diff. (theory)	conversion [%]	target (theory) [g]	loading [mmol/g]
1	10.00	17.0	1.804	quant.	11.812 (11.804)	
2	5.0	8.5	0.902	quant.	5.923 (5.902)	
3	5.0	8.5	0.902	quant.	5.899 (5.902)	

2.2 Immobilization and modification of the benzimidazole building block



Scheme 2. Immobilization of benzimidazole and subsequent bromination on bead.

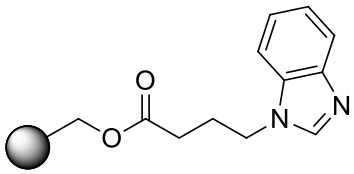
*GP2: Attachment of benzimidazole **6** to benzimidazolebutanoate resin **7.***

The resin **3b** was swollen in DMF (8.00 mL of solvent per 1.00 g resin). Afterwards 3.00 equiv. of benzimidazole, 3.00 equiv. of K_2CO_3 and 1.00 equiv. of KI were added to the mixture. The mixture was shaken at 80 °C over a period of 18 h. The resin was washed according to GWP2 and was dried in an oven at 90 °C.

GWP2: Washing after immobilization of the benzimidazole unit.

Resin was washed successively three times with dist. water, three times with MeOH and three times with CH_2Cl_2.

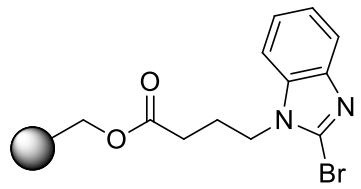
***Polystyrene- 4-(1H-benzo[d]imidazol-1-yl)butanoate* (7)**



According to GP2, 1.00 g of resin **3b** (loading: 1.44 mmol/g, 1.44 mmol) was swollen in 8.00 mL of DMF and 510 mg of benzimidazole (3.00 equiv., 4.32 mmol), 600 mg of K_2CO_3 (3.00 equiv., 4.32 mmol) and 239 mg of KI (1.00 equiv., 1.44 mmol) were added to the mixture. The mixture was shaken at 80 °C for 18 h. The resin was washed according to GWP2 and was dried in an oven at 90 °C. After the purification, 1.11 g of the target resin **7** were obtained in 94% conversion. Loading: 1.21 mmol/g. [Conversion and loading calculated according to mass difference for 1 step.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 24.9, 30.7, 109.5, 120.3, 122.1, 122.9, 133.5, 142.8, 172.1**.** FTIR (ATR): $\tilde{\nu}$ = 3023, 2920, 2849, 1728, 1611, 1511, 1492, 1450, 1381, 1218, 1156, 1008, 822, 742, 697, 541, 426 cm^{-1}. EA ($C_{54}H_{54}N_2O_3$): calc. C 83.26, H 6.99, N 3.60; found C 83.34, H 6.98, N 2.75.

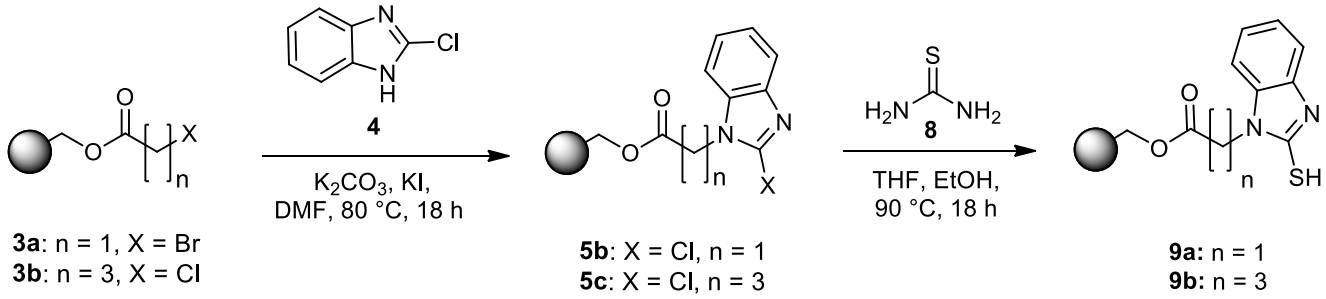
Polystyrene- 4-(2-bromo-1H-benzo[d]imidazol-1-yl)butanoate **(5a)**



200 mg of resin **7** (loading: 1.21 mmol/g, 242 μmol) were swollen in 4.00 mL of DMF and 120 mg CBr_4 (1.50 equiv., 363 μmol) and 154 mg K_3PO_4 (3.00 equiv., 726 μmol) were added to the mixture. The mixture was shaken at 110 °C for 18 h under nitrogen atmosphere. The resin was washed according to GWP2 and was dried in an oven at 90 °C. After the purification, 217 mg of the target resin **5a** were obtained in 89% conversion. Loading: 0.99 mmol/g. [Conversion and loading calculated according to mass difference for 1 step.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 25.1, 30.9, 109.6, 120.5, 122.7. FTIR (ATR): $\tilde{\nu}$ = 3024, 2919, 1727, 1610, 1511, 1491, 1450, 1366, 1237, 1157, 1009, 821, 742, 696, 540, 427 cm^{-1}. EA ($C_{54}H_{53}BrN_2O_3$): calc. C 75.60, H 6.23, N 3.27; found. C 78.14, H 6.47, N 2.91.

2.3 Immobilization and modification of the 2-chlorobenzoimidazole building block



Scheme 3. Immobilization of the first building block and thiolation on bead.

*GP3: Attachment of 2-chlorobenzimidazole **4** to 2-bromobenzimidazole-acetate resin **5a.***

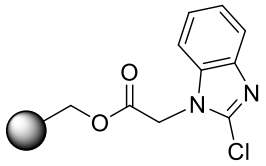
The resin **3a** was swollen in DMF (8.00 mL of solvent per 1.00 g resin). Afterwards 3.00 equiv. of chlorobenzimidazole, 3.00 equiv. of K_2CO_3 and 1.00 equiv. of KI were added to the mixture. The mixture was shaken at 80 °C over a period of 18 h. The resin was washed according to GWP2 and was dried in an oven at 90 °C.

*GP4: Attachment of 2-chlorobenzimidazole **4** to 2-chlorobenzimidazolebutanoate resin **5b.***

The resin **3b** was swollen in DMF (8.00 mL of solvent per 1.00 g resin). Afterwards 3.00 equiv. of 2-chlorobenzimidazole, 3.00 equiv. of K_2CO_3 and 1.00 equiv. of KI were added

to the mixture. The mixture was shaken at 80 °C over a period of 18 h. The resin was washed according to GWP2 and was dried in an oven at 90 °C.

Polystyrene-2-(2-chloro-1H-benzo[d]imidazol-1-yl)acetate **(5b)**

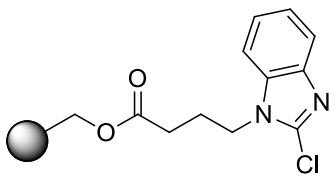


According to GP3, 500 mg of resin **3a** (loading: 1.20 mmol/g, 600 µmol) were swollen in 4.00 mL of DMF and 275 mg of 2-chlorobenzimidazole (3.00 equiv., 1.80 mmol), 249 mg of K_2CO_3 (3.00 equiv., 1.80 mmol) and 100 mg of KI (1.00 equiv., 600 µmol) were added to the mixture. The mixture was shaken at 80 °C for 18 h. The resin was washed according to GWP2 and was dried in an oven at 90 °C. After the purification, 624 mg of the target resin **5b** were obtained. [Conversion and loading calculated according to mass difference for 1 step: see table below.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 45.1 (CH_2N), 109.0, 119.6, 123.0, 123.5, 135.0 (N_2CCl), 140.7, 166.4 (CO). FTIR (ATR): $\tilde{\nu}$ = 3024, 2919, 1747, 1611, 1511, 1492, 1474, 1452, 1367, 1328, 1170, 992, 821, 740, 697, 540, 429, 404 cm^{-1}. EA ($C_{52}H_{49}ClN_2O_3$): calc.: C 79.52, H 6.29, N 3.57, found: C 79.97, H 5.99, N 3.24.

No	start [g]	n [mmol]	diff. (theory)	conversion [%]	target (theory) [g]	loading [mmol/g]
1	0.50	0.600	0.043	quant.	0.624 (0.567)	0.962
2	3.0	3.75	0.268	quant.	3.340 (3.402)	1.12

Polystyrene- 4-(2-chloro-1H-benzo[d]imidazol-1-yl)butanoate **(5c)**



According to GP4, 2.00 g of resin **3b** (loading: 1.44 mmol/g, 2.88 mmol) were swollen in 16.0 mL of DMF and 1.32 g of 2-chlorobenzimidazole (3.00 equiv., 8.64 mmol), 1.19 g of K_2CO_3 (3.00 equiv., 8.64 mmol) and 480 mg of KI (1.00 equiv., 2.88 mmol) were added to the mixture. The mixture was shaken at 80 °C for 18 h. The resin was washed according to GWP2 and was dried in an oven at 90 °C. After the purification, 2.34 g of the target resin **5c** were obtained. [Conversion and loading calculated according to mass difference for 1 step: see table below.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 24.2 ($CH_2CH_2CH_2$), 30.6 ($COCH_2$), 43.2 (CH_2N), 109.3, 119.4, 122.6, 123.1, 134.9, 140.3 (N_2CCl), 141.6, 172.1 (CO). FTIR (ATR): $\tilde{\nu}$ = 3023, 2920, 1728, 1611, 1512, 1492, 1469, 1449, 1375, 1219, 1157, 1007,

821, 741, 697, 540, 433, 401 cm^{-1}. EA ($C_{54}H_{53}ClN_2O_3$): calc.: C 79.73, H 6.57, N 3.44, found: C 77.63, H 6.24, N 3.40.

No	start [g]	n [mmol]	diff. (theory)	conversion [%]	target (theory) [g]	loading [mmol/g]
1	2.00	2.88	0.334	quant.	2.343 (2.334)	1.23
2	2.00	2.88	0.334	quant.	2.397 (2.334)	1.23
3	5.00	7.20	0.835	quant.	5.912 (5.835)	1.23

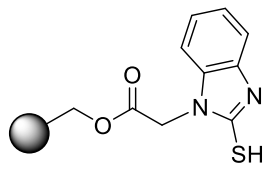
*GP5: Thiolation of immobilized 2-chlorobenzimidazoles to 2-mercaptobenzoimidazoles **9a / 9b:***

The resin was swollen in a mixture of THF and EtOH (6.00 mL THF and 2.00 mL EtOH per 1.00 g resin). Afterwards 10.0 equiv. of thiourea were added to the mixture and the mixture was shaken at 90 °C for 18 h. The resin was washed according to GWP3 and was dried in an oven at 90 °C.

GWP3: Washing after thiolation of the chlorobenzimidazole unit

The resin was washed successively five times with MeOH and five times with CH_2Cl_2

Polystyrene-2-(2-mercapto-1H-benzo[d]imidazol-1-yl)acetate **(9a)**

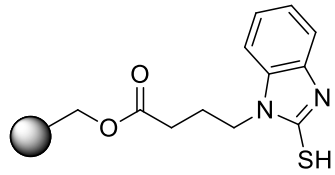


According to GP5, 2.00 g of resin **5b** (loading: 1.12 mmol/g, 2.24 mmol) were swollen in 12.0 mL of THF and 4.00 mL of EtOH and 1.71 g of thiourea (10.0 equiv., 22.4 mmol) were added to the mixture. The mixture was shaken at 90 °C for 18 h. The resin was washed according to GWP3 and dried in an oven at 90 °C. After the purification, 1.98 g of the target resin **9a** were obtained. [Conversion and loading calculated according to mass difference for 1 step: see table below.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 64.7, 109.0, 119.5, 123.6, 140.8, 158.4 (N_2CSH), 166.4 (CO). FTIR: ṽ = 3023, 2917, 1743, 1609, 1510, 1491, 1449, 1338, 1170, 995, 906, 822, 733, 697, 617, 541, 421 cm^{-1}. EA ($C_{52}H_{50}N_2O_3S$): calc.: C 79.76, H 6.44, N 3.58, S 4.09, found: C 77.85, H 6.31, N 3.22, S 3.19.

No	start [g]	n [mmol]	diff. (theory)	conversion [%]	target (theory) [g]	loading [mmol/g]
1	1.00	0.962	0.00456	quant.	1.03 (0.995)	0.967
2	2.00	2.24	0.00533	quant.	1.98 (1.995)	1.13

Polystyrene- 4-(2-mercapto-1H-benzo[d]imidazol-1-yl)butanoate **(9b)**

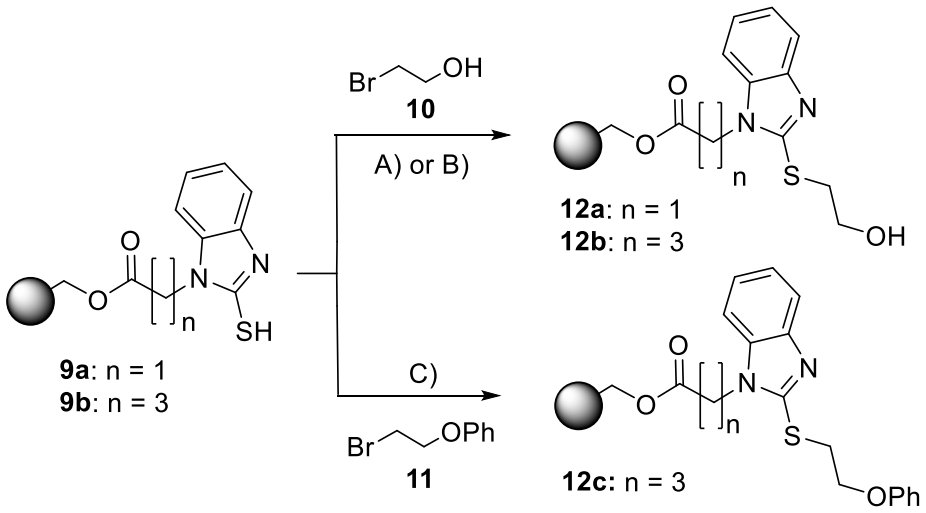


According to GP5, 4.00 g of resin **5c** (loading: 1.23 mmol/g, 4.92 mmol) were swollen in 24.0 mL of THF and 8.00 mL of EtOH and 3.75 g of thiourea (10.0 equiv., 49.2 mmol) were added to the mixture. The mixture was shaken at 90 °C for 18 h. The resin was washed according to GWP3 and dried in an oven at 90 °C. After the purification, 3.99 g of the target resin **9b** were obtained. [Conversion and loading calculated according to mass difference for 1 step: see table below.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 23.08, 31.04, 43.03, 109.19, 122.9, 123.3, 132.6, 167.8, 172.7. FTIR (ATR): $\tilde{\nu}$ = 3022, 2921, 1728, 1609, 1511, 1609, 1511, 1492, 1449, 1377, 1340, 1219, 1155, 1082, 1012, 821, 736, 696, 614, 539, 506, 420 cm^{-1}. EA ($C_{54}H_{54}N_2O_3S$): calc.: C 79.97, H 6.71, N 3.45, S 3.95, found: C 77.65, H 6.51, N 3.92, S 4.09.

No	start [g]	n [mmol]	diff. (theory)	conversion [%]	target (theory) [g]	loading [mmol/g]
1	4.00	4.92	0.0116	quant.	3.99 (3.9884)	1.233
2	2.00	2.46	0.0058	quant.	2.07 (1.9942)	1.233
3	2.00	2.46	0.0058	quant.	2.02 (1.9942)	1.233

2.4 Alkylation of immobilized 2-mercaptobenzoimidazoles



Scheme 4. Alkylation of immobilized 2-mercaptobenzoimidazoles.

*GP6: Alkylation of immobilized 2-mercaptobenzoimidazoles **9a** or **9b:***

A) The resin was swollen in DMF (8.00 mL per 1.00 g resin). Afterwards 5.00 equiv. of Et_3N and 5.00 equiv. of 2-bromoethanol were given to the mixture and the mixture

was shaken at 90 °C for 3 h. The resin was washed according to GWP4 and was dried in an oven at 90 °C.

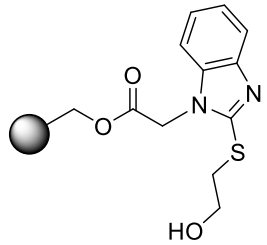
B) The resin was swollen in DMF (8.00 mL per 1.00 g resin). Afterwards 3.00 equiv. of K_2CO_3, 1.00 equiv. of KI and 5.00 equiv. of 2-bromoethanol were given to the mixture and the mixture was shaken at 90 °C for 18 h. The resin was washed according to GWP4 and was dried in an oven at 90 °C.

C) The resin was swollen in DMF (8.00 mL per 1.00 g resin). Afterwards 3.00 equiv. of K_2CO_3, 1.00 equiv. of KI and 5.00 equiv. of (2-bromoethoxy)benzene were given to the mixture and the mixture was shaken at 90 °C for 18 h. The resin was washed according to GWP4 and was dried in an oven at 90 °C.

GWP4: Washing after alkylation

The resin was washed successively two times with DMF, three times with dist. water, three times with MeOH and three times with CH_2Cl_2

***Polystyrene-2-(2-((2-hydroxyethyl)thio)-1H-benzo[d]imidazol-1-yl)acetate* (12a)**

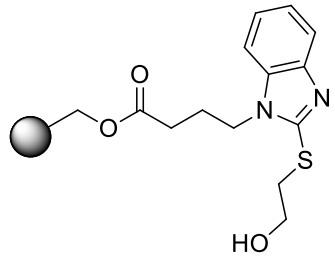


According to GP6A, 500 mg of resin **9a** (loading: 1.13 mmol/g, 565 µmol) were swollen in 4.00 mL of DMF and 392 µL of Et_3N (5.00 equiv., 2.83 mmol) and 200 µL 2-bromoethanol (5.00 equiv., 2.83 mmol) were added to the mixture. The mixture was shaken at 90 °C for 3 h. The resin was washed according to GWP4 and dried in an oven at 90 °C. After the purification, 527 mg of the target resin **12a** were obtained. [Conversion and loading calculated according to mass difference for 1 step: see table below.]

No	start [g]	n [mmol]	diff. (theory)	conversion [%]	target (theory) [g]	loading [mmol/g]
1	0.5	0.565	0.0198	quant.	0.522 (0.520)	1.072
2	1.0	1.13	0.0198	quant	1.054 (1.040)	1.072

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 35.8 (CH_2S), 62.6 (CH_2OH), 108.4, 118.3, 122.7, 135.7, 142.3, 152.2 (N_2CS), 166.9 (CO). FTIR (ATR): $\tilde{\nu}$ = 3024, 2918, 1746, 1610, 1512, 1492, 1446, 1369, 1170, 1012, 820, 738, 697, 540 cm^{-1}. EA ($C_{54}H_{54}N_2O_4S$): calc.: C 78.42, H 6.58, N 3.39, S 3.88, found: C 79.60, H 6.41, N 2.79, S 1.85.

Polystyrene- 4-(2-((2-hydroxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate **(12b)**

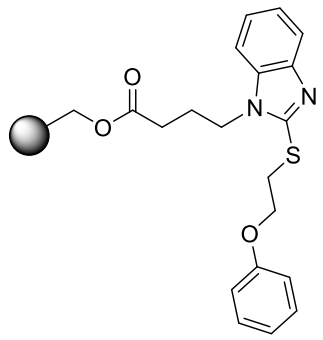


According to GP6B, 2.00 g of resin **9b** (loading: 1.233 mmol/g, 2.47 mmol) were swollen in 16.0 mL of DMF and 1.02 g of K_2CO_3 (3.00 equiv., 7.41 mmol), 410 mg of KI (1.00 equiv., 2.47 mmol) and 875 µL of 2-bromoethanol (5.00 equiv., 12.3 mmol) were added to the mixture. The mixture was shaken at 90 °C for 18 h. The resin was washed according to GWP4 and dried in an oven at 90 °C. After the purification, 2.08 g of the target resin **12b** were obtained. [Conversion and loading calculated according to mass difference for 1 step: see table below.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 24.1, 30.7 (CO*C*H_2), 35.3, 43.2 (CH_2N), 63.2 (O*C*H_2), 108.8, 117.9, 122.1, 133.9, 142.3, 152.1 (N_2*C*S), 172.2 (CO). FTIR (ATR): $\tilde{\nu}$ = 3024, 2919, 1728, 1609, 1511, 1492, 1436, 1380, 1218, 1155, 1008, 821, 739, 697, 542, 419 cm^{-1}. EA ($C_{56}H_{58}N_2O_4S$): calc.: C 78.65, H 6.84, N 3.28, S 3.75, found: C 77.50, H 6.67, N 3.39, S 3.64.

No	start [g]	n [mmol]	diff. (theory)	conversion [%]	target (theory) [g]	loading [mmol/g]
1	1.00	1.233	0.0543	90	1.049 (1.0543)	1.06
2	1.00	1.24	0.0543	96	1.052 (1.0543)	1.12
3	2.00	2.47	0.109	76	2.083 (2.109)	0.90
4	2.00	2.47	0.109	76	2.081 (2.109)	0.90

Polystyrene-4-(2-((2-phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate **(12c)**

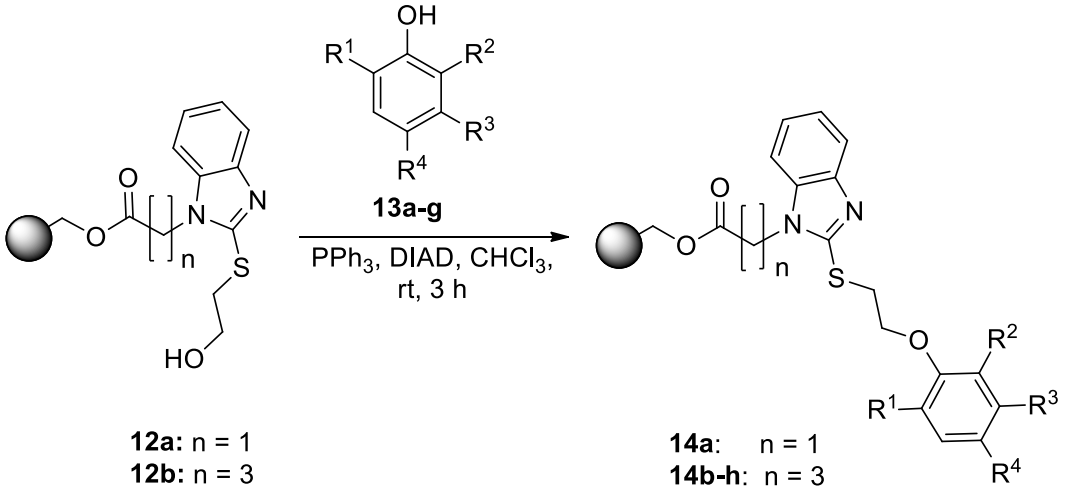


According to GP6C, 2.00 g of resin **9b** (loading: 1.233 mmol/g, 2.47 mmol) were swollen in 16.00 mL of DMF and 1.02 g of K_2CO_3 (3.00 equiv., 7.41 mmol), 420 mg of KI (1.00 equiv., 2.47 mmol) and 1.84 mL of (2-bromoethoxy)benzene (5.00 equiv. 12.4 mmol) were added to the mixture. The mixture was shaken at 90 °C for 18 h. The resin was washed according to GWP4 and dried in an oven at 90 °C. After the purification, 2.20 g of the target resin **12c** were obtained in 68 % conversion. Loading: 0.757 mmol/g. [Conversion and loading calculated according to mass difference for 1 step.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm) δ = 24.5, 30.9 (CO*C*H_2), 66.4 (CH_2O), 110.0, 121.8, 123.9, 158.9 (OC-Ar), 173.2 (CO). FTIR (ATR): $\tilde{\nu}$ = 3024, 2921, 1726, 1600, 1511, 1492,

1450, 1379, 1238, 1157, 1014, 821, 745, 697, 542 cm^{-1}. EA ($C_{62}H_{62}O_4N_2S$): calc. C 79.97, H 6.71, N 3.01, S 3.44, found: C 78.68, H 6.53, N 3.01, S 3.79.

2.5 Mitsunobu etherification



Scheme 5: Mitsunobu etherification of alkylated 2-mercaptobenzoimidazoles.

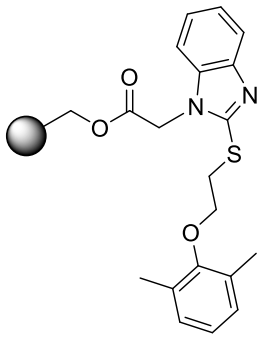
*GP7: Mitsunobu etherification of alkylated 2-mercaptobenzoimidazole **12a / 12b:***

The resin was swollen in $CHCl_3$ (1.00 mL per 0.100 g resin). Afterwards 10.0 equiv. of the corresponding phenol were added to the resin and shaken at room temperature. During this, 10.0 equiv. of PPh_3 were dissolved in 6.00 mL of $CHCl_3$ and the mixture was stirred at 0 °C. Then 10.0 equiv. of DIAD dissolved in 4.00 mL of $CHCl_3$ were added dropwise to the stirred PPh_3-containing solution. The slurry yellow mixture was added rapidly to the resin and shaken at room temperature for three hours. The resin was washed according to GWP5 and was dried in an oven at 90 °C.

GWP5: Washing after Mitsunobu etherification

The resin was washed successively three times with DMF, three times with dist. Water, five times with MeOH and five times with CH_2Cl_2

***Polystyrene-2-(2-((2-(2,6-dimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)acetate* (14a)**

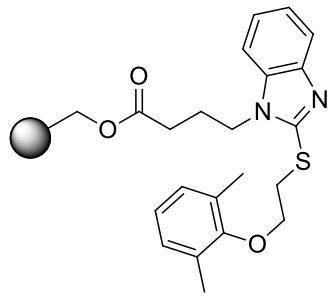


According to GP7, 500 mg of resin **12a** (loading: 1.072 mmol/g, 536 µmol) were swollen in 5.00 mL of $CHCl_3$ and 655 mg of 2,6-dimethylphenol (10.0 equiv., 5.36 mmol) were added and shaken at room temperature. Then a freshly prepared mixture of 1.41 g of

PPh_3 (10.0 equiv., 5.36 mmol) and 1.05 mL of DIAD (10.0 equiv., 5.36 mmol) in 10.0 mL of $CHCl_3$ was added drop wise to the resin and the mixture was shaken at room temperature for three hours. The resin was washed according to GWP5 and dried in an oven at 90 °C. After the purification, 557 mg of the target resin **14a** were obtained in quantitative conversion. Loading: 0.962 mmol/g [Conversion and loading calculated according to mass difference for 1 step.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 16.2 (CH_3), 21.9, 33.0, 67.3 (OCH_2), 108.4, 118.3, 123.0, 123.9, 130.6, 151.5 (N_2CS), 155.1 (OC-Ar), 166.6 (CO). FTIR (ATR): $\tilde{\nu}$ = 3023, 2923, 1745, 1610, 1511, 1492, 1447, 1369, 1170, 1092, 1011, 821, 759, 739, 697, 538, 429, 408 cm^{-1}. EA ($C_{62}H_{62}N_2O_4S$): calc.: C 79.97, H 6.71, N 3.01, S 3.44; found: C 79.42, H 6.38, N 3.18, S 3.08.

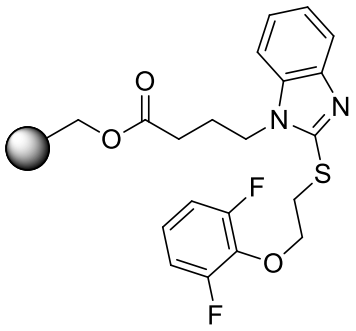
***Polystyrene-4-(2-((2-(2,6-dimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (14b)**



According to GP7, 500 mg of resin **12b** (loading: 1.12 mmol/g, 560 µmol) were swollen in 5.00 mL of $CHCl_3$ and 684 mg of 2,6-dimethylphenol (10.0 equiv., 5.60 mmol) were added and shaken at room temperature. Then a freshly prepared mixture of 1.47 g of PPh_3 (10.0 equiv., 5.60 mmol) and 1.10 mL of DIAD (10.0 equiv., 5.60 mmol) in 10.0 mL of $CHCl_3$ was added drop wise to the resin and the mixture was shaken at room temperature for three hours. The resin was washed according to GWP5 and dried in an oven at 90 °C. After the purification, 561 mg of the target resin **14b** were obtained in 98% conversion. Loading: 0.998 mmol/g [Conversion and loading calculated according to mass difference for 1 step.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 16.3 (CH_3), 24.3, 30.8, 42.8 (CH_2N), 70.0 (OCH_2), 108.6, 118.1, 121.8, 123.9, 128.7, 130.7, 136.1, 151.1 (N_2CS), 155.2 (OC-Ar), 172.5 (CO). FTIR (ATR): $\tilde{\nu}$ = 3025, 2919, 1729, 1611, 1512, 1492, 1437, 1377, 1156, 1089, 1007, 821, 738, 697, 542 cm^{-1}. EA ($C_{64}H_{66}N_2O_4S$): calc.: C 80.13, H 6.94, N 2.92, S 3.34, found: C 77.65, H 6.65, N 3.23, S 3.35.

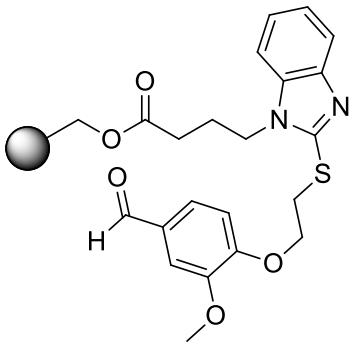
***Polystyrene-4-(2-((2-(2,6-difluorophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (14c)**



According to GP7, 500 mg of resin **12b** (loading: 0.90 mmol/g, 450 µmol) were swollen in 5.00 mL of $CHCl_3$ and 585 mg of 2,6-difluorophenol (10.0 equiv., 4.50 mmol) were added and shaken at room temperature. Then a freshly prepared mixture of 1.18 g of PPh_3 (10.0 equiv., 4.50 mmol) and 883 µL of DIAD (10.0 equiv., 4.50 mmol) in 10.0 mL of $CHCl_3$ was added drop wise to the resin and the mixture was shaken at room temperature for three hours. The resin was washed according to GWP5 and dried in an oven at 90 °C. After the purification, 573 mg of the target resin **14c** were obtained in quantitative conversion. Loading: 0.785 mmol/g [Conversion and loading calculated according to mass difference for 1 step.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 24.2, 30.7 ($OCCH_2$), 43.9 (CH_2N), 72.6, 108.7, 112.2, 118.1, 121.8, 123.0, 128.5, 136.2, 150.8 (N_2CS), 154.3 (OC-Ar), 172.4 (CO). FTIR: $\tilde{\nu}$ = 3024, 2920, 1730, 1602, 1511, 1493, 1451, 1375, 1220, 1157, 1005, 822, 740, 697, 540 cm^{-1}. EA ($C_{62}H_{60}F_2N_2O_4S$): calc.: C 76.99, H 6.25, N 2.90, S 3.31, found: C 72.64, H 5.87, N 2.31, S 2.21.

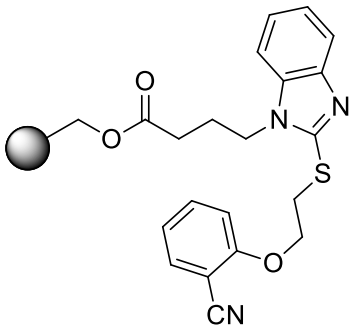
***Polystyrene-4-(2-((2-(4-formyl-2-methoxyphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (14d)**



According to GP7, 500 mg of resin **12b** (loading: 0.900 mmol/g, 450 µmol) were swollen in 5.00 mL of $CHCl_3$ and 685 mg of 4-hydroxy-3-methoxybenzaldehyde (10.0 equiv., 4.50 mmol) were added and shaken at room temperature. Then a freshly prepared mixture of 1.18 g of PPh_3 (10.0 equiv., 4.50 mmol) and 883 µL of DIAD (10.0 equiv., 4.50 mmol) in 10.0 mL of $CHCl_3$ was added drop wise to the resin and the mixture was shaken at room temperature for three hours. The resin was washed according to GWP5 and dried in an oven at 90 °C. After the purification, 583 mg of the target resin **14d** were obtained in quantitative conversion. Loading: 0.772 mmol/g [Conversion and loading calculated according to mass difference for 1 step.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 21.8, 24.3, 30.7 ($COCH_2$), 56.0 (OCH_3), 110.6, 114.7, 121.8, 132.8, 151.1 (N_2CS), 154.6 (OC-Ar), 172.1 (CO), 190.6 (HCO). FTIR (ATR): ṽ = 2922, 1727, 1600, 1511, 1492, 1451, 1381, 1234, 1161, 1107, 1018, 907, 822, 727, 698, 646, 540, 430 cm^{-1}. EA ($C_{64}H_{64}N_2O_6S$): calc.: C 77.70, H 6.52, N 2.83, S 3.24, found: C 69.23, H 5.79, N 2.47, S 1.96.

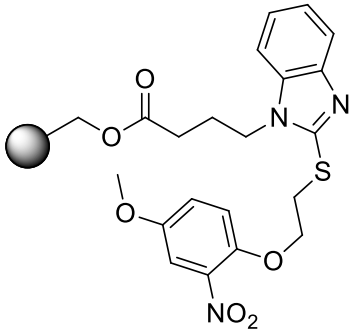
***Polystyrene-4-(2-((2-(2-cyanophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (14e)**



According to GP7, 500 mg of resin **12b** (loading: 0.90 mmol/g, 450 µmol) were swollen in 5.00 mL of $CHCl_3$ and 536 mg of 2-hydroxybenzonitrile (10.0 equiv., 4.50 mmol) were added and shaken at room temperature. Then a freshly prepared mixture of 1.18 g of PPh_3 (10.0 equiv., 4.50 mmol) and 883 µL of DIAD (10.0 equiv., 4.50 mmol) in 10.0 mL of $CHCl_3$ was added drop wise to the resin and the mixture was shaken at room temperature for three hours. The resin was washed according to GWP5 and dried in an oven at 90 °C. After the purification, 549 mg of the target resin **14e** were obtained in quantitative conversion. Loading: 0.820 mmol/g [Conversion and loading calculated according to mass difference for 1 step.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 21.8, 24.2, 30.6 ($COCH_2$), 112.5, 116.2, 121.0, 121.8, 134.2, 150.6 (N_2CS), 156.8, 159.8 (OC-Ar), 172.9 (CO). FTIR (ATR): ṽ 3024, 2922, 2227, 1728, 1599, 1511, 1491, 1450, 1375, 1239, 1161, 1110, 1009, 906, 823, 727, 697, 647, 540, 406 cm^{-1}. EA ($C_{63}H_{61}N_3O_4S$): calc.: C 79.13, H 6.43, N 4.39, S 3.35, found: C 71.45, H 5.94, N 2.86, S 2.11.

***Polystyrene-4-(2-((2-(4-methoxy-2-nitrophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (14f)**

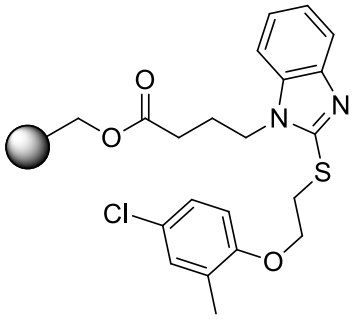


According to GP7, 500 mg of resin **12b** (loading: 0.900 mmol/g, 450 µmol) were swollen in 5.00 mL of $CHCl_3$ and 761 mg of 4-methoxy-2-nitrophenol (10.0 equiv., 4.50 mmol) were added and shaken at room temperature. Then a freshly prepared mixture of 1.18 g of PPh_3 (10.0 equiv., 4.50 mmol) and 883 µL of DIAD (10.0 equiv., 4.35 mmol) in

10.0 mL of $CHCl_3$ was added drop wise to the resin and the mixture was shaken at room temperature for three hours. The resin was washed according to GWP5 and dried in an oven at 90 °C. After the purification, 594 mg of the target resin **14f** were obtained in quantitative conversion. Loading: 0.758 mmol/g [Conversion and loading calculated according to mass difference for 1 step.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 24.2, 30.8 ($COCH_2$), 42.8 (CH_2N), 55.8 (OCH_3), 68.8 (OCH_2), 108.7, 109.6, 117.2, 120.6, 121.8, 136.2, 140.0, 143.3 (OC-Ar), 150.7 (N_2CS), 153.2 (CH_3OC-Ar), 172.8 (CO). FTIR (ATR): $\tilde{\nu}$ = 3023, 2919, 1728, 1602, 1528, 1511, 1492, 1451, 1351, 1219, 1155, 1106, 1030, 907, 820, 734, 697, 540, 396 cm^{-1}. EA ($C_{63}H_{63}N_3O_7S$): calc.: C 75.20, H 6.31, N 4.18, S 3.19, found: C 71.32, H 6.07, N 4.30, S 2.83.

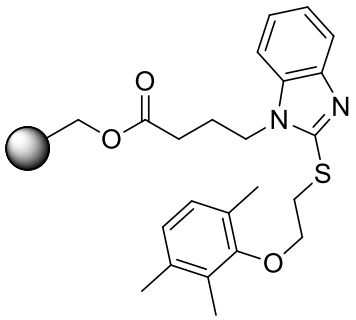
Polystyrene-4-(2-((2-(4-chloro-3-methylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate **(14g)**



According to GP7, 500 mg of resin **12b** (loading: 0.900 mmol/g, 450 µmol) were swollen in 5.00 mL of $CHCl_3$ and 642 mg of 4-chloro-2-methylphenol (10.0 equiv., 4.50 mmol) were added and shaken at room temperature. Then a freshly prepared mixture of 1.18 g of PPh_3 (10.0 equiv., 4.50 mmol) and 880 µL of DIAD (10.0 equiv., 4.50 mmol) in 10.0 mL of $CHCl_3$ was added drop wise to the resin and the mixture was shaken at room temperature for three hours. The resin was washed according to GWP5 and dried in an oven at 90 °C. After the purification, 562 mg of the target resin **14g** were obtained in quantitative connversion. Loading: 0.801 mmol/g [Conversion and loading calculated according to mass difference for 1 step.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 20.2 (CH_3), 24.2, 31.1 ($COCH_2$), 43.9 (CH_2N), 109.7, 113.3, 114.7, 121.9, 129.5, 136.0, 143.3, 150.8 (N_2CS), 156.7 (OC-Ar), 171.8 (CO). FTIR (ATR): $\tilde{\nu}$ = 2919, 1728, 1610, 1511, 1492, 1450, 1374, 1240, 1160, 1106, 1028, 906, 821, 736, 697, 540 cm^{-1}. EA ($C_{63}H_{63}ClN_2O_4S$): calc.: C 77.24, H 6.48, N 2.86, S 3.27, found: C 71.86, H 6.22, N 2.57, S 3.58.

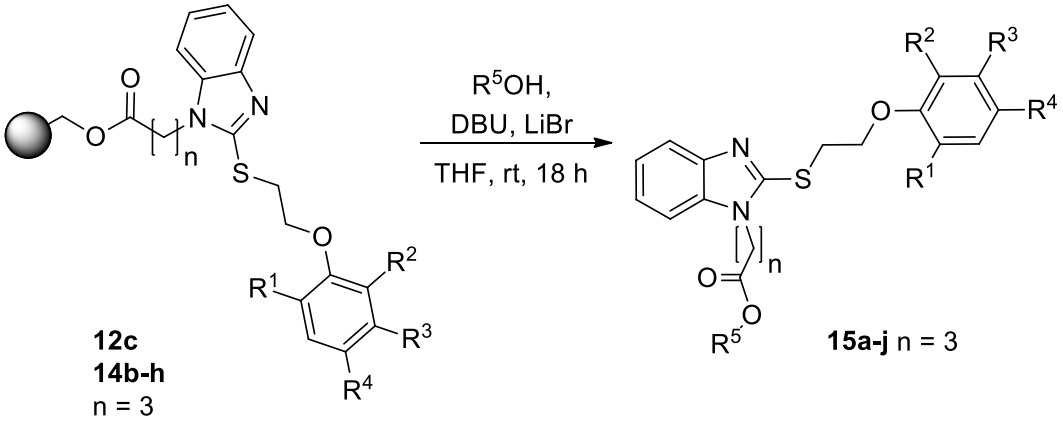
Polystyrene-4-(2-((2-(2,3,6-trimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate **(14h)**



According to GP7, 500 mg of resin **12b** (loading: 0.90 mmol/g, 450 µmol) were swollen in 5.00 mL of $CHCl_3$ and 613 mg of 2,3,6-trimethylphenol (10.0 equiv., 4.50 mmol) were added and shaken at room temperature. Then a freshly prepared mixture of 1.18 g of PPh_3 (10.0 equiv., 4.50 mmol) and 880 µL of DIAD (10.0 equiv., 4.50 mmol) in 10.0 mL of $CHCl_3$ was added drop wise to the resin and the mixture was shaken at room temperature for three hours. The resin was washed according to GWP5 and dried in an oven at 90 °C. After the purification, 562 mg of the target resin **14h** were obtained in quantitative conversion. Loading: 0.801 mmol/g [Conversion and loading calculated according to mass difference for 1 step.]

^{13}C GEL-NMR (75 MHz, $CDCl_3$, ppm), δ = 12.4 (CH_3), 16.2 (CH_3), 19.8 (CH_3), 21.9, 24.3, 70.3 (OCH_2), 108.6, 118.1, 121.8, 125.3, 129.4, 130.1, 135.7, 151.2 (N_2CS), 155.1 (OC-Ar), 172.2 (CO). FTIR (ATR): $\tilde{\nu}$ = 3024, 2919, 1729, 1610, 1511, 1491, 1450, 1376, 1239, 1157, 1084, 1008, 907, 821, 736, 697, 541, 433 cm^{-1}. EA ($C_{65}H_{68}N_2O_4S$): calc.: C 80.21, H 7.04, N 2.88, S 3.29, found: C 74.67, H 6.34, N 2.85, S 2.48.

3. Cleavage of target compounds from the solid phases



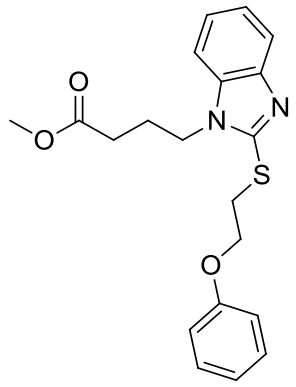
Scheme 6: Cleavage of the immobilized precursors.

3.1 Transesterification of immobilized 2-mercaptobenzooimidazoles

GP8: Transesterification of immobilized 2-mercaptobenzoimidazoles ***12c and 14b-h*** *to the corresponding ester derivatives* ***15a-j:***

Resin was swollen in a mixture of THF and MeOH or EtOH or ^{i}PrOH (0.50 mL of both solvents per 100 mg resin) and 5 equiv. LiBr and 5 equiv. of DBU were given to the mixture. The mixture was shaken at room temperature for 18 h. After that, the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography to give the pure compounds.

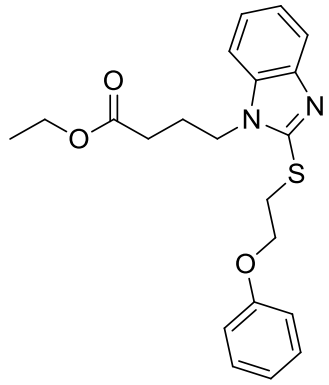
Methyl 4-(2-((2-phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate **(15a)**



According to GP8, 200 mg of resin **12c** (loading: 0.757 mmol/g, 0.151 mmol) were swollen in a mixture of 1.00 mL of THF and 1.00 mL of MeOH. After that 66.0 mg of LiBr (5.00 equiv., 0.760 mmol) and 110 µL of DBU (5.00 equiv., 0.760 mmol) were added and the mixture was shaken at room temperature for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 10:1 → 1:1) to give 12.2 mg (33.0 µmol) of **15a** as an oily liquid. Yield of the target compound calculated for the last step: 22% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 5 steps: 68%.

R_f = 0.80 (CH/EE: 1/1). ^{1}H-NMR (300 MHz, $CDCl_3$, ppm), δ = 2.13 (quin, ^{3}J = 7.1 Hz), 2.36 (t, ^{3}J = 7.1 Hz, 2 H), 3.65 (s, 3 H), 3.78 (t, ^{3}J = 6.0 Hz, 2 H), 4.16 (t, ^{3}J = 7.1 Hz, 2 H), 4.36 (t, ^{3}J = 6.0 Hz, 2 H), 7.02 - 6.86 (m, 3 H), 7.35 - 7.15 (m, 5 H), 7.75 - 7.60 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm), δ = 24.3, 30.6, 31.6, 43.0, 51.8, 66.5, 108.8, 114.7 (2 C), 118.3, 121.1, 121.9, 122.0, 129.5 (2 C), 136.2, 143.5, 151.1, 158.4, 172.9. FTIR (ATR): $\tilde{\nu}$ = 2946, 1731, 1598, 1586, 1495, 1460, 1433, 1379, 1363, 1276, 1238, 1166, 1080, 1031, 907, 876, 819, 740, 691, 596, 511, 435, 405 cm^{-1}. EI-MS (70 eV, 150 °C), *m/z* (%): 370 $[M]^+$ (15), 250 (100), 217 (28), 189 (12), 164 (12), 150 (15). HRMS ($C_{20}H_{22}O_3N_2S$): calc. 370.1347; found. 370.1346,

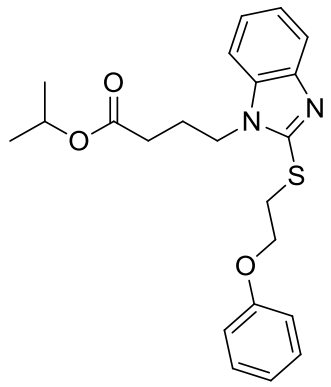
Ethyl 4-(2-((2-phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate **(15b)**



According to GP8, 200 mg of resin **12c** (loading: 0.757 mmol/g, 0.151 mmol) were swollen in a mixture of 1.00 mL of THF and 1.00 mL of EtOH. After that 66.0 mg of LiBr (5.00 equiv., 0.760 mmol) and 110 µL of DBU (5.00 equiv., 0.760 mmol) were added and the mixture was shaken at room temperature for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 10:1 → 1:1) to give 12.2 mg (32.0µmol) of **15b** as an oily liquid. Yield of the target compound calculated for the last step: 21% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 5 steps: 68%.

R_f = 0.77 (CH/EE: 1/1). ^{1}H NMR (300 MHz, $CDCl_3$, ppm), δ = 1.26 (t, ^3J = 7.2 Hz, 3 H), 2.14 (quin, ^3J = 7.2 Hz, 2 H), 2.36 (t, ^3J = 6.7 Hz, 2 H), 3.80 (t, ^3J = 6.1 Hz, 2 H), 4.16 (m, 4 H), 4.38 (t, ^3J = 6.0 Hz, 2 H), 7.05 - 6.84 (m, 3 H), 7.39 - 7.15 (m, 5 H), 7.78 - 7.59 (m, 1 H). C NMR (75 MHz, $CDCl_3$, ppm), δ = 14.2, 24.3, 30.8, 31.6, 43.0, 60.7, 66.4, 108.8, 114.6 (2 C, Ar), 118.2, 121.0, 121.9, 122.0, 129.4 (2 C), 136.2, 143.4, 151.1, 158.4, 172.7. – FTIR (ATR): ṽ = 3057, 2936, 1727, 1598, 1586, 1495, 1461, 1432, 1377, 1276, 1238, 1197, 1164, 1066, 1030, 908, 876, 740, 691, 597, 510, 433, 404 cm^{-1}. EI-MS (70 eV, 110 °C), *m/z* (%): 384 $[M]^+$ (12), 294 (14), 264 (69), 254 (13), 248 (35), 246 (35), 231 (24), 202 (48), 200 (99), 198 (50), 167 (19), 150 (19), 135 (20), 126 (14), 121 (99), 119 (100), 66 (41), 85 (53), 84 (46). HRMS ($C_{21}H_{24}O_3N_2S$): calc. 384.1500; found. 384.1502.

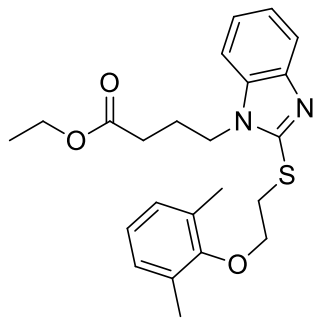
Isopropyl 4-(2-((2-phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate **(15c)**



According to GP8, 200 mg of resin **12c** (loading: 0.757 mmol/g, 0.151 mmol) were swollen in a mixture of 1.00 mL of THF and 1.00 mL of ^{i}PrOH. After that 66.0 mg of LiBr (5.00 equiv., 0.760 mmol) and 110 µL of DBU (5.00 equiv., 0.760 mmol) were added and the mixture was shaken at room temperature for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 10:1 → 1:1) to give 9.10 mg (23.0 µmol) of **15c** as an oily liquid. Yield of the target compound calculated for the last step: 15% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 5 steps: 63%.

R_f = 0.68 (Cyclohexane/EtOAc 1/1). – ^{1}H-NMR (300 MHz, $CDCl_3$, ppm), δ = 1.23 (s, 3H), 1.25 (s, 3H), 2.13 (quin, *J* = 7.0 Hz, 2 H), 2.34 (t, *J* = 7.0 Hz, 2 H), 3.80 (t, *J* = 6.1 Hz, 2 H), 4.18 (t, *J* = 7.2 Hz, 2 H), 4.38 (t, *J* = 6.1 Hz, 2 H), 5.04 (sept, *J* = 6.2 Hz, 1 H), 7.00 - 6.91 (m, 3 H), 7.34 - 7.18 (m, 5 H), 7.72 - 7.65 (m, 1 H). ^{13}C NMR (75 MHz, CDCl3, ppm), δ = 21.8 (2 C), 24.4, 31.2, 31.6, 43.1, 66.5, 68.1, 108.8, 114.7 (2 C), 118.3, 121.1, 121.9, 122.0, 129.5, 136.3 (2 C), 143.5, 151.1, 158.4, 172.0. FTIR (ATR): $\tilde{\nu}$ = 2977, 2934, 1723, 1598, 1586, 1495, 1462, 1435, 1374, 1276, 1238, 1168, 1106, 1080, 1032, 877, 822, 741, 692, 597, 510, 434 cm–1. EI-MS (70 eV, 110 °C), *m/z* (%): 398 $[M]^+$ (14), 278 (100). HRMS ($C_{22}H_{26}O_3N_2S$): calc. 398.1661; found. 398.1659.

Ethyl-4-(2-((2-(2,6-dimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate **(15d)**

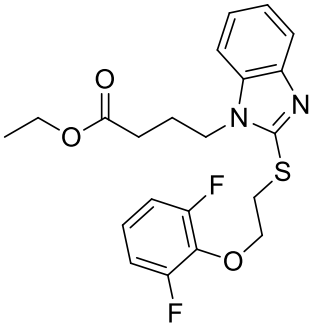


According to GP8, 200 mg of resin **14b** (loading: 0.998 mmol/g, 199.6 µmol) were swollen in a mixture of 1.00 mL of THF and 1.00 mL of EtOH. After that 85.0 mg of LiBr (5.00 equiv., 0.980 mmol) and 150 µL DBU (5.00 equiv., 0.980 mmol) were added and the mixture was shaken at room temperature for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 10:1 → 1:1) to give 15.2 mg (37.0 µmol) of **15d** as an oily liquid. Yield of the target compound calculated

for the last step: 19% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 6 steps: 75%.

R_f = 0.69 (CH/EE: 1/1). ^{1}H NMR (300 MHz $CDCl_3$, ppm), δ = 1.27 (t, *J* = 7.10 Hz, 3 H), 2.17 (quin, *J* = 6.90 Hz, 2 H), 2.31 (s, 6 H), 2.39 (t, *J* = 6.80 Hz, 2 H), 3.85 (t, *J* = 6.00 Hz, 2 H), 4.10 - 4.25 (m, 6 H), 6.89 - 7.03 (m, 3 H), 7.19 - 7.35 (m, 3 H), 7.64 - 7.70 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm), δ = 14.2, 16.3 (2 C), 24.3, 30.9, 32.6, 43.1, 60.7, 70.0, 108.7, 118.2, 121.9, 122.0, 124.0, 128.8 (2 C), 130.8 (2 C), 136.2 (2 C), 151.3, 155.3, 172.5. FTIR (ATR): $\tilde{\nu}$ = 2931, 1729, 1610, 1461, 1433, 1372, 1313, 1275, 1261, 1240, 1197, 1161, 1089, 1008, 918, 874, 767, 740, 670, 434, 401 cm^{-1}. EI-MS (70 eV, 100 °C), *m/z* (%): 412 $[M]^+$ (28), 291 (41), 264 (100), 231 (40), 150 (40) 119 (36), 69 (96), 57 (47). HRMS ($C_{23}H_{28}O_3N_2S$): calc. 412.1817; found. 412.1815.

Ethyl-4-(2-((2-(2,6-difluorophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate (15e)

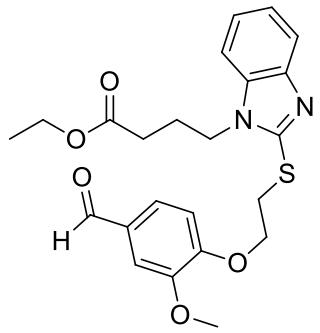


According to GP8, 200 mg of resin **14c** (loading: 0.785 mmol/g, 0.157 mmol) were swollen in a mixture of 1.00 mL of THF and 1.00 mL of EtOH. After that 68.0 mg LiBr (5.00 equiv., 0.785 mmol) and 110 µL DBU (5.00 equiv., 0.785 mmol) were added and the mixture was shaken at room temperature for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 100:1 → 10:1) to give 14.4 mg (34.0 µmol) of **15e** as an oily liquid. Yield of the target compound calculated for the last step: 22% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 6 steps: 74%.

R_f = 0.65 (CH/EE: 1/1). ^{1}H NMR (400 MHz $CDCl_3$, ppm), δ = 1.26 (t, *J* = 7.1 Hz, 3 H), 2.15 (quin, *J* = 7.1 Hz, 2 H), 2.37 (t, *J* = 6.8 Hz, 2 H), 3.79 (t, *J* = 6.0 Hz, 2 H), 4.15 (q, *J* = 7.2 Hz, 2 H), 4.20 (t, *J* = 7.2 Hz, 2 H), 4.50 (t, *J* = 6.0 Hz, 2 H), 6.84 - 7.00 (m, 3 H), 7.19 - 7.25 (m, 2 H), 7.28 - 7.34 (m, 1 H), 7.62 – 7.67 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm), δ = 14.2, 24.3, 30.8, 32.2, 43.1, 60.7, 72.7, 108.8, 112.2 (dd, *J* = 10.2, 6.6 Hz, 2 C), 118.2, 121.9, 122.0, 123.12 (t, *J* = 9.1 Hz, 1 C), 135.2 (t, *J* = 14.3 Hz, 1 C), 136.2, 143.4, 151.0, 156.1 (dd, J = 243, 5.1 Hz, 2 C), 172.5.

FTIR (ATR): $\tilde{\nu}$ = 2936, 1727, 1595, 1495, 1474, 1434, 1376, 1288, 1238, 1162, 1062, 1005, 875, 776, 740, 677, 577, 501, 434 cm^{-1}. EI-MS (70 eV, 100 °C), *m/z* (%): 420 $[M]^+$ (22), 290 (100). HRMS ($C_{21}H_{22}O_3N_2F_2S$): calc. 420.1316; found. 420.1314.

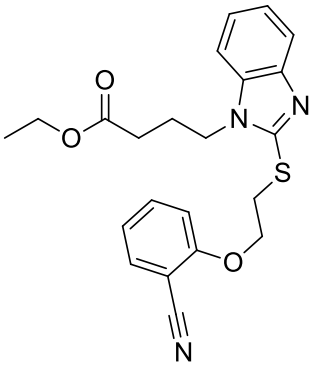
Ethyl-4-(2-((2-(4-formyl-2-methoxyphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate **(15f)**



According to GP8, 200 mg of resin **14d** (loading: 0.772 mmol/g, 0.154 mmol) were swollen in a mixture of 1.00 mL of THF and 1.00 mL of EtOH. After that 67.0 mg of LiBr (5.00 equiv., 0.770 mmol) and 117 µL of DBU (5.00 equiv., 0.770 mmol) were added and the mixture was shaken at room temperature for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 100:1 → 10:1) to give 16.4 mg (37.0 µmol) of **15f** as an oily liquid. Yield of the target compound calculated for the last step: 24% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 6 steps: 75%.

R_f = 0.69 (CH/EE: 1/1). ^{1}H NMR (400 MHz $CDCl_3$, ppm), δ = 1.25 (t, *J* = 7.1 Hz, 3 H), 2.14 (quin, *J* = 7.1 Hz, 2 H), 2.36 (t, *J* = 7.1 Hz, 2 H), 3.85 (t, *J* = 6.3 Hz, 2 H), 3.89 (s, 3 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 4.19 (t, *J* = 7.1 Hz, 2 H), 4.52 (t, *J* = 6.6 Hz, 2 H), 6.97 (d, *J* = 8.1 Hz, 1 H), 7.20 - 7.26 (m, 2 H), 7.28 - 7.35 (m, 1 H), 7.49 (dd, *J* = 8.10, 1.8 Hz, 1 H), 7.63 (d, *J* = 1.50 Hz, 1 H), 7.75 (d, *J* = 8.10 Hz, 1 H), 9.87 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm), δ = 14.2, 24.3, 30.8, 43.1, 56.1, 60.7, 67.7, 77.2, 108.8, 110.8, 111.8, 118.4, 122.1, 126.5, 130.1 (2 C), 136.2, 143.3, 148.3, 150.8, 154.7, 172.5, 190.8. FTIR (ATR): $\tilde{\nu}$ = 2933, 1726, 1682, 1583, 1509, 1461, 1433, 1379, 1262, 1235, 1159, 1132, 1016, 859, 807, 740, 640, 586, 434 cm^{-1}. EI-MS (70 eV, 160 °C), *m/z* (%): 442 $[M]^+$ (10), 264 (100). HRMS ($C_{23}H_{26}O_5N_2S$): calc. 442.1559; found. 442.1557.

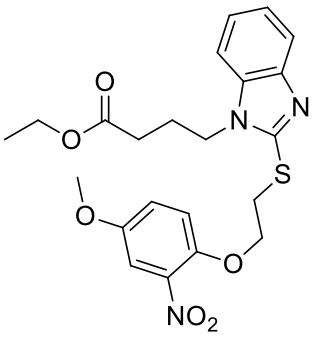
***Ethyl 4-(2-((2-(2-cyanophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (15g)**



According to GP8, 200 mg of resin **14e** (loading: 0.820 mmol/g, 0.164 mmol) were swollen in a mixture of 1.00 mL of THF and 1.00 of mL EtOH. After that 72.0 mg LiBr (5.00 equiv., 0.820 mmol) and 120 µL DBU (5.00 equiv., 0.820 mmol) were added and the mixture was shaken at room temperature for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 100:1 → 10:1) to give 13.8 mg (33.7 µmol) of **15g** as an oily liquid. Yield of the target compound calculated for the last step: 21% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 6 steps: 74%.

R_f = 0.61 (CH/EE: 1/1). ^{1}H NMR (300 MHz $CDCl_3$, ppm), δ = 1.26 (t, *J* = 7.10 Hz, 3 H), 2.14 (quin, *J* = 7.10 Hz, 2 H), 2.37 (t, *J* = 7.2 Hz, 2 H), 3.81 (t, *J* = 6.40 Hz, 2 H), 4.14 (q, *J* = 7.1, 2 H), 4.19 (t, *J* = 7.1 Hz, 2 H), 4.54 (t, *J* = 6.4 Hz, 2 H), 7.02 (m, 1 H), 7.20 -7.26 (m, 3 H), 7.29 - 7.36 (m, 1 H), 7.50 - 7.59 (m, 2 H), 7.63 - 7.69 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm), δ = 14.2, 24.3, 30.6, 30.8, 43.2, 60.7, 67.4, 102.1, 108.9, 112.7, 116.4, 118.2, 121.1, 122.0, 122.1, 133.8, 134.3, 136.3, 143.3, 150.8, 160.1, 172.5. FTIR (ATR): $\tilde{\nu}$ = 2936, 2226, 1726, 1597, 1579, 1492, 1435, 1377, 1287, 1255, 1201, 1163, 1110, 1008, 876, 742, 566, 498, 434 cm^{-1}. EI-MS (70 eV, 150 °C), *m/z* (%): 409 $[M]^+$ (41), 264 (100). – HRMS ($C_{22}H_{23}O_3N_3S$): calc. 409.1456; found 409.1455.

***Ethyl-4-(2-((2-(4-methoxy-2-nitrophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (15h)**

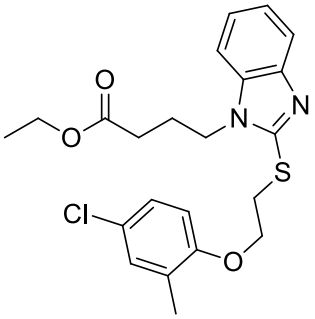


According to GP8, 200 mg of resin **14f** (loading: 0.758 mmol/g, 0.152 mmol) were swollen in a mixture of 1.00 mL of THF and 1.00 of mL EtOH. After that 66.0 mg of LiBr (5.00 equiv., 0.760 mmol) and 110 µL DBU (5.00 equiv., 0.760 mmol) were added and the mixture was shaken at room temperature for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography

(CH/EE 100:1 → 10:1) to give 13.9 mg (30.3 µmol) of **15h** as an oily liquid. Yield of the target compound calculated for the last step: 20% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 6 steps: 73%.

R_f = 0.44 (CH/EE: 1/1). ^{1}H NMR (300 MHz $CDCl_3$, ppm), δ = 1.25 (t, *J* = 7.2 Hz, 3 H), 2.14 (quin, *J* = 7.0 Hz, 2 H), 2.37 (t, *J* = 7.0 Hz, 2 H), 3.77 (t, *J* = 6.4 Hz, 2 H), 3.82 (s, 3 H), 4.10 - 4.21 (m, 4 H), 4.50 (t, *J* = 6.2 Hz, 2 H), 7.07 - 7.11 (m, 1 H), 7.19 - 7.25 (m, 3 H), 7.28 - 7.38 (m, 2 H), 7.64 - 7.67 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm), δ = 14.2, 24.4, 30.9, 31.1, 43.2, 56.0, 60.7, 69.2, 108.9, 109.8, 117.4, 118.2, 120.7, 121.9, 122.0, 136.3, 140.3, 143.4, 146.1, 150.9, 153.4, 172.4. FTIR (ATR): $\tilde{\nu}$ = 2936, 1726, 1526, 1498, 1460, 1435, 1349, 1274, 1218, 1159, 1034, 915, 855, 807, 741, 434 cm^{-1}. EI-MS (70 eV, 180 °C), *m/z* (%): 459 $[M]^+$ (16), 264 (100). HRMS ($C_{22}H_{25}O_6N_3S$): calc. 459.1457; found. 459.1459.

***Ethyl-4-(2-((2-(4-chloro-2-methylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (15i)**

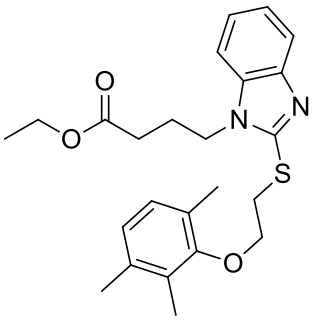


According to GP8, 200 mg of resin **14g** (loading: 0.801 mmol/g, 0.160 mmol) were swollen in a mixture of 1.00 mL of THF and 1.00 mL of EtOH. After that 70.0 mg LiBr (5.00 equiv., 0.800 mmol) and 110 µL of DBU (5.00 equiv., 0.80 mmol) were added and the mixture was shaken at room temperature for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 100:1 → 10:1) to give 12.5 mg (28.9 µmol) of **15i** as an oily liquid. Yield of the target compound calculated for the last step: 18% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 5 steps: 72%.

R_f = 0.67 (CH/EE: 1/1). ^{1}H NMR (400 MHz $CDCl_3$, ppm), δ = 1.26 (t, *J* = 7.1 Hz, 3 H), 2.14 (quin, *J* = 7.1 Hz, 2 H), 2.34 (s, 3H), 2.36 (t, *J* = 7.3 Hz, 2 H), 3.76 (t, *J* = 6.3 Hz, 2 H), 4.14 (q, *J* = 7.1 Hz, 2 H) 4.18 (t, *J* = 7.2 Hz, 2 H), 4.35 (t, *J* = 6.2 Hz, 2 H), 6.74 (dd, *J* = 8.8, 3.0 Hz, 1 H), 6.85 (d, *J* = 2.8 Hz, 1H), 7.20 - 7.26 (m, 3 H), 7.28 -7.34 (m, 1 H), 7.65 -7.70 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm), δ = 14.2, 20.3, 24.3, 30.9, 31.3, 43.1, 60.7, 66.8, 108.8, 113.4, 117.1, 118.3, 121.9, 122.0, 126.1, 129.6,

136.2, 137.0, 143.4, 151.0, 156.9, 172.5. FTIR (ATR): $\tilde{\nu}$ = 2932, 1728, 1594, 1479, 1461, 1435, 1377, 1308, 1276, 1240, 1166, 1027, 858, 807, 740, 652, 632, 443 cm^{-1}. EI-MS (70 eV, 100 °C), *m/z* (%): 432 $[M]^+$ (10), 290 (100), 87 (46). HRMS ($C_{22}H_{25}O_3N_2ClS$): calc. 432.1269; found. 432.1269.

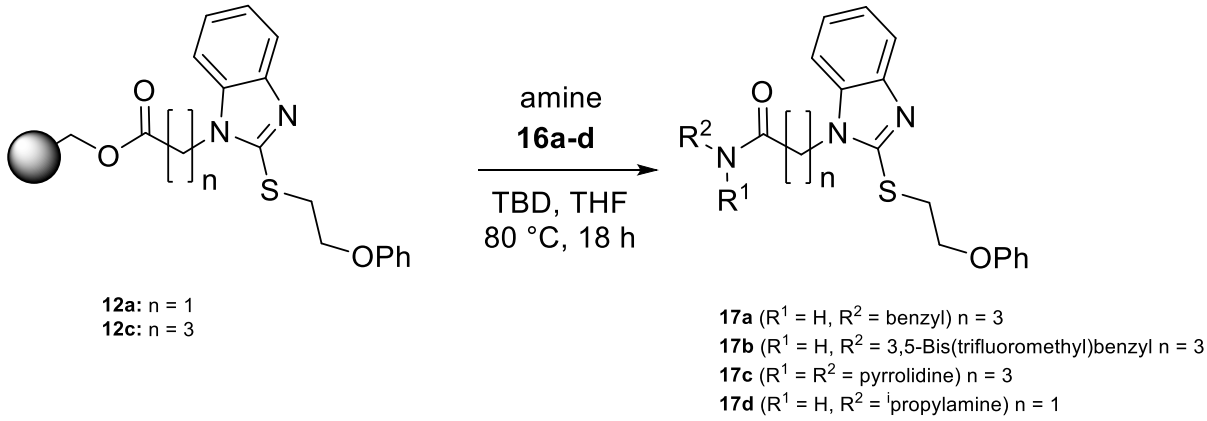
***Ethyl-4-(2-((2-(2,3,6-trimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (15j)**



According to GP8, 200 mg of resin **14h** (loading: 0.801 mmol/g, 160.0 µmol) were swollen in a mixture of 1.00 mL of THF and 1.00 mL of EtOH. After that 68.0 mg of LiBr (5.00 equiv., 0.790 mmol) and 120 µL of DBU (5.00 equiv., 0.790 mmol) were added and the mixture was shaken at room temperature for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 100:1 → 10:1) to give 8.70 mg (20.4 µmol) of **15j** as an oily liquid. Yield of the target compound calculated for the last step: 13% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 6 steps: 72%.

R_f = 0.67 (CH/EE: 1/1). ^{1}H NMR (300 MHz $CDCl_3$, ppm), δ = 1.26 (t, *J* = 7.1 Hz, 3 H), 2.11 - 2.23 (m, 8 H), 2.27 (s, 3 H), 2.39 (t, *J* = 6.8 Hz, 2 H), 3.85 (t, *J* = 6.0 Hz, 2 H), 4.08 - 4.26 (m, 6 H), 6.81 - 6.92 (m, 2 H), 7.19 - 7.26 (m, 2 H), 7.28 - 7.34 (m, 1 H), 7.62 - 7.69 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm), δ = 12.5, 14.2, 16.3, 19.9, 24.4, 30.9, 32.5, 43.1, 60.7, 70.3, 108.7, 118.2, 121.9, 121.9, 125.4, 127.9, 128.0, 129.5, 135.8 (2 C), 136.2, 151.3, 155.1, 172.5. FTIR (ATR): $\tilde{\nu}$ = 2923, 1730, 1609, 1460, 1436, 1368, 1312, 1262, 1240, 1208, 1161, 1084, 1008, 805, 739, 673, 433 cm^{-1}. EI-MS (70 eV, 120 °C), *m/z* (%): 426 $[M]^+$ (42) 290 (100), 264 (98), 129 (69). HRMS ($C_{24}H_{30}O_3N_2S$): calc. 426,1970; found. 426.1972.

3.2 Aminolysis of attached 2-Mercaptobenzoimidazoles

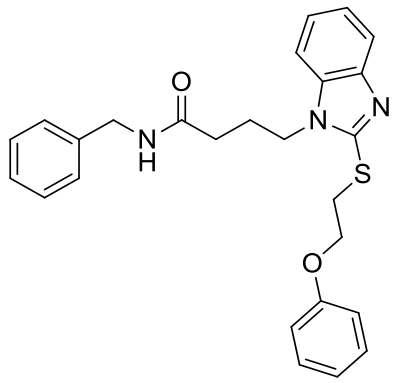


Scheme 7*:* Aminolysis of attached 2-Mercaptobenzoimidazoles.

*GP9: Aminolysis of attached 2-Mercaptobenzoimidazoles **12a and 12c** to the corresponding amide derivatives **17a - d:***

Resin was swollen in THF (0.50 mL of solvent per 100 mg resin) and 5.00 equiv. of TBD (1,5,7-Triazabicyclo[4.4.0]dec-5-ene) and 5.00 equiv. of amine were given to the mixture. The mixture was shaken at 80 °C for 18 h. After that, the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography to give the pure compounds.

N-Benzyl-4-(2-((2-phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanamide **(17a)**

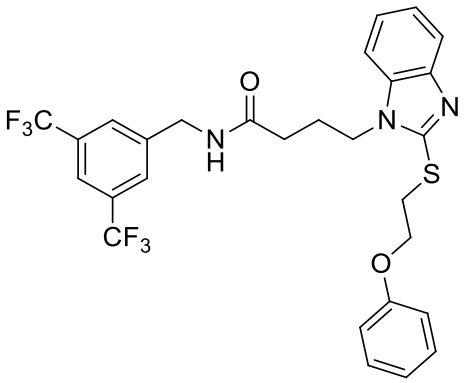


According to GP9, 200 mg of resin **12c** (loading: 0.757 mmol/g, 0.151 mmol) were swollen in 1.50 mL of THF and 106 mg of TBD (5.00 equiv., 0.760 mmol) and 83 µL of Benzylamin (5.00 equiv., 0.760 mmol) were added and the mixture was shaken at 80 °C for 18 h. Afterwards the resin was removed by filtration and washed three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 100:1 → 10:1) to give 24.3 mg (54.5 µmol) of **17a** as an oily liquid. Yield of the target compound calculated for the last step: 36% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 5 steps: 75%.

R_f = 0.31 (CH/EE: 1/1). ^{1}H NMR (300 MHz $CDCl_3$, ppm), δ = 2.16 - 2.22 (m, 4 H), 3.77 (t, *J* = 6.0 Hz, 2 H), 4.20 (t, *J* = 6.8 Hz, 2 H), 4.34 (t, *J* = 6.0 Hz, 2 H),

4.40 (d, *J* = 5.6 Hz, 2 H), 5.77 (bs, 1 H, N*H*), 6.88 - 6.98 (m, 3 H), 7.16 - 7.37 (m, 10 H), 7.65 - 7.71 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm), δ = 24.7, 31.7, 32.4, 43.3, 43.7, 66.3, 109.0, 114.6 (2 C), 118.1, 121.1, 122.0, 122.1, 127.6, 127.9 (2 C), 128.7 (2 C), 129.5 (2 C), 136.1, 138.0, 143.0, 151.0, 158.3, 171.1. FTIR (ATR): $\tilde{\nu}$ = 3293, 3059, 2930, 1645, 1598, 1542, 1494, 1454, 1430, 1379, 1238, 1170, 1079, 1031, 908, 737, 693, 511 cm^{-1}. EI-MS (70 eV, 200 °C), *m/z* (%): 445 $[M]^+$ (8), 325 (100), 176 (57), 91 (50). HRMS ($C_{26}H_{27}O_2N_3S$): calc. 445.1820; found. 445.1819.

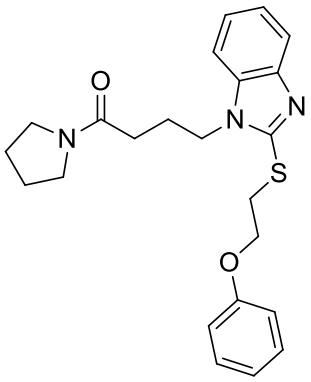
N-(3,5-Bis(trifluoromethyl)benzyl)-4-(2-((2-phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanamide **(17b)**



According to GP9, 200 mg of resin **12c** (loading: 0.757 mmol/g, 0.151 mmol) were swollen in 1.50 mL of THF and 106 mg of TBD (5.00 equiv., 0.760 mmol) and 300 mg of 3,5-Bis(trifluoromethyl)benzylamine (5.00 equiv., 0.760 mmol) were added and the mixture was shaken at 80 °C for 18 h. Afterwards the resin was removed by filtration and washed three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 100:1 → 10:1) to give 9.3 mg (16.0 µmol) of **17b** as an oily liquid. Yield of the target compound calculated for the last step: 11% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 5 steps: 60%.

R_f = 0.39 (CH/EE: 1/1). ^{1}H NMR (400 MHz $CDCl_3$, ppm), δ = 2.22 - 2.45 (m, 4 H), 3.79 (t, *J* = 5.70 Hz, 2 H), 4.19 - 4.25 (m, 2 H), 4.35 (t, *J* = 5.8 Hz, 2 H), 4.45 (d, *J* = 6.1 Hz, 2 H), 5.82 (br.s., 1 H, N*H*), 6.92 (m, 3 H), 7.25 (m, 5 H), 7.68 (br. s., 3 H), 7.79 (br. s., 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm), δ = 24.2, 31.8, 32.3, 42.7, 43.2, 66.3, 109.0, 114.6 (2 C), 118.2, 121.2 (2 C), 121.5 (quin, *J* = 3.7 Hz), 121.8 (q, *J* = 273.0 Hz), 122.2, 127. 8 (2 C), 129.6 (2 C), 131.9 (q, *J* = 33.0 Hz), 136.0, 140.9, 143.2, 151.0, 158.3, 171.6. FTIR (ATR): $\tilde{\nu}$ = 3310, 2937, 1555, 1602, 1539, 1498, 1468, 1443, 1427, 1379, 1348, 1291, 1242, 1171, 1154, 1120, 1009, 890, 799, 755, 735, 704, 694, 681, 567, 509, 428, 396 cm^{-1}. EI-MS (70 eV, 220 °C), *m/z* (%): 581 $[M]^+$ (16), 461 (97), 190 (63), 151 (100), 69 (73). HRMS ($C_{28}H_{25}O_2N_3F_6S$): calc. 581.1565; found. 581.1566.

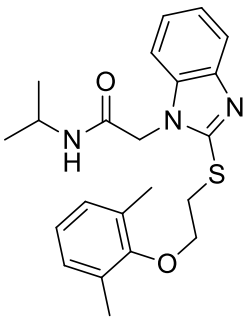
***4-(2-((2-Phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)-1-(pyrrolidin-1-yl)butan-1-one* (17c)**



According to GP9, 200 mg of resin **12c** (loading: 0.757 mmol/g, 0.151 mmol) were swollen in 1.50 mL of THF and 106 mg of TBD (5.00 equiv., 0.760 mmol) and 60 µL of pyrrolidine (5.00 equiv., 0.760 mmol) were added and the mixture was shaken at 80 °C for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 100:1 → 10:1) to give 18.3 mg (44.7 µmol) of **17c** as an oily liquid. Yield of the target compound calculated for the last step: 29% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 5 steps: 72%.

R_f = 0.12 (CH/EE: 1/1). ^{1}H NMR (300 MHz $CDCl_3$, ppm), δ = 1.83 (m, 4 H), 2.13 - 2.24 (m, 4 H), 3.16 (t, *J* = 6.2 Hz, 2 H), 3.48 (t, *J* = 5.9 Hz, 2 H), 3.80 (t, *J* = 6.0 Hz, 2 H), 4.24 (br.s., 2 H), 4.37 (t, *J* = 6.0 Hz, 2 H), 6.94 (m, 3 H), 7.28 (m, 5 H), 7.67 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm), δ = 23.9, 24.3, 25.9, 30.5, 31.6, 43.2, 45.7, 46.3, 66.5, 109.1, 114.6 (2 C), 118.0, 121.0, 121.8, 129.5 (2 C), 136.4, 143.2, 151.1, 158.4, 169.81. FTIR (ATR): $\tilde{\nu}$ = 2946, 2871, 1633, 1598, 1495, 1431, 1378, 1274, 1236, 1171, 1079, 1031, 908, 877, 802, 740, 691, 522, 434 cm^{-1}. EI-MS (70 eV, 170 °C), *m/z* (%): 409 $[M]^+$ (21), 289 (73), 140 (100), 139 (55). HRMS ($C_{23}H_{27}O_2N_3S$): calc. 409.1820; found. 409.1819.

***2-(2-((2-(2,6-Dimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)-N-isopropylacetamide* (19)**



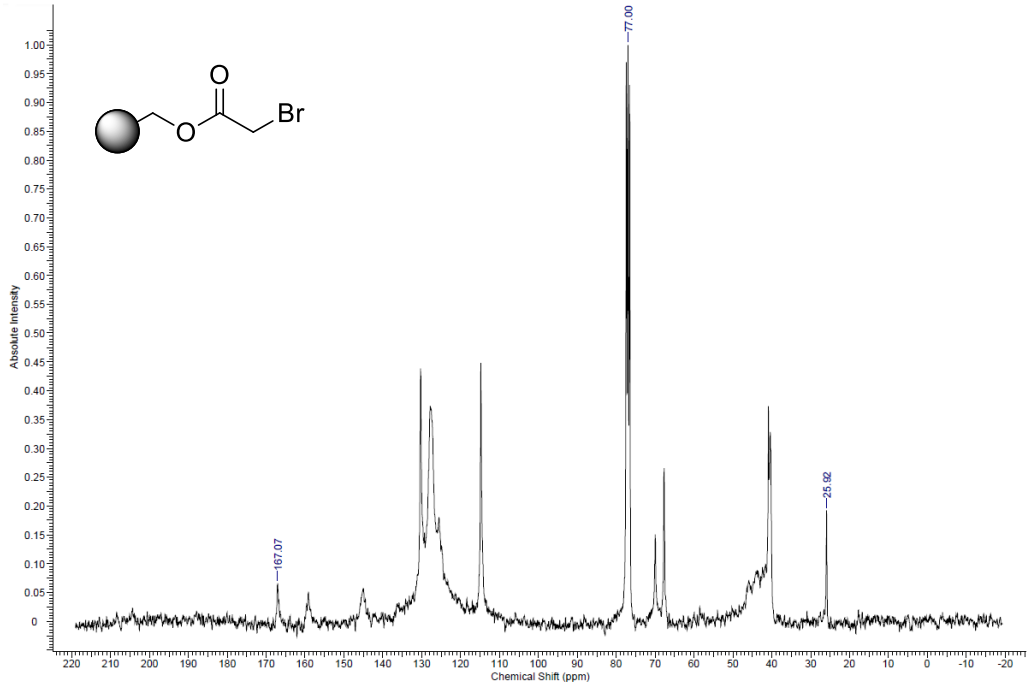
According to GP9, 300 mg of resin **12a** (loading: 0.962 mmol/g, 0.289 mmol) were swollen in 1.50 mL of THF and 200 mg of TBD (5.00 equiv., 1.44 mmol) and 123 µL of ^{i}PrNH$_2$ (5.00 equiv., 1.44 mmol) were added and the mixture was shaken at 80 °C for 18 h. Afterwards the resin was removed by filtration and washed additionally three times with THF. The resulting filtrate was evaporated and the crude material was purified *via* flash chromatography (CH/EE 100:1 → 10:1) to give 15.2 mg (38.2 µmol) of **17d** as an oily liquid. Yield of the

target compound calculated for the last step: 11% (based on calculations of previous resin-conversion *via* mass difference of the single resins). Average yield per step for the whole sequence calculated over 6 steps: 69%.

R_f = 0.44 (CH/EE: 1/1). ^{1}H NMR (300 MHz $CDCl_3$, ppm), δ = 1.04 (s, 3 H), 1.06 (s, 3 H), 2.30 (s, 6 H), 3.84 (t, *J* = 6.0 Hz, 2 H), 4.09 - 4.19 (m, 3 H), 4.75 (s, 2 H), 5.27 (br. s., N*H*), 6.90 - 7.01 (m, 3 H), 7.25 – 7.32 (m, 3 H), 7.69 - 7.72 (m, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$, ppm), δ = 16.3 (2 C), 22.4 (2 C), 28.6, 41.9, 47.6, 70.1, 108.6, 115.2, 118.7, 122.8, 124.1, 128.9 (2 C), 130.8 (2 C), 136.1, 143.6, 152.0, 155.3, 165.1. FTIR (ATR): $\tilde{\nu}$ = 3276, 2970, 1653, 1559, 1462, 1446, 1406, 1366, 1324, 1262, 1238, 1201, 1087, 1059, 1010, 980, 931, 880, 825, 798, 764, 734, 714, 584, 542, 454, 438, 414 cm^{-1}. EI-MS (70 eV, 130 °C), *m/z* (%): 397 $[M]^+$ (58), 249 (100), 163 (81). HRMS ($C_{22}H_{27}O_2N_3S$): calc. 397.1818; found. 397.1819.

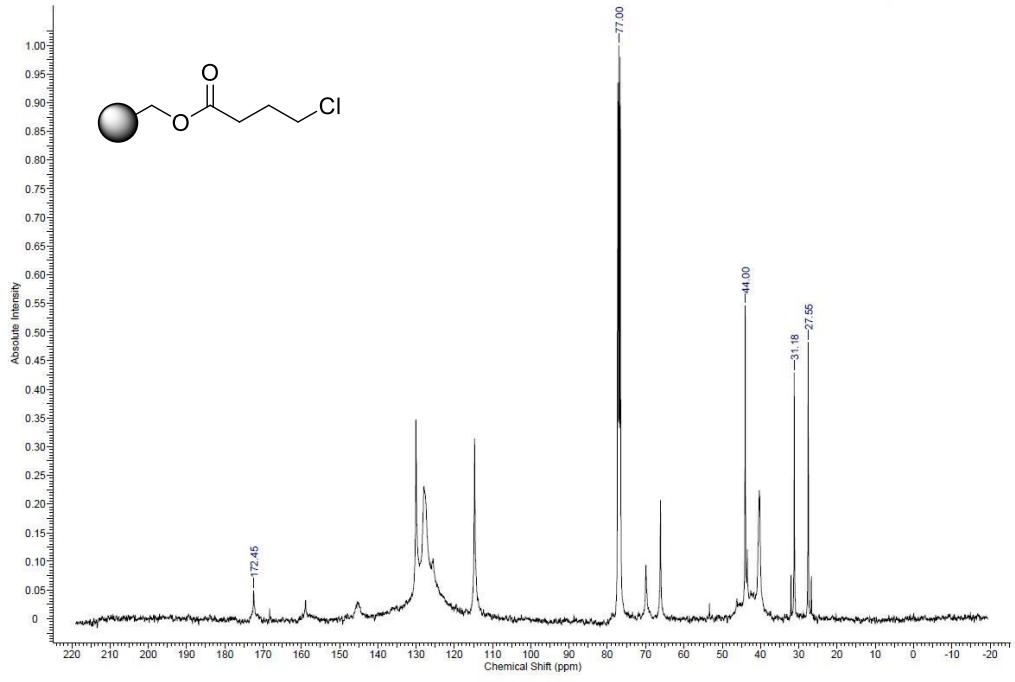
4. Spectra

Polystyrene-2-bromoacetate (3a)



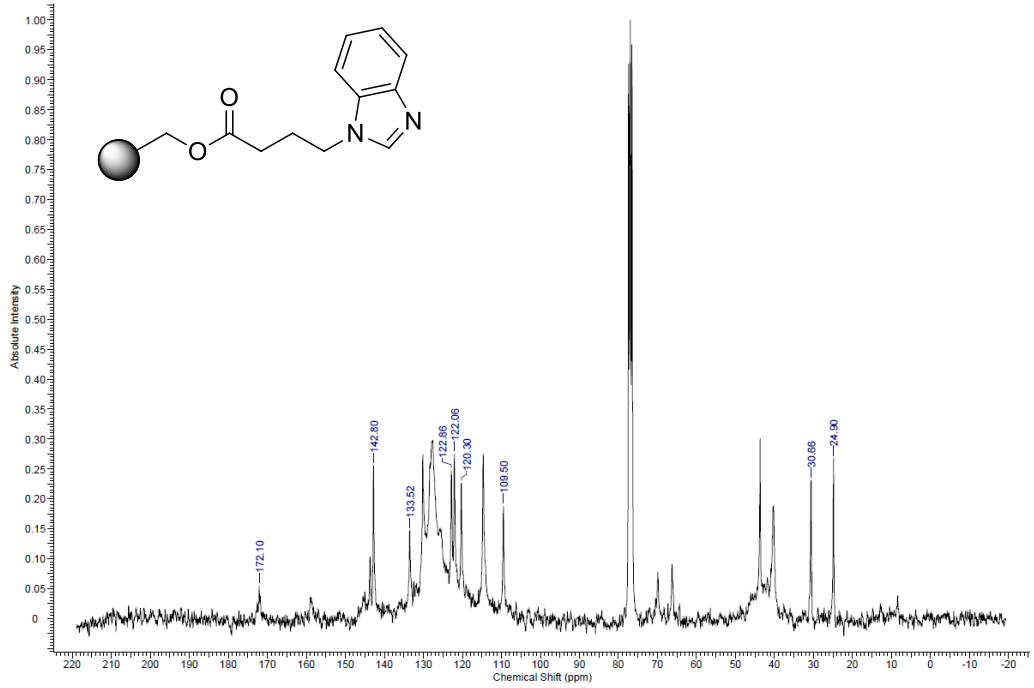
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

Polystyrene-4-chlorobutanoate (3b)



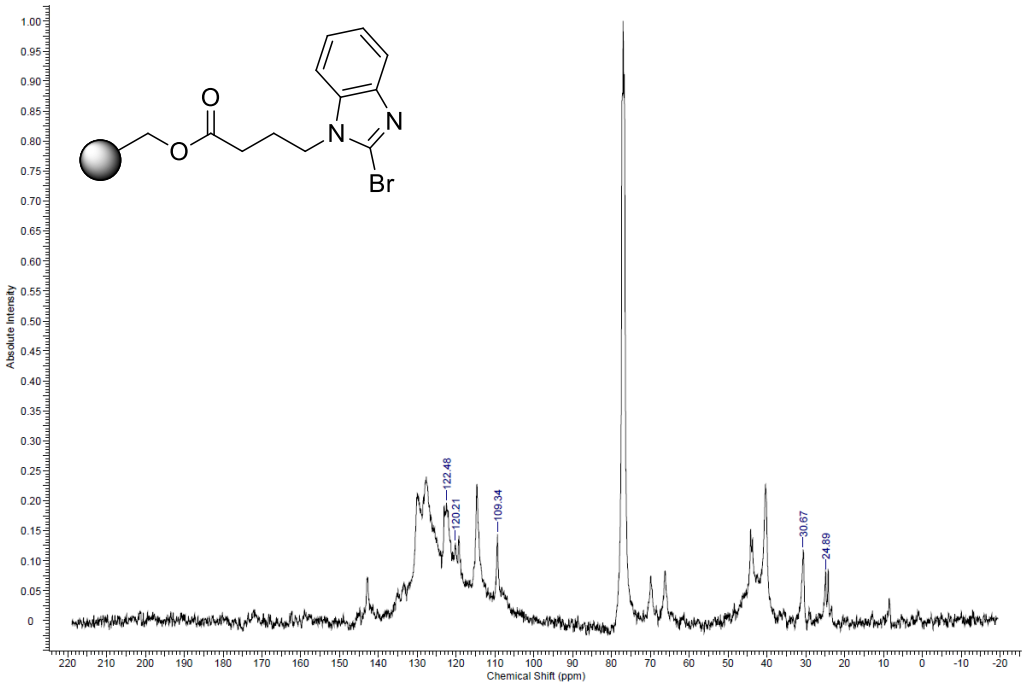
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene- 4-(1H-benzo[d]imidazol-1-yl)butanoate* (5)**



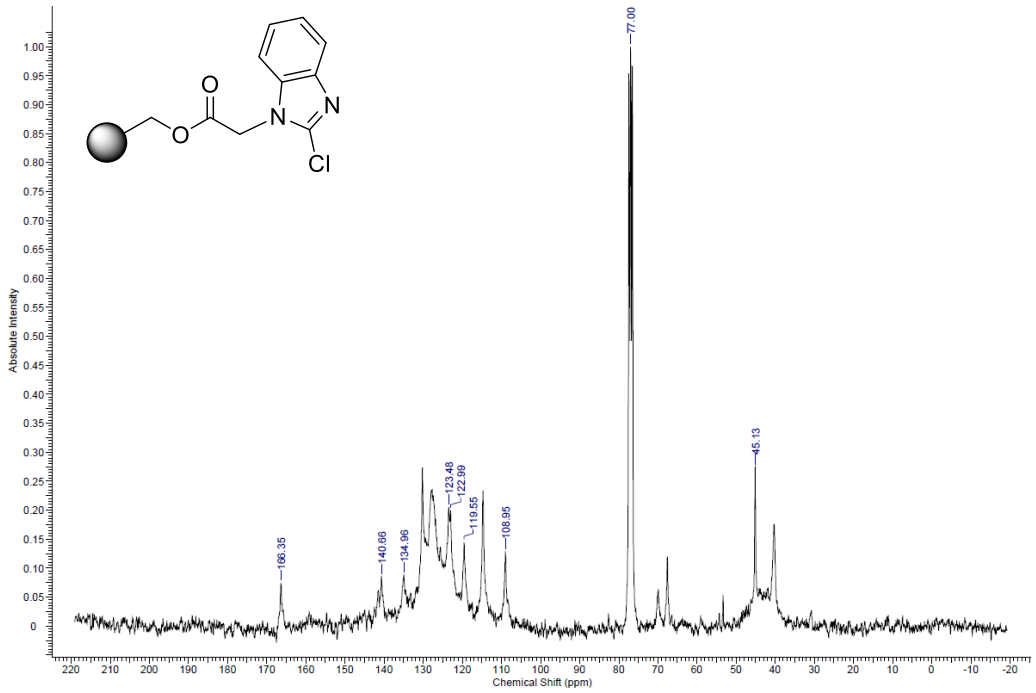
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene- 4-(2-bromo-1H-benzo[d]imidazol-1-yl)butanoate* (4b)**



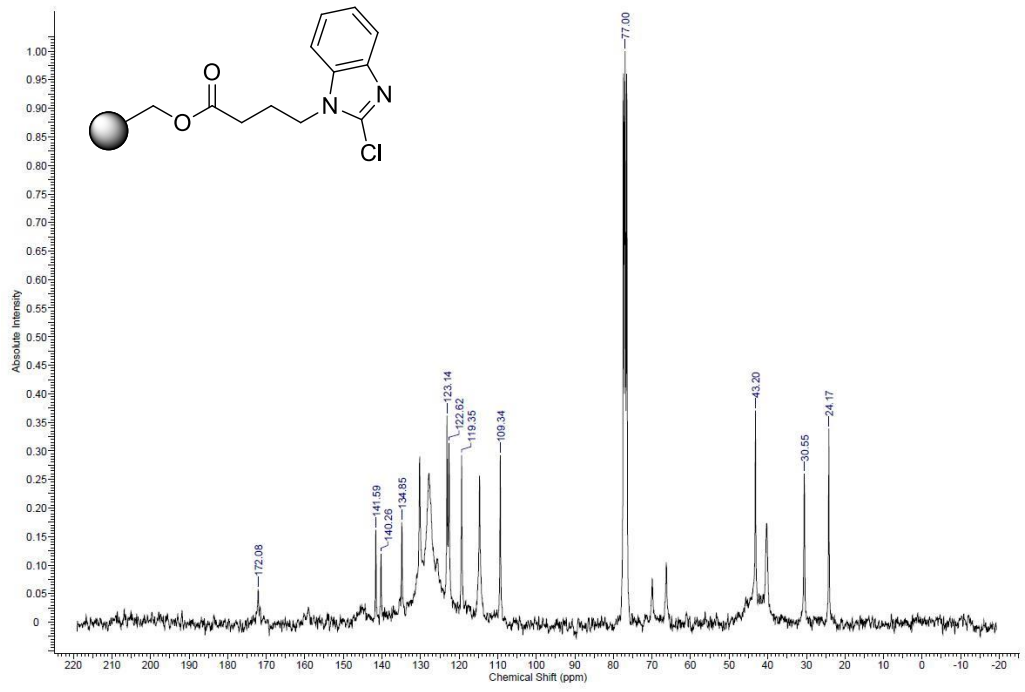
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene-2-(2-chloro-1H-benzo[d]imidazol-1-yl)acetate* (7a)**



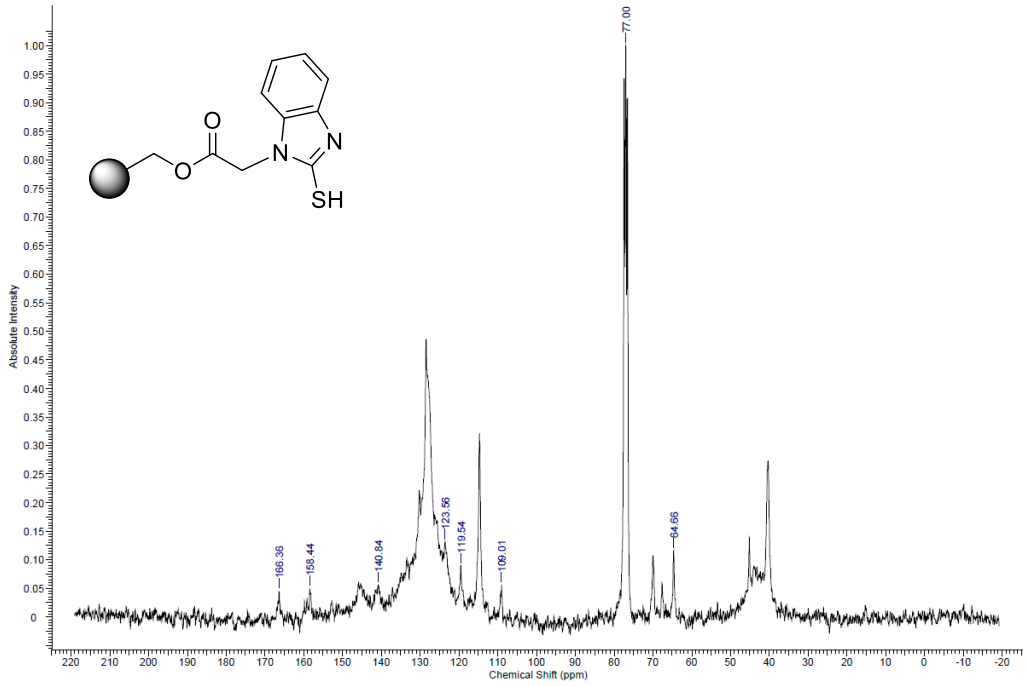
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene- 4-(2-chloro-1H-benzo[d]imidazol-1-yl)butanoate* (7b)**



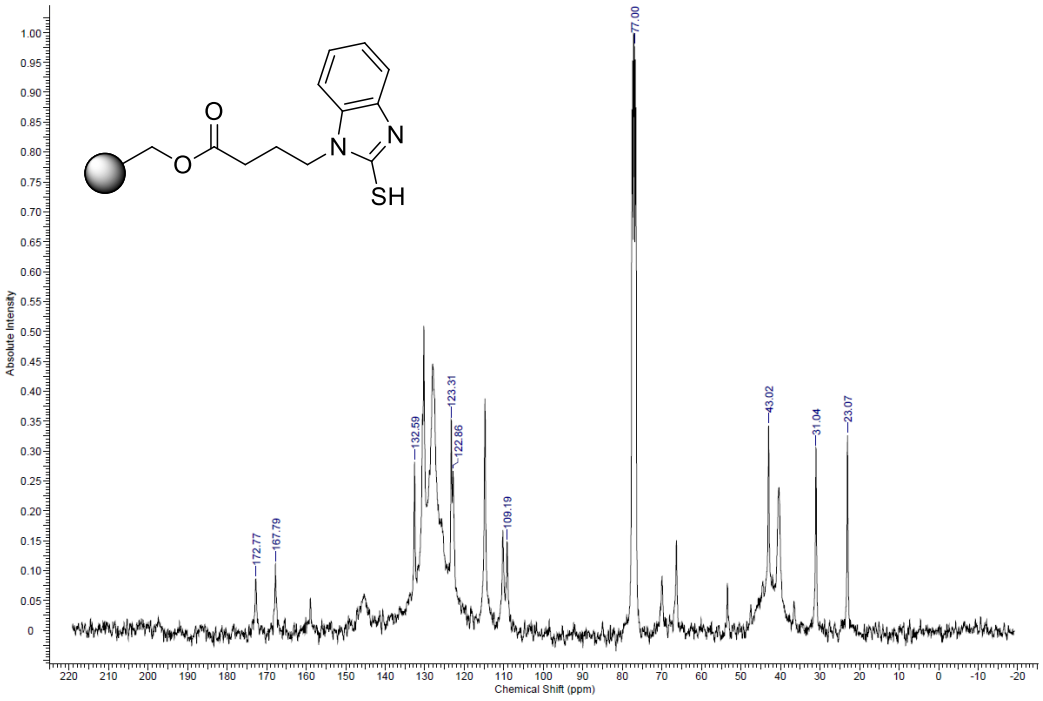
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

Polystyrene-2-(2-mercapto-1H-benzo[d]imidazol-1-yl)acetate **(9a)**



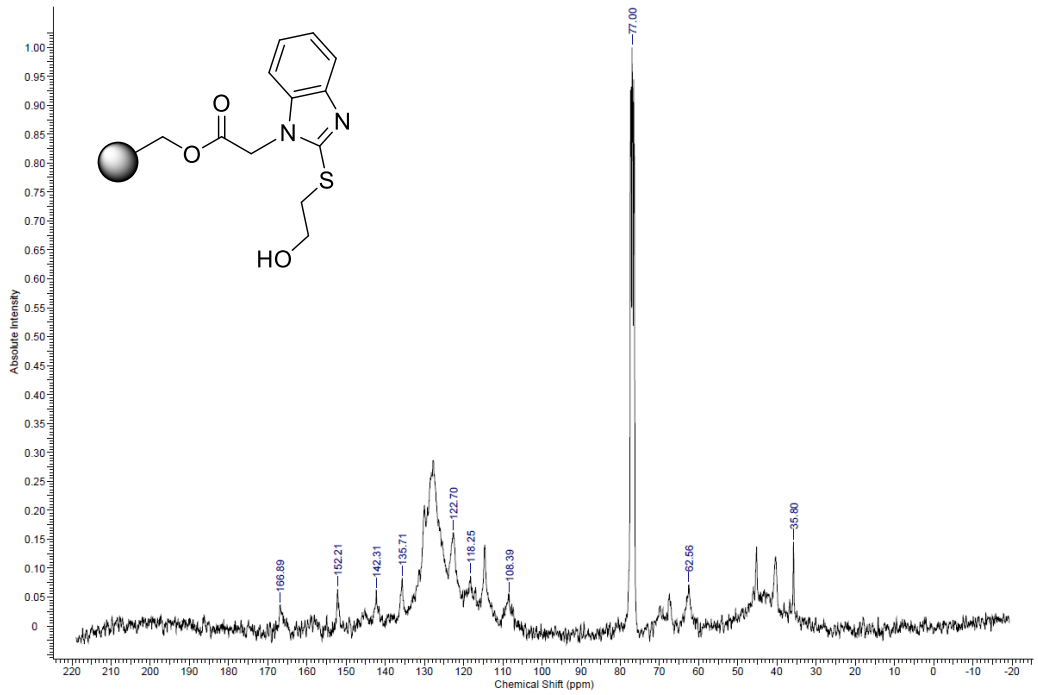
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

Polystyrene- 4-(2-mercapto-1H-benzo[d]imidazol-1-yl)butanoate **(9b)**



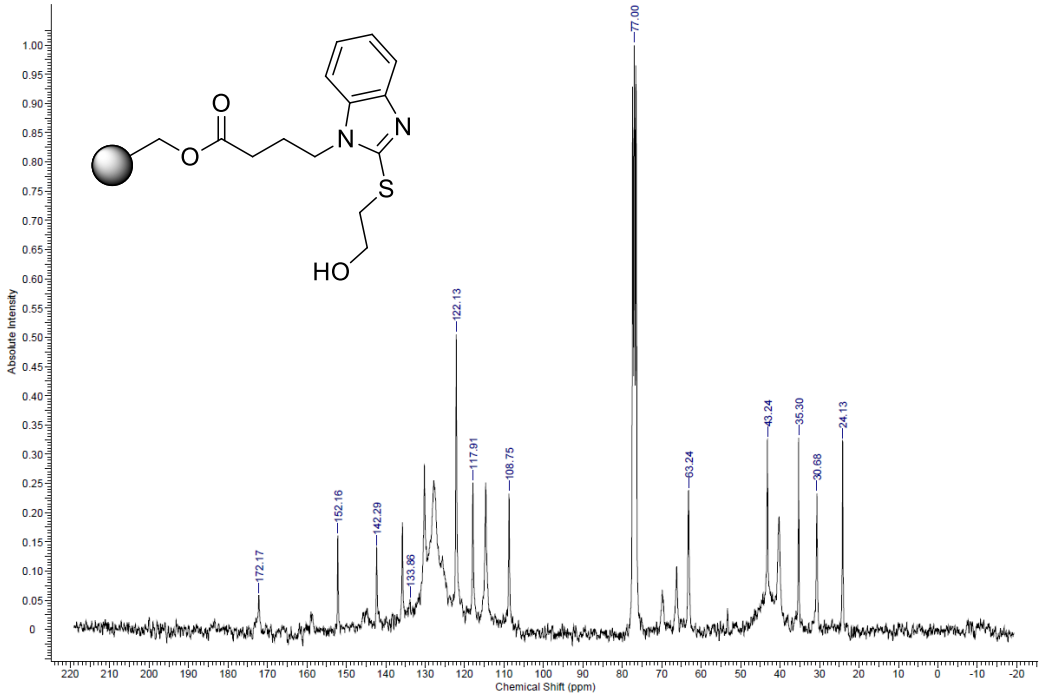
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

Polystyrene-2-(2-((2-hydroxyethyl)thio)-1H-benzo[d]imidazol-1-yl)acetate **(12a)**



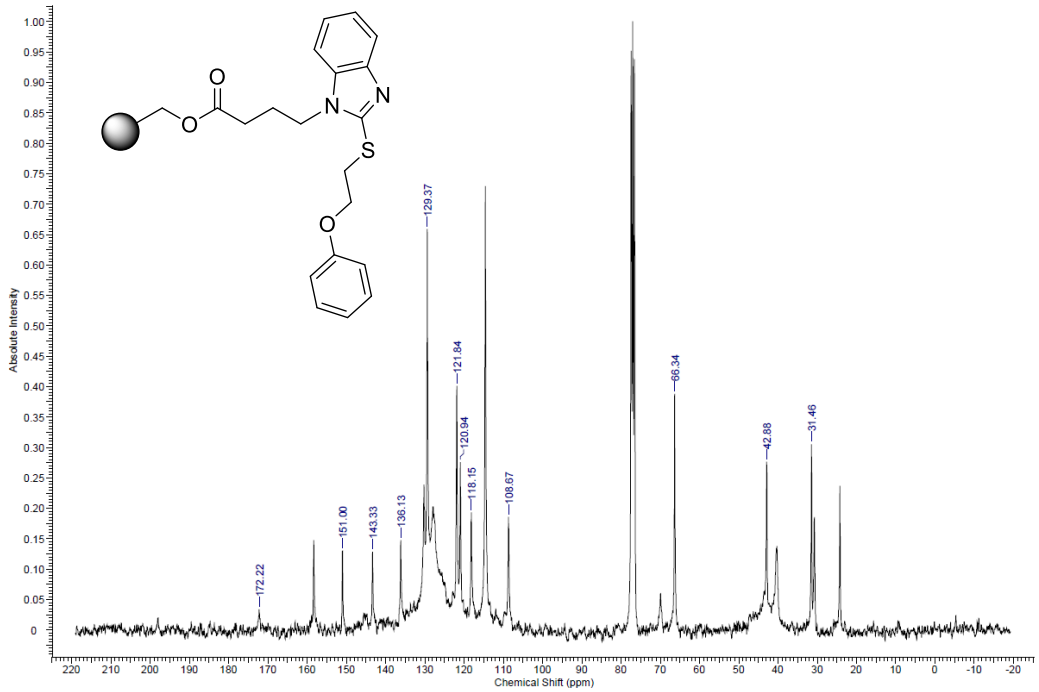
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

Polystyrene- 4-(2-((2-hydroxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate **(12b)**



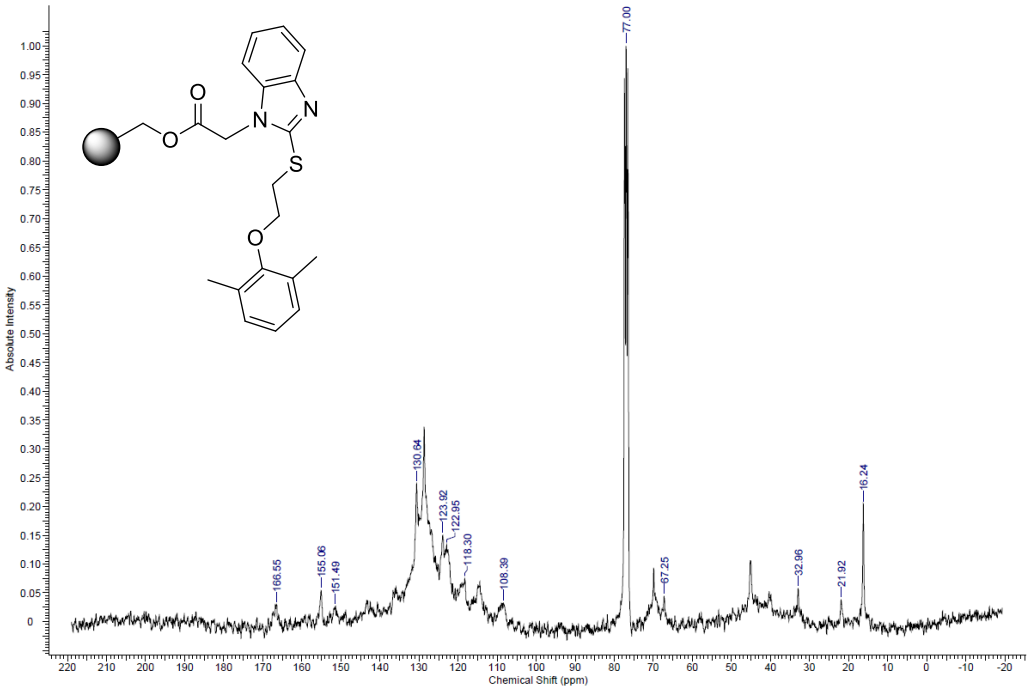
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene-4-(2-((2-phenoxyethyl)thio)-1-benzo[d]imidazol-1-yl)butanoate* (12c)**



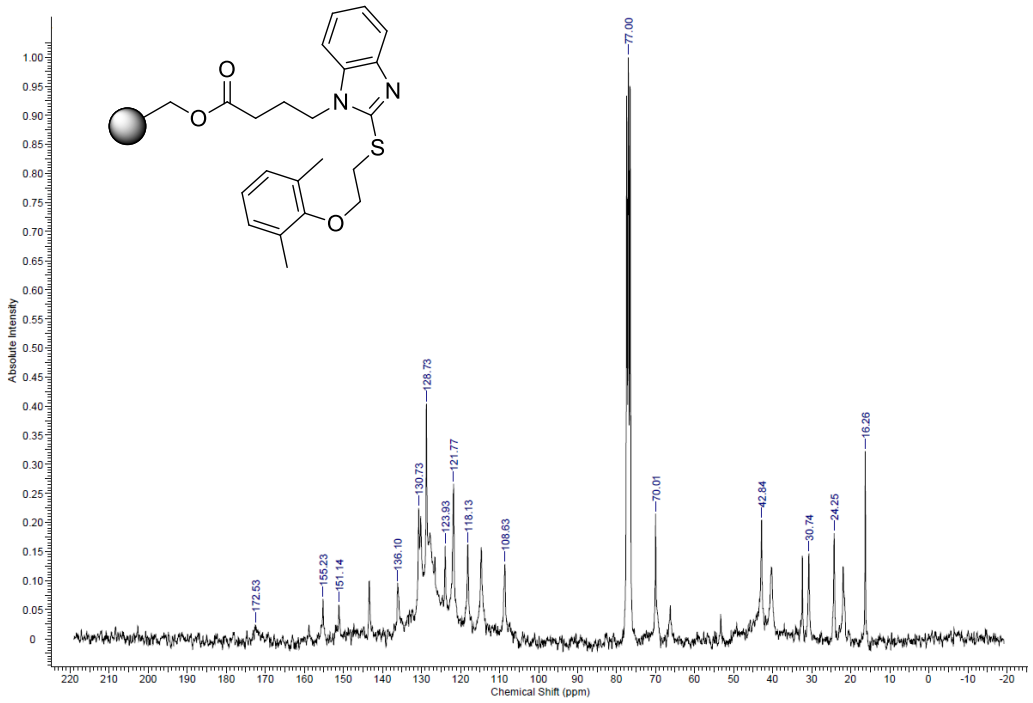
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene-2-(2-((2-(2,6-dimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)acetate* (14a)**



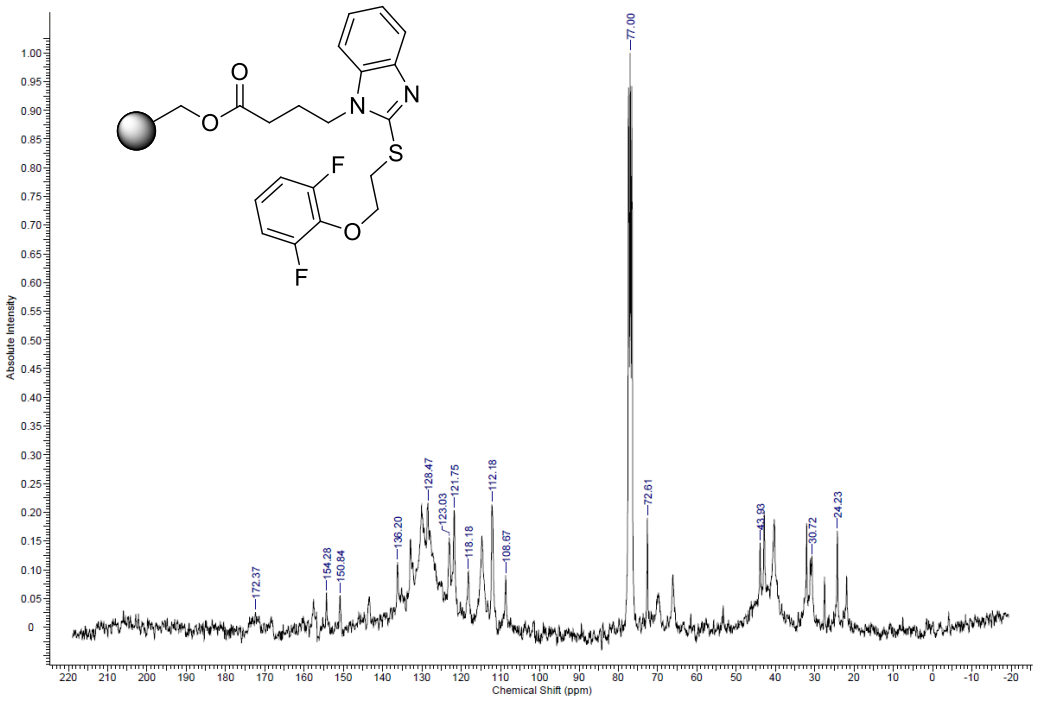
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene-4-(2-((2-(2,6-dimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (14b)**



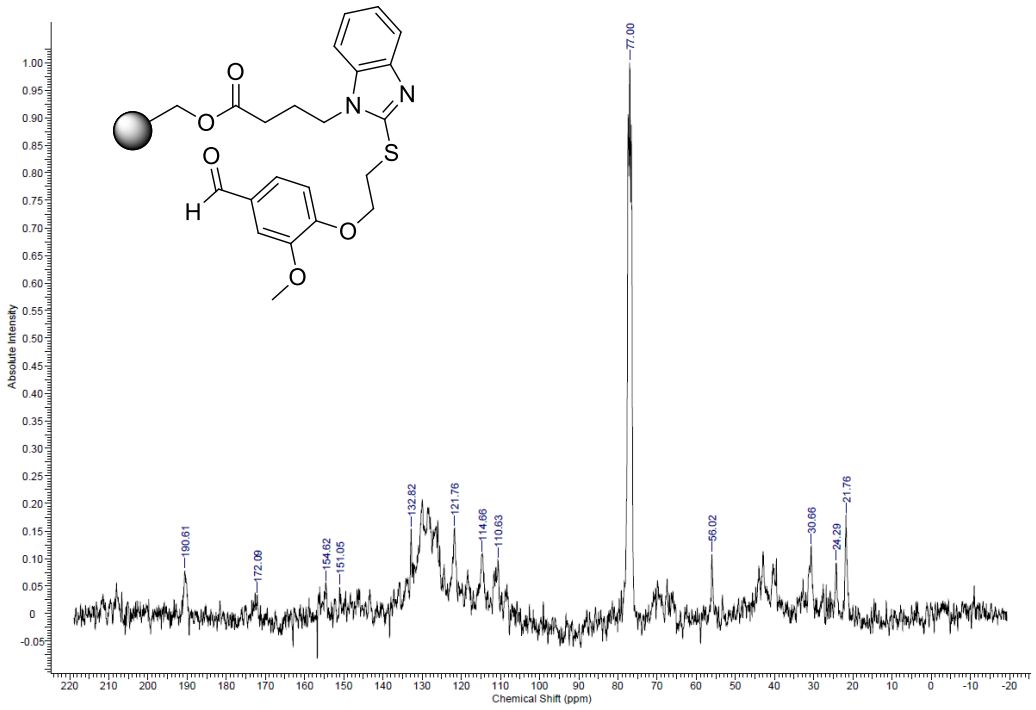
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene-4-(2-((2-(2,6-difluorophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (14c)**



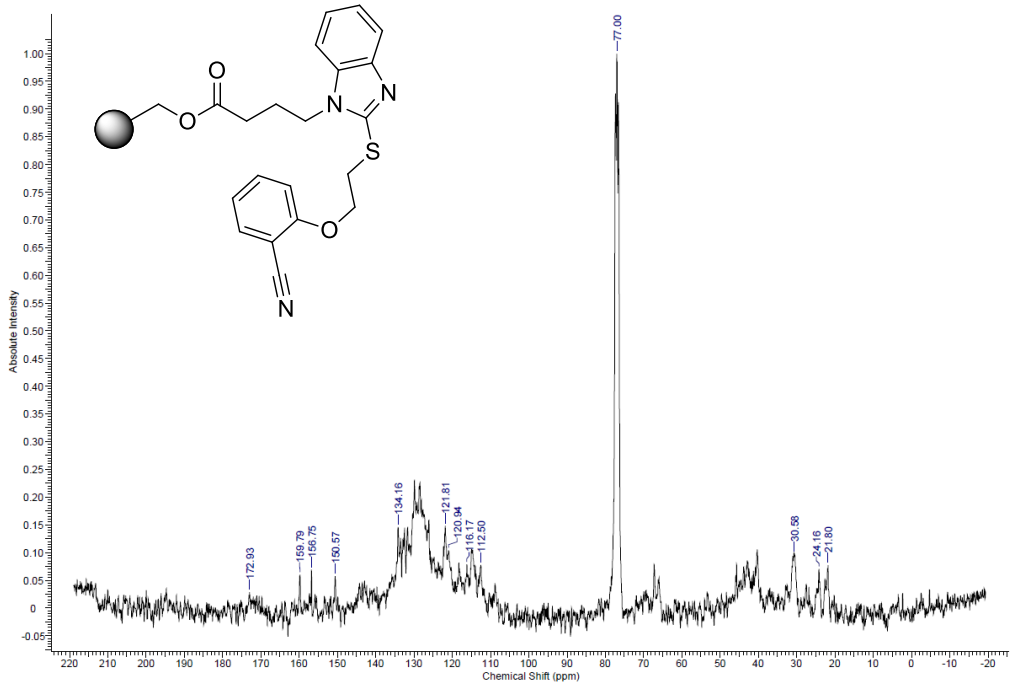
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Ethyl-4-(2-((2-(4-formyl-2-methoxyphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (15f)**



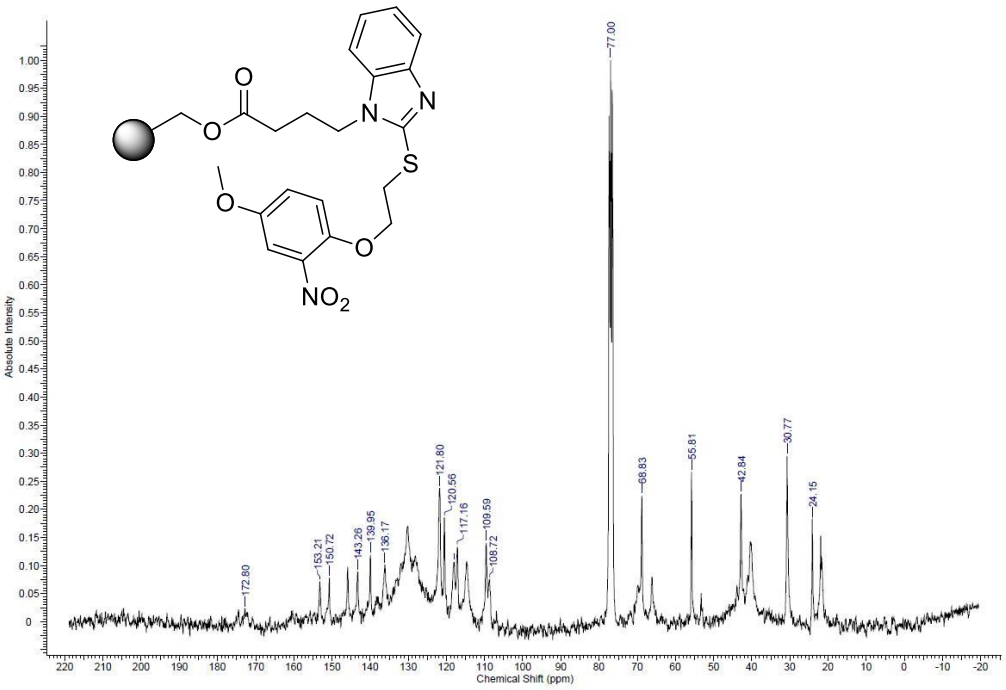
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene-4-(2-((2-(2-cyanophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (14e)**



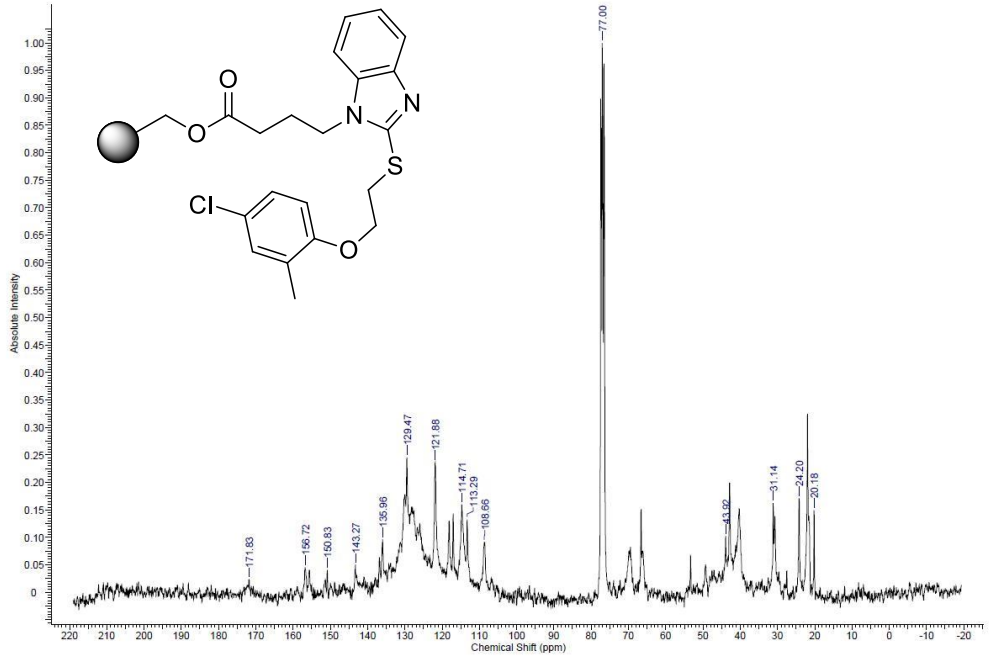
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene-4-(2-((2-(4-methoxy-2-nitrophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (14f)**



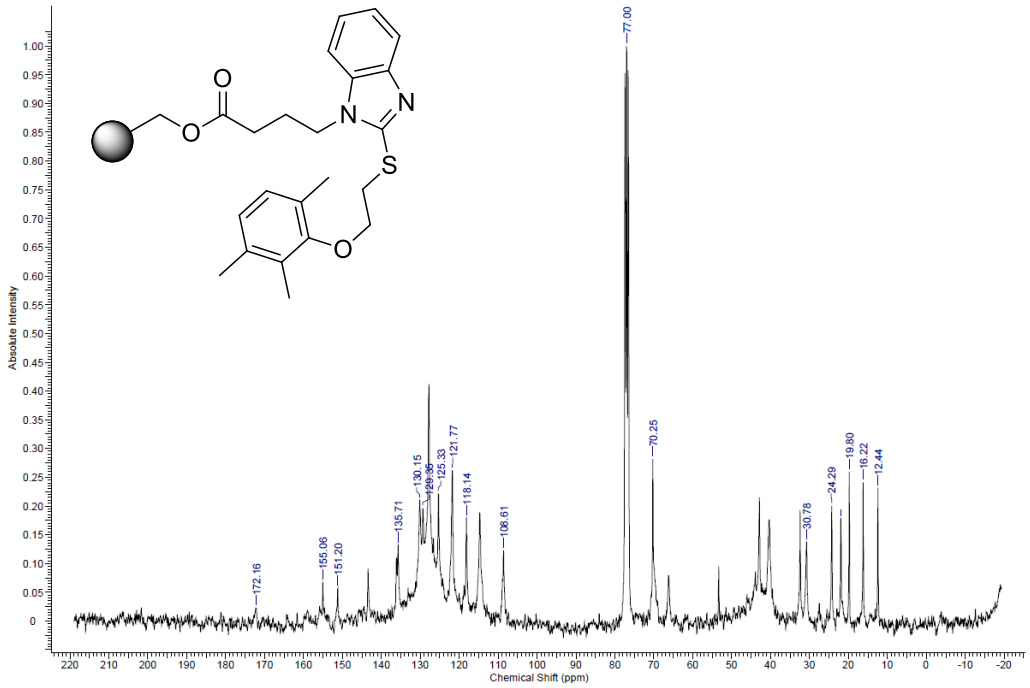
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene-4-(2-((2-(4-chloro-3-methylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (14g)**



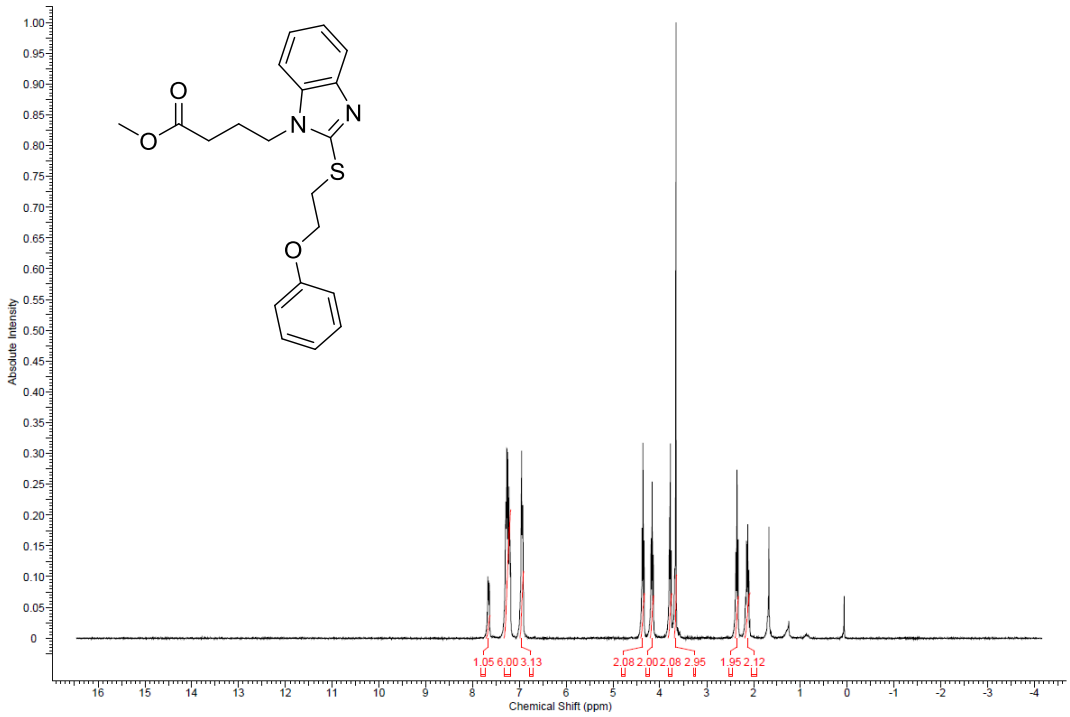
^{13}C Gel-NMR, 75 MHz, $CDCl_3$

***Polystyrene-4-(2-((2-(2,3,6-trimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (14h)**

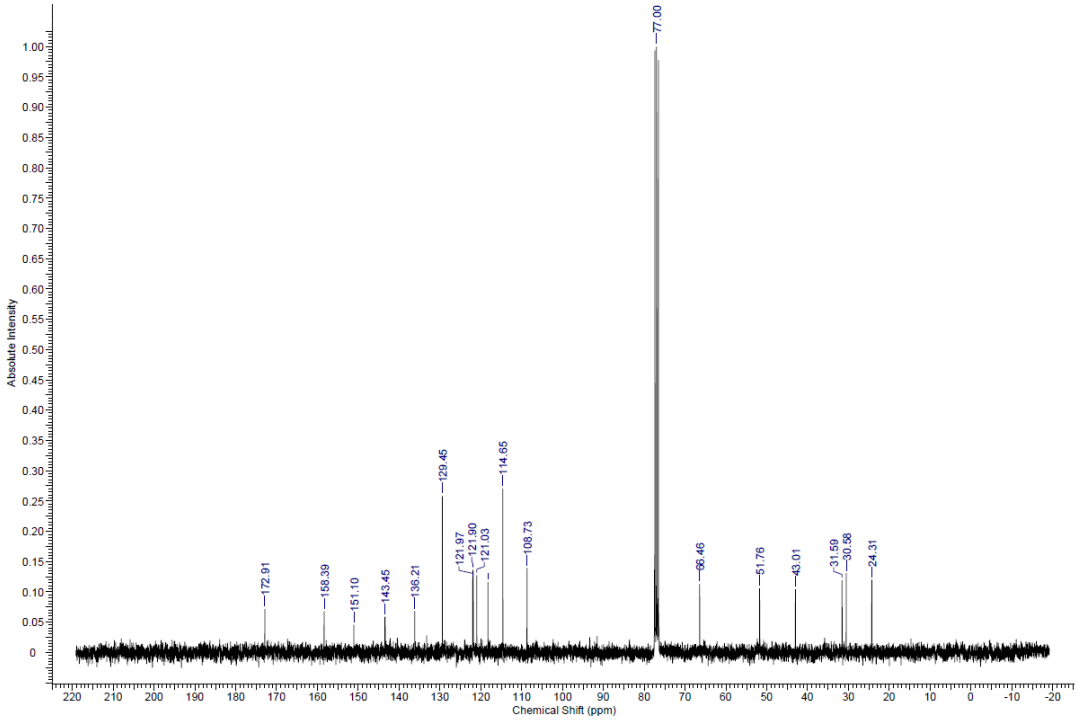


^{13}C Gel-NMR, 75 MHz, $CDCl_3$

Methyl 4-(2-((2-phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate (15a)

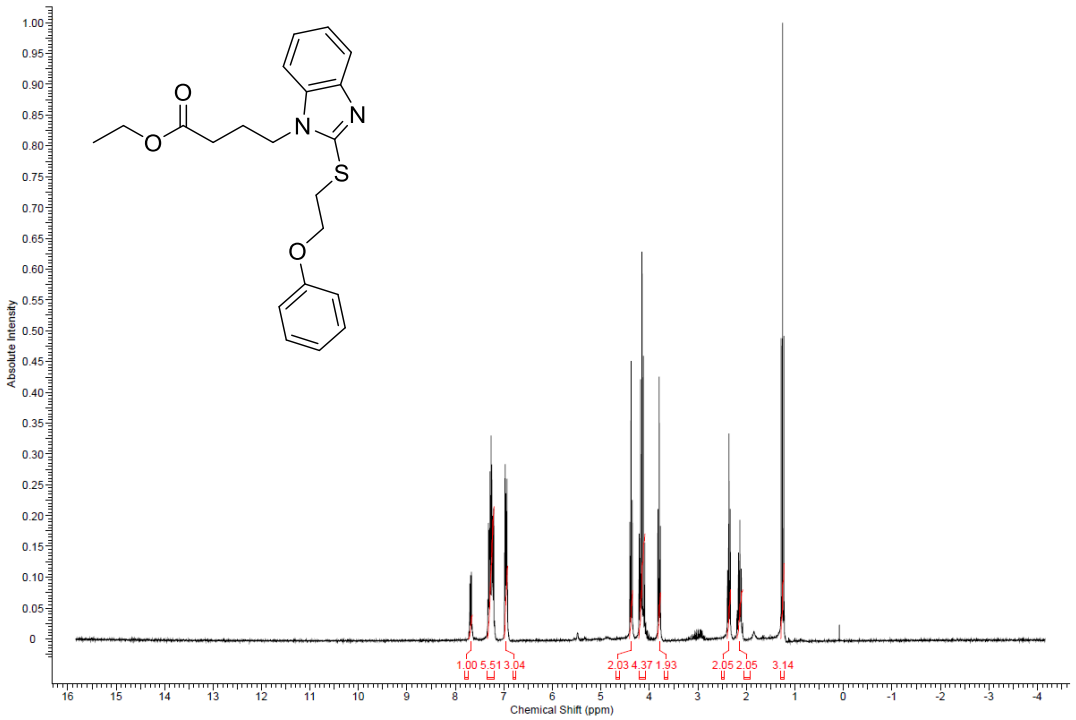


^{1}H NMR, 300 MHz, $CDCl_3$

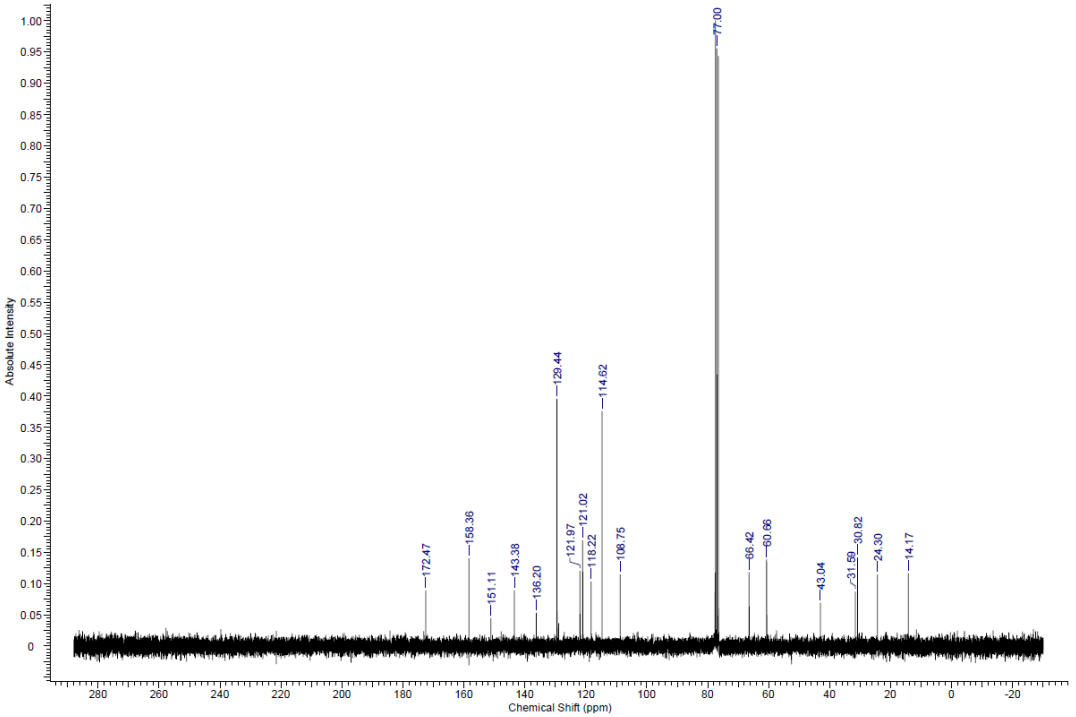


^{13}C NMR, 75 MHz, $CDCl_3$

Ethyl 4-(2-((2-phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate (15b)

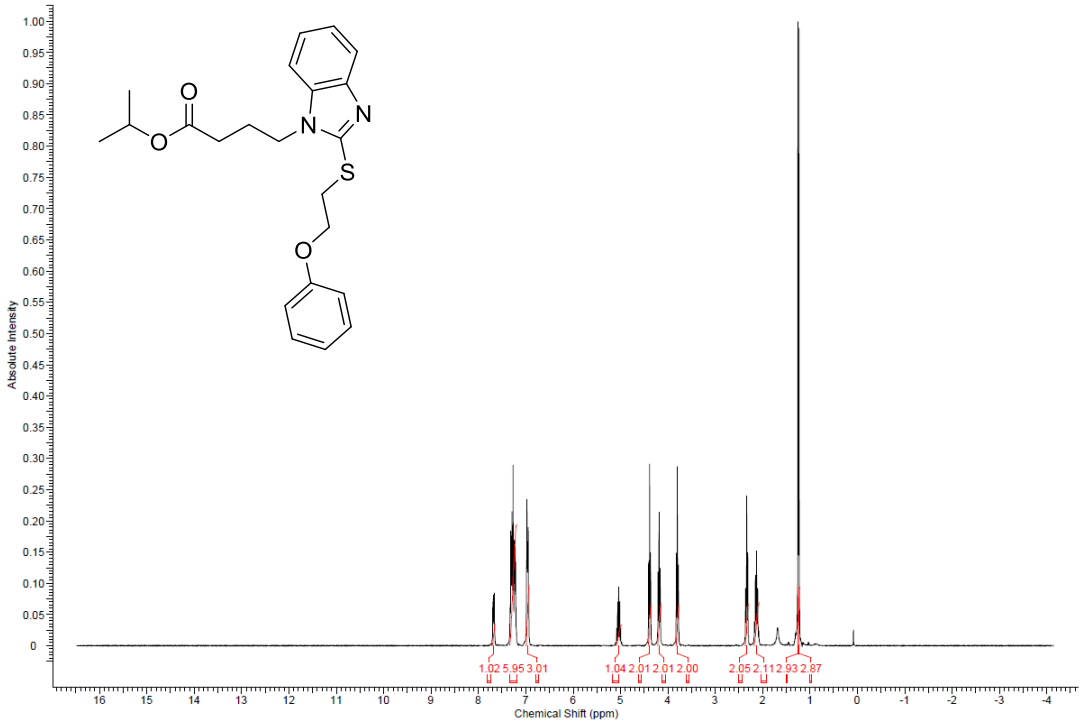


^{1}H NMR, 300 MHz, $CDCl_3$

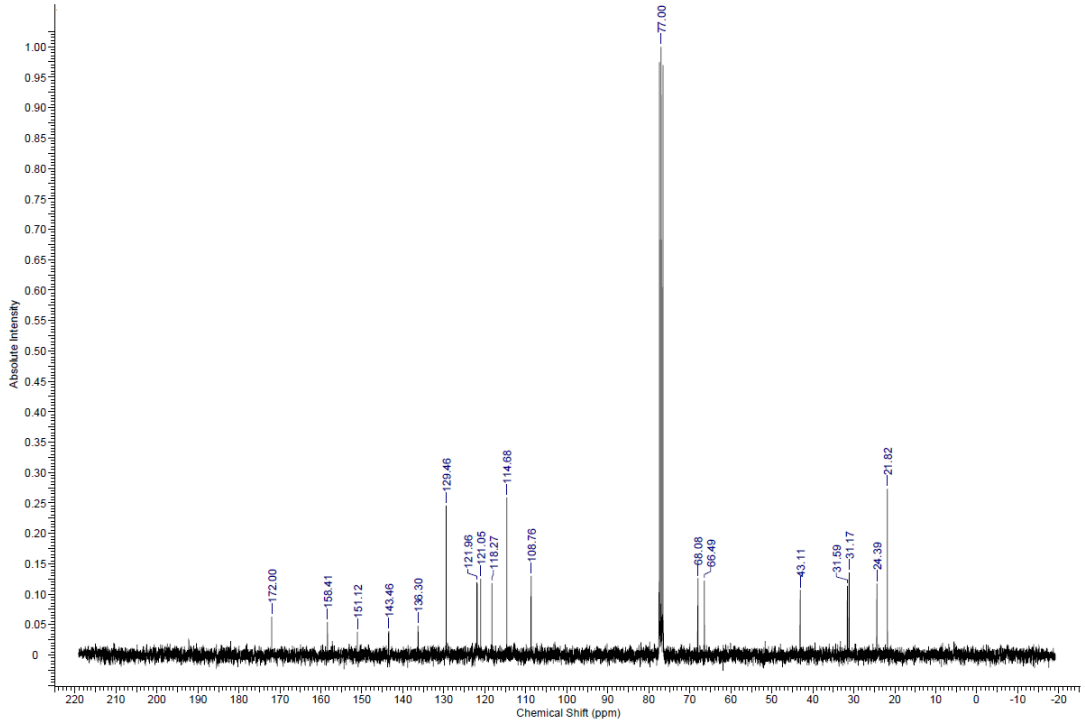


^{13}C NMR, 75 MHz, $CDCl_3$

Isopropyl 4-(2-((2-phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate (15c)

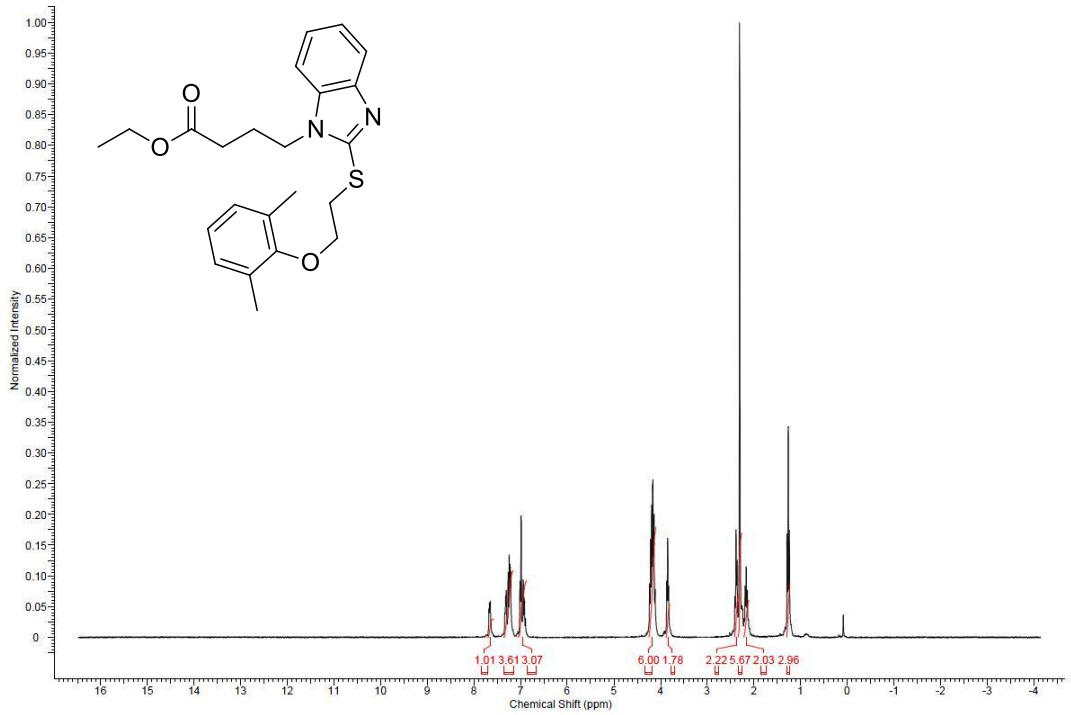


^{1}H NMR, 300 MHz, $CDCl_3$

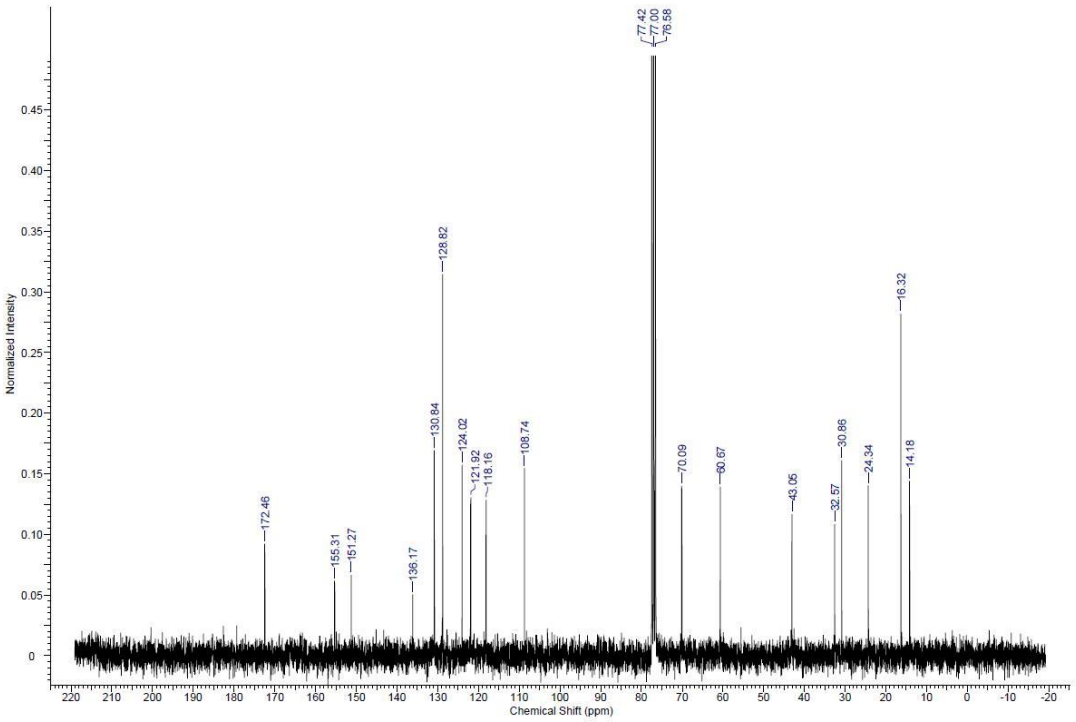


^{13}C NMR, 75 MHz, $CDCl_3$

Ethyl-4-(2-((2-(2,6-dimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate **(15d)**

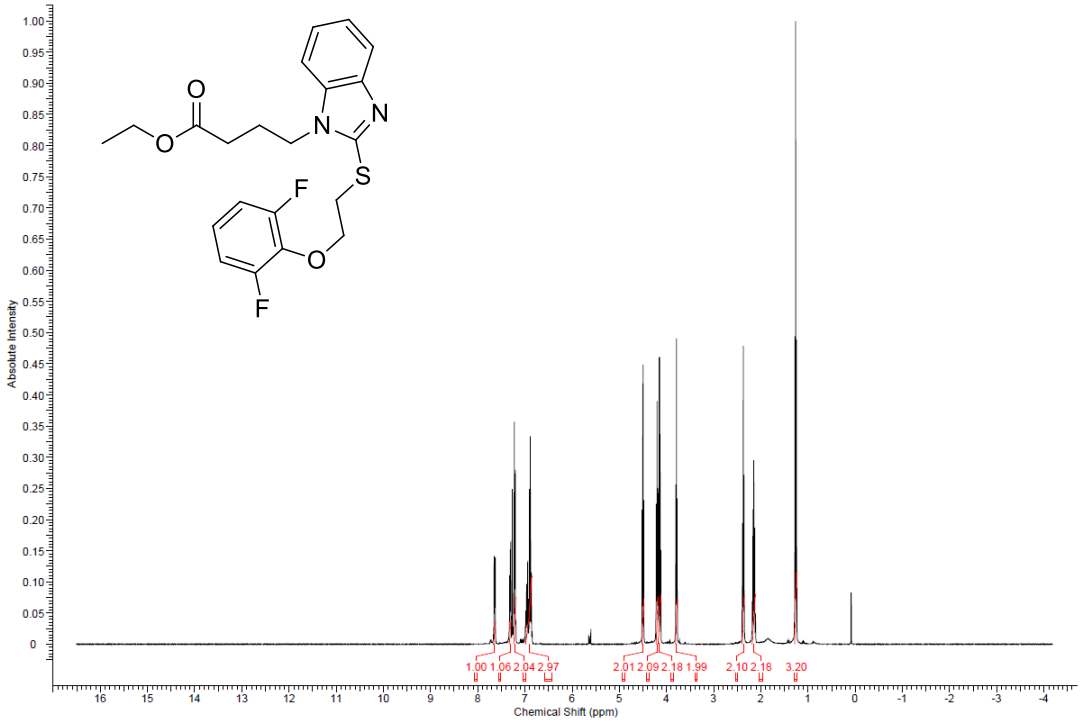


^{1}H NMR, 300 MHz, $CDCl_3$

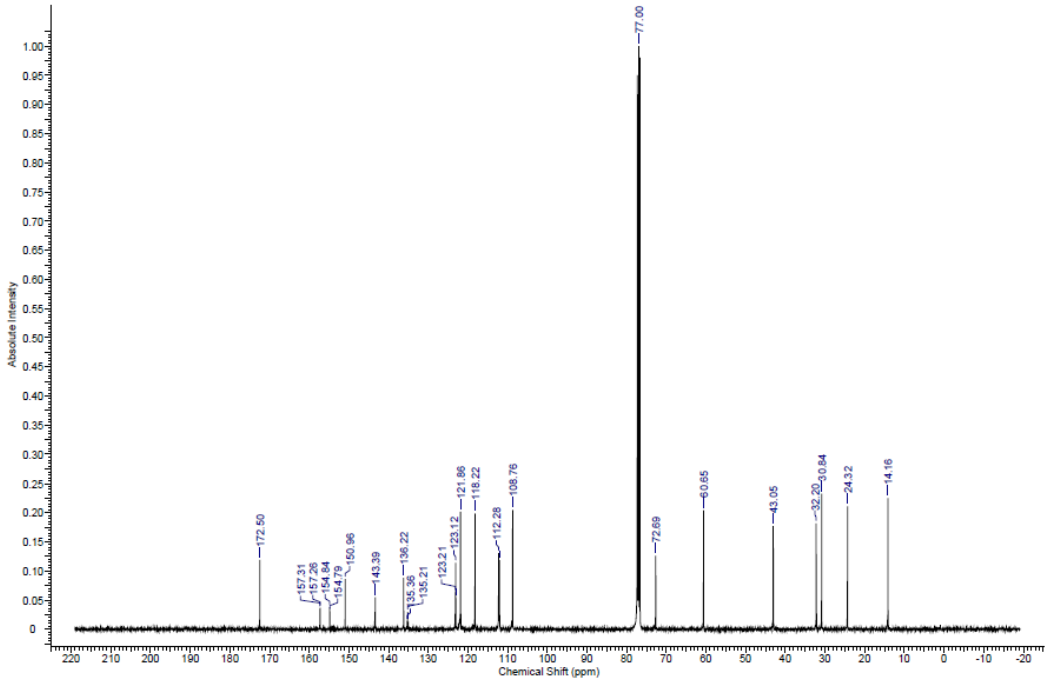


^{13}C NMR, 75 MHz, $CDCl_3$

***Ethyl*-4-(2-((2-(2,6-difluorophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate (15e)**

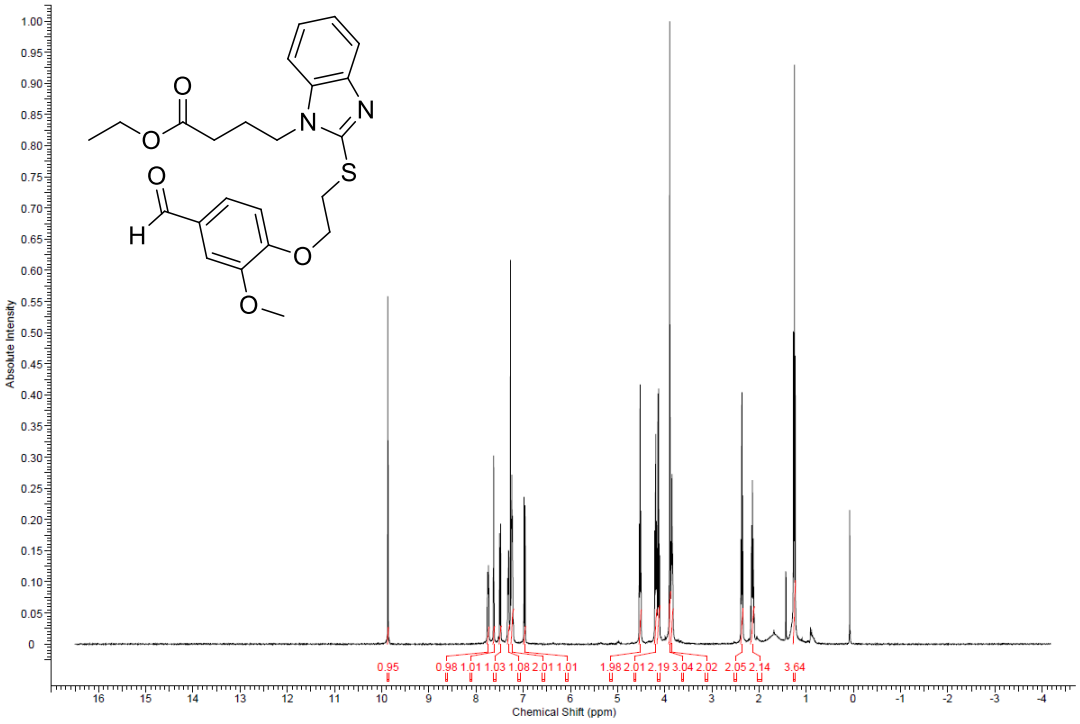


^{1}H NMR, 400 MHz, $CDCl_3$

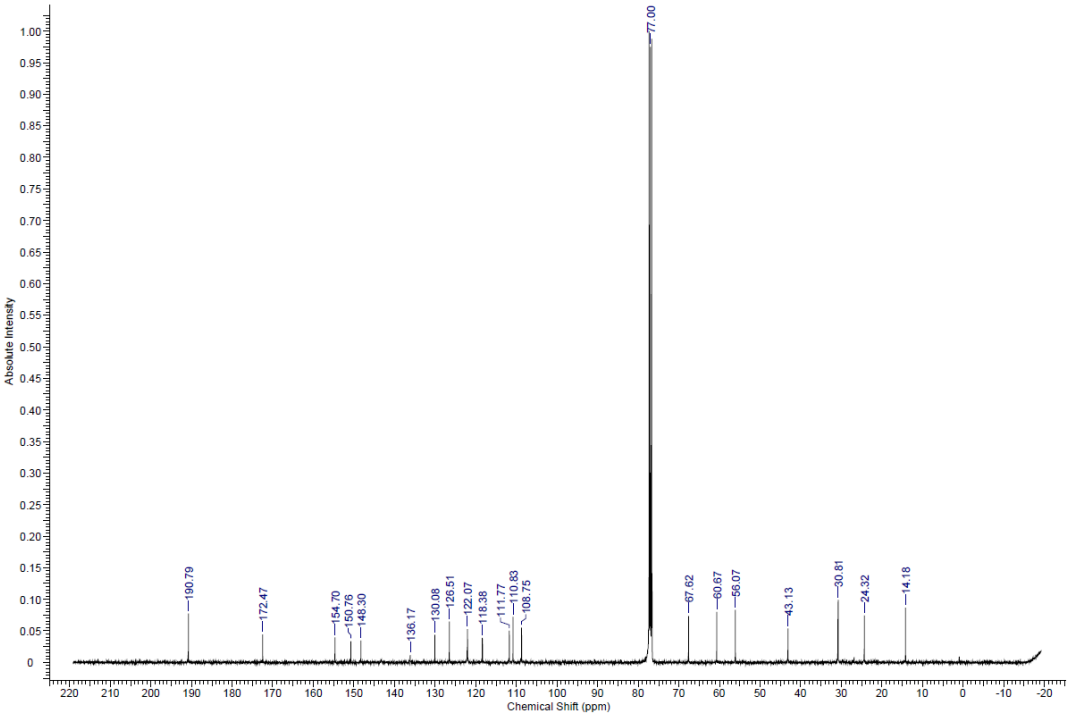


^{13}C NMR, 100 MHz, $CDCl_3$

***Ethyl-4-(2-((2-(4-formyl-2-methoxyphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (15f)**

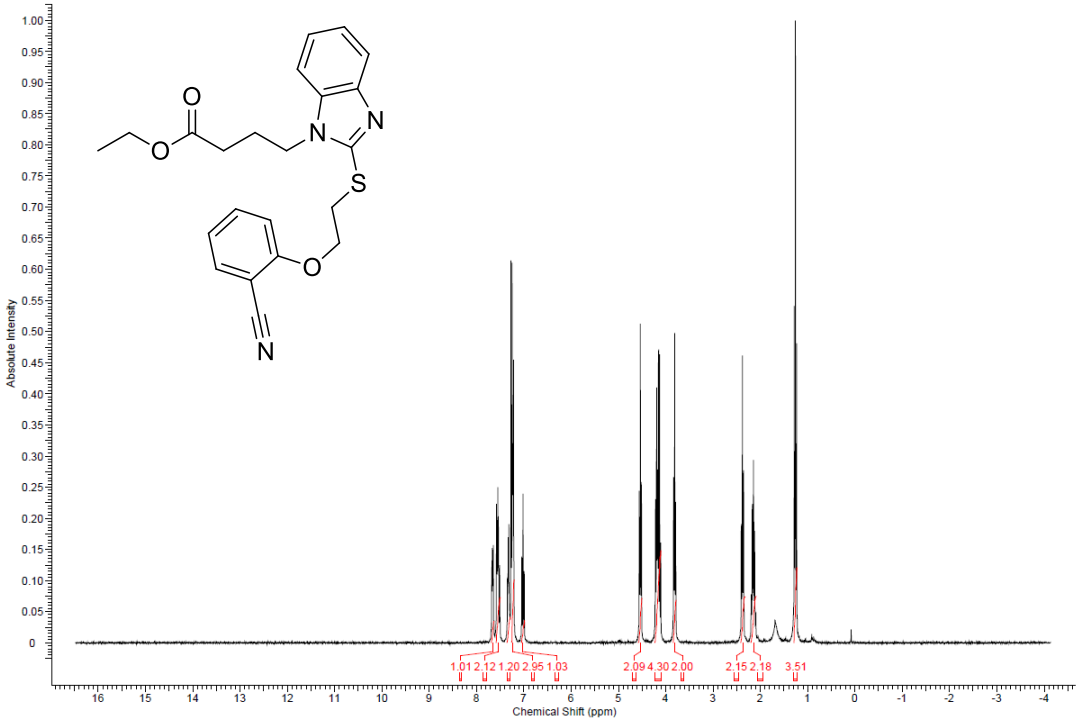


^{1}H NMR, 400 MHz, $CDCl_3$

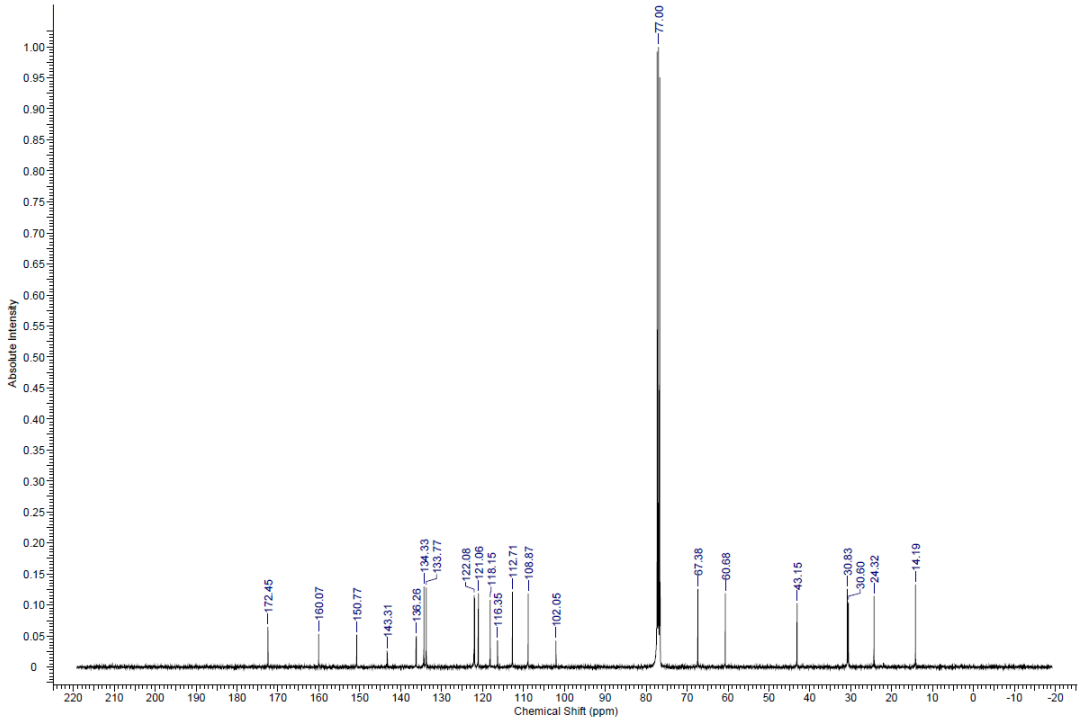


^{13}C NMR, 100 MHz, $CDCl_3$

***Ethyl 4-(2-((2-(2-cyanophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (15g)**

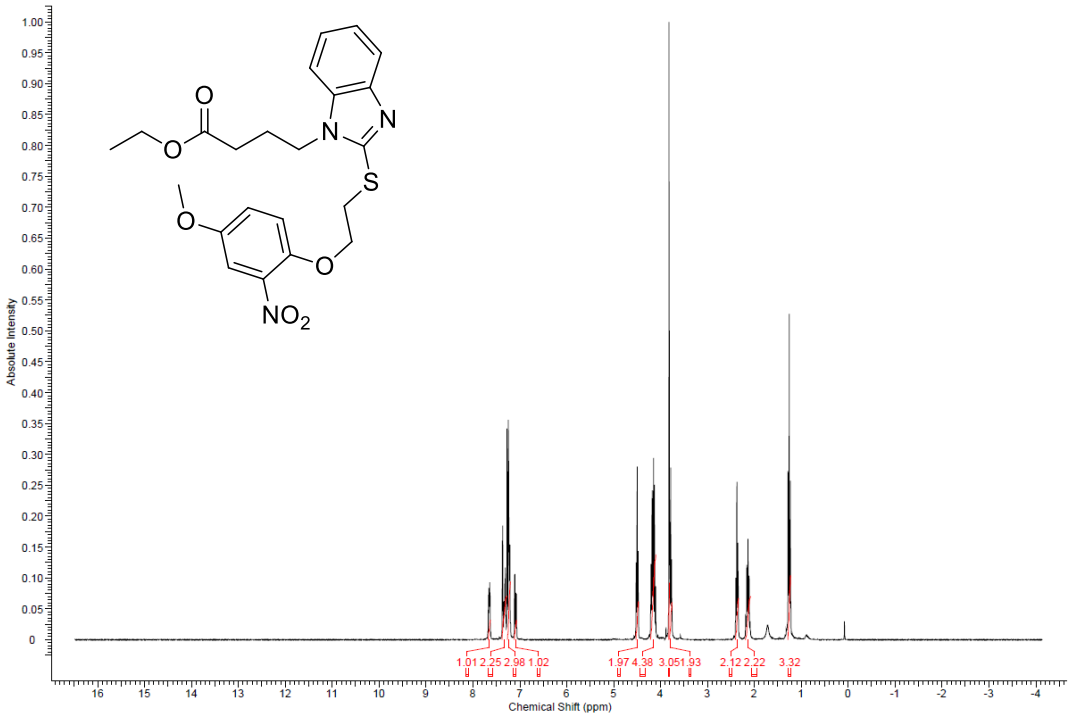


^{1}H NMR, 300 MHz, $CDCl_3$

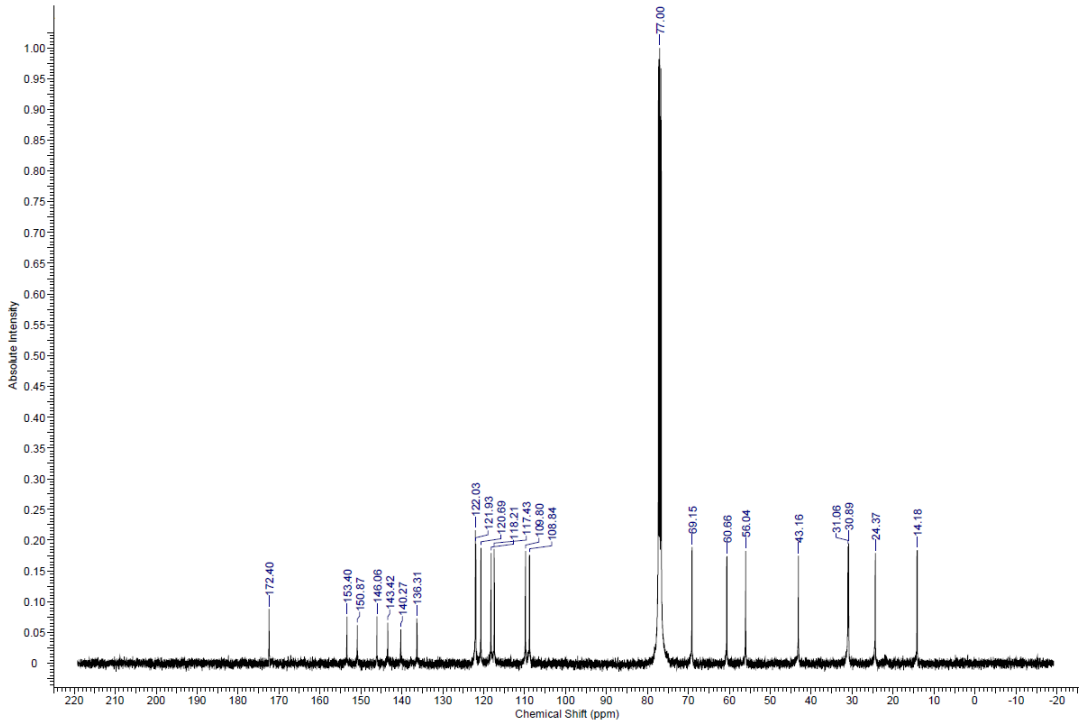


^{13}C NMR, 100 MHz, $CDCl_3$

***Ethyl-4-(2-((2-(4-methoxy-2-nitrophenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (15h)**

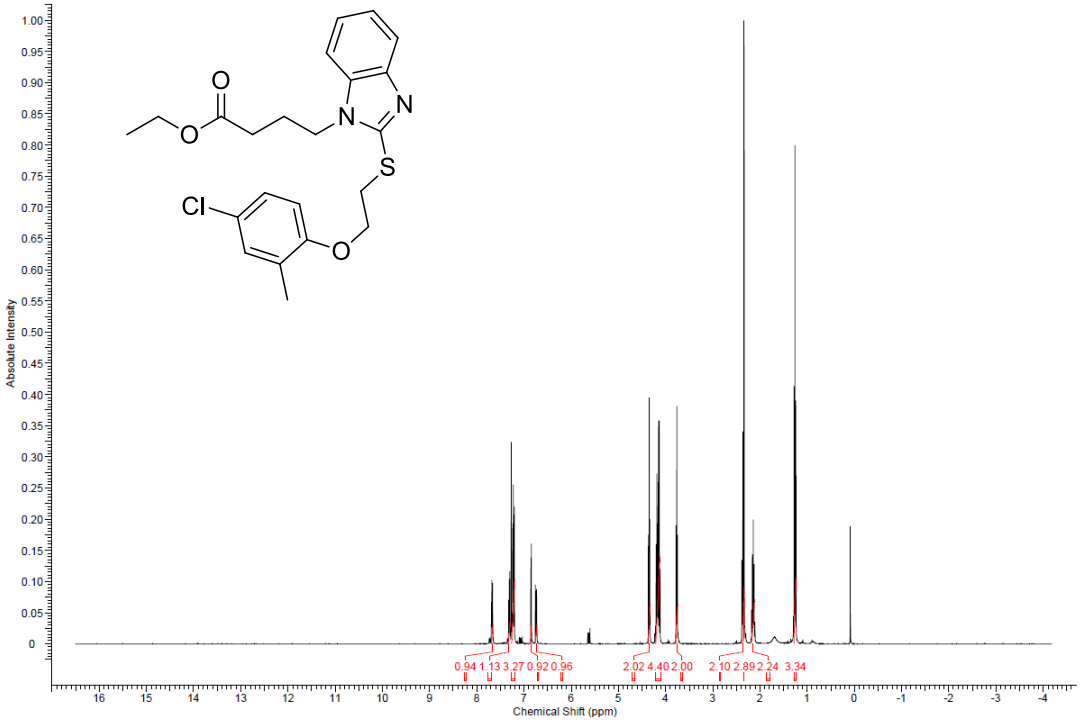


^{1}H NMR, 300 MHz, $CDCl_3$

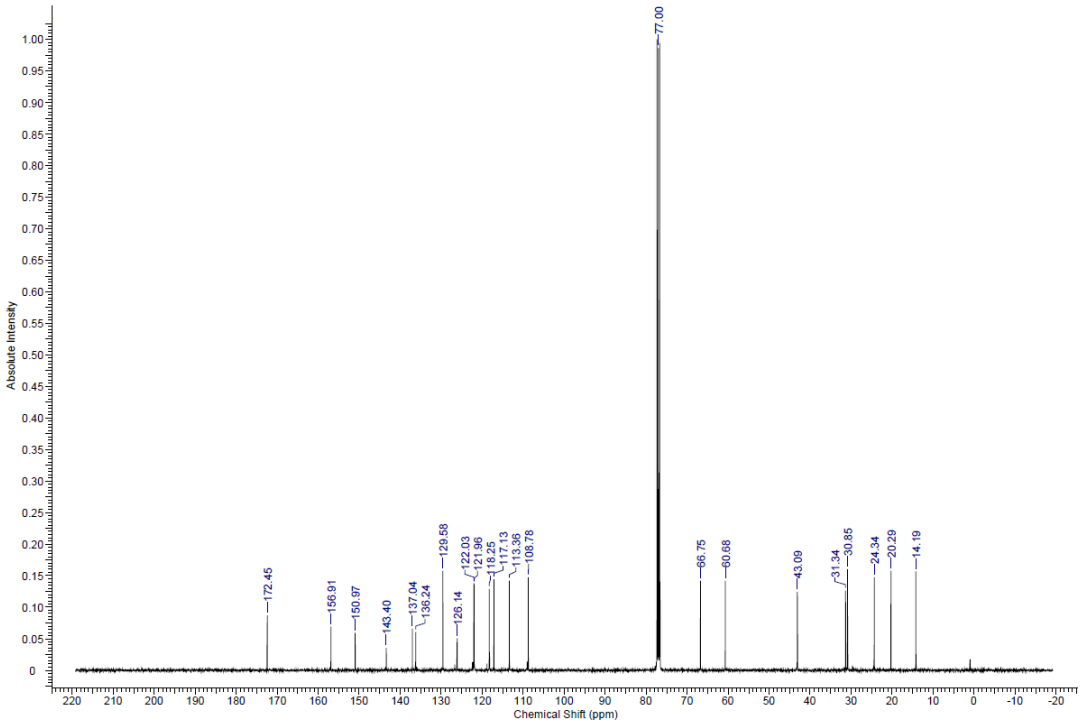


^{13}C NMR, 75 MHz, $CDCl_3$

***Ethyl-4-(2-((2-(4-chloro-2-methylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate* (15i)**



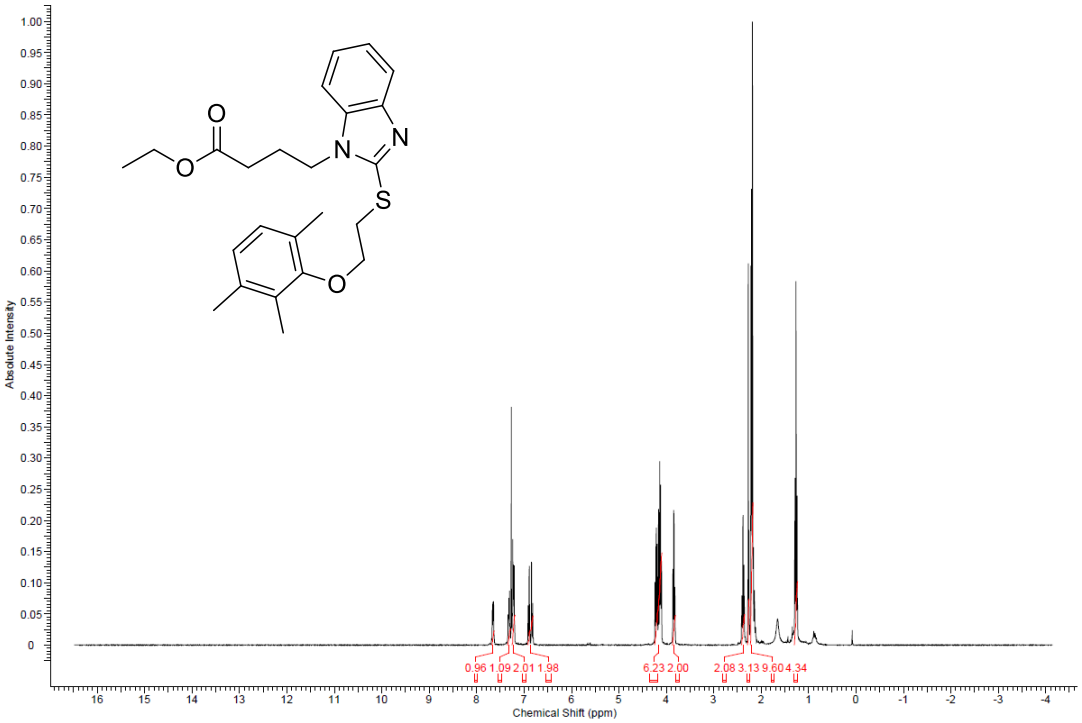
^{1}H NMR, 400 MHz, $CDCl_3$



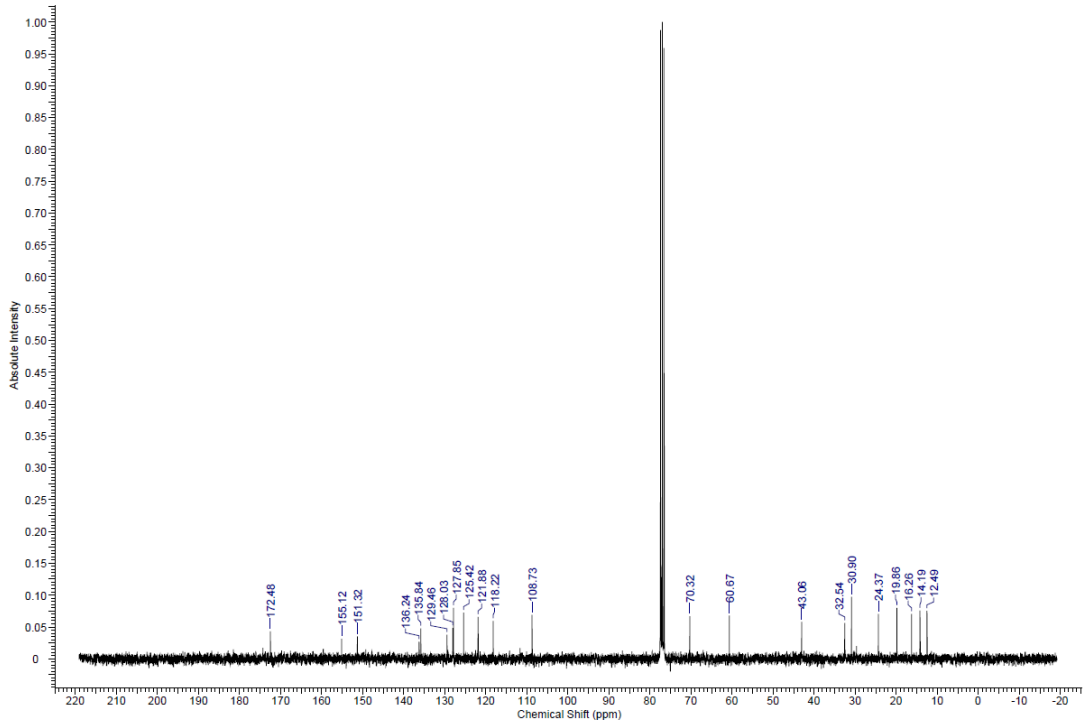
^{13}C NMR, 100 MHz, $CDCl_3$

Ethyl-4-(2-((2-(2,3,6-trimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)butanoate

(15j)

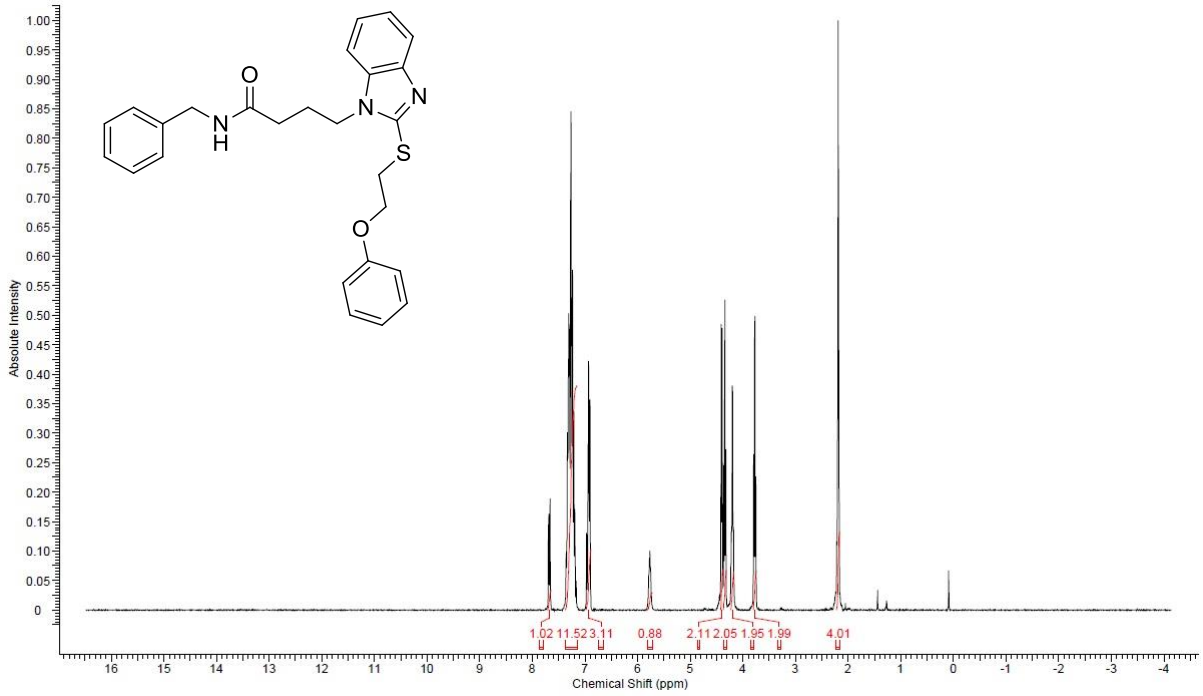


^{1}H NMR, 300 MHz, $CDCl_3$

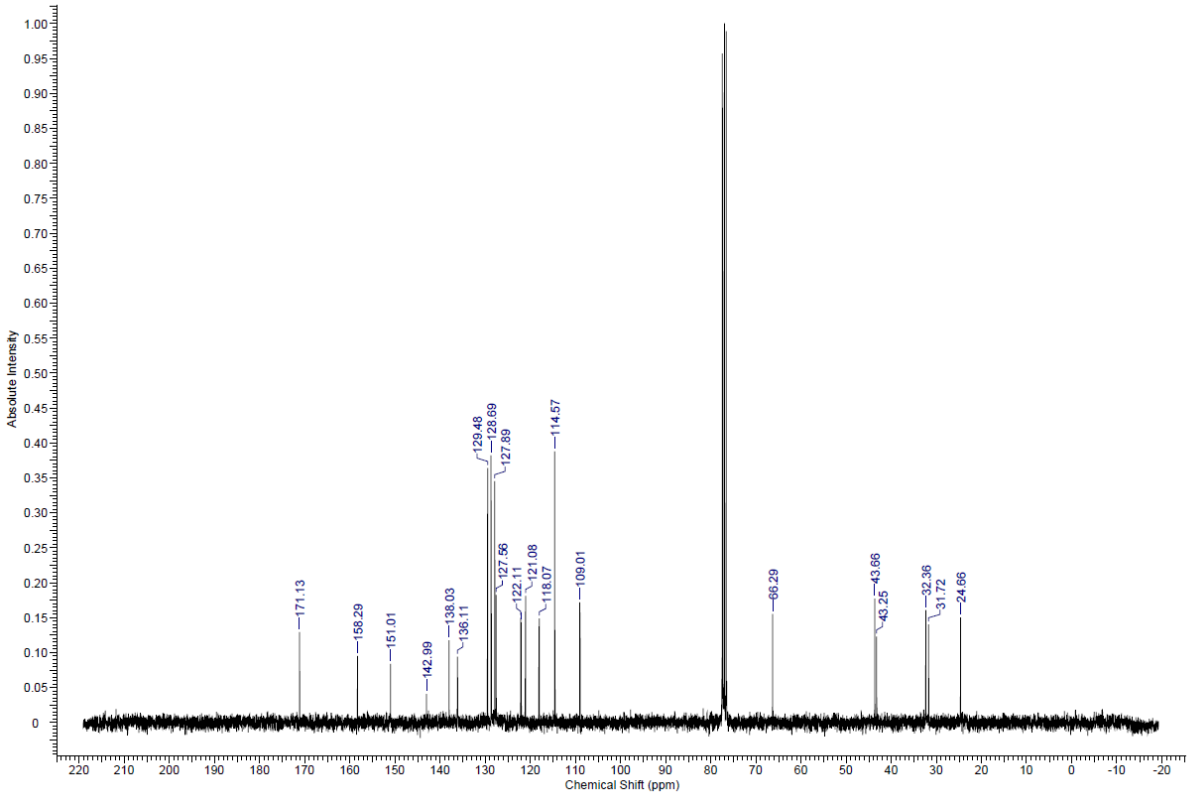


^{13}C NMR, 75 MHz, $CDCl_3$

N-Benzyl-4-(2-((2-phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanamide **(17a)**

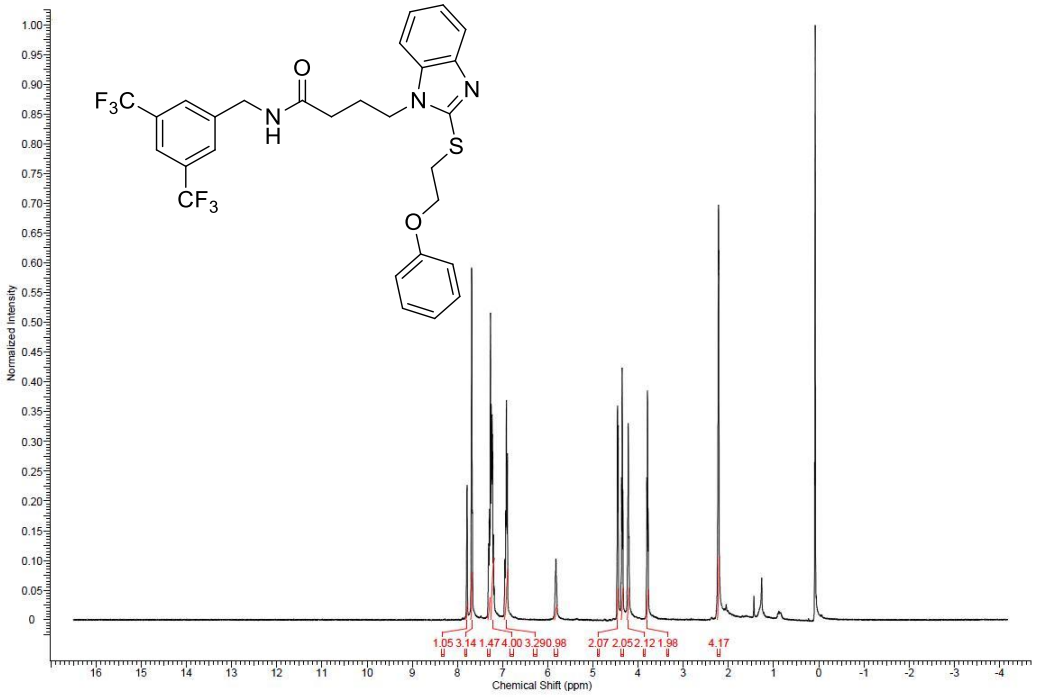


^{1}H NMR, 300 MHz, $CDCl_3$

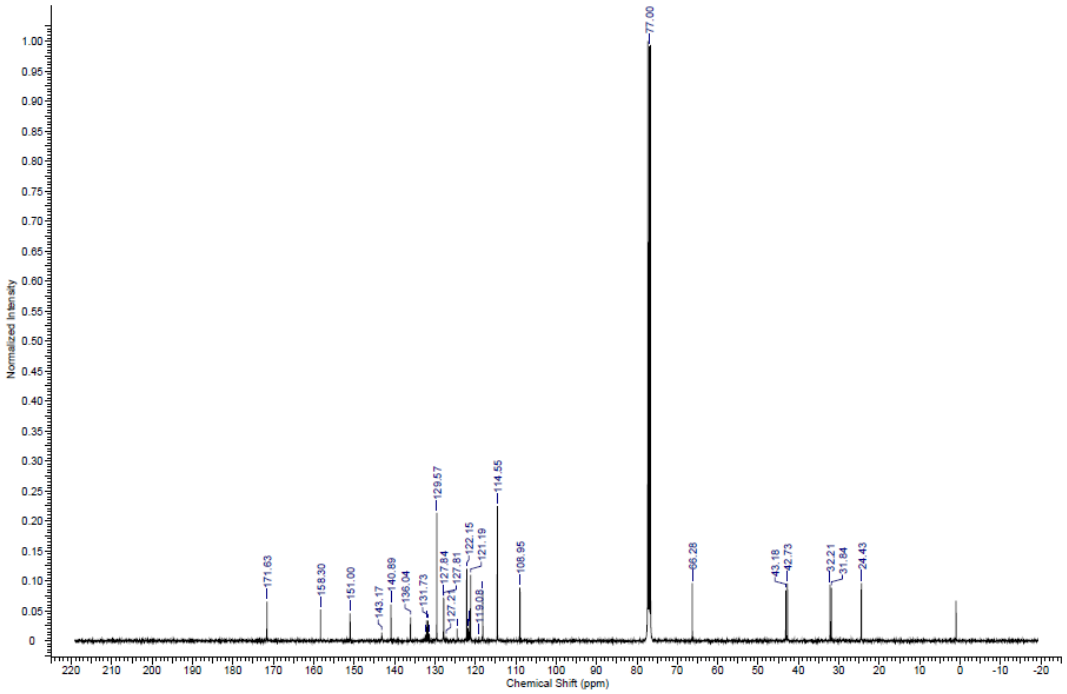


^{13}C NMR, 75 MHz, $CDCl_3$

***N*-(3,5-Bis(trifluoromethyl)benzyl)-4-(2-((2-phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)butanamide** **(17b)**



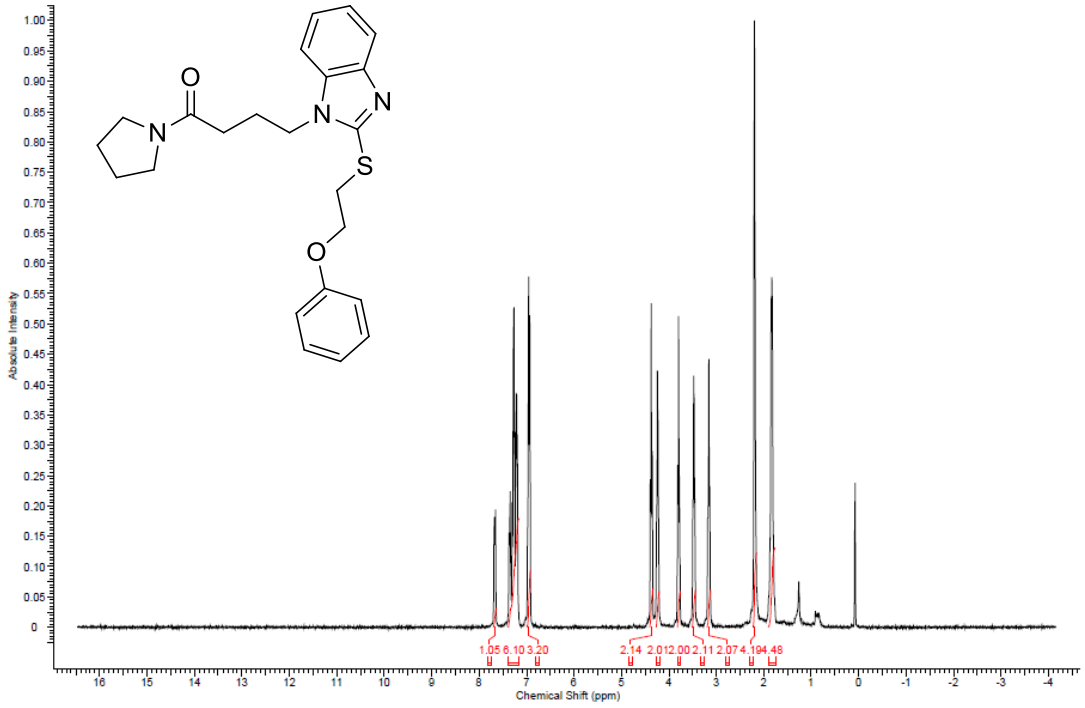
^{1}H NMR, 400 MHz, $CDCl_3$



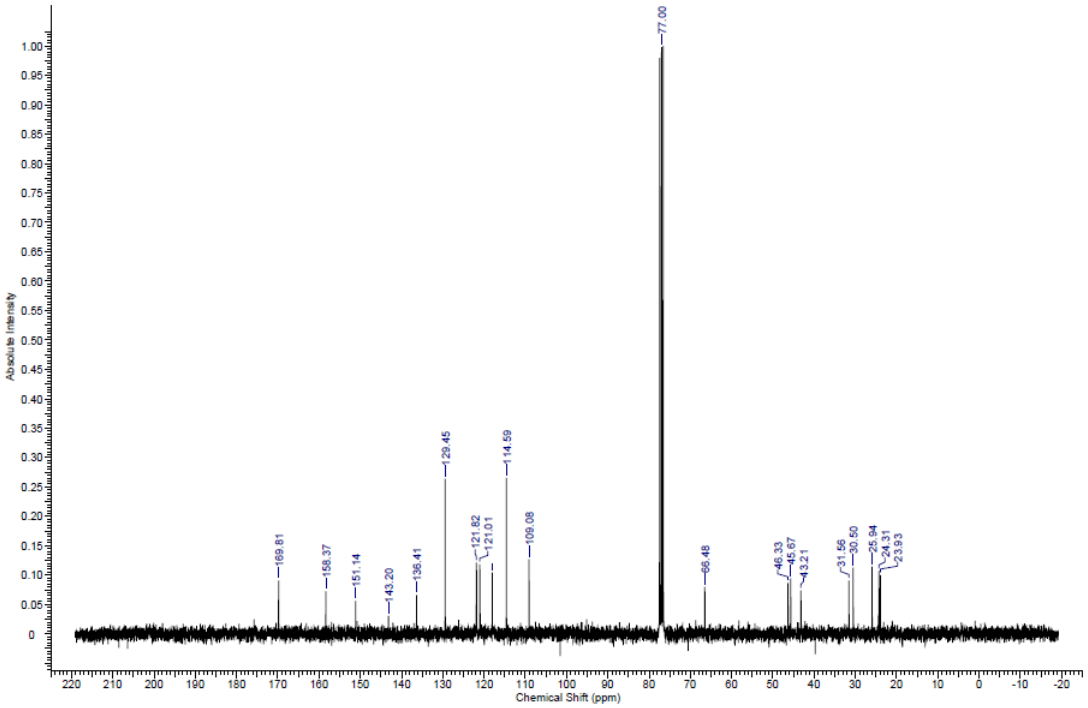
^{13}C NMR, 100 MHz, $CDCl_3$

4-(2-((2-Phenoxyethyl)thio)-1H-benzo[d]imidazol-1-yl)-1-(pyrrolidin-1-yl)butan-1-one

(17c)

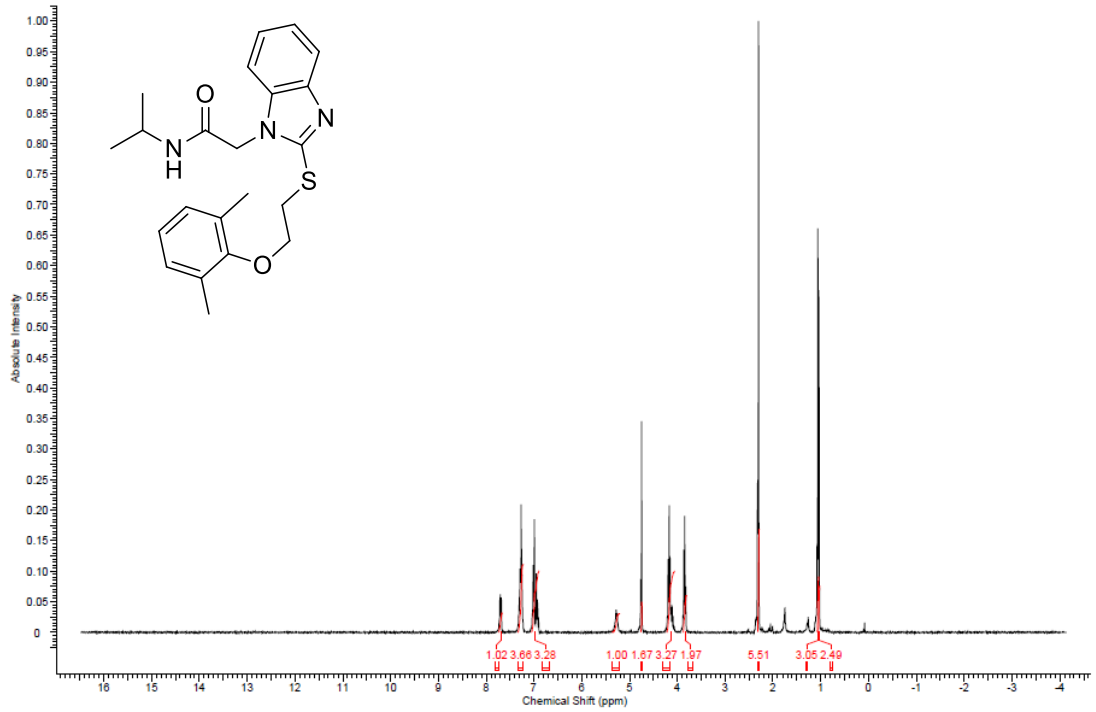


^{1}H NMR, 300 MHz, $CDCl_3$

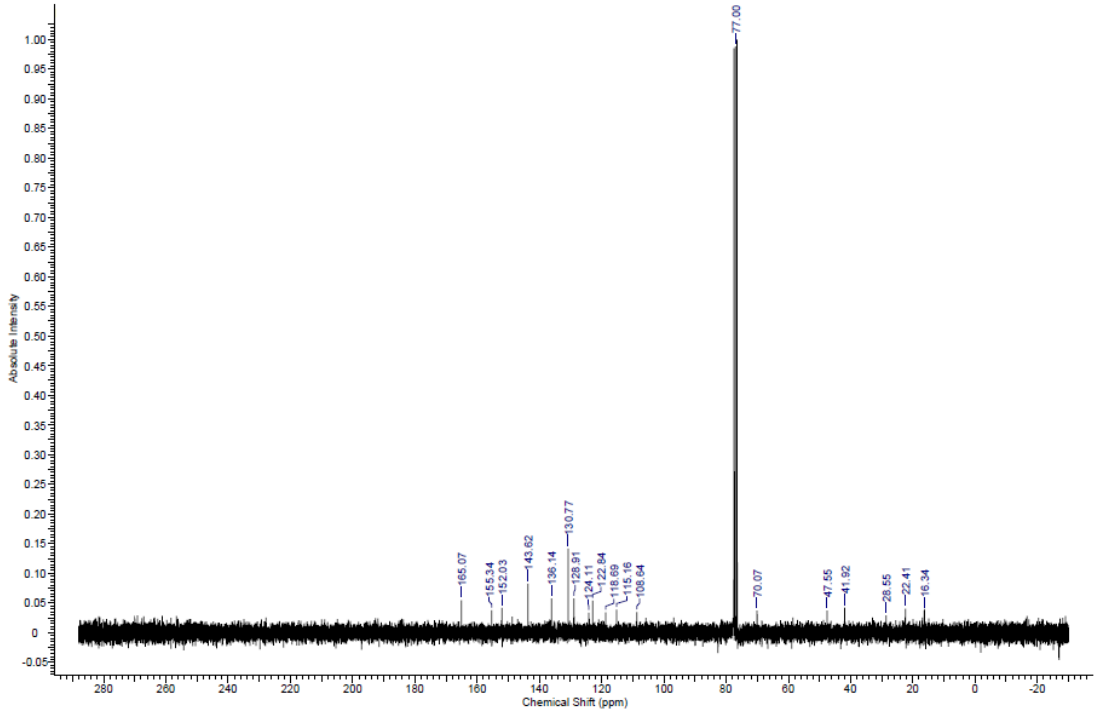


^{13}C NMR, 75 MHz, $CDCl_3$

2-(2-((2-(2,6-Dimethylphenoxy)ethyl)thio)-1H-benzo[d]imidazol-1-yl)-N-isopropylacetamide **(19)**



^{1}H NMR, 300 MHz, $CDCl_3$



^{13}C NMR, 63 MHz, $CDCl_3$