Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Fused azole-thiazolines via one-pot cyclization of functionalized N-heterocyclic carbene precursors

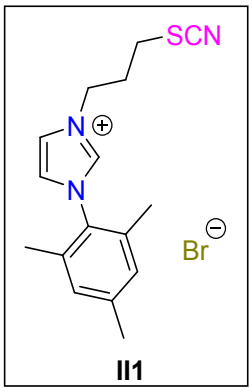
Qiaoqiao Teng,[a,b] Chandan Singh[a] Yuan Han[a] and Han Vinh Huynh[a,*]

[a] Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543 Singapore, Republic of Singapore.

[b]Present address: School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China.

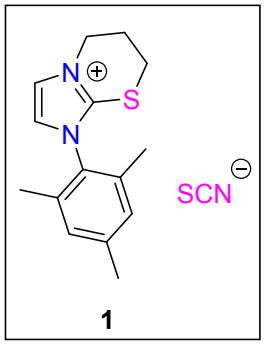
Corresponding author E-mail: chmhhv@nus.edu.sg

Table of Contents



II1

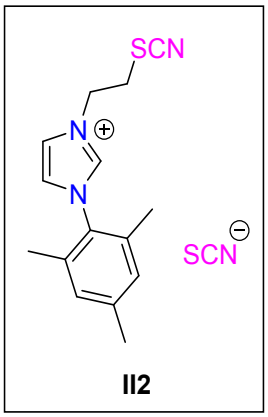
The bromopropyl-imidazolium salt **I1** (388 mg, 1.00 mmol) and KSCN (107 mg, 1.10 mmol) were suspended in CH_3CN (50 mL) and stirred overnight before the solvent was removed under reduced pressure. CH_2Cl_2 (120 mL) was added to dissolve the product and the resulting suspension was filtered and dried to afford the product as a yellowish solid. Yield: 337 mg, 0.92 mmol, 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.98 (s, 1 H, NCHN), 8.24 (s, 1 H, Imi–H), 7.18 (s, 1 H, Imi–H), 6.93 (s, 2 H, Ar–H), 4.85 (t, ^3J(H,H) = 7 Hz, 2 H, NCH_2), 3.20 (t, ^3J(H,H) = 7 Hz, 2 H, SCH_2), 2.54 (m, ^3J(H,H) = 7 Hz, 2 H, CH_2), 2.26 (s, 3 H, CH_3), 1.99 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): 142.1 (NCHN), 138.6, 134.8, 131.2, 130.6, 124.13, 124.07 (Ar–C), 112.8 (SCN), 49.0 (NCH_2), 31.5, 31.4 (CH_2), 21.7, 18.4 (CH_3). HRMS (ESI) m/z calcd. for $C_{16}H_{20}N_3S$ $[M - Br]^+$ 286.1371; found, 286.1372.



1

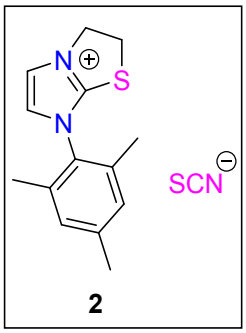
The thiocyanatopropyl-imidazolium salt **II1** (37 mg, 0.10 mmol) and a NaOH aqueous solution (1 M, 10 μL) were mixed in CH_3CN (10 mL) and stirred for 1 h before KSCN (49 mg, 0.50 mmol) was added. The reaction mixture was stirred overnight and the solvent was removed under reduced pressure. CH_2Cl_2 (80 mL) was added and the resulting solution was filtered. Removal of the solvent from the filtrate yielded the product as an off-white solid. Yield: 28 mg, 0.09 mmol, 87%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (s, 1 H, Imi–H), 7.12 (s, 1 H, Imi–H), 6.93 (s, 2 H, Ar–H), 4.59 (br-s, 2 H, NCH_2), 3.45 (br-s, 2 H, SCH_2), 2.50 (br-s, 2 H,

CH_2), 2.25 (s, 3 H, CH_3), 1.95 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): 142.8 (NCN), 142.2, 135.7, 130.4, 129.0, 125.5, 122.0 (Ar–C), 47.3 (NCH_2), 26.4 (SCH_2), 22.4 (CH_2), 21.5, 17.8 (CH_3), SCN^- signal could not be detected. Anal. Calcd. for $C_{16}H_{19}N_3S_2$: C, 60.53; H, 6.03; N, 13.24. Found: C, 60.15; H, 5.79; N, 13.22. HRMS (ESI) m/z calcd. for $C_{15}H_{19}N_2S$ $[M - SCN]^+$ 259.1263; found, 259.1269.



II2

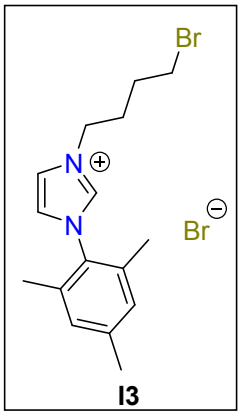
This compound was prepared in analogy to **II1** from **I2** (374 mg, 1.00 mmol) and KSCN (486 mg, 5.00 mmol) as a pinkish solid. Yield: 326 mg, 0.99 mmol, 99%. ^1H NMR (400 MHz, $CDCl_3$ with 5 drops of CD_3CN): δ 9.35 (br-s, 1 H, NCHN), 8.01 (br-s, 1 H, Imi–H), 7.25 (br-s, 1 H, Imi–H), 6.95 (br-s, 2 H, Ar–H), 4.94 (br-s, 2 H, NCH_2), 3.73 (br-s, 2 H, SCH_2), 2.27 (s, 3 H, CH_3), 2.02 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$ with 5 drops of CD_3CN): 141.8 (NCHN), 138.1, 134.7, 130.9, 130.2, 124.5, 124.4 (Ar–C), 111.7 (SCN), 50.0 (NCH_2), 34.4 (SCH_2), 21.4, 17.8 (CH_3), SCN^- signal could not be detected. HRMS (ESI) m/z calcd. for $C_{15}H_{18}N_3S$ $[M - SCN]^+$ 272.1216; found, 272.1224.



2

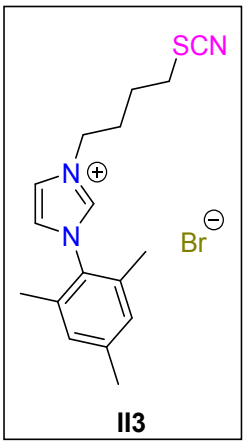
Compound **2** was prepared in analogy to **1** from **II2** (33 mg, 0.10 mmol), NaOH aqueous solution (1M, 10 µL) and KSCN (48 mg, 0.50 mmol) as a white solid. Yield: 28 mg, 0.09 mmol, 92%. ^1H NMR (500 MHz, d_4-Methanol): δ 7.81 (s, 1 H, Imi–H), 7.58 (s, 1 H, Imi–H), 7.13 (s, 2 H, Ar–H), 4.76 (t, ^3J(H,H) = 8 Hz, 2 H,

NCH_2), 4.36 (t, ^3J(H,H) = 8 Hz, 2 H, SCH_2), 2.36 (s, 3 H, CH_3), 2.13 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, d_4-Methanol): 153.8 (NCN), 143.1, 136.1 (Ar–C), 133.6 (SCN^-), 131.8, 131.0, 128.7, 121.9 (Ar–C), 51.1 (NCH_2), 39.1 (SCH_2), 21.2, 17.5 (CH_3). Anal. Calcd. for $C_{15}H_{17}N_3S_2$: C, 59.37; H, 5.65; N, 13.85. Found: C, 59.33; H, 5.57; N, 13.73. HRMS (ESI) m/z calcd. for $C_{14}H_{17}N_2S$ $[M - SCN]^+$ 245.1107; found, 245.1115.



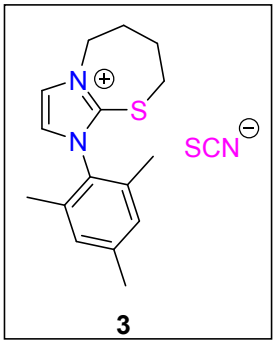
I3

A mixture of *N*-mesityl imidazole (931 mg, 5.00 mmol) and 1,4-dibromobutane (12 mL) was stirred at 90 °C for one day. The excess 1,4-dibromobutane was recovered by vacuum distillation, and CH_2Cl_2 was added to the residue. The resulting suspension was filtered through Celite. The filtrate was dried and washed with diethyl ether (5 × 10 mL) to afford the product as a white solid. Yield: 1.55 g, 3.85 mmol, 77%. ^1H NMR (300 MHz, $CDCl_3$): δ 10.48 (s, 1 H, NCHN), 7.71 (s, 1 H, Imi–H), 7.17 (s, 1 H, Imi–H), 7.01 (s, 2 H, Ar–H), 4.85 (t, ^3J(H,H) = 7 Hz, 2 H, NCH_2), 3.51 (t, ^3J(H,H) = 7 Hz, 2 H, SCH_2), 2.34 (s, 3 H, CH_3), 2.26–2.18 (m, 2 H, CH_2), 2.08 (s, 6 H, CH_3), 2.06–2.01 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 140.6 (NCHN), 136.9, 133.7, 130.3, 129.3, 123.6, 123.0 (Ar–C), 48.6 (NCH_2), 32.4, 28.8, 28.7 (CH_2), 20.7, 17.2 (CH_3). HRMS (ESI) m/z calcd. for $C_{16}H_{22}BrN_2$ $[M - Br]^+$ 321.0961; found, 321.0968.



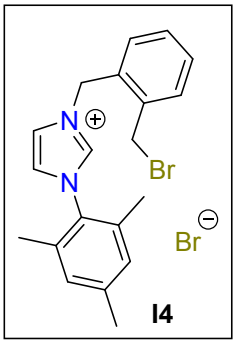
II3

This compound was prepared in analogy to **II1** from **I3** (137 mg, 0.34 mmol) and KSCN (35 mg, 0.36 mmol) as a yellowish solid. Yield: 118 mg, 0.31 mmol, 91%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1 H, NCHN), 8.16 (s, 1 H, Imi–H), 7.18 (s, 1 H, Imi–H), 6.94 (s, 2 H, Ar–H), 4.74 (t, ^{3}J(H,H) = 7 Hz, 2 H, NCH_2), 3.11 (t, ^{3}J(H,H) = 7 Hz, 2 H, SCH_2), 2.28 (s, 3 H, CH_3), 2.23–2.20 (m, 2 H, CH_2), 2.00 (s, 6 H, CH_3), 1.95–1.89 (m, 2 H, CH_2). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 141.8 (NCHN), 137.9, 134.7, 131.1, 130.4, 124.2, 124.0 (Ar–C), 112.9 (SCN), 49.7 (NCH_2), 33.6, 29.1, 26.8 (CH_2), 21.6, 18.1 (CH_3). HRMS (ESI) m/z calcd. for $C_{17}H_{22}N_3S$ $[M - Br]^+$ 300.1529; found, 300.1540.



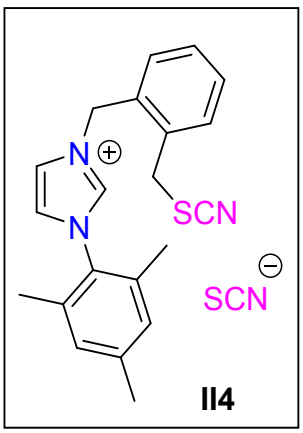
3

Compound **3** was prepared in analogy to **1** from **II3** (148 mg, 0.39 mmol), NaOH aqueous solution (1 M, 39 μL) and KSCN (189 mg, 1.95 mmol) as an off-white solid. Yield: 124 mg, 0.37 mmol, 96%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (s, 1 H, Imi–H), 7.17 (s, 1 H, Imi–H), 6.86 (s, 2 H, Ar–H), 4.57 (br-s, 2 H, NCH_2), 2.89 (br-s, 2 H, SCH_2), 2.17 (br-s, 5 H, CH_2 and CH_3), 2.01 (br-s, 2 H, CH_2), 1.83 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 144.5 (NCN), 141.5, 134.6 (Ar–C), 134.3 (SCN^-), 130.9, 129.8, 127.2, 123.5 (Ar–C), 52.5 (NCH_2), 33.8 (SCH_2), 31.0, 26.1 (CH_2), 21.2, 17.7 (CH_3). HRMS (ESI) m/z calcd. for $C_{16}H_{21}N_2S$ $[M - SCN]^+$ 273.1420; found, 273.1425.



I4

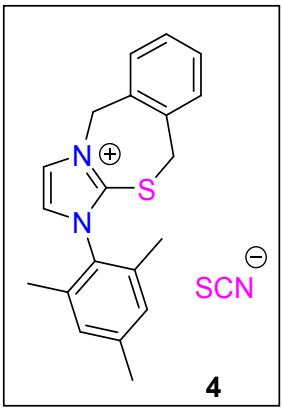
1,2-Bis(bromomethyl)benzene (1.85 g, 7.00 mmol) was heated at 100 °C until it became molten and then *N*-mesityl imidazole (559 mg, 3.00 mmol) was added. The reaction mixture was stirred at 100 °C overnight. After cooling it to ambient temperature, dichloromethane (2 mL) was added. The resulting solution was added to diethyl ether (150 mL) dropwise and a white solid was obtained which was washed with more diethyl ether (4 × 100 mL). The residue was then washed with acetone (2 × 20 mL). Removal of the solvent from the combined acetone washing afforded the product as a white solid. Yield: 293 mg, 0.65 mmol, 22%. ^{1}H NMR (300 MHz, d_6-DMSO): δ 9.59 (s, 1 H, NCHN), 8.04 (s, 1 H, Imi–H), 7.99 (s, 1 H, Imi–H), 7.59–7.33 (m, 4 H, Ar–H), 7.15 (s, 2 H, Ar–H), 5.73 (s, 2 H, NCH_2), 4.95 (s, 2 H, $BrCH_2$), 2.33 (s, 3 H, CH_3), 2.04 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, d_6-DMSO): 140.2 (NCHN), 137.9, 136.6, 134.2, 132.7, 131.4, 131.1, 129.6, 129.5, 129.2, 124.2, 123.5 (Ar–C, two are coincident), 49.3 (NCH_2), 31.7 ($BrCH_2$), 20.5, 17.0 (CH_3). HRMS (ESI) m/z calcd. for $C_{20}H_{22}BrN_2$ $[M - Br]^+$ 369.0961; found, 369.0962.



II4

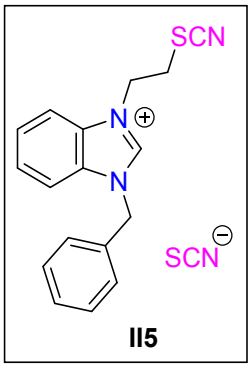
This compound was prepared in analogy to **II1** from **I4** (293 mg, 0.65 mmol) and KSCN (316 mg, 3.25 mmol) as a pale-pink spongy solid. Yield: 233 mg, 0.57 mmol, 88%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.45 (s, 1 H, NCHN), 7.57 (s, 1 H, Imi–H), 7.54–7.43 (m, 4 H, Ar–H), 7.16 (s, 1 H, Imi–H), 6.99 (s, 2 H, Ar–H), 5.99 (s, 2 H, NCH_2), 4.52 (s, 2 H, SCH_2),

2.32 (s, 3 H, CH_3), 2.08 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): 142.2 (NCHN), 138.2, 135.6, 134.9, 133.1, 132.3, 131.6, 131.3, 130.8, 130.6, 124.0, 123.6 (Ar–C, two are coincident), 112.5 (SCN), 51.6 (NCH_2), 36.1 (SCH_2), 21.7, 18.3 (CH_3), SCN^- signal could not be detected. HRMS (ESI) m/z calcd. for $C_{21}H_{22}N_3S$ $[M - SCN]^+$ 348.1529; found, 348.1525.



4

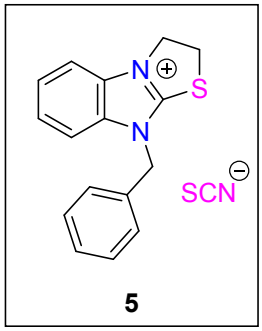
Compound **4** was prepared in analogy to **1** from **II4** (89 mg, 0.22 mmol), NaOH aqueous solution (1 M, 22 μL) and KSCN (107 mg, 1.10 mmol) as an off-white solid. Yield: 80 mg, 0.21 mmol, 95%. ^1H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, ^3J(H,H) = 2 Hz, 1 H, Imi–H), 7.77–7.75 (m, 1 H, Ar–H), 7.41–7.40 (m, 2 H, Ar–H), 7.35–7.33 (m, 1 H, Ar–H), 7.07 (d, ^3J(H,H) = 2 Hz, 1 H, Imi–H), 6.97 (s, 2 H, Ar–H), 6.07 (s, 2 H, NCH_2), 4.75 (s, 2 H, SCH_2), 2.32 (s, 3 H, CH_3), 1.92 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): 144.1 (NCN), 142.6, 136.8, 135.9, 133.8, 131.5, 131.3, 130.6, 130.4, 129.5, 129.1, 127.5, 122.0 (Ar–C), 53.5 (NCH_2), 32.9 (SCH_2), 21.8, 18.2 (CH_3), SCN^- signal could not be detected. HRMS (ESI) m/z calcd. for $C_{20}H_{21}N_2S$ $[M - SCN]^+$ 321.1420; found, 321.1424.



II5

This compound was prepared in analogy to **II1** from **I5** (396 mg, 1.00 mmol) and KSCN (486 mg, 5.00 mmol) as a pale-pink solid. Yield: 349 mg, 0.99 mmol, 99%. ^1H NMR (300 MHz, $CDCl_3$): δ

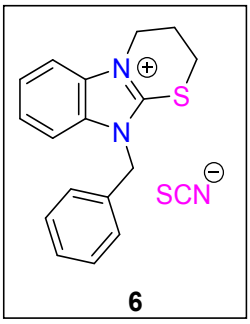
10.23 (s, 1 H, NCHN), 7.98 (d, ^{3}J(H,H) = 8 Hz, 1 H, Ar–H), 7.64–7.28 (m, 8 H, Ar–H), 5.79 (s, 2 H, NCH_2Ph), 5.12 (br-s, 2 H, NCH_2), 3.78 (br-s, 2 H, SCH_2). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): 143.2 (NCHN), 132.7, 132.3, 131.6, 130.0, 129.9, 129.0, 128.3, 128.1, 114.5, 113.9 (Ar–C), 112.3 (SCN), 52.5 (NCH_2Ph), 47.5 (NCH_2), 34.1 (CH_2), SCN^- signal could not be detected. HRMS (ESI) m/z calcd. for $C_{17}H_{16}N_3S$ $[M - SCN]^+$ 294.1059; found, 294.1064.



5

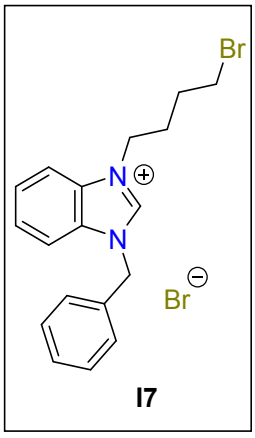
Compound **5** was prepared in analogy to **1** from **II5** (232 mg, 0.66 mmol), NaOH aqueous solution (1 M, 66 µL) and KSCN (321 mg, 3.30 mmol) as an off-white solid. Analytically pure product was obtained by recrystallization from a concentrated MeOH solution. Yield: 184 mg, 0.56 mmol, 85%. ^{1}H NMR (500 MHz, d_4-Methanol): δ 7.80–7.79 (m, 1 H, Ar–H), 7.73–7.71 (m, 1 H, Ar–H), 7.60–7.54 (m, 2 H, Ar–H), 7.50–7.42 (m, 5 H, Ar–H), 5.58 (s, 2 H, NCH_2Ph), 4.77 (t, ^{3}J(H,H) = 8 Hz, 2 H, NCH_2), 4.34 (t, ^{3}J(H,H) = 8 Hz, 2 H, SCH_2). $^{13}C\{^{1}H\}$ NMR (126 MHz, d_4-Methanol): 161.1 (NCN), 137.8, 133.6 (Ar–C), 133.5 (SCN^-), 131.8, 130.5, 130.4, 130.1, 127.4, 126.9, 113.8, 113.4 (Ar–C), 51.9 (NCH_2Ph), 48.0 (NCH_2), 39.1 (CH_2). Anal. Calc. for $C_{17}H_{15}N_3S_2$: C, 62.74; H, 4.65; N, 12.91. Found: C, 62.37; H, 4.59; N, 12.71. HRMS (ESI) m/z calcd. for $C_{16}H_{15}N_2S$ $[M - SCN]^+$ 267.0950; found, 267.0947.

A mixture of bromopropyl-benzimidazolium bromide (41 mg, 0.10 mmol) and KSCN (49 mg, 0.50 mmol) was suspended in CH_3CN (10 mL) and stirred overnight. An aqueous NaOH solution (1 M, 10 µL) was subsequently added and the suspension was



6

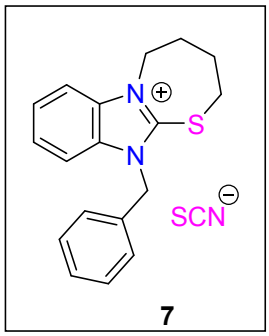
stirred for another 12 h. Dichloromethane (50 mL) was added and the resulting solution was filtered. Removal of the solvent yielded the product as a yellowish solid. The yellowish solid was further purified by column chromatography using silica gel as a stationary phase and by eluting with a mixture of CH_2Cl_2/CH_3OH (95:5 v/v) to obtain the pure compound. Yield: 32 mg, 0.10 mmol, 95%. ^{1}H NMR (500 MHz, CD_3CN): δ 7.74 (d, 1H, ^3J(H,H) = 8 Hz, Ar–H), 7.67 (d, 1H, ^3J(H,H) = 8 Hz, Ar–H), 7.55 (m, 2H, Ar–H), 7.39–7.35 (m, 5H, Ar–H), 5.49 (s, 2H, NCH_2Ph), 4.44 (t, 2H, ^3J(H,H) = 6 Hz, NCH_2), 3.55 (t, 2H, ^3J(H,H) = 6 Hz, SCH_2), 2.53 (q, 2H, ^3J(H,H) = 6 Hz, CH_2). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN): 151.6 (NCN), 134.1, 134.0, 132.3, 130.0, 129.7, 128.6, 127.2, 126.6, 112.6, 112.5 (Ar–C), 49.5 (NCH_2Ph), 44.3 (NCH_2), 27.3 (SCH_2), 21.8 (CH_2), SCN^- signal could not be detected. HRMS (ESI) m/z calcd. for $C_{17}H_{17}N_2S$ $[M - SCN]^+$ 281.1107; found, 281.1107.



I7

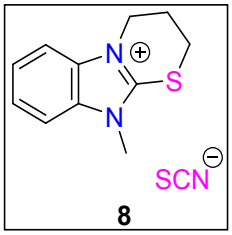
Compound **I7** was synthesized in analogy to **I3** from *N*-benzyl benzimidazole (1.04 g, 5.00 mmol) and 1,4-dibromobutane (12 mL) as a yellowish solid. Yield: 1.42 g, 3.35 mmol, 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.38 (s, 1 H, NCHN), 7.76 (d, ^3J(H,H) = 8 Hz, 1 H, Ar–H), 7.61–7.47 (m, 5 H, Ar–H), 7.33–7.30 (m, 3 H, Ar–H), 5.86 (s, 2 H, NCH_2Ph), 4.72 (br-s, 2 H, NCH_2), 3.47 (t, ^3J(H,H) = 6 Hz, 2 H, $BrCH_2$), 2.25 (br-s, 2 H, CH_2), 2.02 (br-s, 2 H, CH_2). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 143.4 (NCHN), 133.3, 132.0, 131.8, 130.0,

129.8, 129.0, 127.9, 114.6, 113.8 (Ar–C), 52.2, 47.6 (NCH_2), 33.5 ($BrCH_2$), 29.8, 28.5 (CH_3). HRMS (ESI) m/z calcd. for $C_{18}H_{20}BrN_2$ $[M - Br]^+$ 343.0804; found, 343.0808.



7

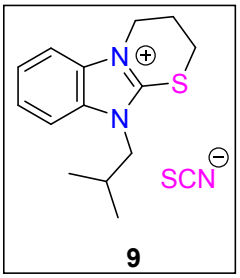
Compound **7** was prepared in analogy to **6** from **I7** (42 mg, 0.10 mmol), KSCN (49 mg, 0.50 mmol), NaOH aqueous solution (1 M, 10 µL) as a pale brown solid. Yield: 35 mg, 0.10 mmol, 98%. ^{1}H NMR (400 MHz, CD_3CN): δ 7.87 (d, ^3J(H,H) = 8 Hz, 1 H, Ar–H), 7.77 (d, ^3J(H,H) = 8 Hz, 1 H, Ar–H), 7.68–7.58 (m, 2 H, Ar–H), 7.39–7.32 (m, 5 H, Ar–H), 5.72 (s, 2 H, NCH_2Ph), 4.64 (t, ^3J(H,H) = 6 Hz, 2 H, NCH_2), 3.25 (t, ^3J(H,H) = 6 Hz, 2 H, SCH_2), 2.31–2.27 (m, 2 H, CH_2), 2.07–2.02 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): 153.9 (NCN), 134.9, 134.2 (Ar–C), 132.9 (SCN^-), 130.1, 129.7, 129.5, 128.5, 128.0, 127.9, 114.0, 113.7 (Ar–C), 51.2, 48.9 (NCH_2), 34.6, 31.1, 25.7 (CH_2). HRMS (ESI) m/z calcd. for $C_{18}H_{19}N_2S$ $[M - SCN]^+$ 295.1263; found, 295.1273.



8

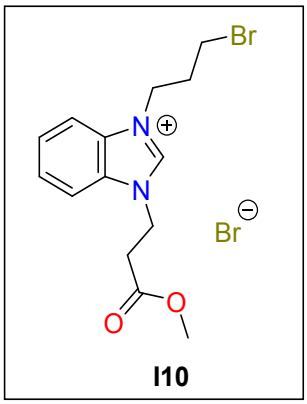
Compound **8** was prepared in analogy to **6** from **I8** (167 mg, 0.50 mmol), KSCN (243 mg, 2.50 mmol), NaOH aqueous solution (1 M, 50 µL) as a pale-yellow solid. Yield: 128 mg, 0.49 mmol, 97%. ^{1}H NMR (400 MHz, CD_3CN): δ 7.72–7.68 (m, 2 H, Ar–H), 7.58–7.55 (m, 2 H, Ar–H), 4.40 (t, ^3J(H,H) = 8 Hz, 2 H, NCH_2), 3.79 (s, 3 H, CH_3), 3.53 (t, ^3J(H,H) = 8 Hz, 2 H, $SCNCH_2$), 2.50 (m, ^3J(H,H) = 7 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): 151.3 (NCN) 133.7, 132.9, 127.0, 126.4, 112.3, 112.2 (Ar–C), 44.1 (NCH_2), 32.0

(CH_3), 27.1 (SCH_2), 21.9 (CH_2), SCN^- signal could not be detected. Anal. Calc. for $C_{12}H_{13}N_3S_2$: C, 54.72; H, 4.98; N, 15.95. Found: C, 54.83; H, 4.67; N, 15.63. HRMS (ESI) m/z calcd. for $C_{11}H_{13}N_2S$ $[M - SCN]^+$ 205.0794; found, 205.0796.



9

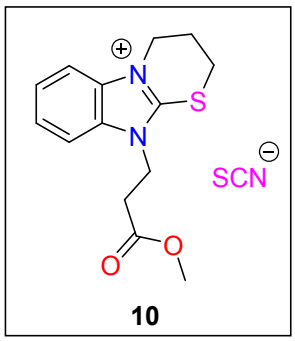
Compound **9** was prepared in analogy to **6** from **I9** (113 mg, 0.30 mmol), KSCN (146 mg, 1.50 mmol), NaOH aqueous solution (1 M, 30 μL) as a pale-yellow solid. Yield: 89 mg, 0.29 mmol, 97%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.65–7.63 (m, 1 H, Ar–H), 7.56–7.54 (m, 1 H, Ar–H), 7.45–7.38 (m, 2 H, Ar–H), 4.55 (t, ^3J(H,H) = 6 Hz, 2 H, NCH_2), 3.99 (d, ^3J(H,H) = 7 Hz, 2 H, NCH_2), 3.61 (t, ^3J(H,H) = 6 Hz, 2 H, SCH_2), 2.57 (m, ^3J(H,H) = 6 Hz, 2 H, CH_2), 2.22 (m, ^3J(H,H) = 7 Hz, 1 H, CH), 0.91 (d, ^3J(H,H) = 7 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): 150.0 (NCN), 133.0, 131.9 (Ar–C), 131.2 (SCN^-), 127.8, 126.9, 126.3, 112.1 (Ar–C), 53.3, 44.0 (NCH_2), 28.8, 27.1, 21.9 (CH and CH_2), 20.5 (CH_3). HRMS (ESI) m/z calcd. for $C_{14}H_{19}N_2S$ $[M - SCN]^+$ 247.1263; found, 247.1271.



I10

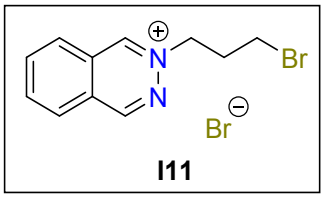
Compound **I10** was synthesized in analogy to **I3** from *N*-methylpropionato benzimidazole (1.02 g, 5.00 mmol) and 1,3-dibromopropane (10 mL) as a yellowish solid. Yield: 1.36 g, 3.35 mmol, 67%. ^1H NMR (400 MHz, $CDCl_3$): δ 10.79 (s, 1 H, NCHN), 7.83–7.78 (m, 2 H, Ar–H), 7.51–7.49 (m, 2 H, Ar–H), 4.82 (t, ^3J(H,H) = 7 Hz, 2 H, NCH_2), 4.73

(t, ^3J(H,H) = 7 Hz, 2 H, NCH_2), 3.47 (s, 3 H, CH_3), 3.42 (t, ^3J(H,H) = 7 Hz, 2 H, $BrCH_2$), 3.10 (t, ^3J(H,H) = 7 Hz, 2 H, $COCH_2$), 2.54 (m, ^3J(H,H) = 7 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 170.9 (CO), 143.3 (NCHN), 131.42, 131.37, 127.62, 127.57, 113.9, 113.5 (Ar–C), 52.6, 46.2, 43.4, 33.7, 32.2 (CH_2), 30.1 (CH_3). Anal. Calcd. for $C_{14}H_{18}Br_2N_2O_2$: C, 41.41; H, 4.47; N, 6.90. Found: C, 41.96; H, 4.79; N, 7.02. HRMS (ESI) m/z calcd. for $C_{14}H_{18}BrN_2O_2$ $[M - Br]^+$ 325.0546; found, 325.0545.



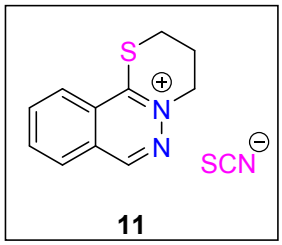
10

Compound **10** was prepared in analogy to **6** from **I10** (406 mg, 1.00 mmol), KSCN (486 mg, 5.00 mmol), NaOH aqueous solution (1 M, 100 µL) as an off-white solid. Yield: 329 mg, 0.98 mmol, 98%. ^1H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, ^3J(H,H) = 7 Hz, 1 H, Ar–H), 7.70 (d, ^3J(H,H) = 7 Hz, 1 H, Ar–H), 7.51–7.46 (m, 2 H, Ar–H), 4.68 (t, ^3J(H,H) = 7 Hz, 2 H, NCH_2), 4.60 (t, ^3J(H,H) = 7 Hz, 2 H, NCH_2), 3.79 (t, ^3J(H,H) = 7 Hz, 2 H, SCH_2), 3.62 (s, 3 H, CH_3), 3.00 (t, ^3J(H,H) = 7 Hz, 2 H, $COCH_2$), 2.64 (m, ^3J(H,H) = 7 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 171.0 (CO), 150.7 (NCN), 133.3, 131.6, 127.2, 126.7, 112.42, 112.38 (Ar–C), 53.0, 44.4, 42.0, 32.9, 27.7 (CH_2), 22.0 (CH_3), SCN^- signal could not be detected. HRMS (ESI) m/z calcd. for $C_{14}H_{17}N_2O_2S$ $[M - SCN]^+$ 277.1005; found, 277.1013.



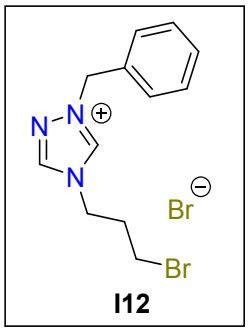
I11

Compound **I11** was synthesized in analogy to **I3** from phthalazine (651 mg, 5.00 mmol) and 1,3-dibromopropane (10 mL) as a pale-yellow solid. Yield: 1.49 g, 4.48 mmol, 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.95 (s, 1 H, NCH), 10.00 (s, 1 H, NCH), 8.82 (d, ^{3}J(H,H) = 8 Hz, 1 H, Ar–H), 8.62 (d, ^{3}J(H,H) = 8 Hz, 1 H, Ar–H), 8.36 (t, ^{3}J(H,H) = 8 Hz, 1 H, Ar–H), 8.25 (t, ^{3}J(H,H) = 8 Hz, 1 H, Ar–H), 5.21 (t, ^{3}J(H,H) = 7 Hz, 2 H, NCH_2), 3.53 (t, ^{3}J(H,H) = 7 Hz, 2 H, $BrCH_2$), 2.74 (m, ^{3}J(H,H) = 7 Hz, 2 H, CH_2). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): 155.2 (NCH), 152.5 (NCH), 140.1, 136.9, 131.7, 129.0, 128.5, 128.4 (Ar–C), 63.0 (NCH_2), 32.8 ($BrCH_2$), 29.6 (CH_2). HRMS (ESI) m/z calcd. for $C_{11}H_{12}BrN_2$ $[M - Br]^+$ 251.0178; found, 251.0181.



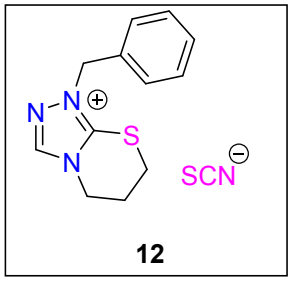
11

Compound **11** was prepared in analogy to **6** from **I11** (33 mg, 0.10 mmol), KSCN (49 mg, 0.5 mmol), NaOH aqueous solution (1 M, 10 µL) as a dark-brown solid. Yield: 24 mg, 0.09 mmol, 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (d, ^{3}J(H,H) = 7 Hz, 1 H, Ar–H), 8.12 (s, 1 H, NCH), 7.77–7.63 (m, 3 H, Ar–H), 4.29 (t, ^{3}J(H,H) = 7 Hz, 2 H, NCH_2), 2.74 (t, ^{3}J(H,H) = 7 Hz, 2 H, SCH_2), 2.21 (m, ^{3}J(H,H) = 7 Hz, 2 H, CH_2). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): 159.9 (NCH), 138.4, 133.6, 132.2, 130.1, 128.4, 127.2, 126.6 (Ar–C), 50.3 (NCH_2), 36.5 (SCH_2), 28.7 (CH_2), SCN^- signal could not be detected. HRMS (ESI) m/z calcd. for $C_{11}H_{11}N_2S$ $[M - SCN]^+$ 203.0637; found, 203.0643.



I12

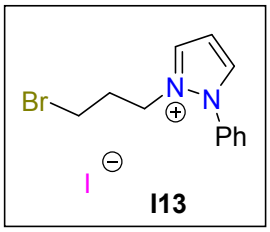
Compound **I12** was synthesized in analogy to **I3** from 1-benzyl triazole (796 mg, 5.00 mmol) and 1,3-dibromopropane (10 mL) as a yellowish solid. Yield: 1.17 g, 3.25 mmol, 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.60 (s, 1 H, NCHN), 9.09 (s, 1 H, NCHN), 7.54–7.51 (m, 2 H, Ar–H), 7.36–7.34 (m, 3 H, Ar–H), 5.68 (s, 2 H, NCH_2Ph), 4.72 (t, ^{3}J(H,H) = 7 Hz, 2 H, NCH_2), 3.47 (t, ^{3}J(H,H) = 7 Hz, 2 H, $BrCH_2$), 2.60 (m, ^{3}J(H,H) = 7 Hz, 2 H, CH_2). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): 144.9 (NCHN), 143.7 (NCHN), 132.4, 130.3, 130.1, 129.9 (Ar–C), 57.1, 48.0 (NCH_2), 32.7 ($BrCH_2$), 29.8 (CH_2). HRMS (ESI) m/z calcd. for $C_{12}H_{15}BrN_3$ $[M - Br]^+$ 280.0444; found, 280.0446.



12

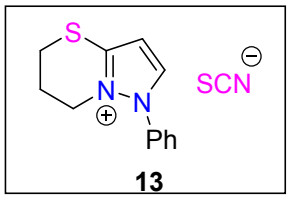
Compound **12** was prepared in analogy to **6** from **I12** (36 mg, 0.10 mmol), KSCN (49 mg, 0.5 mmol), NaOH aqueous solution (1 M, 10 μL) as a dark-brown solid. Yield: 23 mg, 0.08 mmol, 80%. ^{1}H NMR (300 MHz, d_6-DMSO): δ 9.16 (s, 1 H, NCHN), 7.41–7.34 (m, 5 H, Ar–H), 5.43 (s, 2 H, NCH_2Ph), 4.31 (t, ^{3}J(H,H) = 6 Hz, 2 H, NCH_2), 3.50 (t, ^{3}J(H,H) = 6 Hz, 2 H, SCH_2), 2.31 (m, ^{3}J(H,H) = 6 Hz, 2 H, CH_2). $^{13}C\{^{1}H\}$ NMR (75 MHz, d_6-DMSO): 149.1 (NCN), 145.0 (NCHN), 132.8 (SCN^-), 129.6, 128.9, 128.7, 128.4 (Ar–C), 53.0, 44.9 (NCH_2), 26.6 (SCH_2), 20.5 (CH_2). HRMS (ESI) m/z calcd. for $C_{12}H_{14}N_3S$ $[M - SCN]^+$ 232.0903; found, 232.0911.

N-phenyl pyrazole (721 mg, 5.00 mmol) and a CH_3CN (10 mL) solution of NaI (749



I13

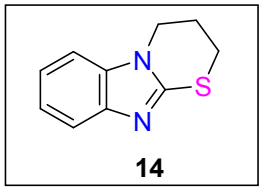
mg, 5.00 mmol) was added to 1,3-dibromopropane (10 mL). The mixture was stirred at 90 °C for one day. The excess 1,3-dibromopropane was recovered by vacuum distillation, and CH_2Cl_2 was added to the residue. The resulting suspension was filtered through Celite. The filtrate was dried and washed with ethyl acetate (3 × 10 mL) to afford the product as a red oil. Yield: 688 mg, 1.75 mmol, 35%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, ^3J(H,H) = 3 Hz, 1 H, NCH), 8.26 (d, ^3J(H,H) = 3 Hz, 1 H, NCH), 7.80–7.73 (m, 5 H, Ar–H), 7.08 (t, ^3J(H,H) = 3 Hz, 1 H, CH), 4.63 (t, ^3J(H,H) = 6 Hz, 2 H, NCH_2), 3.41 (t, ^3J(H,H) = 6 Hz, 2 H, $BrCH_2$), 2.38 (m, ^3J(H,H) = 6 Hz, 2 H, CH_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 139.9, 139.7 (NCH), 134.0, 132.1, 131.8, 128.6 (Ar–C), 110.4 (CH), 50.7 (NCH_2), 32.3 ($BrCH_2$), 29.5 (CH_2). HRMS (ESI) m/z calcd. for $C_{12}H_{14}BrN_2$ [M – I]$^+$ 265.0335; found, 265.0336.



13

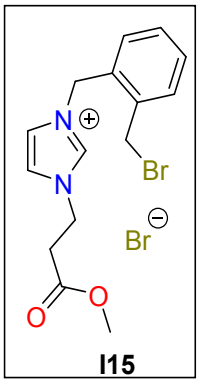
Compound **13** was prepared in analogy to **6** from **I13** (39 mg, 0.10 mmol), KSCN (49 mg, 0.5 mmol) and NaOH aqueous solution (1 M, 10 μL) as an orange oil. Yield: 24 mg, 0.09 mmol, 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, ^3J(H,H) = 3 Hz, 1 H, NCH), 7.86–7.83 (m, 2 H, Ar–H), 7.65–7.60 (m, 3 H, Ar–H), 6.70 (d, ^3J(H,H) = 3 Hz, 1 H, CH), 4.41 (t, ^3J(H,H) = 6 Hz, 2 H, NCH_2), 3.46 (t, ^3J(H,H) = 6 Hz, 2 H, SCH_2), 2.55 (m, ^3J(H,H) = 6 Hz, 2 H, CH_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 146.3 (NCH),

137.0 (NCS), 133.1, 132.4, 131.3, 128.9 (Ar–C), 107.6 (CH), 47.8 (NCH_2), 25.0 (SCH_2), 23.6 (CH_2), SCN^- signal could not be detected. HRMS (ESI) m/z calcd. for $C_{12}H_{13}N_2S$ $[M - SCN]^+$ 217.0794; found, 217.0791.



14

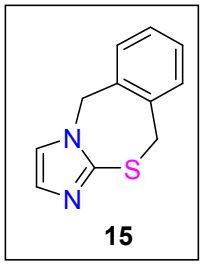
Compound **10** (34 mg, 0.10 mmol) was mixed with an aqueous NaOH solution (1 M, 100 μL) in CH_3CN (5 mL), and the reaction mixture was stirred at 70 °C overnight. After the solvent was removed in vacuum, the product **14** was washed out by diethyl ether (5 × 10 mL) and dried as a white solid. Yield: 18 mg, 0.10 mmol, 97%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, ^3J(H,H) = 7 Hz, 1 H, Ar–H), 7.21–7.19 (m, 3 H, Ar–H), 4.17 (t, ^3J(H,H) = 7 Hz, 2 H, NCH_2), 3.22 (t, ^3J(H,H) = 7 Hz, 2 H, SCH_2), 2.45 (m, ^3J(H,H) = 7 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 147.6 (NCN), 141.6, 135.7, 123.5, 122.5, 118.0, 108.7 (Ar–C), 43.2 (NCH_2), 26.4 (SCH_2), 23.7(CH_2). HRMS (ESI) m/z calcd. for $C_{10}H_{10}N_2S$ $[M + H]^+$ 191.0637; found, 191.0642. Same as in literature.[1]



I15

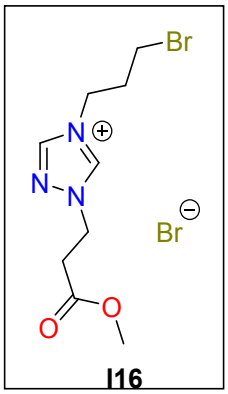
This compound was synthesized in analogy to **I4** from 1,2-bis(bromomethyl)benzene (1.85 g, 7.00 mmol) and *N*-methylpropionato imidazole (154 mg, 1.00 mmol) as a yellow solid. The yellow solid was further purified by column chromatography using silica gel as a stationary phase and by eluting with a CH_2Cl_2/CH_3OH mixture (90:10 v/v) to obtain the pure compound.Yield: 163 mg, 0.39 mmol, 39%. ^1H NMR (400 MHz, CD_3CN): δ 9.64 (br, 1 H, NCHN), 7.72–7.66 (m, 1

H, Imi–H), 7.55–7.53 (m, 1 H, Imi–H), 7.47 (br, 1 H, Ar–H), 7.37 (br, 3 H, Ar–H), 5.71 (s, 2 H, NCH_2), 4.81 (s, 2 H, $BrCH_2$), 4.48–4.45 (m, 2H, NCH_2), 3.60 (s, 3 H, CH_3), 2.99–2.96 (m, 2H, $COCH_2$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ 171.5 (CO), 137.92, 137.87 (Ar–C), 133.2 (NCHN), 132.2, 131.3, 130.7, 130.4, 123.9, 123.2 (Ar–C), 52.6, 50.5, 46.0, 34.8 (CH_2), 32.2 (CH_3). HRMS (ESI) m/z calcd. for $C_{15}H_{18}BrN_2O_2$ $[M - Br]^+$ 337.0546; found, 337.0545.



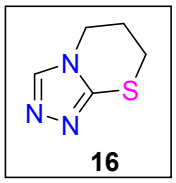
15

Compound **I15** (84 mg, 0.20 mmol) and KSCN (97 mg, 1.00 mmol) were suspended in CH_3CN (10 mL) and stirred overnight. An aqueous solution of NaOH (1 M, 220 μL) was subsequently added, and the resulting mixture was stirred at ambient temperature for 4 h and then heated at 70 °C overnight. After the solvent was removed in vacuum, the product **15** was washed out with ether (5 × 10 mL) and dried as a white solid. The white solid was purified by recrystallization from $CHCl_3$. Yield: 32 mg, 0.16 mmol, 80%. Single crystal was obtained by slow evaporation of a saturated solution in CH_2Cl_2/diethyl ether. ^1H NMR (500 MHz, $CDCl_3$): δ 7.38–7.32 (m, 2 H, Ar–H), 7.30–7.29 (m, 2 H, Imi–H), 6.97–6.96 (m, 2 H, Ar–H), 5.21 (s, 2 H, NCH_2), 4.29 (s, 2 H, SCH_2). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.9 (NCN), 138.1, 134.7, 130.3, 129.8, 129.5, 128.9, 128.5, 122.6 (Ar–C), 50.9 (NCH_2), 32.7 (SCH_2). Anal. Calcd. for $C_{11}H_{10}N_2S$: C, 65.32; H, 4.98; N, 13.85. Found: C, 65.48; H, 5.06; N, 13.83. HRMS (ESI) m/z calcd. for $C_{11}H_{10}N_2S$ $[M + H]^+$ 203.0637; found, 203.0639.



I16

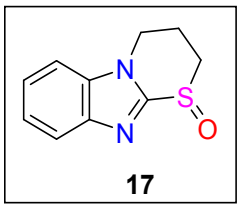
Compound **I16** was synthesized in analogy to **I3** from 1-methylpropionato triazole (776 mg, 5.00 mmol) and 1,3-dibromopropane (10 mL) as a yellowish and sticky solid. Yield: 696 mg, 1.95 mmol, 39%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.31 (s, 1 H, NCHN), 9.11 (s, 1 H, NCHN), 4.85 (t, ^{3}J(H,H) = 6 Hz, 2 H, NCH_2), 4.75 (t, ^{3}J(H,H) = 6 Hz, 2 H, NCH_2), 3.69 (s, 3 H, CH_3), 3.54 (t, ^{3}J(H,H) = 6 Hz, 2 H, $BrCH_2$), 3.13 (t, ^{3}J(H,H) = 6 Hz, 2 H, $COCH_2$), 2.65 (m, ^{3}J(H,H) = 6 Hz, 2 H, CH_2). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 170.9 (CO), 144.9, 144.5 (NCHN), 53.2, 49.1, 48.0, 33.0, 32.8 (CH_2), 30.0 (CH_3). HRMS (ESI) m/z calcd. for $C_9H_{15}BrN_3O_2$ [M – Br]$^{+}$ 276.0342; found, 276.0346.



16

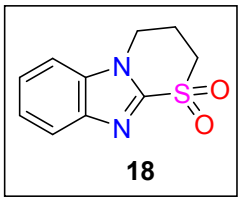
Compound **16** was prepared in analogy to **15** from **I16** (71 mg, 0.2 mmol), KSCN (97 mg, 1.00 mmol) and a NaOH aqueous solution (1 M, 220 µL) as a yellowish oil. Yield: 27 mg, 0.19 mmol, 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1 H, NCHN), 4.10 (t, ^{3}J(H,H) = 6 Hz, 2 H, NCH_2), 3.13 (t, ^{3}J(H,H) = 6 Hz, 2 H, SCH_2), 2.31 (m, ^{3}J(H,H) = 6 Hz, 2 H, CH_2). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ 146.4 (NCN), 144.0 (NCHN), 44.0 (NCH_2), 26.4 (SCH_2), 23.9 (CH_2). Anal. Calcd. for $C_5H_7N_3S$: C, 42.53; H, 5.00; N, 29.76. Found: C, 42.90; H, 5.04; N, 30.00. HRMS (ESI) m/z calcd. for $C_5H_7N_3S$ [M + H]$^{+}$ 142.0433; found, 142.0432.

Compound **17** was purified using column chromatography (Rf: 0.05,



17

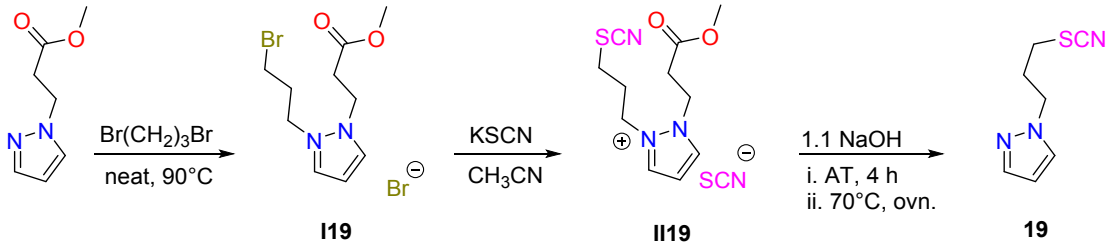
hexane/EA/CH2Cl2: 1/2/1,) and isolated as a white solid. Yield: 17 mg, 0.08 mmol, 31%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, ^{3}J(H,H) = 8 Hz, 1 H, Ar–H), 7.44–7.37 (m, 3 H, Ar–H), 4.54–4.48 (m, 1 H, NCH_2), 4.21–4.14 (m, 1 H, NCH_2), 3.50–3.46 (m, 1 H, SCH_2), 3.27–3.15 (m, 2 H, SCH_2 and CH_2), 2.47–2.40 (m, 1 H, CH_2). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 148.8 (NCN), 142.7, 135.0, 126.1, 124.8, 122.2, 110.7 (Ar–C), 46.1, 43.8, 14.2 (CH_2). Anal. Calcd. for $C_{10}H_{10}N_2OS$: C, 58.23; H, 4.89; N, 13.58. Found: C, 58.44; H, 5.08; N, 13.73. HRMS (ESI) m/z calcd. for $C_{10}H_{10}N_2OS$ $[M + H]^+$ 207.0587; found, 207.0588.

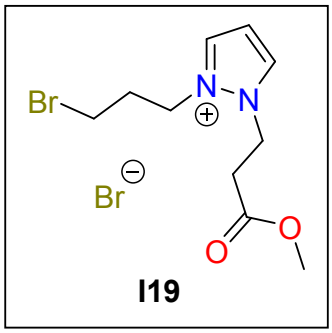


18

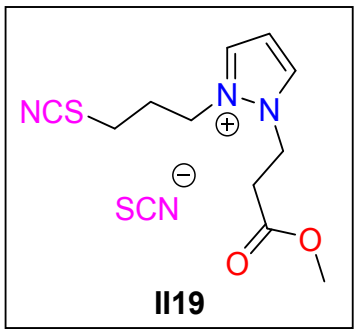
Compound **18** was purified using column chromatography (Rf: 0.33, hexane/EA/CH2Cl2: 1/2/1,) and isolated as a white solid. Yield: 14 mg, 0.06 mmol, 24%. ^{1}H NMR (500 MHz, CD_3CN): δ 7.82 (d, ^{3}J(H,H) = 8 Hz, 1H, Ar–H), 7.52 (d, ^{3}J(H,H) = 8 Hz, 1H, Ar–H), 7.48 (t, ^{3}J(H,H) = 8 Hz, 1H, Ar–H), 7.41 (t, ^{3}J(H,H) = 8 Hz, 1H, Ar–H), 4.32 (t, ^{3}J(H,H) = 6 Hz, 2H, NCH_2), 3.67–3.64 (m, 2H, SCH_2), 2.77–2.73 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN): δ 149.4 (NCN), 142.1, 135.0, 126.3, 125.0, 121.9, 112.4 (Ar–C), 51.8, 43.9, 22.6 (CH_2). Anal. Calcd. for $C_{10}H_{10}N_2O_2S$: C, 54.04; H, 4.54; N, 12.60. Found: C, 53.85; H, 4.72; N, 12.46. HRMS (ESI) m/z calcd. for $C_{10}H_{10}N_2O_2S$ $[M + H]^+$ 223.0536; found, 223.0532.

Scheme S1. Formation of SCN-propyl-pyrazole.



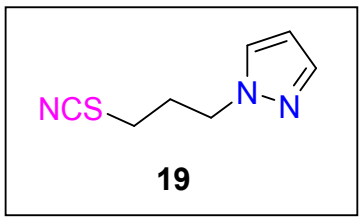


Compound **I19** was synthesized in analogy to **I3** from *N*-methylpropionato pyrazole (771 mg, 5.00 mmol) and 1,3-dibromopropane (10 mL) as a colorless oil. Yield: 1.42 g, 4.00 mmol, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, ^{3}J(H,H) = 3 Hz, 1 H, NCH), 8.73 (d, ^{3}J(H,H) = 3 Hz, 1 H, NCH), 6.74 (t, ^{3}J(H,H) = 3 Hz, 1 H, CH), 5.02–4.99 (m, 4 H, NCH_2), 3.61 (s, 3 H, CH_3), 3.53 (t, ^{3}J(H,H) = 6 Hz, 2 H, $BrCH_2$), 3.17 (t, ^{3}J(H,H) = 6 Hz, 2 H, $COCH_2$), 2.53 (m, ^{3}J(H,H) = 6 Hz, 2 H, CH_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 170.9 (CO), 138.98, 138.88 (NCH), 108.9 (CH), 53.1, 49.7, 46.7, 34.5, 32.8 (CH_2), 29.7 (CH_3). HRMS (ESI) m/z calcd. for $C_{10}H_{16}BrN_2O_2$ $[M - Br]^+$ 275.0390; found, 275.0389.



This compound was prepared in analogy to **II1** from **I19** (356 mg, 1.00 mmol) and KSCN (486 mg, 5.00 mmol) as a pinkish oil. Yield: 291 mg, 0.93 mmol, 93%. ^{1}H NMR (400 MHz, CD_3CN): δ 8.28 (d, ^{3}J(H,H) = 3 Hz, 1 H, NCH), 8.26 (d, ^{3}J(H,H) = 3 Hz, 1 H, NCH), 6.78 (t, ^{3}J(H,H) = 3 Hz, 1 H, CH), 4.70 (t, ^{3}J(H,H) = 6 Hz, 2 H, NCH_2), 4.62 (t, ^{3}J(H,H) = 6

Hz, 2 H, NCH_2), 3.64 (s, 3 H, CH_3), 3.15 (t, ^3J(H,H) = 6 Hz, 2 H, $SCNCH_2$), 3.02 (t, ^3J(H,H) = 6 Hz, 2 H, $COCH_2$), 2.41 (m, ^3J(H,H) = 6 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ 171.3 (CO), 139.1, 138.5 (NCH), 113.0 (SCN), 109.0 (CH), 52.8, 49.1, 46.5, 33.8, 30.9 (CH_2), 30.2 (CH_3), SCN^- signal could not be detected. HRMS (ESI) m/z calcd. for $C_{11}H_{16}N_3O_2S$ $[M - SCN]^+$ 254.0958; found, 254.0965.



19

Compound **II19** (81 mg, 0.26 mmol) was dissolved in CH_3CN and an aqueous solution of NaOH (1 M, 286 μL) was added. The suspension was stirred at ambient temperature for four hours and then heated at 80 °C overnight. After the solvent was removed in vacuum, the product was washed out by ether (5 × 10 mL) as a colorless oil (41 mg, 0.25 mmol, 95%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, ^3J(H,H) = 3 Hz, 1 H, NCH), 7.45 (d, ^3J(H,H) = 3 Hz, 1 H, NCH), 6.30 (t, ^3J(H,H) = 3 Hz, 1 H, CH), 4.37 (t, ^3J(H,H) = 6 Hz, 2 H, NCH_2), 2.91 (t, ^3J(H,H) = 6 Hz, 2 H, $SCNCH_2$), 2.42 (m, ^3J(H,H) = 6 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 140.0, 130.6 (NCH), 112.4 (SCN), 106.8 (CH), 49.7 (NCH_2), 31.5 (SCH_2), 31.0 (CH_2). Anal. Calcd. for $C_7H_9N_3S$: C, 50.28; H, 5.42; N, 25.13. Found: C, 49.92; H, 5.31; N, 25.49. HRMS (ESI) m/z calcd. for $C_7H_9N_3S$ $[M + H]^+$ 168.0590; found, 168.0596.

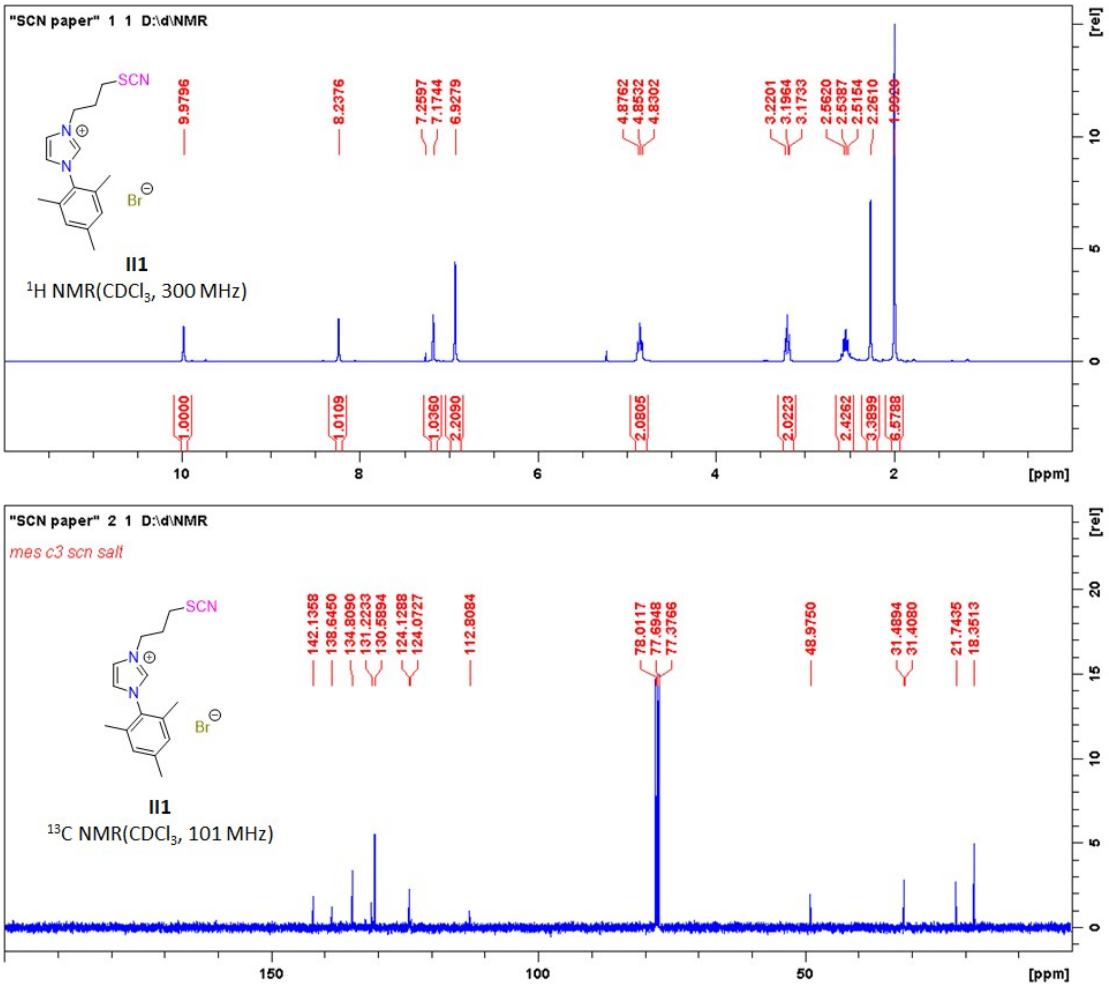


Figure S1. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **II1** in $CDCl_3$.

Mass Spectrum SmartFormula Report

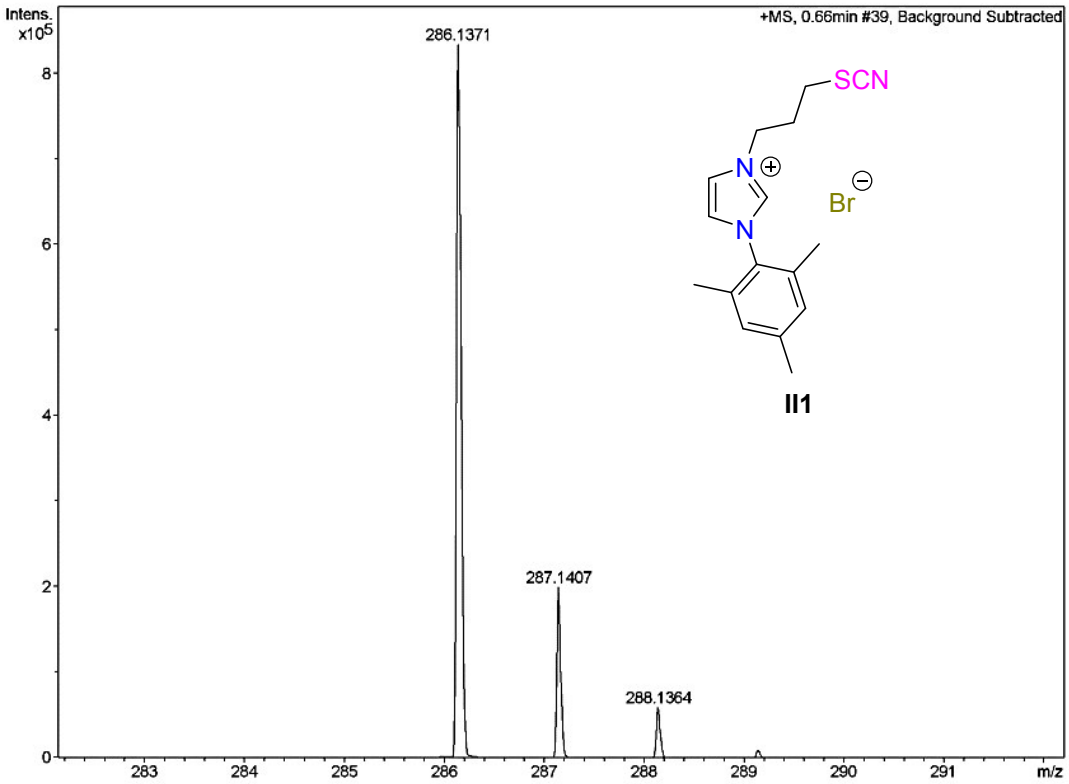
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-II1-1.d	Acquisition Date	1/22/2020 10:18:55 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-II1	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
286.1371	1	C 16 H 20 N 3 S	286.1372	0.4	8.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 10:23:11 AM Page 1 of 1

Figure S2. HR-MS (ESI) data of **II1**.

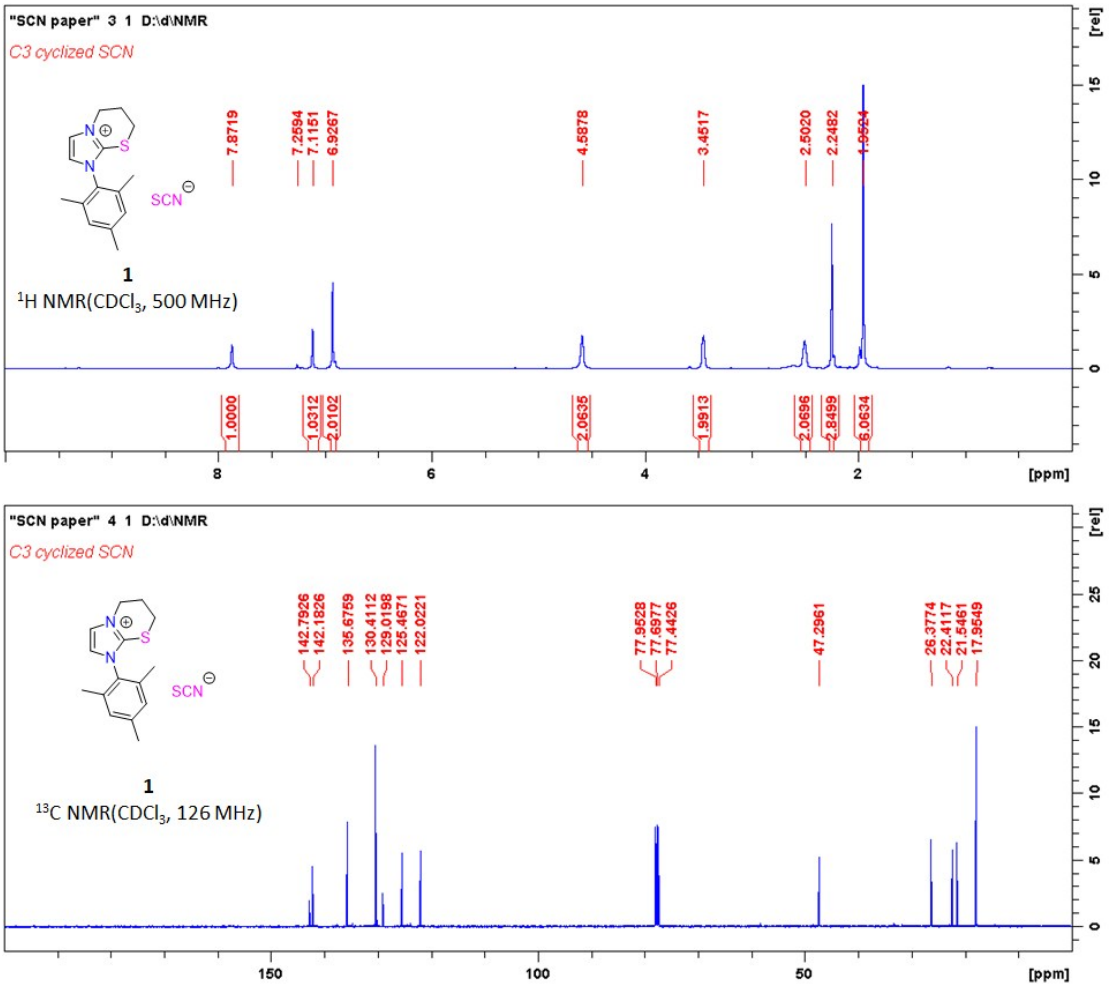


Figure S3. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** in $CDCl_3$.

Mass Spectrum SmartFormula Report

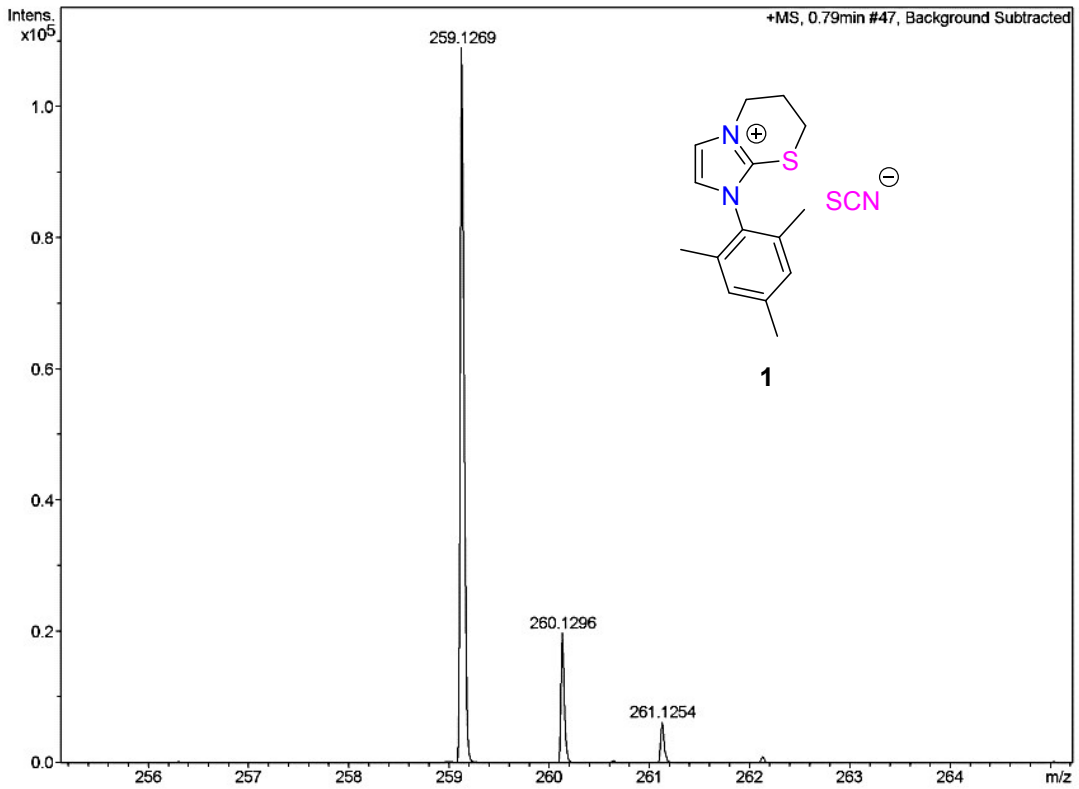
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS1.d	Acquisition Date	1/10/2020 2:31:13 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS1	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
259.1269	1	C 15 H 19 N 2 S	259.1263	-2.1	7.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 2:34:25 PM Page 1 of 1

Figure S4. HR-MS (ESI) data of **1**.

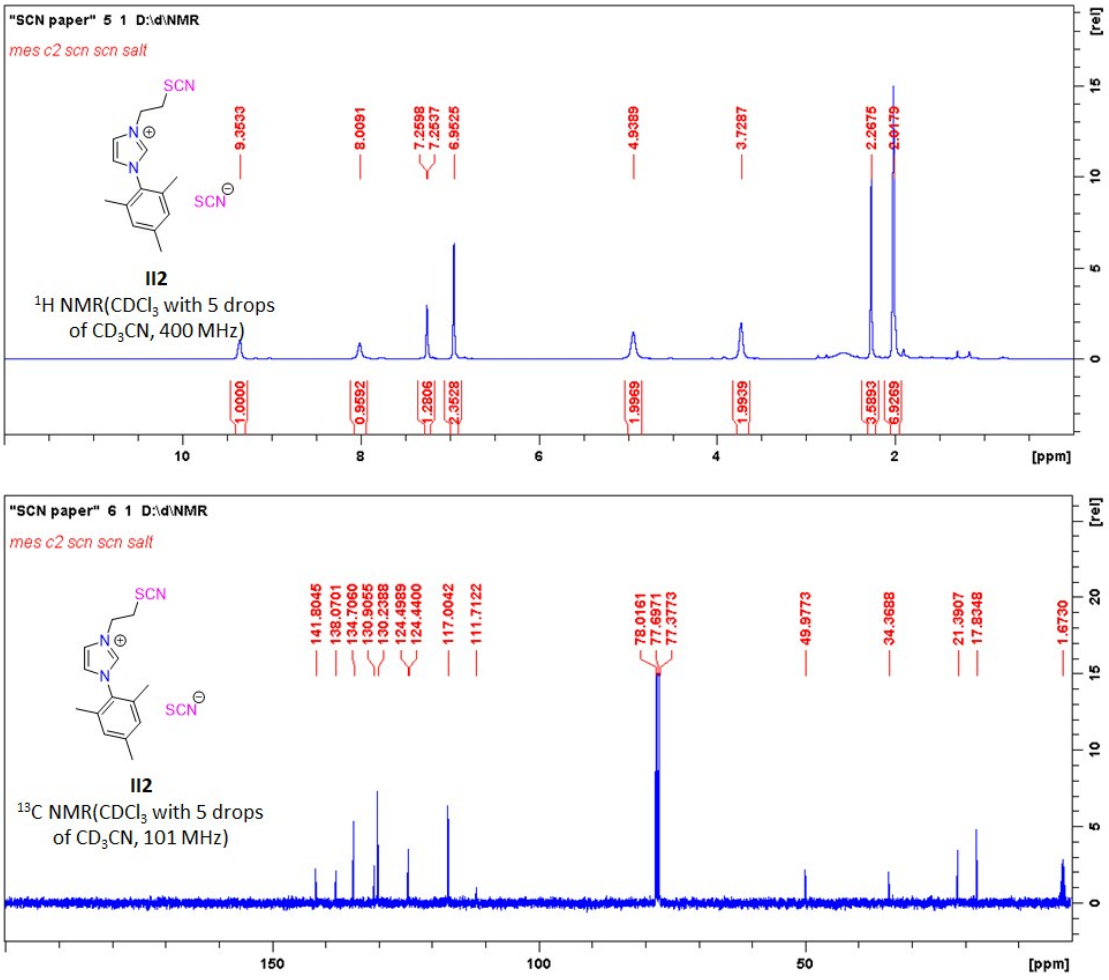


Figure S5. ^{1}H NMR and ^{13}C{^{1}H} NMR spectrum of compound **II2** in $CDCl_3$.

Mass Spectrum SmartFormula Report

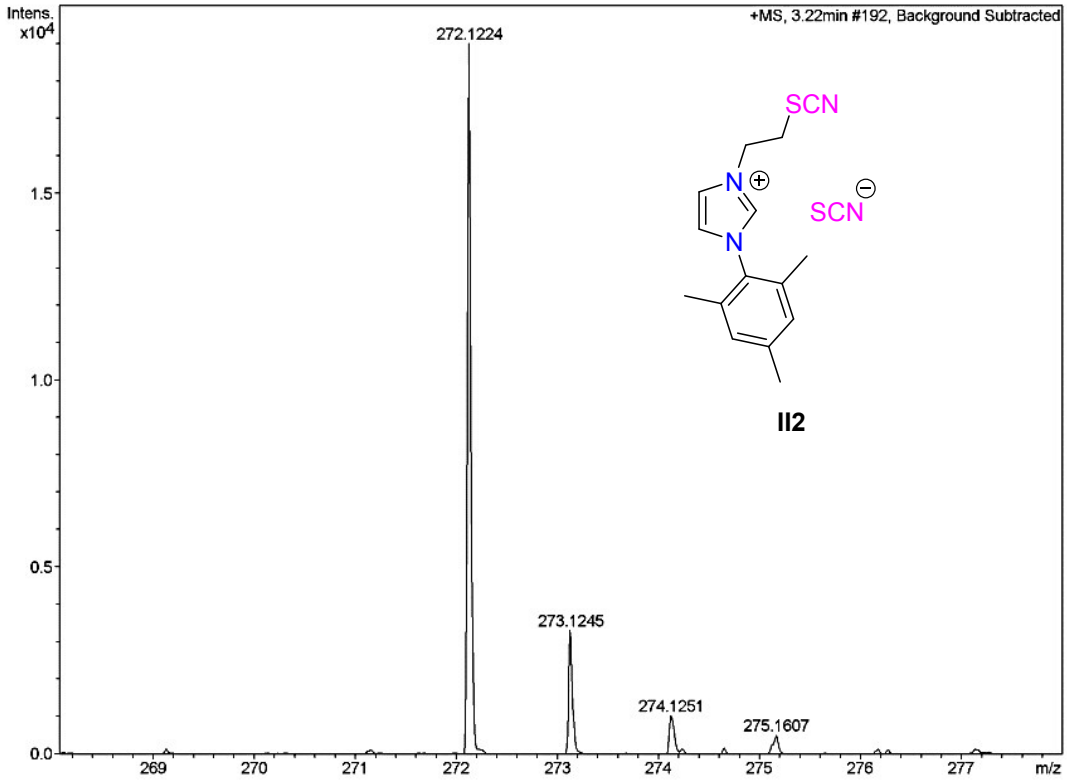
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CSII2.d	Acquisition Date	1/10/2020 2:54:50 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CSII2	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
272.1224	1	C 15 H 18 N 3 S	272.1216	-2.9	8.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 2/11/2020 3:05:18 PM Page 1 of 1

Figure S6. HR-MS (ESI) data of **II2**.

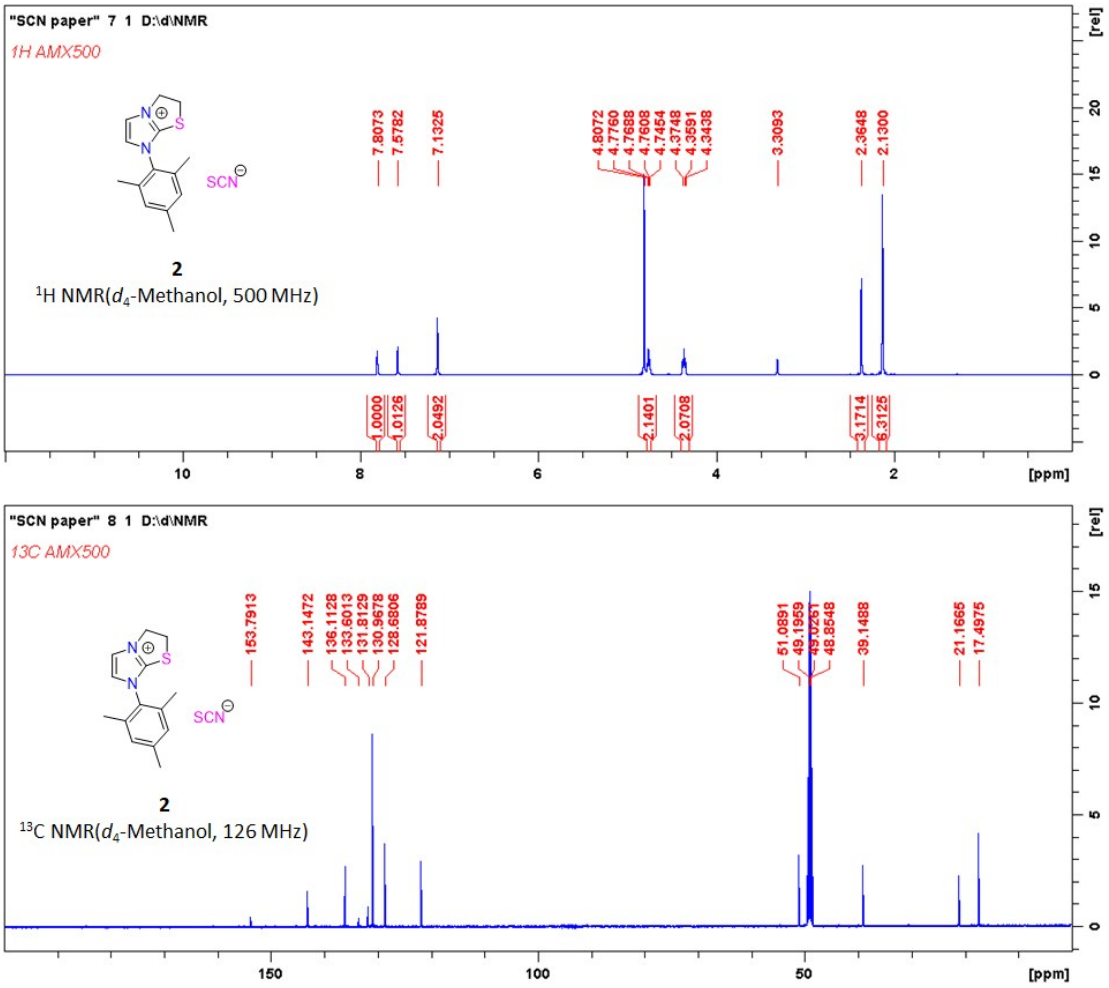


Figure S7. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **2** in CD_3OD.

Mass Spectrum SmartFormula Report

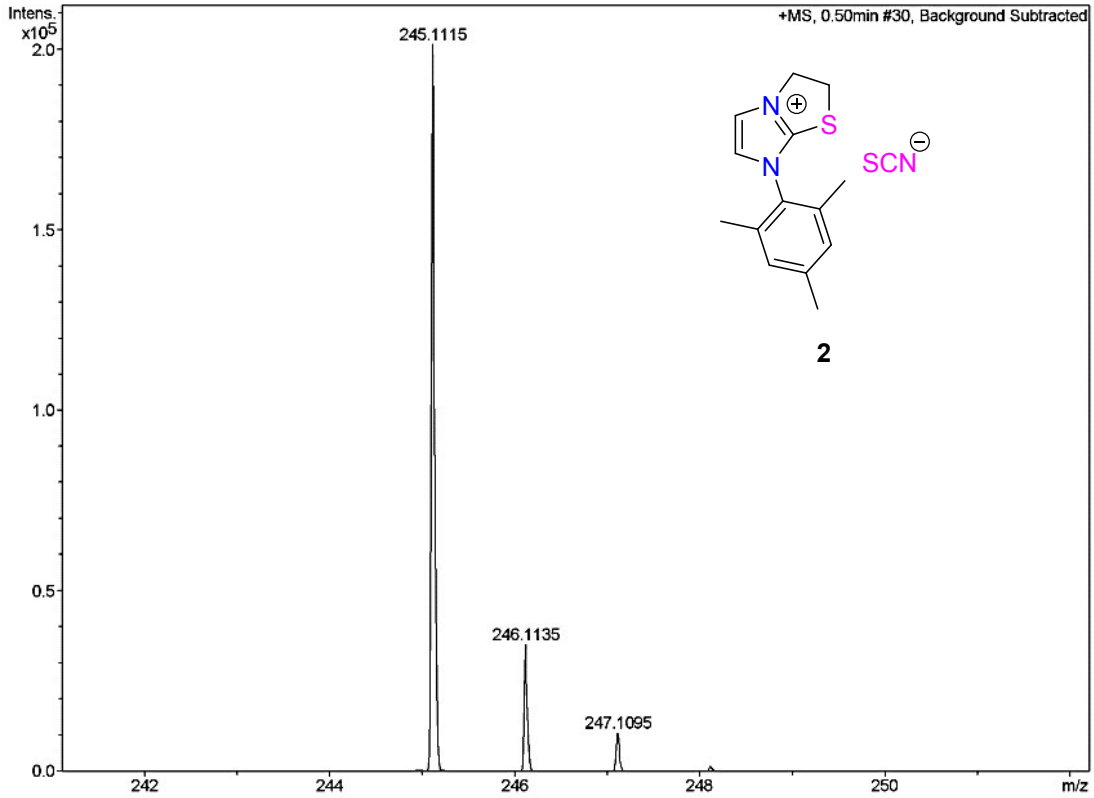
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS2.d	Acquisition Date	1/10/2020 2:43:48 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS2	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
245.1115	1	C 14 H 17 N 2 S	245.1107	-3.4	7.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 2:46:32 PM Page 1 of 1

Figure S8. HR-MS (ESI) data of **2**.

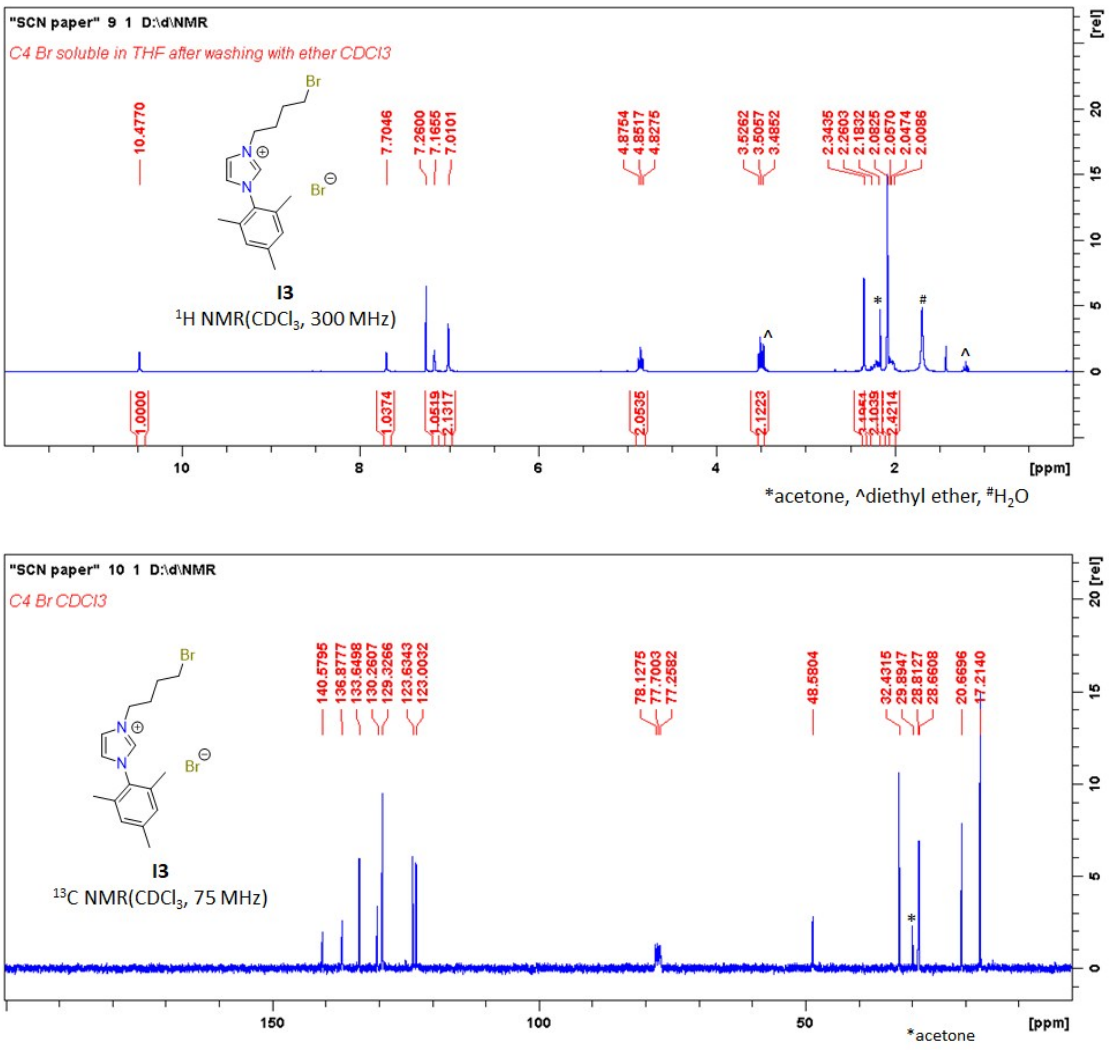


Figure S9. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **I3** in $CDCl_3$.

Mass Spectrum SmartFormula Report

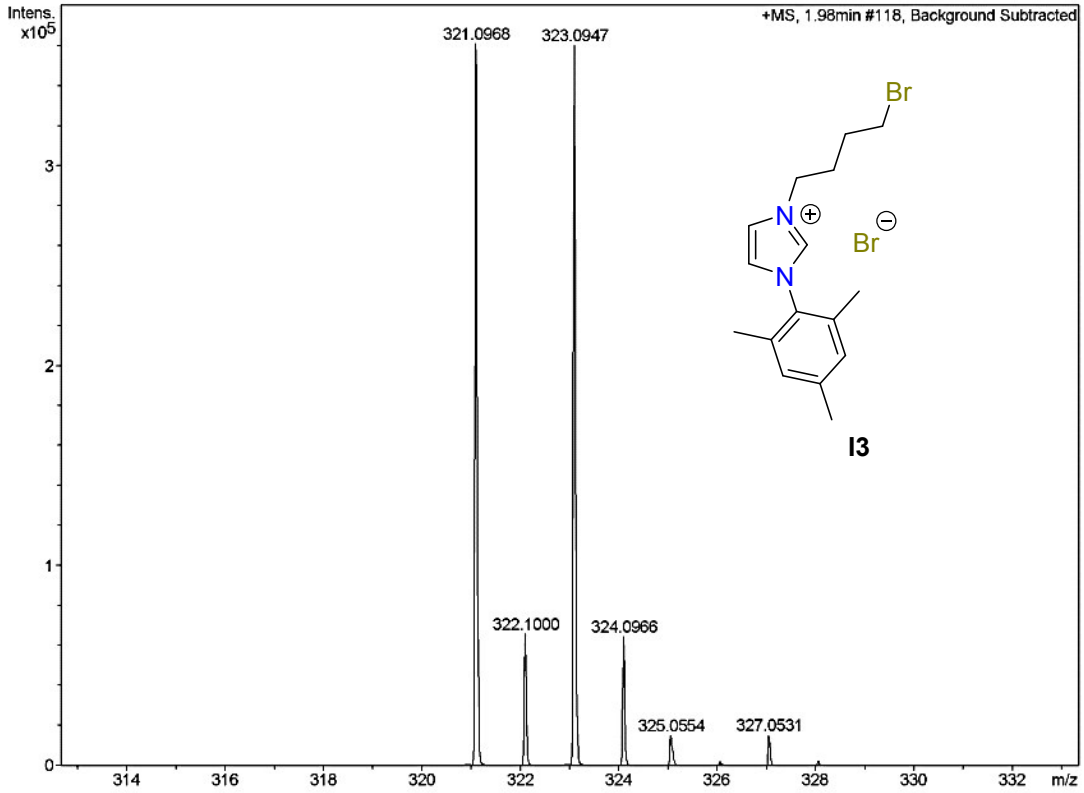
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-I3.d	Acquisition Date	1/22/2020 10:24:28 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-I3	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
321.0968	1	C 16 H 22 Br N 2	321.0961	-2.3	6.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 10:28:47 AM Page 1 of 1

Figure S10. HR-MS (ESI) data of **I3**.

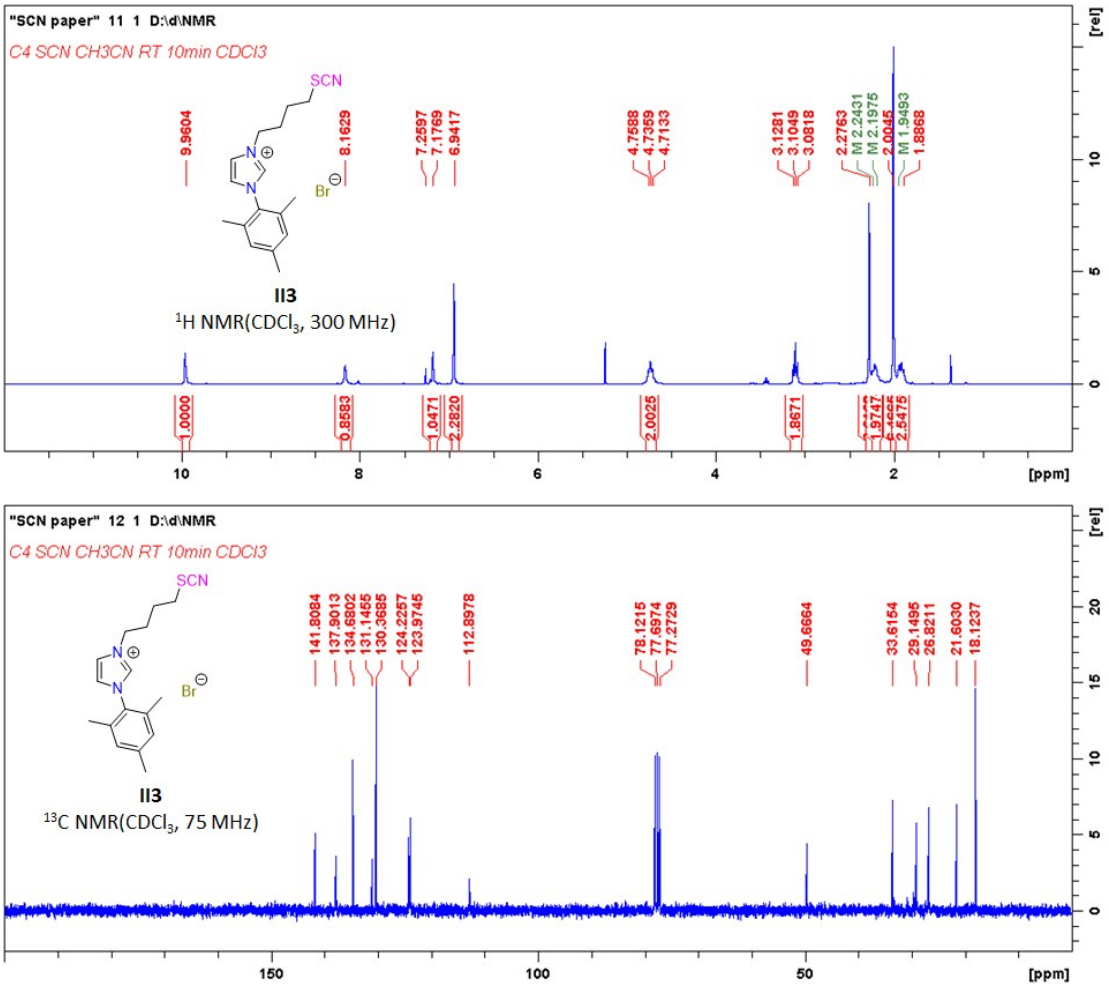


Figure S11. ^{1}H NMR and ^{13}C{^{1}H} NMR spectrum of compound **II3** in $CDCl_3$.

Mass Spectrum SmartFormula Report

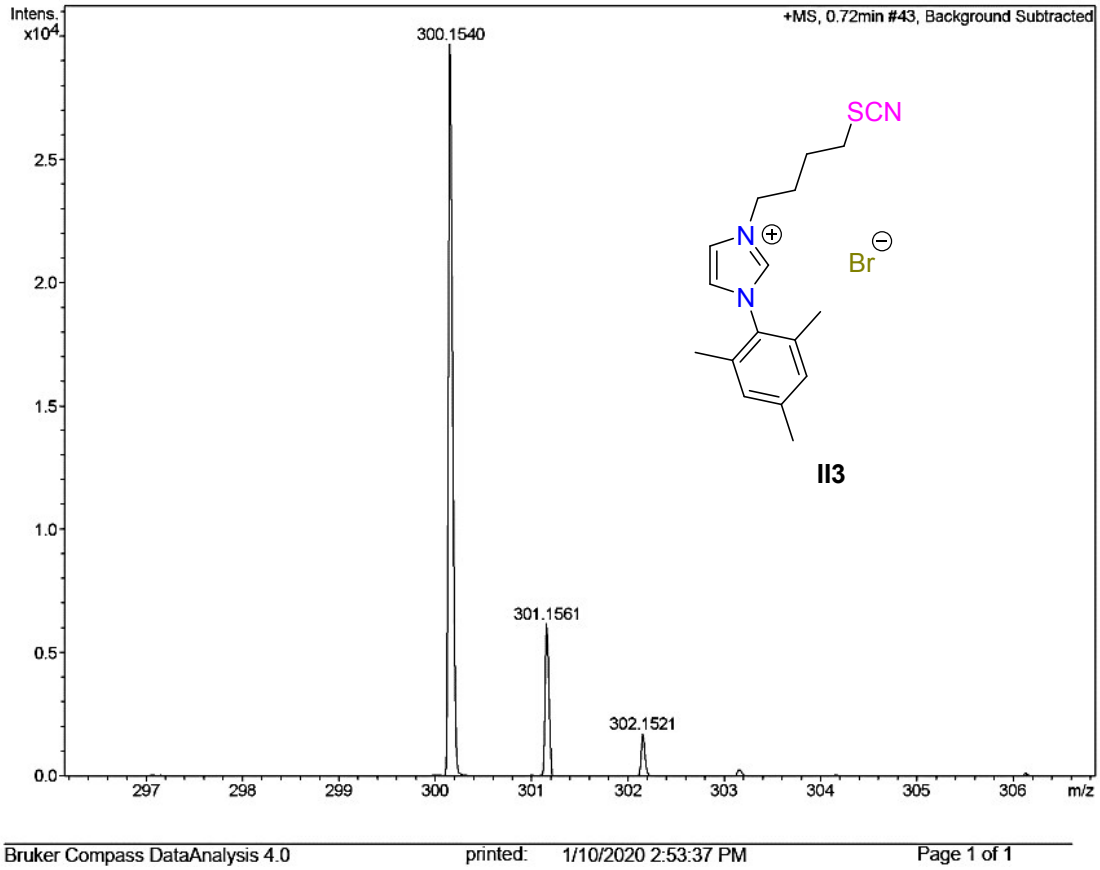
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CSII3-1.d	Acquisition Date	1/10/2020 2:50:46 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CSII3	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
300.1540	1	C 17 H 22 N 3 S	300.1529	-3.8	8.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 2:53:37 PM Page 1 of 1

Figure S12. HR-MS (ESI) data of **II3**.

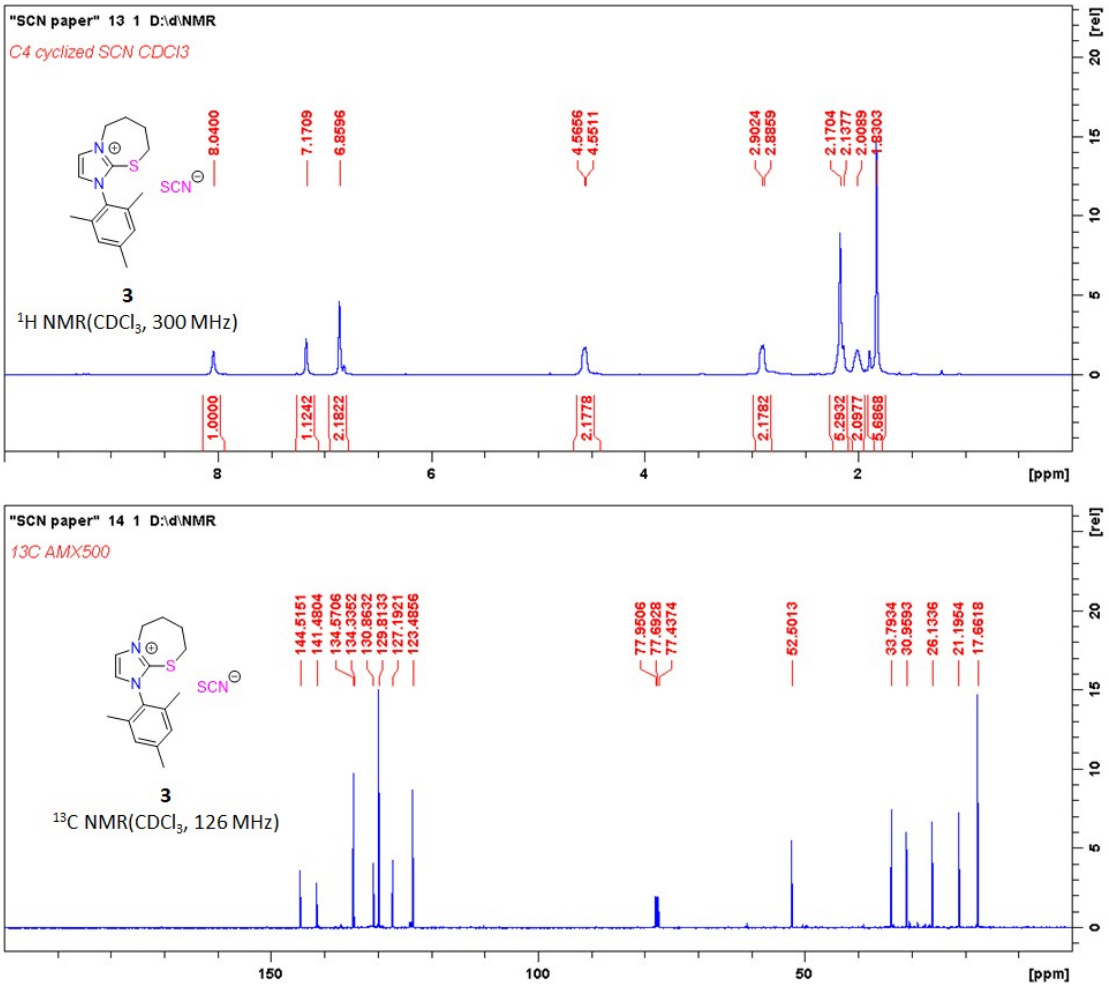


Figure S13. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **3** in $CDCl_3$.

Mass Spectrum SmartFormula Report

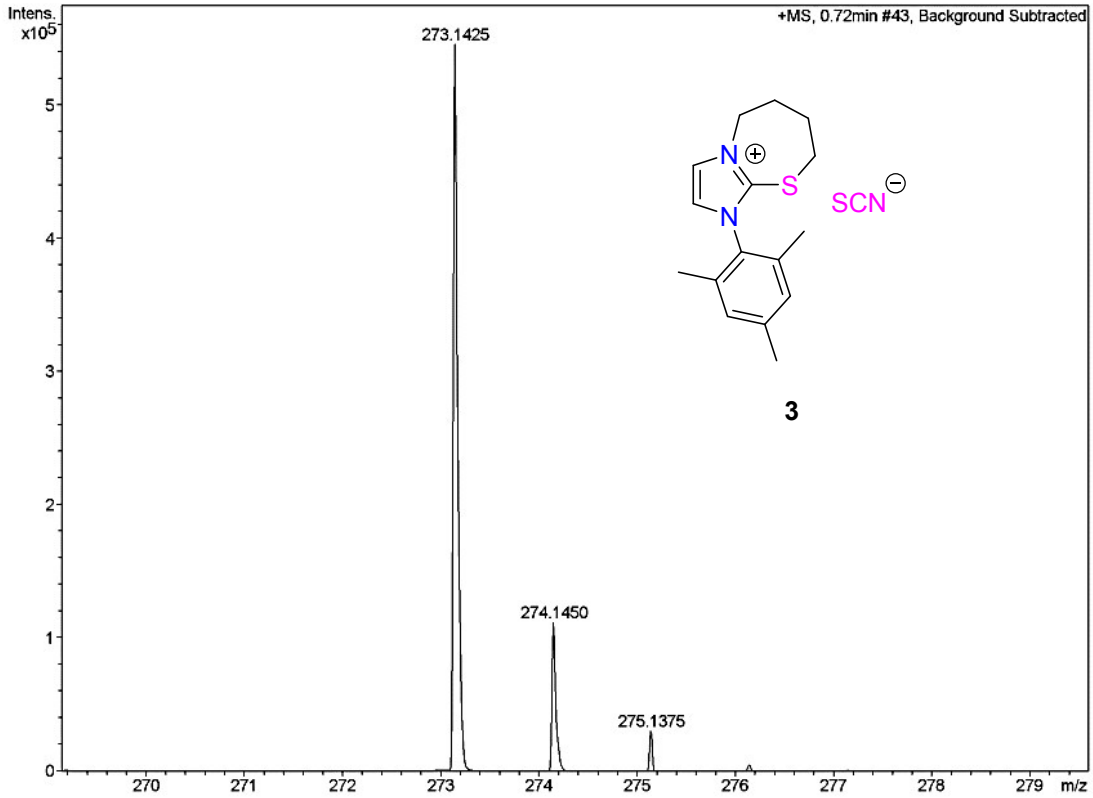
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-3.d	Acquisition Date	1/22/2020 10:30:19 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-3	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
273.1425	1	C 16 H 21 N 2 S	273.1420	-2.0	7.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 10:32:49 AM Page 1 of 1

Figure S14. HR-MS (ESI) data of **3**.

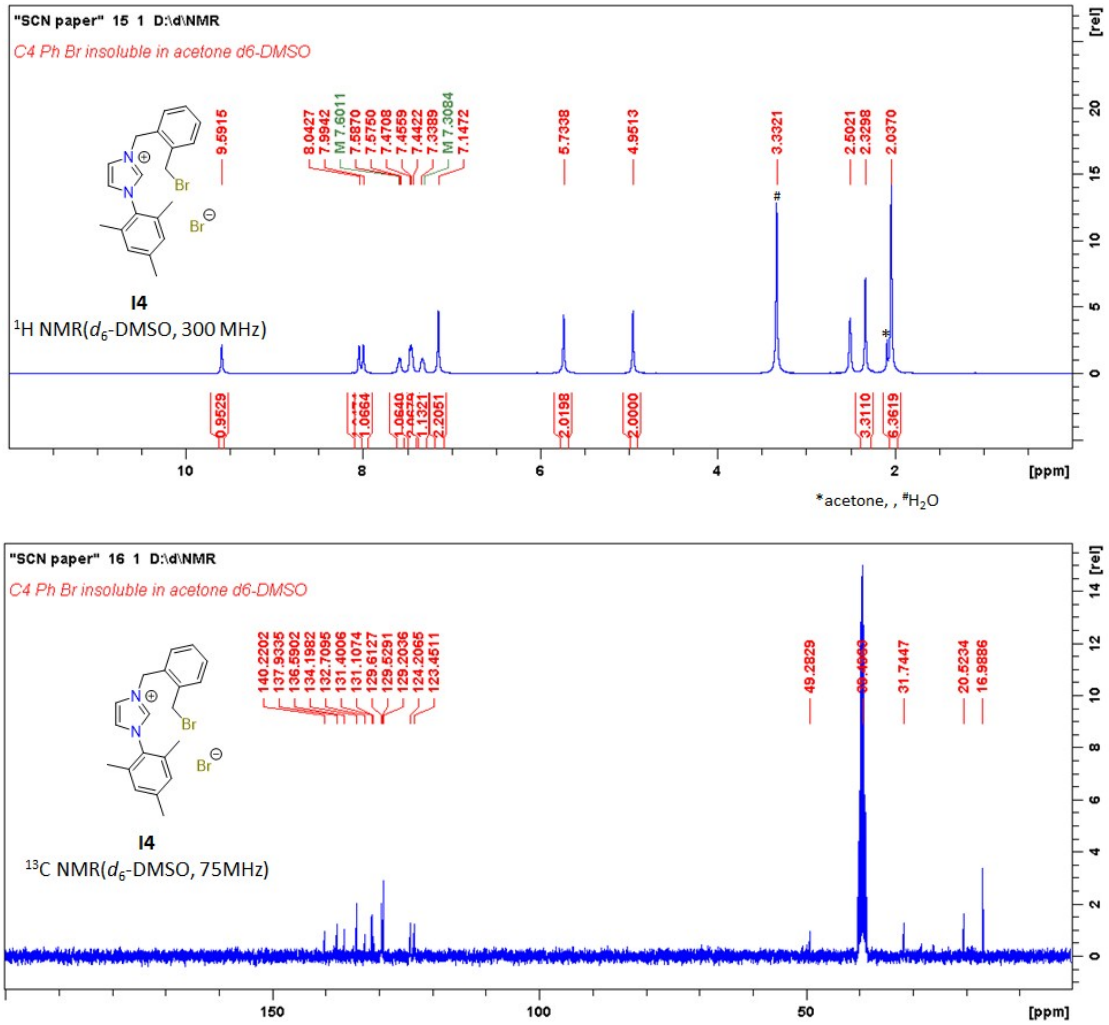


Figure S15. ^{1}H NMR and ^{13}C{^{1}H} NMR spectrum of compound **I4** in d_6-DMSO.

Mass Spectrum SmartFormula Report

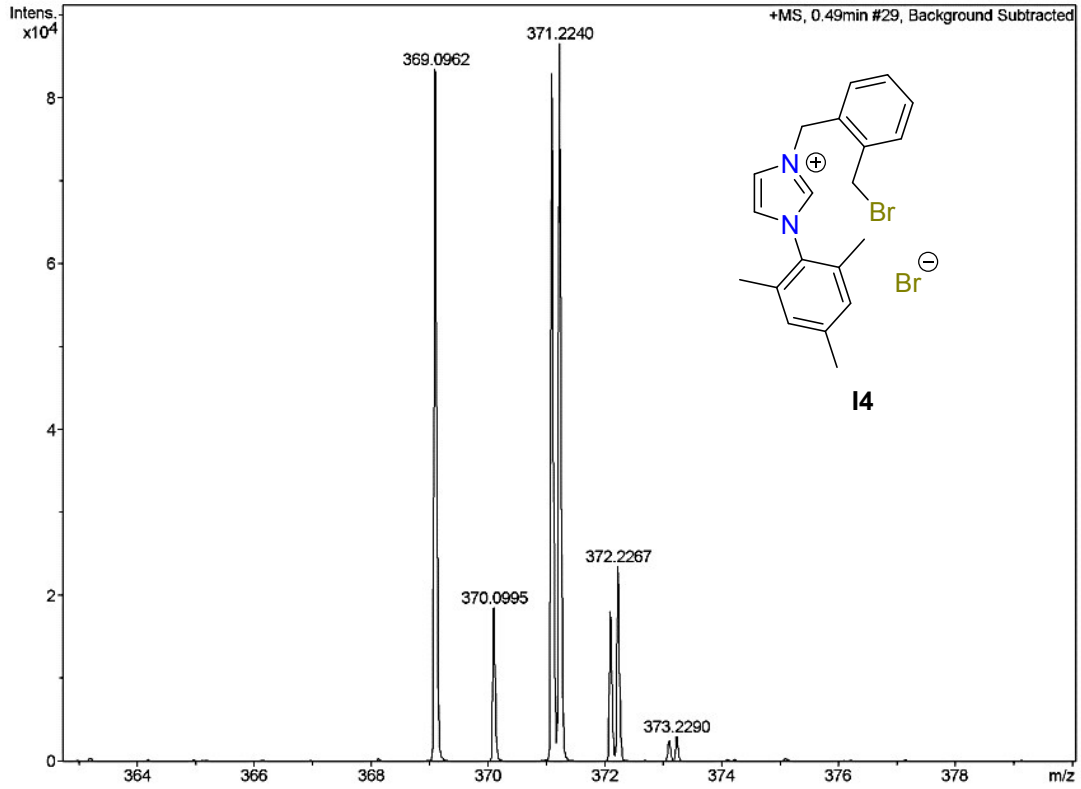
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-I4.d	Acquisition Date	1/22/2020 11:12:18 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-I4	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
369.0962	1	C 20 H 22 Br N 2	369.0961	-0.3	10.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 11:17:08 AM Page 1 of 1

Figure S16. HR-MS (ESI) data of **I4**.

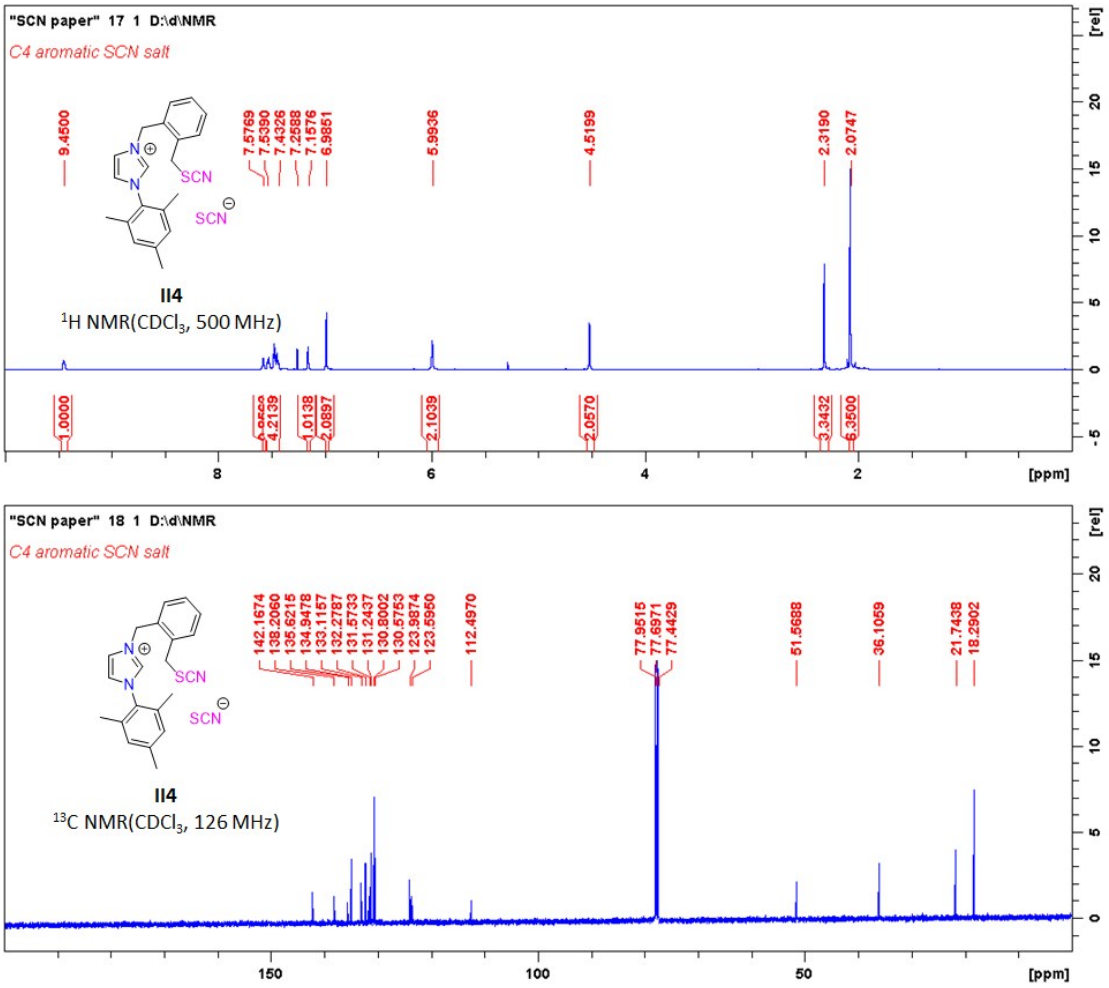


Figure S17. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **II4** in $CDCl_3$.

Mass Spectrum SmartFormula Report

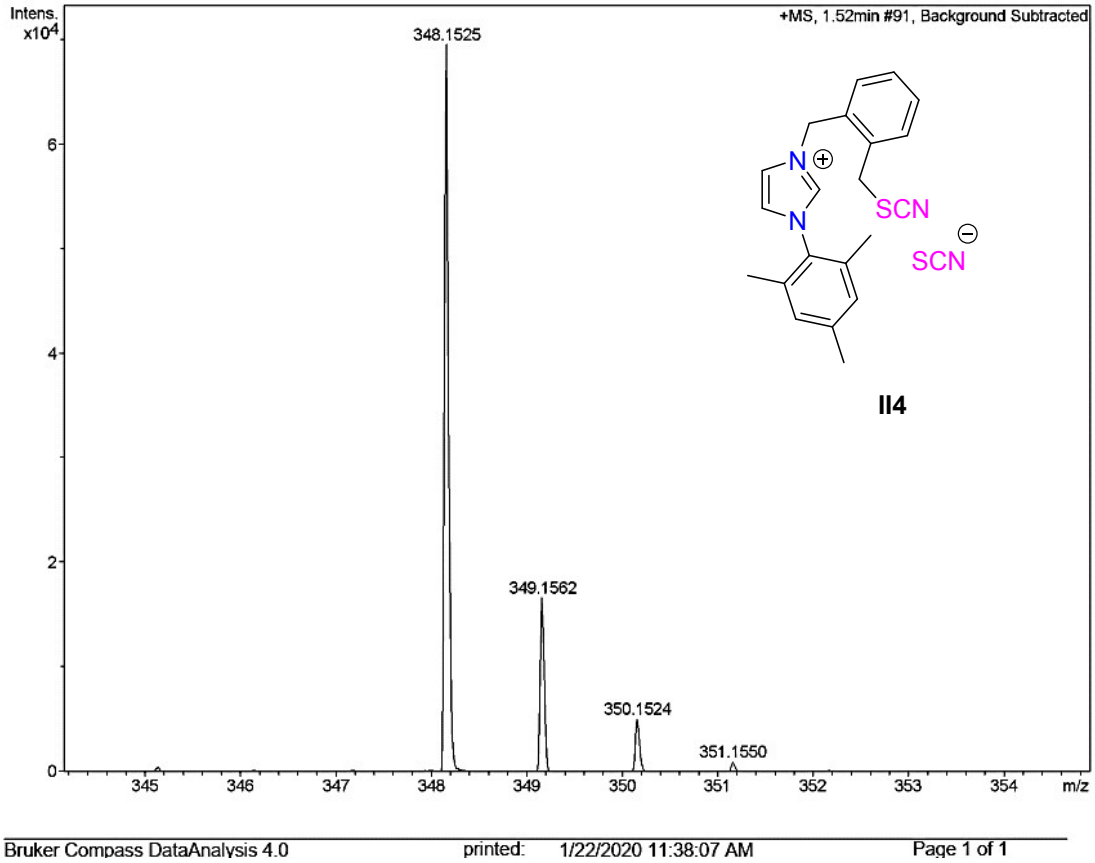
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-II4.d	Acquisition Date	1/22/2020 11:19:09 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-II4	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
348.1525	1	C 21 H 22 N 3 S	348.1529	1.0	12.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 11:38:07 AM Page 1 of 1

Figure S18. HR-MS (ESI) data of **II4**.

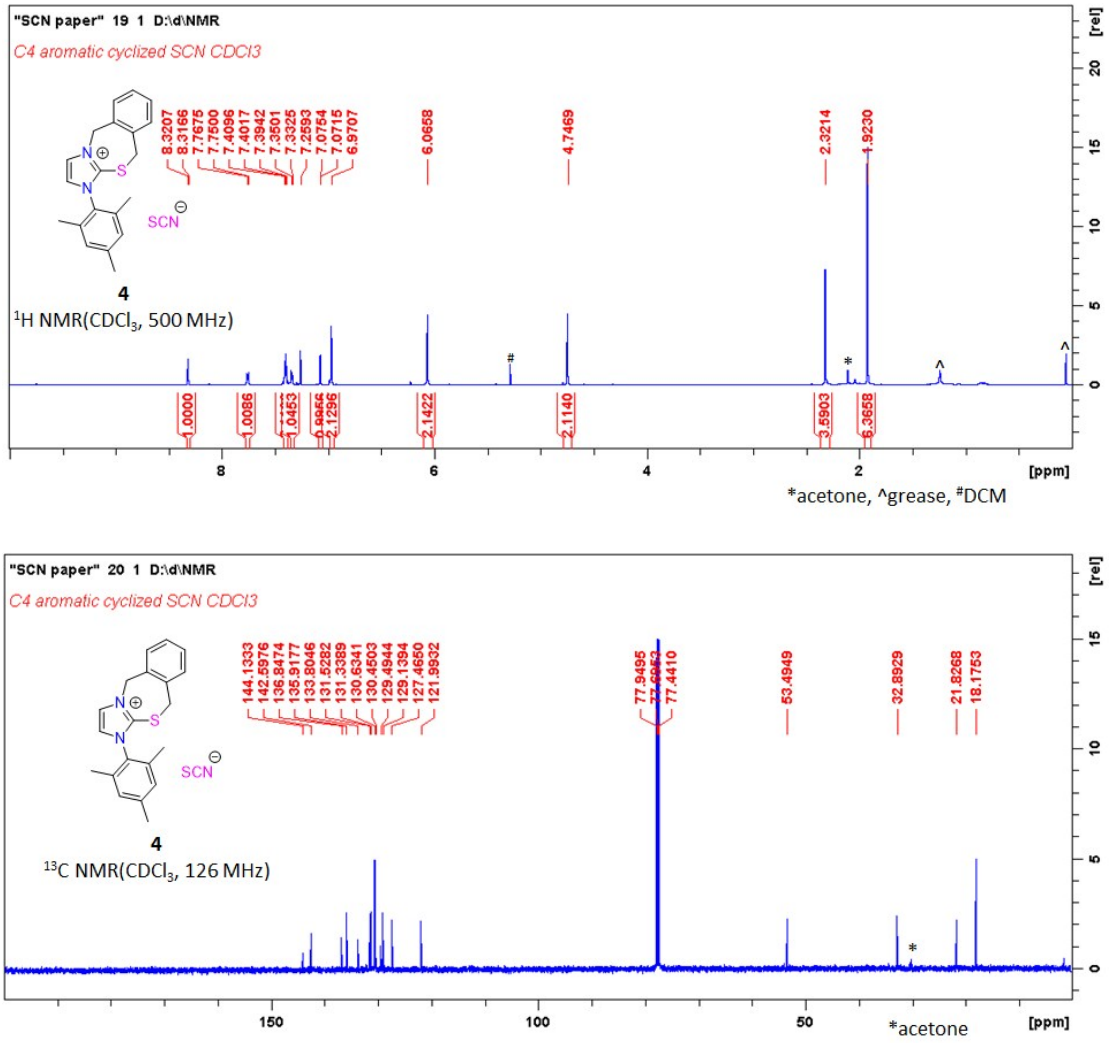


Figure S19. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **4** in $CDCl_3$.

Mass Spectrum SmartFormula Report

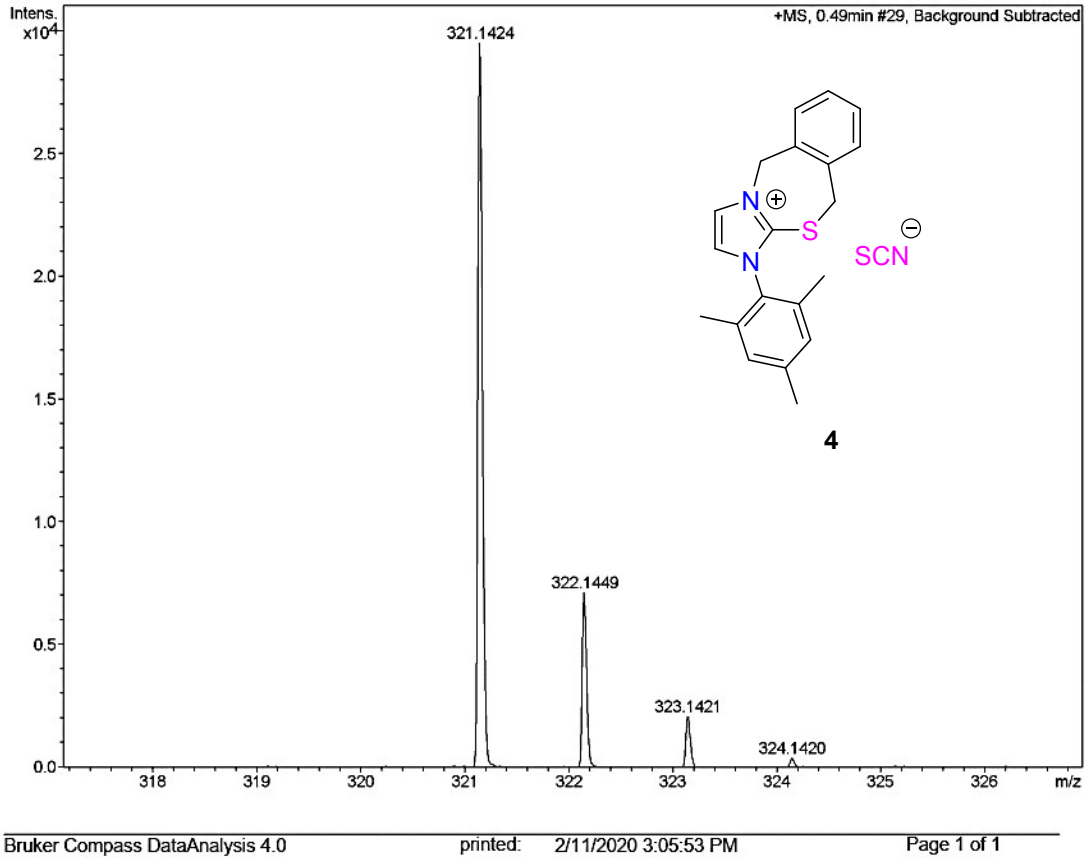
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS4.d	Acquisition Date	1/10/2020 3:14:31 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS4	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
321.1424	1	C 20 H 21 N 2 S	321.1420	-1.4	11.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 2/11/2020 3:05:53 PM Page 1 of 1

Figure S20. HR-MS (ESI) data of **4**.

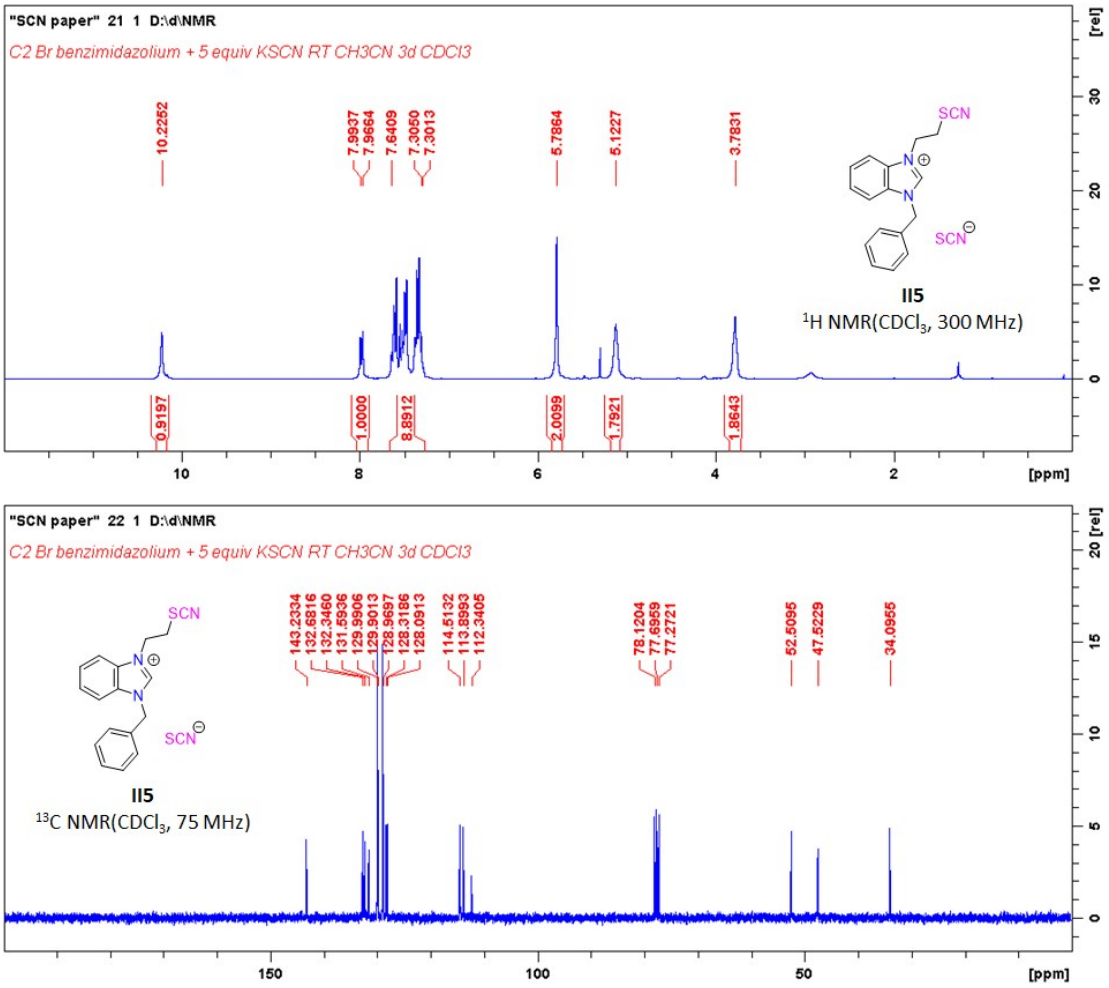


Figure S21. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **II5** in $CDCl_3$.

Mass Spectrum SmartFormula Report

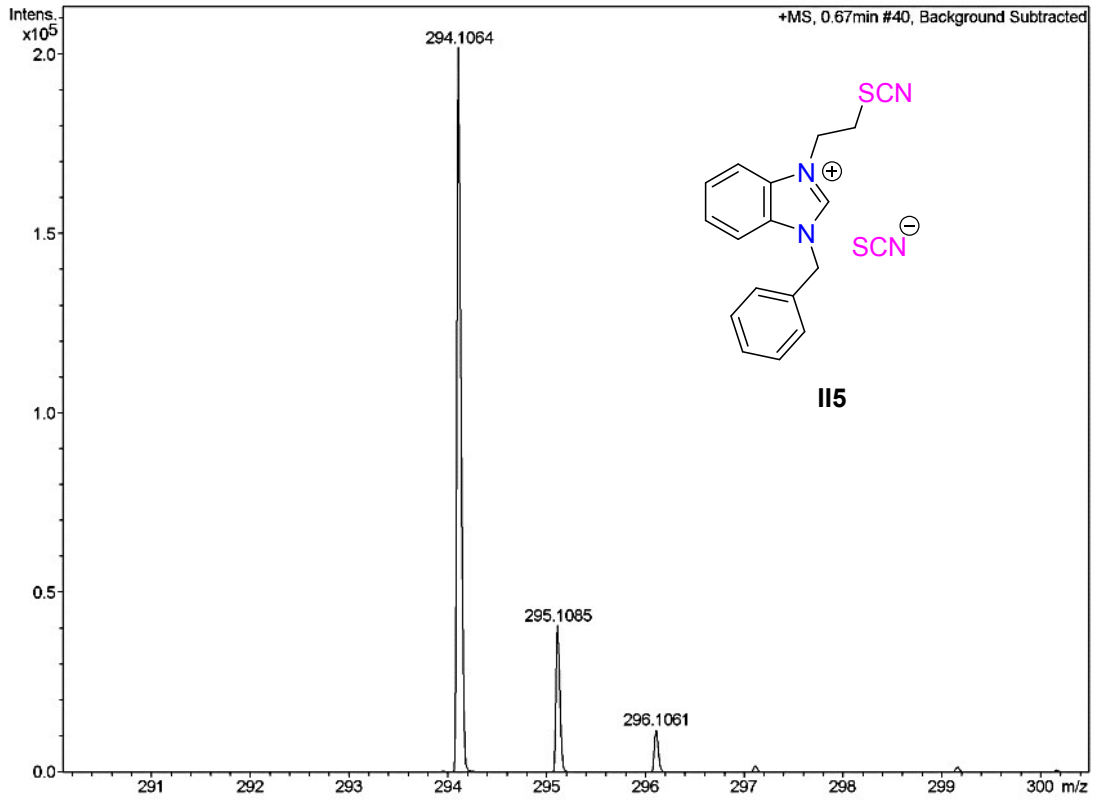
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CSII5.d	Acquisition Date	1/10/2020 3:04:59 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CSII5	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
294.1064	1	C 17 H 16 N 3 S	294.1059	-1.6	11.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 3:07:57 PM Page 1 of 1

Figure S22. HR-MS (ESI) data of **II5**.

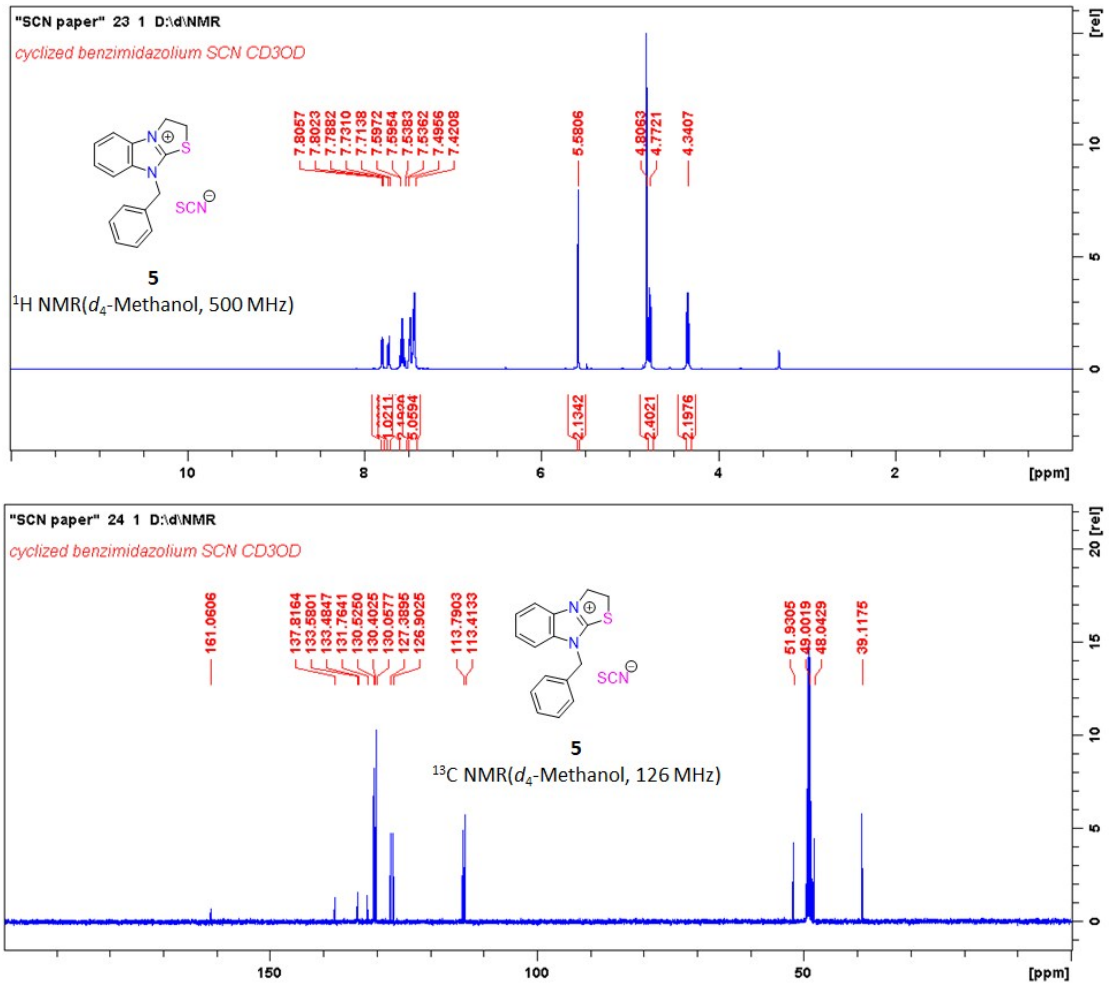


Figure S23. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **5** in CD_3OD.

Mass Spectrum SmartFormula Report

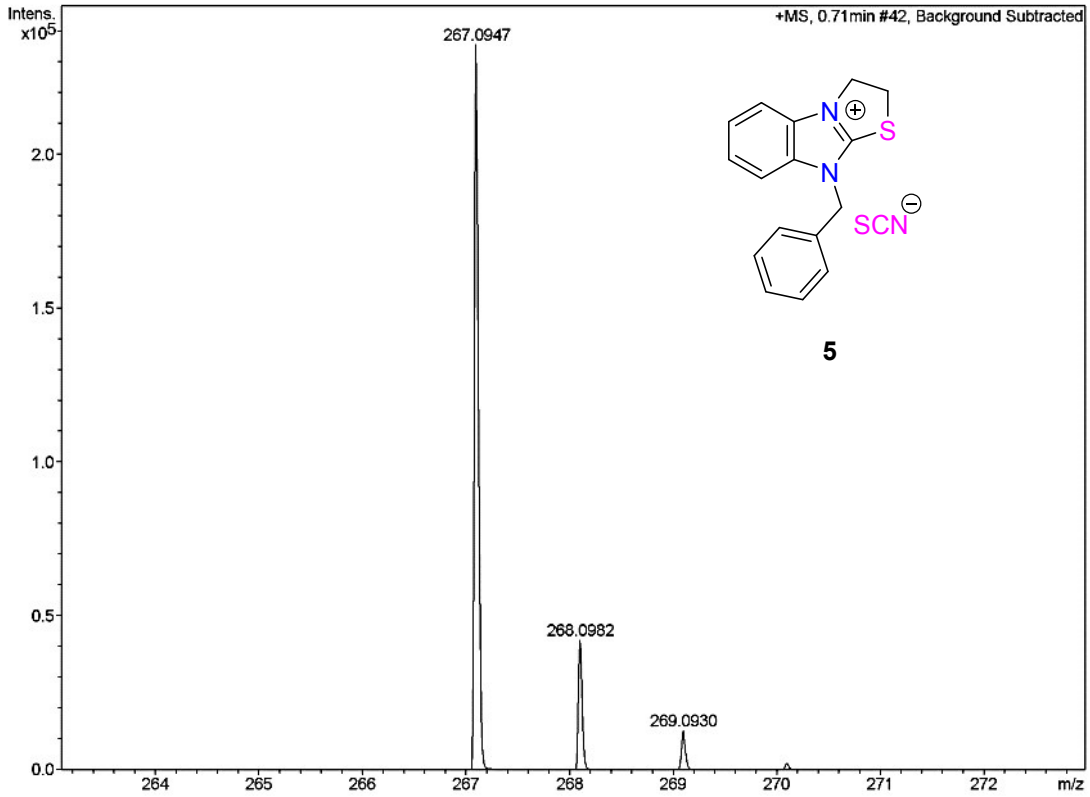
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS5.d	Acquisition Date	1/10/2020 3:19:52 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS5	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
267.0947	1	C 16 H 15 N 2 S	267.0950	1.3	10.5	even	ok



5

Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 3:21:54 PM Page 1 of 1

Figure S24. HR-MS (ESI) data of **5**.

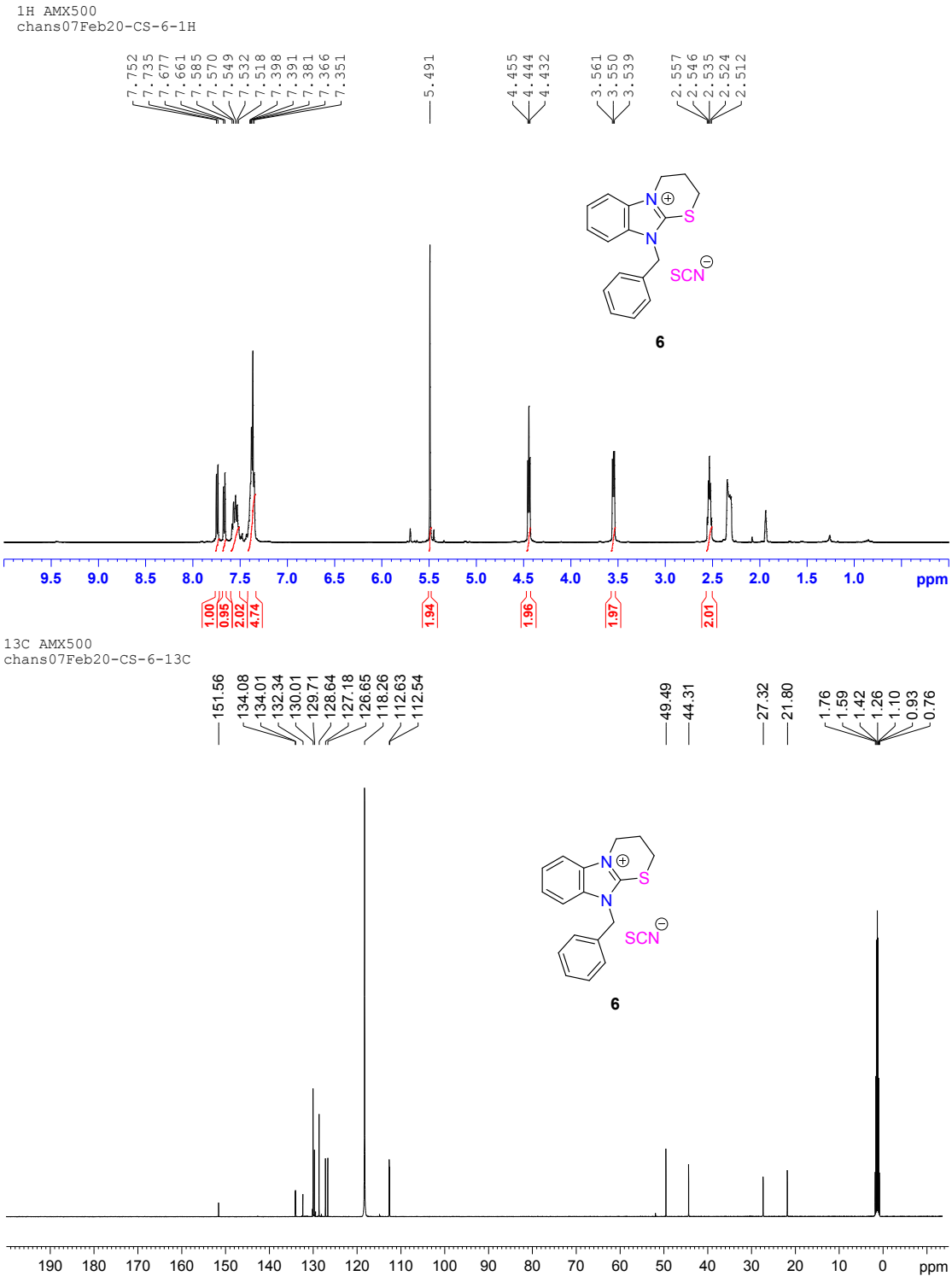


Figure S25. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** in CD_3CN.

Mass Spectrum SmartFormula Report

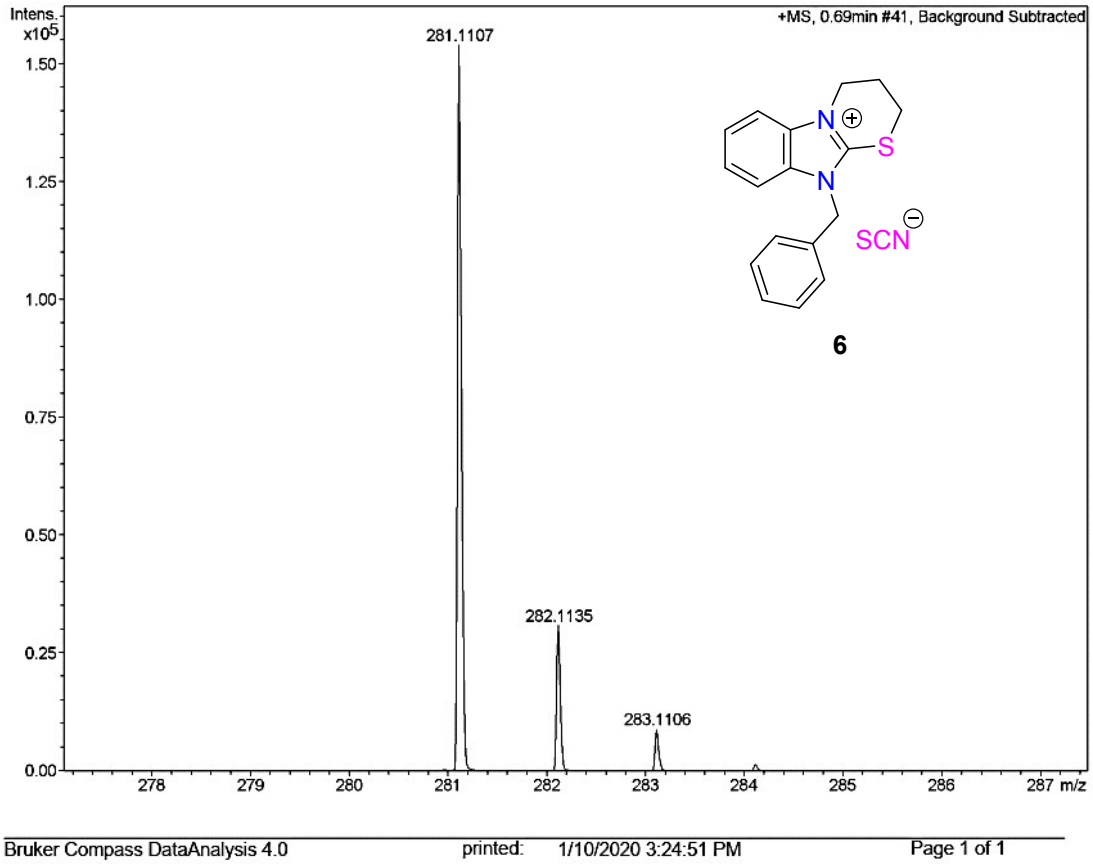
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS6.d	Acquisition Date	1/10/2020 3:22:51 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS6	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
281.1107	1	C 17 H 17 N 2 S	281.1107	-0.1	10.5	even	ok



6

Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 3:24:51 PM Page 1 of 1

Figure S26. HR-MS (ESI) data of **6**.

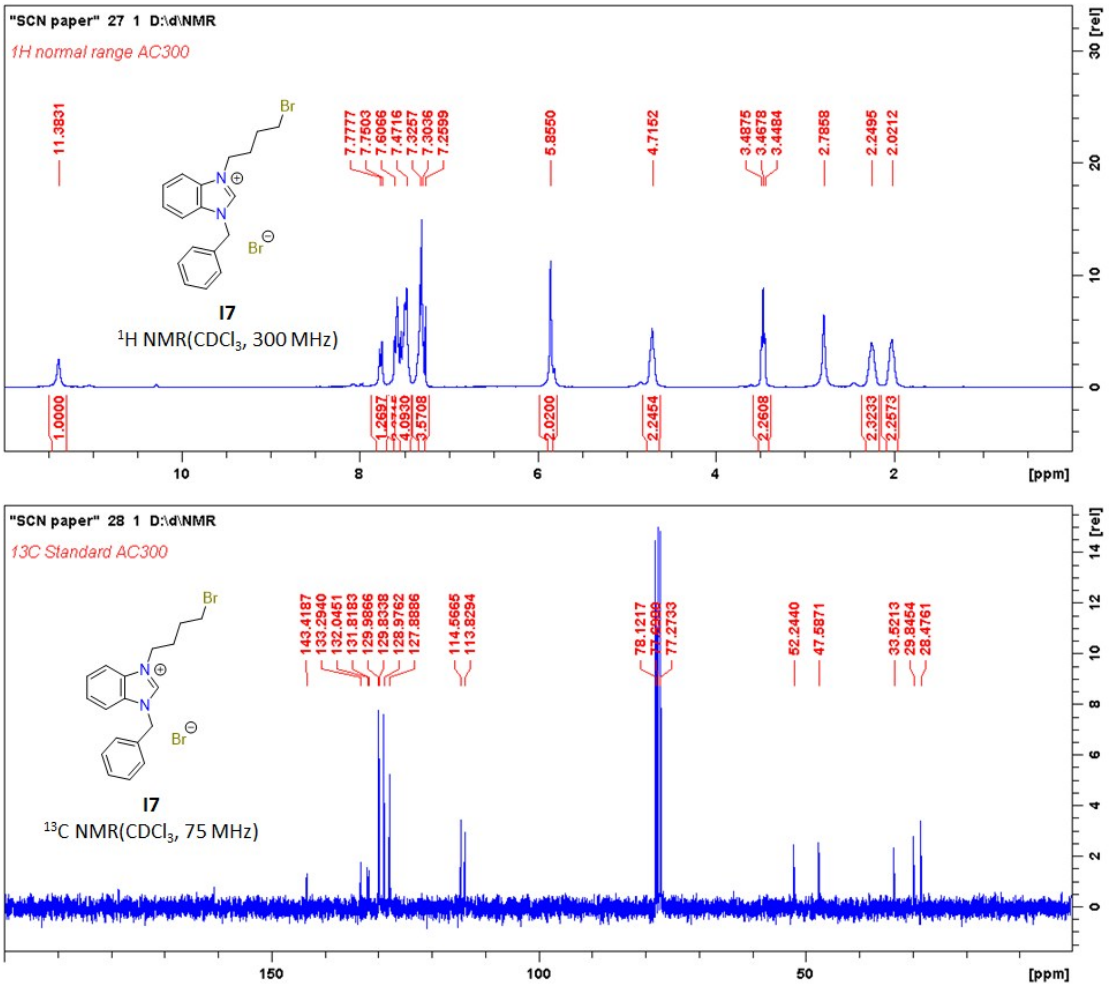


Figure S27. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **I7** in $CDCl_3$.

Mass Spectrum SmartFormula Report

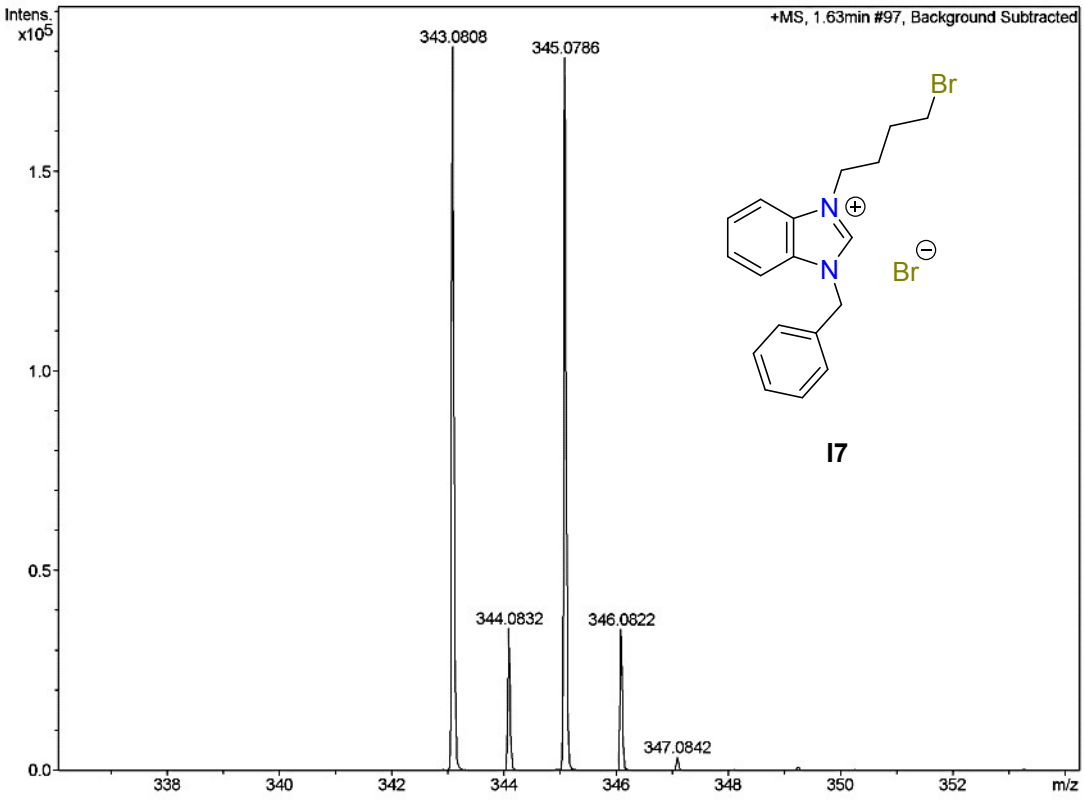
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-I7-1.d	Acquisition Date	1/22/2020 12:07:28 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-I7	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
343.0808	1	C 18 H 20 Br N 2	343.0804	-1.1	9.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 12:11:28 PM Page 1 of 1

Figure S28. HR-MS (ESI) data of **I7**.

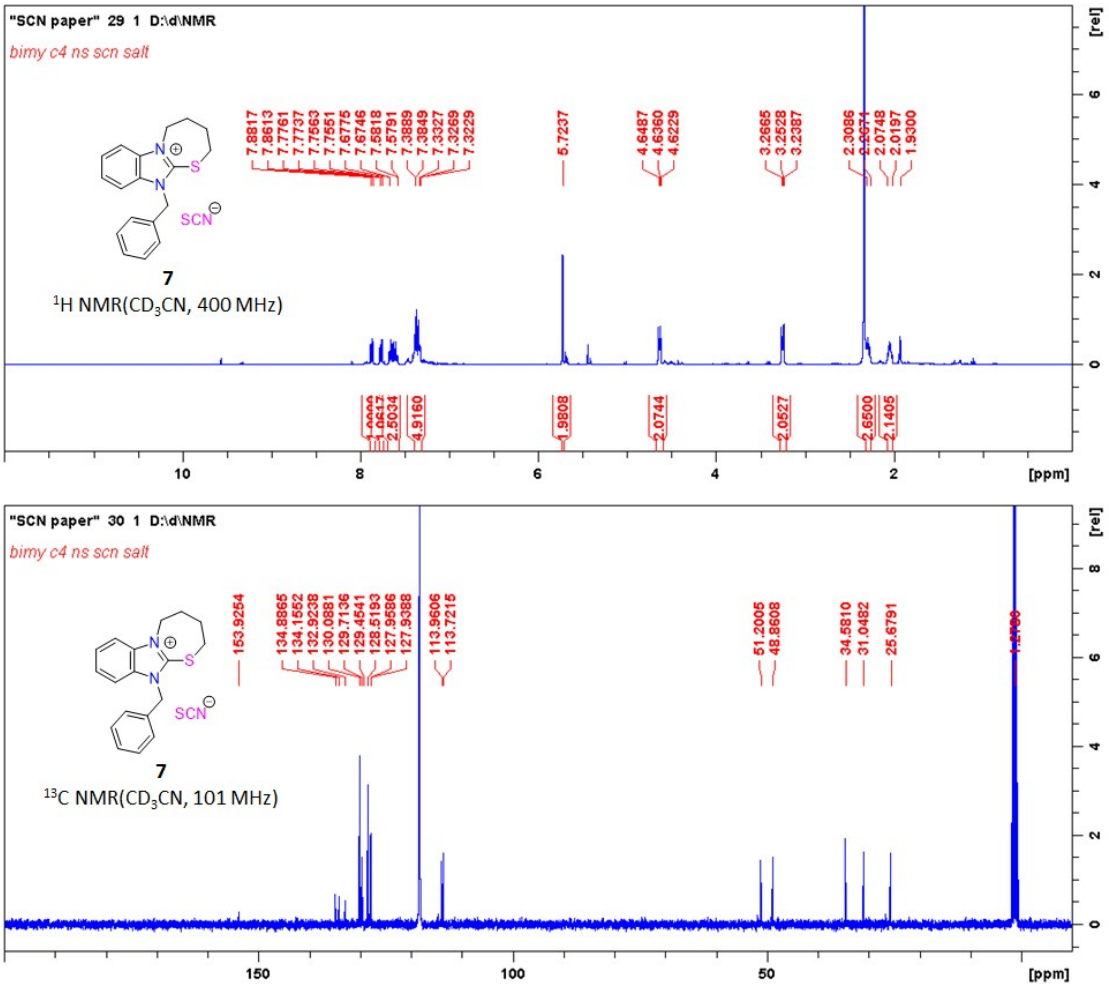


Figure S29. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **7** in CD_3CN.

Mass Spectrum SmartFormula Report

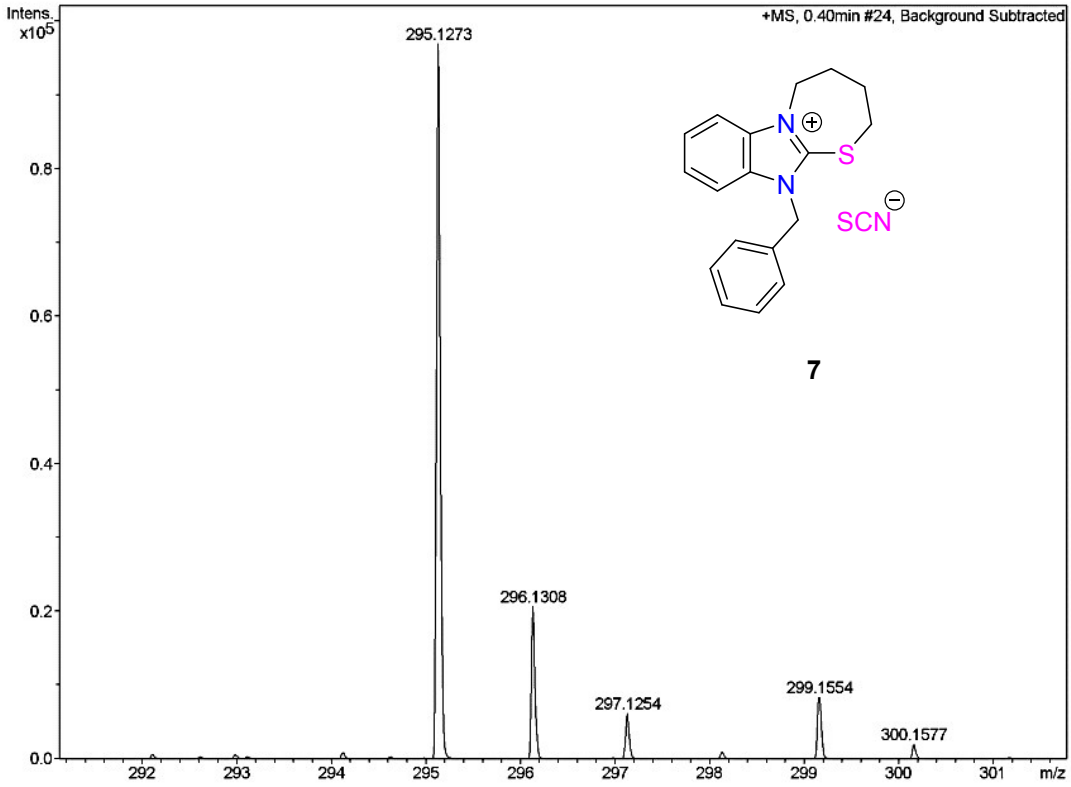
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202002\0206\CS-7.d	Acquisition Date	2/6/2020 2:39:51 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-7	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
295.1273	1	C 18 H 19 N 2 S	295.1263	-3.3	10.5	even	ok



7

Bruker Compass DataAnalysis 4.0 printed: 2/6/2020 2:45:31 PM Page 1 of 1

Figure S30. HR-MS (ESI) data of **7**.

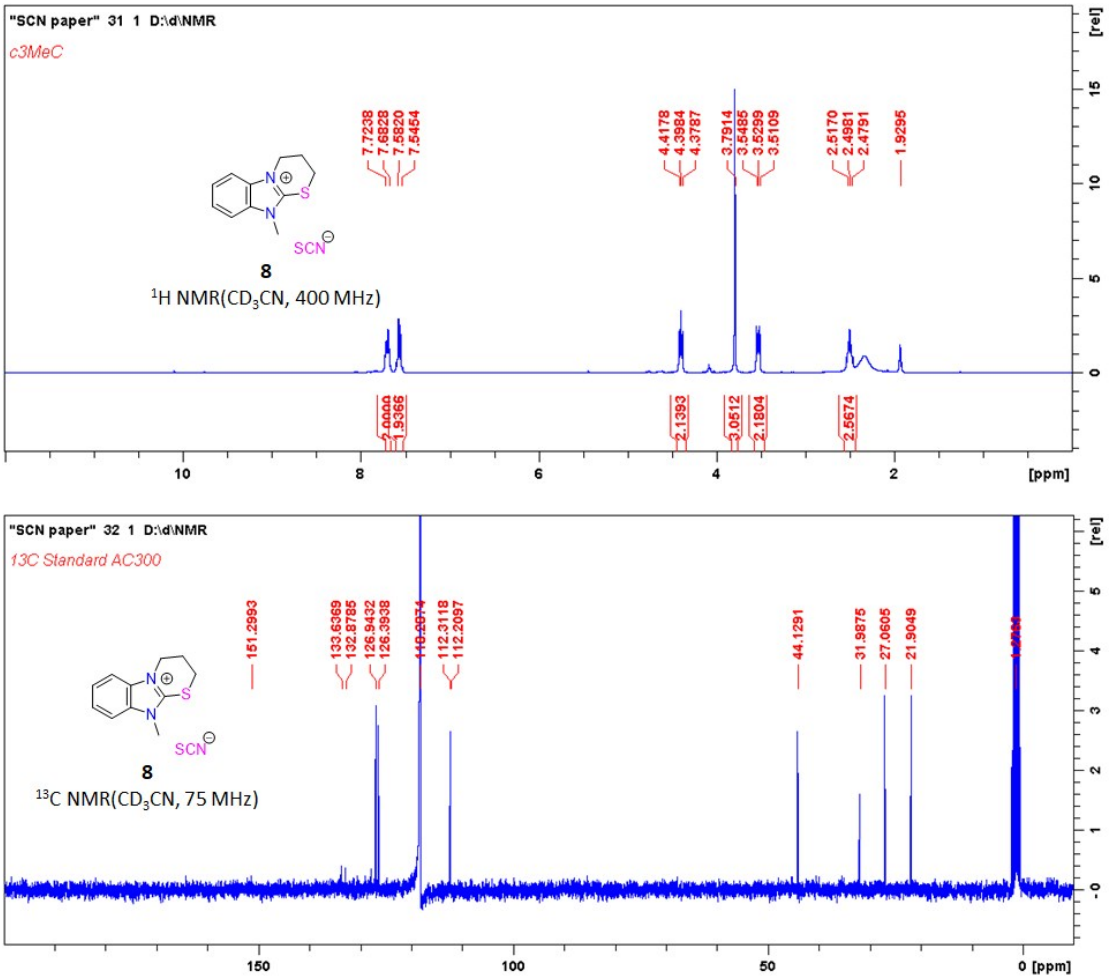


Figure S31. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **8** in CD_3CN.

Mass Spectrum SmartFormula Report

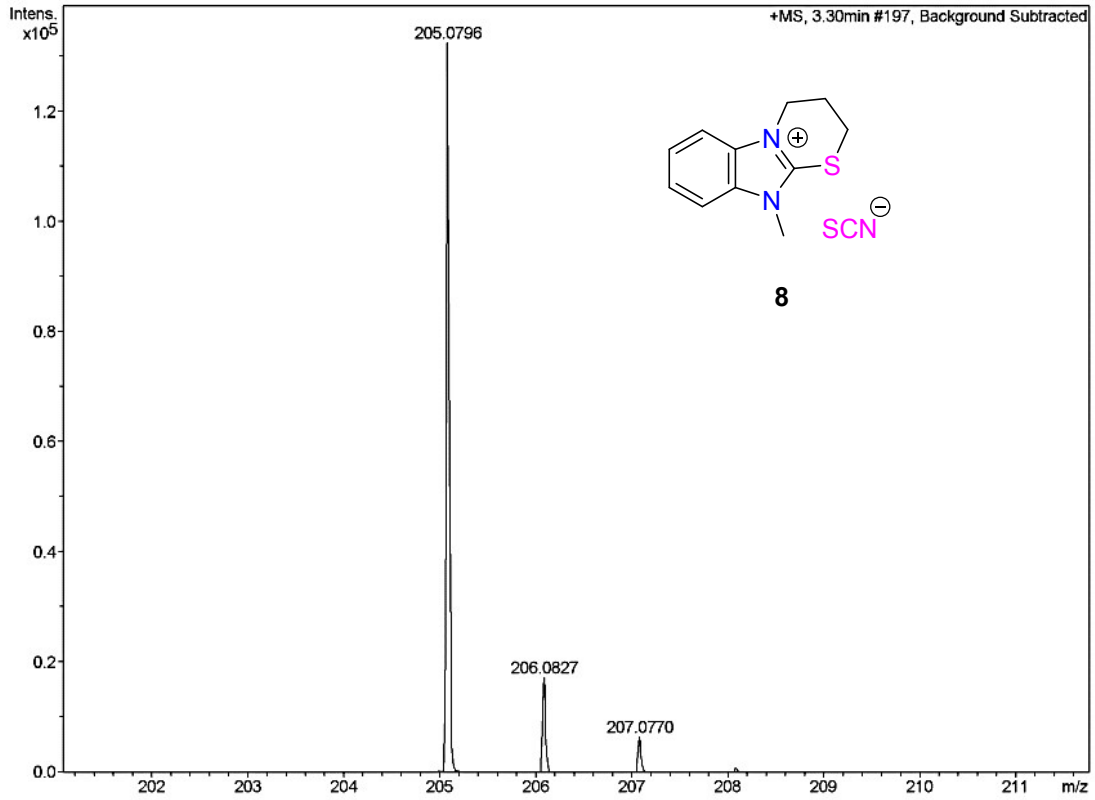
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202002\0206\CS-8.d	Acquisition Date	2/6/2020 2:46:48 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-8	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
205.0796	1	C 11 H 13 N 2 S	205.0794	-1.1	6.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 2/6/2020 2:51:46 PM Page 1 of 1

Figure S32. HR-MS (ESI) data of **8**.

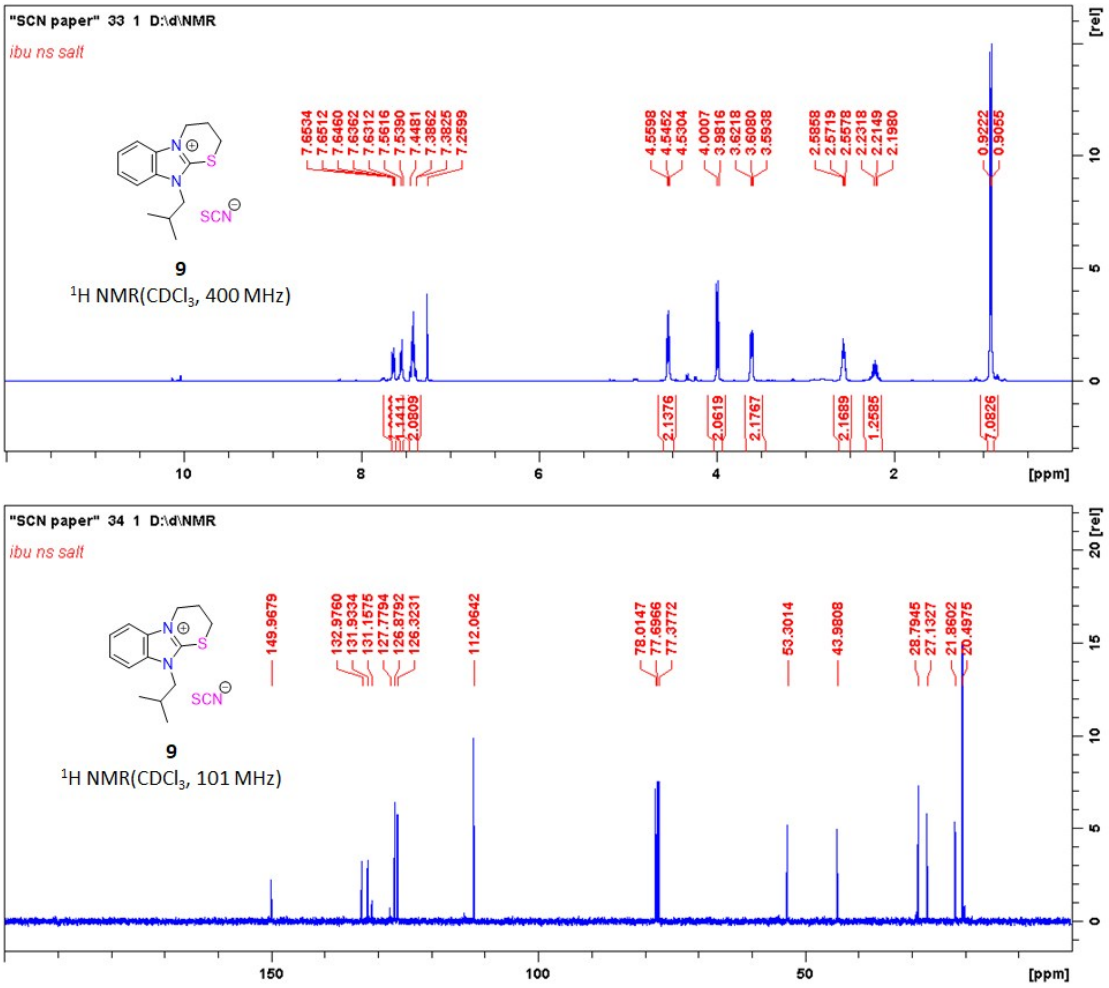


Figure S33. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **9** in $CDCl_3$.

Mass Spectrum SmartFormula Report

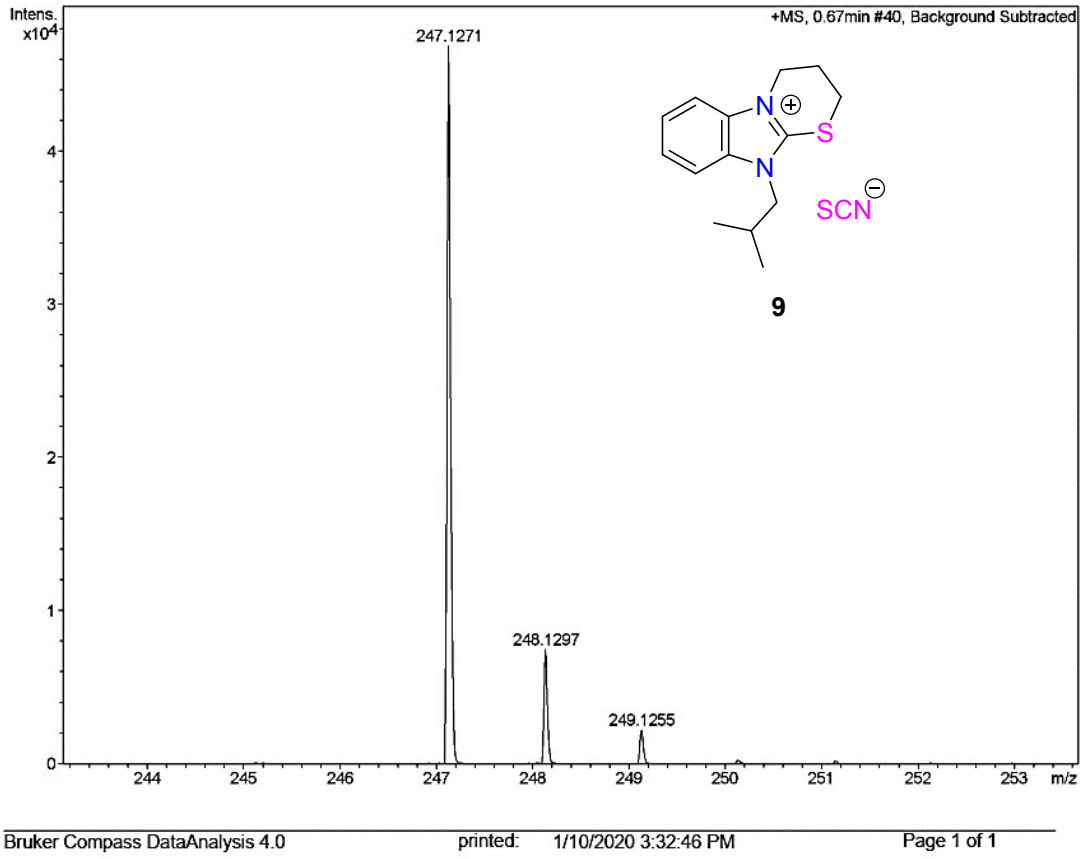
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS9-1.d	Acquisition Date	1/10/2020 3:28:56 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS9	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
247.1271	1	C 14 H 19 N 2 S	247.1263	-2.9	6.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 3:32:46 PM Page 1 of 1

Figure S34. HR-MS (ESI) data of **9**.

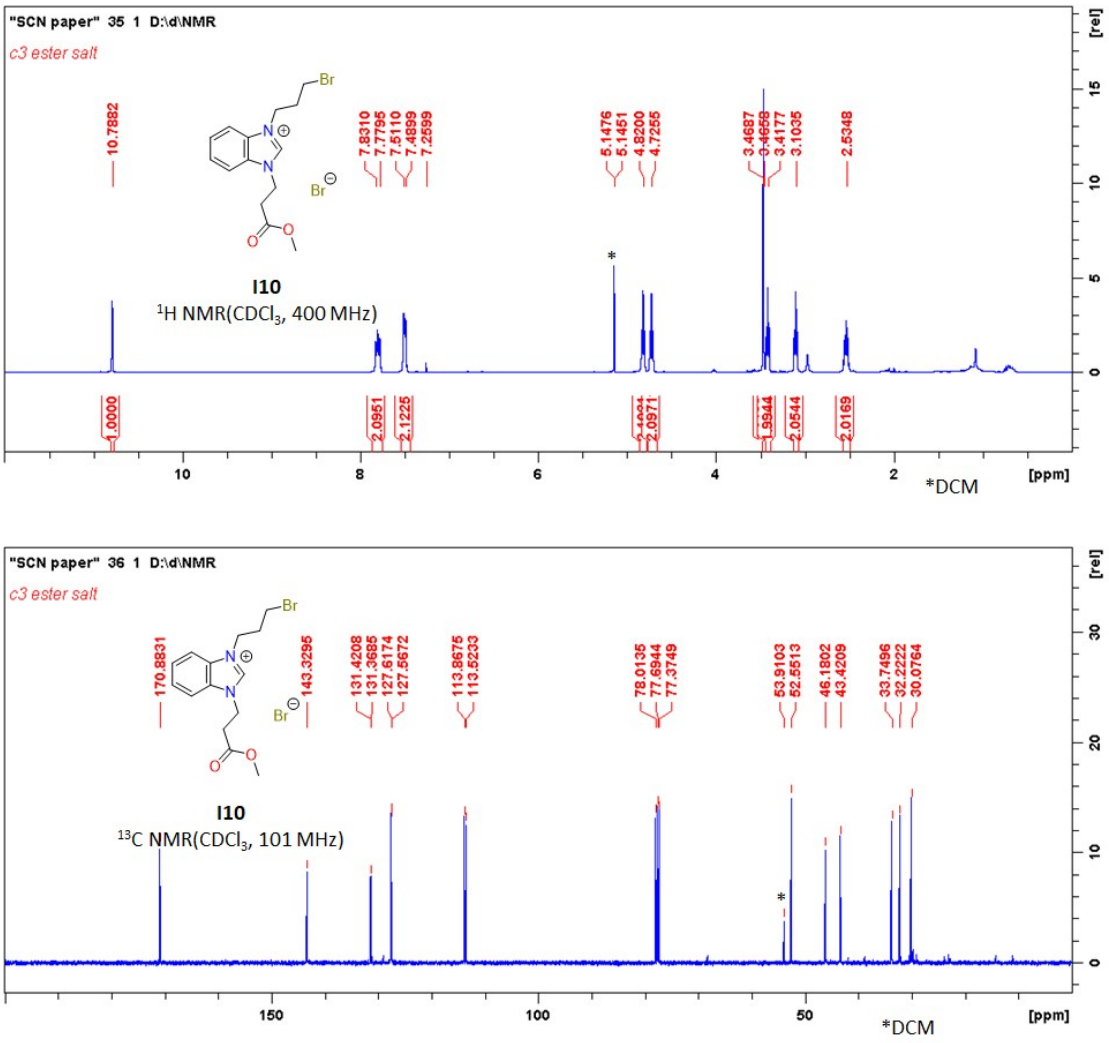


Figure S35. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **I10** in $CDCl_3$.

Mass Spectrum SmartFormula Report

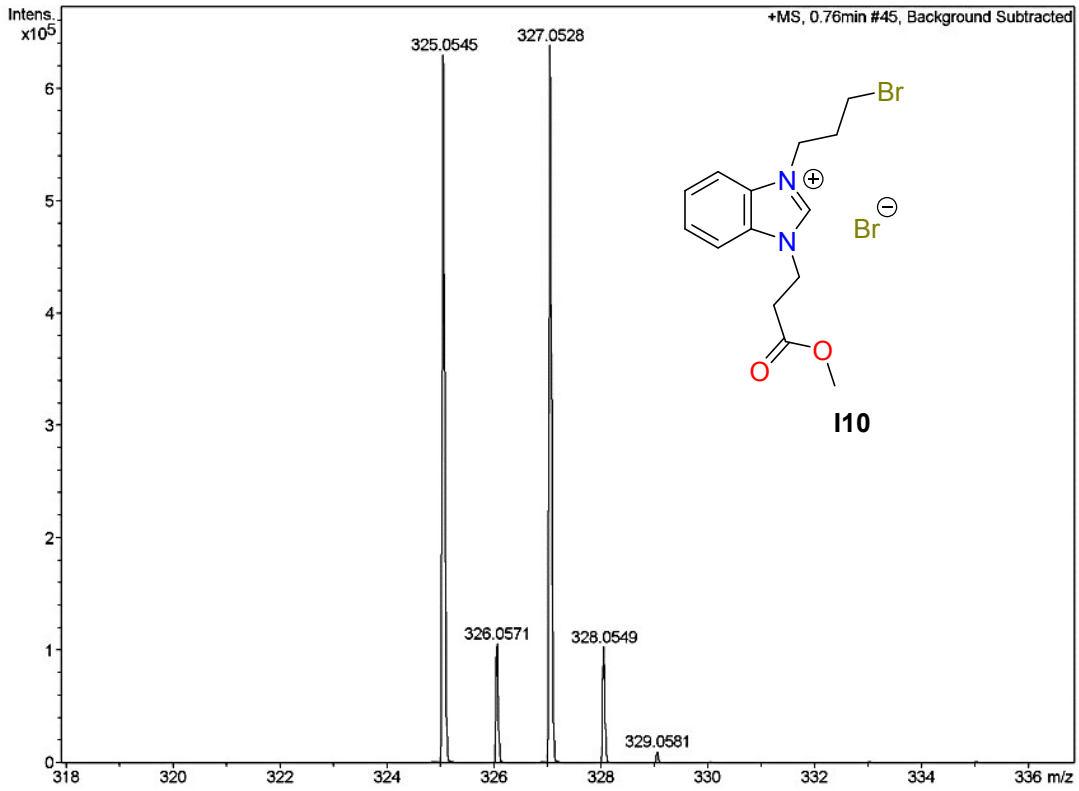
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-I10.d	Acquisition Date	1/22/2020 11:39:31 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-I10	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
325.0545	1	C 14 H 18 Br N 2 O 2	325.0546	0.5	6.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 11:42:27 AM Page 1 of 1

Figure S36. HR-MS (ESI) data of **I10**.

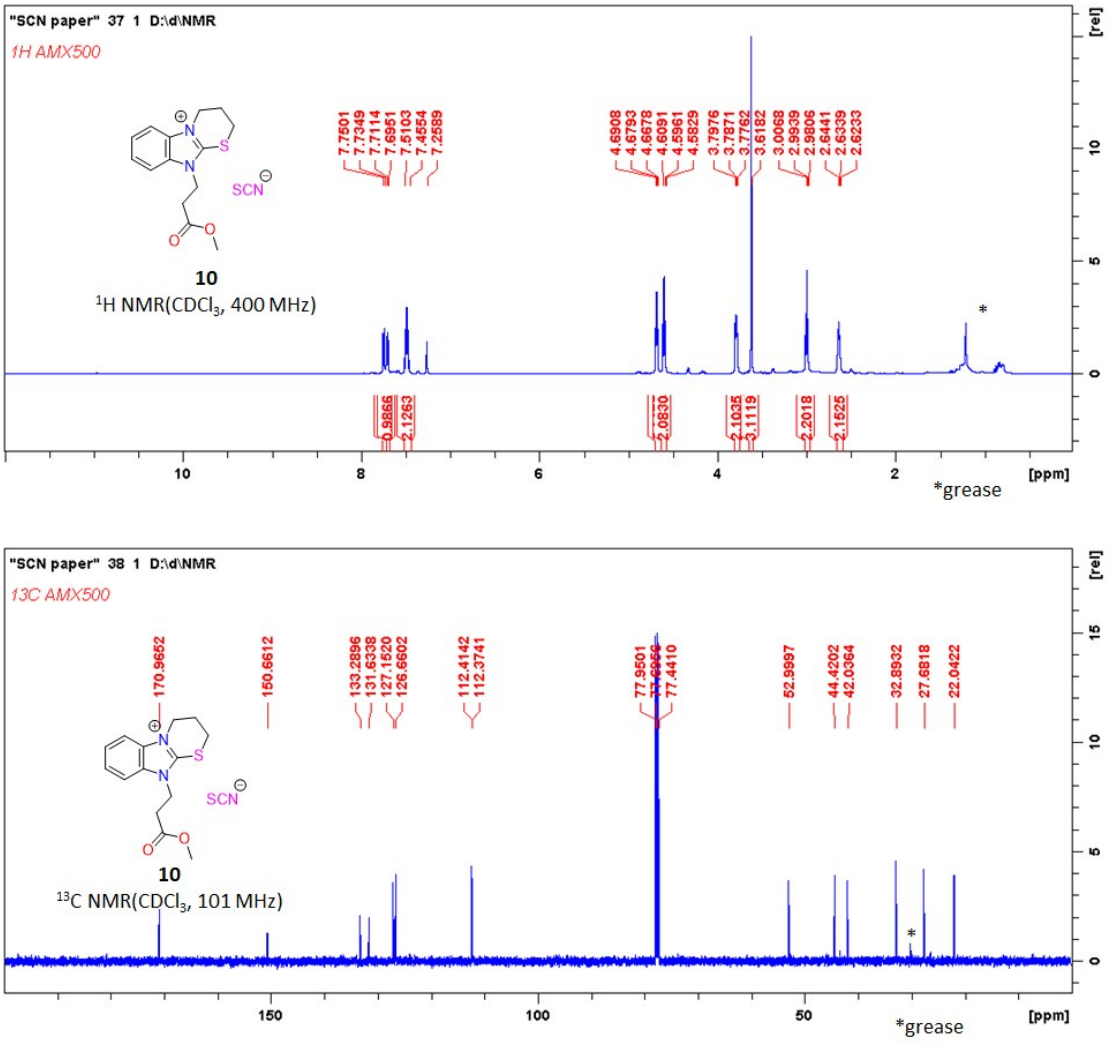


Figure S37. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **10** in $CDCl_3$.

Mass Spectrum SmartFormula Report

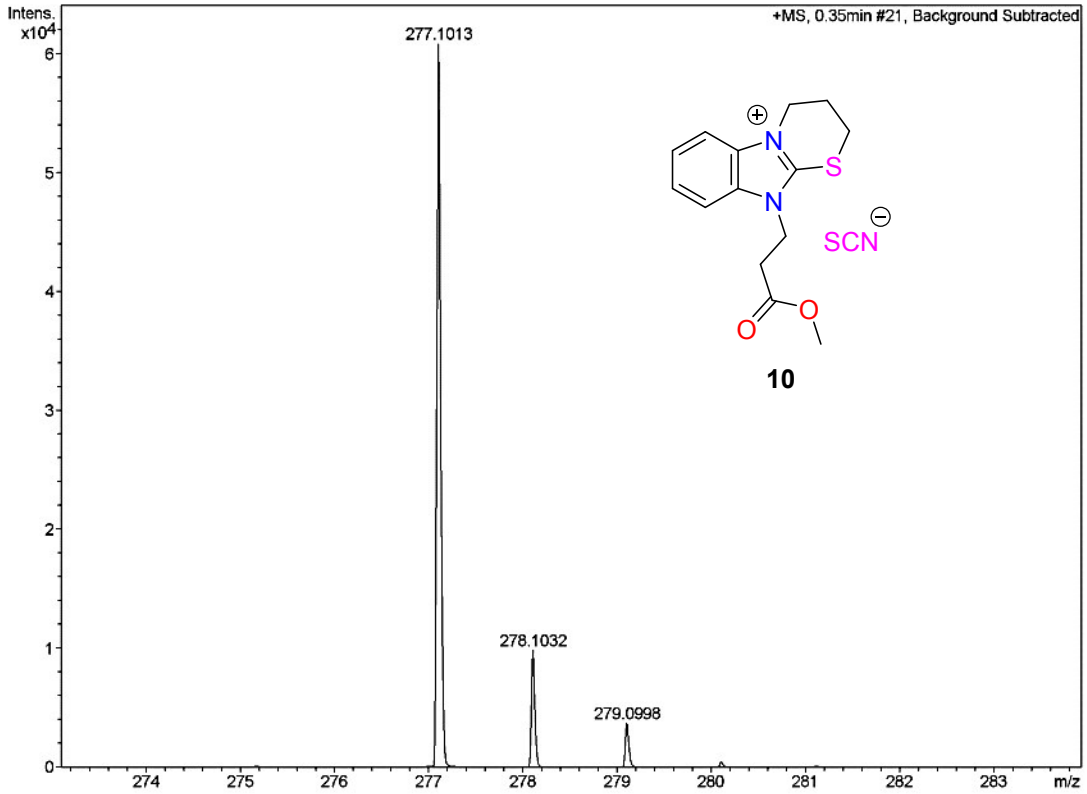
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS10.d	Acquisition Date	1/10/2020 3:34:49 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS10	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
277.1013	1	C 14 H 17 N 2 O 2 S	277.1005	-2.8	7.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 3:36:58 PM Page 1 of 1

Figure S38. HR-MS (ESI) data of **10**.

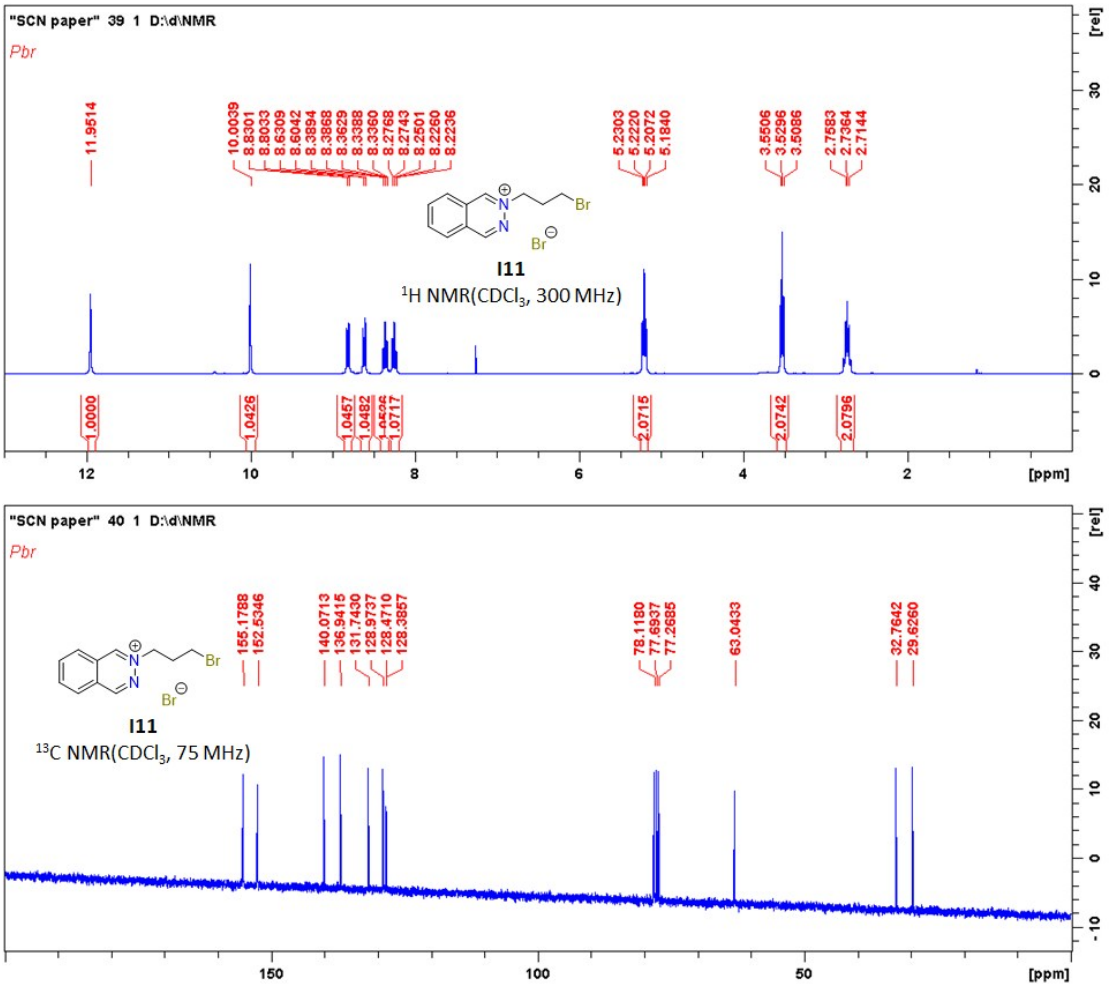


Figure S39. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **I11** in $CDCl_3$.

Mass Spectrum SmartFormula Report

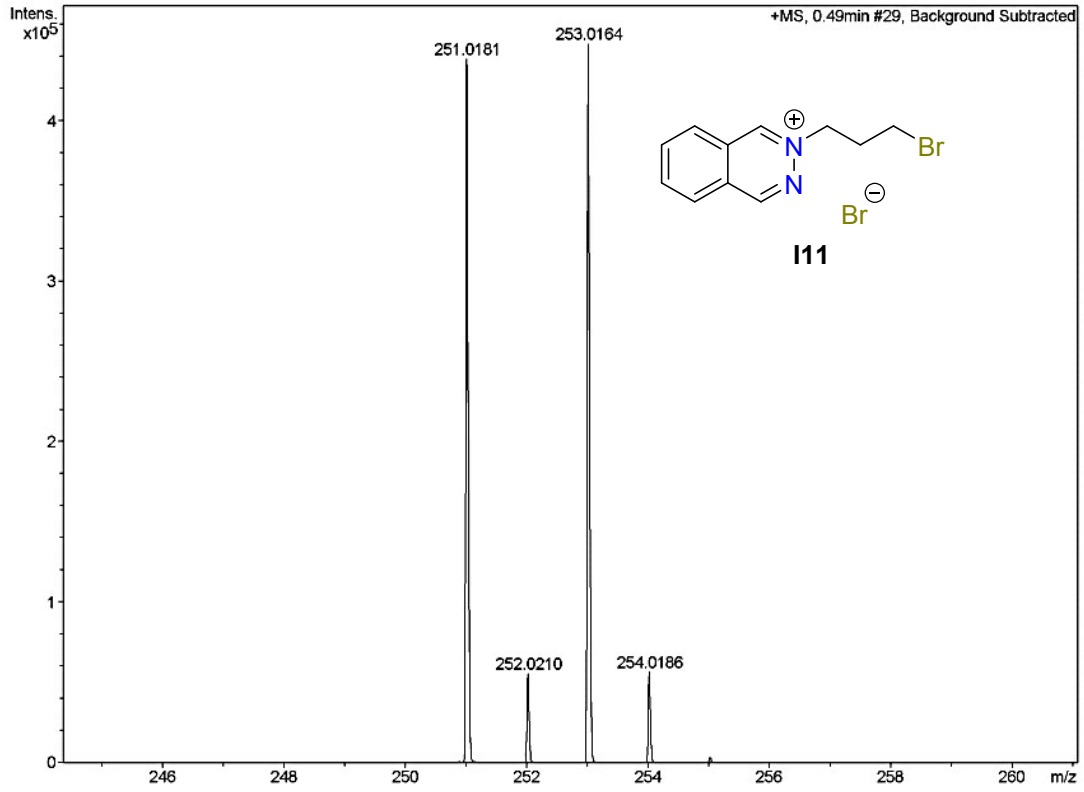
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-I11.d	Acquisition Date	1/22/2020 10:37:53 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-I11	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
251.0181	1	C 11 H 12 Br N 2	251.0178	-1.0	6.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 10:43:16 AM Page 1 of 1

Figure S40. HR-MS (ESI) data of **I11**.

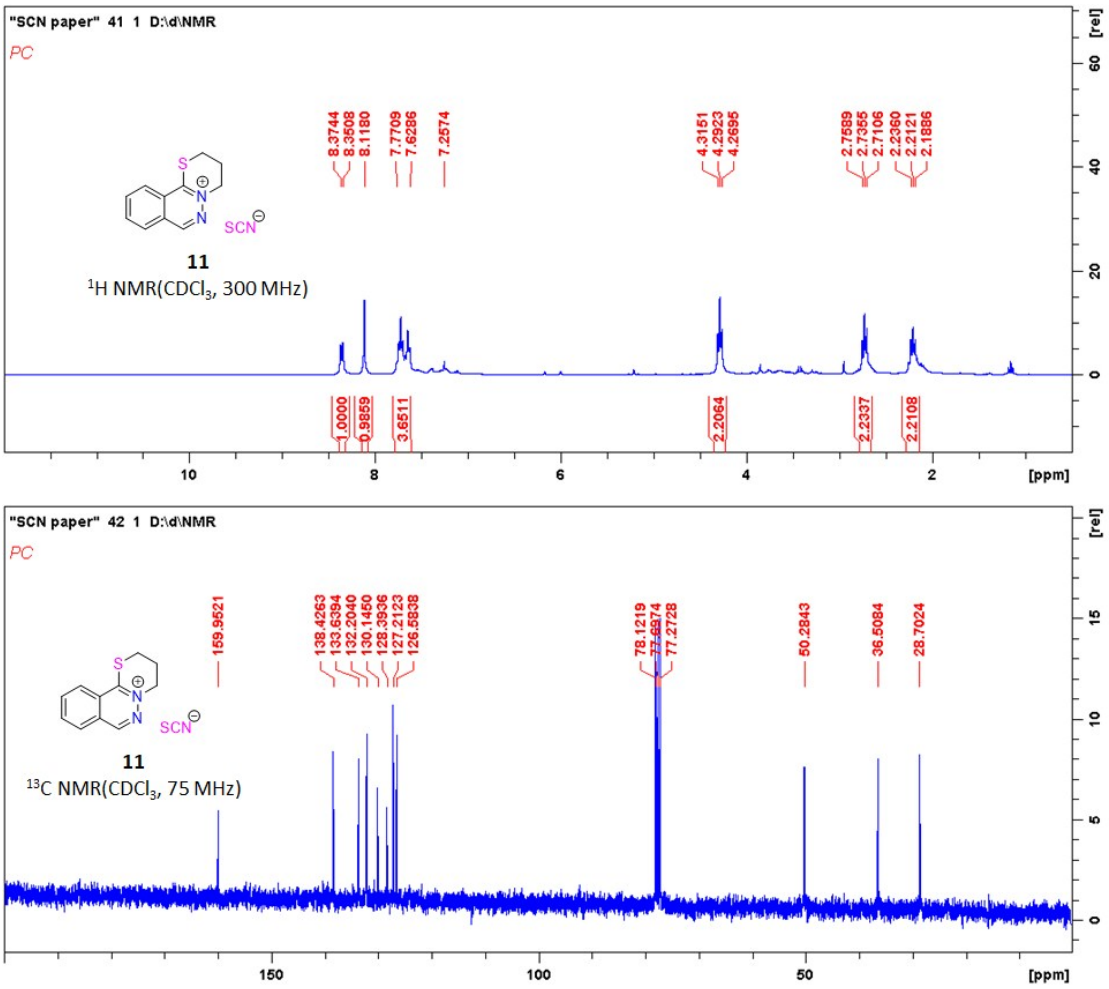


Figure S41. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **11** in $CDCl_3$.

Mass Spectrum SmartFormula Report

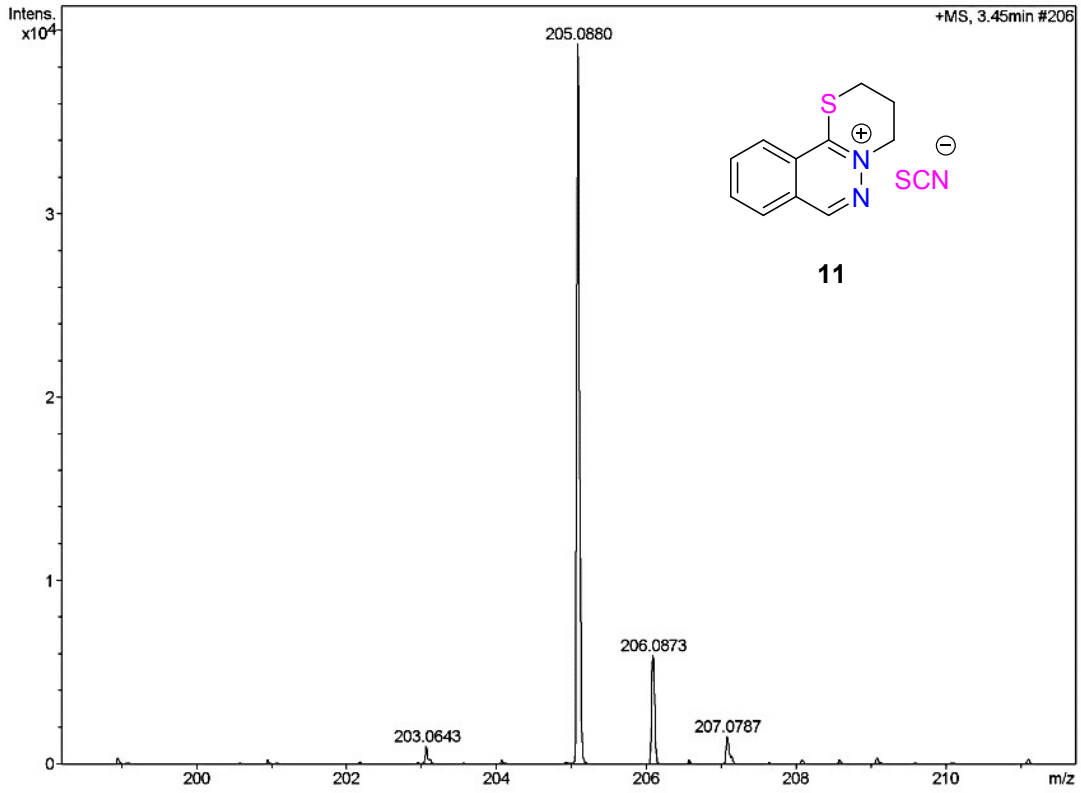
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-11.d	Acquisition Date	1/22/2020 10:45:00 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-11	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
203.0643	1	C 11 H 11 N 2 S	203.0637	-2.5	7.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 10:53:28 AM Page 1 of 1

Figure S42. HR-MS (ESI) data of **11**.

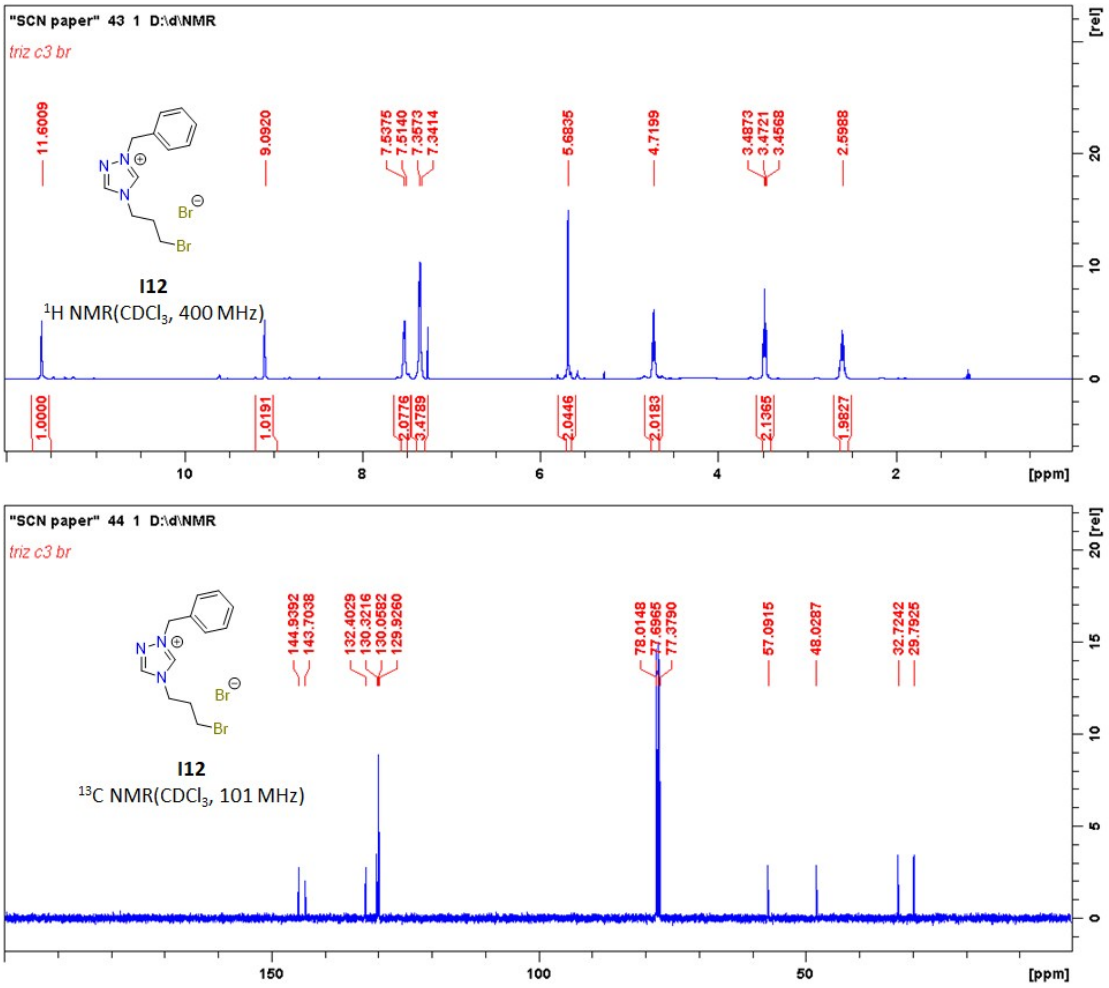


Figure S43. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **I12** in $CDCl_3$.

Mass Spectrum SmartFormula Report

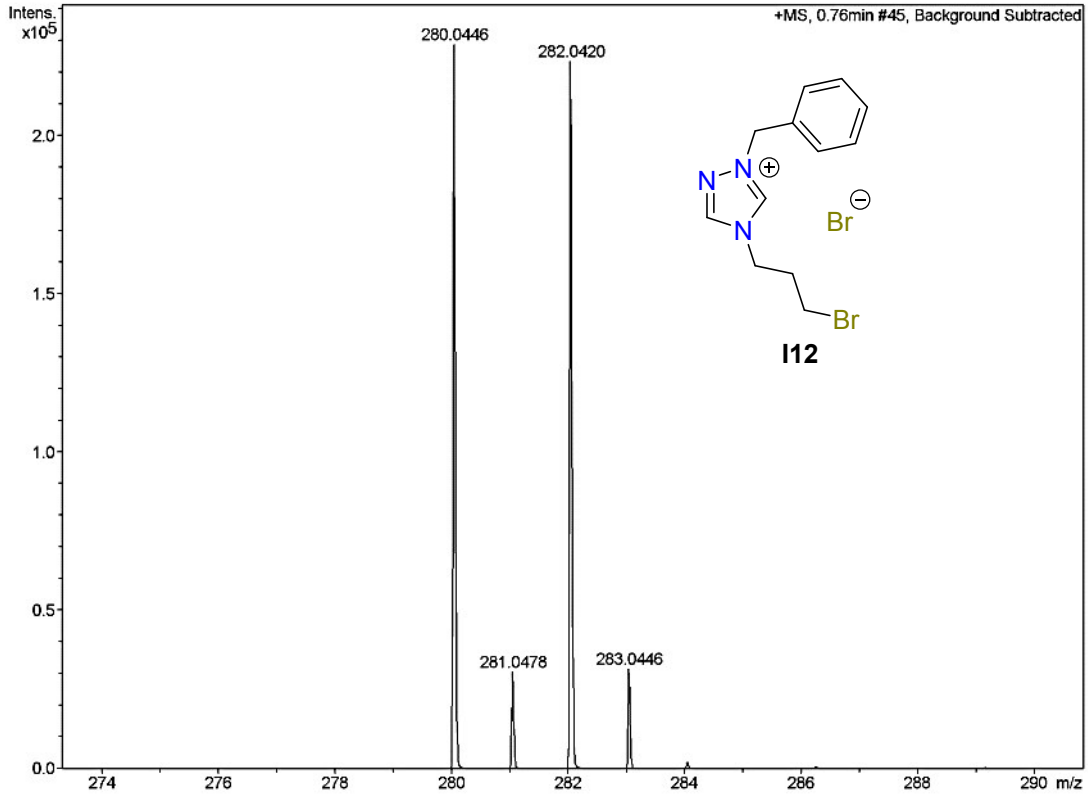
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-I12.d	Acquisition Date	1/22/2020 11:44:43 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-I12	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
280.0446	1	C 12 H 15 Br N 3	280.0444	-0.9	6.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 11:47:08 AM Page 1 of 1

Figure S44. HR-MS (ESI) data of **I12**.

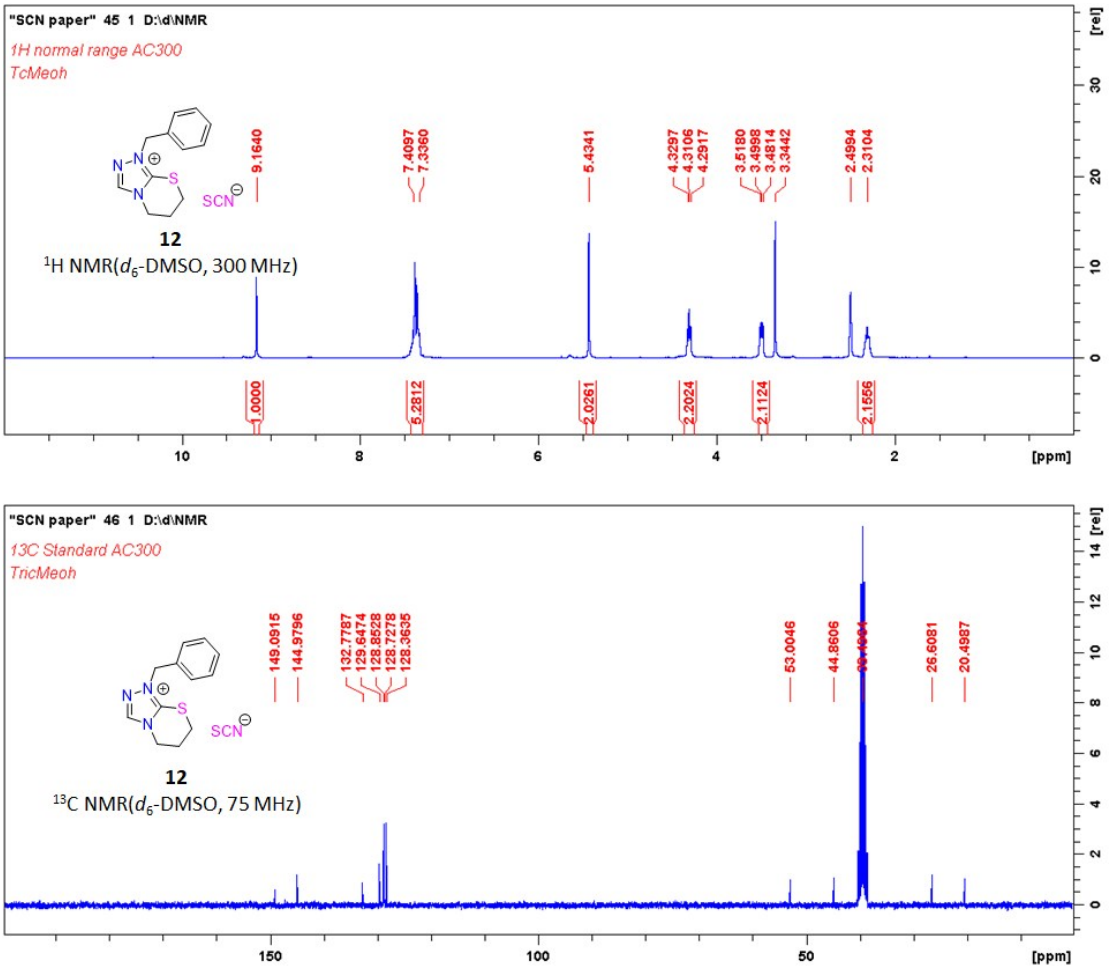


Figure S45. ^{1}H NMR and ^{13}C{^{1}H} NMR spectrum of compound **12** in d_6-DMSO.

Mass Spectrum SmartFormula Report

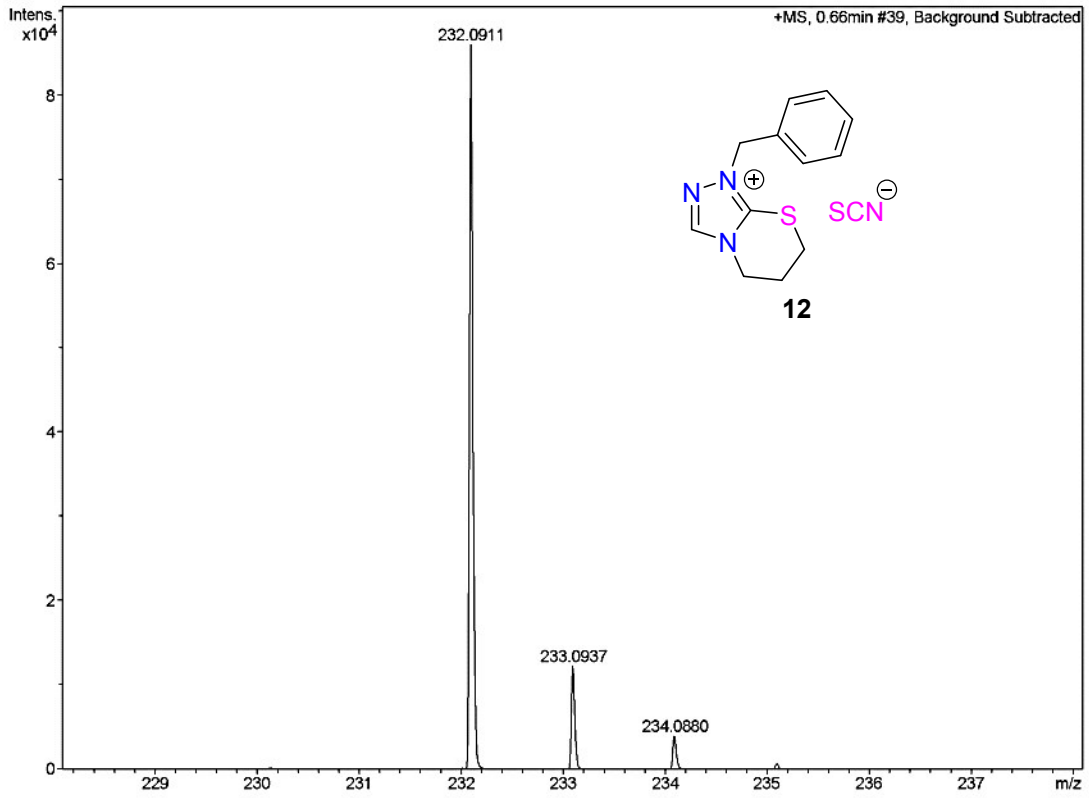
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS12.d	Acquisition Date	1/10/2020 3:38:05 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS12	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
232.0911	1	C 12 H 14 N 3 S	232.0903	-3.5	7.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 3:42:08 PM Page 1 of 1

Figure S46. HR-MS (ESI) data of **12**.

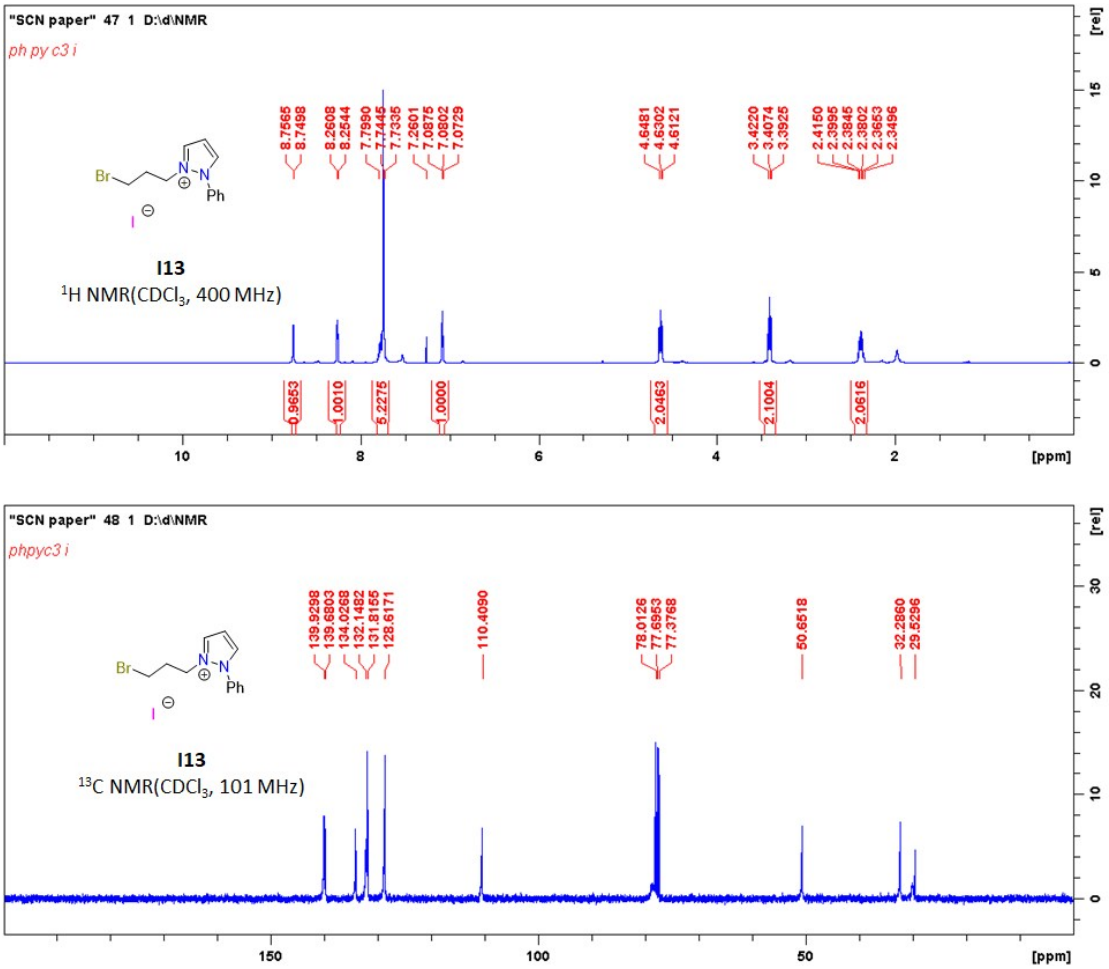


Figure S47. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **I13** in $CDCl_3$.

Mass Spectrum SmartFormula Report

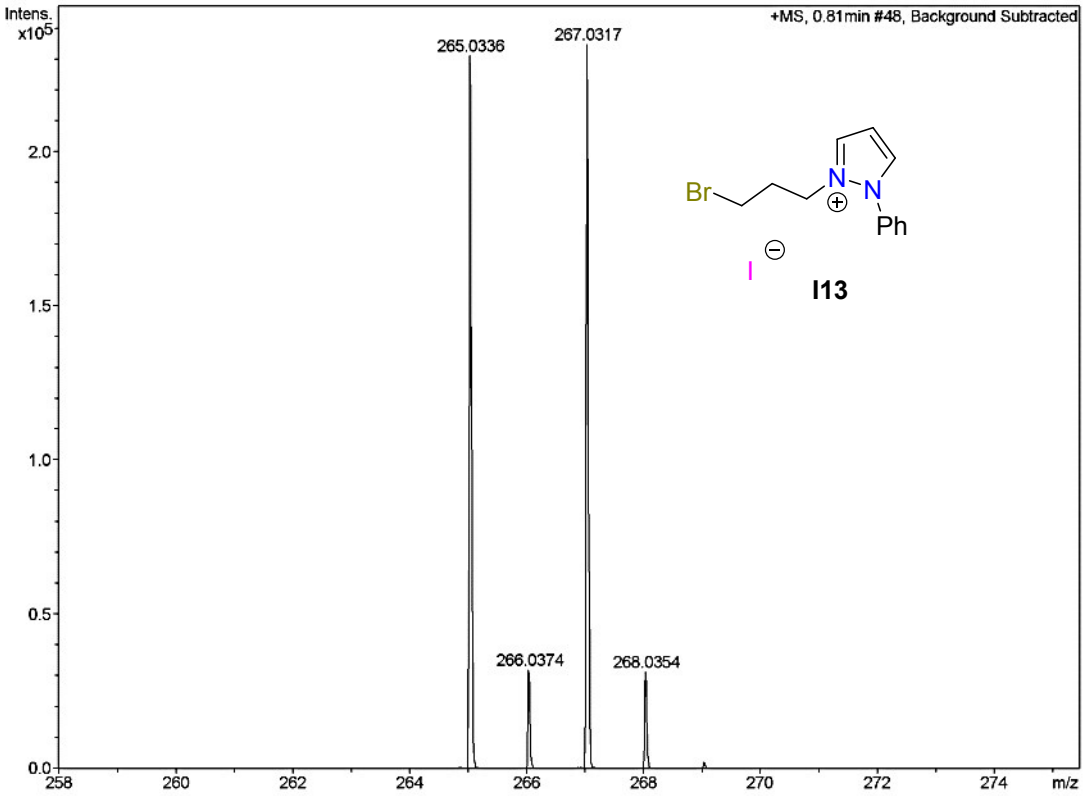
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-I13.d	Acquisition Date	1/22/2020 10:54:55 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-I13	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
265.0336	1	C 12 H 14 Br N 2	265.0335	-0.5	6.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 10:57:24 AM Page 1 of 1

Figure S48. HR-MS (ESI) data of **I13**.

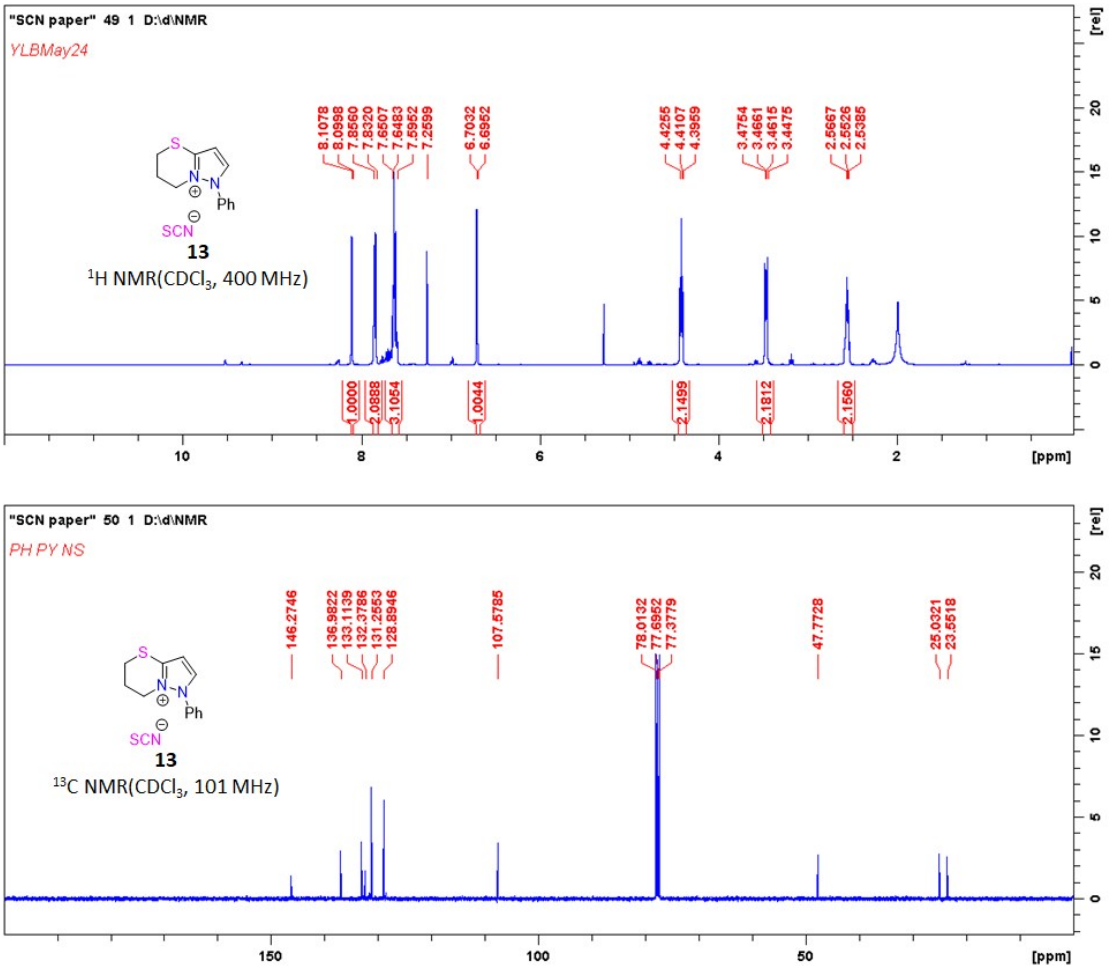


Figure S49. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **13** in $CDCl_3$.

Mass Spectrum SmartFormula Report

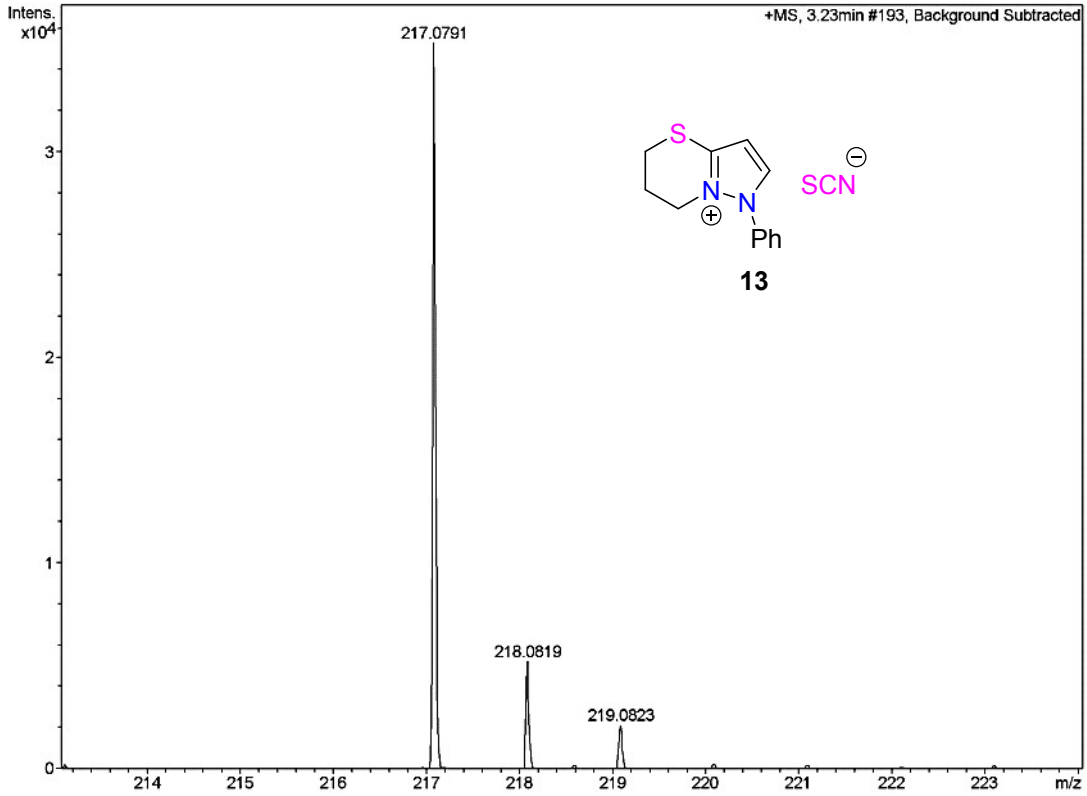
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-13.d	Acquisition Date	1/22/2020 10:59:48 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-13	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
217.0791	1	C 12 H 13 N 2 S	217.0794	1.6	7.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 11:05:01 AM Page 1 of 1

Figure S50. HR-MS (ESI) data of **13**.

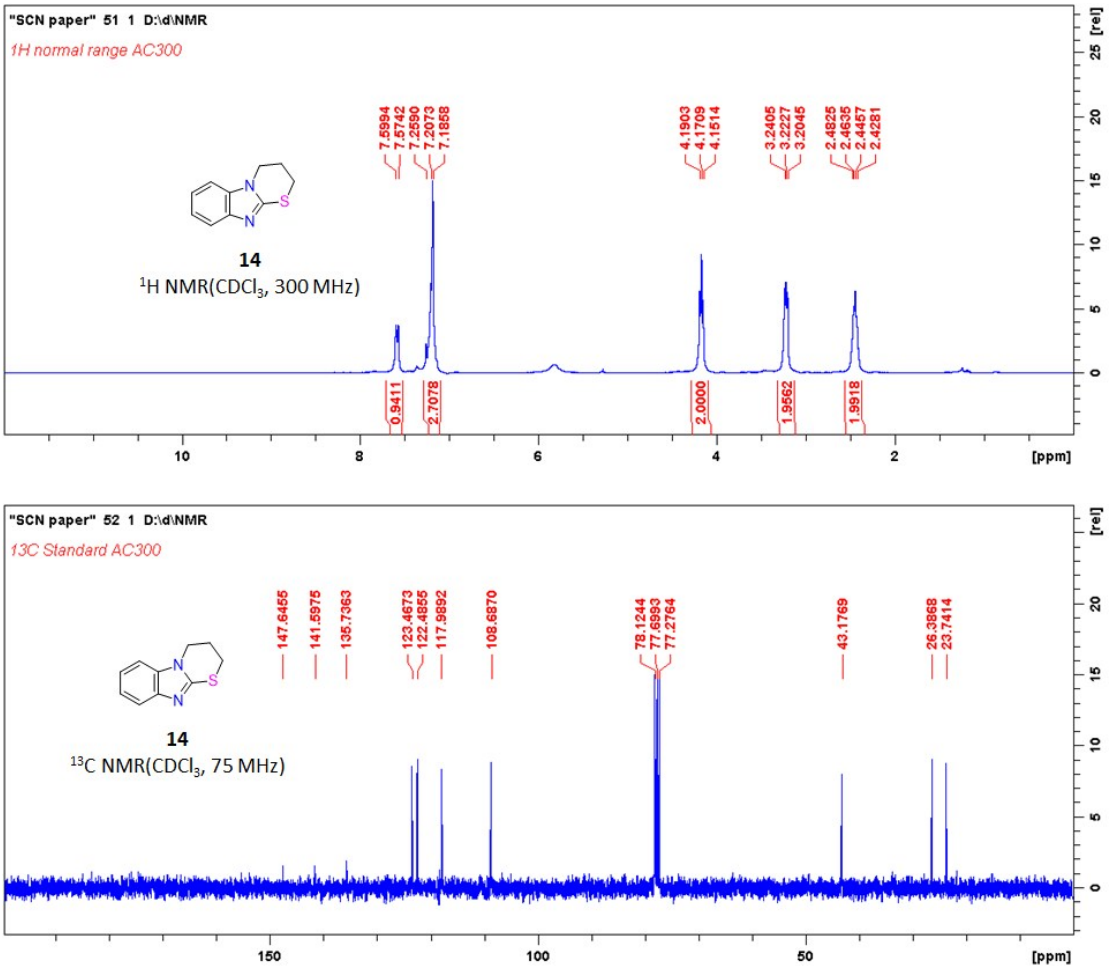


Figure S51. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **14** in $CDCl_3$.

Mass Spectrum SmartFormula Report

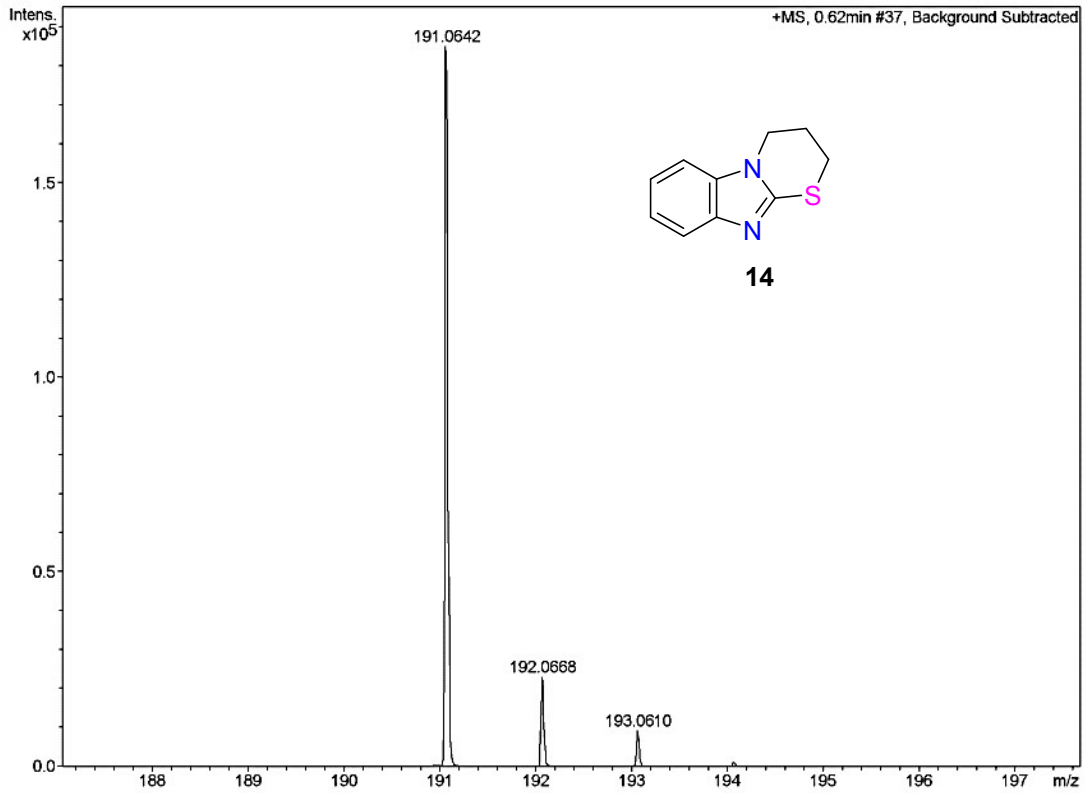
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS14.d	Acquisition Date	1/10/2020 3:43:32 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS14	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	60.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
191.0642	1	C 10 H 11 N 2 S	191.0637	-2.2	6.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 3:46:34 PM Page 1 of 1

Figure S52. HR-MS (ESI) data of **14**.

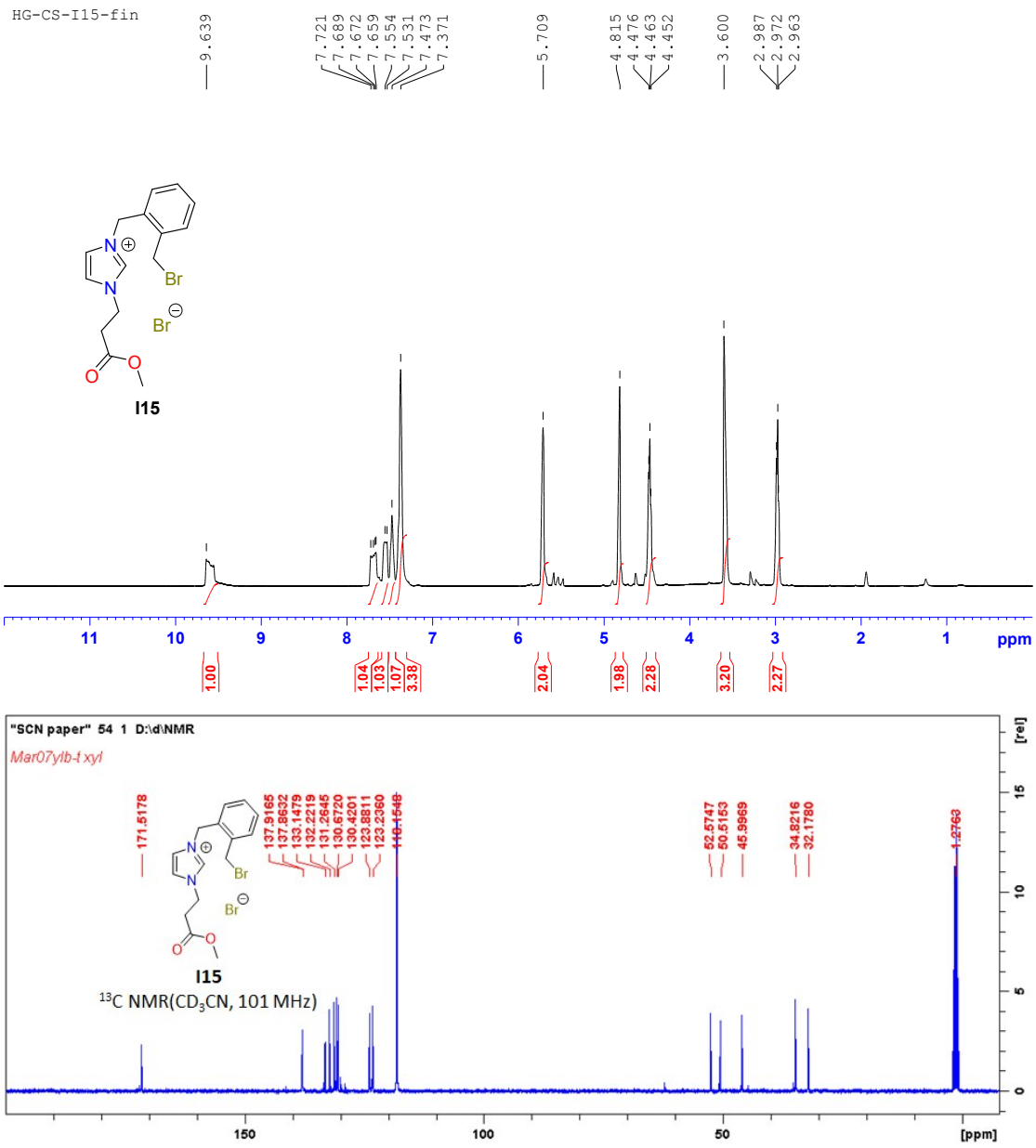


Figure S53. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **I15** in CD_3CN.

Mass Spectrum SmartFormula Report

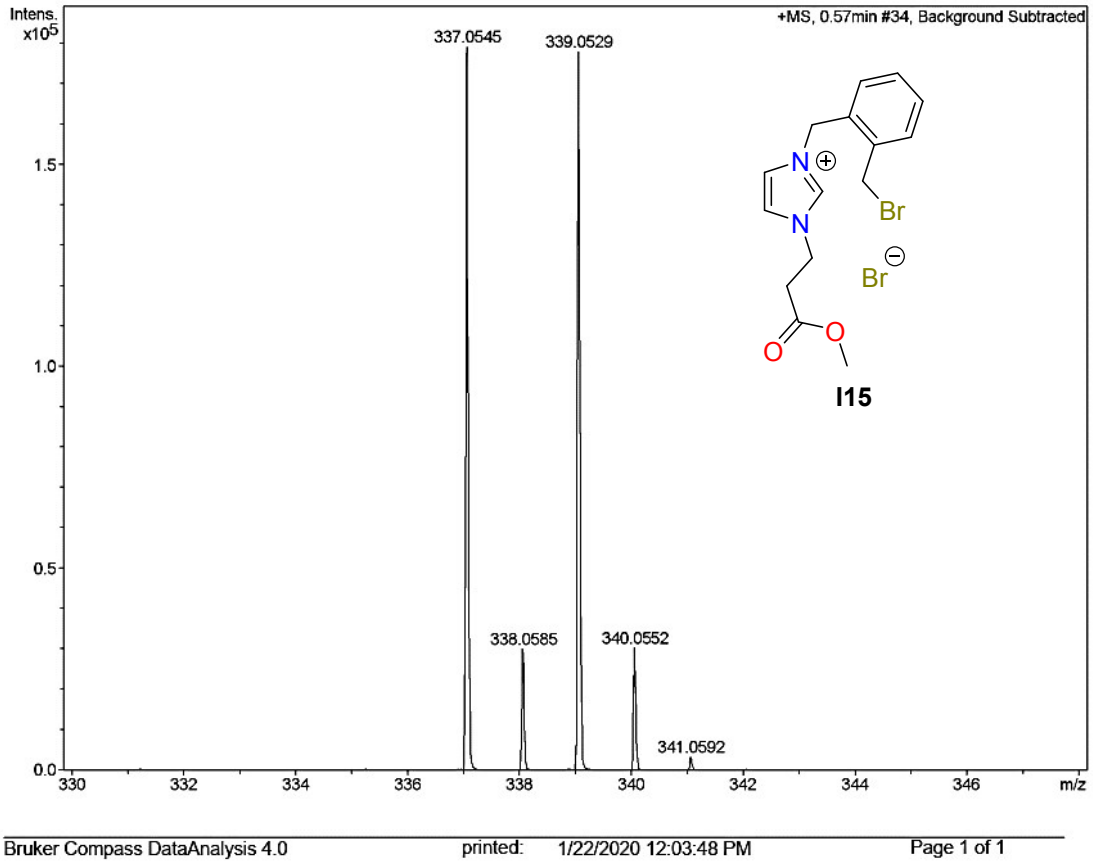
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-I15.d	Acquisition Date	1/22/2020 12:00:10 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-I15	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
337.0545	1	C 15 H 18 Br N 2 O 2	337.0546	0.3	7.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 12:03:48 PM Page 1 of 1

Figure S54. HR-MS (ESI) data of **I15**.

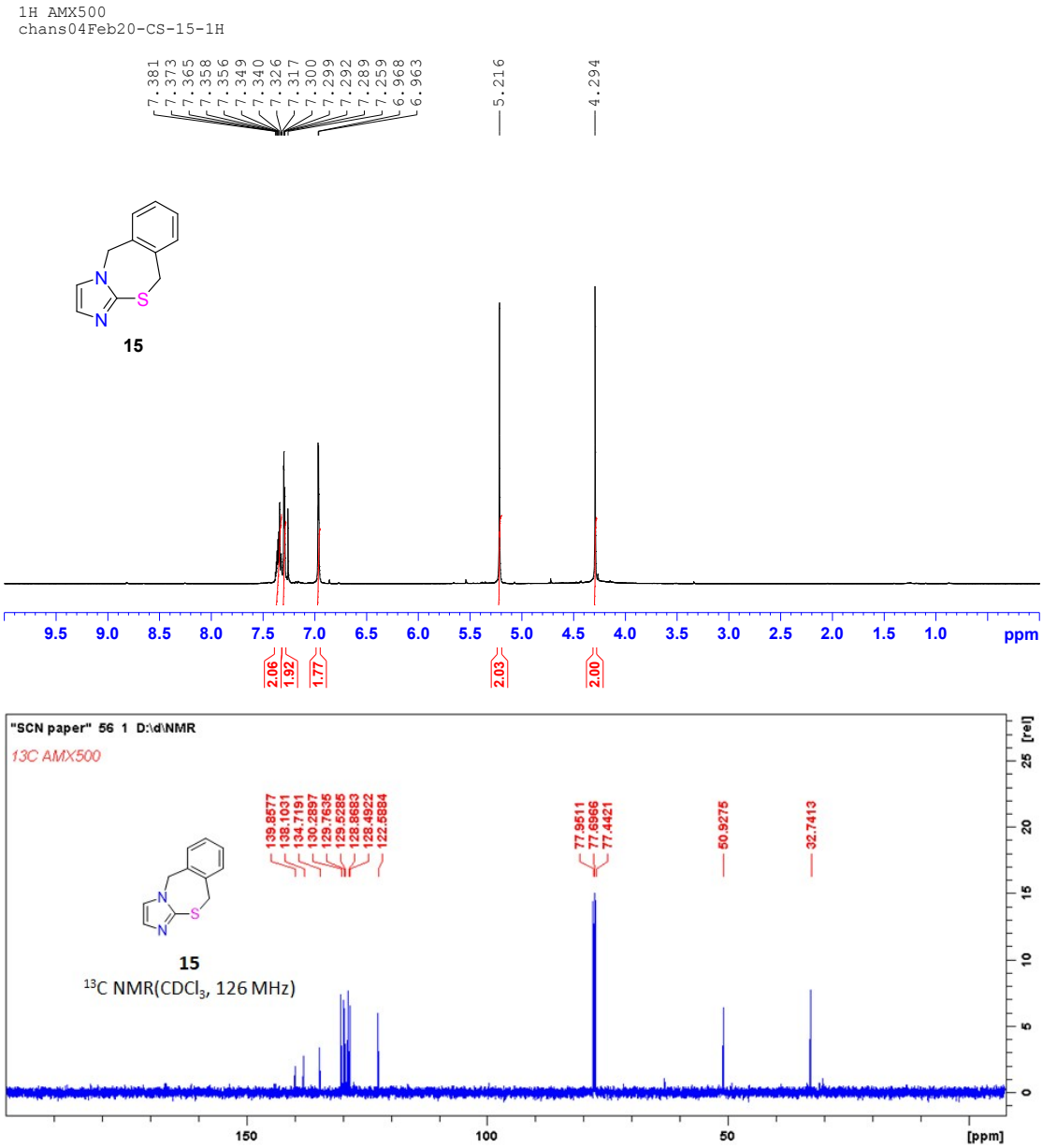


Figure S55. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **15** in $CDCl_3$.

Mass Spectrum SmartFormula Report

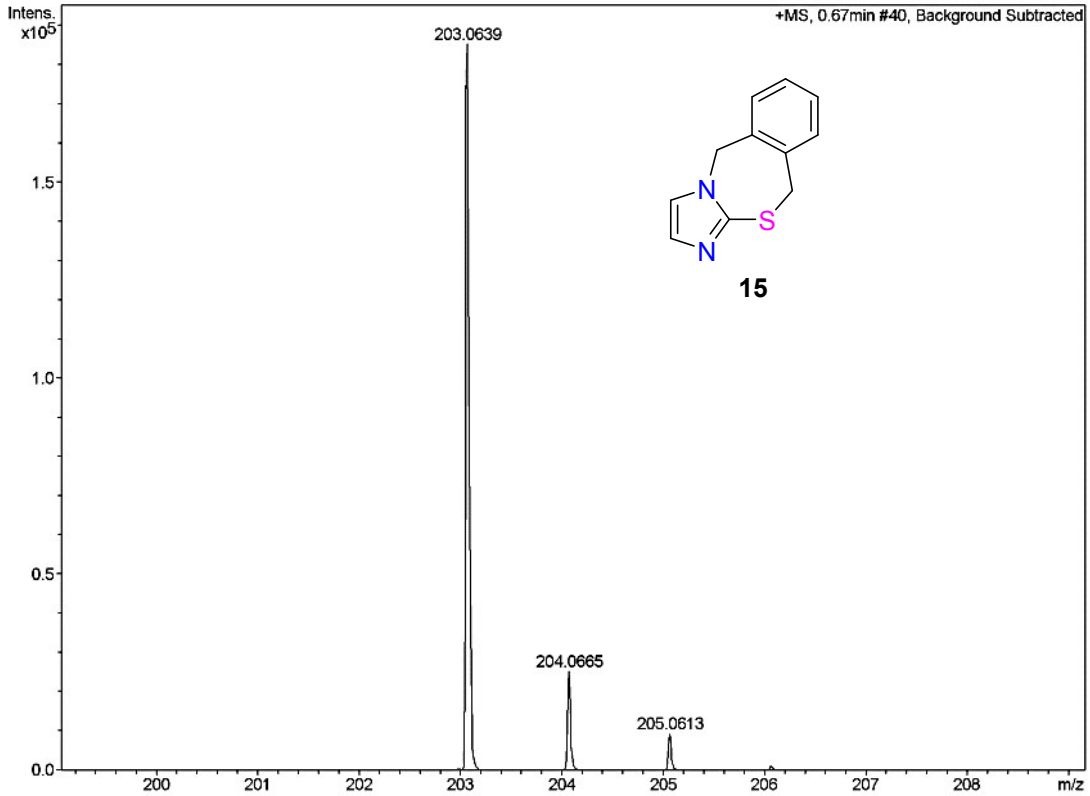
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS15.d	Acquisition Date	1/10/2020 3:47:43 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS15	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	60.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
203.0639	1	C 11 H 11 N 2 S	203.0637	-0.6	7.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 3:50:13 PM Page 1 of 1

Figure S56. HR-MS (ESI) data of **15**.

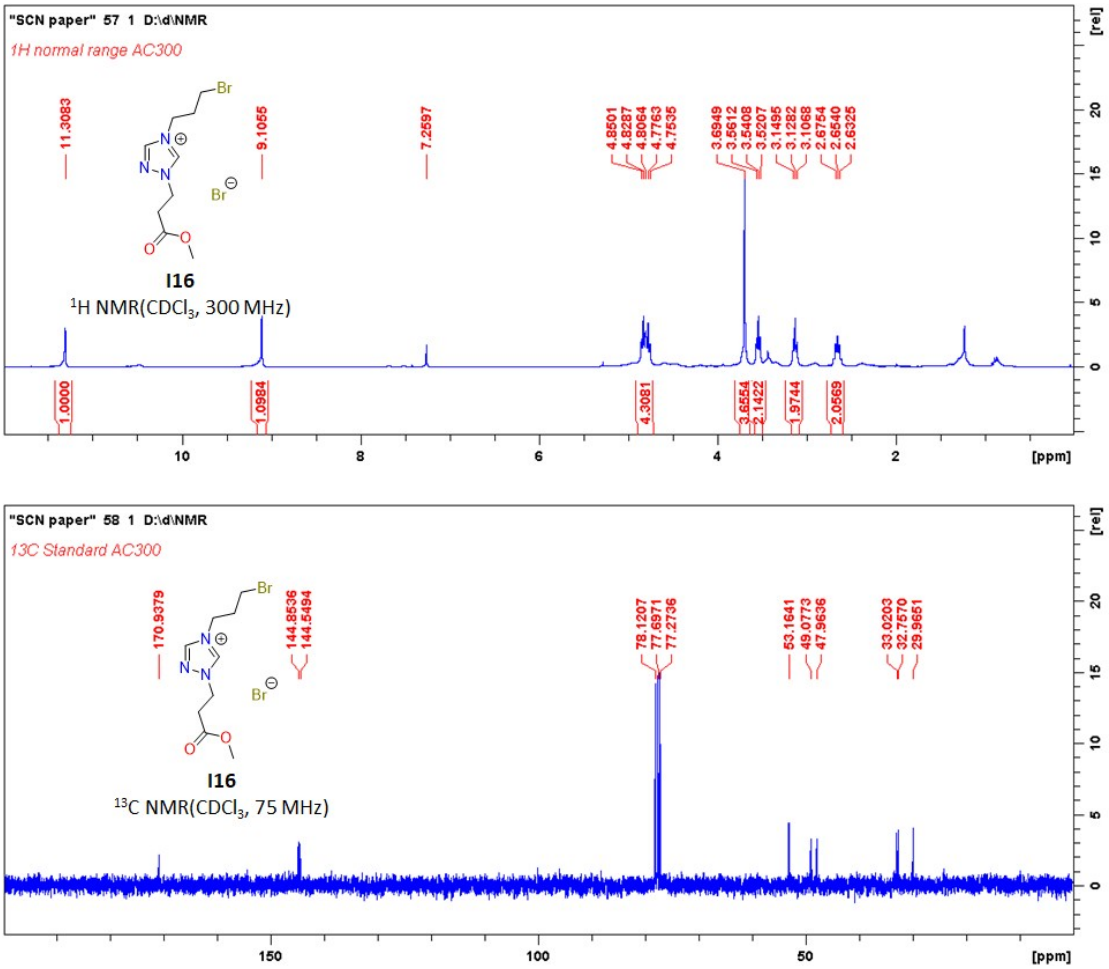


Figure S57. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **I16** in $CDCl_3$.

Mass Spectrum SmartFormula Report

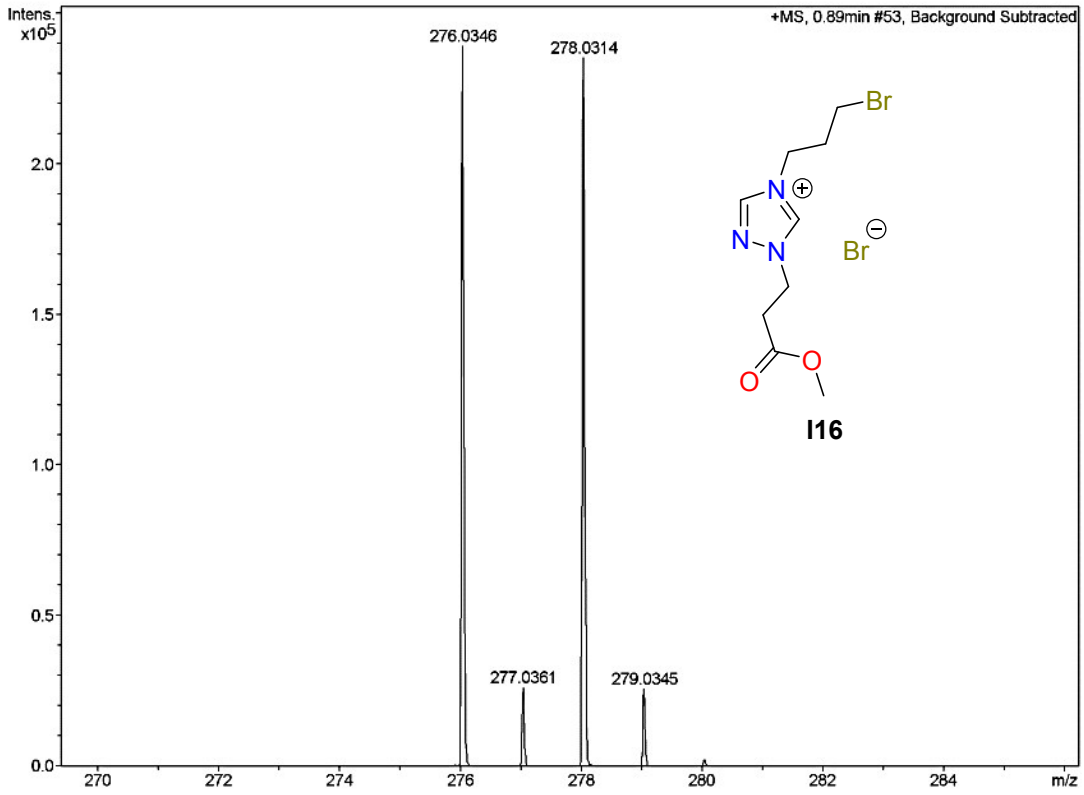
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-I16.d	Acquisition Date	1/22/2020 11:48:20 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-I16	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
276.0346	1	C 9 H 15 Br N 3 O 2	276.0342	-1.3	3.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 11:51:04 AM Page 1 of 1

Figure S58. HR-MS (ESI) data of **I16**.

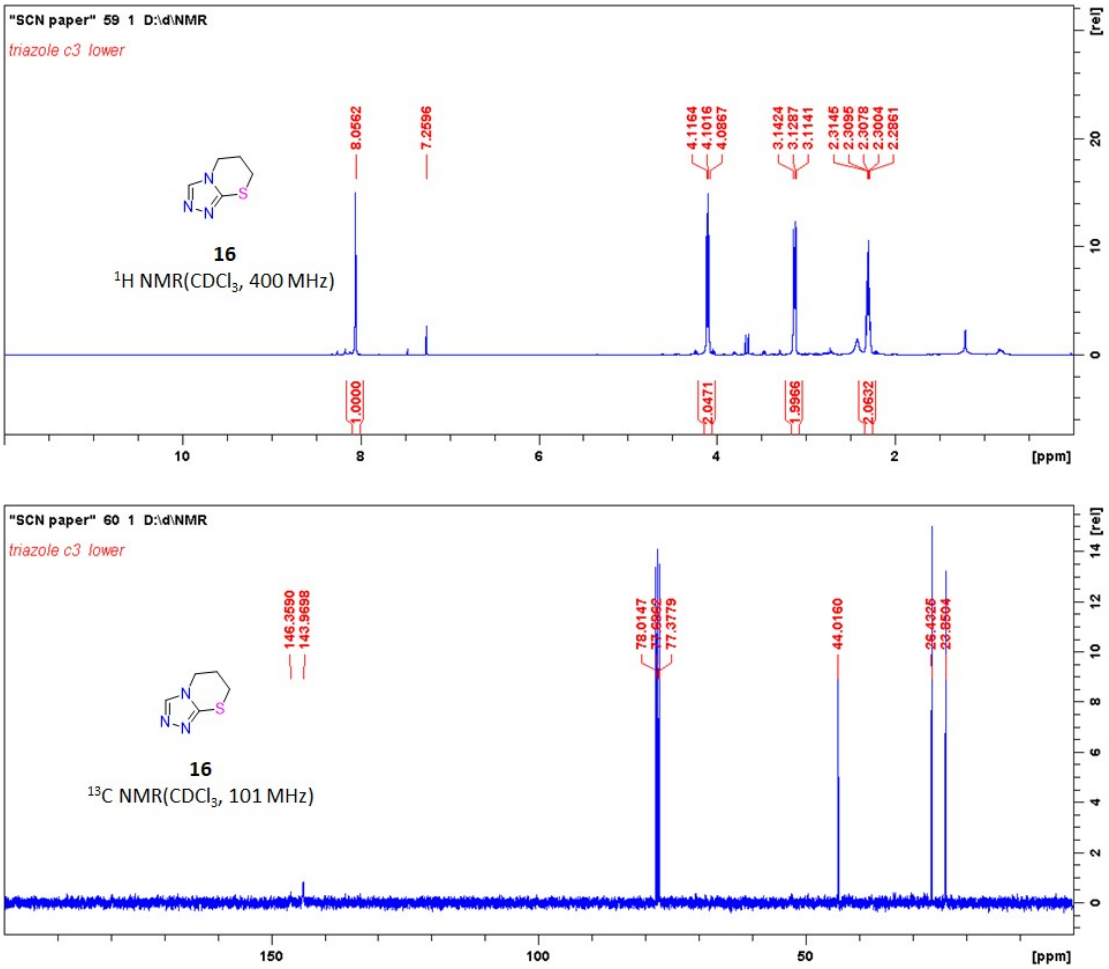


Figure S59. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **16** in $CDCl_3$.

Mass Spectrum SmartFormula Report

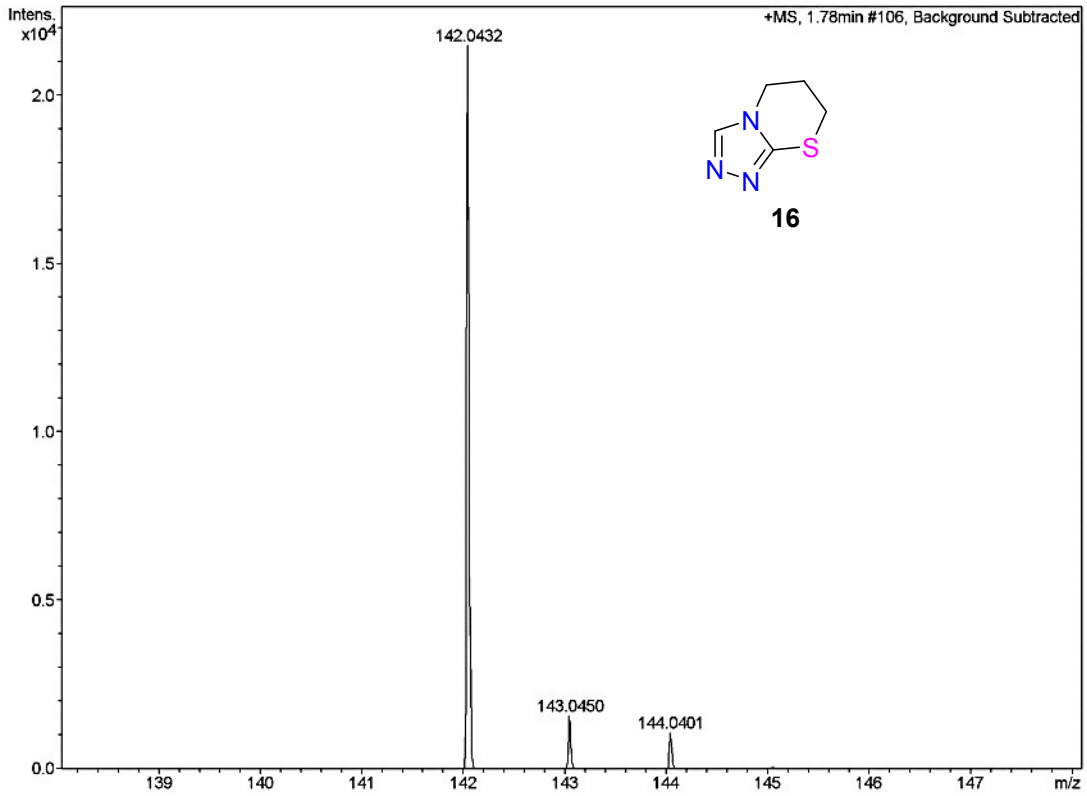
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS16.d	Acquisition Date	1/10/2020 3:51:10 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS16	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	60.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
142.0432	1	C 5 H 8 N 3 S	142.0433	0.8	3.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 3:55:12 PM Page 1 of 1

Figure S60. HR-MS (ESI) data of **16**.

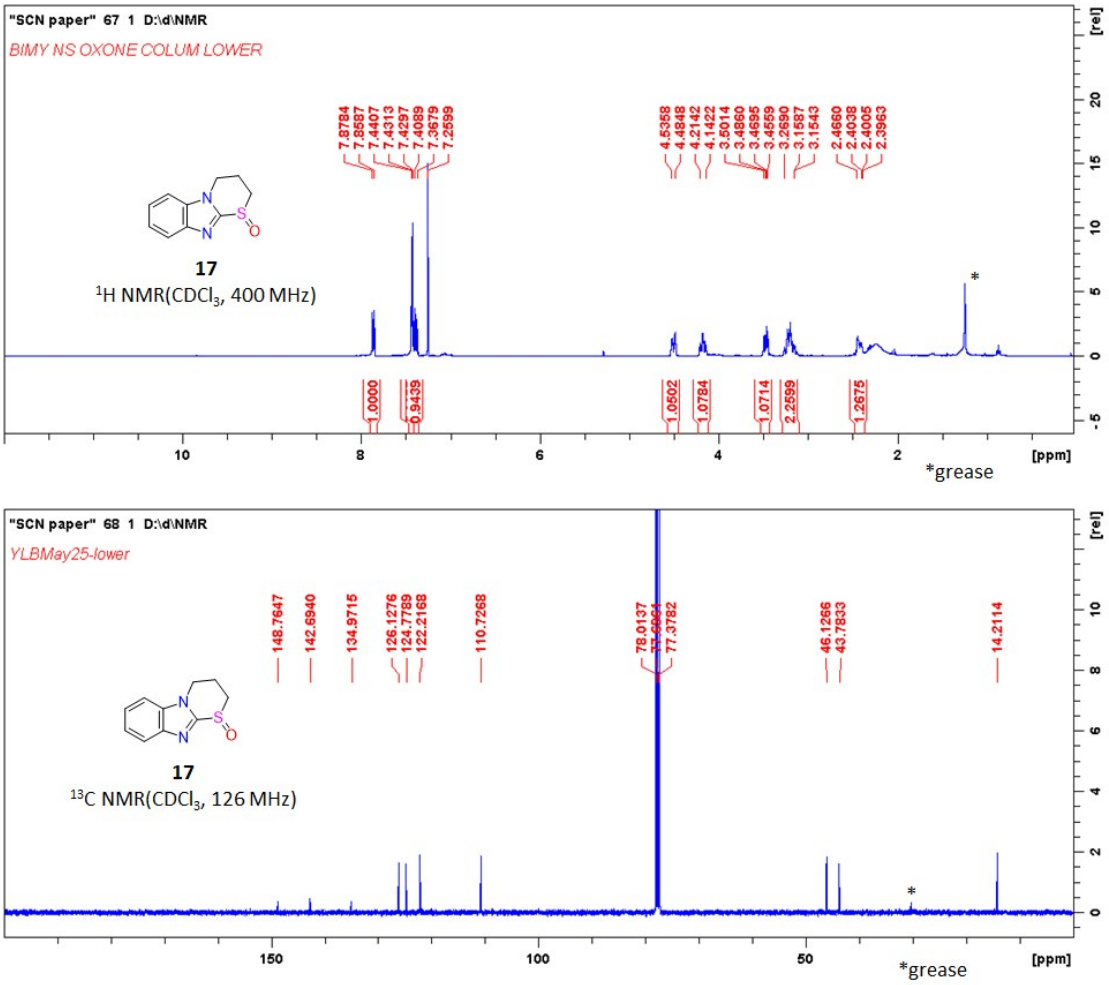


Figure S61. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **17** in $CDCl_3$.

Mass Spectrum SmartFormula Report

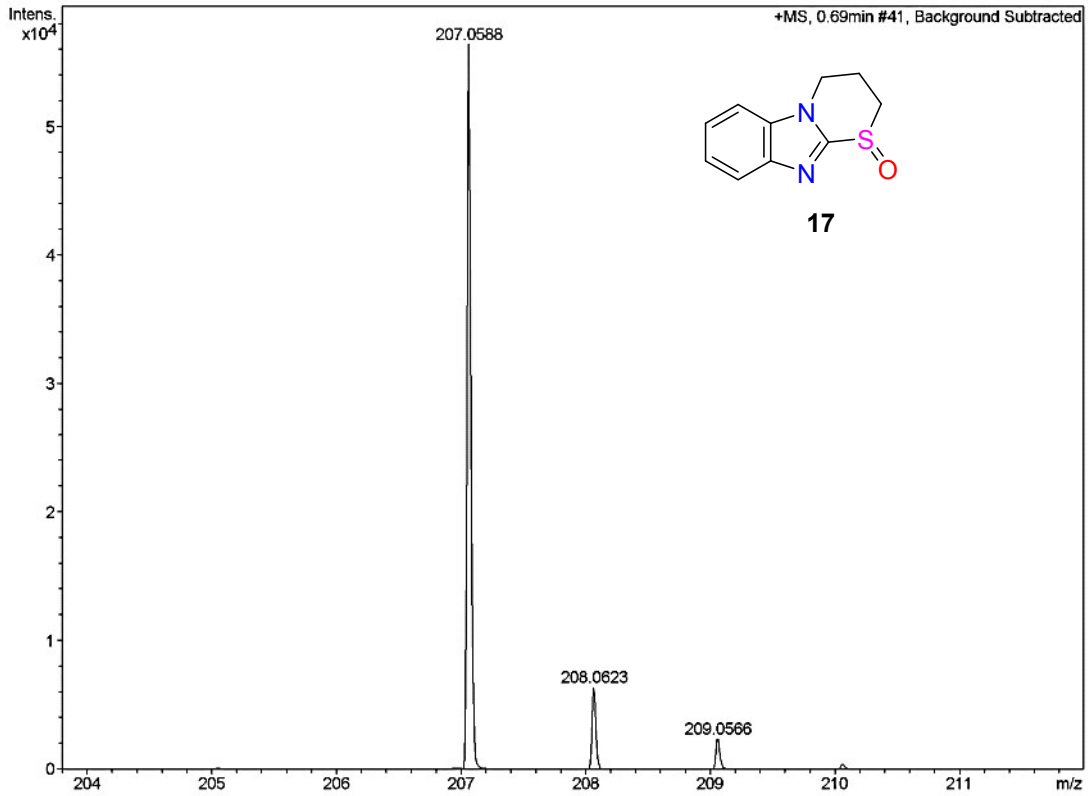
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS17.d	Acquisition Date	1/10/2020 3:56:14 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS17	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	60.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
207.0588	1	C 10 H 11 N 2 O S	207.0587	-0.8	6.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 3:59:23 PM Page 1 of 1

Figure S62. HR-MS (ESI) data of **17**.

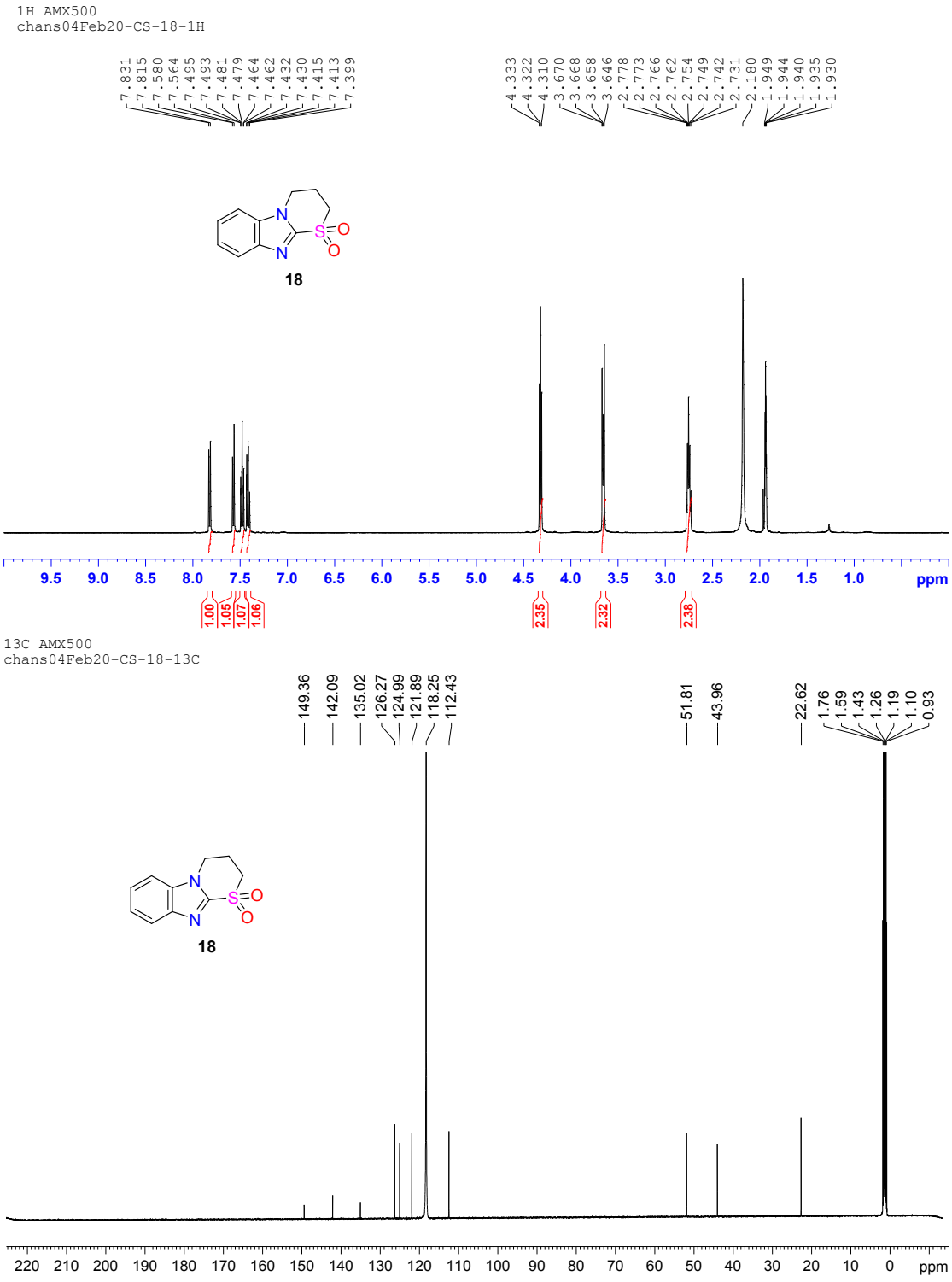


Figure S63. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **18** in CD_3CN.

Mass Spectrum SmartFormula Report

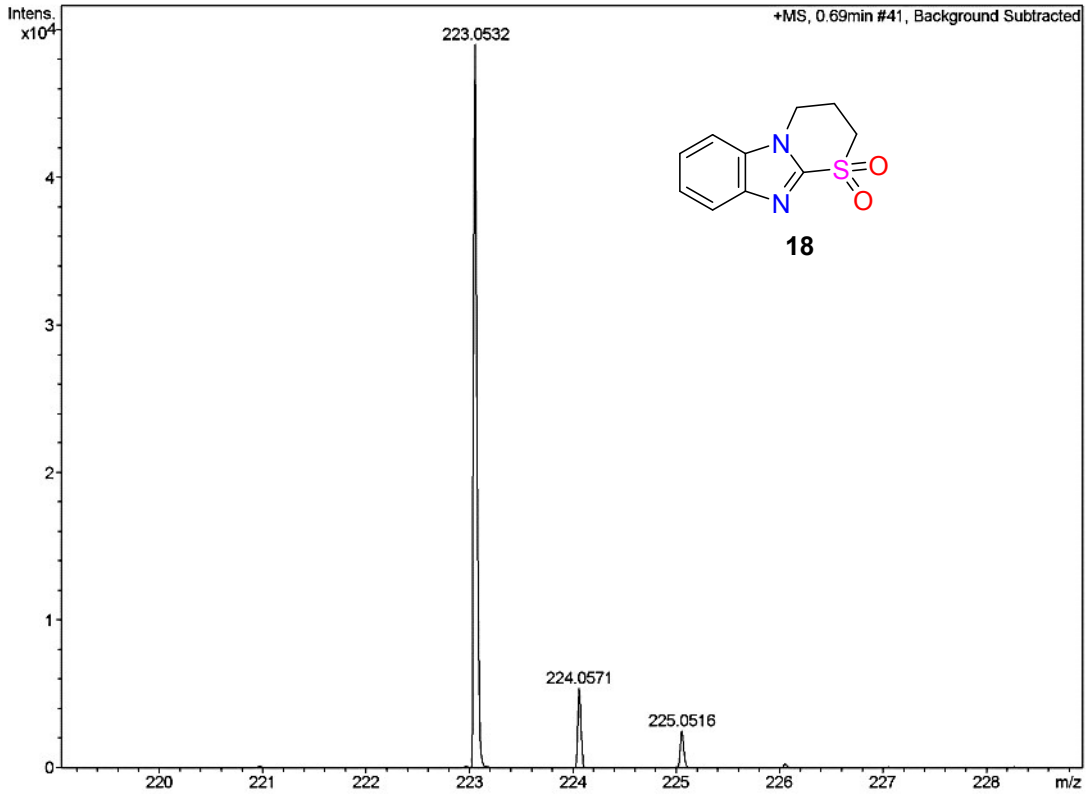
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CS18.d	Acquisition Date	1/10/2020 4:00:20 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS18	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	60.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
223.0532	1	C 10 H 11 N 2 O 2 S	223.0536	1.8	6.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 4:03:07 PM Page 1 of 1

Figure S64. HR-MS (ESI) data of **18**.

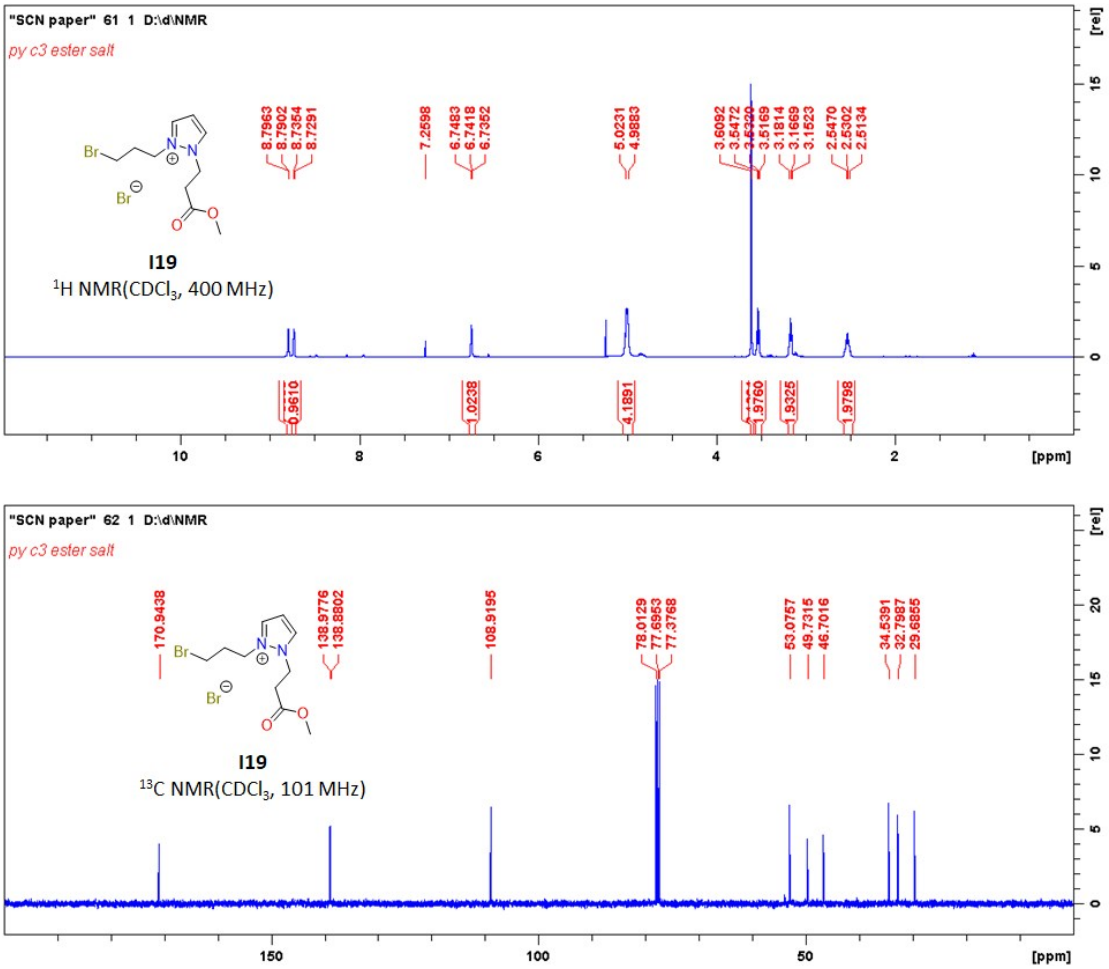


Figure S65. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **I19** in $CDCl_3$.

Mass Spectrum SmartFormula Report

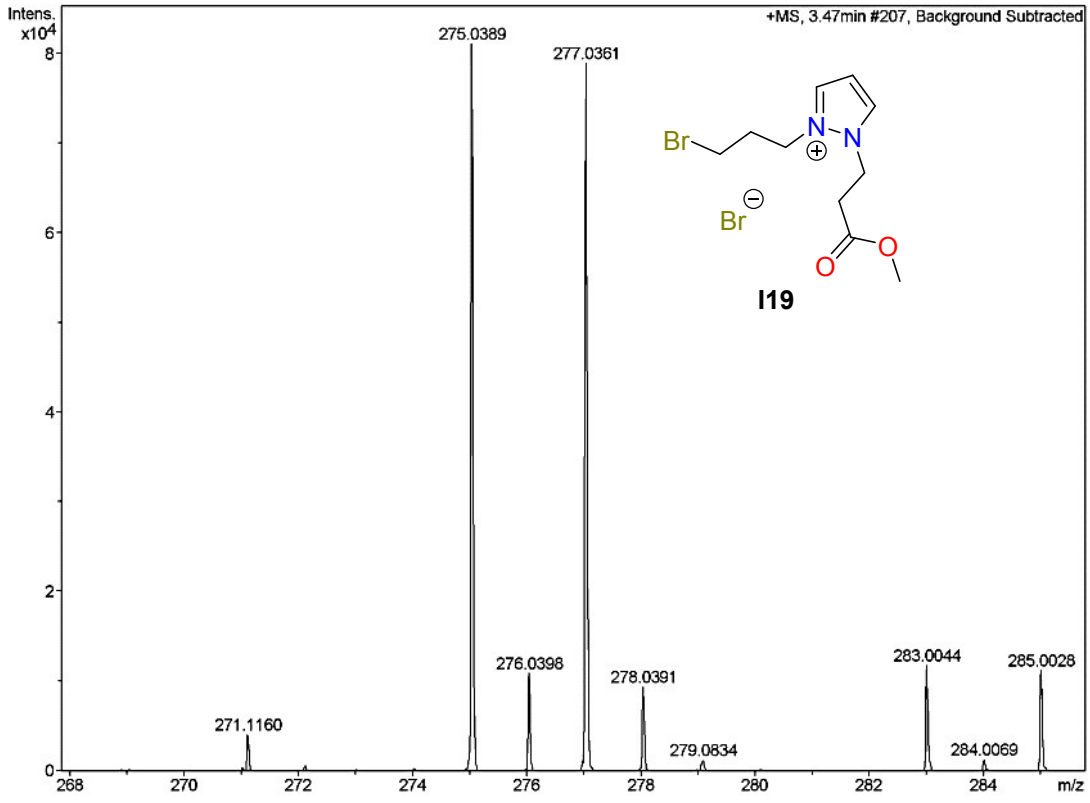
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0122\CS-I19.d	Acquisition Date	1/22/2020 11:52:21 AM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-I19	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
275.0389	1	C 10 H 16 Br N 2 O 2	275.0390	0.2	3.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/22/2020 11:57:38 AM Page 1 of 1

Figure S66. HR-MS (ESI) data of **I19**.

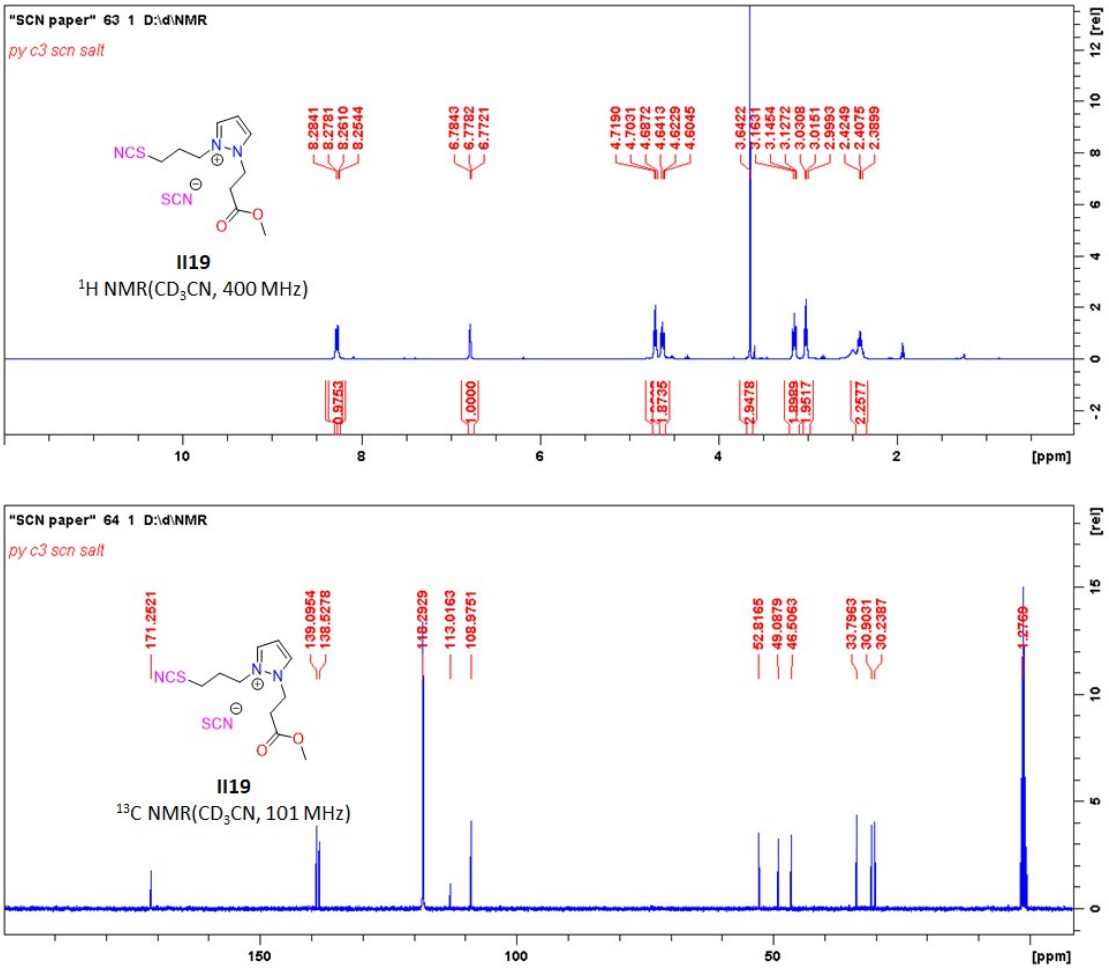


Figure S67. ^{1}H NMR and ^{13}C{^{1}H} NMR spectrum of compound **II19** in CD_3CN.

Mass Spectrum SmartFormula Report

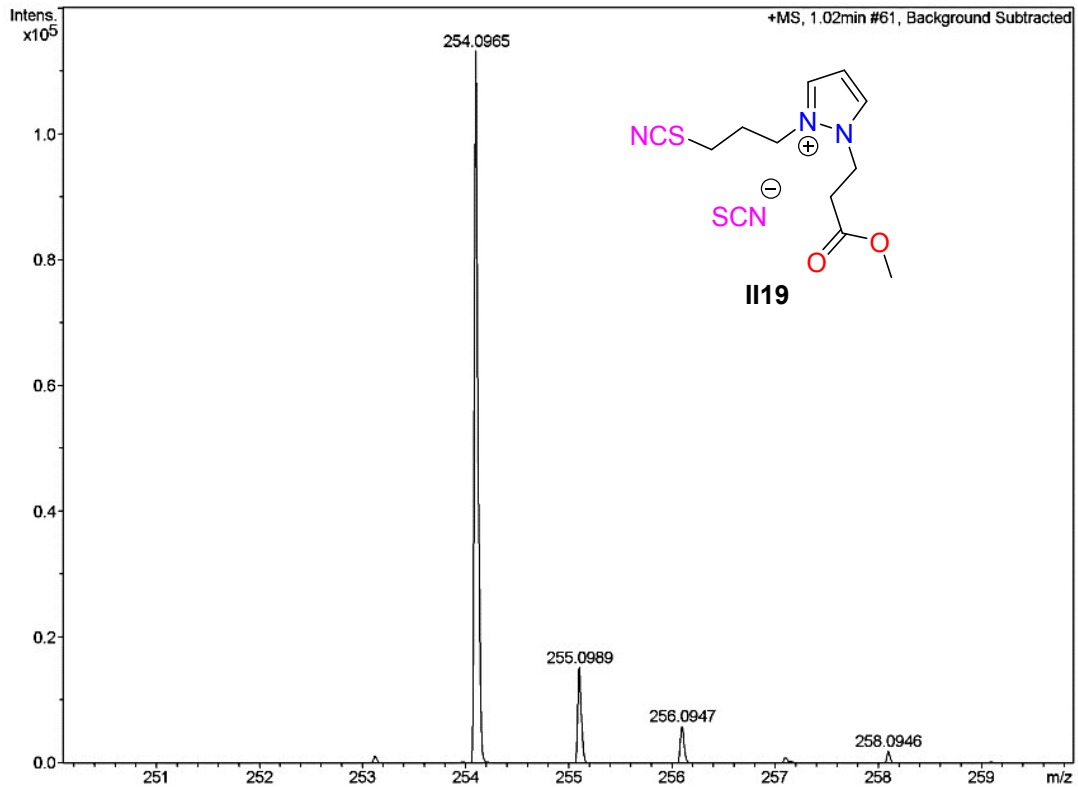
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202001\0109\CSII19.d	Acquisition Date	1/10/2020 3:10:42 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CSII19	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
254.0965	1	C 11 H 16 N 3 O 2 S	254.0958	-2.8	5.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 1/10/2020 3:13:25 PM Page 1 of 1

Figure S68. HR-MS (ESI) data of **II19**.

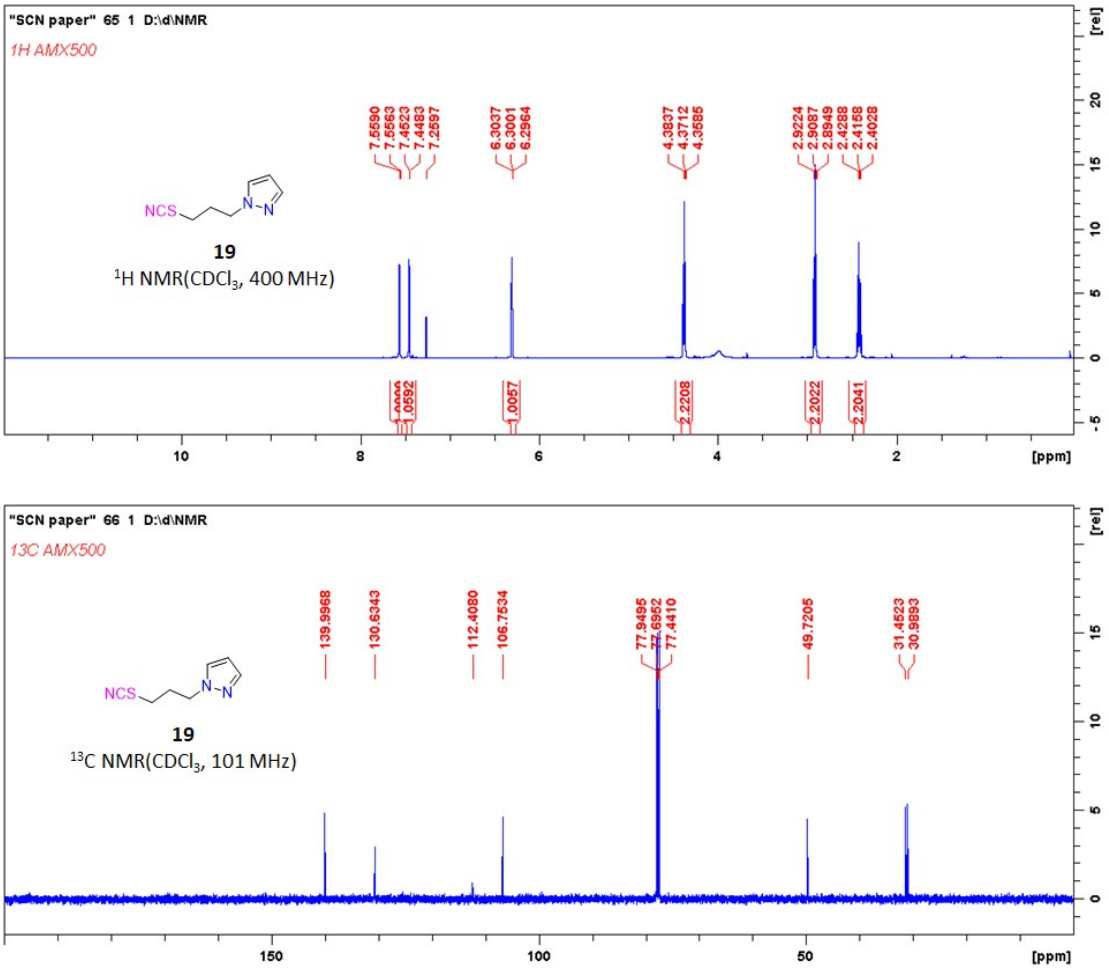


Figure S69. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectrum of compound **19** in $CDCl_3$.

Mass Spectrum SmartFormula Report

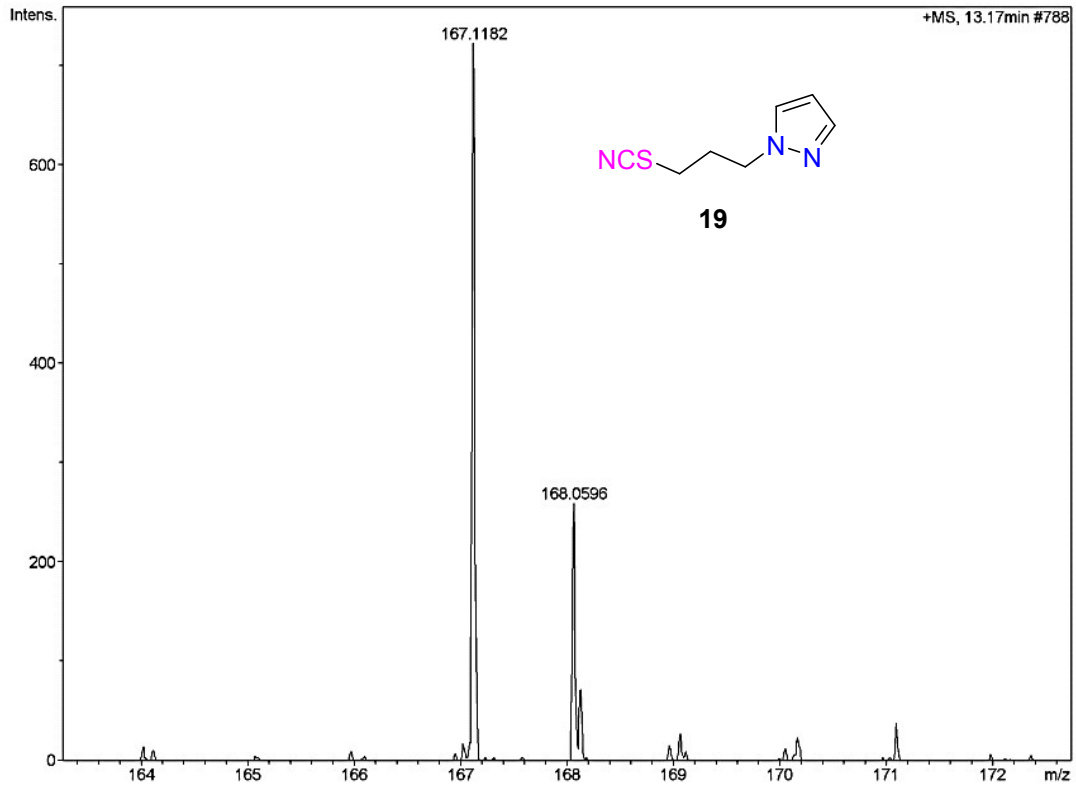
Analysis Info

Analysis Name	D:\Data\Chem\2020 Samples\202002\0206\CS-19-1.d	Acquisition Date	2/6/2020 3:02:37 PM
Method	YCH-50-500.m	Operator	default user
Sample Name	CS-19	Instrument / Ser#	micrOTOF-Q II 10269
Comment	A/P Huynh Han Vinh		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	500 m/z	Set Collision Cell RF	50.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
168.0596	1	C 7 H 10 N 3 S	168.0590	-3.7	4.5	even	ok



Bruker Compass DataAnalysis 4.0 printed: 2/6/2020 3:23:24 PM Page 1 of 1

Figure S70. HR-MS (ESI) data of **19**.

X-ray Diffraction Studies. Single crystals of **2**, **4**, **5**, **12**, **15** were obtained by slow evaporation of a concentrated solution in CH_2Cl_2/diethyl ether or CH_2Cl_2/hexane. X-ray data for them were collected with a Bruker AXS SMART APEX diffractometer, using Mo- or Cu-K_α radiation with the SMART suite of Programs.[2] Data were processed and corrected for Lorentz and polarization effects with SAINT,[3] and for absorption effect with SADABS.[4] Structural solution and refinement were carried out with the SHELXTL suite of programs.[5] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H-atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table S1.

Table S1. Selected X-ray crystallographic data for complexes **2**, **4**, **5**, **12**, **15**.

	2	**4**	**5**
formula	$C_{15}H_{17}N_3S_2$	$C_{21}H_{21}N_3S_2$	$C_{17}H_{15}N_3S_2$
fw	303.44	379.53	325.44
color, habit	yellow, block	colorless, block	colorless, block
cryst size [mm]	0.60 x 0.30 x 0.15	0.16 x 0.14 x 0.12	0.46 x0.26 x0.20
temp [K]	100(2)	223(2)	100(2)
crystsyst	orthorhombic	monoclinic	monoclinic
space group	*P*bca	*P*21/c	*P*21/n
a[Å]	10.5462(6)	8.1553(5)	5.3591(3)
b [Å]	11.8138(6)	16.6915(10)	19.3576(11)
c [Å]	24.1532(13)	14.5815(9)	15.0546(8)
α [deg]	90.00	90.00	90.00
β [deg]	90.00	102.2050(10)	96.0410(10)
γ [deg]	90.00	90.00	90.00
V [Å^3]	3009.3(3)	1940.0(2)	1553.08(15)
Z	8	4	4
D_c [g cm^{-3}]	1.340	1.299	1.392
radiation used	Mo Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	0.347	0.284	0.342
θ range [deg]	1.69–27.50	1.88–27.50	2.10–27.48
no. of unique data	20165	13597	10876
max., min. transmn	0.9498, 0.8188	0.9667, 0.9560	0.9348, 0.8586
final R indices	R_1 = 0.0467,	R_1 = 0.0591	R1 = 0.0391,
[$I > 2\sigma(I)$]	wR_2 = 0.1138	wR_2 = 0.1310	wR2 = 0.1026
R indices (all data)	R_1 = 0.0517,	R_1 = 0.0925	R1 = 0.0437,
	wR_2 = 0.1167	wR_2 = 0.1459	wR2 = 0.1057
goodness-of-fit	1.096	1.043	1.057
Largest diff. peak	0.542/–0.304	0.308/–0.211	0.361/–0.216

Table S1 (cont.)

	12	**15**
formula	$C_{13}H_{14}N_4S_2$	$C_{11}H_{10}N_2S$
fw	290.40	202.27
color, habit	red, rod	colorless, thin plate
cryst size [mm]	0.60 x0.36 x0.30	0.20 x 0.16 x 0.04
temp [K]	223(2)	100(2)
crystsyst	orthorhombic	monoclinic
space group	*P*2(1)2(1)2(1)	*P*21/n
a[Å]	9.035(5)	11.0937(7)
b [Å]	11.727(7)	6.0127(4)
c [Å]	13.103(8)	13.9608(10)
α [deg]	90.00	90.00
β [deg]	90.00	93.459(5)
γ [deg]	90.00	90.00
V [Å^3]	1388.4(14)	929.53(11)
Z	4	4
D_c [g cm^{-3}]	1.389	1.445
radiation used	Mo Kα	Cu Kα
μ [mm^{-1}]	0.375	2.716
θ range [deg]	2.33–27.50	4.949–70.072
no. of unique data	9140	7913
max., min. transmn	0.8959, 0.8064	0.7533, 0.5482
final R indices	R1 = 0.0369,	R_1 = 0.0556,
[$I > 2\sigma(I)$]	wR2= 0.0893	wR_2 = 0.1304
R indices (all data)	R1 = 0.0391,	R_1 = 0.0809,
	wR2 = 0.0906	wR_2 = 0.1447
goodness-of-fit	1.071	1.024
Largest diff. peak	0.333/–0.176	0.540/–0.420

References

S5 E. S. H. E. Ashry, Y. E. Kilany, N. M. Nahas, A. Barakat, N. A.-Qurashi, H. A. Ghabbour, H.-K. Fun, *Molecules* **2016**, *21*, 12–23.

S2 *SMART,* version 5.628; Bruker AXS Inc.: Madison, WI, 2001.

S3 *SAINT+,* version 6.22a; Bruker AXS Inc.: Madison, WI, 2001.

S4 G. W. Sheldrick, *SADABS* version 2.10; University of Göttingen: Göttingen, Germany, 2001.

S5 *SHELXTL,*version 6.14; Bruker AXS Inc.: Madison, WI, 2000.