**Supporting Information**

A Non-Isocyanate Approach to Preparing Carbamate- and Thiocarbamate-Containing Ionic Liquids

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**Additional Experimental Procedures.**

**Synthesis of butyl-1-imidazolecarboxylate**(**O4-CDI**)*.*1 In a 250-mL round-bottomed flask with magnetic stirring was dissolved *n*-butanol (50.00 g, 0.675 mol). CDI (10.94 g, 0.0675 mol) was added in portions over a 5 min period, and the resulting solution was stirred at rt overnight. The solvent was then removed under reduced pressure and the residue was purified by column chromatography on silica gel with an eluent of 50:50 hexanes:ethyl acetate. Purification resulted in 7.63 (67 %) of a clear, colorless oil. 1H NMR (CDCl3):  8.05 (s, 1 H), 7.35 (s, 1 H), 6.98 (s, 1 H), 4.34 (t, 2 H, *J* = 6.8 Hz), 1.70 (m, 2 H), 1.40 (m, 2 H), 0.91 (t, 3 H, *J* = 7.4 Hz). 13C NMR (CDCl3):  148.59, 136.90, 130.40, 16.90, 68.03, 30.29, 18.79, 13.42. Anal. Calcd. For C8H12N2O2: C 57.13, H 7.19, N 16.66. Found: C 57.29, H 7.75, N 16.46.

**Synthesis of O4-API.** In a 250-mL round-bottomed flask with magnetic stirring was dissolved O4-CDI (9.00 g, 0.0535 mol) in CH2Cl2 (100 mL). API (8.03 g, 0.0642 mol) was added and the resulting solution was stirred at rt overnight. An additional 100 mL of CH2Cl2 was added and the solution was washed with DI water (2 x 100 mL) and brine (100 mL), dried over Na2SO4/MgSO4, filtered, and solvent removed to provide 9.93 g (82 %) of a clear, colorless oil. 1H NMR (CDCl3):  7.41 (s, 1 H), 6.96 (s, 1 H), 6.87 (s, 1 H), 5.53 (bs, 1 H), 3.97 (t, 2 H, *J* = 6.8 Hz), 3.92 (t, 2 H, *J* = 6.8 Hz), 3.10 (m, 2 H), 1.91 (quintet, 2 H, *J* = 6.7 Hz), 1.51 (m, 2 H), 1.30 (quintet, 2 H, *J* = 7.6 Hz), 0.85 (t, 3 H, *J* = 7.2 Hz). 13C NMR (CDCl3):  156.97, 136.95, 129.24, 118.70, 64.59, 44.11, 37.68, 31.35, 30.87, 18.88, 13.57. Anal. Calcd. For C11H19N3O2: C 58.64, H 8.50, N 18.65. Found: C 58.27, H 8.75, N 19.45.

**Synthesis of octyl-1-imidazolecarboxylate (O8-CDI).**2 In a 250-mL round-bottomed flask with magnetic stirring was dissolved 1-octanol (5.00 g, 0.0384 mol) in EtOAc (60 mL). To this stirred solution was added CDI (6.54 g, 0.0403 mol) in portions over a 15 min period. The resulting solution was stirred at rt overnight. The solvent was then removed under reduced pressure and the resulting oil was purified by column chromatography on silica gel with a gradient elution of 30-50 % EtOAc in hexanes. Purification resulted in 7.23 g (84 %) of a clear, colorless liquid, which solidified upon standing. 1H NMR (CDCl3):  8.11 (s, 1 H), 7.40 (s, 1 H), 7.05 (s, 1 H), 4.38 (t, 2 H, *J* = 6.6 Hz), 1.76 (m, 2 H), 1.20-1.45 (m, 10 H), 0.86 (t, 3 H, *J* = 6.8 Hz). 13C NMR (CDCl3):  148.65, 136.96, 130.49, 116.97, 68.40, 31.62, 28.99, 28.36, 25.60, 22.50, 13.95. Anal. Calcd. For C12H20N2O2: C 64.26, H 8.99, N 8.99. Found: C 65.01, H 8.87, N 9.10.

**Synthesis of O8-API.** In a 100-mL round-bottomed flask was dissolved octyl-1-imidazolecarboxylate (7.10 g, 0.0317 mol) in CH2Cl2 (70 mL). API (5.94 g, 0.0475 mol) was added and the resulting solution was stirred magnetically at rt overnight. The reaction was washed with DI water (2 x 50 mL) and brine (50 mL), dried over Na2SO4/MgSO4, filtered, and solvent removed under reduced pressure to afford 8.25 g (93 %) of a yellow oil. 1H NMR (CDCl3):  7.42 (s, 1 H), 6.99 (s, 1 H), 6.88 (s, 1 H), 5.32 (bs, 1 H), 3.99 (t, 2 H, *J* = 6.4 Hz), 3.94 (t, 2 H, *J* = 7.2 Hz), 3.11 (m, 2 H), 1.93 (quintet, 2 H, *J* = 6.9 Hz), 1.54 (m, 2 H), 1.15-1.30 (m, 10 H), 0.81 (t, 3 H, *J* = 6.8 Hz). 13C NMR (CDCl3):  156.97, 137.00, 129.40, 118.71, 65.02, 44.15, 37.78, 31.64, 31.44, 29.11, 29.07, 28.90, 25.72, 22.50, 13.97. Anal. Calcd. For C15H27N3O2: C 64.02, H 9.67, N 14.93. Found: C 62.52, H 9.32, N 15.11.

**Synthesis of dodecyl-1-imidazolecarboxylate (O12-CDI).**3 In a 250-mL round-bottomed flask with magnetic stirring was dissolved 1-dodecanol (5.00 g, 0.0268 mol) in EtOAc (60 mL). To this stirred solution was added CDI (4.56 g, 0.0281 mol) in portions over a 20 min period. The resulting solution was stirred at rt overnight. The solvent was then removed under reduced pressure and the resulting oil was quickly purified by column chromatography on silica gel in order to avoid solidification. A 50:50 EtOAc:hexanes solution was used for elution. The purification resulted in 6.09 g (81 %) of a clear, colorless liquid, which solidified upon standing. 1H NMR (CDCl3):  8.11 (s, 1 H), 7.40 (s, 1 H), 7.04 (s, 1 H), 4.38 (t, 2 H, *J* = 6.6 Hz), 1.75 (m, 2 H), 1.18-1.58 (m, 18 H), 0.85 (t, 3 H, *J* = 6.8 Hz). 13C NMR (CDCl3):  148.75, 137.06, 130.56, 117.07, 68.51, 68.02, 31.88, 29.59, 29.53, 29.50, 29.47, 29.42, 29.31, 29.20, 29.12, 28.65, 28.44, 25.69, 22.66, 14.10. Anal. Calcd. For C16H28N2O2: C 68.53, H 10.07, N 9.99. Found: C 70.13, H 10.08, N 9.54.

**Synthesis of O12-API.** Dodecyl-1-imidazolecarboxylate (1.50 g, 5.35 mmol) was dissolved in CH2Cl2 (15 mL) in a 100-mL round-bottomed flask equipped with a magnetic stir bar. API (0.74 g, 5.88 mmol) was added and the resulting solution was stirred at RT for 48 hr. The reaction was further diluted with CH2Cl2 (35 mL), washed with DI water (2 x 25 mL) and brine (25 mL), dried over Na2SO4/MgSO4, filtered, and the solvent removed under reduced pressure to give 1.63 g (90 %) of an off-white solid. 1H NMR (CDCl3):  7.45 (s, 1 H), 7.02 (s, 1 H), 6.90 (s, 1 H), 5.11 (bs, 1 H), 4.01 (t, 2 H, *J* = 6.8 Hz), 3.97 (t, 2 H, *J* = 7.0 Hz), 3.14 (m, 2 H), 1.96 (quintet, 2 H, *J* = 6.8 Hz), 1.57 (m, 2 H), 1.15-1.31 (m, 18 H), 0.84 (t, 3 H, *J* = 6.8 Hz). 13C NMR (CDCl3):  156.95, 137.03, 129.54, 118.72, 65.13, 62.73, 44.21, 37.98, 32.78, 31.84, 31.52, 29.56, 29.51, 29.48, 29.27, 29.22, 28.95, 25.79, 22.61, 14.04. Anal. Calcd. For C19H35N3O2: C 67.62, H 10.45, N 12.45. Found: C 66.82, H 10.23, N 12.35.

**Synthesis of 2-methoxyethyl-1-imidazolecarboxylate (OM-CDI).** In a 250-mL round-bottomed flask with a magnetic stir bar was dissolved 2-methoxyethanol (4.00 g, 0.0526 mol) in EtOAc (50 mL). CDI (12.79 g, 0.0789 mol) was added in portions over a 15 min period and the resulting solution was stirred at rt overnight. The resulting solution was stirred at rt overnight. The solvent was then removed under reduced pressure and the resulting oil was purified by column chromatography on silica gel with a gradient elution of 30-50 % EtOAc in hexanes. Purification resulted in 7.25 g (80 %) of a clear, colorless liquid, which solidified upon standing. 1H NMR (CDCl3):  8.12 (s, 1 H), 7.40 (s, 1 H), 7.02 (s, 1 H), 4.51 (m, 2 H), 3.68 (m, 2 H), 3.37 (s, 3 H). 13C NMR (CDCl3):  148.56, 137.01, 130.46, 117.02, 69.72, 66.86, 58.88. Anal. Calcd. For C7H10N2O3: C 49.41, H 5.92, N 16.46. Found: C 48.59, H 5.88, N 16.91.

**Synthesis of OM-API.** 2-Methoxyethyl-1-imidazolecarboxylate (6.85 g, 0.0400 mol) was dissolved in CH2Cl2 (75 mL) in a 250-mL round-bottomed flask with magnetic stirring. API (7.47 g, 0.0597 mol) was then added and the resulting solution was stirred at rt for 48 hours. The resulting solution was stirred at rt overnight. The reaction was then purified by extraction, washing the organic phase sequentially with DI water (2 x 25 mL) and brine (25 mL). The organic phase was then isolate, dried over Na2SO4/MgSO4, filtered, and the solvent removed under reduced pressure to give 8.01 g (88 %) of an off-white solid. 1H NMR (CDCl3):  7.62 (s, 1 H), 7.03 (s, 1 H), 6.92 (s, 1 H), 5.31 (bs, 1 H), 4.18 (t, 2 H, *J* = 6.9 Hz), 3.99 (t, 2 H, *J* = 7.2 Hz), 3.53 (t, 2 H, *J* = 6.9 Hz), 3.34 (s, 3 H), 3.14 (m, 2 H), 1.96 (t, 3 H, *J* = 6.6 Hz). 13C NMR (CDCl3):  156.58, 137.02, 128.73, 118.90, 70.76, 63.87, 58.87, 44.34, 37.83, 31.35. Anal. Calcd. For C10H17N3O3: C 52.85, H 7.54, N 18.49. Found: C 53.15, H 7.85, N 19.05.

**Synthesis of butylthio-1-imidazolecarboxylate.** In a 250-mL round-bottomed flask with a magnetic stir bar was dissolve 1-butanethiol (5.00 g, 0.0554 mol) in EtOAc (50 mL). CDI (8.99 g, 0.0554 mol) was added in portions over a 20-minute period and the resulting solution was stirred at rt overnight. The solvent was then removed under reduced pressure and the crude yellow oil was purified by column chromatography on silica gel with 15-30 % EtOAc in hexanes. Purification resulted in 8.32 g (81 %) of a clear colorless oil. 1H NMR (CDCl3):  8.14 (s, 1 H), 7.42 (s, 1 H), 7.04 (s, 1 H), 3.08 (t, 2 H, *J* = 7.4 Hz), 1.66 (quintet, 2 H, *J* = 6.6 Hz), 1.41 (quintet, 2 H, *J* = 6.8 Hz), 0.91 (t, 3 H, *J* = 7.2). 13C NMR (CDCl3):  166.19, 135.29, 130.71, 115.77, 31.11, 30.23, 21.66, 13.37. Anal. Calcd. For C8H12N2OS: C 52.15, H 6.56, N 15.20, S 17.40. Found: C 52.13, H 6.85, N 14.55, S 17.22.

**Synthesis of S4-API.** Butylthio-1-imidazolecarboxylate (8.00 g, 0.0434 mol) was dissolve in CH2Cl2 (100 mL) in a 250-mL round-bottomed flask with magnetic stirring. To this solution was added API (8.15 g, 0.0651 mol) and the resulting solution was stirred at rt for 24 hr. The solution was transferred to a separatory funnel and washed with DI water (50 mL) and brine (50 mL). The organic phase was dried over Na2SO4/MgSO4, filtered, and the solvent removed under reduced pressure to give 6.50 g (62 %) of a light, yellow oil. 1H NMR (CDCl3):  7.41 (s, 1 H), 7.02 (s, 1 H), 6.90 (s, 1 H), 6.89 (bs, 1 H), 3.96 (t, 2 H, *J* = 6.8 Hz), 3.24 (m, 2 H), 2.87 (m, 2 H), 1.98 (m, 2 H), 1.55 (m, 2 H), 1.36 (m, 2 H), 0.87 (t, 3 H, *J* = 6.8 Hz). 13C NMR (CDCl3):  168.05, 137.05, 129.27, 118.77, 44.18, 37.97, 32.40, 31.02, 29.38, 21.79, 13.51. Anal. Calcd. For C11H19N3OS: C 57.74, H 7.94, N 17.41, S 13.28. Found: C 56.92, H 8.16, N 17.21, S 13.08.

**Synthesis of O2-C2-Br.** O2-API (2.60 g, 0.0142 mol) was dissolved in acetonitrile (30 mL) in a 100-mL round-bottomed flask with magnetic stirring. Ethyl bromide (3.09 g, 0.0284 mol) was added and the resulting solution was heated to 40 °C where it was held stirring for 24 hr. The volatiles were then removed under reduced pressure, and the residue was washed vigorously with anhydrous THF (3 x 30 mL), then dried under reduced pressure (0.1 mm Hg at 60 °C) for 48 hr, resulting in a viscous light brown oil (3.78 g, 91 %). 1H NMR (DMSO-*d*6):  9.29 (s, 1 H), 7.82 (s, 1 H), 7.80 (s, 1 H), 7.21 (t, 1 H, *J* = 5.8 Hz), 4.13-4.19 (m, 4 H), 3.92 (q, 2 H, *J* = 7.1 Hz), 2.97 (m, 2 H), 1.89 (m, 2 H), 1.38 (t, 3 H, *J* = 7.4 Hz), 1.10 (t, 3 H, *J* = 7.1 Hz). 13C NMR (DMSO-*d*6):  156.33, 135.94, 122.38, 122.14, 59.67, 46.52, 44.20, 36.81, 29.78, 15.02, 14.64. Anal. Calcd. For C11H20BrN3O2: C 43.15, H 6.58, N 13.72. Found: C 41.92, H 7.05, N 13.91.

**Synthesis of O2-C2-NTf2.** O2-C2-Br (2.54 g, 8.69 mmol) was dissolved in DI water (25 mL) in a 250-mL round-bottomed flask with magnetic stirring. A solution of LiNTf2 (2.99 g, 10.43 mmol) in DI water (5 mL) was added and the resulting mixture was stirred at RT overnight. CH2Cl2 (100 mL) was then added and stirring continued for one hour. The organic layer was separated, washed with DI water (3 x 30 mL), and solvent removed under reduced pressure, resulting in 3.95 g (92 %) of a light, yellow oil.  1H NMR (DMSO-*d*6):  9.14 (s, 1 H), 7.78 (s, 1 H), 7.77 (s, 1 H), 7.21 (t, 1 H, *J* = 5.6 Hz), 4.12-4.20 (m, 4 H), 3.96 (q, 2 H, *J* = 7.1 Hz), 2.97 (m, 2 H), 1.92 (m, 2 H), 1.41 (t, 3 H, *J* = 7.2 Hz), 1.14 (t, 3 H, *J* = 7.0 Hz). 13C NMR (DMSO-*d*6):  156.39, 135.90, 122.42, 122.15, 119.49 (q, *J* = 320 Hz, -CF3), 59.71, 46.58, 44.23, 36.84, 29.83, 14.93, 14.61. Anal. Calcd. For C13H20F6N4O6S2: C 30.83, H 3.98, N 11.06, S 12.66. Found: C 30.74, H 3.21, N 11.66, S 12.95.

**Synthesis of O2-C8-Br.** In a 250-mL round-bottomed flask with a magnetic stir bar was dissolved O2-API (4.00 g, 0.0218 mol) in acetonitrile (50 mL). 1-Bromooctane (5.06 g, 0.0262 mol) was added and the resulting solution was stirred at 60 °C for 24 hr. The solvent was then removed under reduced pressure and the resulting oil was washed vigorously with anhydrous THF (3 x 50 mL). After removal of the final THF washing, the residue was dried in a vacuum oven (0.1 mm Hg, 60 °C) for 48 hr. Yield = 7.90 g (96 %) of a viscous, light brown oil. 1H NMR (DMSO-*d*6):  9.24 (s, 1 H), 7.81 (s, 2 H), 7.23 (bs, 1 H), 4.12-4.17 (m, 4 H), 3.94 (m, 2 H), 2.95 (m, 2 H), 1.91 (m, 2 H), 1.78 (m, 2 H), 1.12-1.30 (m, 10 H), 0.83 (t, 3 H, *J* = 6.6 Hz). 13C NMR (DMSO-*d*6):  156.33, 136.17, 122.43, 59.67, 48.83, 46.55, 36.78, 31.15, 29.81, 29.27, 28.47, 28.32, 25.48, 22.05, 14.63, 13.93. Anal. Calcd. For C17H32BrN3O2: C 52.31, H 8.26, N 10.76. Found: C 52.92, H 8.59, N 10.85.

**Synthesis of O2-C8-NTf2.** O2-C8-Br (1.50 g, 3.84 mmol) was dissolve in DI water (10 mL) in a 100-mL round-bottomed flask with magnetic stirring. To this solution was added a solution of LiNTf2 (1.16 g, 4.03 mmol) in DI water (8 mL) and the resulting mixture was stirred at rt overnight. Dichloromethane (40 mL) was then added and stirring continued at rt for 1 hr, followed by separation of the organic phase and washing with DI water (3 x 20 mL). The solvent was then removed from the organic phase under reduced pressure, resulting in 2.08 g (92 %) of a light, yellow oil. 1H NMR (DMSO-*d*6):  9.15 (s, 1 H), 7.78 (s, 2 H), 7.22 (bs, 1 H), 4.09-4.19 (m, 4 H), 3.96 (m, 2 H), 2.95 (m, 2 H), 1.92 (m, 2 H), 1.79 (m, 2 H), 1.11-1.31 (m, 10 H), 0.84 (t, 3 H, *J* = 6.8 Hz). 13C NMR (DMSO-*d*6):  156.38, 136.14, 122.46, 119.49 (q, *J* = 320 Hz, -CF3), 59.69, 48.88, 46.58, 36.80, 31.15, 29.84, 29.26, 28.47, 28.32, 25.48, 22.05, 14.61, 13.91. Anal. Calcd. For C19H32F6N4O6S2: C 38.64, H 5.46, N 9.49, S 10.86. Found: C 38.22, H 4.92, N 9.82, S 11.48.

**Synthesis of O2-C12-Br**. In a 250-mL round-bottomed flask was dissolved O2-API (2.50 g, 0.0137 mol) in acetonitrile (50 mL) with magnetic stirring. 1-Bromododecane (4.08 g, 0.0164 mol) was added and the resulting solution was stirred at 60 °C for 24 hr. The solvent was then removed and the residue was washed with several portions of THF (3 x 40 mL), then placed in a vacuum oven for 24 hr to remove trace solvent impurities. A viscous brown oil was obtained (5.49 g, 90 %). 1H NMR (DMSO-*d*6):  9.23 (s, 1 H), 7.81 (s, 2 H), 7.22 (t, 1 H, *J* = 5.5 Hz), 4.15 (m, 4 H), 3.95 (t, 2 H, *J* = 6.9 Hz), 2.98 (q, 2 H, *J* = 6.3 Hz), 1.93 (quintet, 2 H, *J* = 6.6 Hz), 1.76 (m, 2 H), 1.16-1.30 (m, 18 H), 1.14 (t, 3 H, *J* = 7.1 Hz), 0.83 (t, 3 H, *J* = 6.6 Hz). 13C NMR (DMSO-*d*6):  156.34, 136.16, 122.46, 59.67, 48.83, 46.55, 36.78, 31.29, 29.81, 29.26, 29.02, 29.00, 28.94, 28.81, 28.72, 28.36, 25.48, 22.09, 14.63, 13.96. Anal. Calcd. For C21H40BrN3O2: C 56.49, H 9.03, N 9.41. Found: C 56.30, H 9.27, N 9.76.

**Synthesis of O2-C12-NTf2.** In a 100-mL round-bottomed flask was dissolved O2-C12-Br (3.05 g, 6.83 mmol) in CHCl3 (40 mL) with magnetic stirring. A solution of LiNTf2 (2.06 g, 7.17 mmol) in DI water (30 mL) was added and the mixture was stirred for 24 hr. The organic layer was then separated, and the solvent was removed under reduced pressure, resulting in 4.21 g (95 %) of a yellow oil. 1H NMR (DMSO-*d*6):  9.12 (s, 1 H), 7.75 (s, 1 H), 7.74 (s, 1 H), 7.19 (t, 1 H, *J* = 5.5 Hz), 4.11 (m, 4 H), 3.95 (t, 2 H, *J* = 6.8 Hz), 2.93 (q, 2 H, *J* = 6.6 Hz), 1.89 (quintet, 2 H, *J* = 6.6 Hz), 1.76 (m, 2 H), 1.15-1.29 (m, 18 H), 1.14 (t, 3 H, *J* = 7.0 Hz), 0.81 (t, 3 H, *J* = 6.6 Hz). 13C NMR (DMSO-*d*6):  156.38, 136.16, 122.46, 119.50 (q, *J* = 320 Hz, -CF3), 59.69, 48.90, 46.58, 36.78, 31.31, 29.84, 29.28, 29.04, 28.96, 28.82, 28.74, 28.38, 25.49, 22.10, 14.57, 13.89. Anal. Calcd. For C23H40F6N4O6S2: C 42.72, H 6.23, N 8.66, S 9.91. Found: C 42.86, H 5.89, N 9.01, S 10.55.

**Synthesis of OM-C2-Br.** In a 100-mL round-bottomed flask with magnetic stirring was dissolved ME-API (2.65 g, 0.0116 mol) in acetonitrile (30 mL). Ethyl bromide (2.52 g, 0.0231 mol) was added and the solution was stirred at 50 C for 24 hr. The removal of solvent and excess ethyl bromide was then completed under reduced pressure to afford a viscous yellow oil (3.75 g, 96 %). 1H NMR (CDCl3):  9.23 (s, 1 H), 7.81 (s, 1 H), 7.78 (s, 1 H), 7.32 (t, 1 h, *J* = 5.6 Hz), 4.15 (m, 4 H), 4.01 (t, 2 H, *J* = 6.8 Hz), 3.43 (t, 2 H, *J* = 6.6 Hz), 3.20 (s, 3 H), 2.93 (m, 2 H), 1.90 (quintet, 2 H, *J* = 6.8 Hz), 1.38 (t, 3 H, *J* = 7.2 Hz). 13C NMR (CDCl3):  156.25, 135.92, 122.38, 122.16, 70.24, 62.97, 57.95, 46.51, 44.21, 36.87, 29.76, 14.99. Anal. Calcd. For C12H22BrN3O3: C 42.87, H 6.60, N 12.50. Found: C 41.42, H 7.07, N 12.58.

**Synthesis of OM-C2-NTf2.** In a 100-mL round-bottomed flask with magnetic stirring was dissolved ME-C2-Br (3.70 g, 0.0109 mol) in DI water (30 mL). A solution of LiNTf2 (4.71 g, 0.0164 mol) in DI water (25 mL) was added and the resulting mixture was stirred overnight at RT. Dichloromethane (75 mL) was then added and the mixture stirred for an additional hour, followed by separation of the organic phase, washing with DI water (3 x 50 mL), and removal of solvent under reduced pressure. The reaction yielded 5.43 g (92 %) of a light-yellow oil. 1H NMR (CDCl3):  9.12 (s, 1 H), 7.75 (s, 1 H), 7.74 (s, 1 H), 7.32 (t, 1 H, *J* = 5.5 Hz), 4.13 (m, 4 H), 4.02 (t, 2 H, *J* = 6.8 Hz), 3.44 (m, 2 H), 3.21 (s, 3 H), 2.94 (m, 2 H), 1.90 (quintet, 2 H, *J* = 6.6 Hz), 1.39 (t, 3 H, *J* = 7.2 Hz). 13C NMR (CDCl3):  156.37, 135.95, 122.45, 122.18, 119.53 (q, *J* = 320 Hz, -CF3), 70.29, 63.04, 57.94, 46.58, 44.29, 36.90, 29.82, 14.92. Anal. Calcd. For C14H22F6N4O7S2: C 31.35, H 4.13, N 10.44, S 11.95. Found: C 31.32, H 4.02, N 10.67, S 12.54.

**Synthesis of O4-C2-Br.** In a 250-mL round-bottomed flask with magnetic stirring was dissolved O4-API (9.40 g, 0.0417 mol) in acetonitrile (100 mL). Ethyl bromide (13.64 g, 0.0125 mol) was added and the resulting solution was stirred at 50 °C for 24 hr. The solvent was then removed under reduced pressure, followed by washing the residual oil with anhydrous THF (3 x 50 mL). The residue was then dried under vacuum (0.1 mm Hg, 60 °C), resulting in 13.26 g (95 %) of a light brown oil. 1H NMR (DMSO-*d*6):  9.33 (s, 1 H), 7.84 (s, 1 H), 7.81 (s, 1 H), 7.21 (t, 1 H, *J* = 5.6 Hz), 4.11-4.20 (m, 4 H), 3.87 (q, 2 H, *J* = 6.7 Hz), 2.92 (q, 2 H, *J* = 6.3 Hz), 1.89 (quintet, 2 H, *J* = 6.6 Hz), 1.43 (quintet, 2 H, *J* = 7.6 Hz), 1.38 (t, 3 H, *J* = 7.4 Hz), 1.26 (quintet, 2 H, *J* = 7.5 Hz), 0.82 (t, 3 H, *J* = 7.2 Hz). 13C NMR (DMSO-*d*6):  156.41, 135.95, 122.36, 122.13, 63.44, 46.50, 44.18, 36.83, 30.70, 29.78, 18.57, 15.02, 13.60. Anal. Calcd. For C13H24BrN3O2: C 46.71, H 7.24, N 12.57. Found: C 45.14, H 7.68, N 12.38.

**Synthesis of O4-C2-NTf2.** O4-C2-Br (3.00 g, 8.98 mmol) was dissolved in DI water (30 mL) with magnetic stirring in a 250-mL round-bottomed flask. A solution of LiNTf2 (3.09 g, 10.77 mmol) in DI water (20 mL) was then added and the resulting mixture was stirred at rt overnight. CH2Cl2 (50 mL) was then added and stirring continued for an additional hour, followed by removal of the organic phase and washing with DI water (3 x 30 mL). The organic phase was separated and the volatiles were removed under reduced pressure, resulting in 4.61 g (96 %) of a light, yellow oil. 1H NMR (DMSO-*d*6):  9.14 (s, 1 H), 7.78 (s, 1 H), 7.77 (s, 1 H), 7.23 (t, 1 H, *J* = 5.8 Hz), 4.12-4.20 (m, 4 H), 3.92 (t, 2 H, *J* = 6.6 Hz), 2.97 (q, 2 H, *J* = 6.3 Hz), 1.91 (quintet, 2 H, *J* = 6.6 Hz), 1.50 (quintet, 2 H, *J* = 6.8 Hz), 1.41 (t, 3 H, *J* = 7.4 Hz), 1.31 (quintet, 2 H, *J* = 6.8 Hz), 0.87 (t, 3 H, *J* = 7.2 Hz). 13C NMR (DMSO-*d*6):  156.53, 135.91, 122.43, 122.15, 119.51 (q, *J* = 320 Hz, -CF3), 63.54, 46.60, 44.26, 36.87, 30.74, 29.84, 18.62, 14.90, 13.56. Anal. Calcd. For C15H24F6N4O6S2: C 33.71, H 4.53, N 10.48, S 12.00. Found: C 34.66, H 4.29, N 10.65, S 12.50.

**Synthesis of O4-C2-OTf.** O4-C2-Br (2.00 g, 5.98 mmol) was dissolved in DI water (20 mL) in a 100-mL round-bottomed flask with magnetic stirring. A solution of silver triflate (1.58 g, 6.16 mmol) in DI water (5 mL) was added and the resulting mixture was stirred in the dark for 24 hr. CH2Cl2 (50 mL) was then added and stirring continued for an additional hour. The solids were then filtered, and the organic layer was separated, washed with DI water (3 x 25 mL), and solvent removed under reduced pressure to give 2.07 g (86 %) of a light, yellow oil. 1H NMR (DMSO-*d*6):  9.11 (s, 1 H), 7.76 (s, 1 H), 7.74 (s, 1 H), 7.16 (t, 1 H, *J* = 5.6 Hz), 4.11-4.18 (m, 4 H), 3.90 (t, 2 H, *J* = 6.6 Hz), 2.95 (q, 2 H, *J* = 6.3 Hz), 1.89 (quintet, 2 H, *J* = 6.6 Hz), 1.48 (m, 2 H), 1.39 (t, 3 H, *J* = 7.2 Hz), 1.28 (quintet, 2 H, *J* = 6.6 Hz), 0.84 (t, 3 H, *J* = 7.2 Hz). 13C NMR (DMSO-*d*6):  156.51, 135.90, 122.42, 122.16, 120.67 (q, *J* = 320 Hz, -CF3), 63.53, 46.59, 44.26, 36.89, 30.74, 29.82, 18.62, 14.93, 13.60. Anal. Calcd. For C14H24F3N3O5S2: C 41.68, H 6.00, N 10.42, S 7.95. Found: C 41.12, H 6.12, N 10.73, S 8.11.

**Synthesis of O4-C2-OMs.** O4-C2-Br (4.00 g, 0.0120 mmol) was dissolved in DI water (40 mL) in a 100-mL round-bottomed flask with magnetic stirring. A solution of silver mesylate (2.50 g, 0.0123 mmol) in DI water (10 mL) was added and the resulting mixture was stirred in the dark for 24 hr. CH2Cl2 (75 mL) was then added and stirring continued for an additional hour. The solids were then filtered, and the organic layer was separated, washed with DI water (3 x 35 mL), and solvent removed under reduced pressure to give 3.60 g (86 %) of a yellow oil. 1H NMR (DMSO-*d*6):  9.21 (s, 1 H), 7.79 (s, 1 H), 7.77 (s, 1 H), 7.20 (t, 1 H, *J* = 5.6 Hz), 4.12-4.17 (m, 4 H), 3.88 (t, 2 H, *J* = 6.6 Hz), 2.94 (q, 2 H, *J* = 6.3 Hz), 2.29 (s, 3 H), 1.89 (quintet, 2 H, *J* = 6.6 Hz), 1.45 (m, 2 H), 1.38 (t, 3 H, *J* = 7.2 Hz), 1.26 (m, 2 H), 0.84 (t, 3 H, *J* = 7.2 Hz). 13C NMR (DMSO-*d*6):  159.07, 138.63, 125.03, 124.76, 66.06, 49.14, 46.79, 42.35, 39.50, 33.33, 32.39, 21.20, 17.60, 16.21. Anal. Calcd. For C14H27N3O5S2: C 48.12, H 7.79, N 12.03, S 9.17. Found: C 48.20, H 7.52, N 11.09, S 9.02.

**Synthesis of O4-C2-NFBSI.** In a 100-mL round-bottomed flaks equipped with a magnetic stir bar was dissolved O4-C2-Br (1.35 g, 4.04 mmol) in DI water (12 mL). A solution of LiNFSI (2.50 g, 4.24 mmol) in DI water (10 mL) was then added and the resulting mixture was stirred at rt overnight. Dichloromethane (50 mL) was then added and stirring continued for 1 hour. The organic phase was separated, washed with DI water (3 x 25 mL), and the solvent was removed to afford 3.26 g (97%) of a light, yellow oil. 1H NMR (DMSO-*d*6):  9.15 (s, 1 H), 7.79 (s, 1 H), 7.77 (s, 1 H), 7.21 (t, 1 H, *J* = 5.6 Hz), 4.13-4.20 (m, 4 H), 3.92 (t, 2 H, *J* = 6.6 Hz), 2.97 (q, 2 H, *J* = 6.3 Hz), 1.91 (quintet, 2 H, *J* = 6.4 Hz), 1.50 (quintet, 2 H, *J* = 6.8 Hz), 1.41 (t, 3 H, *J* = 7.2 Hz), 1.30 (quintet, 2 H, *J* = 6.8 Hz), 0.87 (t, 3 H, *J* = 7.2 Hz). 13C NMR (DMSO-*d*6):  156.51, 135.92, 122.44, 122.16, 105-122 (m, -CF2CF2CF2CF3), 63.51, 46.58, 44.24, 36.87, 30.74, 29.86, 18.61, 14.91, 13.54. Anal. Calcd. For C21H24F18N4O6S2: C 30.22, H 2.90, N 6.71, S 7.68. Found: C 30.11, H 3.04, N 7.33, S 8.09.

**Synthesis of O8-C2-Br.** O8-API (5.00 g, 0.0178 mol) was dissolved in acetonitrile (50 mL) in a 250-mL round-bottomed flask with magnetic stirring. Ethyl bromide (5.81 g, 0.0533 mol) was added and the resulting solution was stirred at 50 °C overnight, followed by removal of volatiles under reduced pressure. The residue was washed with anhydrous THF (3 x 30 mL) and then underwent additional drying in the vacuum oven (0.1 mm Hg, 60 °C), resulting in 6.45 g (93 %) of a viscous, light brown oil. 1H NMR (DMSO-*d*6):  9.34 (s, 1 H), 7.87 (s, 1 H), 7.84 (s, 1 H), 7.23 (t, 1 H, *J* = 5.6 Hz), 4.16-4.23 (m, 4 H), 3.89 (t, 2 H, *J* = 6.6 Hz), 2.96 (q, 2 H, *J* = 6.3 Hz), 1.92 (quintet, 2 H, *J* = 6.8 Hz), 1.51 (m, 2 H), 1.41 (t, 3 H, *J* = 7.2 Hz), 1.18-1.30 (m, 10 H), 0.82 (t, 3 H, *J* = 6.6 Hz). 13C NMR (DMSO-*d*6):  156.41, 135.94, 122.37, 122.13, 63.75, 46.50, 44.18, 36.83, 31.19, 29.79, 28.65, 28.62, 25.36, 22.05, 15.02, 13.91. Anal. Calcd. For C17H32BrN3O2: C 52.31, H 8.26, N 10.76. Found: C 50.80, H 8.13, N 10.35.

**Synthesis of O8-C2-NTf2.** In a 250-mL round-bottomed flask with magnetic stirring was dissolved O8-C2-Br (3.50 g, 8.97 mmol) in DI water (30 mL). A solution of LiNTf2 (3.86 g, 13.4 mmol) in DI water (15 mL) was added followed by stirring at RT for 2 hr. CH2Cl2 (100 mL) was then added and mixing continued overnight at RT. The organic phase was separated, washed with DI water (3 x 50 mL), and the solvent was removed under reduced pressure to afford 5.21 g (98 %) of a light-yellow oil. 1H NMR (DMSO-*d*6):  9.15 (s, 1 H), 7.78 (s, 1 H), 7.77 (s, 1 H), 7.20 (t, 1 H, *J* = 5.6 Hz), 4.14-4.21 (m, 4 H), 3.92 (t, 2 H, *J* = 6.6 Hz), 2.97 (q, 2 H, *J* = 6.3 Hz), 1.91 (quintet, 2 H, *J* = 6.8 Hz), 1.52 (m, 2 H), 1.42 (t, 3 H, *J* = 7.2 Hz), 1.19-1.31 (m, 10 H), 0.85 (t, 3 H, *J* = 6.6 Hz). 13C NMR (DMSO-*d*6):  156.51, 135.90, 122.43, 122.11, 119.50 (q, *J* = 320 Hz, -CF3), 63.82, 46.58, 44.25, 36.86, 31.23, 29.85, 28.69, 28.67, 25.42, 22.08, 14.91, 13.89. Anal. Calcd. For C19H32F6N4O6S2: C 38.64, H 5.46, N 9.49, S 10.86. Found: C 39.64, H 5.66, N 9.52, S 11.08.

**Synthesis of O12-C2-Br.** In a 250-mL round-bottomed flask was dissolved O12-API (2.50 g, 7.41 mmol) in acetonitrile (30 mL) with magnetic stirring. 1-Bromoethane (2.42 g, 22.2 mmol) was added and the resulting solution was stirred at 50 °C for 24 hr. The solvent was then removed and the residue was washed with several portions of THF (3 x 40 mL), then placed in a vacuum oven for 24 hr to remove trace solvent impurities. A viscous brown oil was obtained (3.01 g, 91 %). 1H NMR (DMSO-*d*6):  9.42 (s, 1 H), 7.83 (s, 1 H), 7.82 (s, 1 H), 7.31 (t, 1 H, *J* = 5.6 Hz), 4.14-4.20 (m, 4 H), 3.89 (t, 2 H, *J* = 6.8 Hz), 2.93 (q, 2 H, *J* = 6.3 Hz), 1.89 (quintet, 2 H, *J* = 6.8 Hz), 1.47 (m, 2 H), 1.38 (t, 3 H, *J* = 7.2 Hz), 1.13-1.7 (m, 18 H), 0.80 (t, 3 H, *J* = 6.6 Hz). 13C NMR (DMSO-*d*6):  156.43, 136.09, 122.39, 122.13, 63.72, 46.47, 44.17, 36.81, 31.30, 29.81, 29.05, 29.00, 28.72, 25.38, 22.09, 15.01, 13.92. Anal. Calcd. For C21H40BrN3O2: C 56.49, H 9.03, N 9.41. Found: C 56.31, H 9.27, N 9.66.

**Synthesis of O12-C2-NTf2.** O12-C2-Br (2.15 g, 4.82 mmol) was dissolved in DI water (20 mL) in a 100-mL round-bottomed flask with magnetic stirring. A solution of LiNTf2 (0.87 g, 3.03 mmol) in DI water (5 mL) was added and the resulting mixture was stirred at rt overnight. CH2Cl2 (50 mL) was added and stirring continued for an additional hour, followed by removal of the organic phase, washing with DI water (3 x 30 mL) and removal of solvents under reduced pressure. Yield = 2.99 g (98 %) of a light yellow oil. 1H NMR (DMSO-*d*6):  9.12 (s, 1 H), 7.76 (s, 1 H), 7.74 (s, 1 H), 7.18 (t, 1 H, *J* = 5.6 Hz), 4.12-4.16 (m, 4 H), 3.88 (t, 2 H, *J* = 6.6 Hz), 2.94 (q, 2 H, *J* = 6.3 Hz), 1.89 (quintet, 2 H, *J* = 6.8 Hz), 1.48 (m, 2 H), 1.38 (t, 3 H, *J* = 7.2 Hz), 1.16-1.28 (m, 18 H), 0.81 (t, 3 H, *J* = 6.6 Hz). 13C NMR (DMSO-*d*6):  156.47, 135.89, 122.41, 122.14, 119.48 (q, *J* = 320 Hz, -CF3), 63.80, 46.56, 44.22, 36.85, 31.30, 29.83, 29.05, 29.02, 29.00, 28.73, 28.66, 25.39, 22.10, 14.93, 13.91. Anal. Calcd. For C23H40F6N4O6S2: C 42.72, H 6.23, N 8.66, S 9.91. Found: C 44.83, H 6.24, N 9.36, S 10.17.

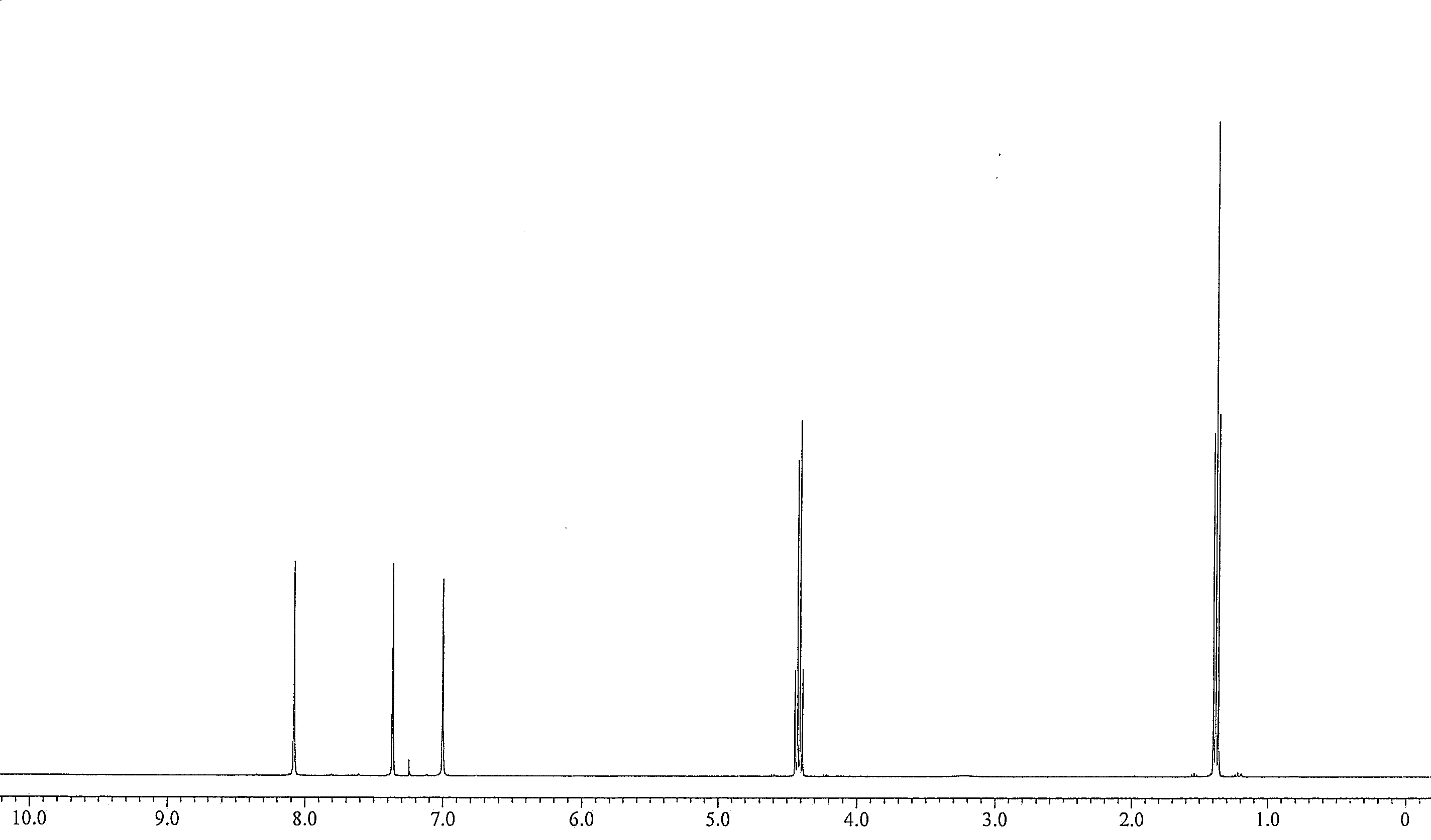
**Synthesis of S4-C2-Br.** In a 100-mL round-bottomed flask with magnetic stirring was dissolved S4-API (1.96 g, 8.12 mmol) in acetonitrile (20 mL). Ethyl bromide (2.65 g, 24.4 mmol) was added to the flask and the solution was stirred at 40 °C for 48 hr. The volatiles were then removed under reduced pressure to afford a dark, yellow oil, which was washed with several portions of diethyl ether (3 x 30 mL). After drying the residue in a vacuum oven for 24 hr, a yellow oil (2.69 g, 95 %) was obtained. 1H NMR (DMSO-*d*6):  9.28 (s, 1 H), 8.25 (t, 1 H, *J* = 5.4 Hz), 7.86 (s, 1 H), 7.82 (s, 1 H), 4.13-4.21 (m, 4 H), 3.09 (q, 2 H, *J* = 6.3 Hz), 2.76 (q, 2 H, *J* = 6.3 Hz), 1.95 (quintet, 2 H, *J* = 6.6 Hz), 1.46 (m, 2 H), 1.38 (t, 3 H, *J* = 7.4 Hz), 1.28 (quintet, 2 H, *J* = 7.4 Hz), 0.84 (t, 3 H, *J* = 7.2 Hz). 13C NMR (DMSO-*d*6):  166.05, 135.92, 122.38, 122.16, 46.64, 44.21, 37.30, 32.27, 29.50, 28.36, 21.29, 15.01, 13.50. Anal. Calcd. For C13H24BrN3OS: C 44.57, H 6.91, N 12.00, S 9.15. Found: C 43.99, H 6.68, N 12.30, S 9.00.

**Synthesis of S4-C2-NTf2.** S4-C2-Br (2.46 g, 7.02 mmol) was dissolved in DI water (20 mL) with magnetic stirring in a 100-mL round-bottomed flask. A solution of LiNTf2 (2.12 g, 7.37 mmol) in DI water (10 mL) was then added and the resulting mixture was stirred at rt overnight. Dichloromethane (50 mL) was then added and stirring continued for an additional hour, followed by removal of the organic phase and washing with DI water (2 x 30 mL). The organic phase was separated and the volatiles were removed under reduced pressure, resulting in 3.59 g (93 %) of a light, yellow oil. 1H NMR (DMSO-*d*6):  9.14 (s, 1 H), 8.18 (bs, 1 H), 7.79 (s, 1 H), 7.77 (s, 1 H), 4.12-4.20 (m, 4 H), 3.12 (m, 2 H), 2.77 (m, 2 H), 1.94 (m, 2 H), 1.43 (m, 2 H), 1.41 (t, 3 H, *J* = 7.2 Hz), 1.39 (m, 2 H), 0.86 (t, 3 H, *J* = 6.8 Hz). 13C NMR (DMSO-*d*6):  166.05, 135.88, 122.40, 122.16, 119.49 (q, *J* = 320 Hz, -CF3), 46.71, 44.29, 37.33, 32.29, 29.53, 28.41, 21.29, 14.92, 13.45. Anal. Calcd. For C15H24F6N4O5S3: C 32.72, H 4.39, N 10.18, S 17.47. Found: C 33.27, H 4.50, N 10.10, S 17.96.

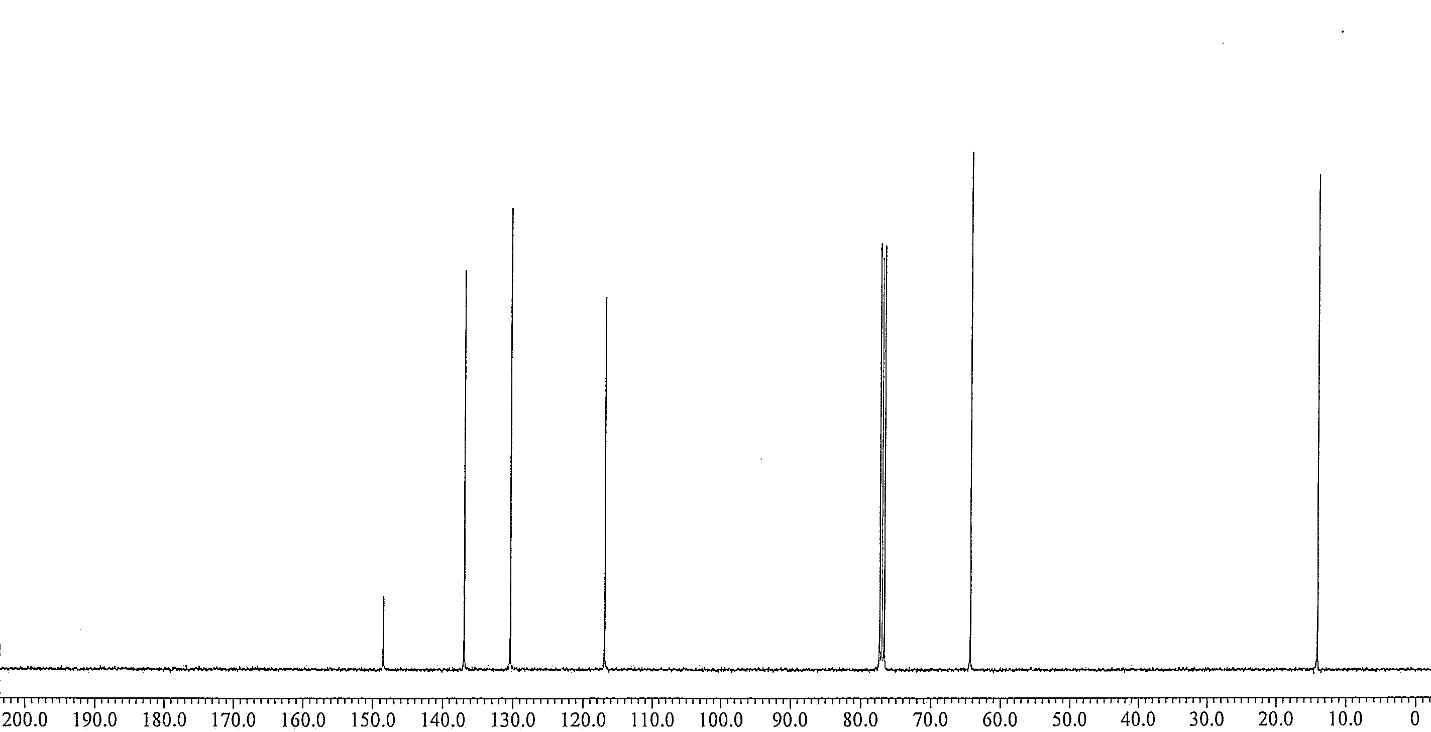
**Synthesis of S4-C8-Br.** In a 100-mL round-bottomed flask with magnetic stirring was dissolved S4-API (2.50 g, 0.0104 mol) in acetonitrile (40 mL). 1-Bromooctane (3.00 g, 0.0155 mol) was added to the flask and the solution was stirred at 60 °C for 48 hr. The solvent was then removed under reduced pressure to afford a dark, yellow oil, which was washed with several portions of diethyl ether (3 x 30 mL). After drying the residue in a vacuum oven for 24 hr, a yellow oil (4.02 g, 89 %) was obtained. 1H NMR (DMSO-*d*6):  9.22 (s, 1 H), 8.22 (t, 1 H, *J* = 5.4 Hz), 7.83 (s, 1 H), 7.80 (s, 1 H), 4.12-4.17 (m, 4 H), 3.07 (m, 2 H), 2.77 (m, 2 H), 1.94 (m, 2 H), 1.76 (m, 2 H), 1.44 (m, 2 H), 1.12-1.34 (m, 14 H), 0.83 (t, 3 H, *J* = 7.2 Hz), 1.28 (quintet, 2 H, *J* = 7.4 Hz), 0.84 (t, 3 H, *J* = 7.2 Hz). 13C NMR (DMSO-*d*6):  166.05, 136.16, 122.42, 48.86, 46.67, 37.26, 32.28, 31.17, 29.50, 29.27, 28.48, 28.37, 28.34, 25.49, 22.07, 21.29, 13.96, 13.49. Anal. Calcd. For C19H36BrN3OS: C 52.52, H 8.35, N 9.67, S 7.38. Found: C 50.91, H 8.86, N 9.36, S 7.44.

**Synthesis of S4-C8-NTf2.** S4-C8-Br (3.50 g, 8.06 mmol) was dissolved in DI water (35 mL) with magnetic stirring in a 100-mL round-bottomed flask. A solution of LiNTf2 (2.43 g, 8.46 mmol) in DI water (20 mL) was then added and the resulting mixture was stirred at rt overnight. Dichloromethane (75 mL) was then added and stirring continued for an additional hour, followed by removal of the organic phase and washing with DI water (2 x 30 mL). The organic phase was separated and the volatiles were removed under reduced pressure, resulting in 4.70 g (92 %) of a light, yellow oil. 1H NMR (DMSO-*d*6):  9.16 (s, 1 H), 8.17 (bs, 1 H), 7.79 (s, 1 H), 7.78 (s, 1 H), 4.11-4.16 (m, 4 H), 3.09 (m, 2 H), 2.76 (m, 2 H), 1.94 (m, 2 H), 1.76 (m, 2 H), 1.45 (m, 2 H), 1.15-1.29 (m, 14 H), 0.85 (t, 3 H, *J* = 7.2 Hz). 13C NMR (DMSO-*d*6):  166.09, 136.12, 122.46, 122.42, 119.48 (q, *J* = 320 Hz, -CF3), 48.90, 46.70, 37.25, 32.27, 31.15, 29.50, 29.25, 28.45, 28.39, 28.32, 25.48, 22.03, 21.27, 13.86, 13.40. Anal. Calcd. For C21H36F6N4O5S3: C 39.74, H 5.72, N 8.83, S 15.15. Found: C 39.19, H 5.54, N 8.91, S 14.95.

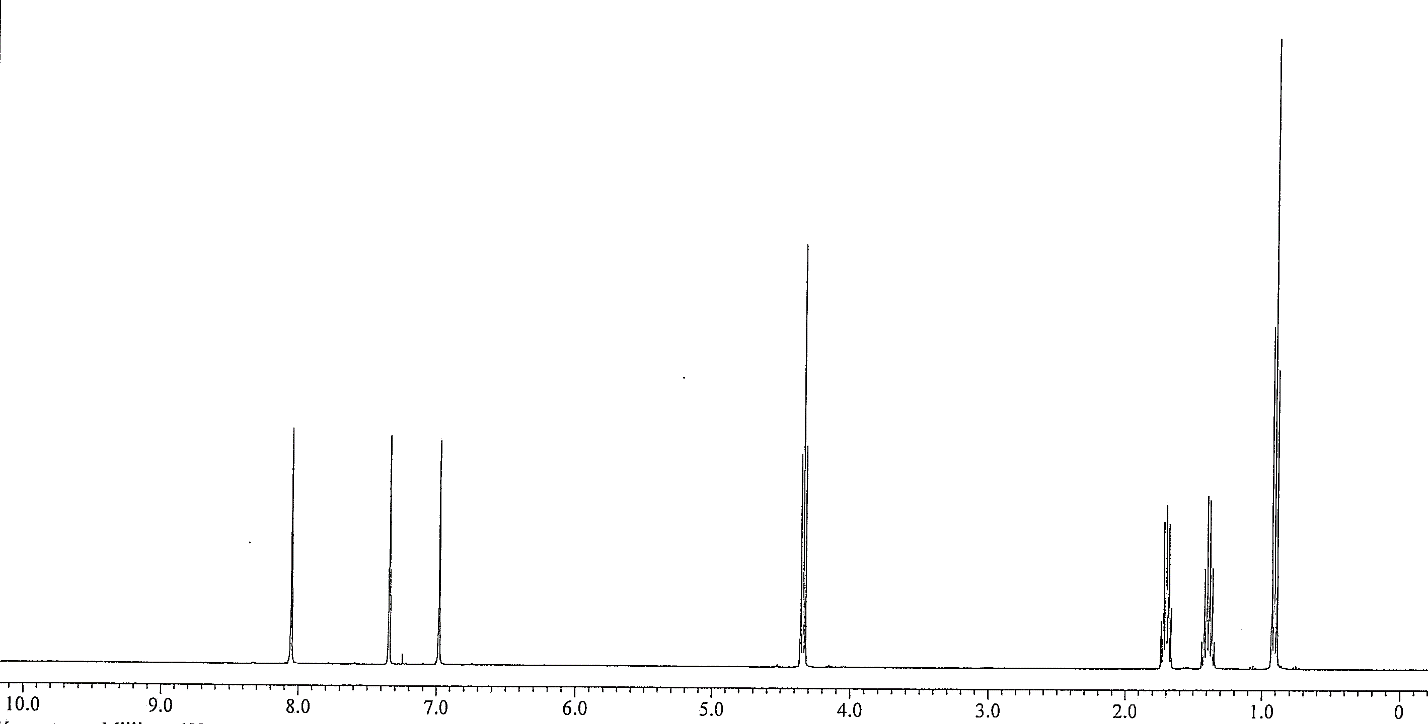
**NMR spectra**

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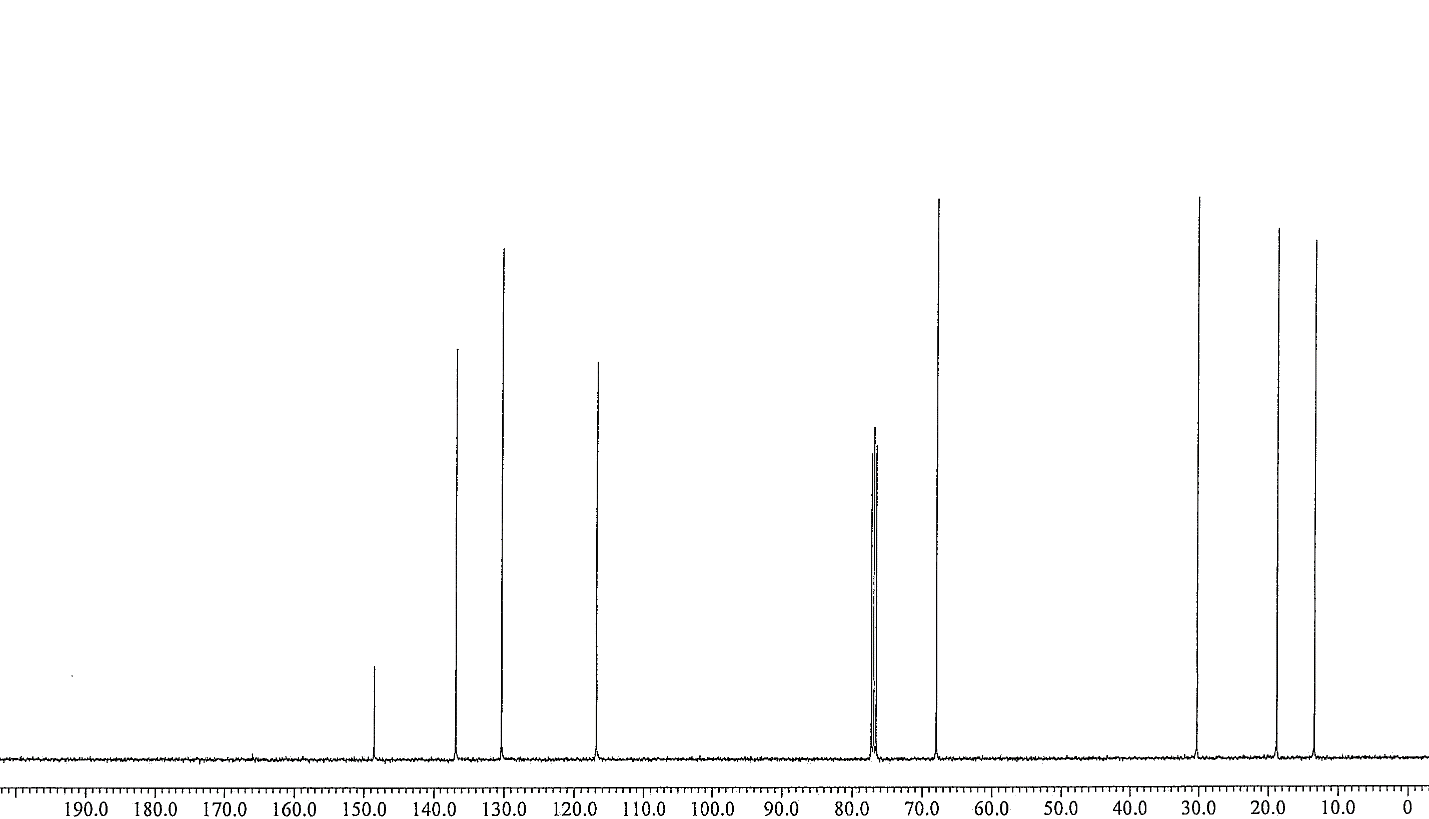
**Figure S1.** 1H NMR spectrum of ethyl-1-imidazolecarboxylate (CDCl3).



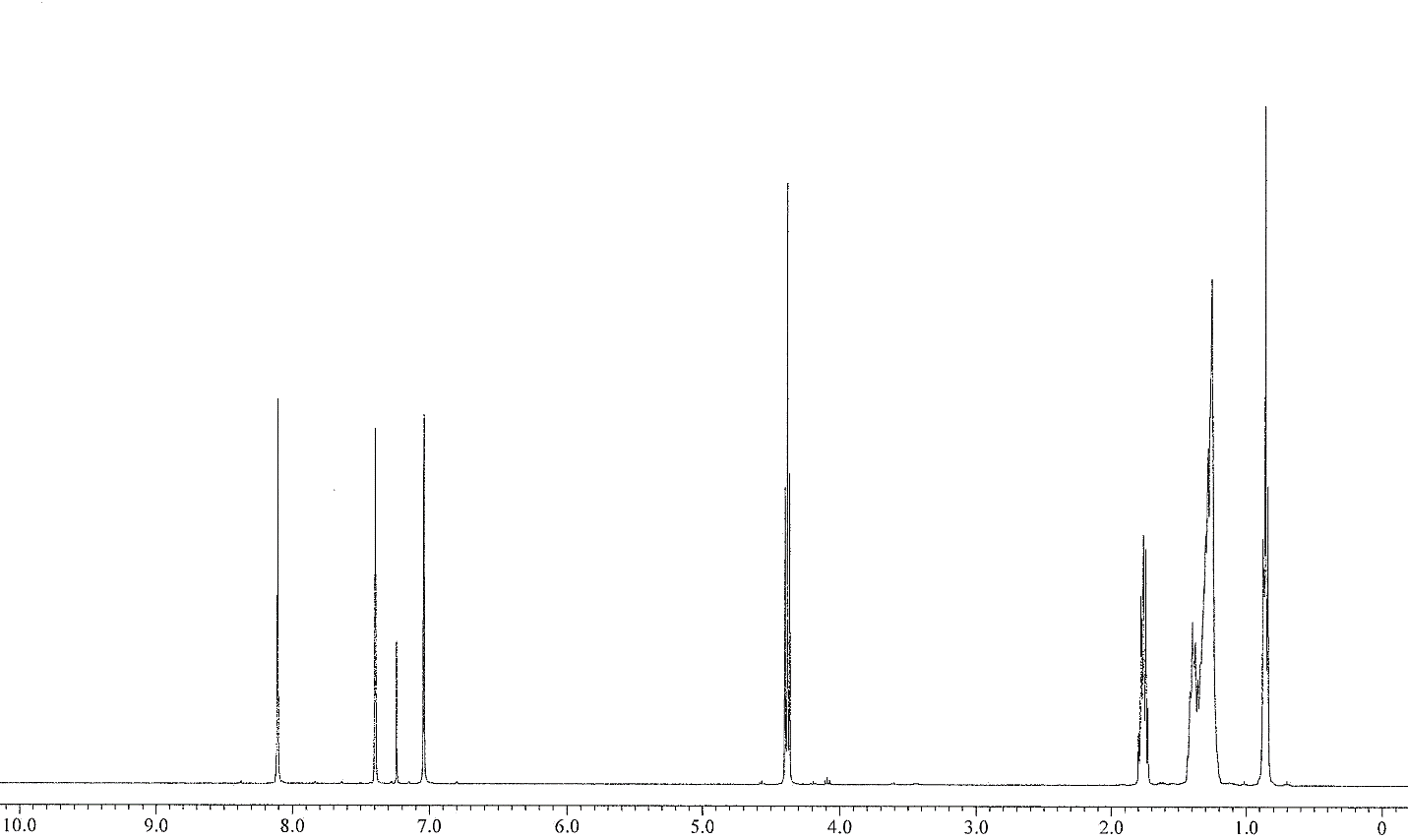
**Figure S2.** 13C NMR spectrum of ethyl-1-imidazolecarboxylate (CDCl3).



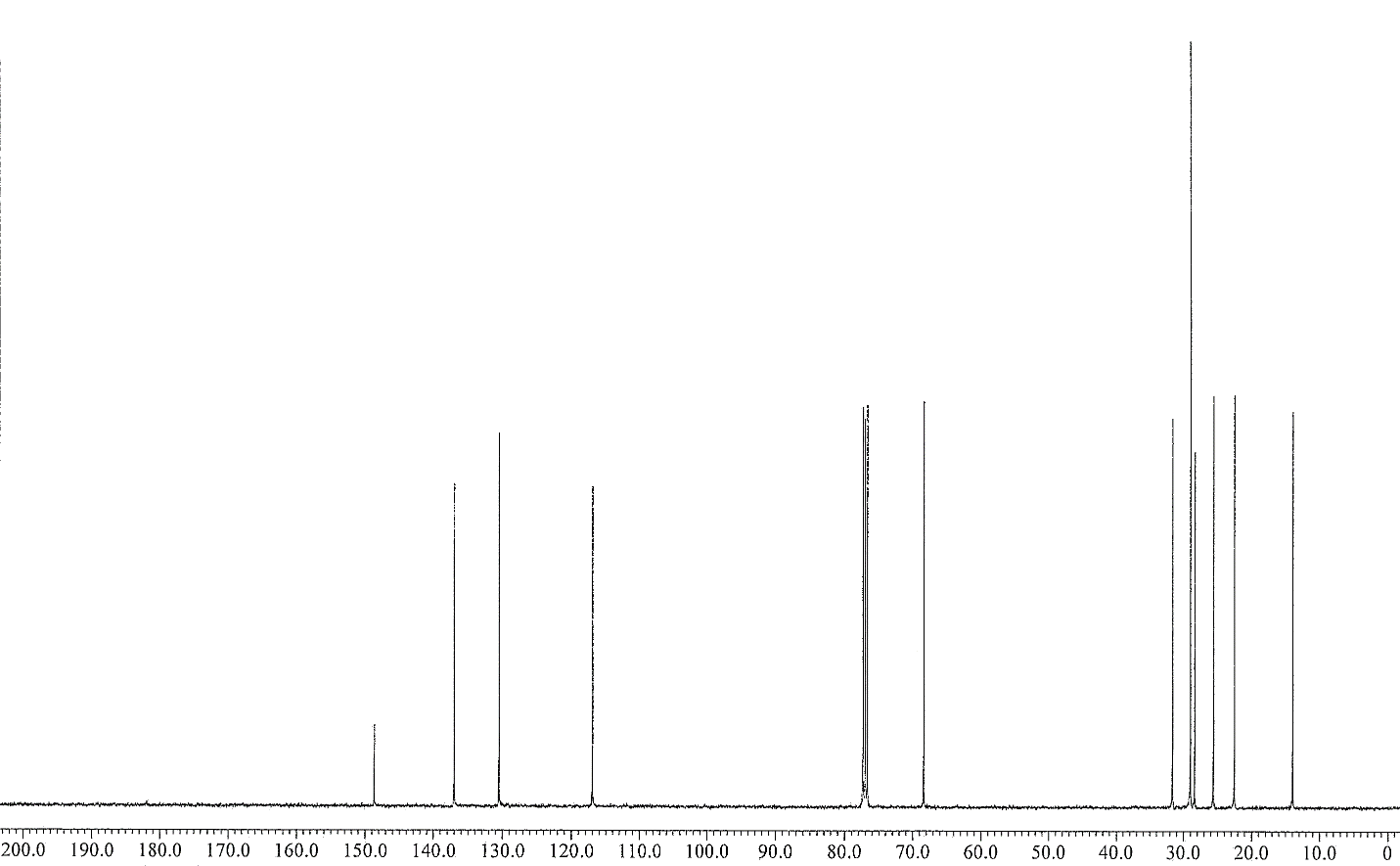
**Figure S3.** 1H NMR spectrum of butyl-1-imidazolecarboxylate (CDCl3).



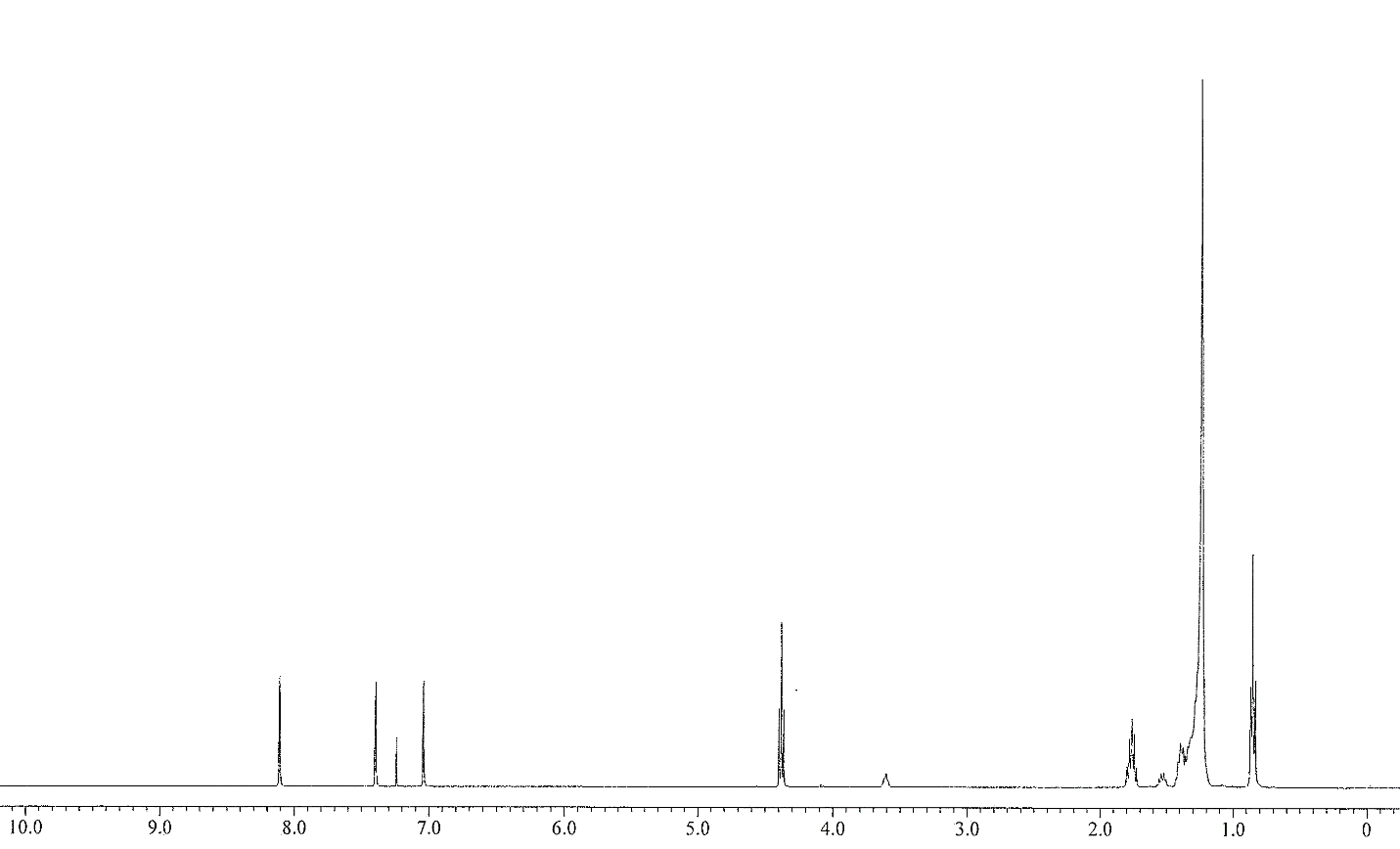
**Figure S4.** 13C NMR spectrum of butyl-1-imidazolecarboxylate (CDCl3).



**Figure S5.** 1H NMR spectrum of octyl-1-imidazolecarboxylate (CDCl3).



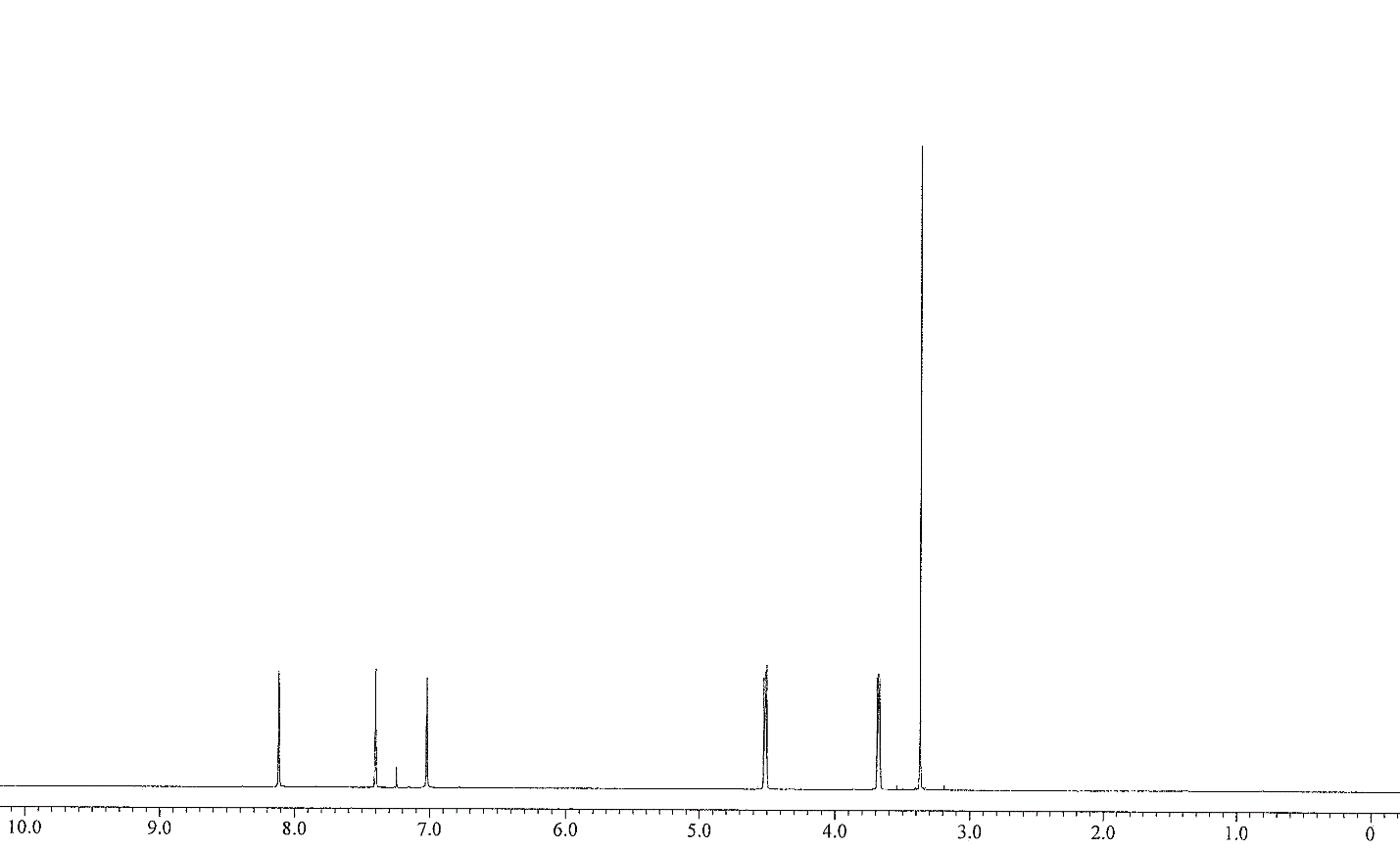
**Figure S6.** 13C NMR spectrum of octyl-1-imidazolecarboxylate (CDCl3).



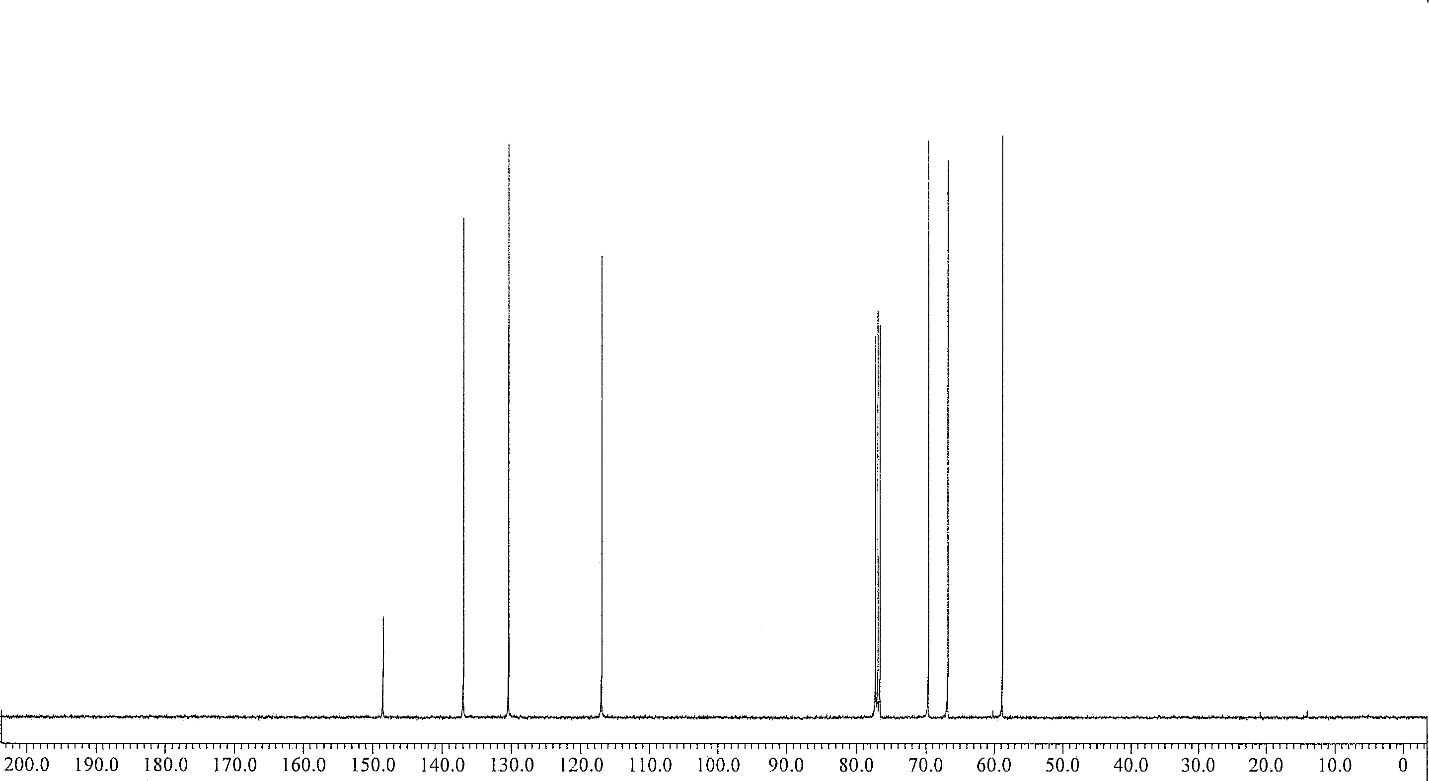
**Figure S7.** 1H NMR spectrum of dodecyl-1-imidazolecarboxylate (CDCl3).



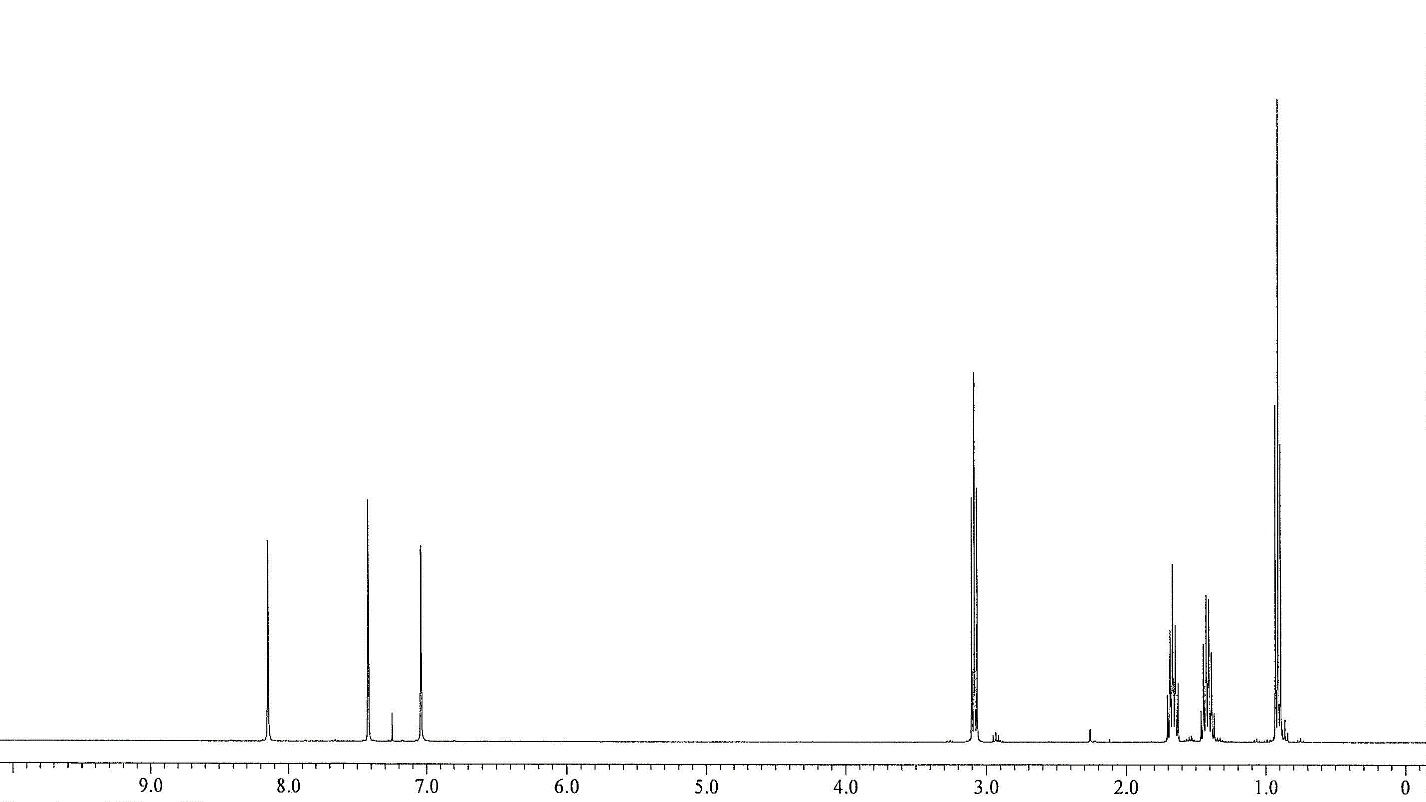
**Figure S8.** 13C NMR spectrum of dodecyl-1-imidazolecarboxylate (CDCl3).



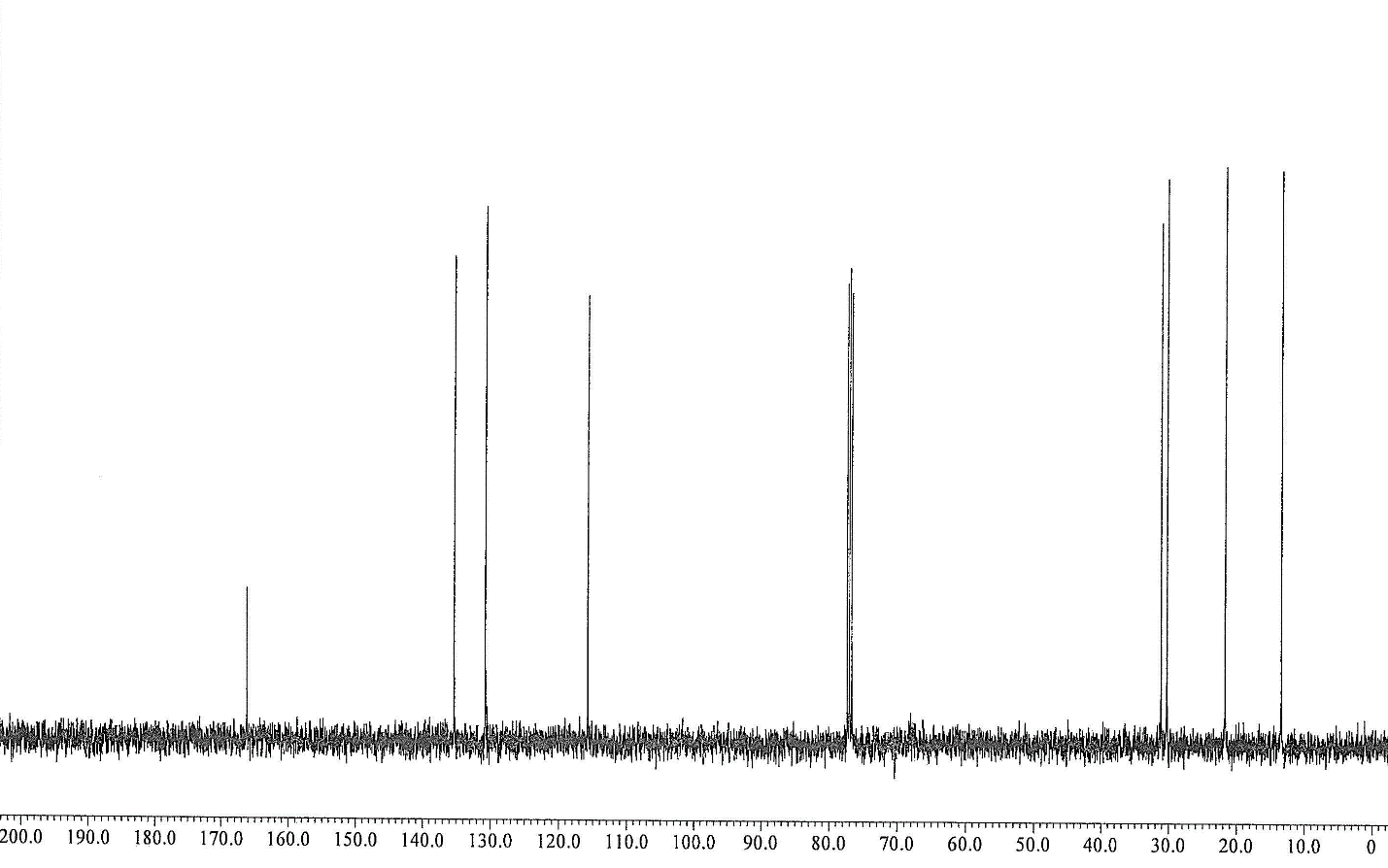
**Figure S9.** 1H NMR spectrum of 2-methoxyethyl-1-imidazolecarboxylate (CDCl3).



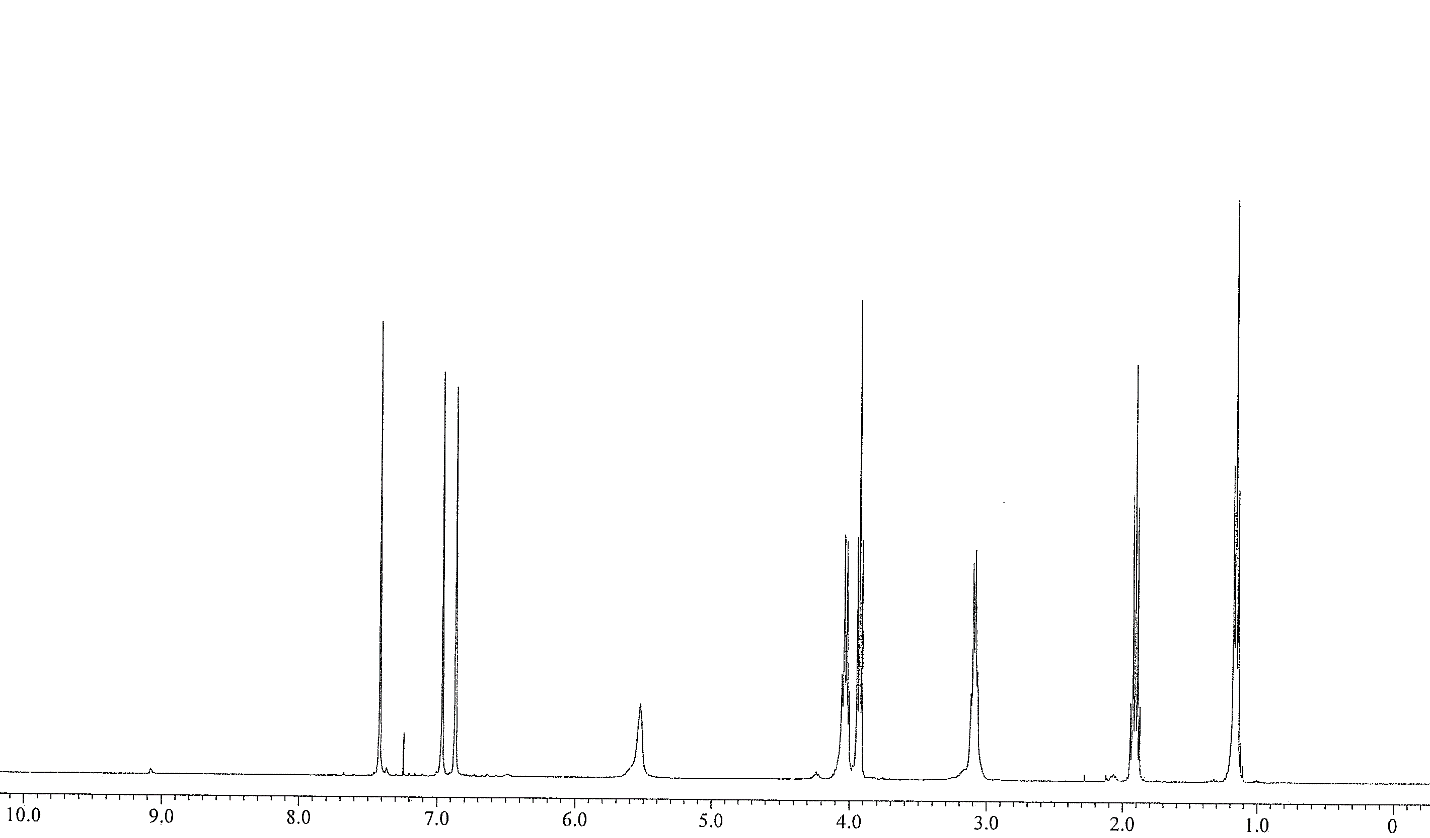
**Figure S10.** 13C NMR spectrum of 2-methoxyethyl-1-imidazolecarboxylate (CDCl3).



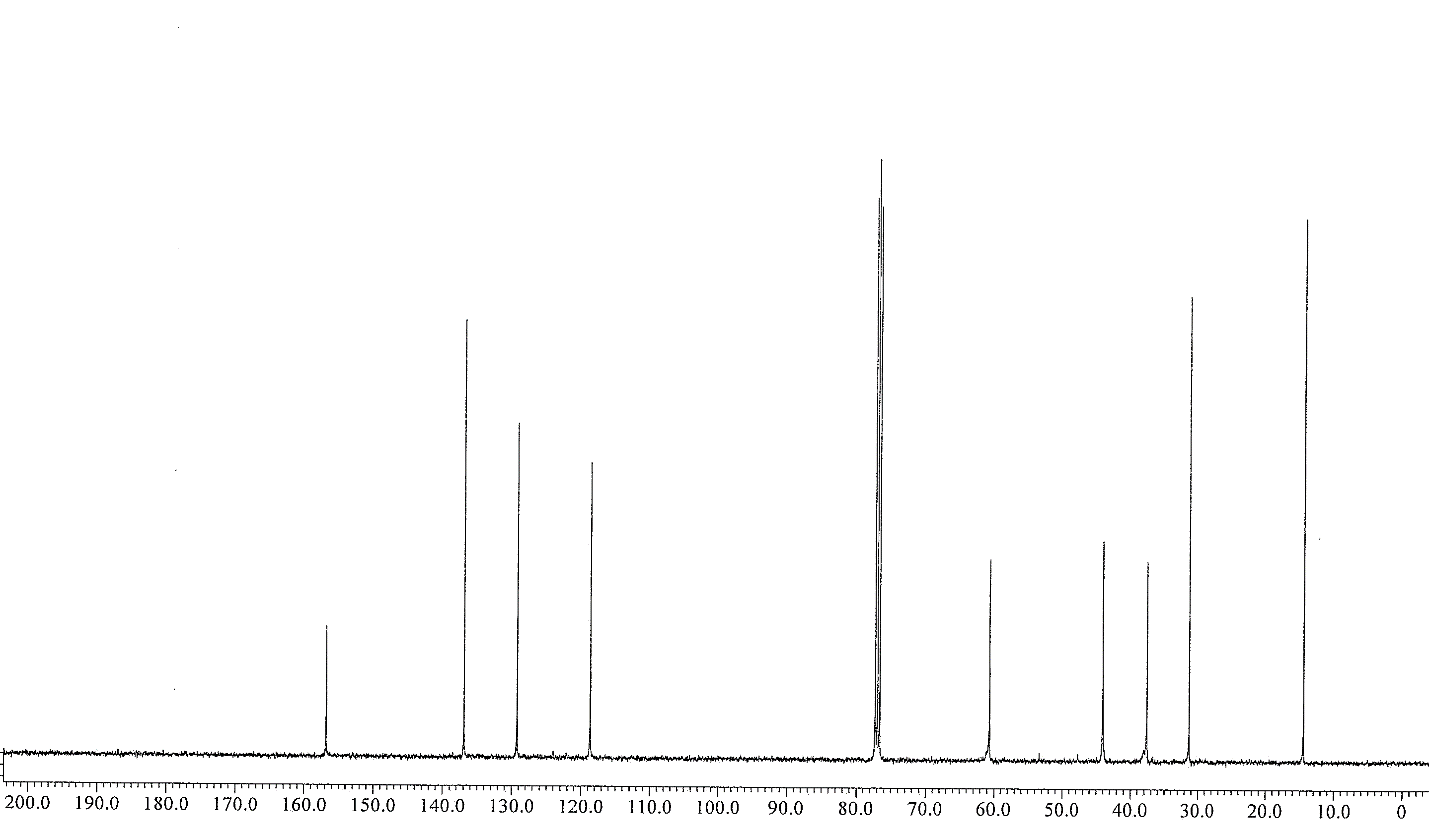
**Figure S11.** 1H NMR spectrum of **S4-CDI** (CDCl3).



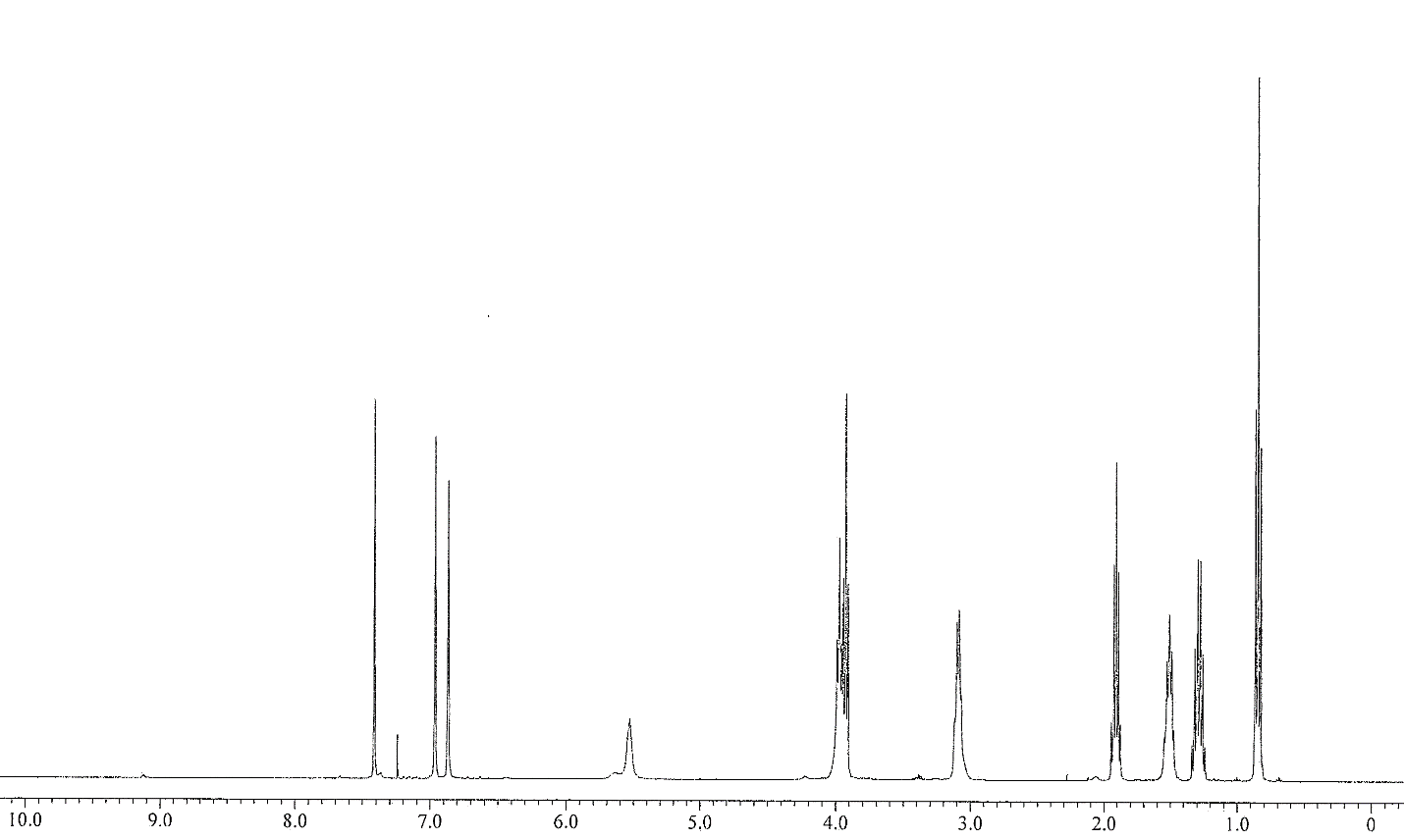
**Figure S12.** 13C NMR spectrum of **S4-CDI** (CDCl3).



**Figure S13.** 1H NMR spectrum of **O2-API** (CDCl3).

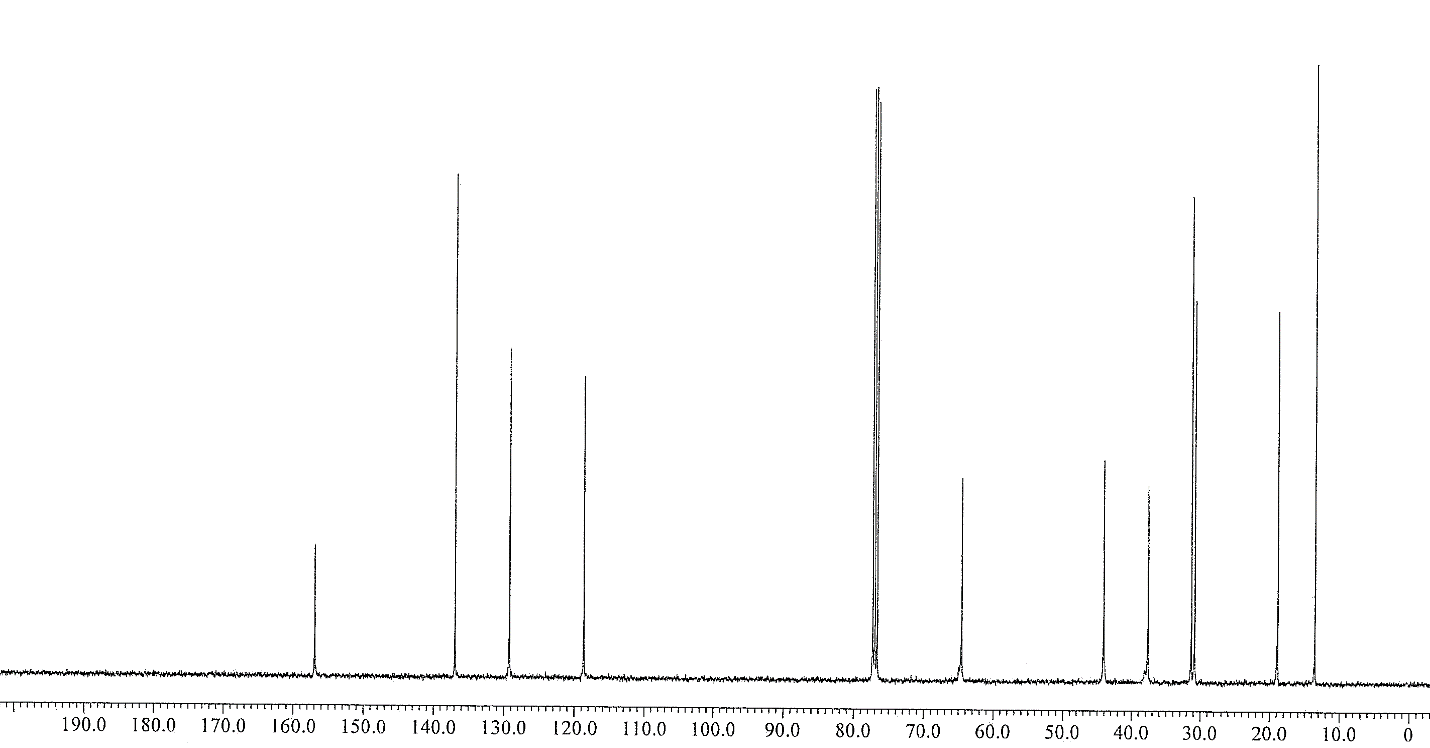


**Figure S14.** 13C NMR spectrum of **O2-API** (CDCl3).

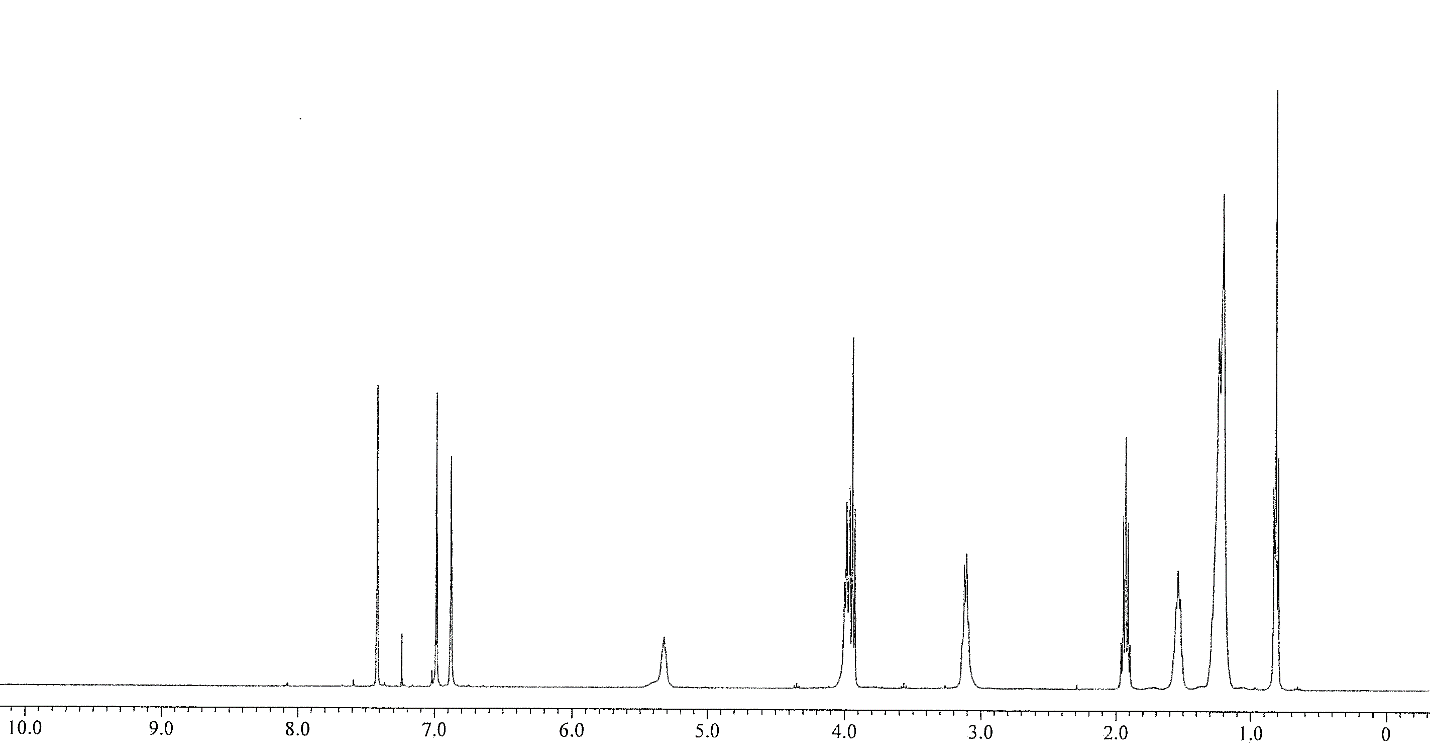


**Figure S15.** 1H NMR spectrum of **O4-API** (CDCl3).

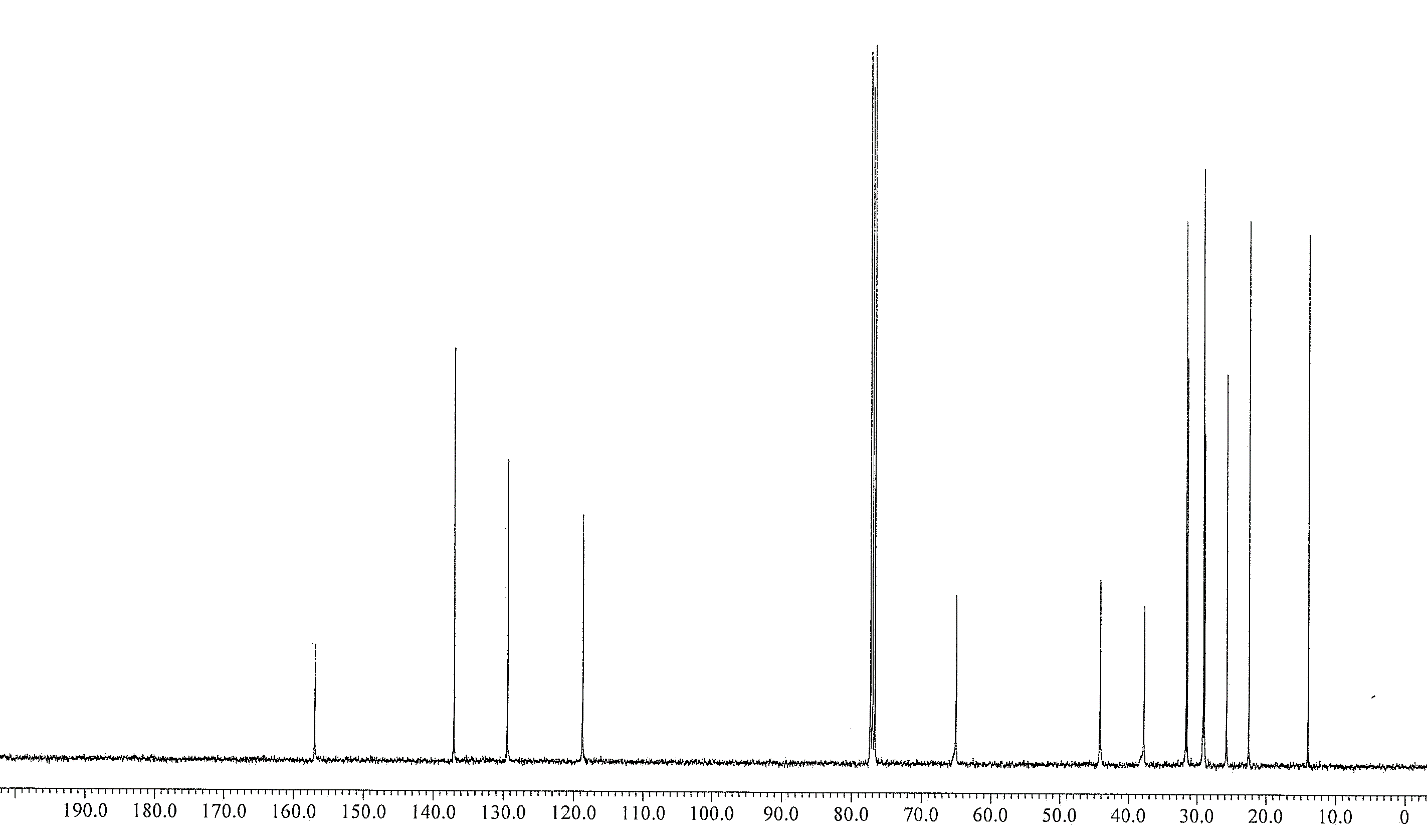




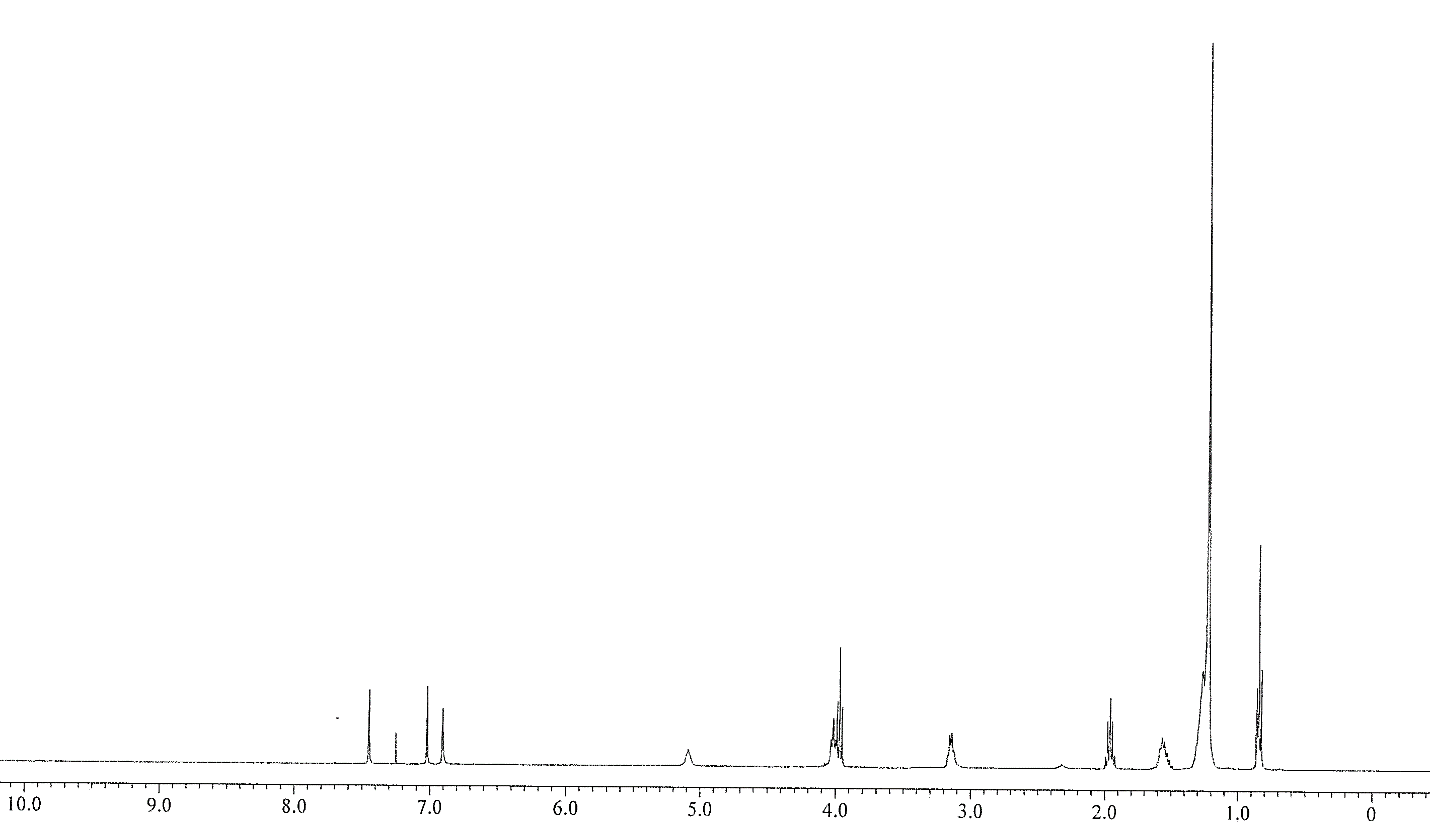
**Figure S16.** 13C NMR spectrum of **O4-API** (CDCl3).



**Figure S17.** 1H NMR spectrum of **O8-API** (CDCl3).

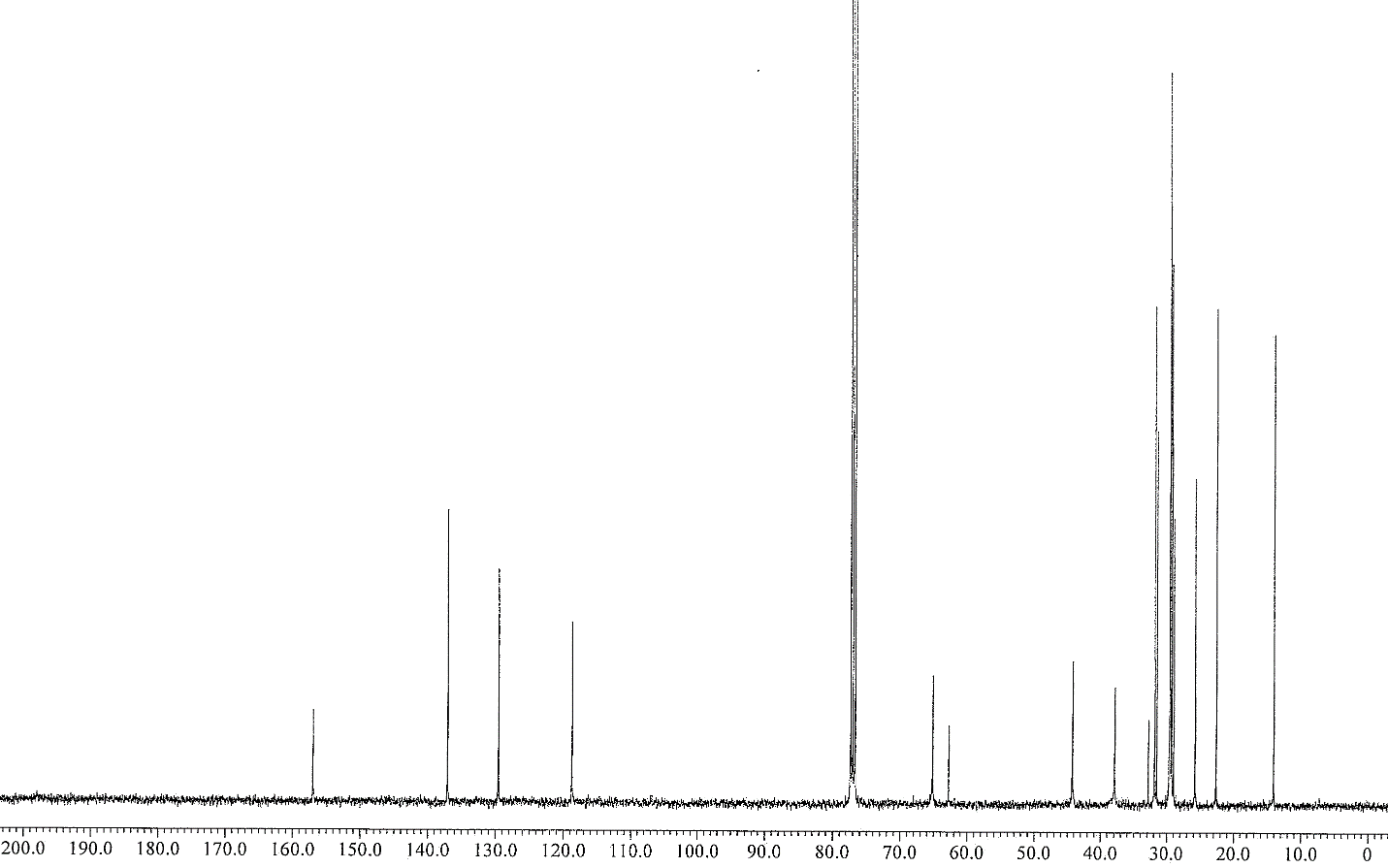


**Figure S18.** 13C NMR spectrum of **O8-API** (CDCl3).

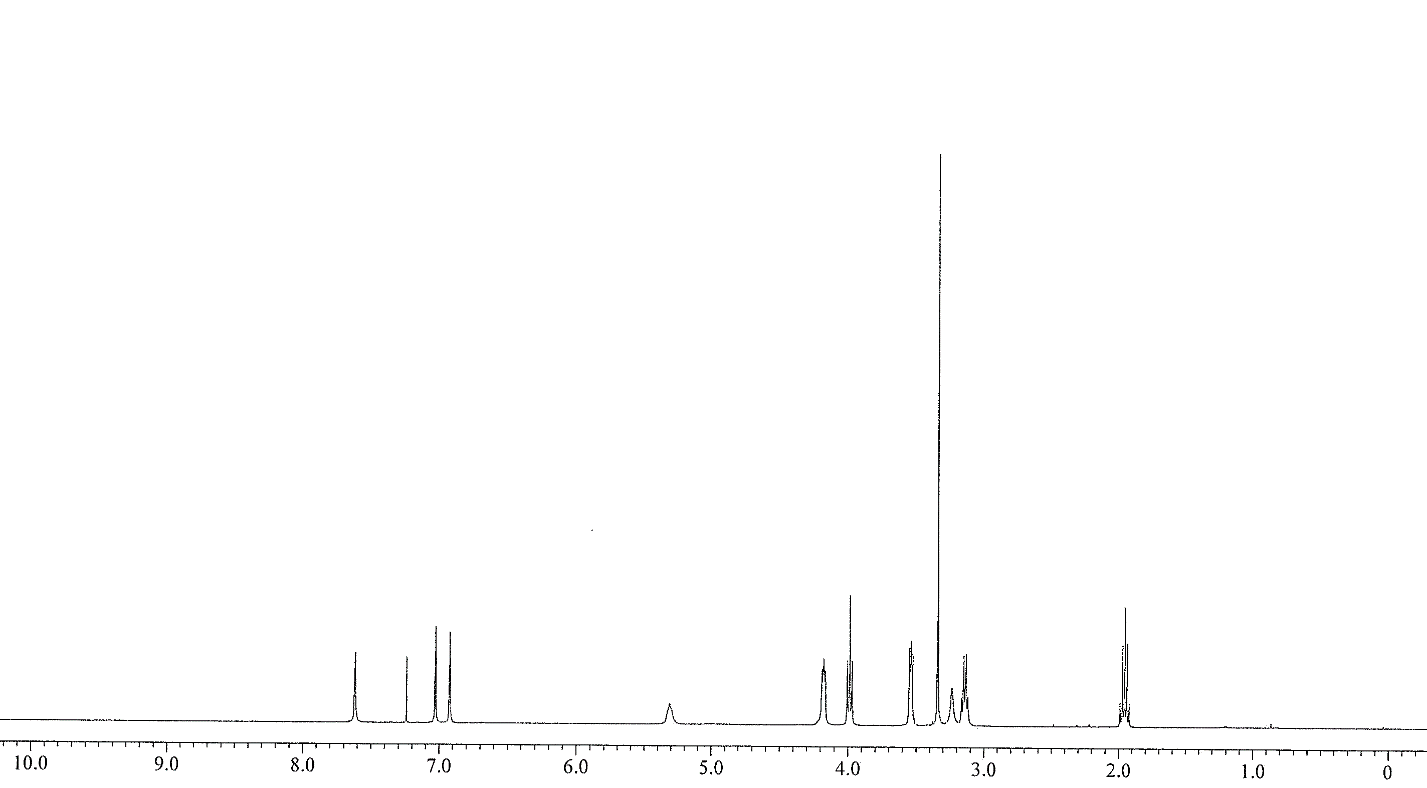
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**Figure S19.** 1H NMR spectrum of **O12-API** (CDCl3).



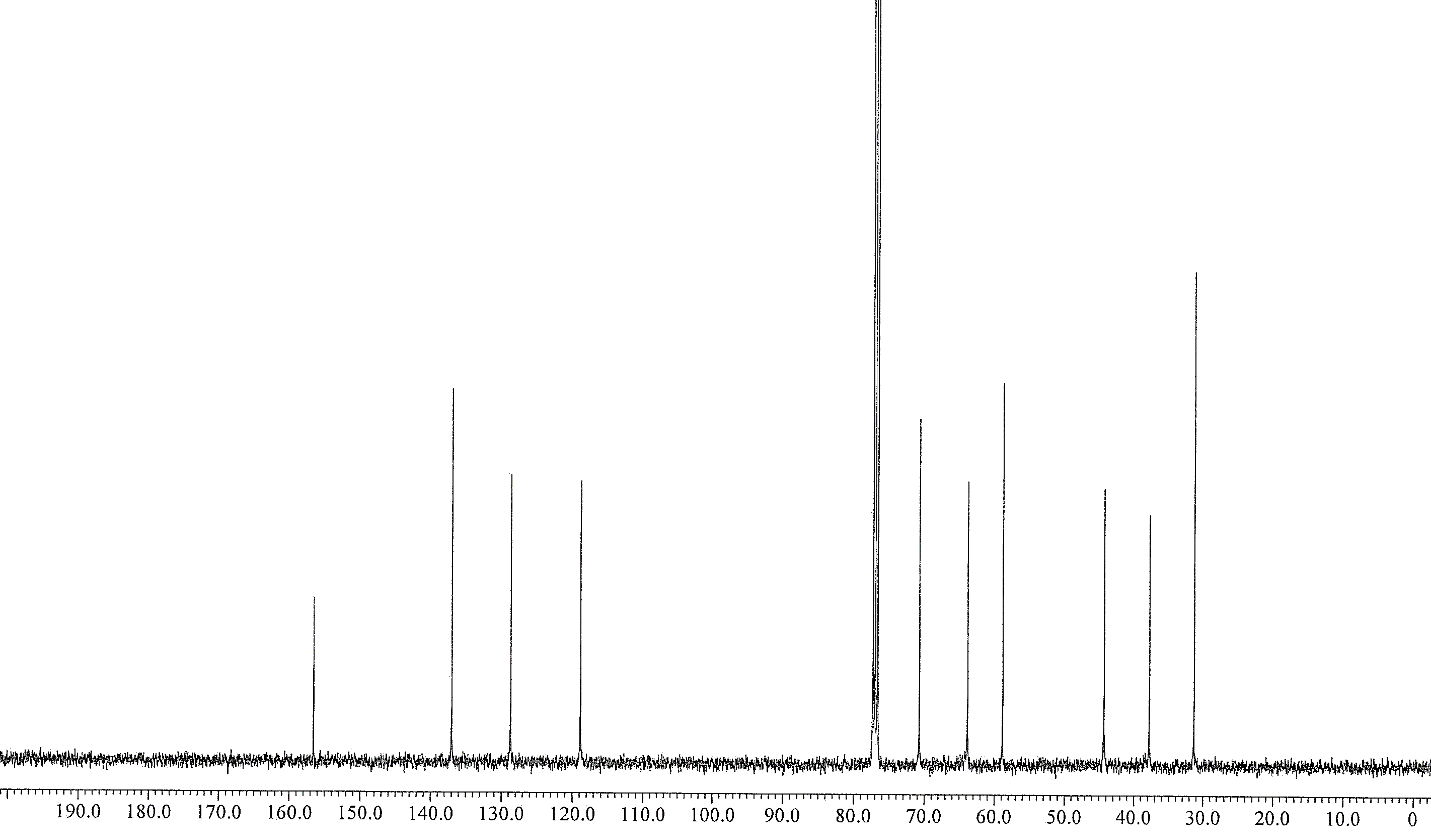


**Figure S20.** 13C NMR spectrum of **O12-API** (CDCl3).

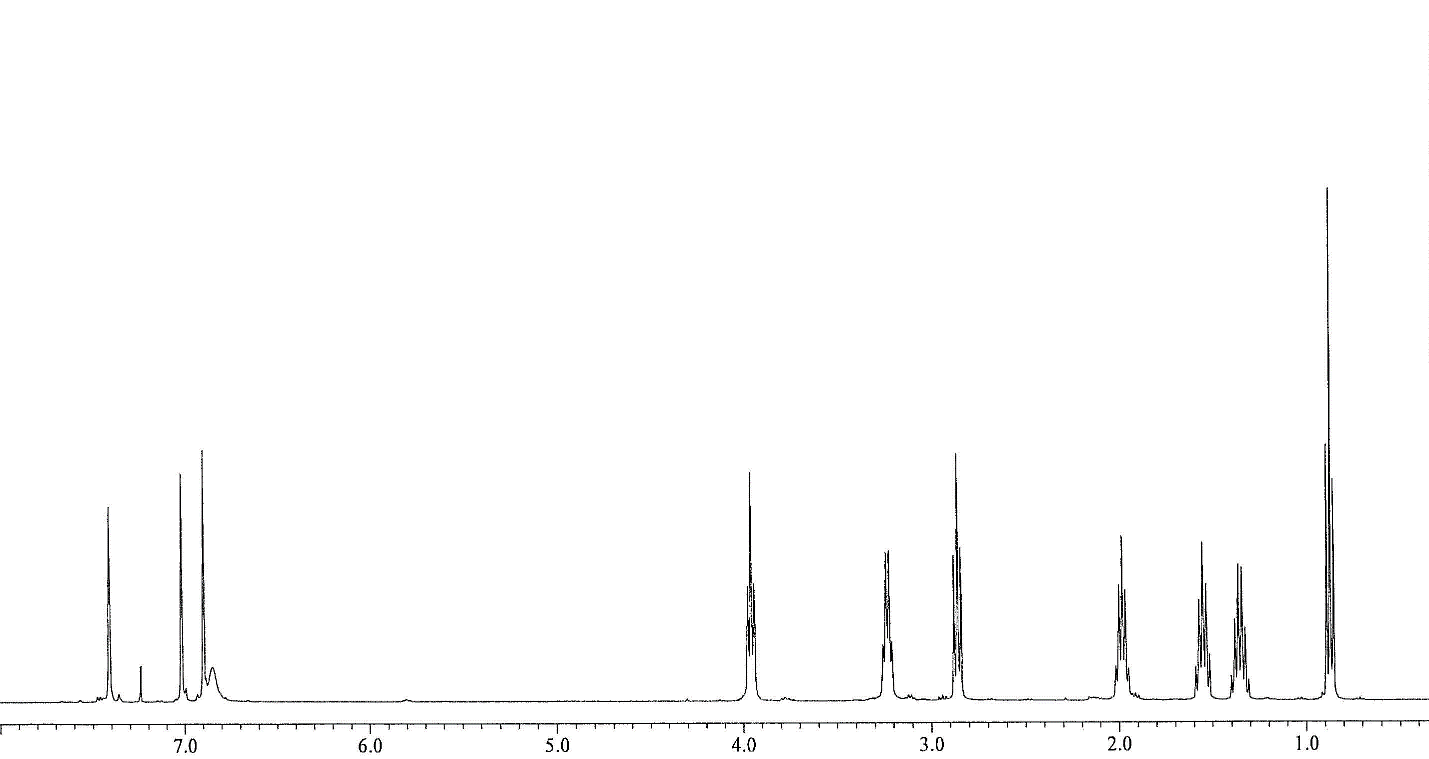


**Figure S21.** 1H NMR spectrum of **OM-API** (CDCl3).

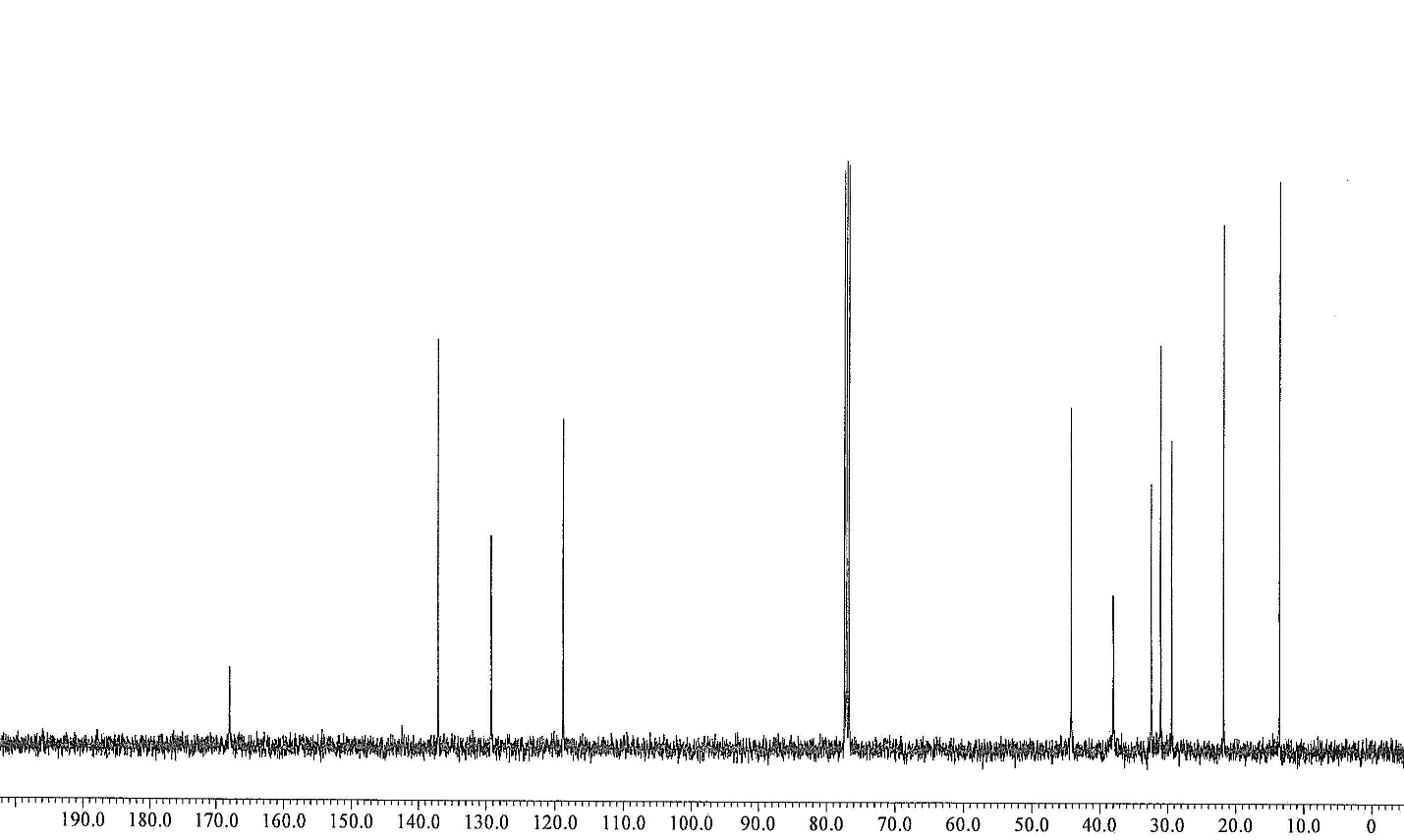




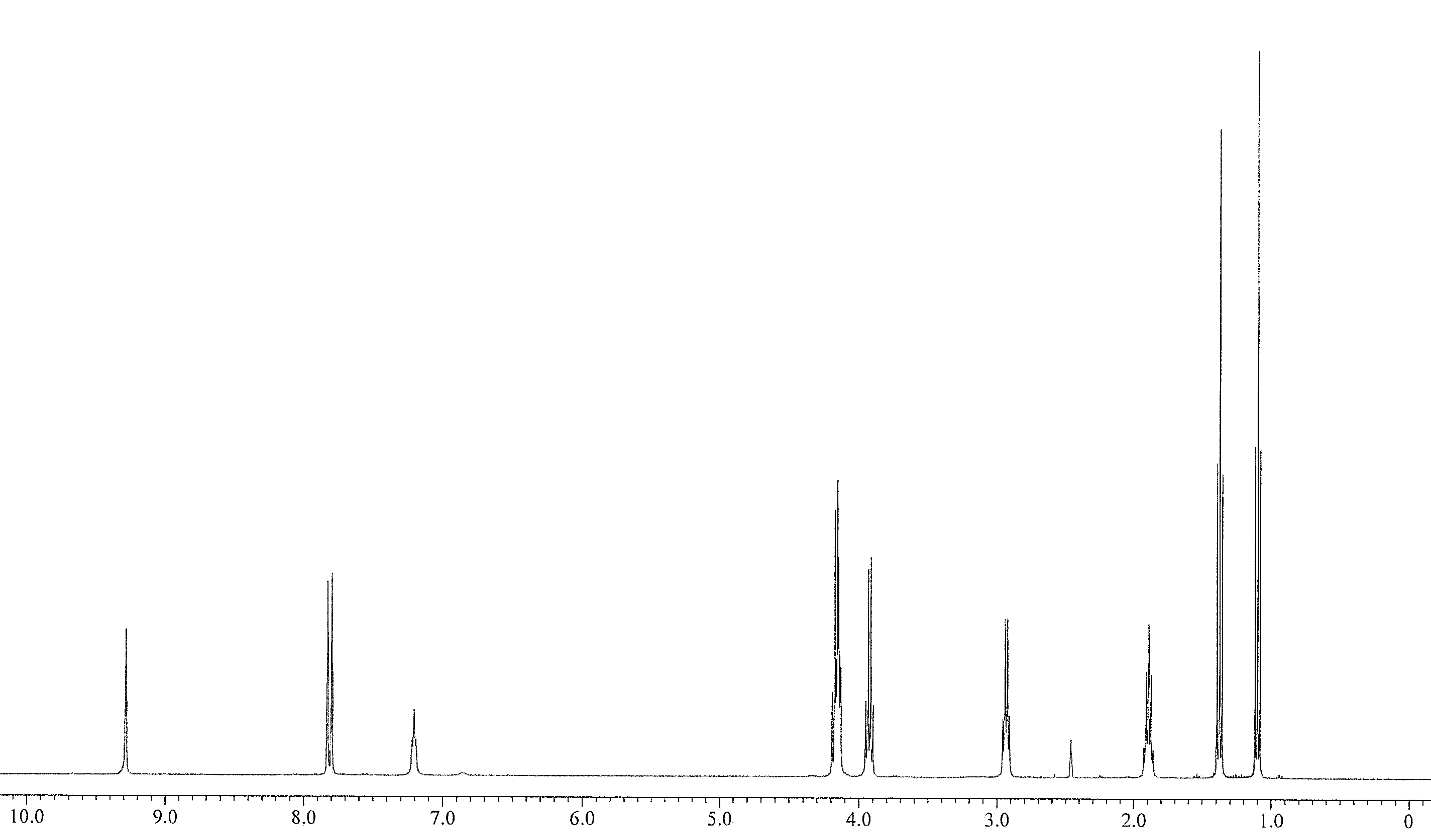
**Figure S22.** 13C NMR spectrum of **OM-API** (CDCl3).

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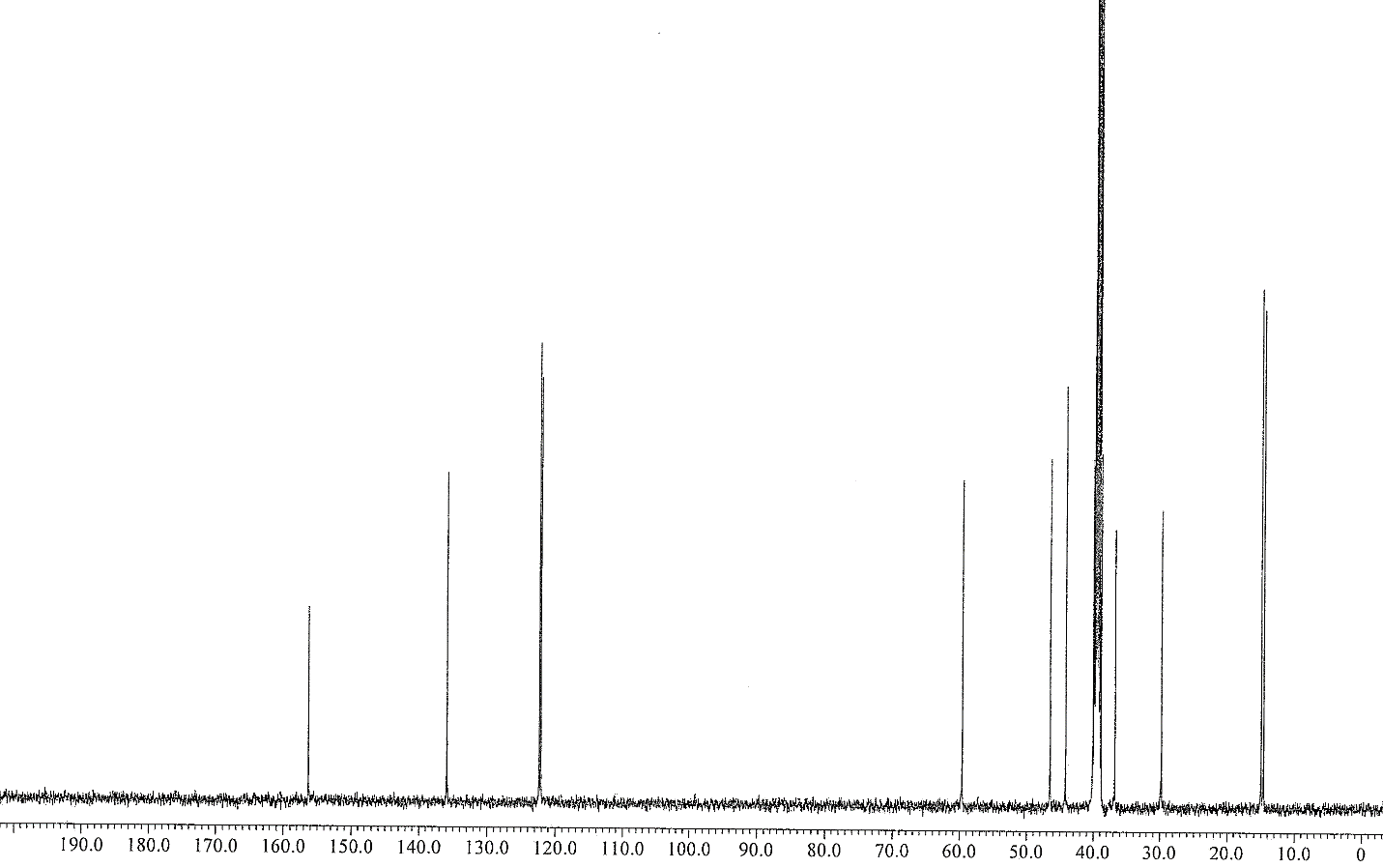
**Figure S23.** 1H NMR spectrum of **S4-API** (CDCl3).



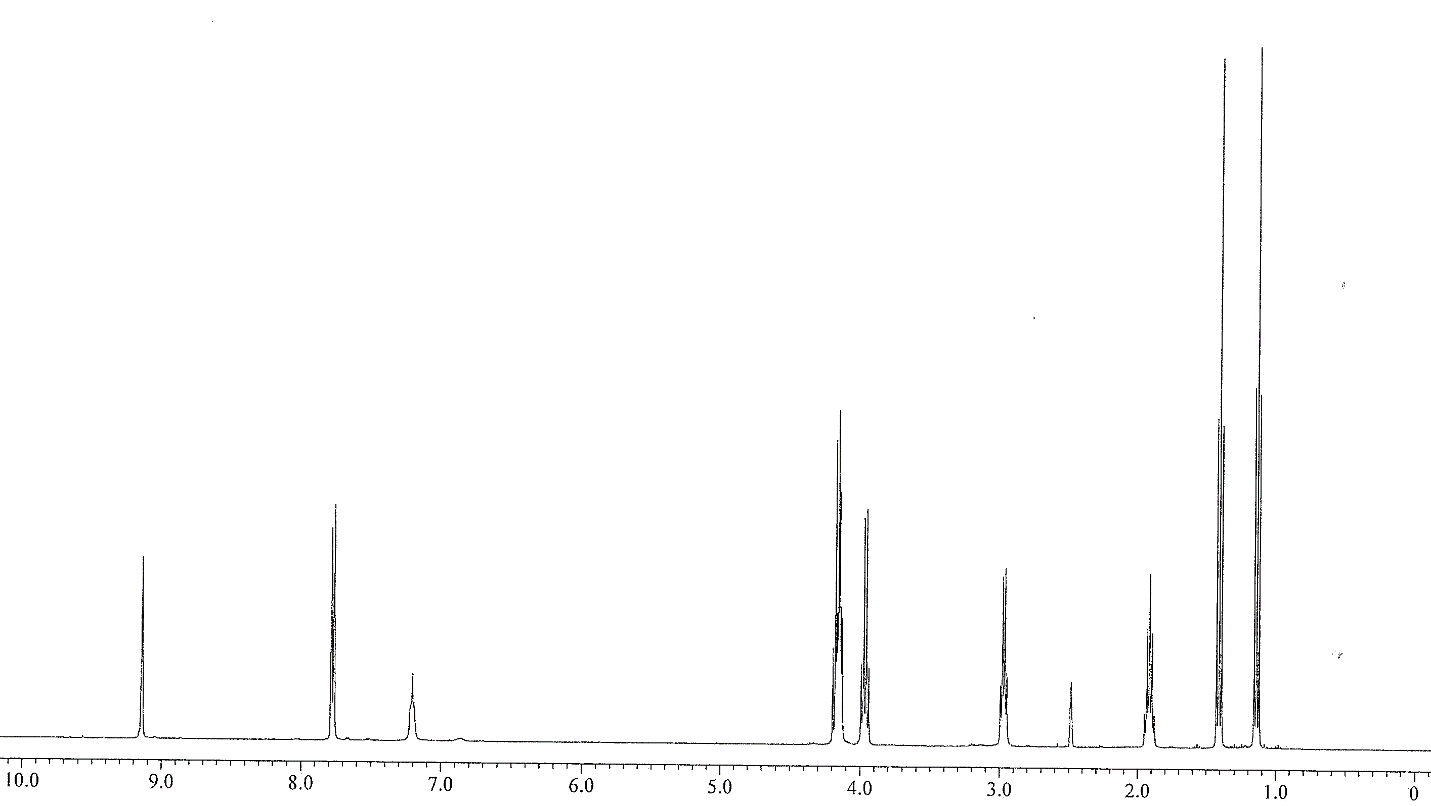
**Figure S24.** 13C NMR spectrum of **S4-API** (CDCl3).



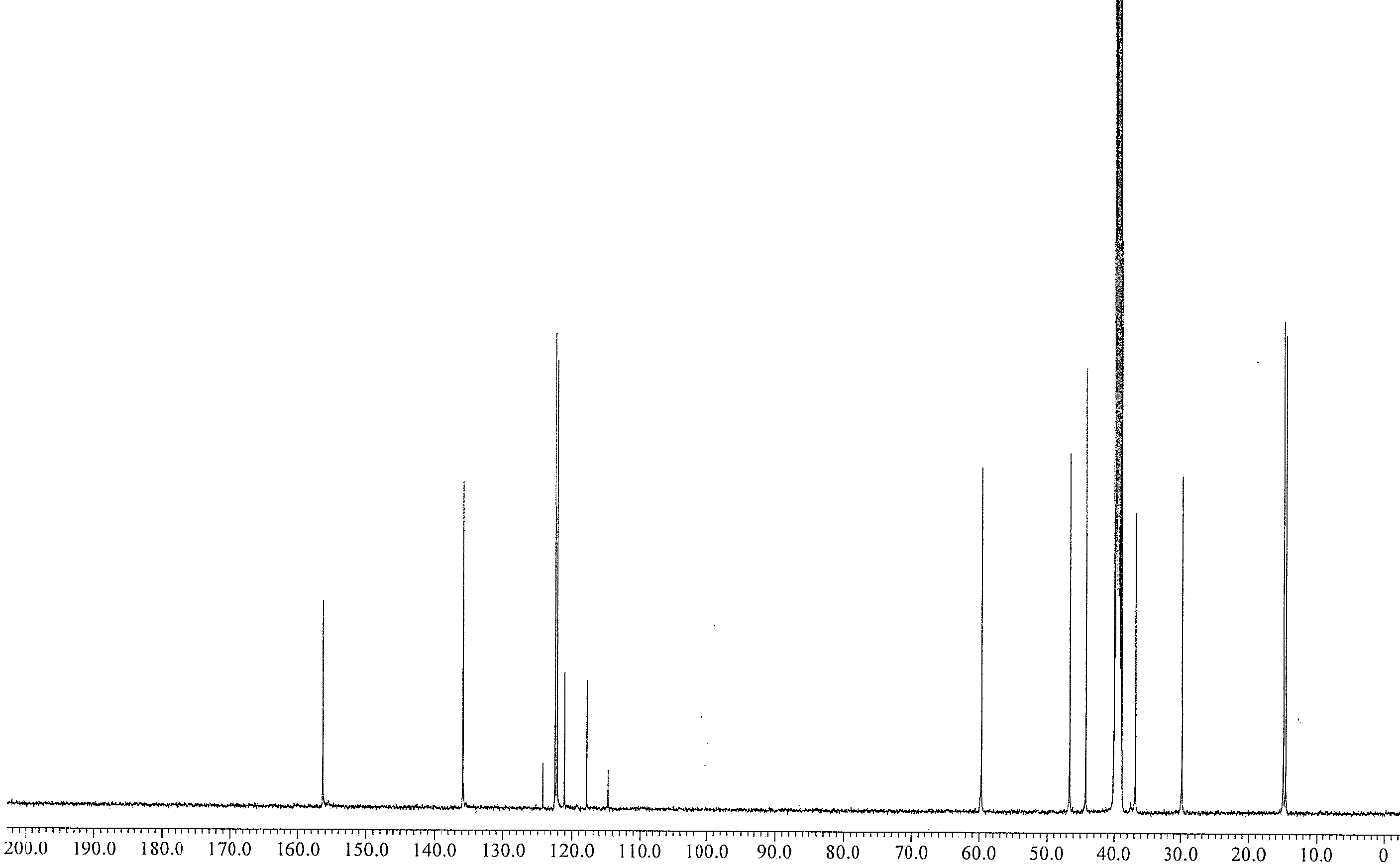
**Figure S25.** 1H NMR spectrum of **O2-C2-Br** (DMSO-*d*6).



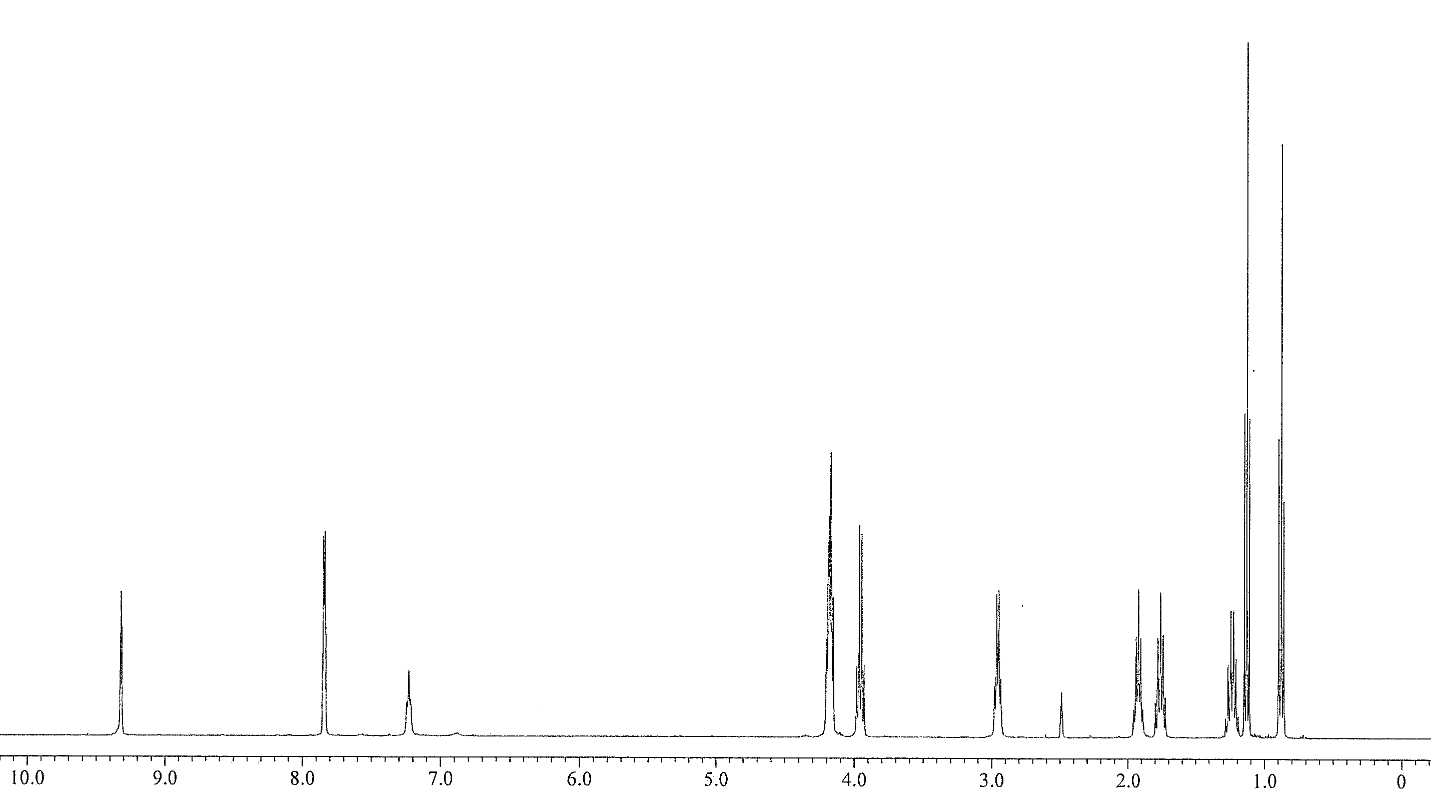
**Figure S26.** 13C NMR spectrum of **O2-C2-Br** (DMSO-*d*6).



**Figure S27.** 1H NMR spectrum of **O2-C2-NTf2** (DMSO-*d*6).

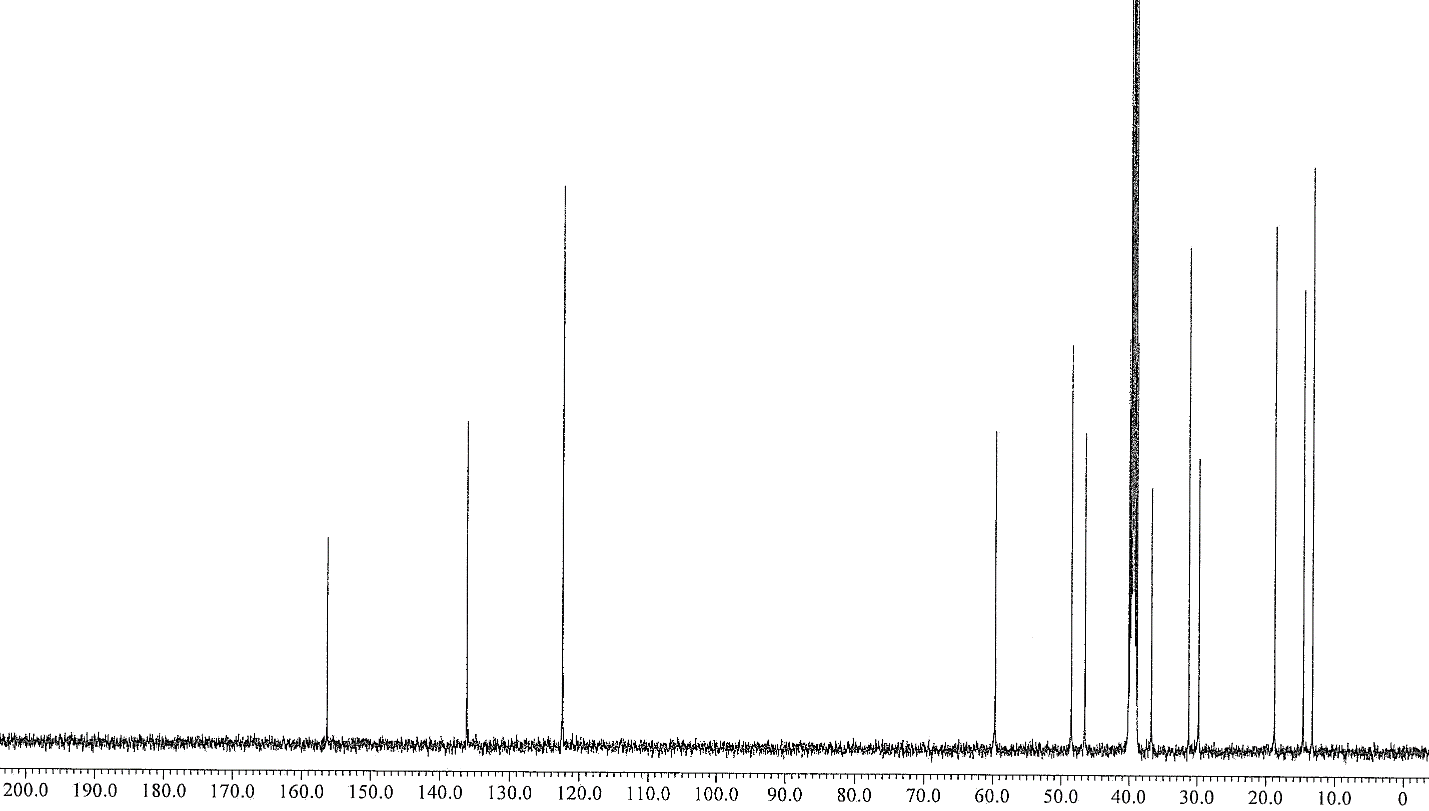


**Figure S28.** 13C NMR spectrum of **O2-C2-NTf2** (DMSO-*d*6).



**Figure S29.** 1H NMR spectrum of **O2-C4-Br** (DMSO-*d*6).



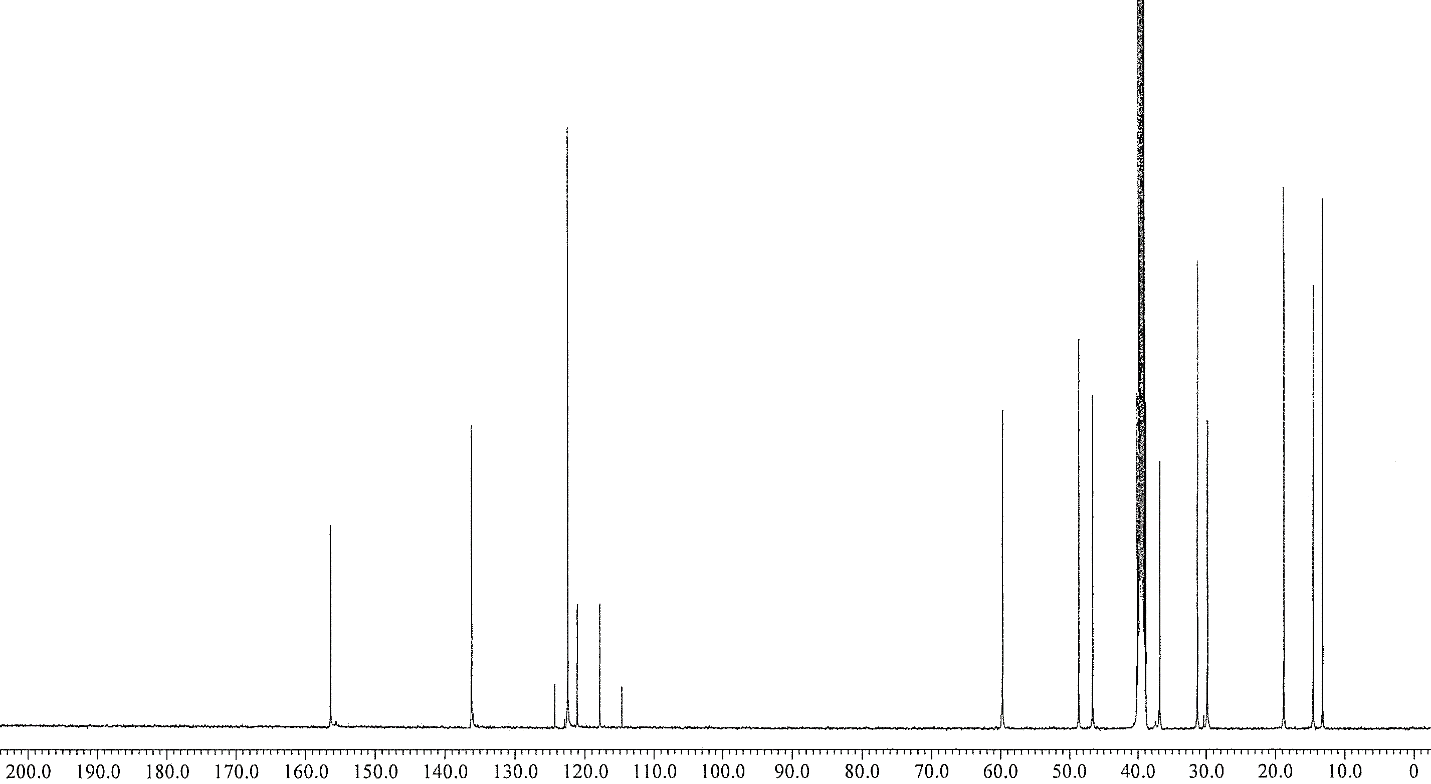


**Figure S30.** 13C NMR spectrum of **O2-C4-Br** (DMSO-*d*6).

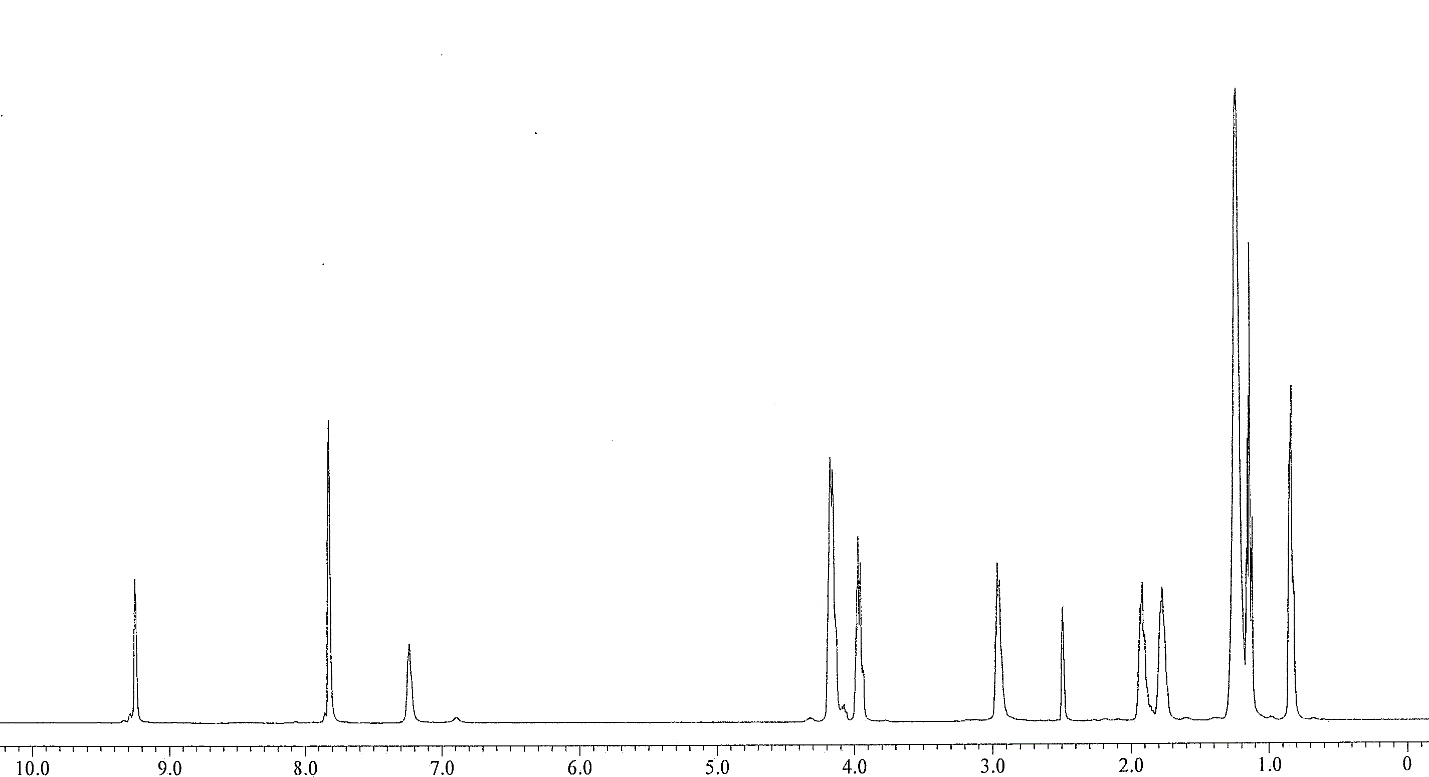


**Figure S31.** 1H NMR spectrum of **O2-C4-NTf2** (DMSO-*d*6).





**Figure S32.** 13C NMR spectrum of **O2-C4-NTf2** (DMSO-*d*6).

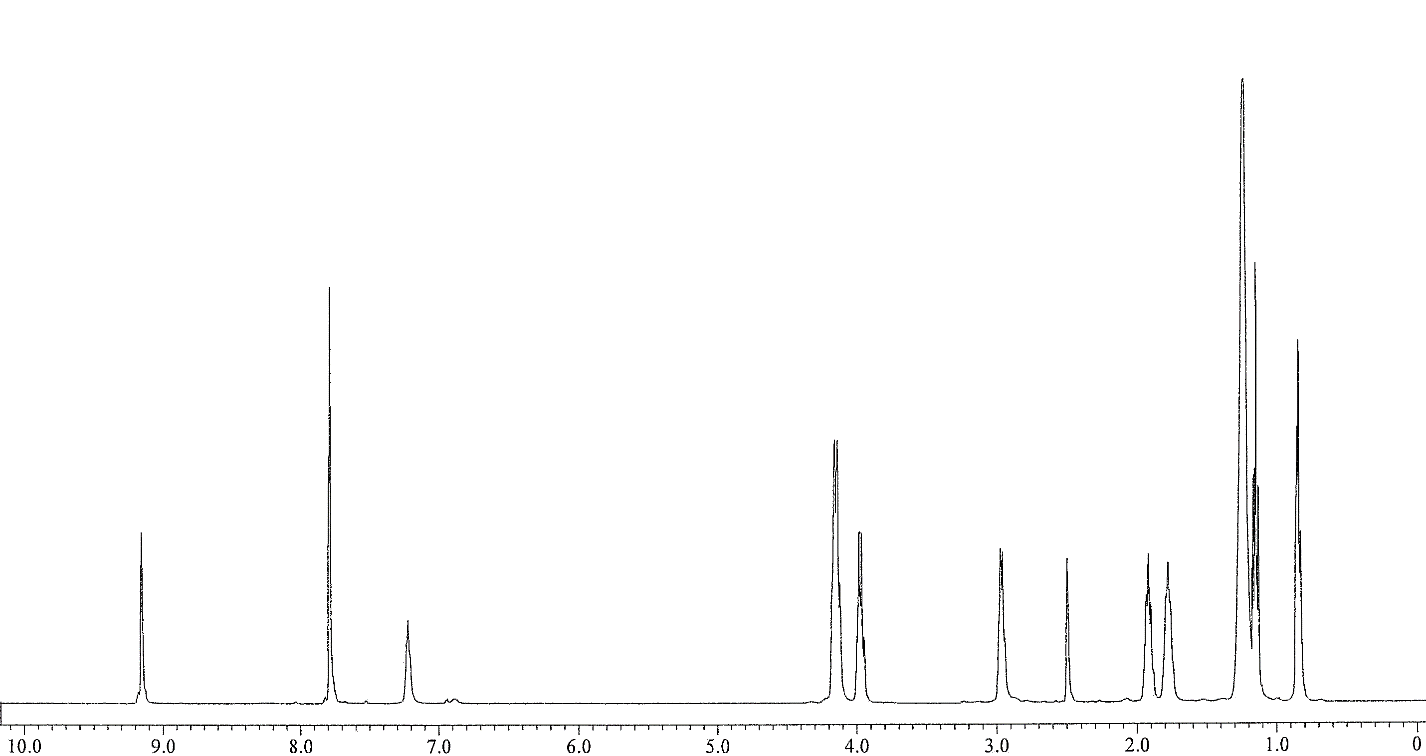


**Figure S33.** 1H NMR spectrum of **O2-C8-Br** (DMSO-*d*6).



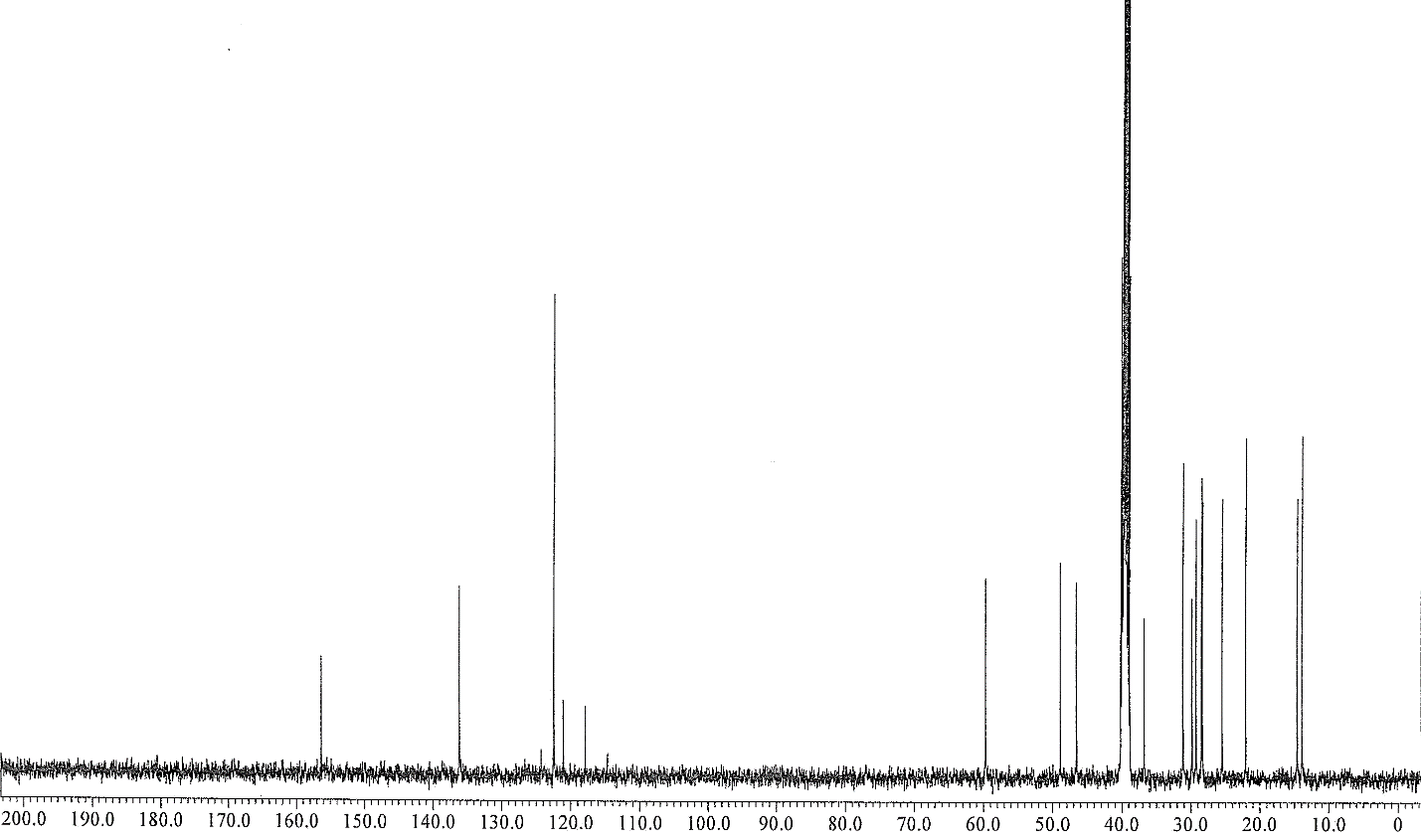


**Figure S34.** 13C NMR spectrum of **O2-C8-Br** (DMSO-*d*6).

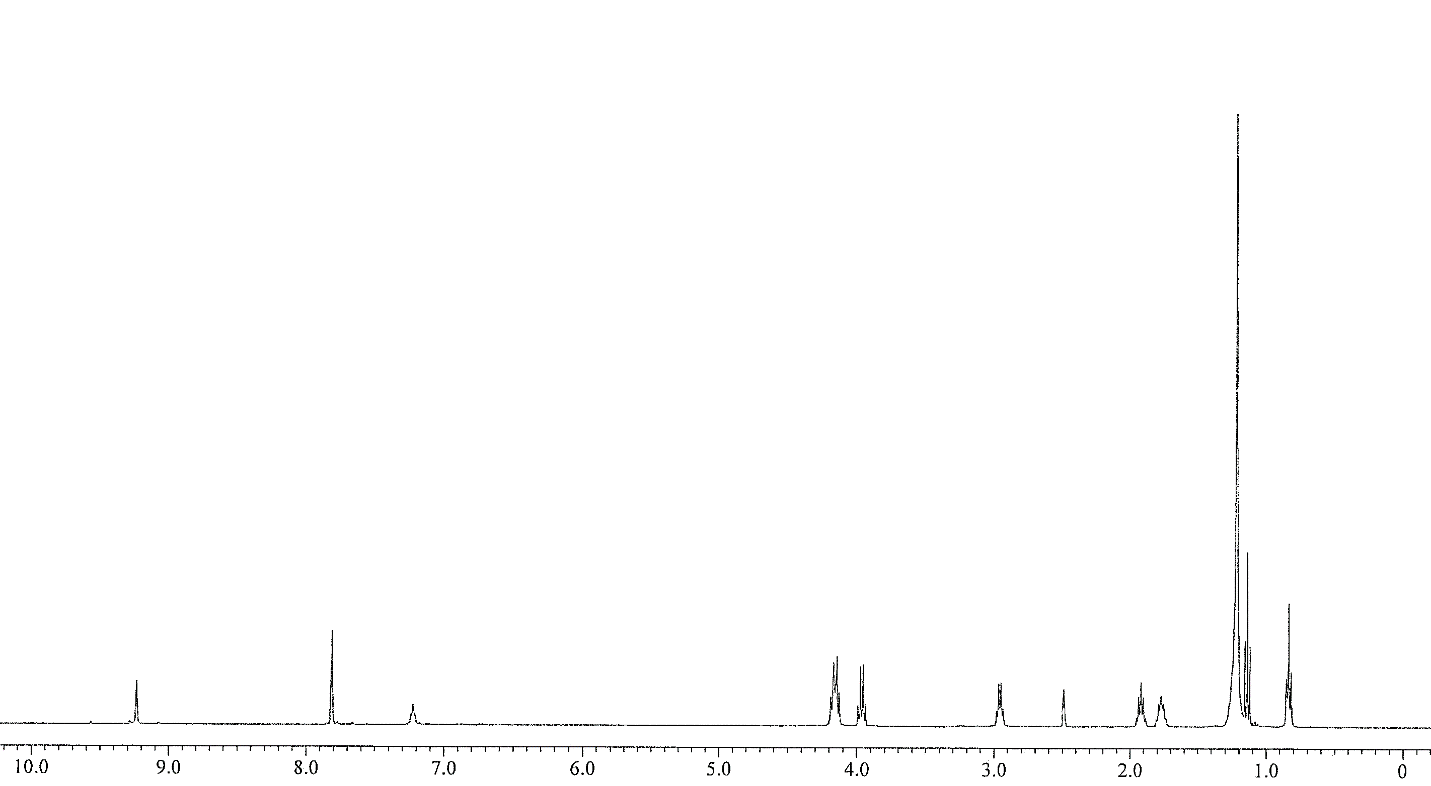


**Figure S35.** 1H NMR spectrum of **O2-C8-NTf2** (DMSO-*d*6).





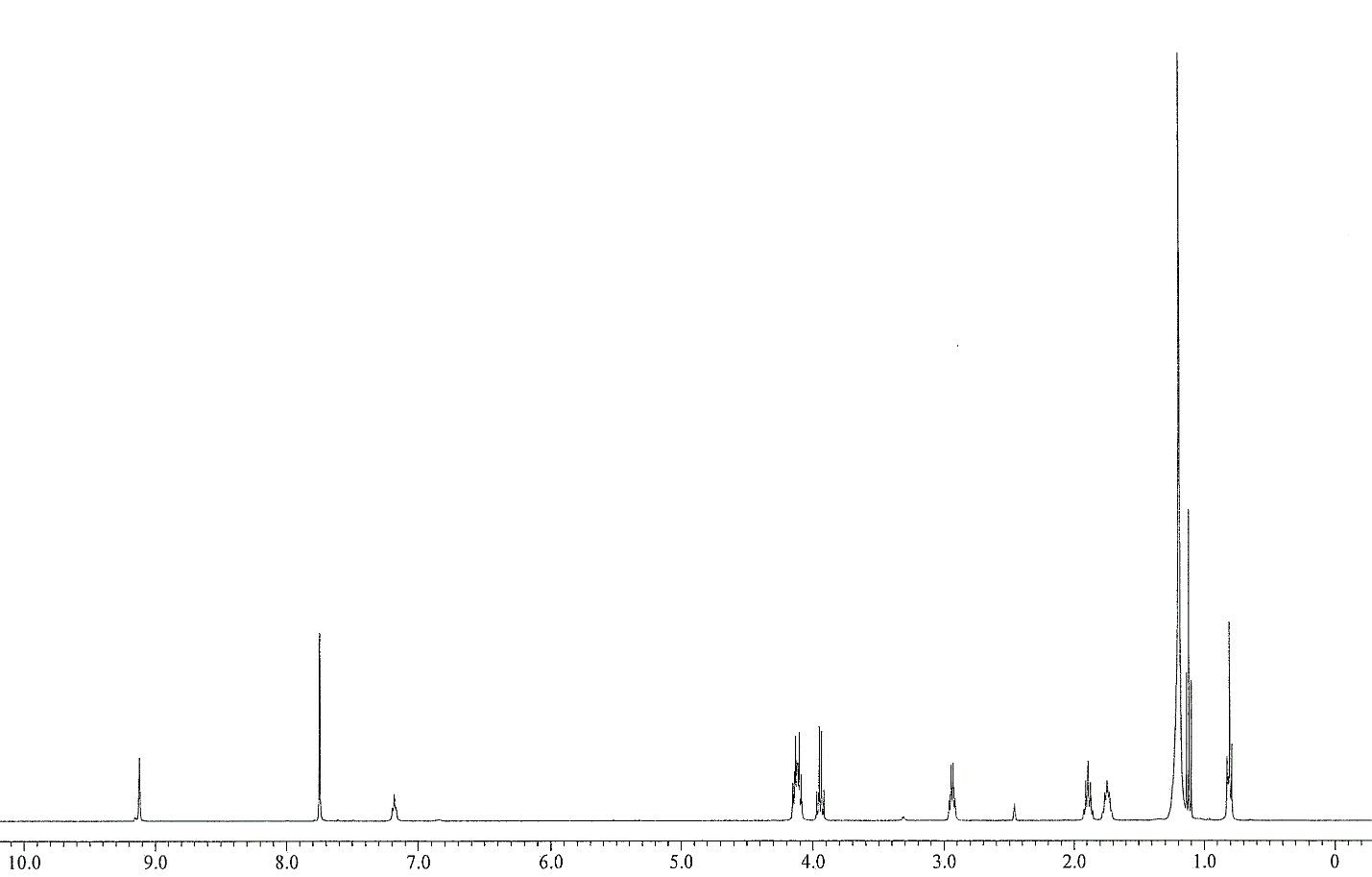
**Figure S36.** 13C NMR spectrum of **O2-C8-NTf2** (DMSO-*d*6).



**Figure S37.** 1H NMR spectrum of **O2-C12-Br** (DMSO-*d*6).

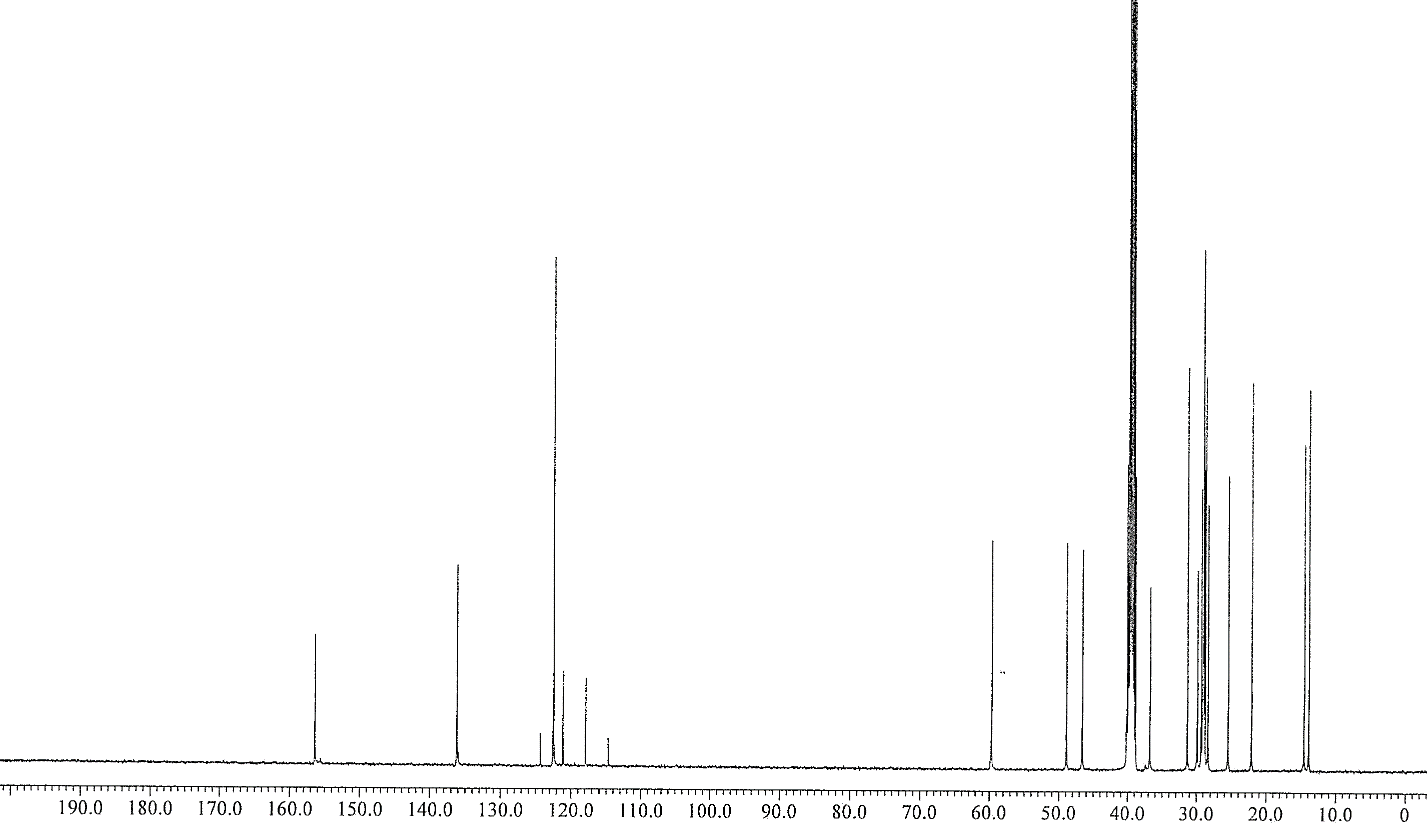


**Figure S38.** 13C NMR spectrum of **O2-C12-Br** (DMSO-*d*6).

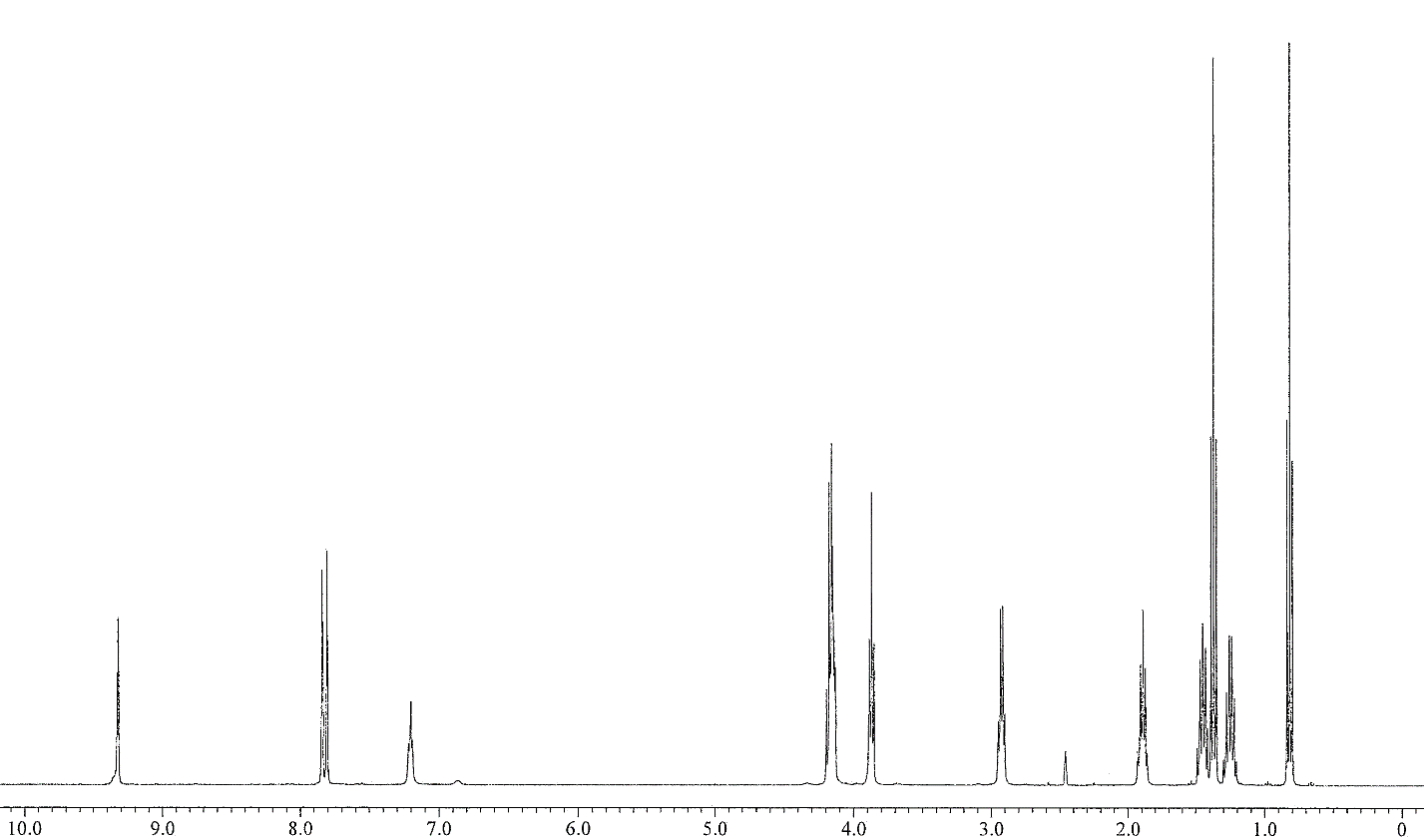


**Figure S39.** 1H NMR spectrum of **O2-C12-NTf2** (DMSO-*d*6).



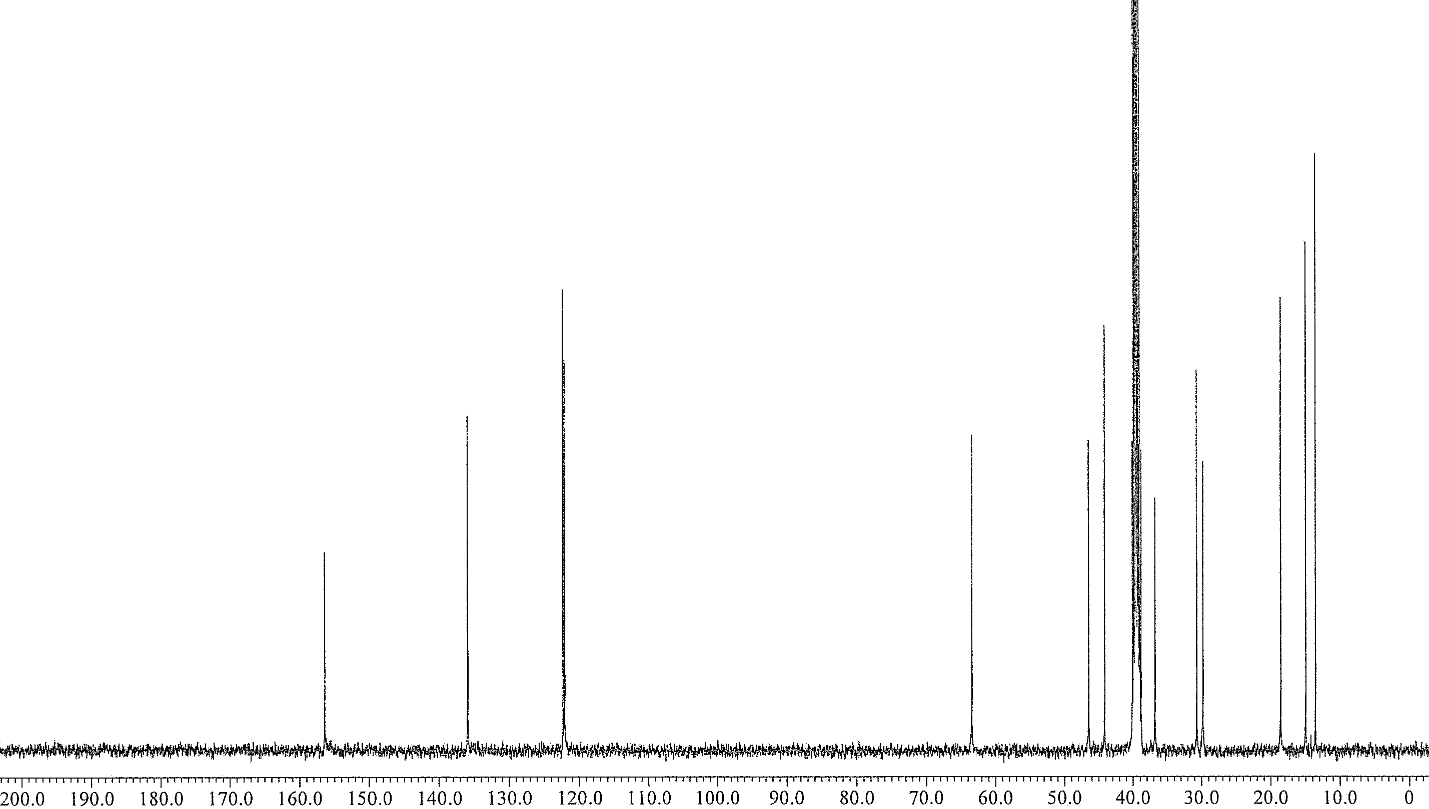


**Figure S40.** 13C NMR spectrum of **O2-C12-NTf2** (DMSO-*d*6).

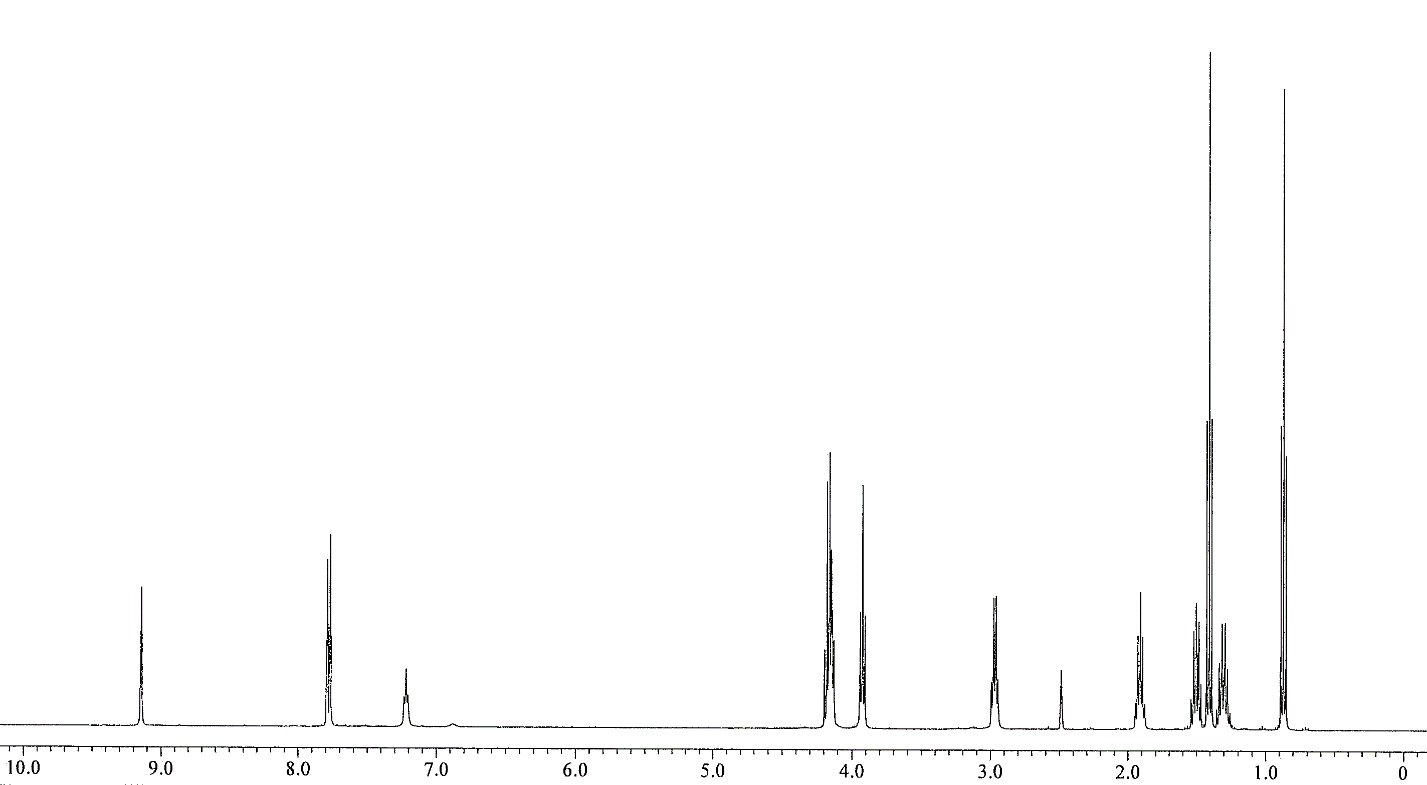


**Figure S41.** 1H NMR spectrum of **O4-C2-Br** (DMSO-*d*6).



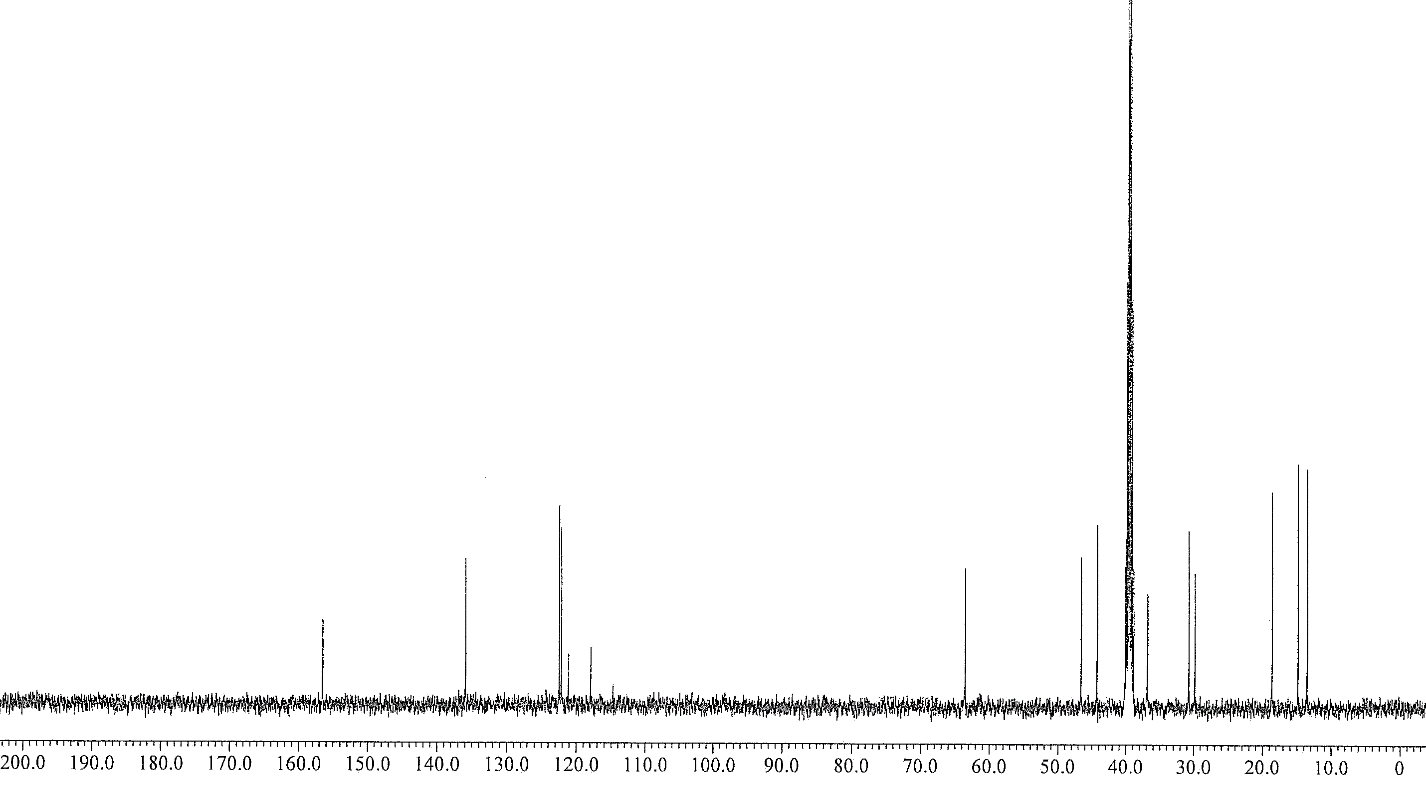


**Figure S42.** 13C NMR spectrum of **O4-C2-Br** (DMSO-*d*6).

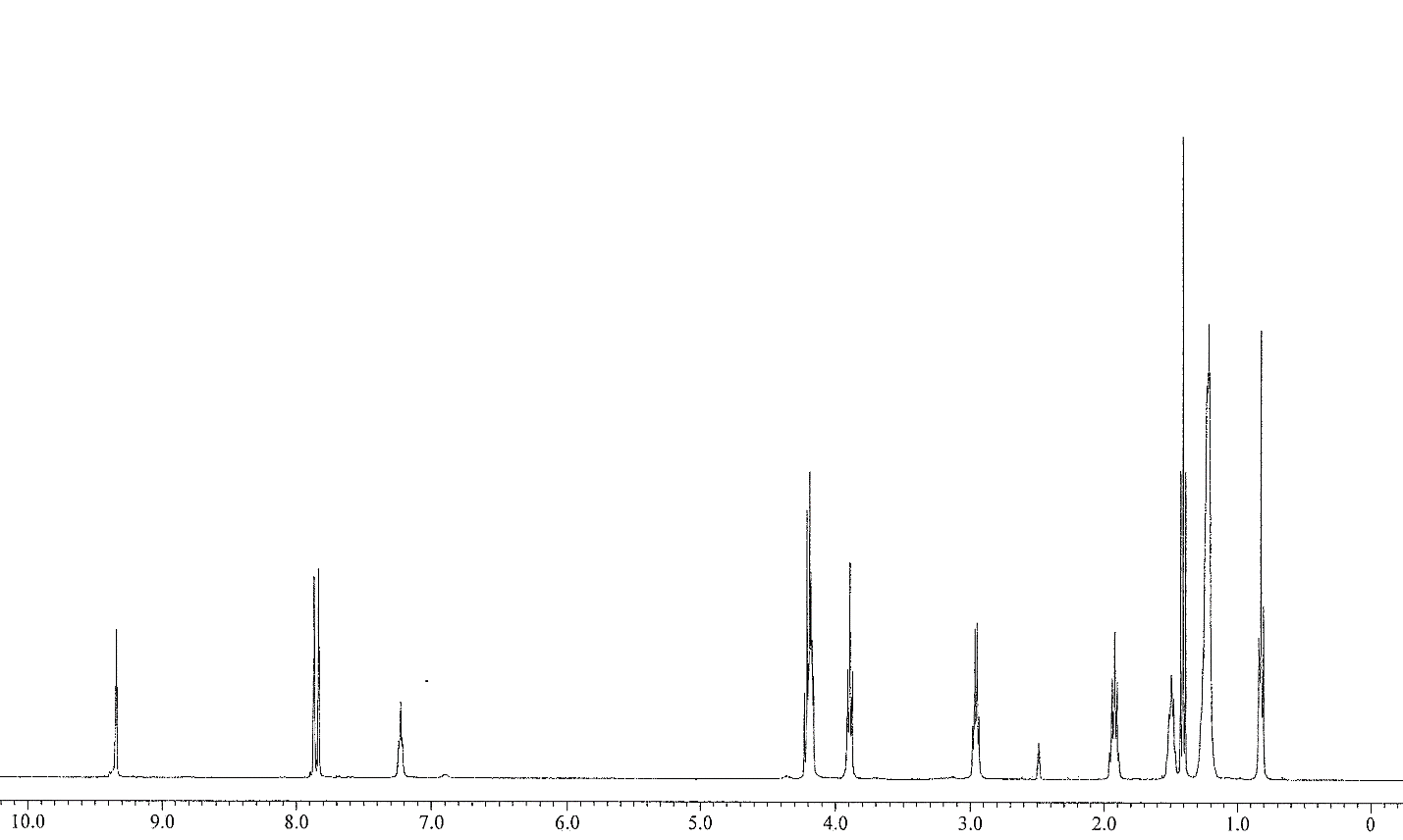


**Figure S43.** 1H NMR spectrum of **O4-C2-NTf2** (DMSO-*d*6).



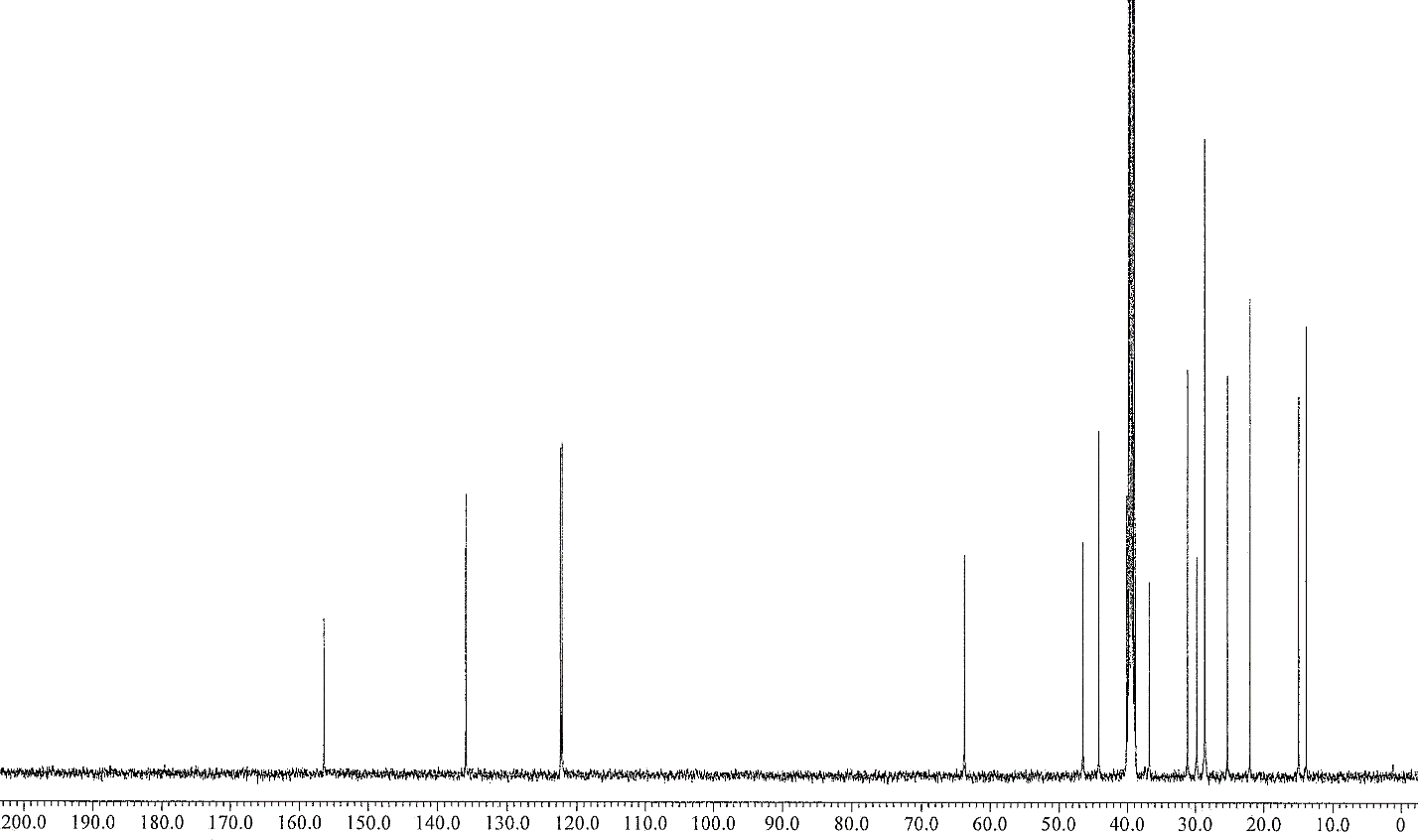


**Figure S44.** 13C NMR spectrum of **O4-C2-NTf2** (DMSO-*d*6).

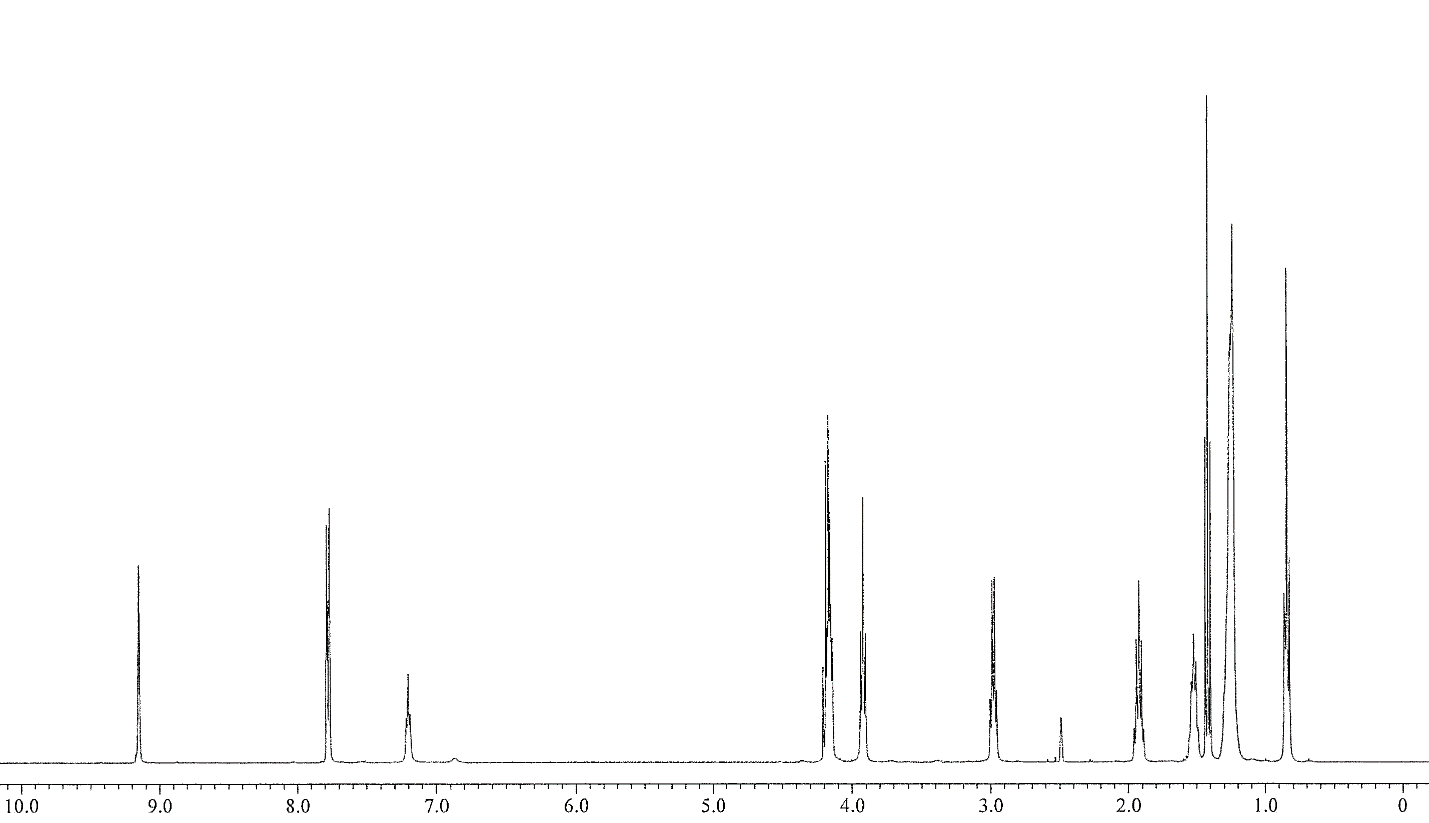


**Figure S45.** 1H NMR spectrum of **O8-C2-Br** (DMSO-*d*6).

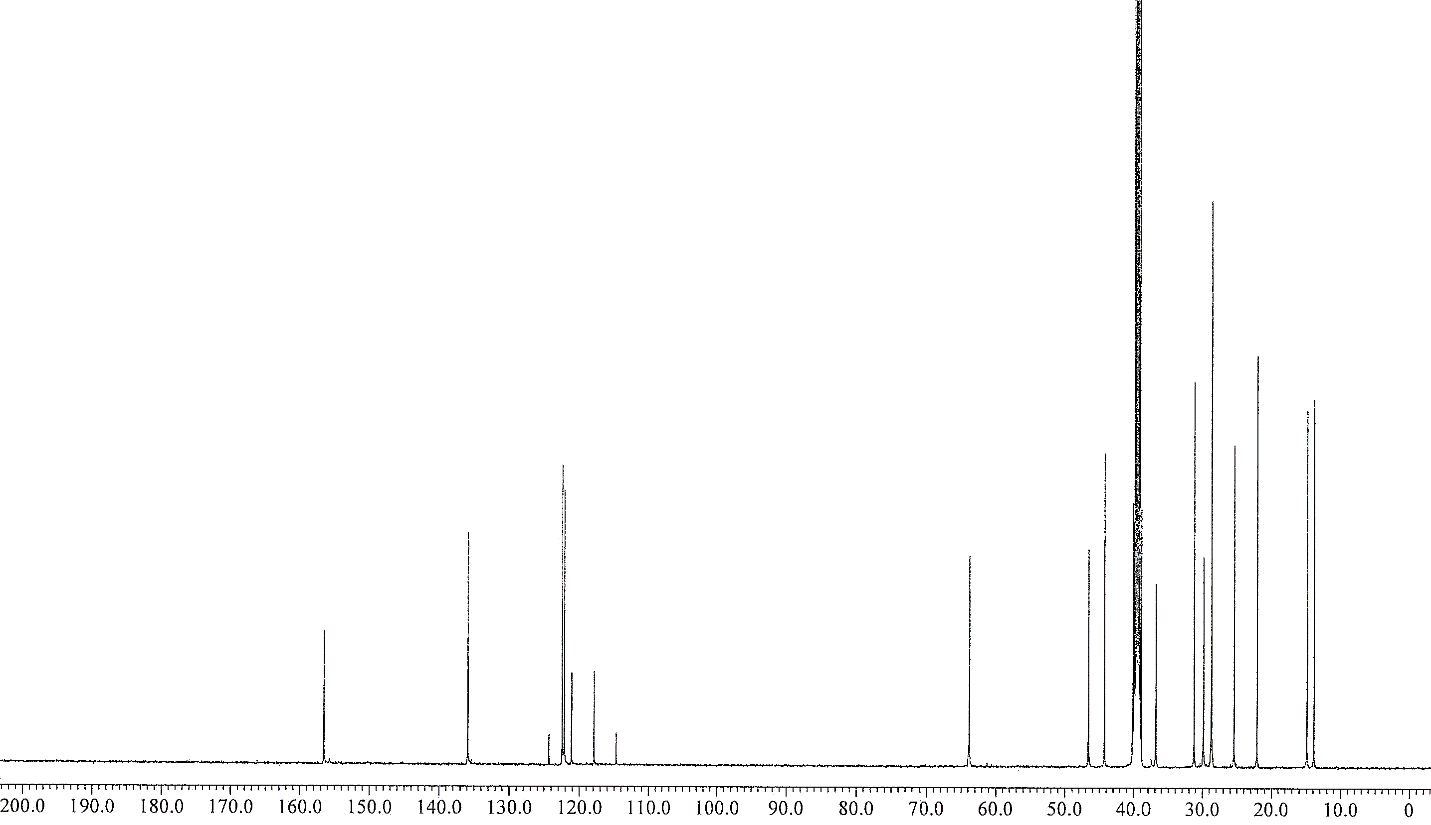




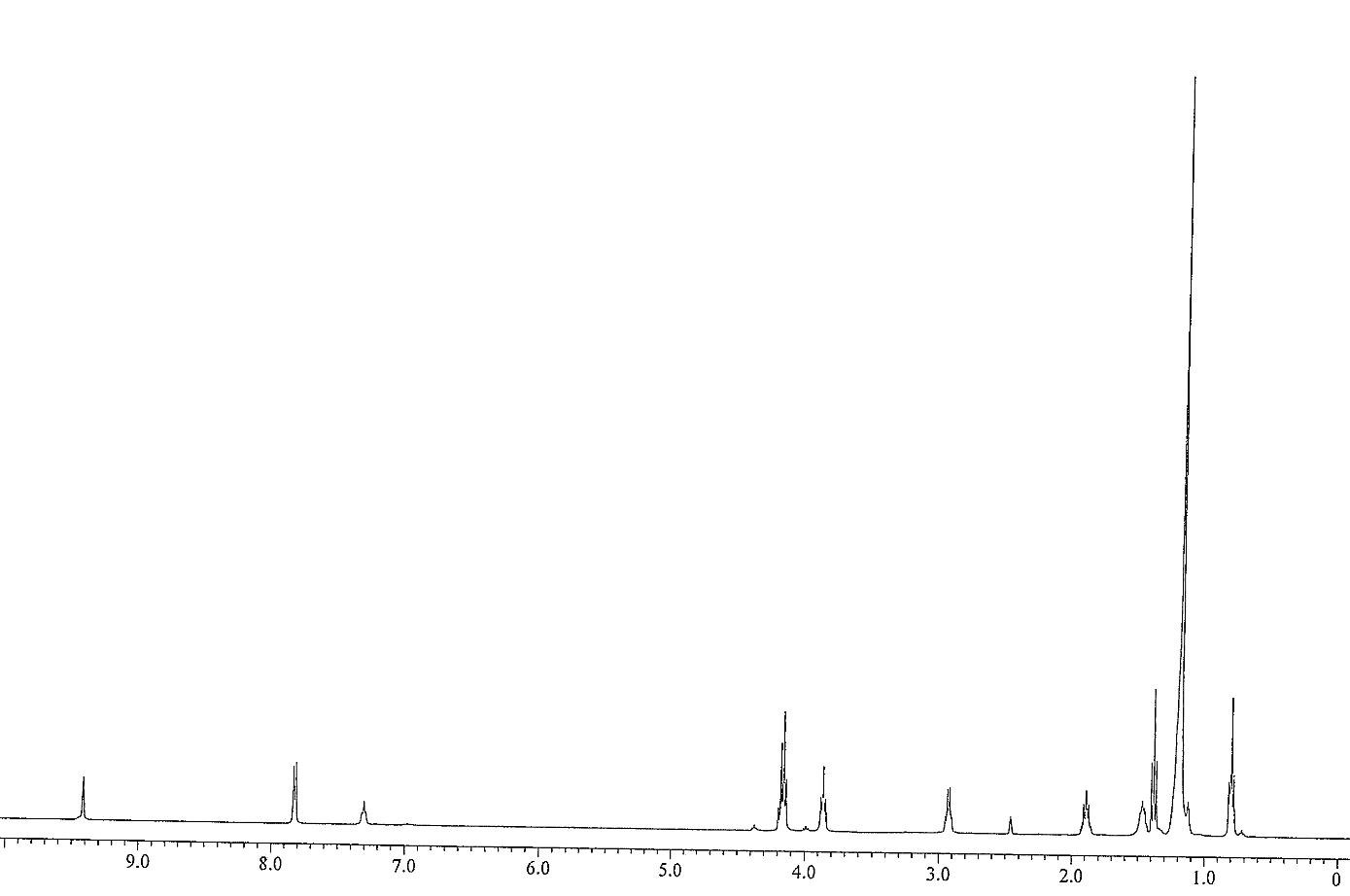
**Figure S46.** 13C NMR spectrum of **O8-C2-Br** (DMSO-*d*6).



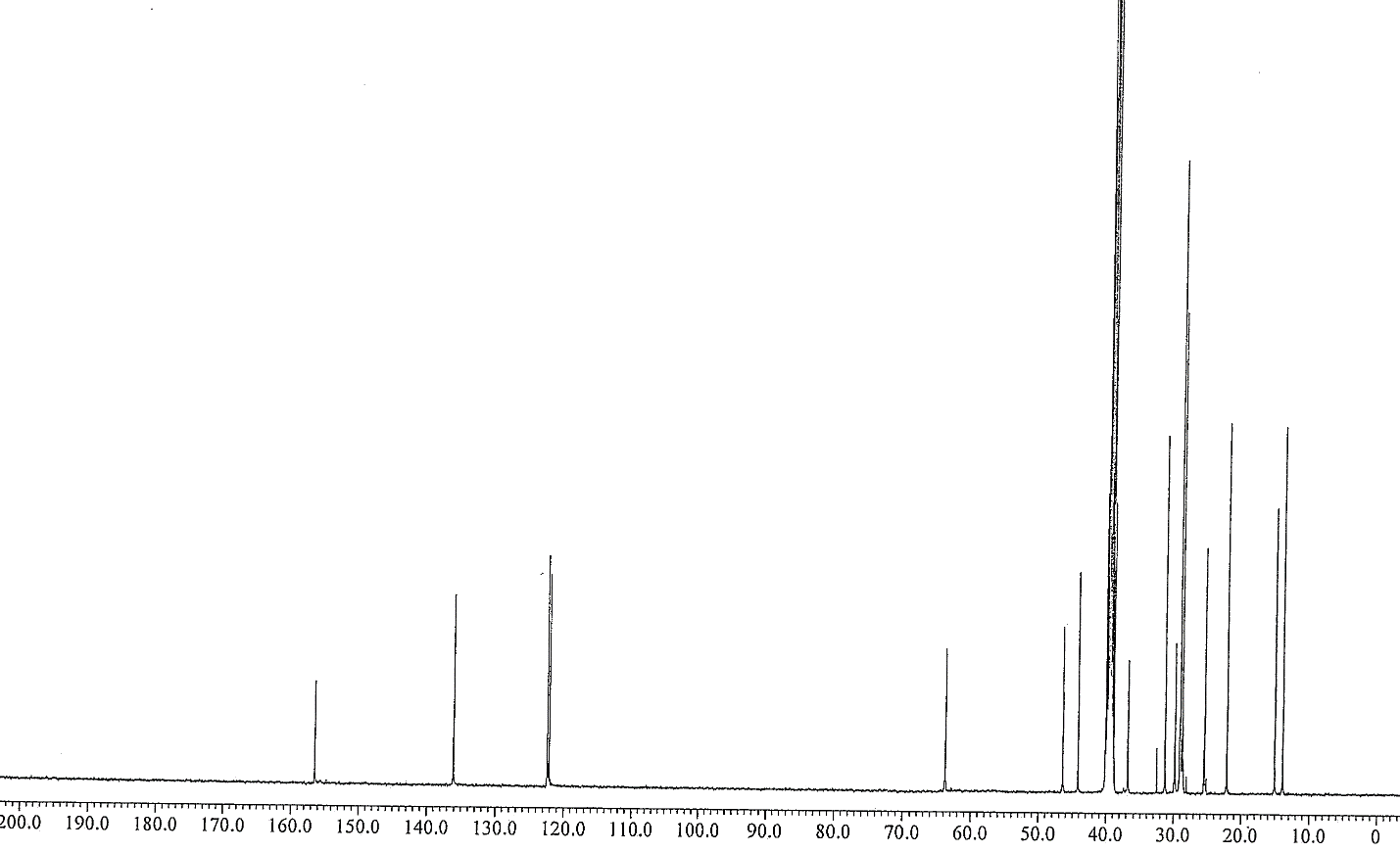
**Figure S47.** 1H NMR spectrum of **O8-C2-NTf2** (DMSO-*d*6).



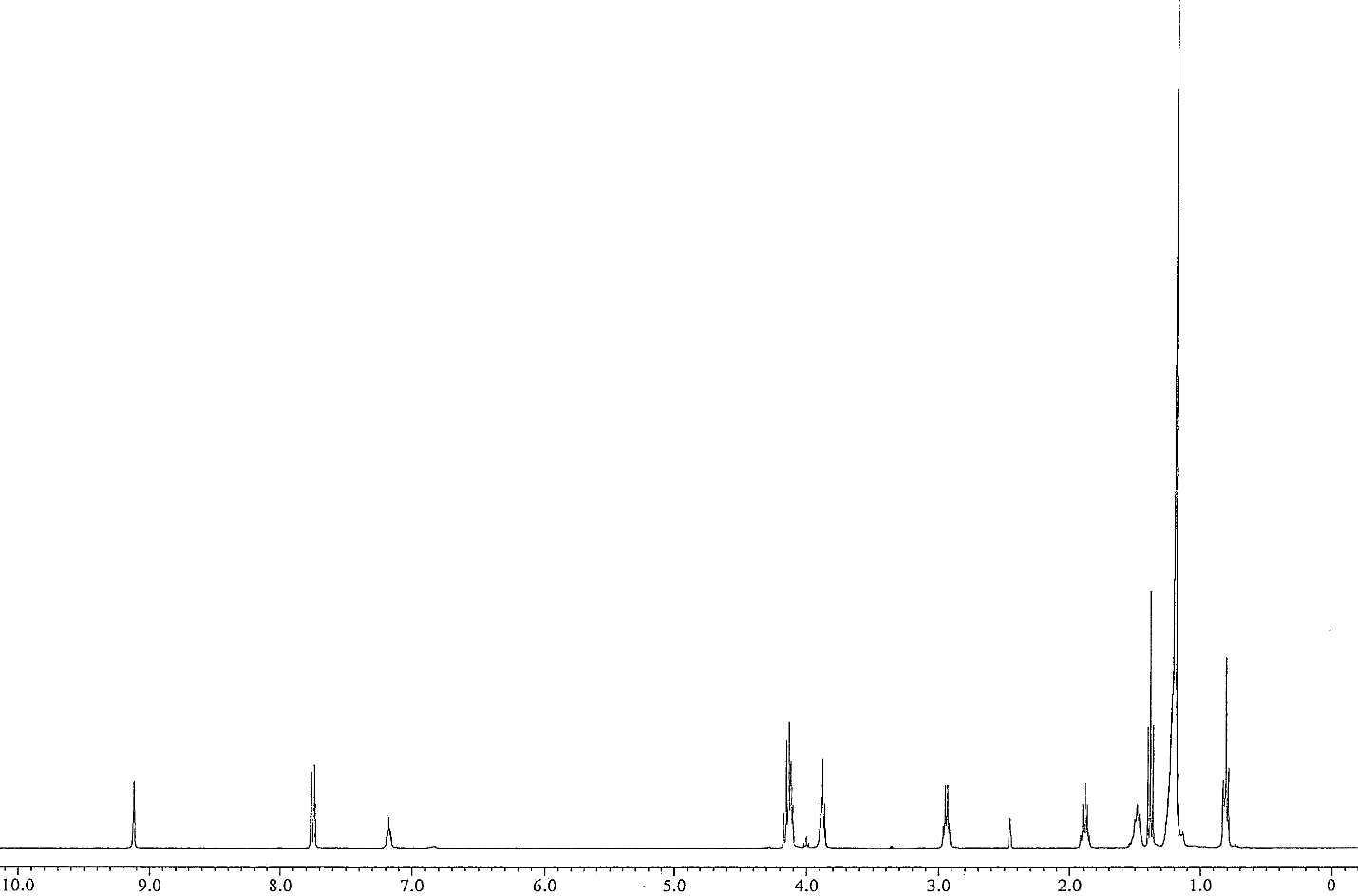
**Figure S48.** 1H NMR spectrum of **O8-C2-NTf2** (DMSO-*d*6).



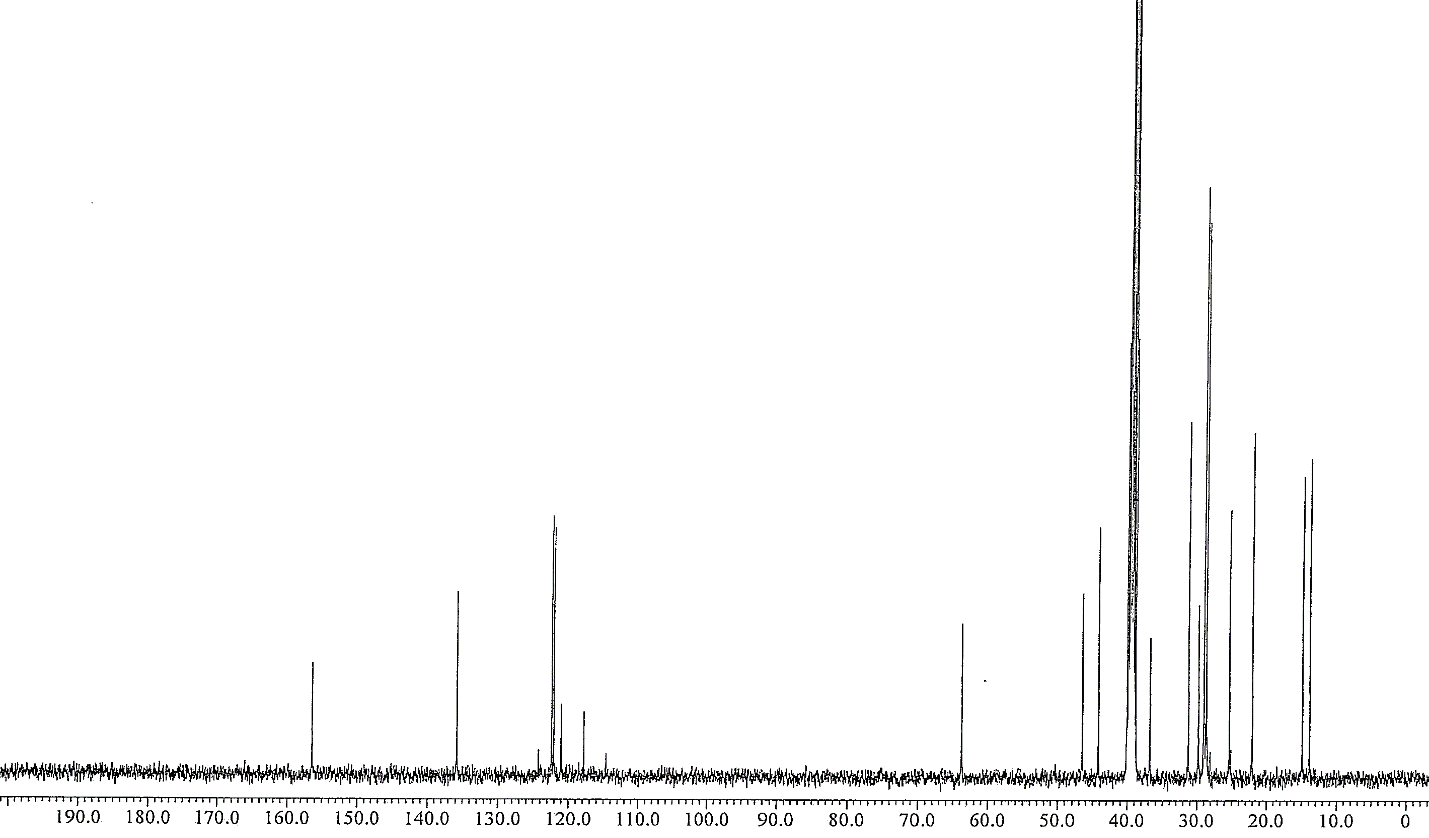
**Figure S49.** 1H NMR spectrum of **O12-C2-Br** (DMSO-*d*6).



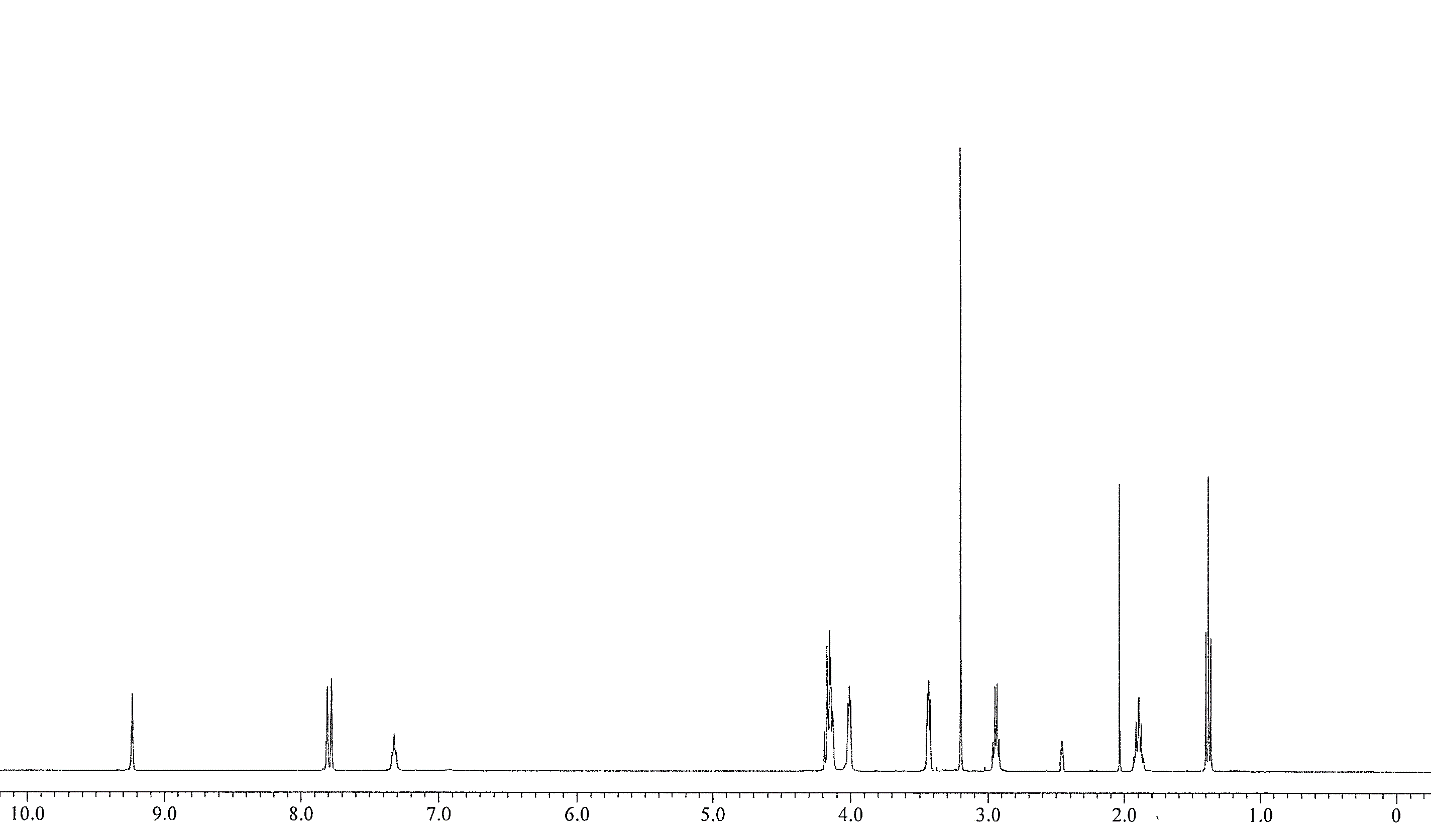
**Figure S50.** 13C NMR spectrum of **O12-C2-Br** (DMSO-*d*6).



**Figure S51.** 1H NMR spectrum of **O12-C2-NTf2** (DMSO-*d*6).

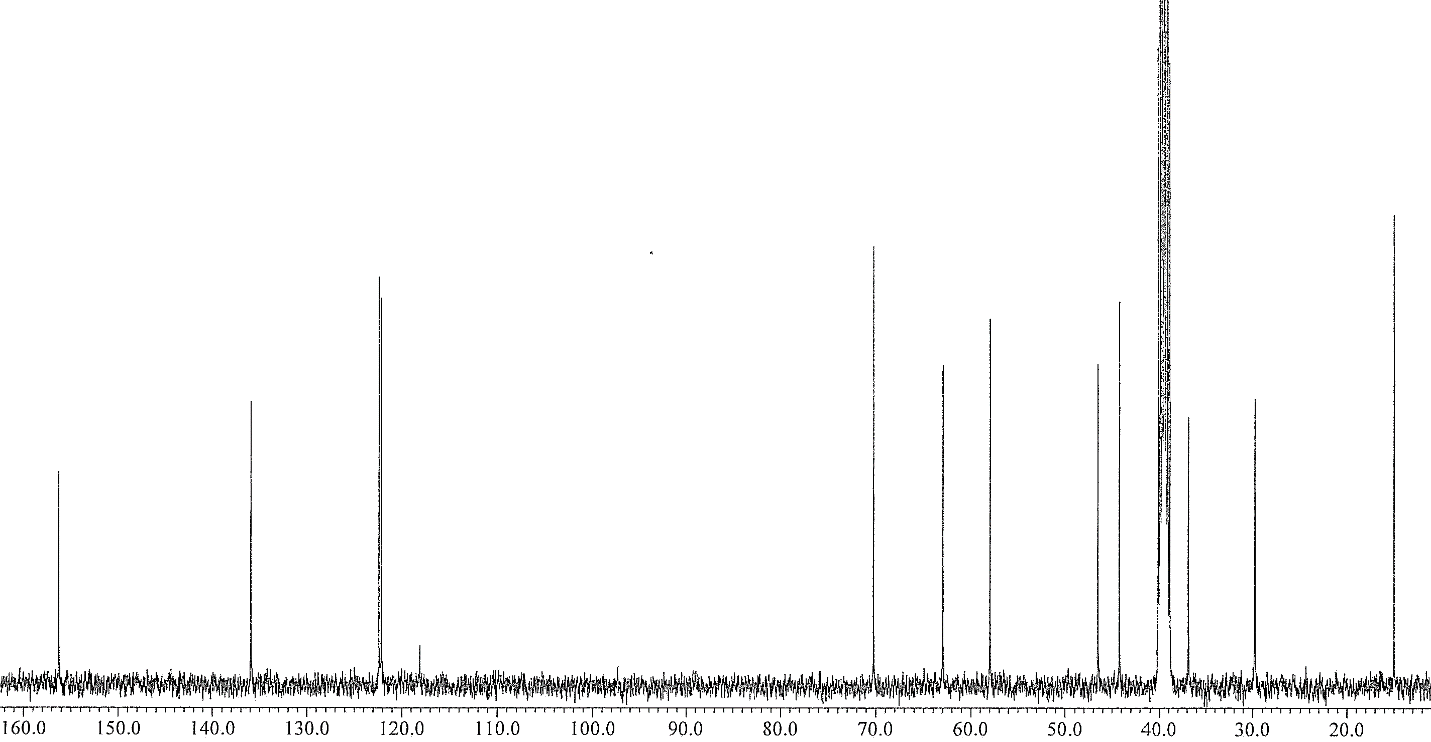


**Figure S52.** 13C NMR spectrum of **O12-C2-NTf2** (DMSO-*d*6).

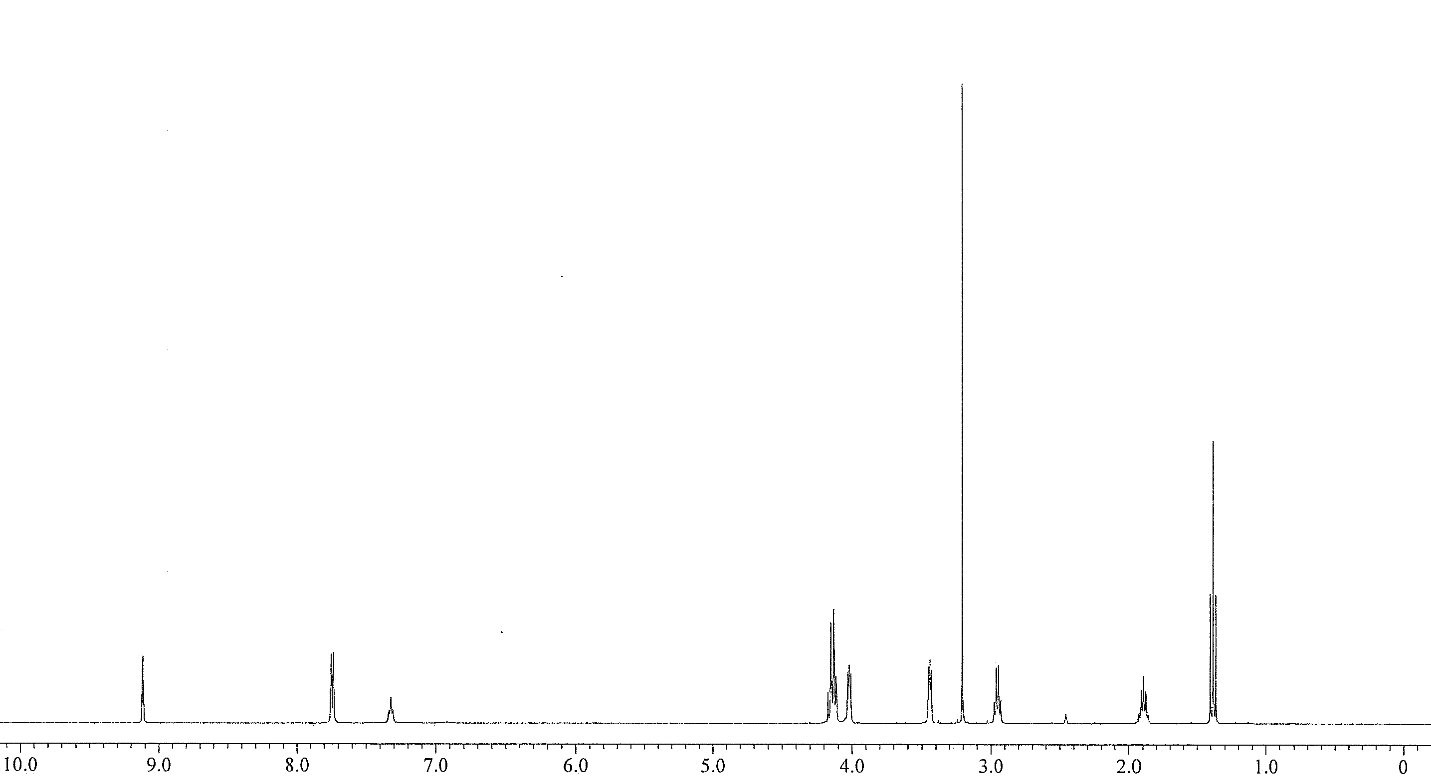


**Figure S53.** 1H NMR spectrum of **OM-C2-Br** (DMSO-*d*6).



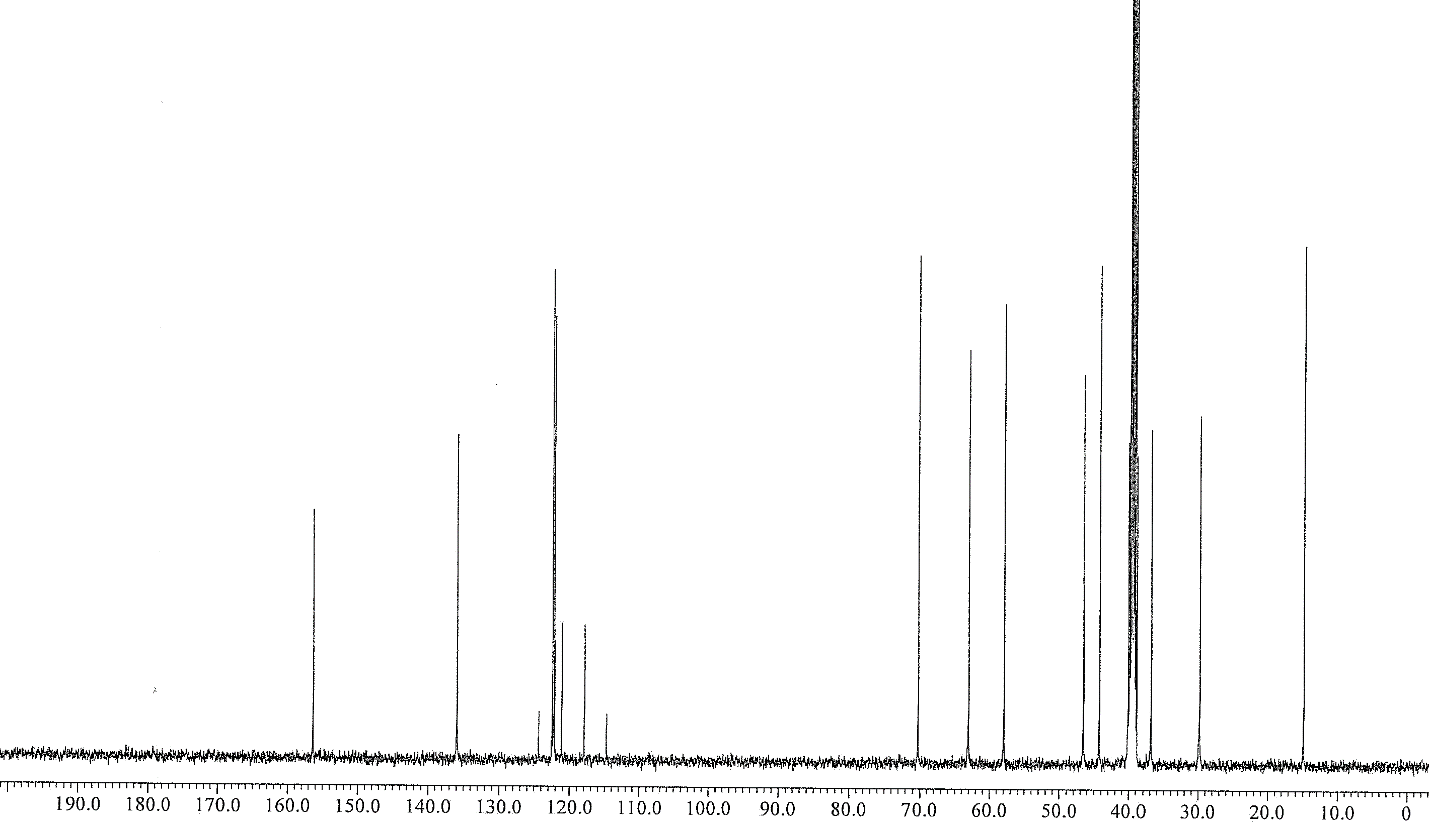


**Figure S54.** 13C NMR spectrum of **OM-C2-Br** (DMSO-*d*6).

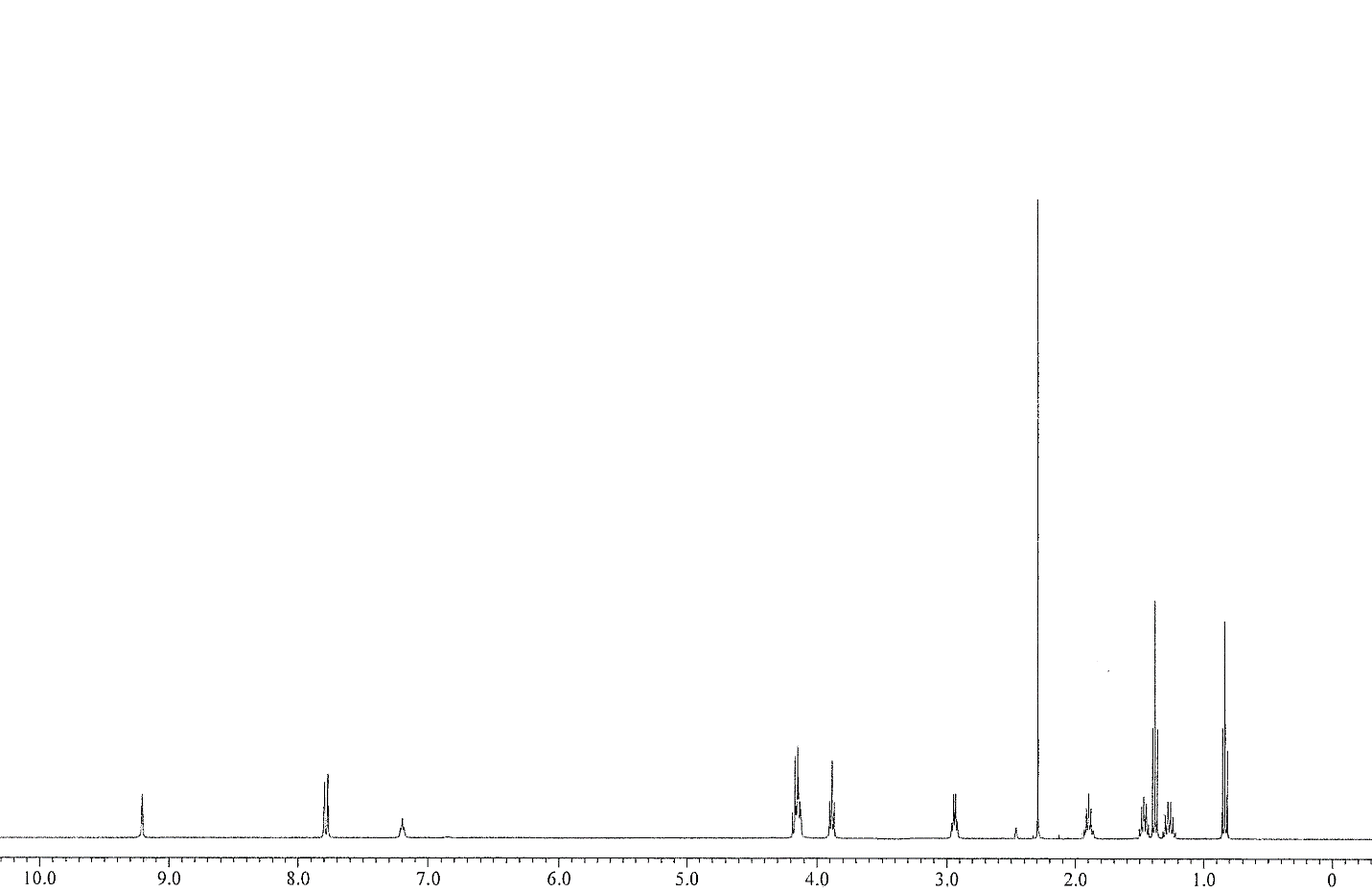


**Figure S55.** 1H NMR spectrum of **OM-C2-NTf2** (DMSO-*d*6).



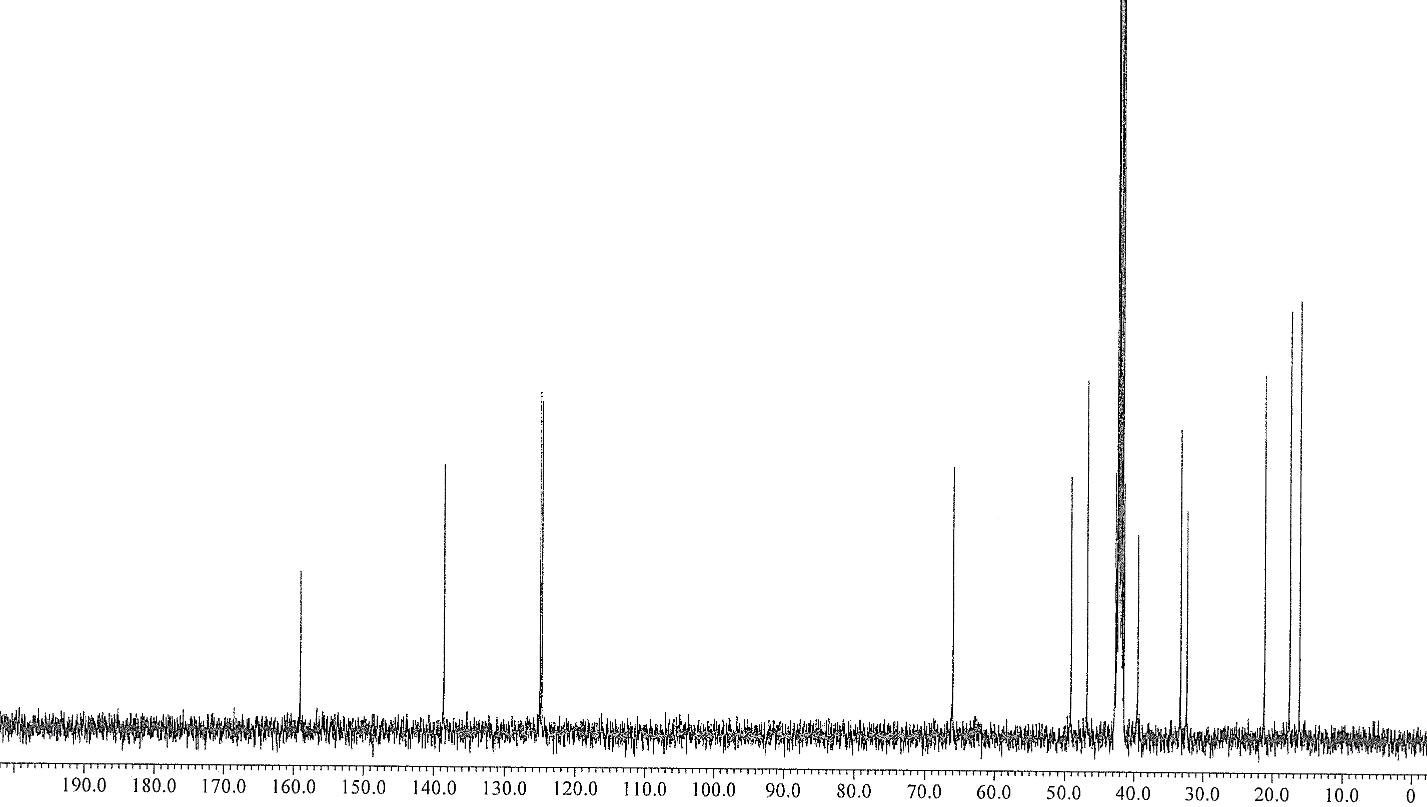


**Figure S56.** 1H NMR spectrum of **OM-C2- NTf2** (DMSO-*d*6).



**Figure S57.** 1H NMR spectrum of **O4-C2-OMs** (DMSO-*d*6).

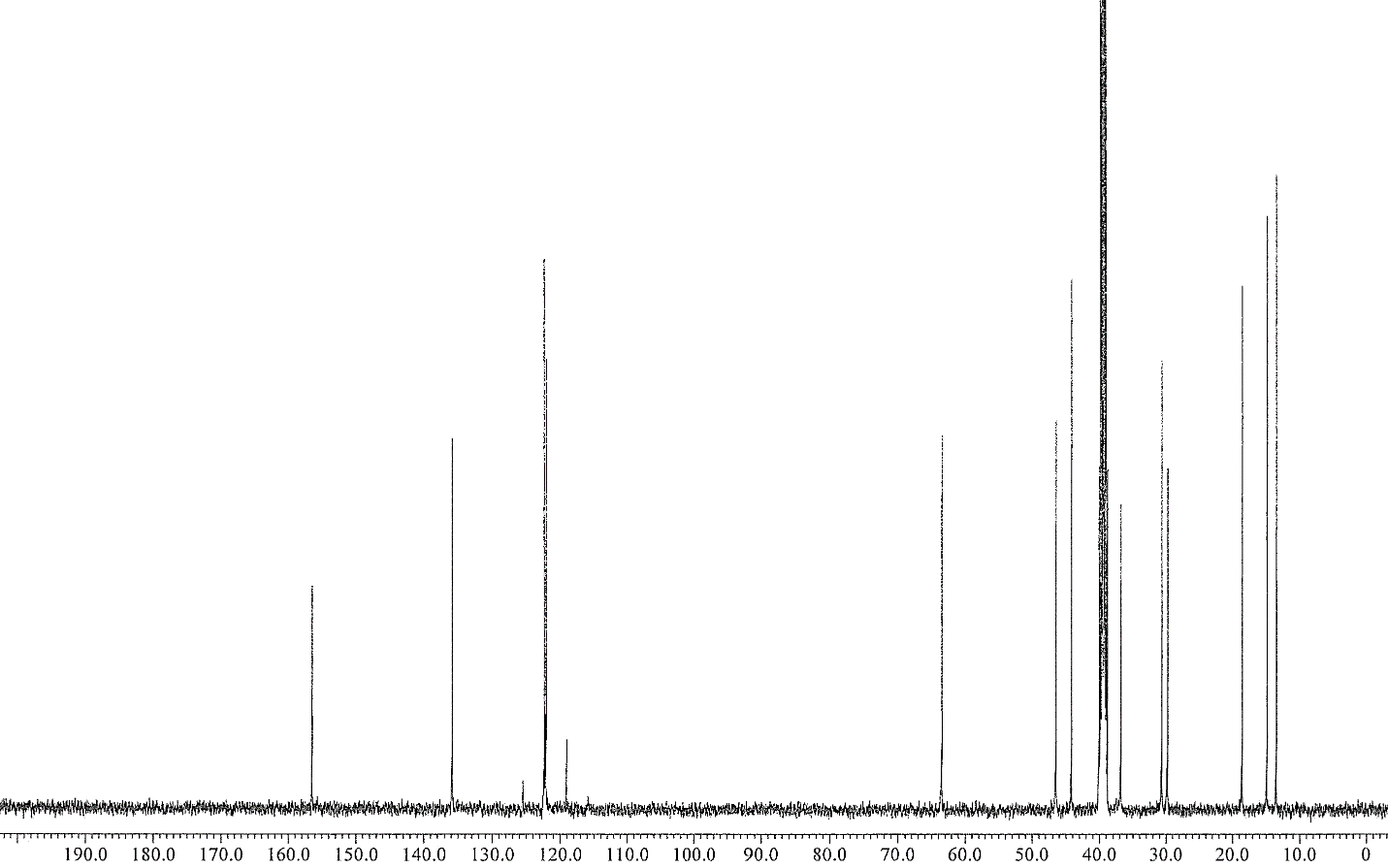




**Figure S58.** 13C NMR spectrum of **O4-C2-OMs** (DMSO-*d*6).

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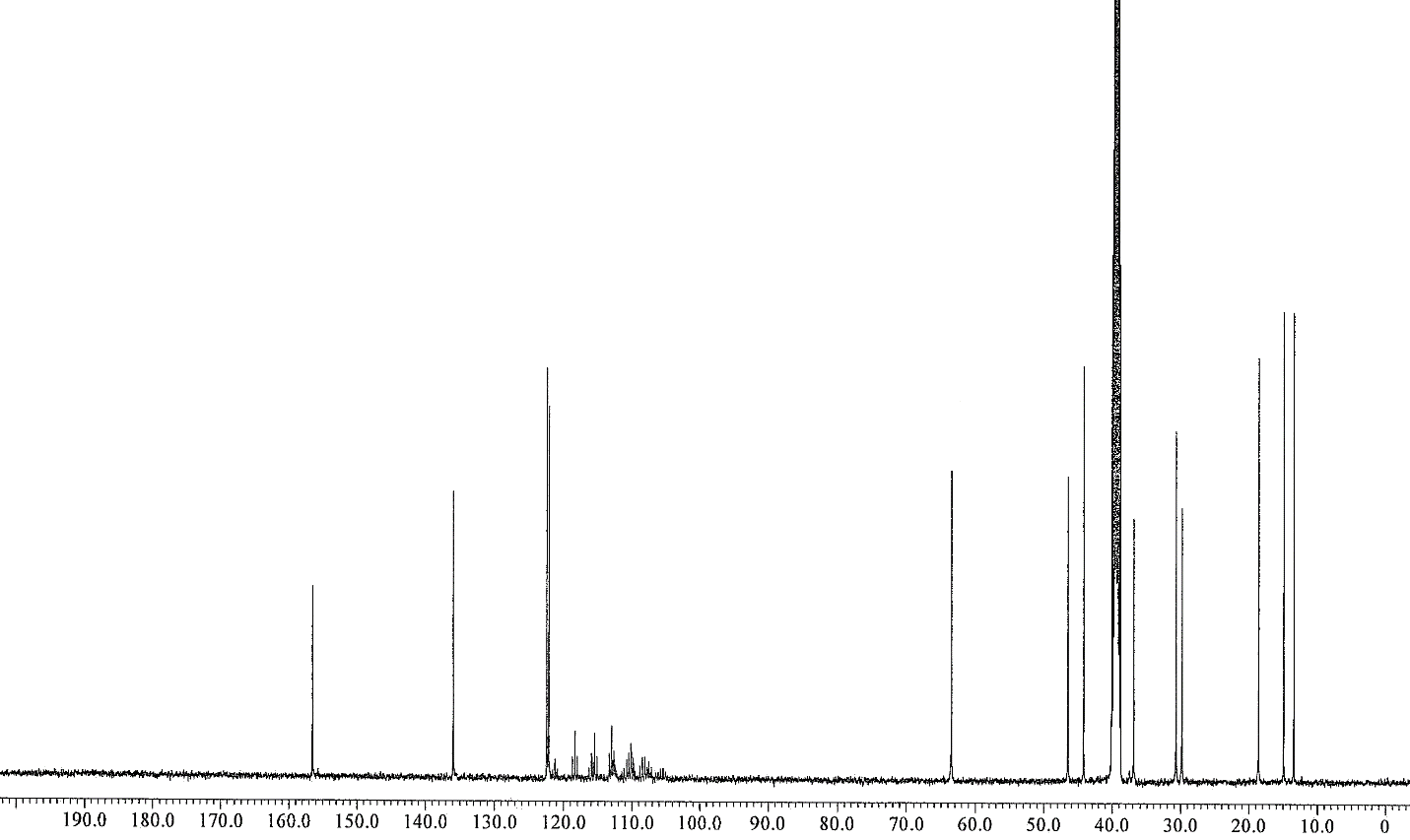
**Figure S59.** 1H NMR spectrum of **O4-C2-OTf** (DMSO-*d*6).



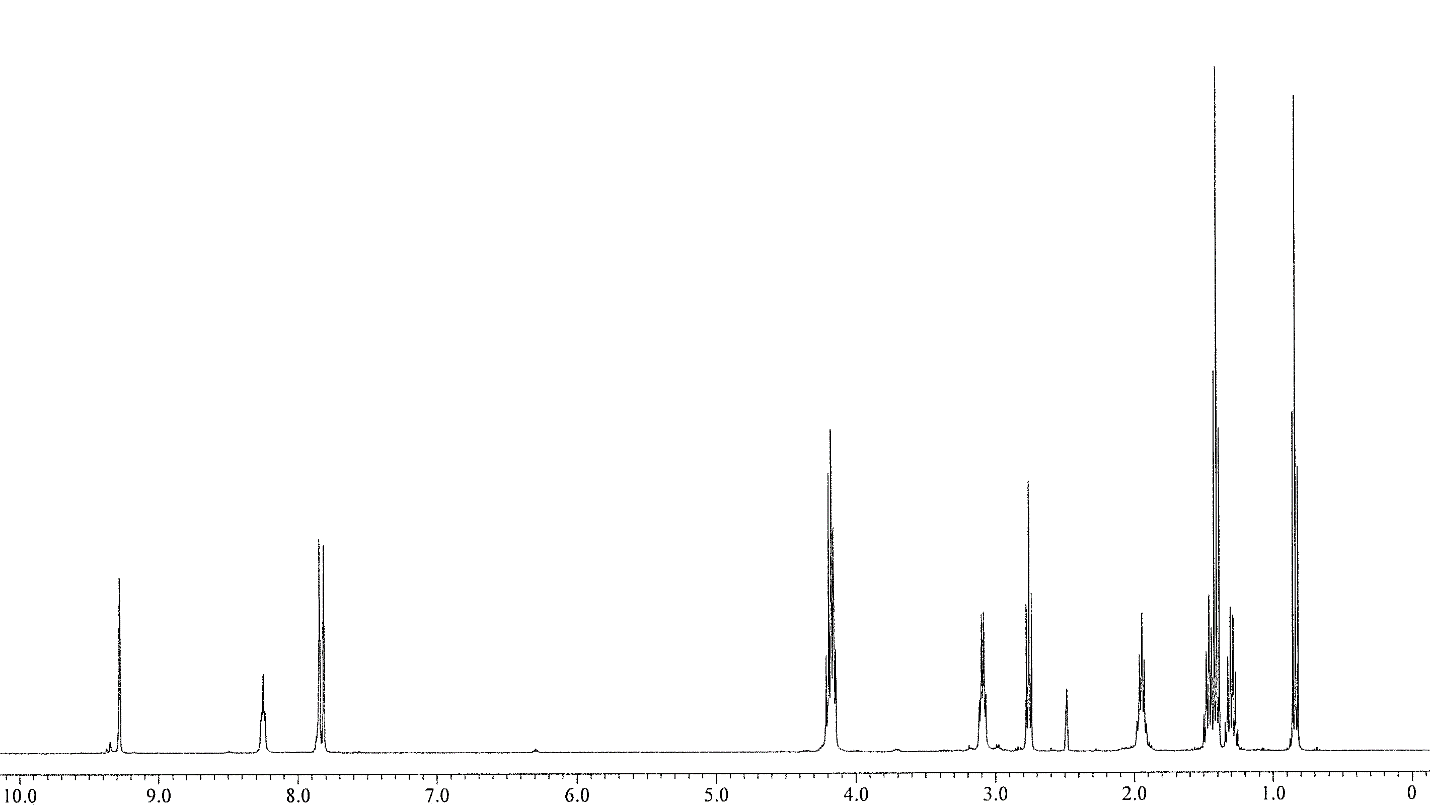
**Figure S60.** 13C NMR spectrum of **O4-C2-OTf** (DMSO-*d*6).



**Figure S61.** 1H NMR spectrum of **O4-C2-NFBSI** (DMSO-*d*6).

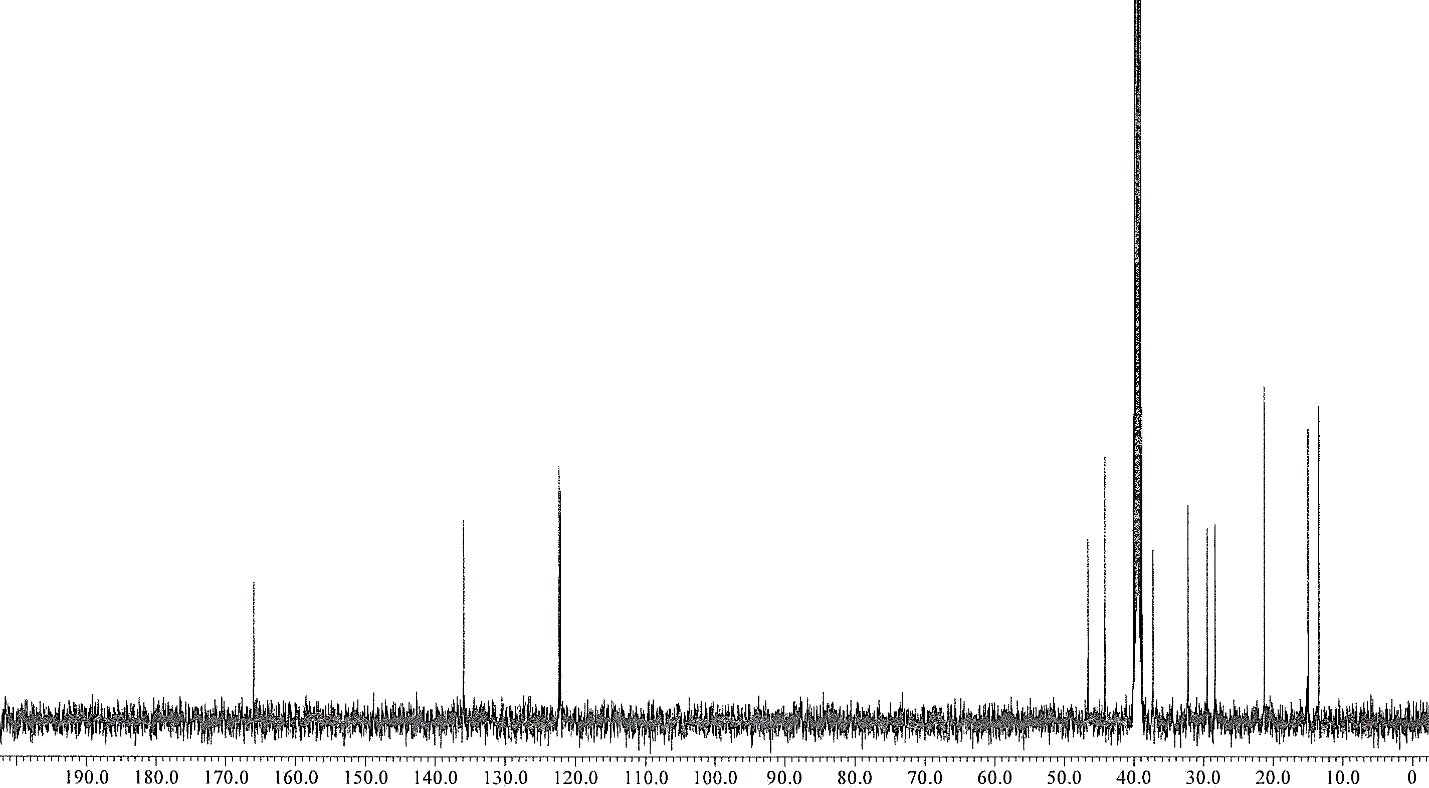


**Figure S62.** 13C NMR spectrum of **O4-C2-NFBSI** (DMSO-*d*6).

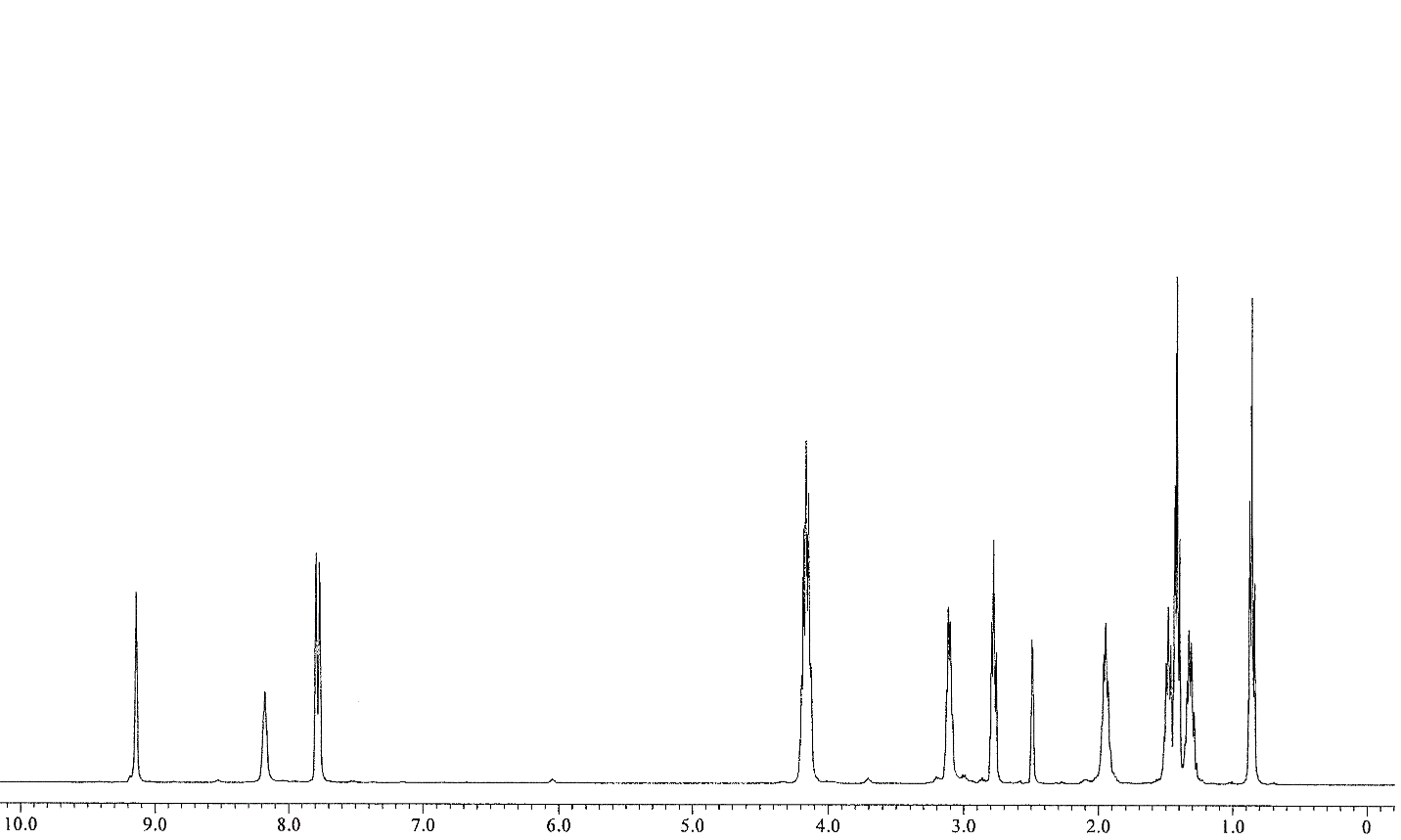


**Figure S63.** 1H NMR spectrum of **S4-C2-Br** (DMSO-*d*6).



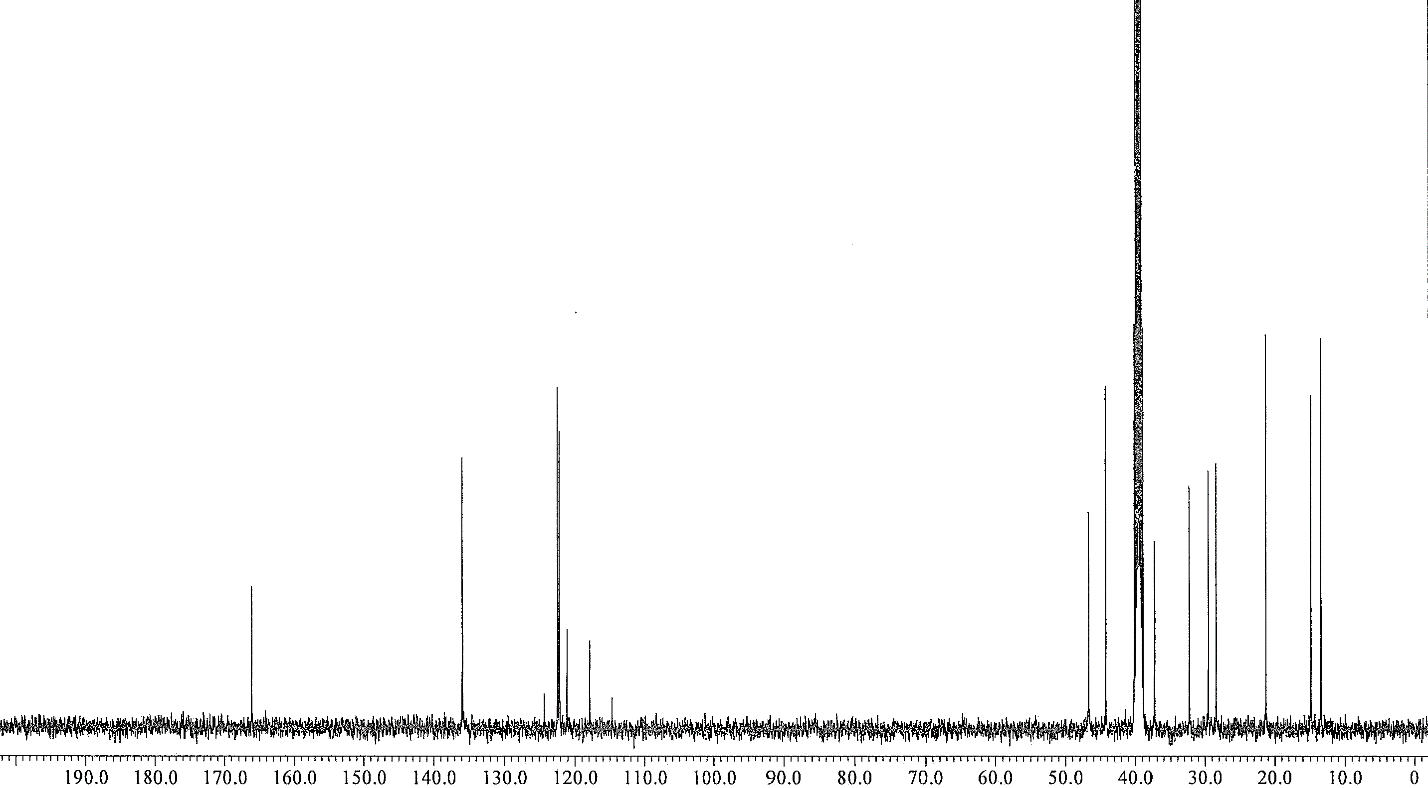


**Figure S64.** 1H NMR spectrum of **S4-C2-Br** (DMSO-*d*6).

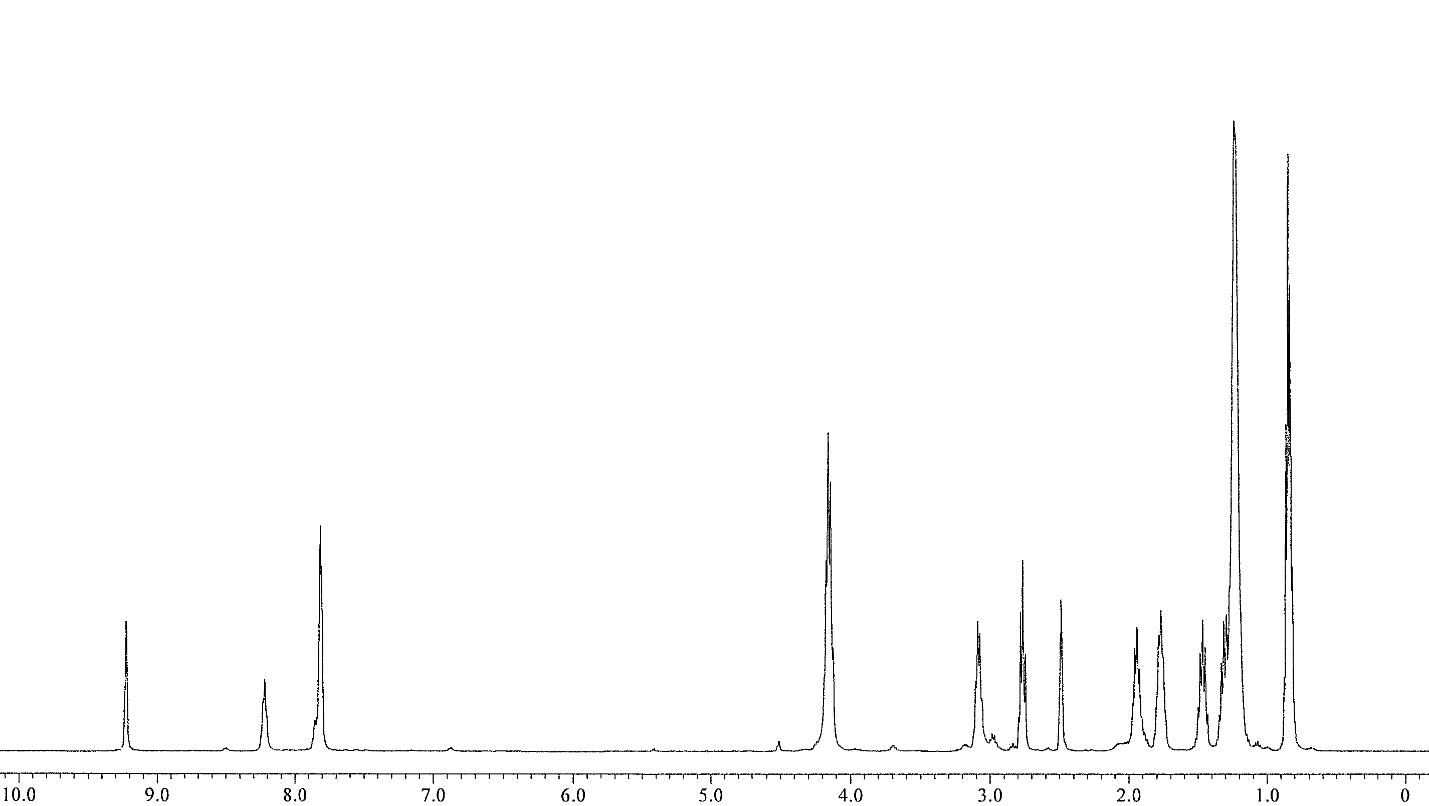


**Figure S65.** 1H NMR spectrum of **S4-C2-NTf2** (DMSO-*d*6).



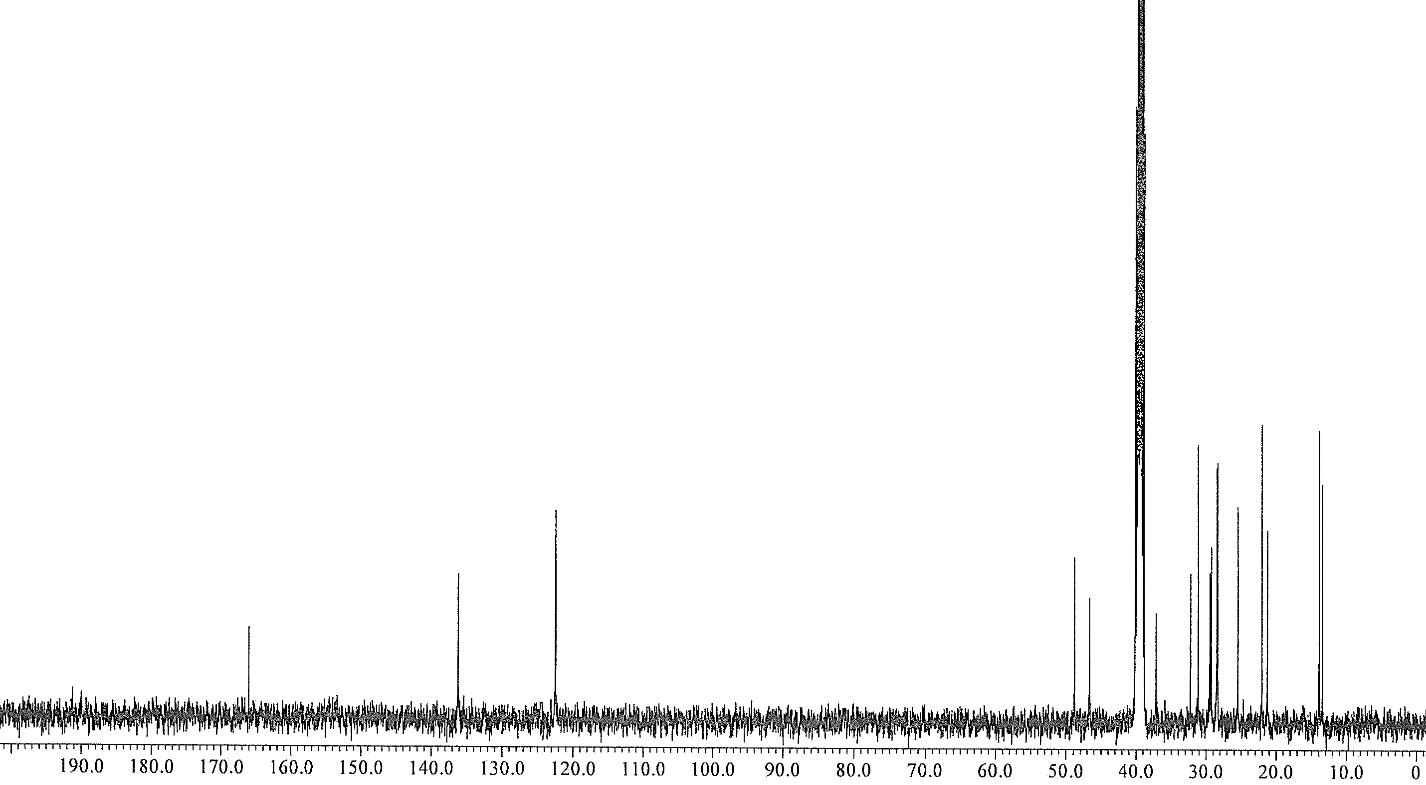


**Figure S66.** 13C NMR spectrum of **S4-C2-NTf2** (DMSO-*d*6).

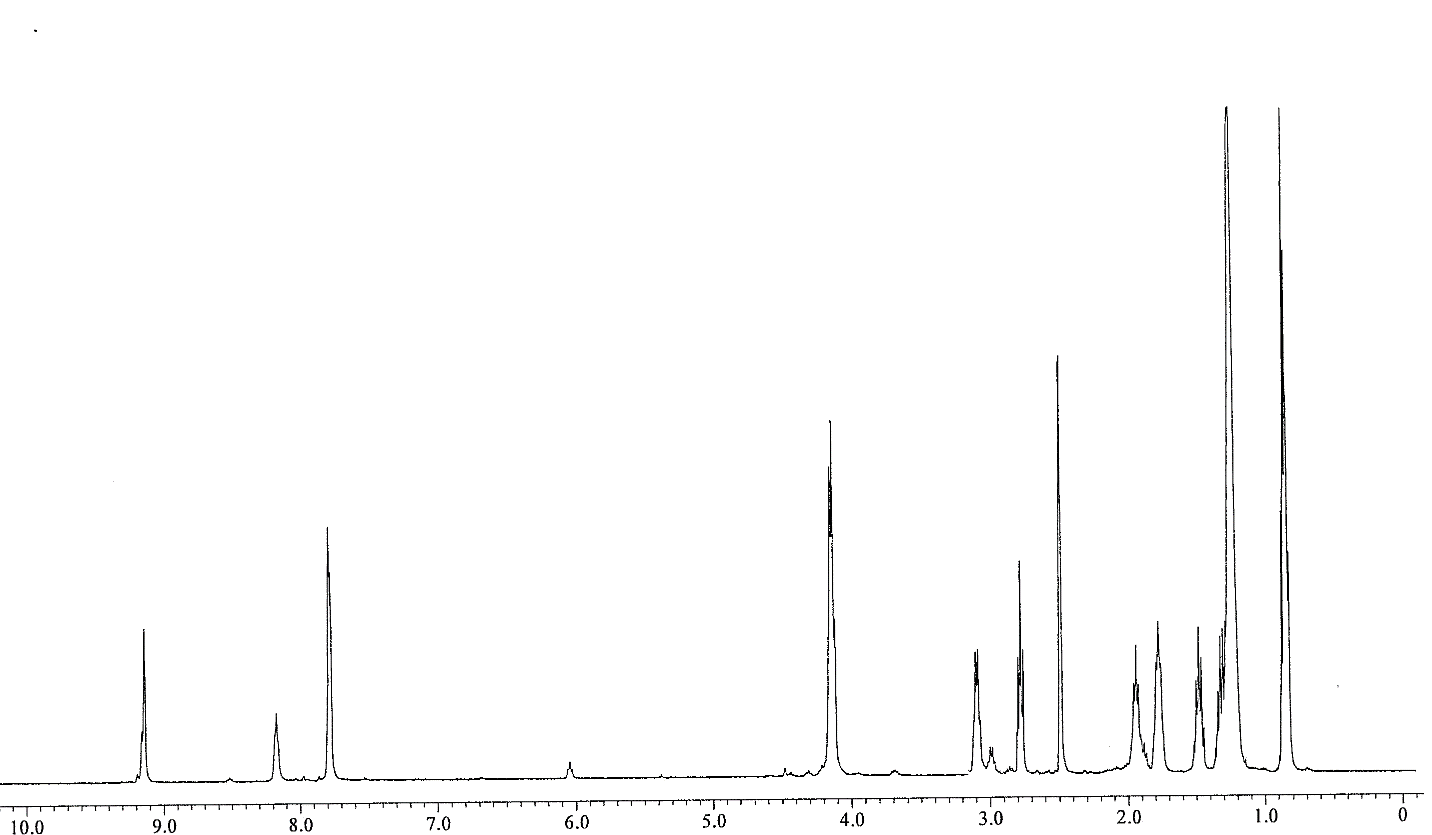


**Figure S67.** 1H NMR spectrum of **S4-C8-Br** (DMSO-*d*6).



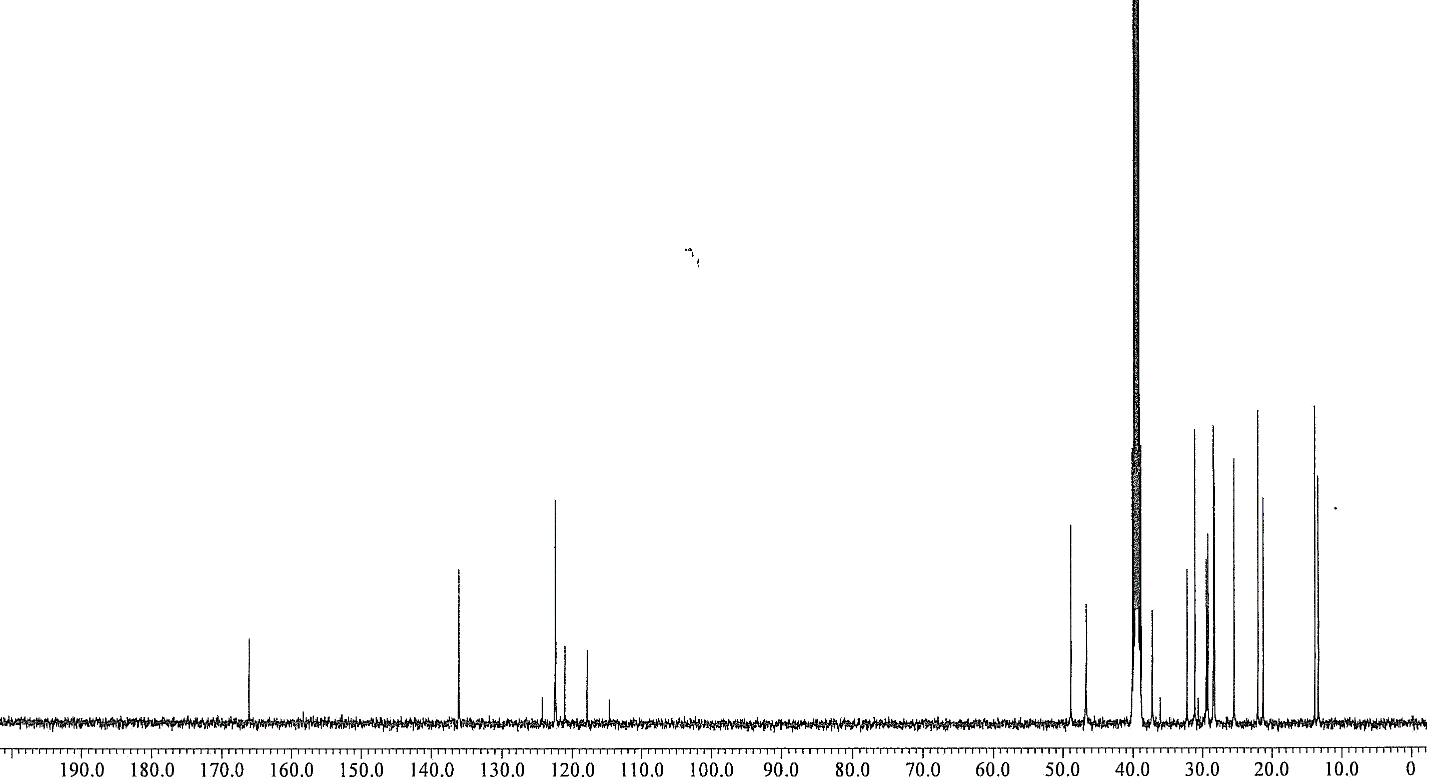


**Figure S68.** 13C NMR spectrum of **S4-C8-Br** (DMSO-*d*6).

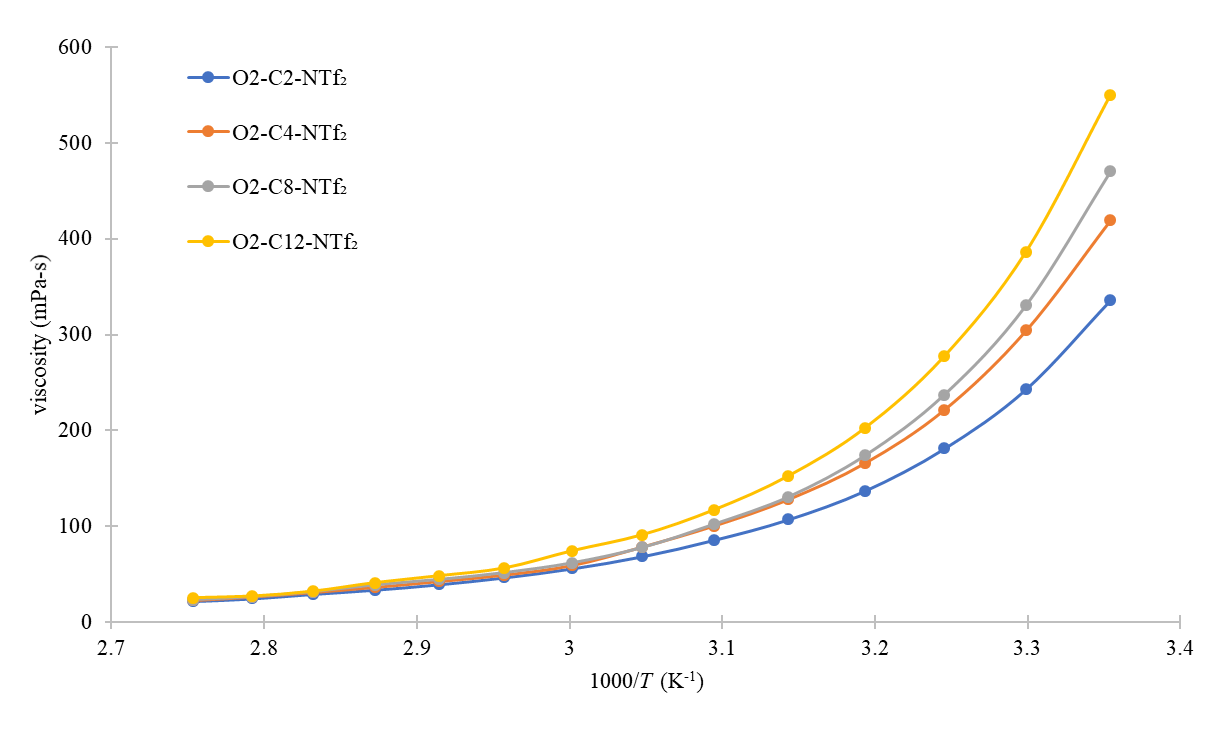


**Figure S69.** 1H NMR spectrum of **S4-C8-NTf2** (DMSO-*d*6).

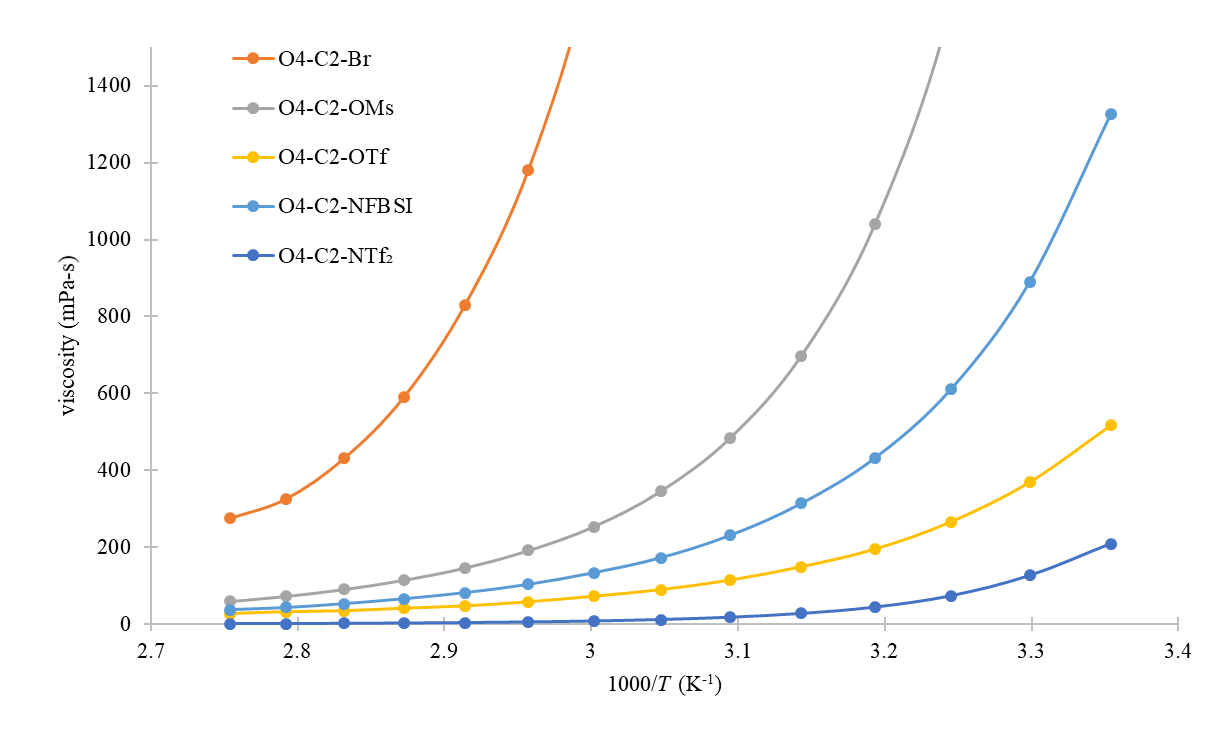




**Figure S70.** 13C NMR spectrum of **S4-C8-NTf2** (DMSO-*d*6).

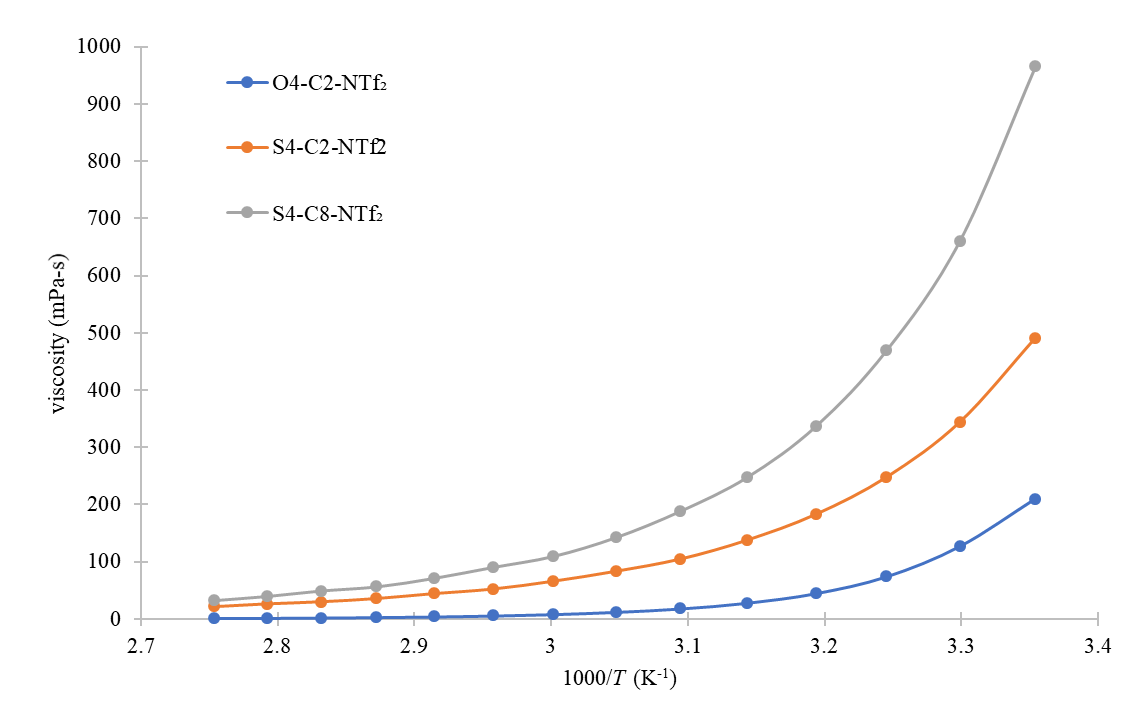


**Figure S71.** Temperature-dependent viscosity overlay of **OA-C2-NTf2**



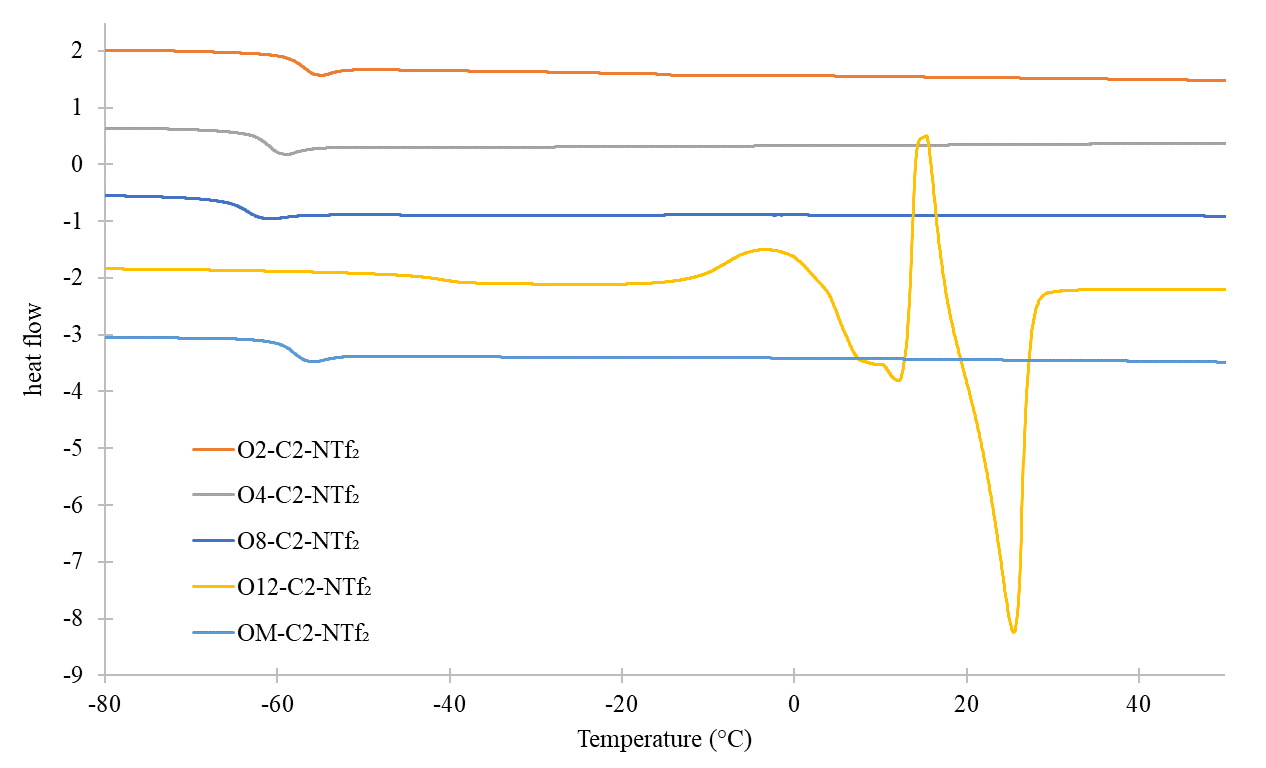
**Figure S72.** Temperature-dependent viscosity overlay of **O4-C2-X**

**Figure S73.** Temperature-dependent viscosity overlay of **O2-CZ-NTf2**

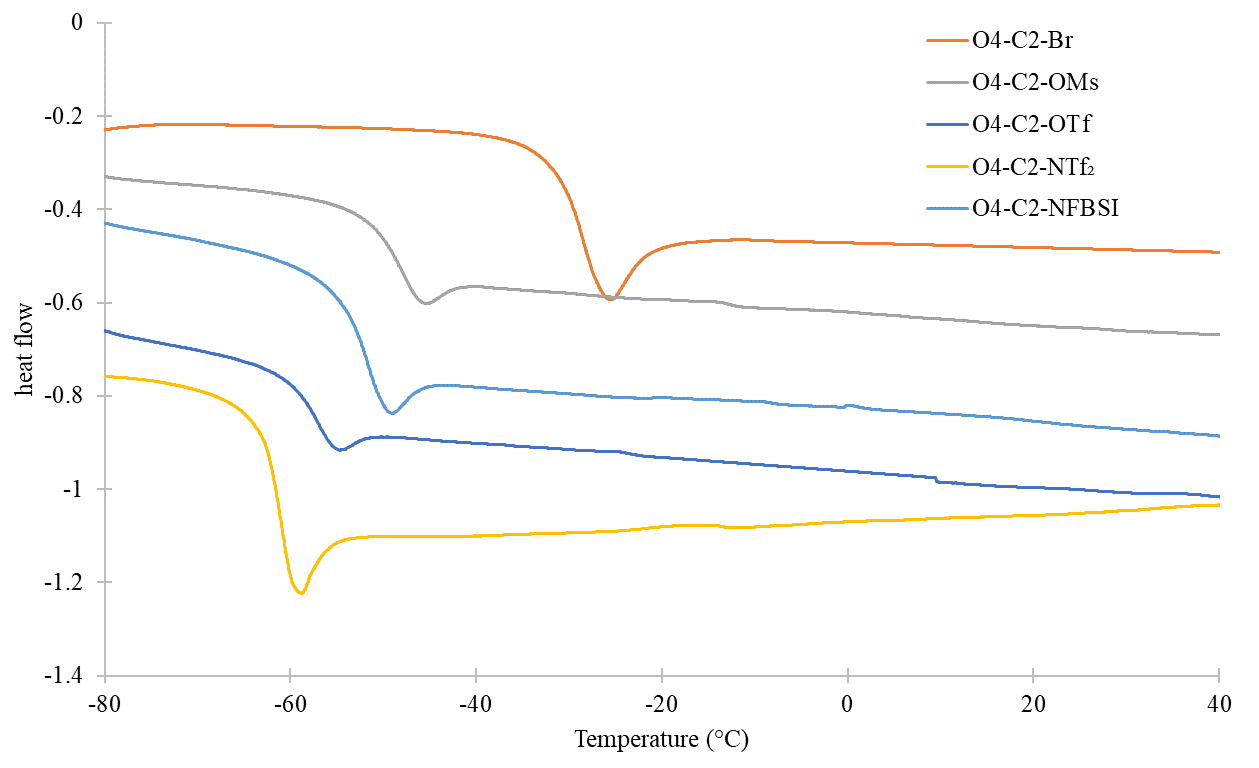


**Figure S74.** Temperature-dependent viscosity overlay of **S4-CZ-NTf2**

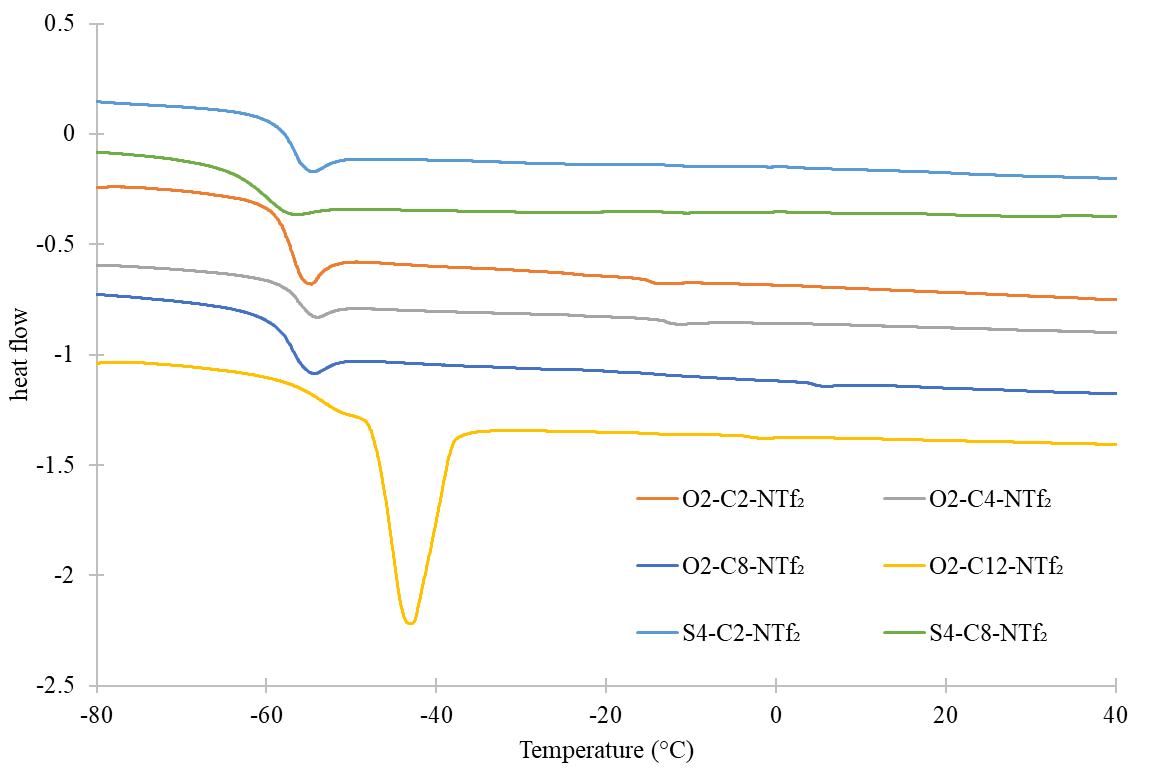
**Figure S75.** Temperature-dependent density overlay of ionic liquids.



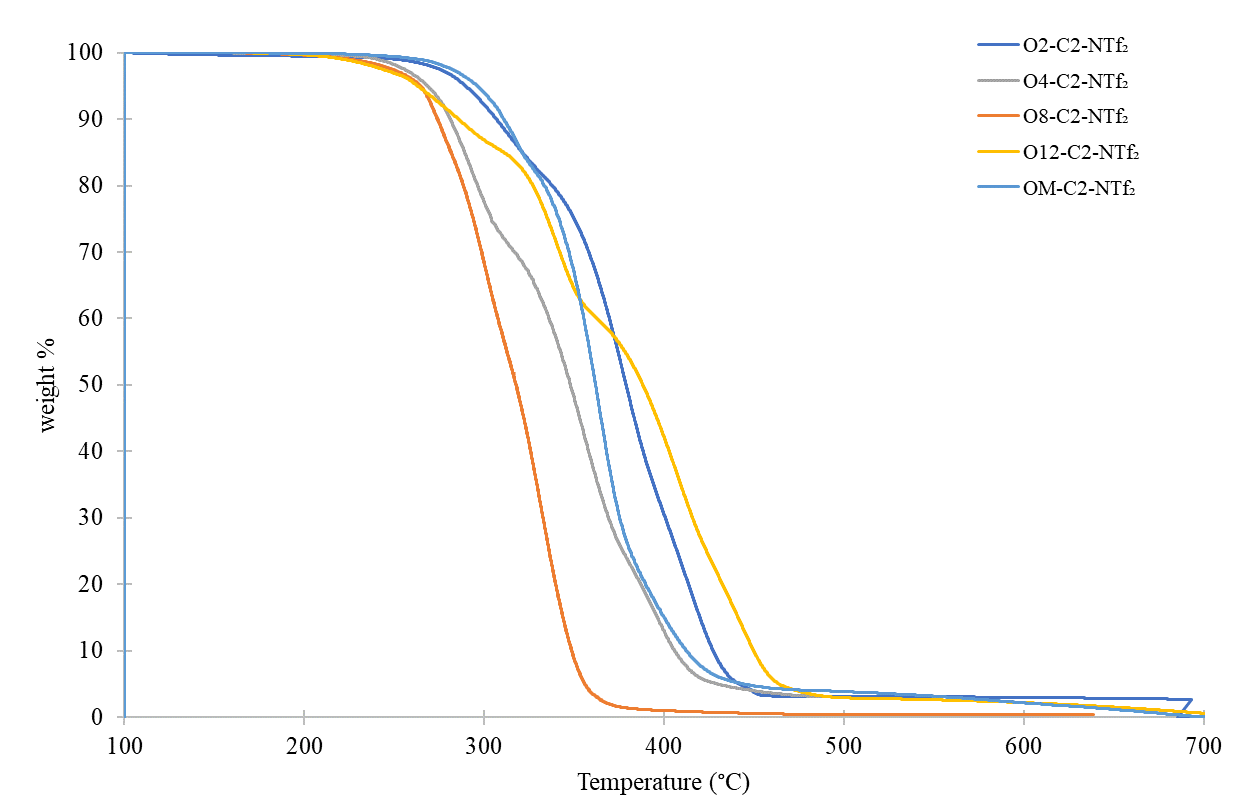
**Figure S76.** DSC overlay of **OA-C2-NTf2**



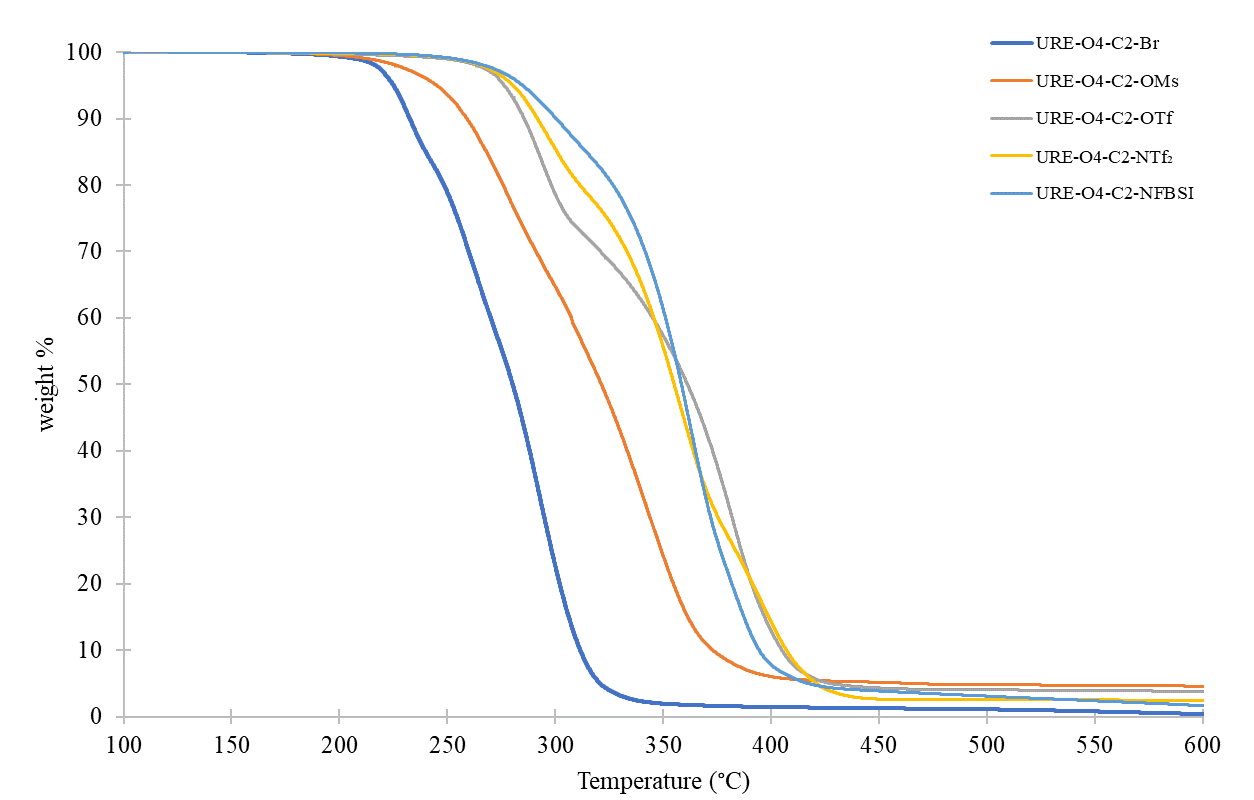
**Figure S77.** DSC overlay of **O4-C2-X**



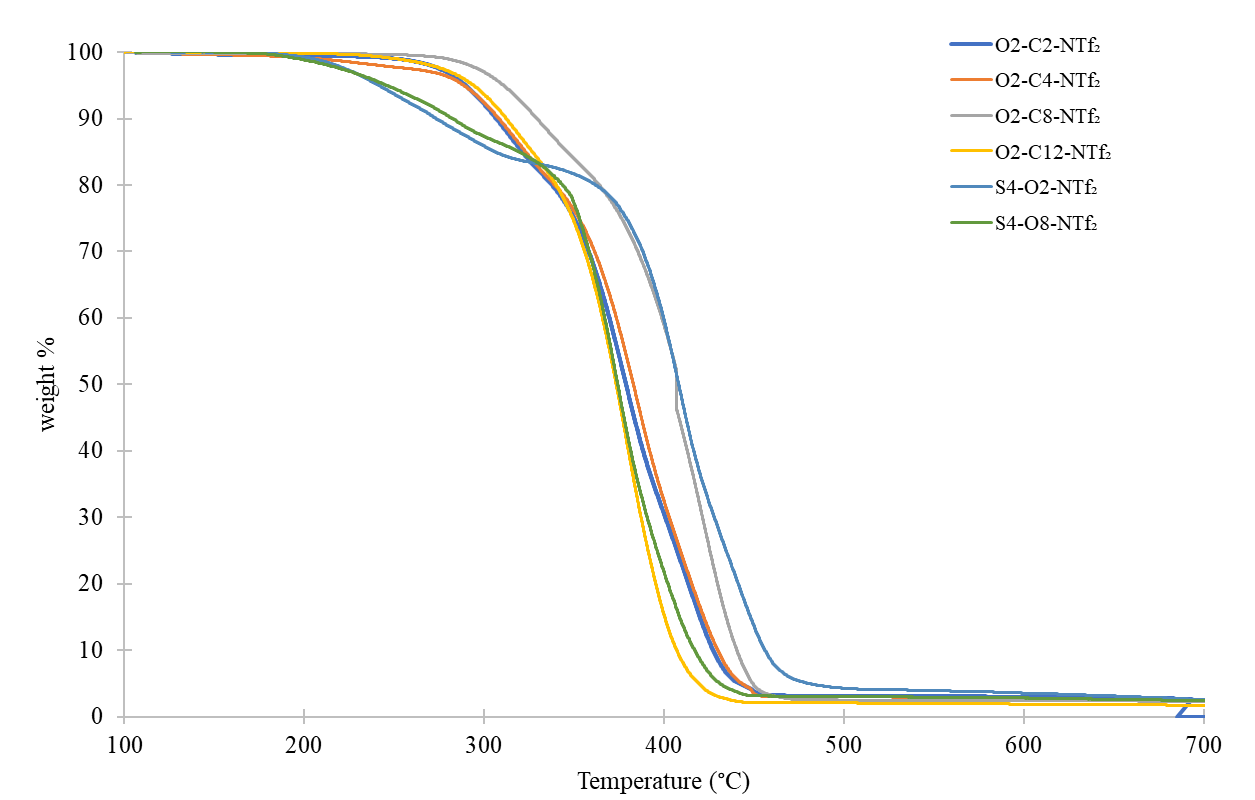
**Figure S78.** DSC overlay of **O2-CZ-NTf2** and **S4-CZ-NTf2**



**Figure S79.** TGA overlay of **OA-C2-NTf2**



**Figure S80.** TGA overlay of **O4-C2-X**



**Figure S81.** TGA overlay of **O2-CZ-NTf2** and **S4-CZ-NTf2**

**Figure S82.** Temperature-dependent ionic conductivity overlay of **OA-C2-NTf2**

**Figure S83.** Temperature-dependent ionic conductivity overlay of **O2-CZ-NTf2**

**Figure S84.** Temperature-dependent ionic conductivity overlay of **S4-CZ-NTf2**

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2. V. A. Vaillard, M. Gonzalez, J. P. Perotti, R. J. A. Grau, S. E. Vaillard, Method for the synthesis of *N*-alkyl-*O*-alkyl carbamates, *RSC Adv.* **2014,** *4*, 13012-13017.

3. X. Yan, Y. Zhang, H. Zhang, P. G. Wang, X. Chu, X. Wang, Amphiphilic polyethylenimine (PEI) as highly efficient non-viral gene carrier, *Org. Biomol. Chem.* **2014,** *12*, 1975-1982.