Electronic Supplementary Material (ESI) for Green Chemistry

Supplementary Information

A new generation of aprotic yet Brønsted acidic imidazolium salts: low toxicity, high recyclability and greatly improved activity

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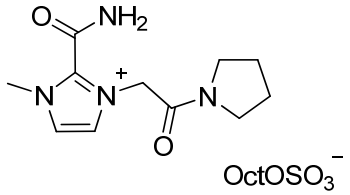
1.0 General

Proton Nuclear Magnetic Resonance spectra were recorded on 400 MHz and 600 MHz spectrometers in $CDCl_3$ referenced relative to residual $CHCl_3$ (δ = 7.26 ppm), DMSO-d_6 referenced relative to residual DMSO (H) (δ = 2.51 ppm). Chemical shifts are reported in ppm and coupling constants in Hertz. Carbon NMR spectra were recorded on the same instruments (100 MHz and 150 MHz) with total proton decoupling. All melting points are uncorrected. Infrared spectra were obtained using neat samples on a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a universal ATR sampling accessory. Flash chromatography was carried out using silica gel, particle size 0.04-0.063 mm. TLC analysis was performed on precoated $60F_{254}$ slides, and visualised by UV irradiation, $KMnO_4$ or anisaldehyde staining. All aldehydes were sourced commercially and either distilled under vacuum (if liquid) or dissolved in CH_2Cl_2 and washed with NaOH (if solid) prior to use. Methanol and THF were distilled from sodium and stored under argon best results were obtained using freshly distilled methanol. All reactions were carried out in oven-dried glassware with magnetic stirrers under an atmosphere of argon, unless specified. Careful drying of all catalysts/salts is essential for best results a convenient procedure for this follows: the catalysts/salts were dissolved in dry toluene under argon. The solvent was removed *in vacuo* and the procedure was repeated twice, taking care the compound was not exposed to air. The catalysts/salts were then dried under high vacuum for 2 h and used in the reaction. Preparation of Catalyst **41**, and **42** included in ESI.

2.0 Catalyst synthesis

1*H*-Imidazolium-2-carboxamide,1-methyl-3-[2-oxo-2-(1-pyrrolidinyl)ethyl] octylsulfate (8):



A flask was charged with 1*H*-Imidazolium-2-carboxamide, 1-methyl-3-[2-oxo-2-(1-pyrrolidinyl)ethyl]-, bromide **9** (1.00 g, 3.15 mmol) and distilled water (10 mL). Sodium octylsulfate (0.731 g, 3.15 mmol) in distilled water (10 mL) was added in one portion and the suspension was stirred vigorously for 24 h at RT. The water was removed on the rotary evaporator and residue was dissolved in dichloromethane (20 mL) and washed with water. Organic layer was dried over anhydrous magnesium sulphate, filtered and solvent removed by rotary evaporation. The product was dried *in vacuo* for 72 h to give **8** as a white solid (0.649 g, 46%).

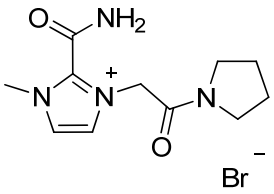
^{1}H-NMR (400 MHz, DMSO-d_6): 0.89 (t, J = 7.2 Hz, 3H), 1.31-1.33 (m, 10H), 1.47-1.54 (m, 2H), 1.87-1.82 (m, 2H), 2.00-1.94 (m, 2H), 3.36 (t, J = 6.8 Hz, 2H), 3.52 (t, J = 6.8 Hz, 2H), 3.70 (t, J = 6.8 Hz, 2H), 4.03 (s, 3H), 5.37 (s, 2H), 7.83 (d, J = 2.0 Hz, 1H), 7.87 (d, J = 2.0 Hz, 1H), 8.83 (bs, 1H), 8.76 (bs, 1H)

^{13}C-NMR (100 MHz, DMSO-d_6): 13.9, 22.1, 23.7, 25.4, 25.5, 28.7, 28.7, 29.0, 31.2, 36.8, 45.1, 46.0, 50.7, 65.5, 123.4, 124.1, 138.9, 154.6, 162.4,

ES-MS (+ve) m/z: Found $[M–OctOSO_3^{-}]^{+}$ 237.1356, $C_{11}H_{17}N_4O_2^{+}$ requires 237.1346

Melting Point: 122-124 °C.

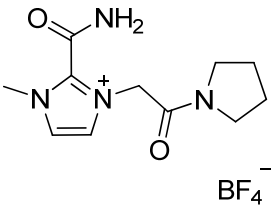
1*H*-Imidazolium-2-carboxamide, 1-methyl-3-[2-oxo-2-(1-pyrrolidinyl) ethyl] Bromide (9):



A round-bottomed flask was charged with 1-methyl-1*H*-imidazole-2-carboxamide (2.00 g, 16.0 mmol) and THF (100 mL) under nitrogen. To this solution was added 2-bromo-1-(pyrrolidin-1-yl)ethanone (3.07 g, 16.0 mmol). The reaction mixture was refluxed for 2 days with vigorous stirring. The product precipitated as a white solid, was then washed with THF (5 x 50 mL). The solvent was removed on the rotary evaporator and the product **9** was dried *in vacuo* for 72 h to give **9** as a white solid (2.35 g, 47%).

^{1}H-NMR (400 MHz, DMSO-d_6): 1.83-1.76 (m, 2H), 1.97-1.90 (m, 2H), 3.28 (t, J = 6.8 Hz, 2H), 3.51 (t, J = 6.8 Hz, 2H), 4.01 (s, 3H), 5.38 (s, 2H), 7.85 (d, J = 2.0 Hz, 1H), 7.88 (d, J = 2.0 Hz, 1H), 8.83 (bs, 1H), 8.73 (bs, 1H)
^{13}C-NMR (150 MHz, DMSO-d_6): 23.7, 25.5, 36.9, 45.2, 46.0, 50.8, 123.4, 124.1, 139.0, 154.6, 162.4.
ES-MS (+ve) m/z: Found $[M–Br^{-}]^{+}$ 237.1361, $C_{11}H_{17}N_4O_2^{+}$ requires 237.1346
Melting Point: 197-198 °C

1*H*-Imidazolium-2-carboxamide, 1-methyl-3-[2-oxo-2-(1-pyrrolidinyl)ethyl] BF_4 (10):

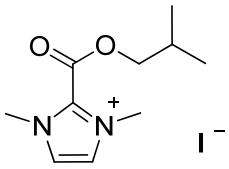


A flask was charged with 1*H*-Imidazolium-2-carboxamide, 1-methyl-3-[2-oxo-2-(1-pyrrolidinyl)ethyl]-, bromide **9** (1.20 g, 3.78 mmol) and ethanol (60 mL) under a Nitrogen atmosphere. Sodium tetrafluoroborate (0.415 g, 3.78 mmol) was added in one portion and the suspension was stirred vigorously for 24 hours at RT. The fine white precipitate was filtered

quickly in air and washed with ethanol. The filtrate and washings were combined and solvent removed by rotary evaporation, then *in vacuo* for 2 days to give **10** as a pale pink solid (0.764 g, 62%).

^{1}H-NMR (600 MHz, DMSO-d_6): 1.79-1.82 (m, 2H), 1.92-1.95 (m, 2H), 3.32 (t, J = 6.6 Hz, 2H), 3.54-3.48 (m, 2H), 4.00 (s, 3H), 5.35 (s, 2H), 7.82 (d, J = 1.8 Hz, 1H), 7.84 (d, J = 1.8 Hz, 1H), 8.73 (bs, 1H), 8.82 (bs, 1H)
^{13}C-NMR (150 MHz, DMSO-d_6): 23.6, 25.4, 36.8, 45.2, 46.0, 50.8, 123.4, 124.1, 138.9, 154.6, 162.4.
ES-MS (+ve) m/z: Found $[M–BF_4^-]^+$ 237.1355, $C_{11}H_{17}N_4O_2^+$ requires 237.1346
Melting point: 145-147 °C

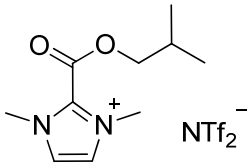
2-(isobutoxycarbonyl)-1,3-dimethyl-1*H*-imidazol-3-ium iodide (11):



A round-bottomed flask was charged with isobutyl 1-methyl-1*H*-imidazole-2-carboxylate (2.00 g, 10.9 mmol) and diethyl ether (100 mL) under nitrogen. To this solution was added methyl iodide (6.24 g, 43.9 mmol) in one portion. The reaction mixture was refluxed for 2 days with vigorous stirring. The product precipitated as a light yellow solid, was filtered then washed with diethyl ether (5 x 50 mL). The residual solvent was removed on the rotary evaporator. The product was dried *in vacuo* for 24 h to give **11** as a light yellow solid (2.21 g, 62%).

^{1}H-NMR (400 MHz, $CDCl_3$): 1.05 (d, J = 6.8 Hz, 6H), 2.16 (sep.t, J = 6.8, 6.4 Hz, 1H), 4.30 (s, 6H), 4.31 (d, J = 6.4 Hz, 2H), 8.24 (s, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$): 14.0, 22.3, 35.1, 69.2, 121.8, 127.1, 148.7.
ES-MS (+ve) m/z: Found $[M–I^-]^+$ 197.1296, $C_{10}H_{17}N_2O_2^+$ requires 197.1285
Melting Point: 116-117 °C.

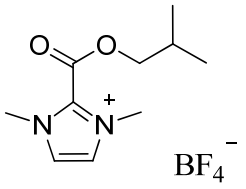
2-(isobutoxycarbonyl)-1,3-dimethyl-1*H*-imidazol-3-ium NTf_2 (12):



A round-bottomed flask was charged with 2-(isobutoxycarbonyl)-1,3-dimethyl-1*H*-imidazol-3-ium iodide **11** (0.500 g, 1.54 mmol) and distilled water (2 mL). Lithium bis(trifluoromethane) sulfonamide (0.443g, 1.54 mmol) in distilled water (2 mL) was added in one portion and the suspension was stirred vigorously for 4 h at RT. The product precipitated as a light yellow solid. The aqueous layer was removed, and the IL washed with water (3 x 4 mL) then the solvent removed on the rotary evaporator. The product was dried *in vacuo* for 48 h to give **12** as a pale yellow solid (0.630 g, 86%).

^{1}H-NMR (400 MHz, $CDCl_3$): 1.07 (d, J = 6.8 Hz, 6H), 2.16 (sep.t, J = 6.8, 6.4 Hz, 1H), 4.19 (s, 6H), 4.32 (d, J = 6.4 Hz, 2H), 7.54 (s, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$): 19.1, 27.5, 39.6, 74.6, 119.7(q, J = 320 Hz, 2 CF_3), 126.5, 132.3, 153.6.
ES-MS (+ve) m/z: Found $[M–NTf_2^-]^+$ 197.1283, $C_{10}H_{17}N_2O_2^+$ requires 197.1285
Melting Point: 45-46 °C

2-(isobutoxycarbonyl)-1,3-dimethyl-1*H*-imidazol-3-ium BF_4 (13):



A round-bottomed flask was charged with isobutyl 1-methyl-1*H*-imidazole-2-carboxylate (0.200 g, 1.1 mmol) and dry diethyl ether (10 mL) under nitrogen. To this solution was added trimethyloxonium tetrafluoroborate (0.162 g, 1.1 mmol) quickly. The reaction mixture was stirred vigorously for 24 h. The product precipitated as a white solid, was filtered, and then washed with diethyl ether (2 x 10 mL). The solvent was removed on the rotary evaporator. The product was dried *in vacuo* for 24 h to give **13** as a white solid (0.302 g, 97%).

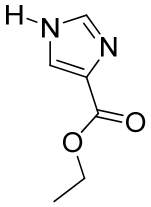
^{1}H-NMR (400 MHz, $CDCl_3$): 1.05 (d, J = 6.8 Hz, 6H), 2.14 (sep.t, J = 6.8, 6.4 Hz, 1H), 4.16 (s, 6H), 4.29 (d, J = 6.4 Hz, 2H), 7.65 (s, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): 19.1, 27.5, 39.3, 74.2, 126.7, 132.2, 153.9.

ES-MS (+ve) m/z: Found $[M–BF_4^–]^+$ 197.1295, $C_{10}H_{17}N_2O_2^+$ requires 197.1285

Melting Point: 64-65 °C.

Ethyl 1*H*-imidazole-4-carboxylate (14a)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with 4-imidazoledicarboxylic acid (250 mg, 2.2 mmol) in ethanol (5 mL). To this DMF (3 drops) was added followed by thionyl chloride (585 µL, 8 mmol). The reaction mixture was fitted with a condenser and stirred at 80 °C for 48 h. Upon completion of the reaction, the solvent was removed *in vacuo* and the residue was dissolved in water (5 mL). Aqueous sodium hydroxide was then added until the solution reached pH 9. The mixture was then extracted with EtOAc (2 x 10 mL) and the organic layer was concentrated *in vacuo* giving the pure ester **14a** (155 mg, 70 %).

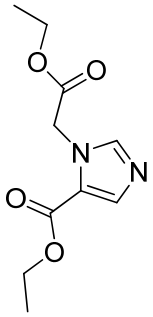
^{1}H NMR (400 MHz, $CDCl_3$): 1.39 (t, J = 7.2 Hz, 3H), 4.38 (q, J = 7.2 Hz, 2H), 7.81 (s, 1H), 7.95 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): 13.9, 60.3, 125.3, 129.4, 136.5, 161.7.

ES-MS (+ve) m/z: Found 140.0479, $C_6H_8N_2O_2$ requires 140.0479

Melting point: 66-69 °C

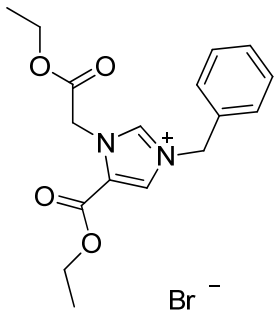
Diethyl 1*H*-imidazole-1,5-dicarboxylate (14b)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **14a** (150 mg, 1.08 mmol) in acetonitrile (2 mL). To this K_2CO_3 (145 mg, 1.08 mmol) was added and the reaction mixture was stirred for 30 min under an argon atmosphere. Ethyl bromoacetate (215 µL, 1.95 mmol) was added and the reaction mixture was stirred at room temperature for 2 days. Upon completion of the reaction, the solvent was removed *in vacuo* and the resulting residue was extracted with dichloromethane (2 x 10 mL). The extracts were combined and concentrated *in vacuo* giving a pale yellow solid. This solid was washed with ether (20 mL) after which the crude product was purified by flash column chromatography (chloroform: MeOH, 10:1) resulting in the pure product **14b** as a pale yellow oil (161 mg, 70 %).

^{1}H NMR (400 MHz, $CDCl_3$): 1.32 (t, J = 7.1 Hz, 3H), 1.38 (t, J = 7.1 Hz , 3H), 4.27 (q, J = 7.1 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 5.04 (s, 2H), 7.63 (s, 1H), 7.80 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): 14.1, 14.2, 29.7, 48.0, 60.7, 62.0, 137.3, 142.6, 160.4, 167.4.
ES-MS (+ve) m/z: Found 226.0949, $C_{10}H_{14}N_2O_2$ requires 226.0954

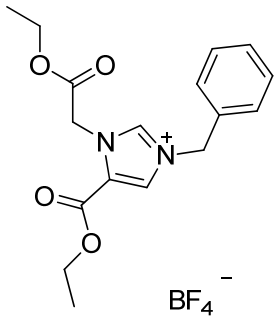
3-Benzyl-1,5-*bis*(ethoxycarbonyl)-1*H*-imidazol-3-ium bromide (14)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **14b** (150 mg, 0.69 mmol) in acetonitrile (2 mL). Benzyl bromide (321 µL, 2.7 mmol) was added and the reaction mixture was stirred at room temperature for 3 days. Upon completion of the reaction, the solvent was removed *in vacuo* resulting in a brown oil. This oil was washed with ether (20 mL) to remove excess benzyl bromide after which the pure product **14** was obtained as a pale yellow oil (174 mg, 65 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.36-1.39 (t, J = 7.0 Hz, 6H), 3.55-3.60 (q, J = 7.0 Hz, 4H), 4.75 (s, 2H), 5.31 (s, 2H), 7.36-7.49 (m, 5H), 7.58 (s, 1H), 7.88 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 15.1, 15.3, 49.2, 57.2, 61.1, 62.5, 126.7, 128.9, 129.7, 129.5, 134.4, 137.2, 145.8, 161.1, 168.4.
ES-MS (+ve) m/z: Found $[M–Br^–]^+$ 317.1412, $C_{17}H_{21}N_2O_4^+$ requires 317.1416.

3-Benzyl-1,5-*bis*(ethoxycarbonyl)-1*H*-imidazol-3-ium tetrafluoroborate (15)

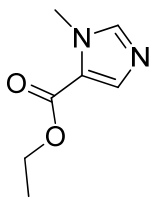


To a 50 mL round bottomed flask fitted with a magnetic stirring bar, **14** (150 mg, 0.38 mmol) was added. To this $NaBF_4$ (75 mg, 0.68 mmol) and acetone (10 mL) were added and the mixture was placed under an argon atmosphere.The resulting suspension was stirred at room

temperature for 4 days, after which time a white precipitate was formed. This precipitate was filtered using a Buchner funnel under vacuum and washed with dry acetone (2 x 5 mL). The combined filtrate and washings were then concentrated *in vacuo* giving the pure product **15** as a pale yellow oil (146 mg, 96 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.32 (t, J = 6.8 Hz, 6H), 3.56 (q, J = 6.8 Hz, 4H), 4.69 (s, 1H), 5.95 (s, 1H), 7.26-7.48 (m, 5H), 7.86 (s, 1H), 8.95 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 15.1, 15.2, 49.5, 58.1, 62.1, 62.5, 126.7, 128.9, 129.7, 130.1, 134.4, 137.5, 146.2, 161.2, 169.0.
ES-MS (+ve) m/z: Found $[M–BF_4^-]^+$ 317.1423, $C_{17}H_{21}N_2O_4^+$ requires 317.1422.

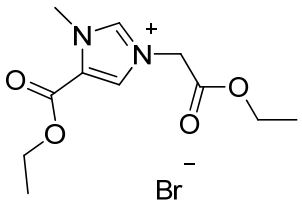
Ethyl 1-methyl-1*H*-imidazole-5-carboxylate (16a)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **14a** (120 mg, 0.86 mmol) dissolved in methanol (7.2 mL). To this methyl iodide (158 µL, 1.71 mmol) in methanol (2.7 mL) was added. The flask was fitted with a condenser and stirred under reflux for 48 h after which the solvent was removed *in vacuo* giving a dark brown oil. This crude oil was purified by flash chromatography ($CHCl_3$: MeOH (1.5%)) giving the pure compound **16a** as a pale yellow oil (87 mg, 71 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.28 (t, J = 7.1, 3H), 3.83 (s, 3H), 4.25 (q, J = 7.1, 2H), 7.62, (s, 1H), 7.91 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 14.2, 60.4, 125.3, 127.7, 133.2, 137.4, 160.4.
ES-MS (+ve) m/z: Found 154.0745, $C_7H_{10}N_2O_2$ requires 154.0742.

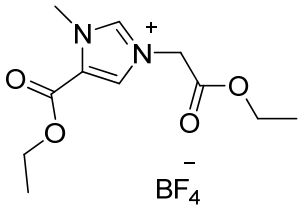
3,5-*bis*(ethoxycarbonyl)-1-methyl-1*H*-imidazol-3-ium bromide (16)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **16a** (200 mg, 1.4 mmol) in acetonitrile (2 mL). Ethyl bromoacetate (320 µL, 2.9 mmol) was added and the reaction mixture was stirred at room temperature for 4 days. Upon completion of the reaction, the solvent was removed *in vacuo* giving a light brown oil. This oil was washed with ether (30 mL) to remove excess ethyl bromoacetate giving the pure product **16** as a pale yellow oil (370 mg, 85 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.33 (t, 3H, J = 7.1), 1.36 (t, 3H, J = 7.1), 4.24 (s, 3H), 4.29 (q, 2H, J = 7.1), 4.41 (q, 2H, J = 7.1), 5.64 (s, 2H), 8.11 (s, 1H), 10.43 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 13.6, 36.6, 50.4, 62.3, 62.7, 123.9, 128.5, 141.3, 156.8, 165.5, 206.1.
ES-MS (+ve) m/z: : Found $[M–Br^{-}]^{+}$ 241.1033, $C_{11}H_{17}N_2O_4$ requires 241.1032.

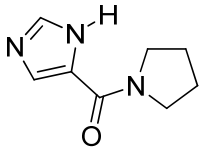
3,5-*bis*(ethoxycarbonyl)-1-methyl-1*H*-imidazol-3-ium tetrafluoroborate (17)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **14b** (150 mg, 0.69 mmol) in acetonitrile (2 mL). Trimethyloxonium tetrafluroborate (103 mg, 0.7 mmol) was added and the reaction mixture was stirred at room temperature for 4 days. Upon completion of the reaction, the solvent was removed *in vacuo* after which the pure product **17** was obtained as a pale yellow oil (197 mg, 90 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.26 (t, J = 7.1 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H), 4.07 (s, 3H), 4.22 (q, J = 7.1 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 8.50 (s, 1H), 9.38 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 13.9, 36.4, 49.9, 62.1, 62.5, 123.8, 129.3, 141.1, 157.2, 166.5, 206.6.
ES-MS (+ve) m/z: Found $[M–BF_4^-]^+$ 241.1035, $C_{11}H_{17}N_2O_4$ requires 241.1032.

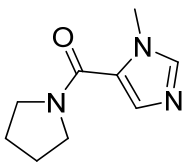
(1*H*-imidazol-5-yl)(pyrrolidin-1-yl)methanone (18a)



A 10 mL microwave reaction vial was fitted with a magnetic stirrer and to this **14a** (250 mg, 1.7 mmol) was added. This was dissolved in distilled pyrrolidine (1.2 mL, 15 mmol). The reaction vessel was fitted with a lid, placed in the microwave under reduced pressure and stirred for 3 h at 110 °C. Upon completion of the reaction the pyrrolidine was removed *in vacuo* and the resulting residue was purified by flash chromatography (CH_2Cl_2:MeOH, 1:0-10:1) giving **18a** as an off-white solid (217 mg, 77%).

^{1}H NMR (400 MHz, DMSO-d_6): 1.93 (m, 2H), 2.05 (m, 2H), 3.66 (t, J = 6.6 Hz, 2H), 3.80 (t, J = 6.6 Hz, 2H), 7.49 (s, 1H), 7.70 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 23.4, 26.0, 46.6, 47.7, 126.4, 129.9, 136.2, 160.4.
ES-MS (+ve) m/z: Found 166.0979, $C_8H_{11}N_3O$ requires 166.0980.
Melting point: 92-93 °C

(1-methyl-1*H*-imidazol-5-yl)(pyrrolidin-1-yl)methanone (18b)

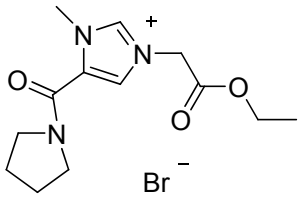


A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **18a** (150 mg, 0.91 mmol) dissolved in methanol (7.2 mL). To this methyl iodide (186 µL, 3 mmol) in methanol (2.7 mL) was added. The flask was fitted with a condenser and stirred under reflux for 48 h after which the solvent was removed *in vacuo* giving a dark brown oil.

This crude oil was purified by flash chromatography ($CHCl_3$:MeOH (5%)) giving the pure compound **18b** as an orange oil (104 mg, 64 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.93-1.96 (m, 2H), 2.05-2.08 (m, 2H), 3.55 (t, J = 6.4 Hz, 2H), 3.67 (t, J = 6.4 Hz, 2H), 3.95 (s, 3H), 7.93 (s, 1H), 8.44 (s, 1H)
^{13}C NMR (100 MHz, DMSO-d_6): 23.2, 26.5, 34.4, 45.5, 46.8, 126.7, 129.9, 138.4, 161.2.
ES-MS (+ve) m/z: Found 179.1053, $C_9H_{13}N_3O$ requires 179.1055.

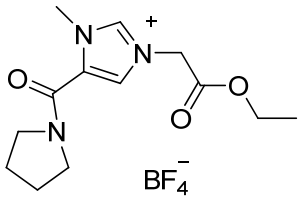
3-(ethoxycarbonyl)-1-methyl-5-(pyrrolidine-1-carbonyl)-1*H*-imidazol-3-ium bromide (18)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **18b** (100 mg, 0.56 mmol) in acetonitrile (2 mL). Ethyl bromoacetate (247 µL, 2.24 mmol) was added and the reaction mixture was stirred at room temperature for 4 days. Upon completion of the reaction, the solvent was removed *in vacuo* giving a dark brown oil. This oil was washed with ether (30 mL) to remove excess ethyl bromoacetate giving the pure product **18** as an orange oil (133 mg, 69 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.13 (t, J = 6.8 Hz, 3H), 1.95-1.97 (m, 2H), 2.04-2.06 (m, 2H), 3.54-3.57 (m, 2H), 3.66-3.69 (m, 2H), 3.75 (s, 3H), 4.16 (q, J = 7.0 Hz, 2H), 4.73 (s, 2H), 7.95 (s, 1H), 8.47 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 13.9, 23.2, 26.6, 34.4, 45.6, 46.8, 50.2, 62.0, 126.8, 130.1, 138.9, 161.5, 166.2.
ES-MS (+ve) m/z: Found $[M–Br^-]^+$ 267.1535, $C_{13}H_{20}N_3O_3^+$ requires 267.1539.

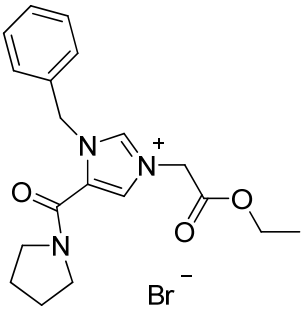
3-(ethoxycarbonyl)-1-methyl-5-(pyrrolidine-1-carbonyl)-1*H*-imidazol-3-ium tetrafluoroborate (19)



To a 50 mL round bottomed flask fitted with a magnetic stirring bar, **18** (100 mg, 0.3 mmol) was added. To this $NaBF_4$ (70 mg, 0.64 mmol) and acetone (10 mL) were added and the mixture was placed under an argon atmosphere.The resulting suspension was stirred at room temperature for 4 days. After which a white precipitate was formed. This precipitate was filtered using a Buchner funnel under vacuum and washed with dry acetone (2 x 5 mL). The combined filtrate and washings were then concentrated *in vacuo* giving the pure product **19** as a yellow solid (100 mg, 98 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.16 (t, J = 6.8 Hz, 3H), 1.95-1.98 (m, 2H), 2.11-2.14 (m, 2H), 3.65-3.67 (m, 2H), 3.71-3.74 (m, 2H), 3.79 (s, 3H), 4.18 (q, J = 6.8 Hz, 2H), 4.77 (s, 2H), 7.96 (s, 1H), 8.97 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 13.9, 23.1, 26.6, 34.4, 45.9, 47.1, 50.6, 62.7, 126.8, 130.4, 138.9, 161.6, 167.3.
ES-MS (+ve) m/z: Found $[M–BF_4^-]^+$ 267.1537, $C_{13}H_{20}N_3O_3^+$ requires 267.1538.
Melting point: 112-115 °C

1-benzyl-3-(2-ethoxy-2-oxoethyl)-5-(pyrrolidine-1-carbonyl)-1H-imidazol-3-ium bromide (18d)

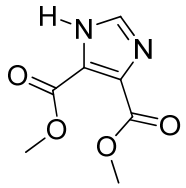


A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **18c** (250 mg, 1.0 mmol) in acetonitrile (2 mL). Benzyl bromide (321 µL, 2.7 mmol) was added and the reaction mixture was stirred at room temperature for 3 days. Upon completion of the reaction, the solvent was removed *in vacuo* resulting in a brown oil. This oil was washed with

ether (20 mL) to remove excess benzyl bromide after which the pure product **18d** was obtained as a pale yellow oil (270 mg, 64 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.13 (t, J = 6.8 Hz, 3H), 1.95-1.98 (m, 2H), 2.04-2.06 (m, 2H), 3.54-3.57 (m, 2H), 3.66-3.69 (m, 2H), 4.16 (q, J = 7.0 Hz, 2H), 4.73 (s, 2H), 5.52 (s, 2H), 7.23-7.27 (m, 5H), 7.95 (s, 1H), 8.47 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 14.2, 25.2, 27.6, 47.3, 49.8, 52.3, 54.1, 63.8, 125.5, 126.9, 127.6, 129.4, 132.5, 137.2, 139.5, 160.4, 167.2.
ES-MS (+ve) m/z: Found $[M–Br^-]^+$ 342.1810, $C_{19}H_{24}N_3O_3^+$ requires 342.1812.

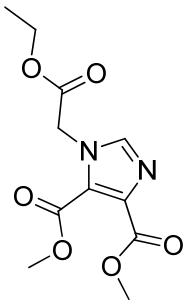
Dimethyl 1*H*-imidazole-4,5-dicarboxylate (20a)



To a 50 mL round-bottomed flask, fitted with a magnetic stirring bar, 4,5-imidazoledicarboxylic acid (500 mg, 3.2 mmol) was added. To this sulfuric acid (3.4 mL, 6.4 mmol) in methanol (10 mL) was added. The reaction mixture was fitted with a condenser and stirred under reflux for 24 h. Upon completion of the reaction the solution was brought to pH 5 with saturated $NaHCO_3$ and the product was extracted using EtOAc. The extracts were combined and concentrated under reduced pressure and the resulting ester **20a** was obtained as an off-white solid (456 mg, 78 %).

^{1}H NMR (400 MHz, DMSO-d_6): 3.80 (s, 6H), 7.91 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 30.7, 52.0, 138.1, 206.6.
ES-MS (+ve) m/z: Found 184.0565, $C_7H_8N_2O_4$ requires 184.0562.
Melting point: 78-82 °C

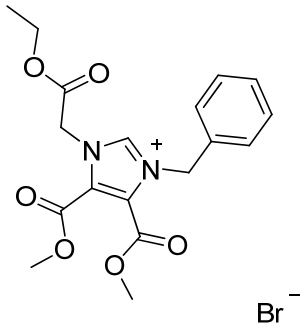
Dimethyl 1-(2-ethoxy-2-oxoethyl)-1*H*-imidazole-4,5-dicarboxylate (20b)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **20a** (500 mg, 2.7 mmol) in acetonitrile (2 mL). To this K_2CO_3 (383 mg, 2.7 mmol) was added and the reaction mixture was stirred for 30 min under an argon atmosphere. Ethyl bromoacetate (598 µL, 5.4 mmol) was added and the reaction mixture was stirred at room temperature for 2 days. Upon completion of the reaction, the solvent was removed *in vacuo* and the resulting residue was extracted with dichloromethane. The extracts were combined and concentrated *in vacuo* giving a pale yellow solid. This solid was washed with ether after which the pure product **20b** was obtained as an off-white solid (597 mg, 82 %).

^{1}H NMR (400 MHz, $CDCl_3$): 1.21 (t, J = 7.0 Hz, 3H), 3.78 (s, 3H), 3.81 (s, 3H), 4.17 (q, J = 7.0 Hz, 2H), 5.14 (s, 2H), 7.98 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): 14.8, 31.5, 48.8, 53.1, 62.2, 124.2, 138.0, 142.7, 160.4, 163.9, 168.5.
ES-MS (+ve) m/z: Found 270.0923, $C_{11}H_{14}N_2O_6$ requires 270.0930.
Melting point: 72-74 °C

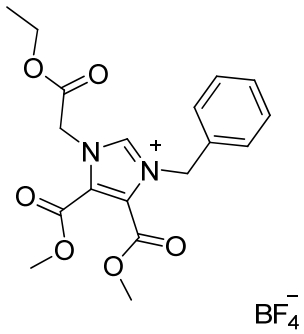
3-Benzyl-1-(2-ethoxy-2-oxoethyl)-4,5-*bis*(methoxycarbonyl)-1H-imidazol-3-ium bromide (20)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **20b** (500 mg, 1.9 mmol) in acetonitrile (2 mL). Benzyl bromide (452 µL, 3.8 mmol) was added and the reaction mixture was stirred at room temperature for 3 days. Upon completion of the reaction, the solvent was removed *in vacuo* resulting in a yellow oil. This oil was washed with ether (15 mL) to remove excess benzyl bromide after which the pure catalyst **20** was obtained as a pale yellow oil (620 mg, 74 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.22-1.25 (m, 3H), 3.86 (s, 3H), 3.88 (s, 3H), 4.23 (q, J = 7.0 Hz, 2H), 5.42 (s, 2H), 5.67 (s, 2H), 7.24 (s, 1H), 7.37 (d, J = 7.3 Hz, 2H), 7.45 (t, J = 7.3 Hz, 2H), 9.61 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 14.0, 48.0, 50.2, 51.4, 54.1, 62.3, 123.4, 128.5, 129.1, 132.9, 137.7, 157.5, 159.5, 163.1, 166.1, 167.7.
ES-MS (+ve) m/z: Found $[M–Br^-]^+$ 361.1390, $C_{18}H_{21}N_2O_6^+$ requires 361.1394

3-Benzyl-1-(2-ethoxy-2-oxoethyl)-4,5-*bis*(methoxycarbonyl)-1*H*-imidazol-3-ium tetrafluoroborate (21)



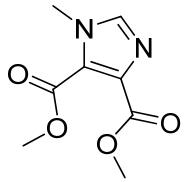
To a 50 mL round bottomed flask fitted with a magnetic stirring bar, **20** (250 mg, 0.57 mmol) was added. To this $NaBF_4$ (74.8 mg, 0.68 mmol) and acetone (10 mL) were added and the mixture was placed under an argon atmosphere. The resulting suspension was stirred at room temperature for 4 days. After which a white precipitate was formed. This precipitate was filtered using a Buchner funnel under vacuum and washed with dry acetone (5 mL X 2). The combined filtrate and washings were then concentrated *in vacuo* giving the pure catalyst **21** as a pale yellow oil (249 mg, 98 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.23-1.26 (m, 3H), 3.78 (s, 3H), 3.81 (s, 3H), 4.22 (q, J = 7.1 Hz, 2H), 5.39 (s, 2H), 5.62 (s, 2H), 7.26 (s, 1H), 7.43 (d, J = 7.2 Hz, 2H), 7.64 (t, J = 7.2 Hz, 2H), 9.89 (s, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): 14.2, 47.9, 50.4, 51.5, 53.9, 62.1, 123.7, 128.9, 129.6, 133.2, 138.7, 157.8, 159.7, 164.2, 166.9, 168.2.

ES-MS (+ve) m/z: Found $[M–BF_4^-]^+$ 361.1392, $C_{18}H_{21}N_2O_6^+$ requires 361.1394

Dimethyl 1-methyl-1*H*-imidazole-4,5-dicarboxylate (22a)



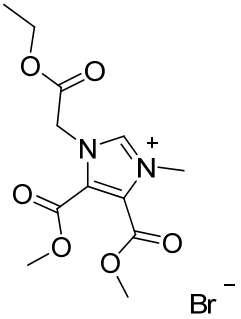
A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **20a** (300 mg, 1.6 mmol) in methanol (7 mL). To this methyl iodide (187 µL, 3 mmol) was added. The reaction mixture was stirred under argon at room temperature for 3 days. Upon completion of the reaction, the solvent was removed *in vacuo* and the resulting residue was extracted with dichloromethane. The extracts were combined and concentrated *in vacuo* giving the pure product **22a** as a pale yellow oil (273 mg, 86 %).

^{1}H NMR (400 MHz, $CDCl_3$): 3.77 (s, 3H), 3.78 (s, 3H), 3.83 (s, 3H), 7.92 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): 33.6, 51.8, 52.4, 124.7, 136.1, 141.2, 160.0, 162.9.

ES-MS (+ve) m/z: Found 198.0717, $C_8H_{10}N_2O_4$ requires 198.0719.

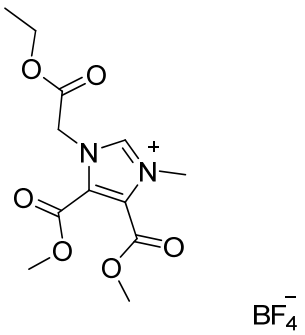
1-(2-ethoxy-2-oxoethyl)-4,5-*bis*(methoxycarbonyl)-3-methyl-1*H*-imidazol-3-ium bromide (22)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **22a** (250 mg, 1.26 mmol) in acetonitrile (2 mL). Ethyl bromoacetate (277 μL, 2.5 mmol) was added and the reaction mixture was stirred at room temperature for 4 days. Upon completion of the reaction, the solvent was removed *in vacuo* giving a light brown oil. This oil was washed with ether (20 mL) to remove excess ethyl bromoacetate giving the pure product **22** as a yellow oil (408 mg, 89 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.25 (t, J = 7.1 Hz, 3H), 3.91 (s, 3H), 3.97 (s, 3H), 4.02 (s, 3H), 4.24 (q, J = 7.1 Hz, 2H), 5.40 (s, 2H), 9.45 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 13.9, 24.5, 25.5, 36.6, 49.9, 53.9, 62.2, 125.6, 127.5, 141.8, 157.0, 166.1.
ES-MS (+ve) m/z: Found $[M–Br^{-}]^{+}$ 285.1084, $C_{12}H_{17}N_2O_6^{+}$ requires 285.1081.

1-(2-ethoxy-2-oxoethyl)-4,5-*bis*(methoxycarbonyl)-3-methyl-1*H*-imidazol-3-ium tetrafluoroborate (23)

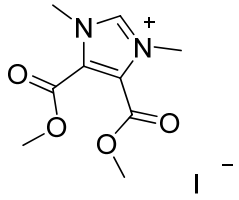


A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **20b** (250 mg, 0.93 mmol) in acetonitrile (2 mL). Trimethyloxonium tetrafluoroborate (137 mg, 0.93 mmol) was added and the reaction mixture was stirred at room temperature for 4 days. Upon completion of the reaction, the solvent was removed *in vacuo* after which the pure product **23** was obtained as a pale yellow oil (318 mg, 92 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.24 (t, J = 7.1 Hz, 3H), 3.91 (s, 3H), 3.97 (s, 3H), 4.01 (s, 3H), 422 (q, J = 7.1 Hz, 2H), 5.39 (s, 2H), 9.45 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 14.8, 24.8, 25.9, 37.4, 50.7, 54.8, 63.1, 126.5, 128.4, 142.6, 157.9, 167.0.

ES-MS (+ve) m/z: Found $[M–BF_4^-]^+$ 285.1079, $C_{12}H_{17}N_2O_6^+$ requires 285.1081

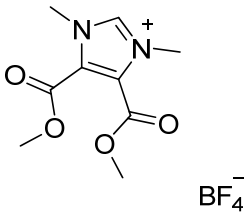
4,5-*bis*(methoxycarbonyl)-1,3-dimethyl-1*H*-imidazol-3-ium iodide (26)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **22a** (250 mg, 1.26 mmol) in acetonitrile (2 mL). Methyl iodide (79 µL, 1.26 mmol) was added and the reaction mixture was stirred at room temperature for 3 days. Upon completion of the reaction, the solvent was removed *in vacuo* giving the pale yellow oil **26** (368 mg, 86 %).

^{1}H NMR (400 MHz, DMSO-d_6): 3.91-4.02 (m, 12H), 9.40 (s, 1H)
^{13}C NMR (100 MHz, DMSO-d_6): 36.2, 53.8, 126.6, 141.2, 157.3
ES-MS (+ve) m/z: Found $[M–I^-]^+$ 213.0877, $C_9H_{13}N_2O_4^+$ requires 213.0875.

4,5-*bis*(methoxycarbonyl)-1,3-dimethyl-1*H*-imidazol-3-ium tetrafluoroborate (27)

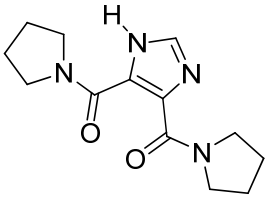


A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **22a** (250 mg, 1.62 mmol) in acetonitrile (2 mL). Triemthyloxonium tetrafluoroborate (240 mg, 1.62 mmol) was added and the reaction mixture was stirred at room temperature for 3 days. Upon completion of the reaction, the solvent was removed *in vacuo* giving the pale yellow solid **27** (344 mg, 91 %).

^{1}H NMR (400 MHz, DMSO-d_6): 3.92-4.02 (br.s, 12H), 9.42 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 38.1, 53.8, 126.7, 141.2, 157.3
ES-MS (+ve) m/z: Found $[M–BF_4^-]^+$ 213.0873, $C_9H_{13}N_2O_4^+$ requires 213.0875.

Melting point: 85-87 °C

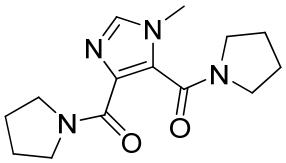
(1H-imidazole-4,5-diyl)*bis*(pyrrolidin-1-ylmethanone) (24a)



A 10 mL microwave reaction vial was fitted with a magnetic stirrer and to this dimethyl imidazole-4,5-dicarboxylate **20a** (500 mg, 2.7 mmol) was added. This was dissolved in distilled pyrrolidine (1.2 mL, 14.4 mmol). The reaction was fitted with a lid, placed in the microwave under reduced pressure and stirred for 3 h at 110 °C. Upon completion of the reaction the pyrrolidine was removed *in vacuo* and the resulting residue was purified by flash chromatography (CH_2Cl_2: MeOH, 1:0-10:1) giving the pure product **24a** as an off-white solid (506 mg, 72 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.95-1.98 (m, 4H), 2.06-2.11 (m, 4H), 3.70 (t, J = 6.8 Hz, 4H), 3.82 (t, J = 6.8 Hz, 4H), 7.50 (s, 1H), 7.72 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 23.8, 26.3, 46.9, 47.8, 126.2, 136.5, 159.6.
ES-MS (+ve) m/z: Found 262.1432, $C_{13}H_{18}N_4O_2$ requires 262.1429.
Melting point: 123-124 °C

(1H-imidazole-4,5-diyl)*bis*(pyrrolidin-1-ylmethanone) (24b)

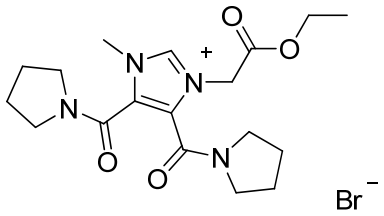


A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **24a** (250 mg, 0.95 mmol) in methanol (7 mL). To this methyl iodide (144 µL, 2.3 mmol) was added. The reaction mixture was stirred under argon at room temperature for 3 days. Upon completion of the reaction, the solvent was removed *in vacuo* and the resulting residue was

extracted with dichloromethane (2 x 5 mL). The organic layer was concentrated *in vacuo* giving the pure product **24b** as a pale yellow oil (220 mg, 84 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.91-1.98 (m, 8H), 3.63-3.70 (m, 8H), 3.79 (s, 3H), 7.93 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 23.9, 24.5, 26.2, 27.6, 35.2, 47.1, 48.2, 48.9, 49.5, 127.3, 138.9, 141.3, 161.2, 167.8.
ES-MS (+ve) m/z: Found 276.1435, $C_{14}H_{20}N_4O_2$ requires 276.1431.

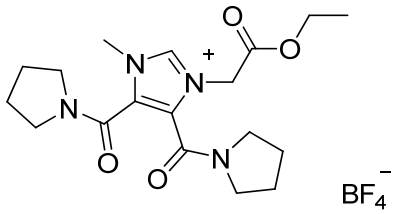
3-(2-methoxyacetyl)-1-methyl-4,5-*bis*[(pyrrolidin-1-yl)carbonyl]-1*H*-imidazol-3-ium bromide (24)



A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **24b** (200 mg, 0.72 mmol) in acetonitrile (2 mL). Ethyl bromoacetate (320 µL, 2.9 mmol) was added and the reaction mixture was stirred at room temperature for 4 days. Upon completion of the reaction, the solvent was removed *in vacuo* giving a light brown oil. This oil was washed with ether (25 mL) to remove excess ethyl bromoacetate giving the pure product **24** as a yellow oil (282 mg, 89 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.36 (t, J = 6.5 Hz, 3H), 1.86-1.89 (m, 8H), 3.61-3.68 (m, 8H), 3.65 (s, 3H), 4.25 (q, J = 6.5 Hz, 2H), 4.73 (s, 2H), 8.96 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 23.4, 24.2, 25.9, 27.1, 33.2, 35.4, 46.9, 47.8, 48.6, 49.5, 53.4, 61.8, 127.3, 138.9, 141.3, 159.5, 161.2, 167.8.
ES-MS (+ve) m/z: Found $[M\text{-}Br^-]^+$ 363.2029, $C_{18}H_{27}N_4O_4^+$ 363.2032.

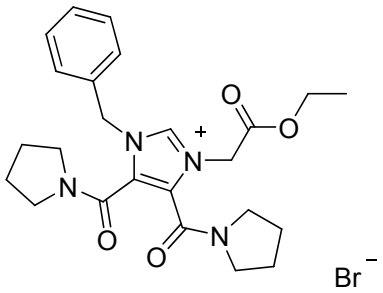
3-(2-methoxyacetyl)-1-methyl-4,5-*bis*[(pyrrolidin-1-yl)carbonyl]-1*H*-imidazol-3-ium tetrafluoroborate (25)



To a 25 mL round bottomed flask fitted with a magnetic stirring bar, **24** (250 mg, 0.56 mmol) was added. To this $NaBF_4$ (74.8 mg, 0.68 mmol) and acetone (10 mL) were added and the mixture was placed under an argon atmosphere. The resulting suspension was stirred at room temperature for 4 days. After which a white precipitate was formed. This precipitate was filtered using a Buchner funnel under vacuum and washed with dry acetone (2 x 5 mL). The combined filtrate and washings were then concentrated *in vacuo* giving the pure product **25** as a pale yellow oil (241 mg, 96 %).

^{1}H NMR (400 MHz, DMSO-d_6): 1.29 (t, J = 6.8 Hz, 3H), 1.82-1.86 (m, 8H), 3.61-3.66 (m, 8H), 3.59 (s, 3H), 4.17 (q, J = 6.8 Hz, 2H), 4.73 (s, 2H), 9.35 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 23.2, 24.5, 26.0, 27.3, 33.5, 35.7, 47.1, 47.9, 48.4, 49.1, 53.5, 62.0, 127.3, 138.6, 142.3, 159.6, 161.2, 167.7.
ES-MS (+ve) m/z: Found $[M\text{-}BF_4^-]^+$ 363.2030, $C_{18}H_{27}N_4O_4^+$ 363.2032.

1-Benzyl-3-(2-ethoxy-2-oxoethyl)-4,5-*bis*(pyrrolidine-1-carbonyl)-1H-imidazol-3-ium bromide (24c)

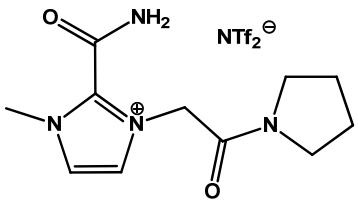


A 25 mL round-bottomed flask, fitted with a magnetic stirring bar, was charged with **24a** (250 mg, 0.95 mmol) in acetonitrile (5 mL). To this K_2CO_3 (135 mg, 0.95 mmol) was added and the reaction mixture was stirred for 30 min under an argon atmosphere. Ethyl bromoacetate (421 µL, 3.8 mmol) was added and the reaction mixture was stirred at room temperature for 2 days. Upon completion of the reaction, the solvent was removed *in vacuo* and the resulting residue was extracted with dichloromethane. The extracts were combined and concentrated *in vacuo* giving a pale yellow solid. This solid was washed with ether after

which the pure product was obtained as an off-white solid. To this benzyl bromide (452 µL, 3.8 mmol) was added and the reaction mixture was stirred at room temperature for 3 days. Upon completion of the reaction, the solvent was removed *in vacuo* resulting in a yellow oil. This oil was washed with ether (15 mL) to remove excess benzyl bromide after which the pure catalyst **24c** was obtained as a pale yellow oil (355 mg, 72%).

^{1}H NMR (400 MHz, DMSO-d_6): 1.25 (t, J = 6.9 Hz, 3H), 1.93-1.95 (m, 4H), 2.03-2.09 (m, 4H), 2.24-2.27 (m, 2H), 3.59-3.69 (m, 8H), 5.23 (s, 2H), 5.84 (s, 2H), 7.23-7.29 (m, 5H), 8.21 (s, 1H).
^{13}C NMR (100 MHz, DMSO-d_6): 21.2, 23.5, 25.8, 26.2, 33.7, 45.6, 46.7, 47.9, 48.1, 52.4, 54.8, 61.6, 125.6, 126.8, 127.6, 129.2, 137.3, 138.3, 141.2, 157.9, 160.6, 167.2.
ES-MS (+ve) m/z: Found $[M\text{-}BF_4^-]^+$ 439.2338, $C_{24}H_{31}N_4O_4^+$ 439.2340.

1*H*-Imidazolium-2-carboxamide,1-methyl-3-[2-oxo-2-(1-pyrrolidinyl)ethyl]-, NTf_2 (41):



A RB flask was charged with 1*H*-Imidazolium-2-carboxamide, 1-methyl-3-[2-oxo-2-(1-pyrrolidinyl) ethyl]-, bromide **9** (1.00 g, 3.15 mmol) and distilled water (5 mL). Lithium bis(trifluoromethane)sulfonamide (0.905 g, 3.15 mmol) in distilled water (5 mL) was added in one portion and the suspension was stirred vigorously for 4 h at RT. The product precipitated as a white solid. The aqueous layer was removed, and the IL washed with water (3 x 10 mL). The solvent was removed on the rotary evaporator and the product was dried *in vacuo* for 72 h to give the title compound **41** as a colorless solid at RT in 73% yield (1.205 g, 2.33 mmol).

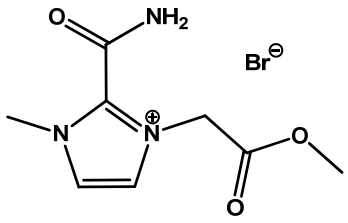
^{1}H-NMR (600 MHz, DMSO-d_6): 1.84-1.79 (m, 2H), 1.97-1.93 (m, 2H), 3.34 (t, J = 7.2 Hz, 2H), 3.49 (t, J = 7.2 Hz, 2H), 4.00 (s, 3H), 5.31 (s, 2H), 7.76 (d, J = 1.8 Hz, 1H), 7.82 (d, J = 2.4 Hz, 1H), 8.74 (bs, 1H), 8.79 (bs, 1H).

^{13}C-NMR (150 MHz, DMSO-d_6): 23.7, 25.4, 36.9, 45.1, 46.0, 50.7, 119.4 (q, J = 319 Hz, 2 CF_3), 123.4, 124.2, 139.0, 154.6, 162.4.

Melting Point: 79-81 °C

ES-MS (+ve) m/z: Found $[M– NTf_2^-]^+$ 237.1348, $C_{11}H_{17}N_4O_2^+$ requires 237.1346

1*H*-Imidazolium-2-carboxamide,3-(2-methoxy-2-oxoethyl)-1-methyl-, Bromide: (42)



A RB flask was charged with 1-methyl-1*H*-imidazole-2-carboxamide (0.500 g, 4.0 mmol) and THF (20 mL) under nitrogen. To this solution was added methyl bromoacetate (0.612 g, 4.0 mmol). The reaction mixture was refluxed for 4 days with vigorous stirring. The product precipitated as a pink colored solid and was then washed with THF (5 x 20 mL). The solvent was removed on the rotary evaporator and the product was dried *in vacuo* for 48 h to give the title compound **42** as a pink colored solid at RT in 17% yield (0.189 g, 0.68 mmol).

^{1}H-NMR (600 MHz, DMSO-d_6): 3.75 (s, 3H), 4.02 (s, 3H), 5.34 (s, 2H), 7.87 (d, J = 1.8 Hz, 1H), 7.88 (d, J = 1.2 Hz, 1H), 8.82 (bs, 1H), 8.87 (bs, 1H)

^{13}C-NMR (150 MHz, DMSO-d_6): 37.0, 49.9, 52.9, 123.9, 124.3, 138.4, 154.3, 166.7

Melting Point: 200 °C (decomposed)

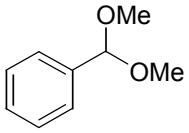
ES-MS (+ve) m/z: Found $[M–Br^-]^+$ 237.1356, $C_8H_{12}N_3O_3^+$ requires 237.1346.

3.0 General Procedure - Acetalisation of aldehydes

A 20 mL reaction vessel was fitted with a magnetic stirring bar, charged with catalyst (0.08 mmol), fitted with a septum and flushed with argon. Benzaldehyde (170 μL, 1.67 mmol) was added followed by dry methanol (3.4 mL) *via* syringe. The solution was then stirred under argon at room temperature for 24 h. When conversion was judged to be either complete or > 95% conversion (by H NMR spectroscopic analysis) the reaction was quenched with $PhNHNH_2$ and solvent was removed *in vacuo*. The crude product was purified by flash-chromatography or yield was calculated using an internal standard.

4.0 Characterization data

Benzaldehyde dimethyl acetal (6)



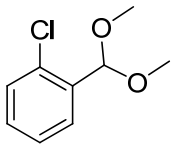
The desired dimethyl acetal was obtained following the general procedure using catalyst **21** (12.5 mg, 0.03 mmol), methanol (6.7 mL) and benzaldehyde (340 μL, 3.34 mmol). After purification of the crude material by flash chromatography (5:1 hexane:EtOAc) the product **6** was obtained as a pale yellow liquid (466 mg, 92%).

The NMR spectra of **6** were consistent with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$): 3.36 (s, 6H,), 5.42 (s, 1H), 7.34-7.39 (m, 3H), 7.47-7.49 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 52.2, 102.7, 126.2, 127.7, 128.0, 137.5.

2-Chlorobenzaldehyde dimethyl acetal (31, Table 4, entry 1)



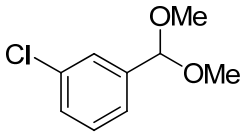
The dimethyl acetal was obtained following the general procedure using catalyst **21** (1.5 mg, 0.003 mmol), methanol (6.8 mL) and 2-chlorobenzaldehyde (400 µL, 2.56 mmol). After purification of crude material by flash chromatography (5:1 hexane: EtOAc) the product **31** was obtained as a pale yellow liquid (455 mg, 95 %).

The NMR spectra of **31** were consistent with those previously reported.[2]

^{1}H NMR (400 MHz, $CDCl_3$): 3.32 (s, 6H), 5.39 (s, 1H), 7.28-7.35 (m, 3H), 7.48-7.52 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): 52.2, 101.6, 124.4, 126.5, 128.1, 129.1, 133.8, 139.8.

3-Chlorobenzaldehyde dimethyl acetal (32, Table 4, entry 2)



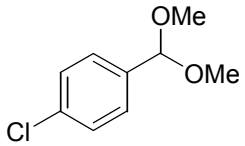
The dimethyl acetal was obtained following the general procedure using catalyst **21**(1.5 mg, 0.003 mmol), methanol (6.8 mL) and 3-chlorobenzaldehyde (400 µL, 2.56 mmol). After purification of crude material by flash chromatography (5:1 hexane: EtOAc) the product **32** was obtained as a pale yellow liquid (461 mg, 96 %).

The NMR spectra of **32** were consistent with those previously reported.[2]

^{1}H NMR (400 MHz, $CDCl_3$): 3.41 (s, 6H), 5.66 (s, 1H), 7.29-7.31 (m, 2H), 7.38-7.40 (m, 1H,), 7.63-7.65 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): 53.4, 100.5, 126.1, 127.6, 129.1, 129.3, 132.7, 134.8.

4-Chlorobenzaldehyde dimethyl acetal (33, Table 4, entry 3)



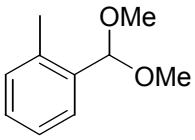
The desired dimethyl acetal was obtained following the general procedure using catalyst **21** (1.3 mg, 0.004 mmol), methanol (7.1 mL) and 4-chlorobenzaldehyde (500 mg, 3.56 mmol). After purification of the crude material by flash chromatography (5:1, hexane:EtOAc) the product **33** was obtained as a pale yellow liquid (653 mg, 98%).

The NMR spectra of **33** were consistent with those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$): 3.34 (s, 6H,), 5.39 (s, 1H), 7.32 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): 52.2, 101.6, 124.6, 126.4, 128.4, 133.8.

2-Methylbenzaldehyde dimethyl acetal (34, Table 4, entry 4)



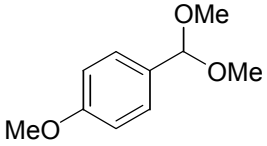
The desired dimethyl acetal was obtained following the general procedure using catalyst **21** (3.9 mg, 0.01 mmol), methanol (2.3 mL) and 2-methylbenzaldehyde (100 μL, 0.86 mmol). After purification of the crude material by flash chromatography (15:1 hexane:EtOAc) the product **34** was obtained as a pale yellow liquid (129 mg, 90%).

The NMR spectra of **34** were consistent with that previously reported.[3]

^{1}H NMR (400 MHz, $CDCl_3$): 2.42 (s, 3H,), 3.37 (s, 6H), 5.51 (s, 1H) 7.06-7.25 (m, 3H), 7.57-7.59 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): 18.4, 52.5, 101.3, 124.9, 126.1, 127.9, 130.1, 135.2, 135.8.

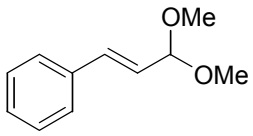
4-Methoxybenzaldehyde dimethyl acetal (35, Table 4, entry 5)



The desired dimethyl acetal was obtained following the general procedure using catalyst **21** (3.8 mg, 0.01 mmol), methanol (2.2 mL) and 4-methoxybenzaldehyde (100 μL, 0.82 mmol). The reaction mixture was then heated at 35 °C for 24 h. **Note:** the use of $PhNHNH_2$ was not required. After purification of the crude material by flash chromatography (5:1 Hexane :EtOAc) the product **35** was obtained as a pale yellow liquid (137 mg, 92%).
The NMR spectra of **35** were consistent with those previously reported.[1]

^{1}H NMR (400 MHz, CD_3OD): 3.30 (s, 6H), 3.81 (s, 3H), 5.34 (s, 1H), 6.92 (d, J = 8.9 Hz, 2H), 7.32 (d, J = 8.9 Hz, 2H)
^{13}C NMR (100 MHz, $CDCl_3$): 51.2, 53.7, 102.7, 112.5, 127.1, 129.7, 160.0.

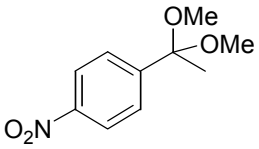
3,3-Dimethoxypropenyl benzene (37, Table 4, entry 7)



The desired dimethyl acetal was obtained following the general procedure using catalyst **21** (2.9 mg, 0.008 mmol), methanol (2.1 mL) and cinnamaldehyde (100 μL, 0.79 mmol). **Note:** the use of $PhNHNH_2$ was not required. After purification of the crude material by flash chromatography (8:1 hexane: EtOAc) the product **37** was obtained as a pale yellow liquid (128 mg, 90%).
The NMR spectra of **37** were consistent with those previously reported.[5]

^{1}H NMR (400 MHz, $CDCl_3$): 3.41 (s, 6H), 5.00 (d, J = 5.1 Hz, 1H), 6.18 (dd, J = 16.4, 5.1 Hz, 1H), 6.69 (d, J = 16.4 Hz, 1H), 7.29-7.38 (m, 3H), 7.44-7.45 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): 52.3, 102.5, 125.2, 126.3, 127.6, 128.2, 133.2, 135.6.

4-nitroacetophenone dimethyl ketal (38, Table 4, entry 8). (35 °C.)

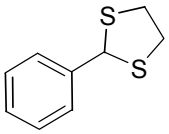


The desired dimethyl ketal was obtained following the general procedure using catalyst **21** (3.7 mg, 0.01 mmol), methanol (2.6 mL) and 4-nitroacetophenone (165.2 mg, 1 mmol). The reaction mixture was then heated at 35 °C for 48 h. **Note:** the use of $PhNHNH_2$ was not required. After purification of the crude material by flash chromatography (15:1 hexane;EtOAc) the product **38** was obtained as a pale yellow solid (133 mg, 63%). M.p. 58-60 °C (lit.,[7a] 60-61.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$): 1.53 (s, 3H), 3.18 (s, 6H), 7.66 (d, J = 8.9 Hz, 2H), 8.17 (d, J = 8.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 26.4, 48.6, 123.1, 123.9, 129.1, 146.7, 151.4

Phenyl-1,3-dithiolane (39)



The desired dithiolane was obtained following the general procedure using catalyst **21** (3.9 mg, 0.01 mmol), 1,2-ethanethiol (100 µL, 1.19 mmol), THF (200 µL) and benzaldehyde (110 µL, 1.08 mmol). After completion of the reaction, the reaction mixture was poured onto a saturated $NaHCO_3$ solution (5 mL) and the product was extracted with ethyl acetate (2 x 10 mL) 25 mL water. The organic layer was separated, dried over $MgSO_4$ and concentrated *in vacuo*. After purification by flash chromatography (5:1 hexane:EtOAc) the product **39** was obtained as a colorless liquid (179 mg, 90 %).

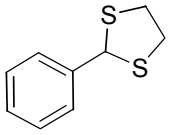
The NMR spectra of **39** were consistent with those previously reported.[7]

^{1}H NMR (400 MHz, $CDCl_3$): 3.34-3.40 (m, 2H), 3.48-3.54 (m, 2H), 5.66 (s, 1H), 7.27-7.35 (m, 3H), 7.54-7.56 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): 39.8, 55.8, 127.5, 127.6, 128.1, 139.9.

5.0 Recyclability study

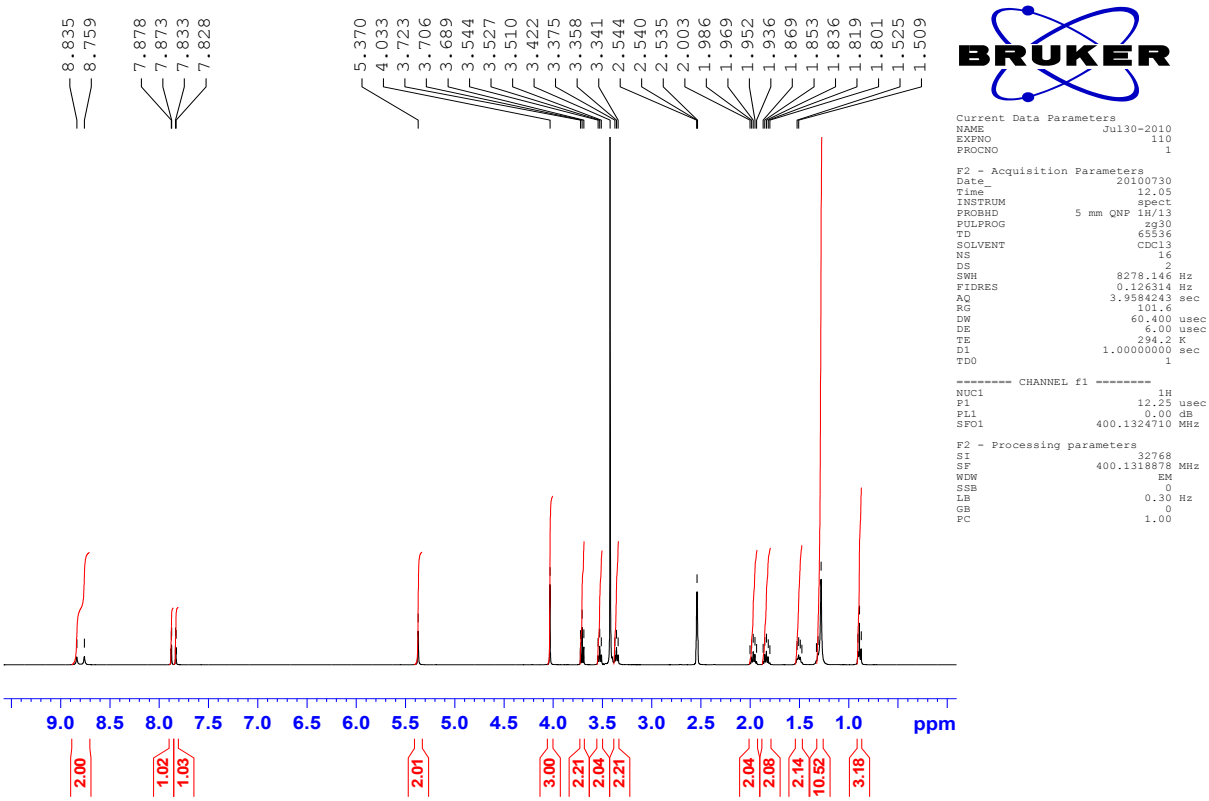
Phenyl-1,3-dithiolane (39)

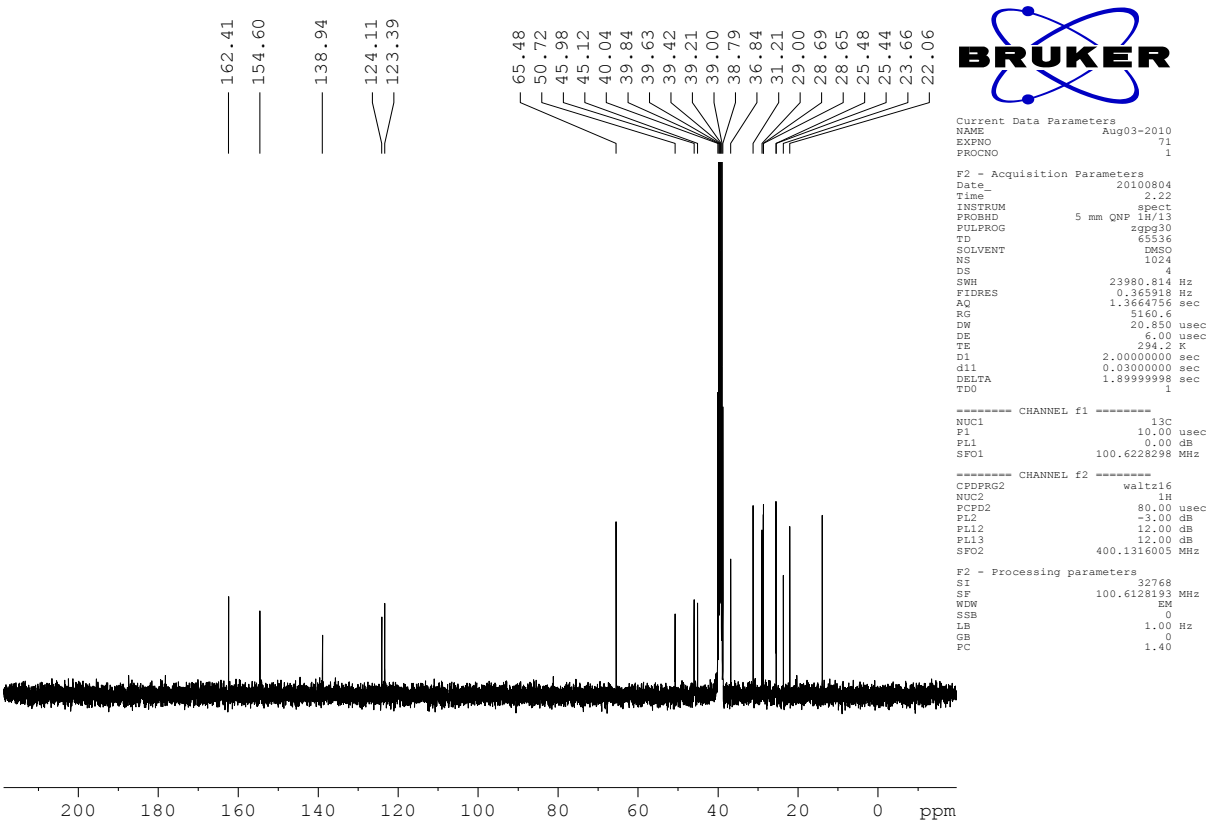


The dithiane was obtained following the general procedure using catalyst **10** (68.3 mg, 0.27 mmol), 1,3-propanedithiol (300 µL, 2.98 mmol), anhydrous THF (9.1 mL) and benzaldehyde (276 µL, 2.71 mmol). (*E*)-stilbene (2.71 mmol) was added as an internal standard. After 24 h, the yield of product **39** was obtained by ^{1}H NMR spectroscopy with the internal standard. The catalyst was preciptated using hexane, dried *in vacuo* and reused in subsequent reaction.

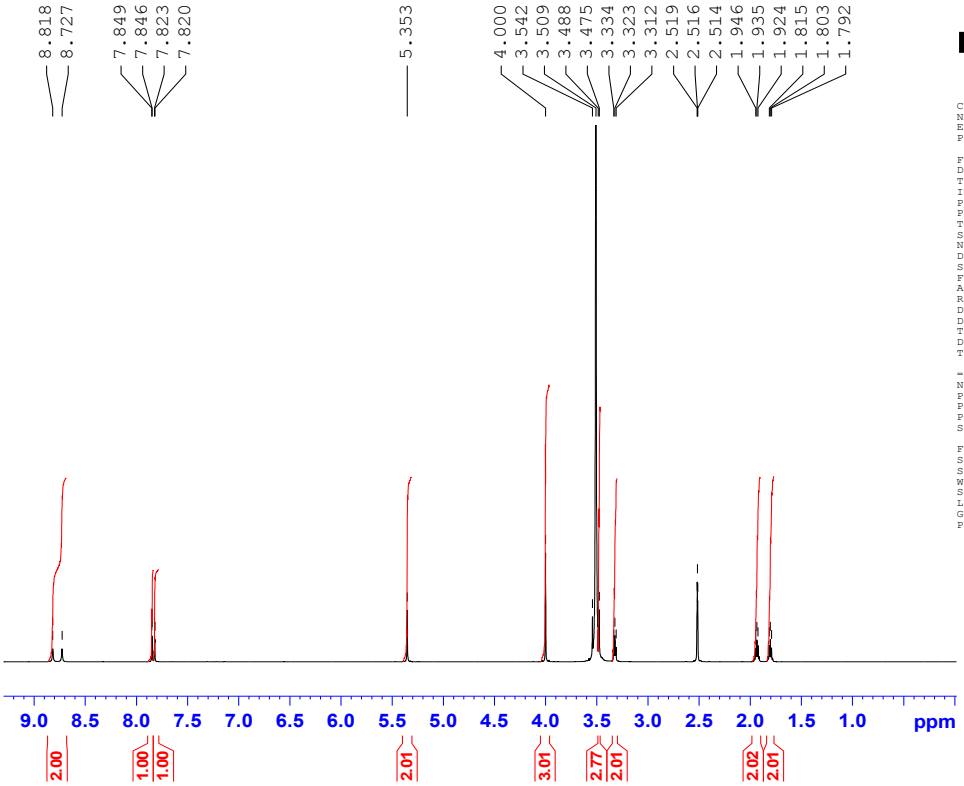
6.0 NMR Spectra

Compound 8





Compound 9



BRUKER

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PROCNO                         1

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TD                      65536
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AQ                 2.6564426 sec
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DE                    10.73 usec
TE                    300.0 K
D1                 1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
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P1                    11.65 usec
PL1                   -5.30 dB
PL1W               25.53414154 W
SFO1              600.3267072 MHz

F2 - Processing parameters
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LB                      0.30 Hz
GB                             0
PC                          1.00
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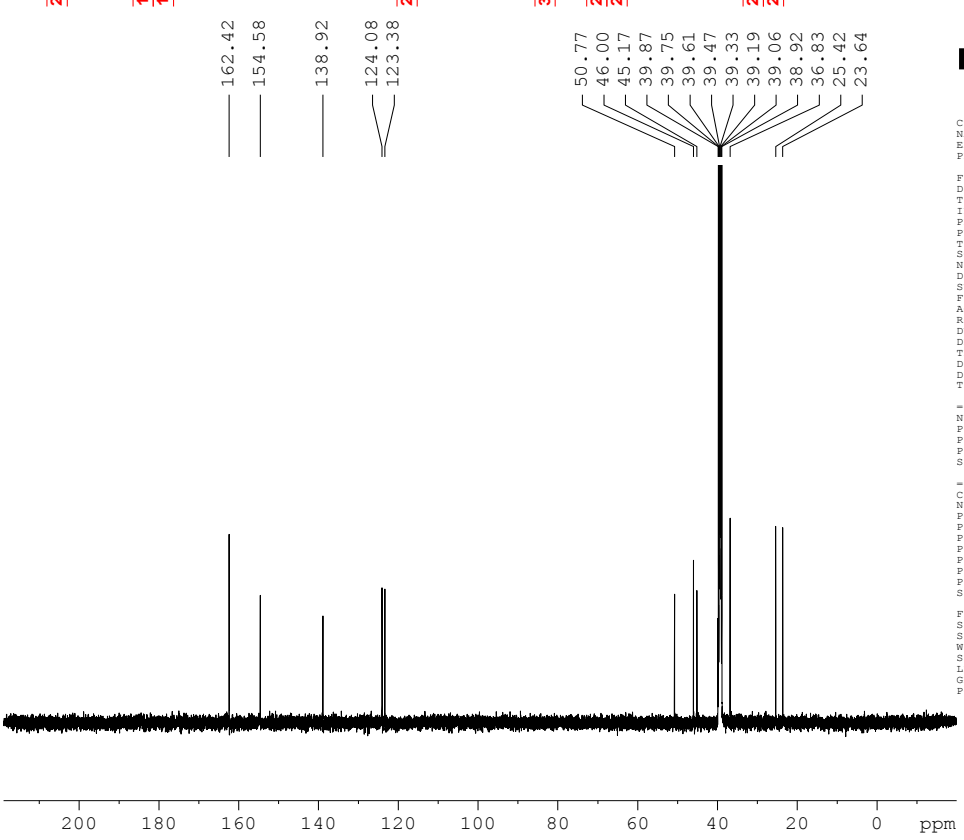

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AQ                 0.9088159 sec
RG                        2050
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DE                    6.50 usec
TE                    300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
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P1                     9.71 usec
PL1                   1.50 dB
PL1W               78.77777863 W
SFO1              150.9664335 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                         1H
PCPD2                 70.00 usec
PL2                   -5.30 dB
PL12                  10.02 dB
PL13                  120.00 dB
PL2W               25.53414154 W
PL12W               0.75010353 W
PL13W               0.00000000 W
SFO2              600.3254013 MHz

F2 - Processing parameters
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GB                             0
PC                          1.40
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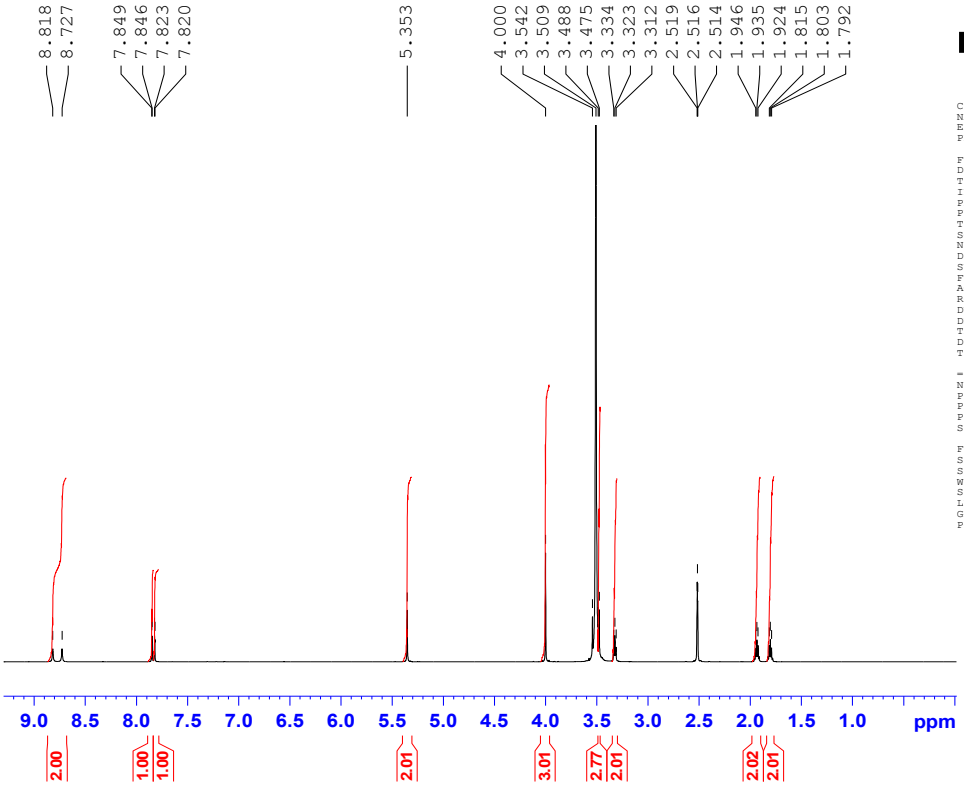
Compound 10



BRUKER

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EXPNO                        110
PROCNO                         1

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SOLVENT                   DMSO
NS                          16
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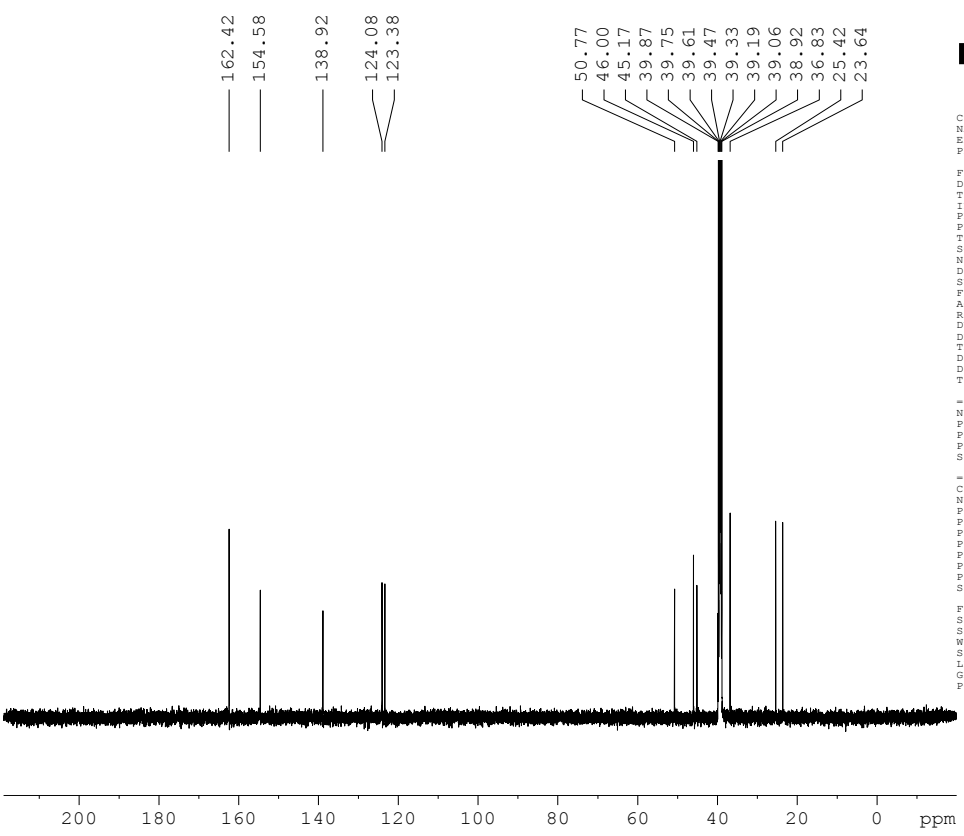
TD0                            1

======== CHANNEL f1 ========
NUC1                         1H
P1                       11.65 usec
PL1                      -5.30 dB
PL1W                25.53414154 W
SFO1               600.3267072 MHz

F2 - Processing parameters
SI                           32768
SF                 600.3230000 MHz
WDW                             EM
SSB                              0
LB                            0.30 Hz
GB                               0
PC                            1.00
```



BRUKER

```
Current Data Parameters
NAME                  Nov04-2010
EXPNO                        111
PROCNO                         1

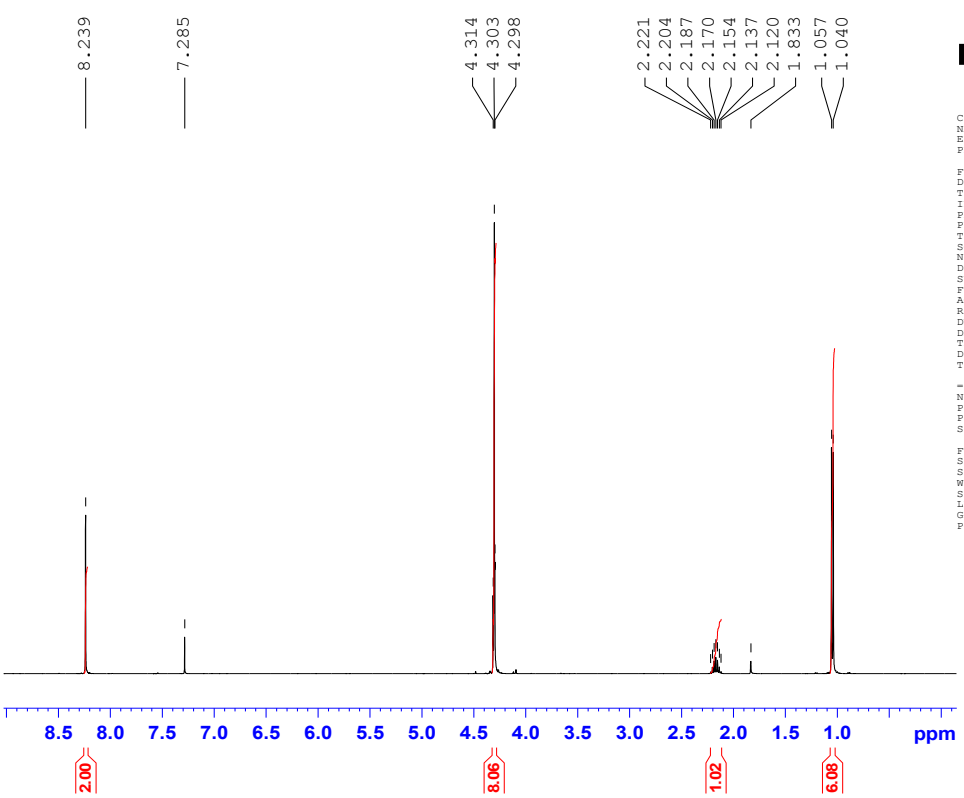
F2 - Acquisition Parameters
Date_                 20101104
Time                      18.19
INSTRUM                   spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                   DMSO
NS                         1024
DS                            4
SWH                  36057.691 Hz
FIDRES                0.550197 Hz
AQ                   0.9088159 sec
RG                         2050
DW                       13.867 usec
DE                        6.50 usec
TE                       300.0 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                        13C
P1                        9.71 usec
PL1                       1.50 dB
PL1W                78.77777863 W
SFO1               150.9664335 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                    70.00 usec
PL2                      -5.30 dB
PL12                     10.02 dB
PL13                    120.00 dB
PL2W                25.53414154 W
PL12W                0.75010353 W
PL13W                0.00000000 W
SFO2               600.3254013 MHz

F2 - Processing parameters
SI                           32768
SF                 150.9514145 MHz
WDW                             EM
SSB                              0
LB                            1.00 Hz
GB                               0
PC                            1.40
```

Compound 11

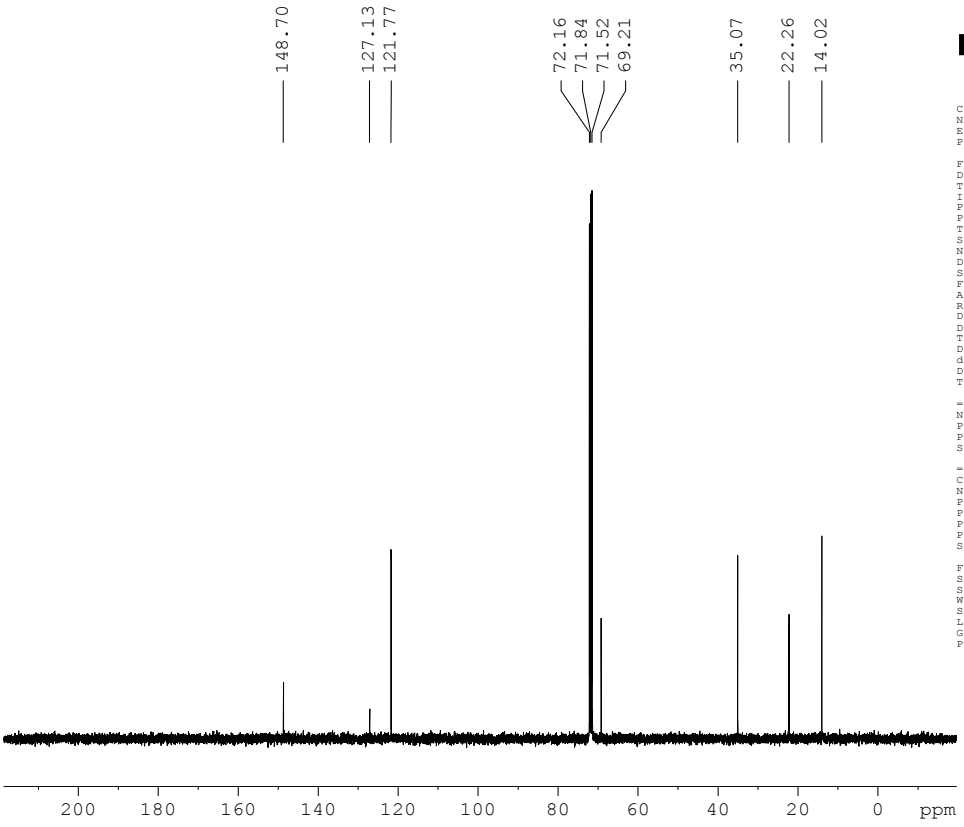



```
Current Data Parameters
NAME                  May26-2010
EXPNO                        120
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20100526
Time                       14.54
INSTRUM                    spect
PROBHD  5 mm QNP 1H/13
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8278.146 Hz
FIDRES                 0.126314 Hz
AQ                     3.9584243 sec
RG                          181
DW                       60.400 usec
DE                        6.00 usec
TE                       293.2 K
D1                    1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          1H
P1                       12.25 usec
PL1                       0.00 dB
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                  400.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```




```
Current Data Parameters
NAME                  May26-2010
EXPNO                         81
PROCNO                         1

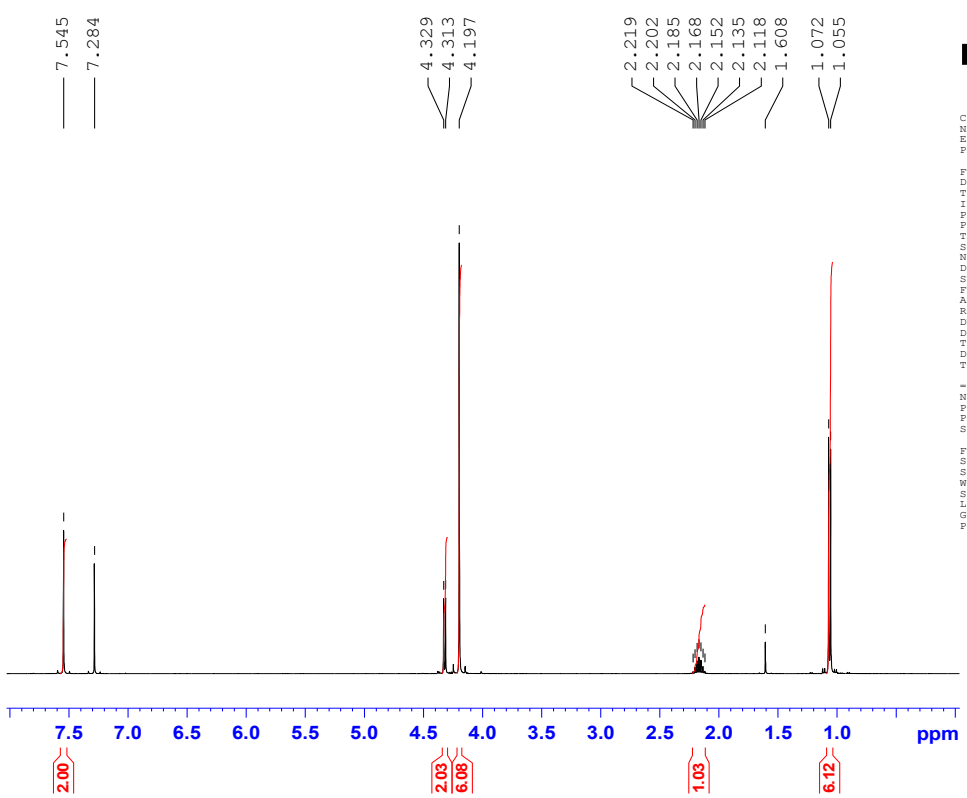
F2 - Acquisition Parameters
Date_                   20100527
Time                        0.48
INSTRUM                    spect
PROBHD  5 mm QNP 1H/13
PULPROG                  zgpg30
TD                        65536
SOLVENT                    DMSO
NS                          1024
DS                             4
SWH                   23980.814 Hz
FIDRES                 0.365918 Hz
AQ                     1.3664756 sec
RG                        2896.3
DW                       20.850 usec
DE                        6.00 usec
TE                       294.2 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          13C
P1                       10.00 usec
PL1                       0.00 dB
SFO1                100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                          1H
PCPD2                    80.00 usec
PL2                      -3.00 dB
PL12                     12.00 dB
PL13                     12.00 dB
SFO2                400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                  100.6128193 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

Compound 12

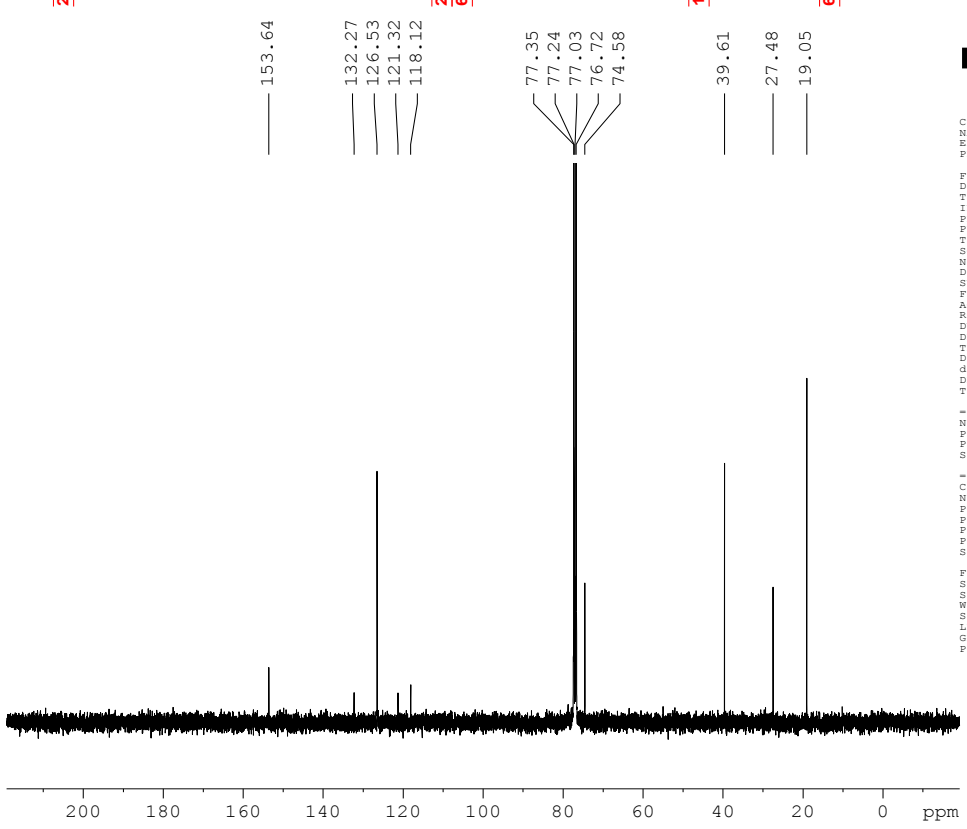



```
Current Data Parameters
NAME                  Jul23-2010
EXPNO                        130
PROCNO                         1

F2 - Acquisition Parameters
Date_                 20100723
Time                     16.28
INSTRUM                  spect
PROBHD     5 mm QNP 1H/13
PULPROG                  zg30
TD                      65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 8278.146 Hz
FIDRES              0.126314 Hz
AQ                  3.9584243 sec
RG                         362
DW                    60.400 usec
DE                     6.00 usec
TE                     294.2 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                     12.25 usec
PL1                     0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF                400.1300000 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```




```
Current Data Parameters
NAME                  Jul23-2010
EXPNO                         71
PROCNO                         1

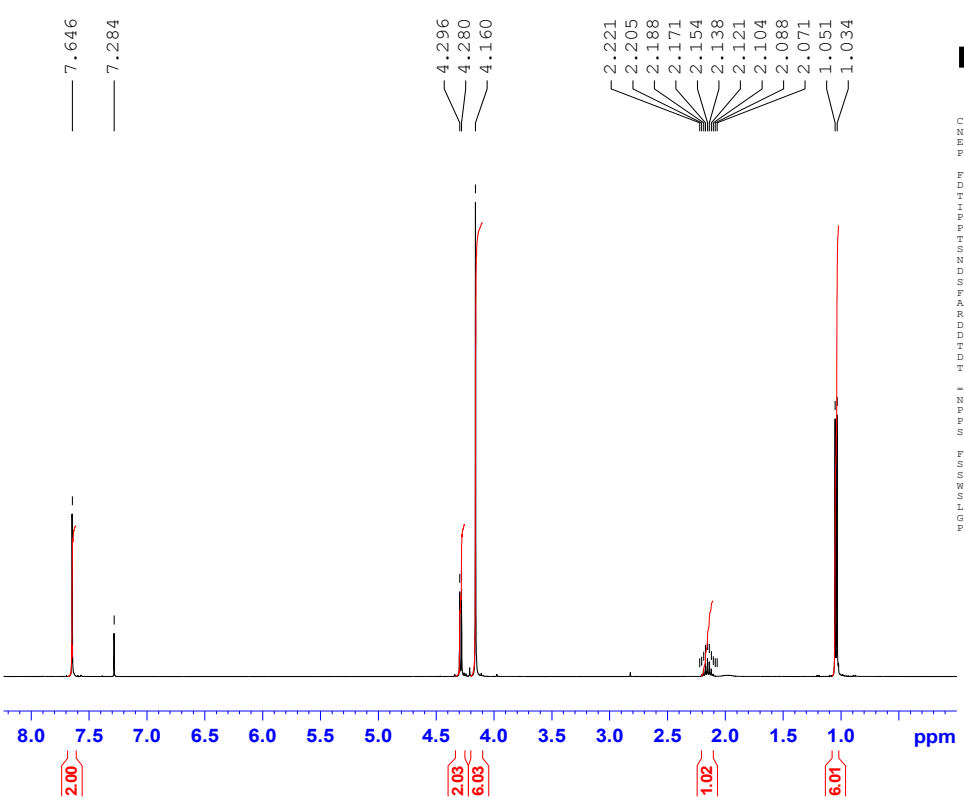
F2 - Acquisition Parameters
Date_                 20100724
Time                      9.43
INSTRUM                  spect
PROBHD     5 mm QNP 1H/13
PULPROG                zgpg30
TD                      65536
SOLVENT                  CDCl3
NS                        3000
DS                           4
SWH                23980.814 Hz
FIDRES              0.365918 Hz
AQ                  1.3664756 sec
RG                       1448.2
DW                    20.850 usec
DE                     6.00 usec
TE                     294.2 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                     10.00 usec
PL1                     0.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                  80.00 usec
PL2                    -3.00 dB
PL12                   12.00 dB
PL13                   12.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF                100.6127690 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

Compound 13



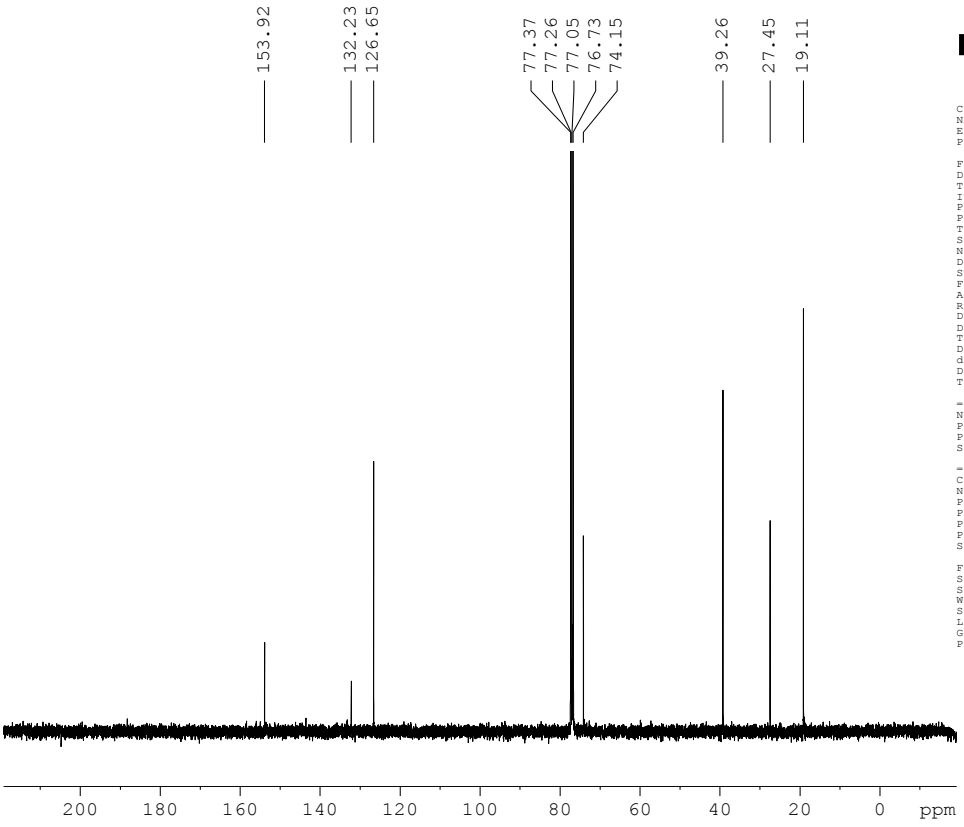
BRUKER

```
Current Data Parameters
NAME                  May28-2010
EXPNO                         70
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20100528
Time                       23.05
INSTRUM                    spect
PROBHD      5 mm QNP 1H/13
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8278.146 Hz
FIDRES                 0.126314 Hz
AQ                     3.9584243 sec
RG                         161.3
DW                        60.400 usec
DE                         6.00 usec
TE                        294.2 K
D1                     1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          1H
P1                        12.25 usec
PL1                        0.00 dB
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                         32768
SF                  400.1300000 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```



BRUKER

```
Current Data Parameters
NAME                  May28-2010
EXPNO                         71
PROCNO                         1

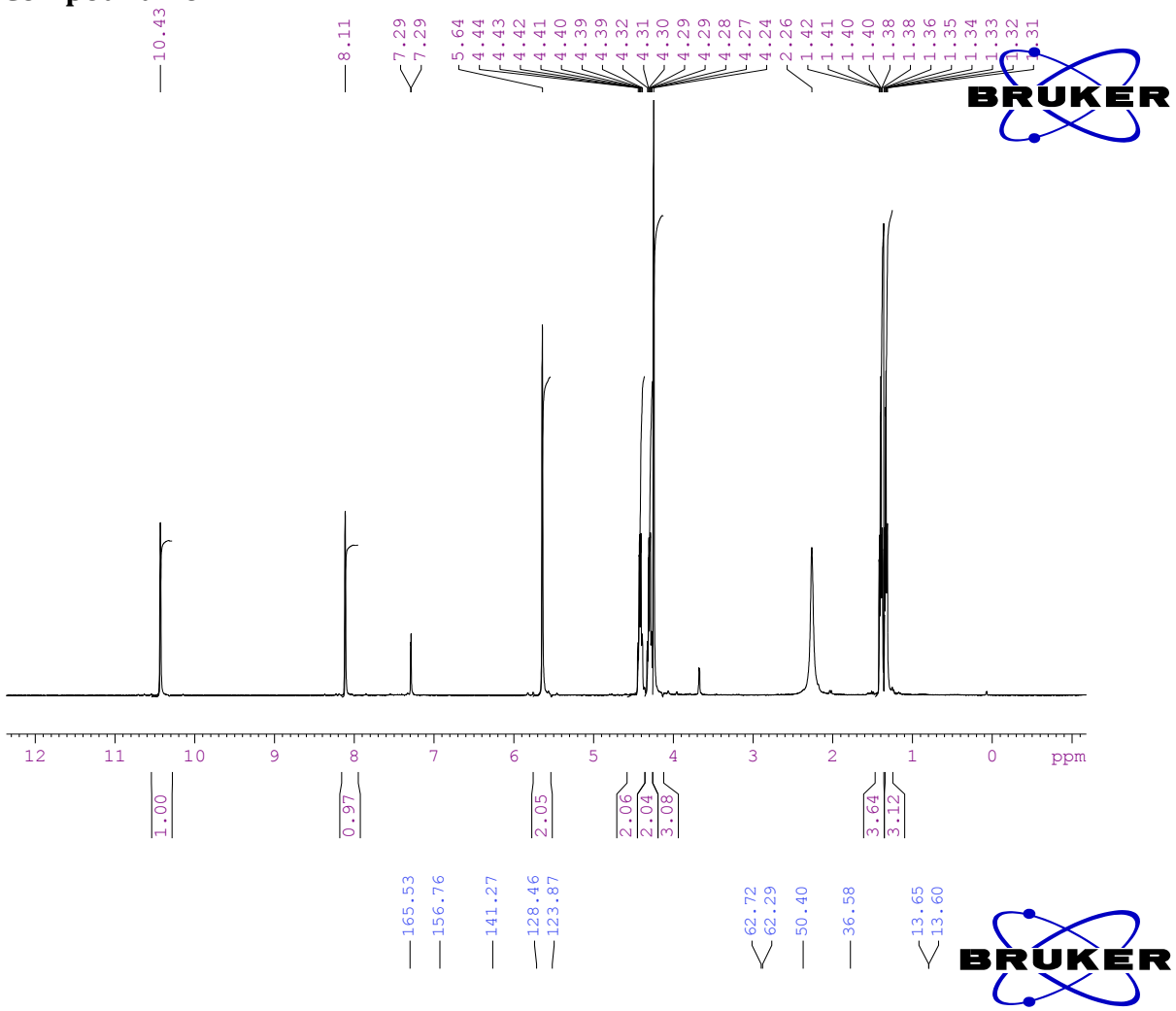
F2 - Acquisition Parameters
Date_                   20100529
Time                        0.05
INSTRUM                    spect
PROBHD      5 mm QNP 1H/13
PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                         1024
DS                            4
SWH                   23980.814 Hz
FIDRES                 0.365918 Hz
AQ                     1.3664756 sec
RG                         5792.6
DW                        20.850 usec
DE                         6.00 usec
TE                        294.2 K
D1                     2.00000000 sec
d11                    0.03000000 sec
DELTA                  1.89999998 sec
TD0                            1

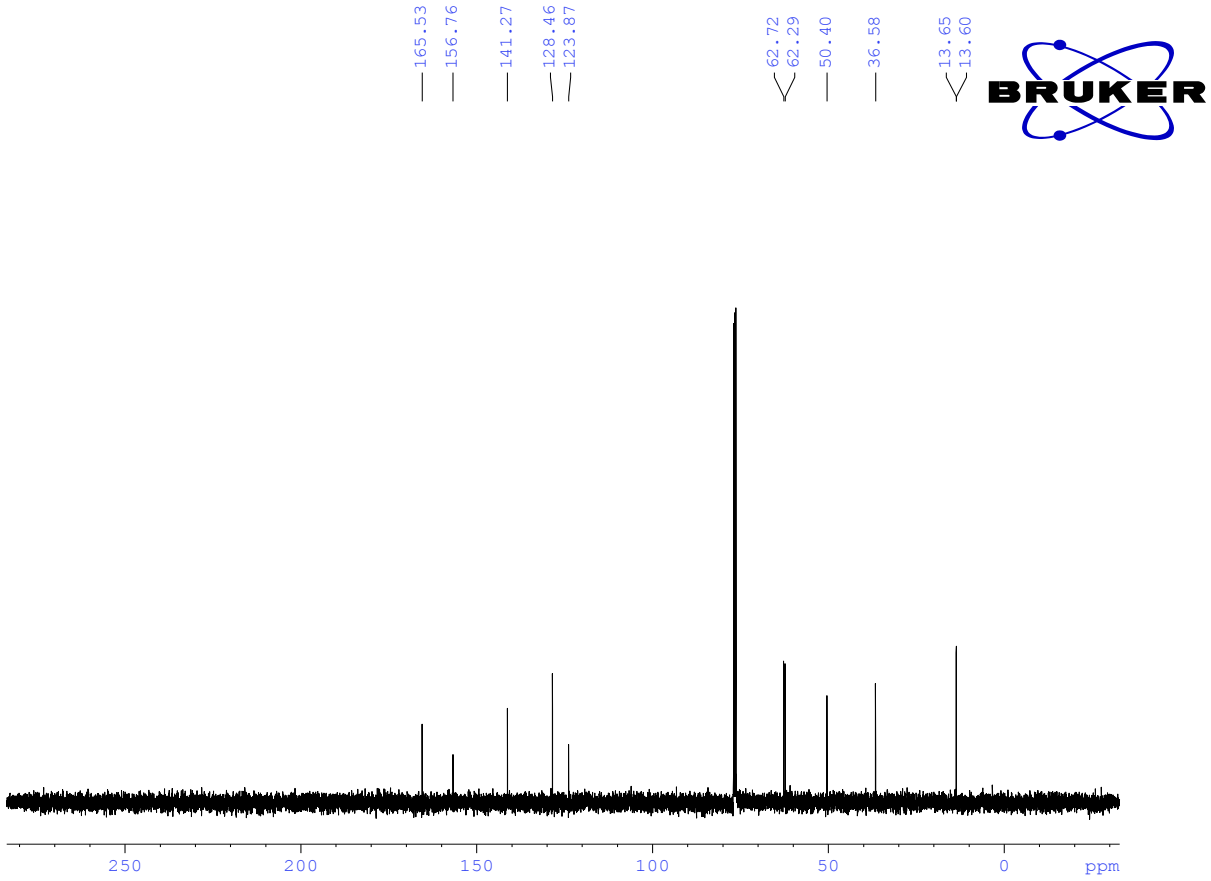
======== CHANNEL f1 ========
NUC1                          13C
P1                        10.00 usec
PL1                        0.00 dB
SFO1                100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                          1H
PCPD2                     80.00 usec
PL2                       -3.00 dB
PL12                      12.00 dB
PL13                      12.00 dB
SFO2                400.1316005 MHz

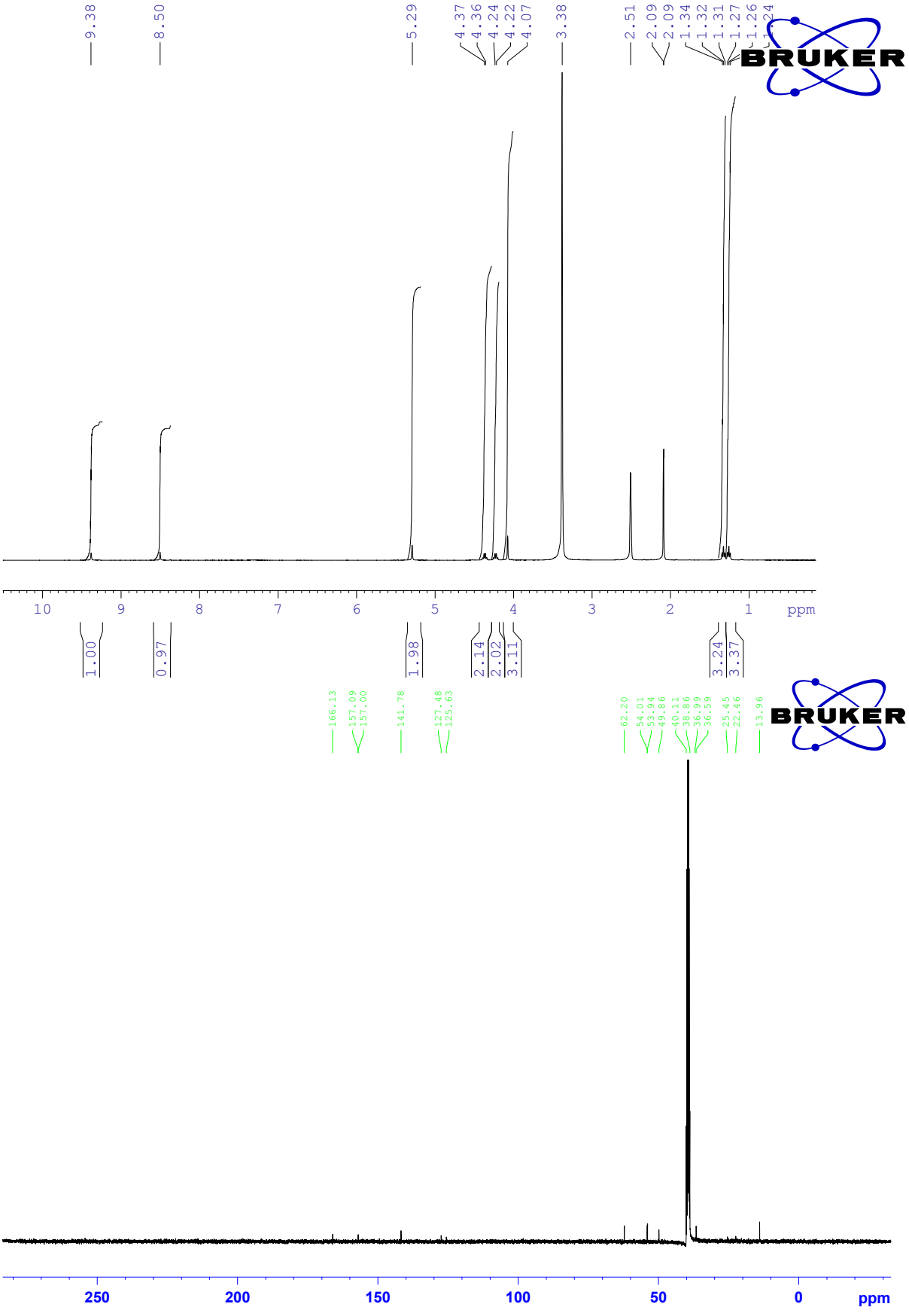
F2 - Processing parameters
SI                         32768
SF                  100.6127690 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

Compound 16

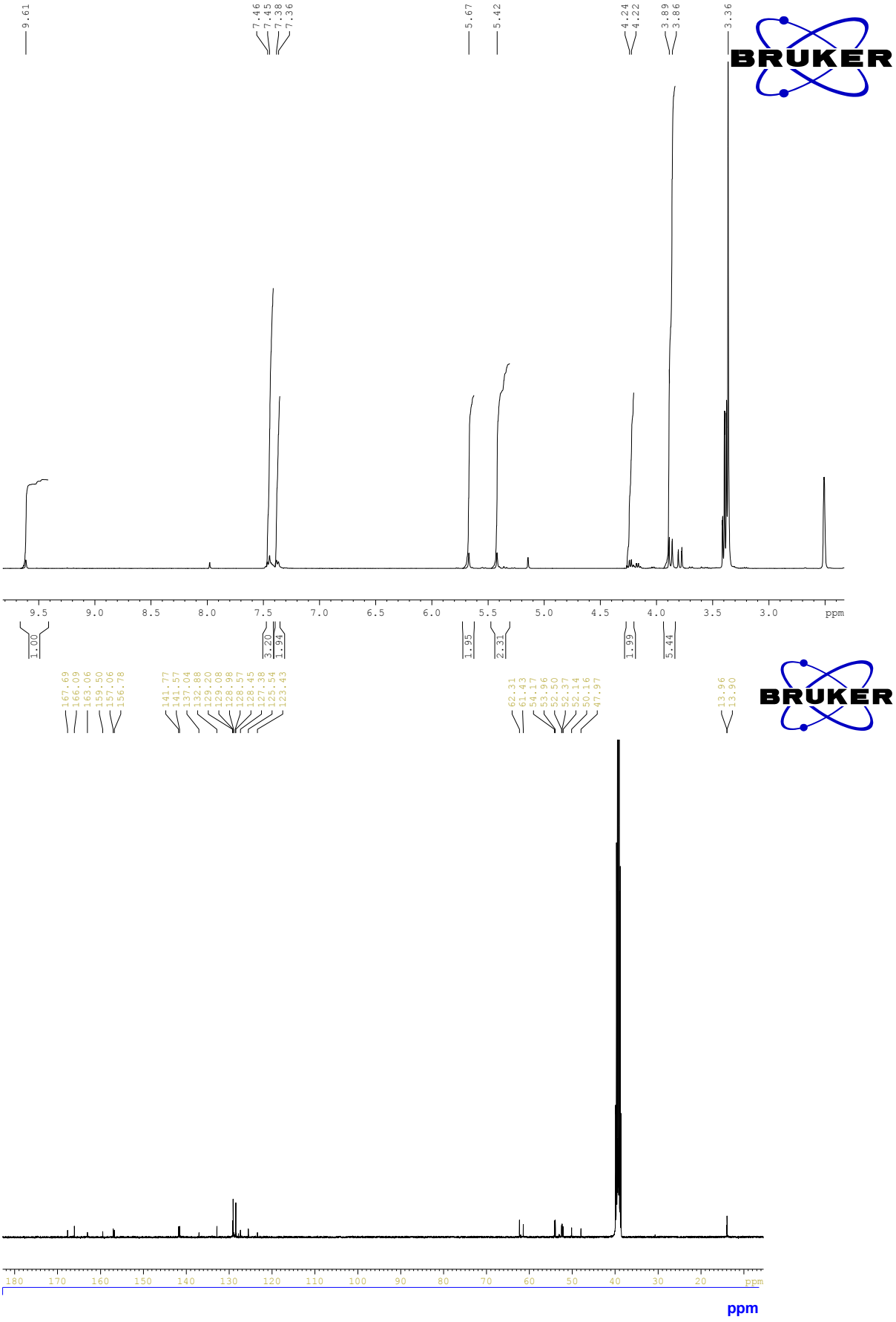




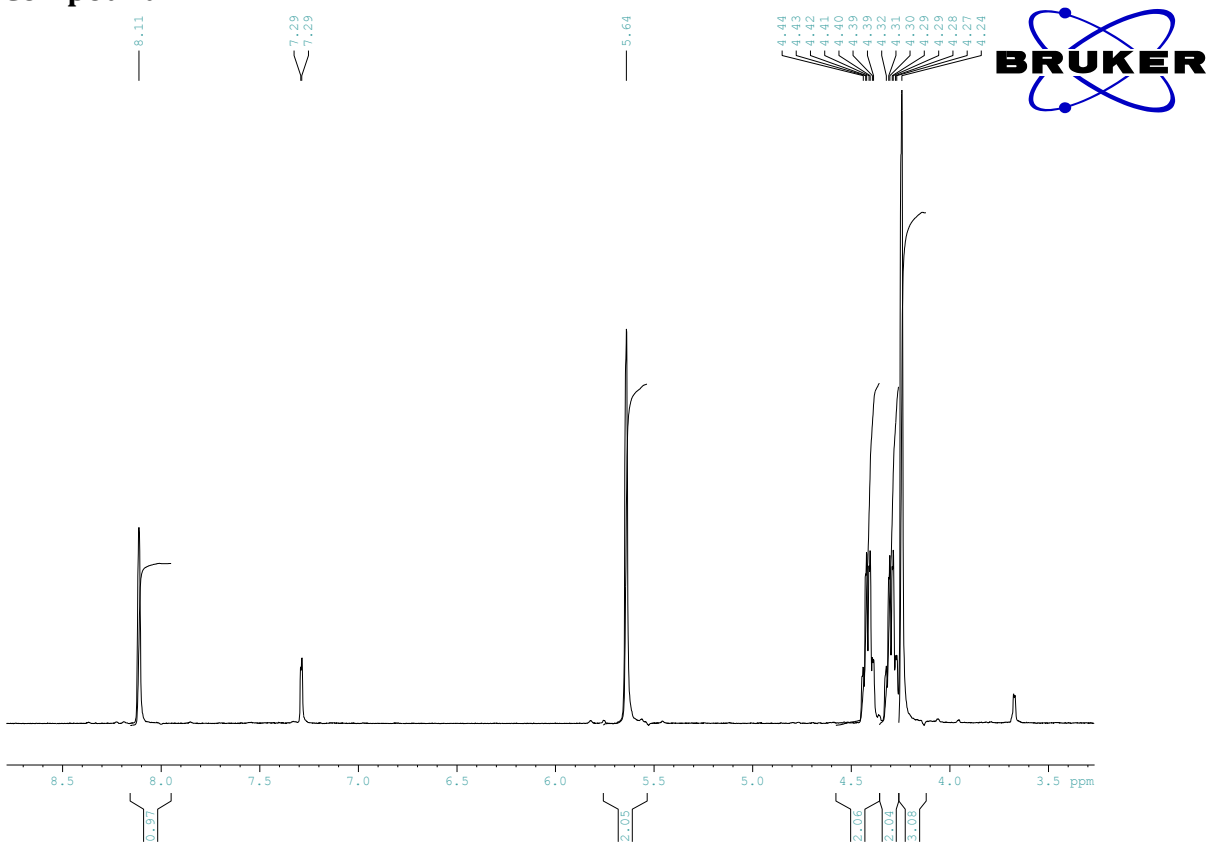
Compound 17

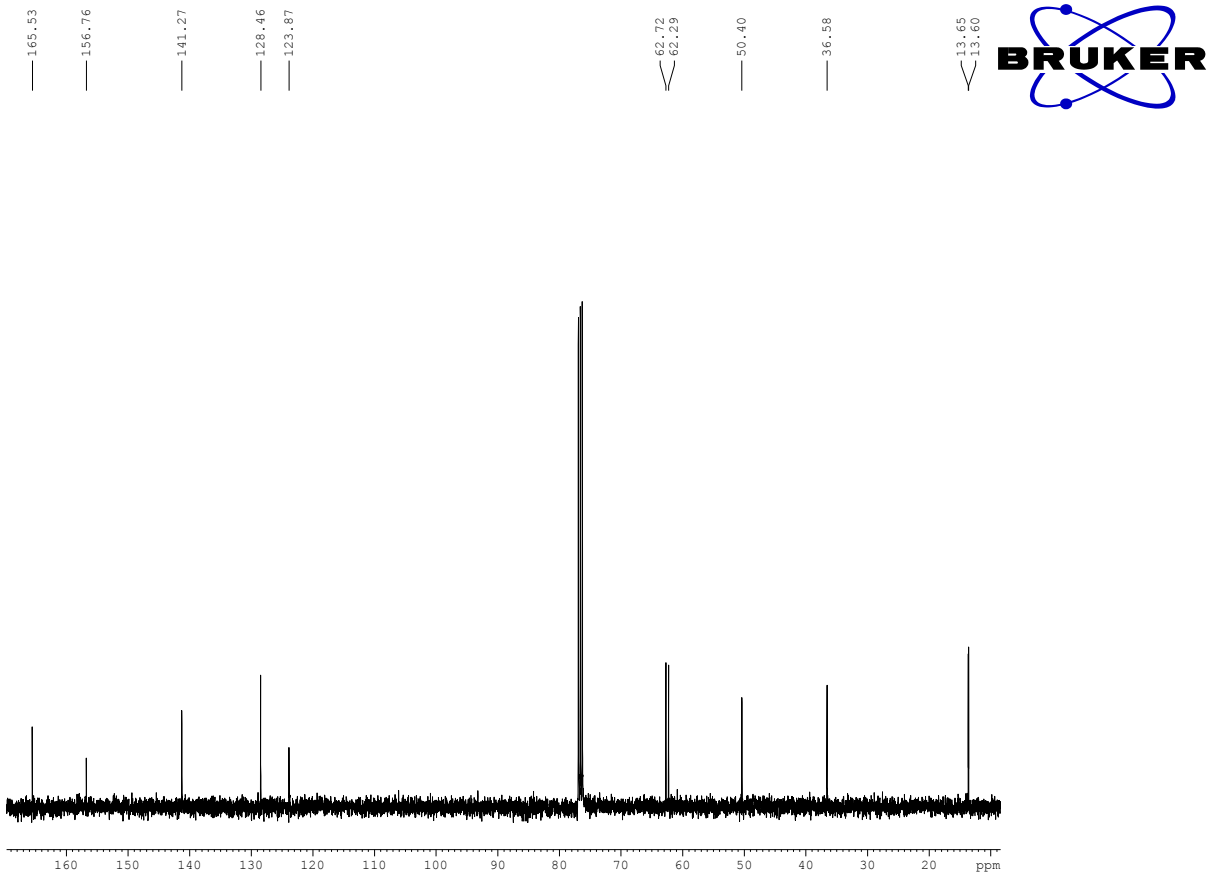


Compound 20

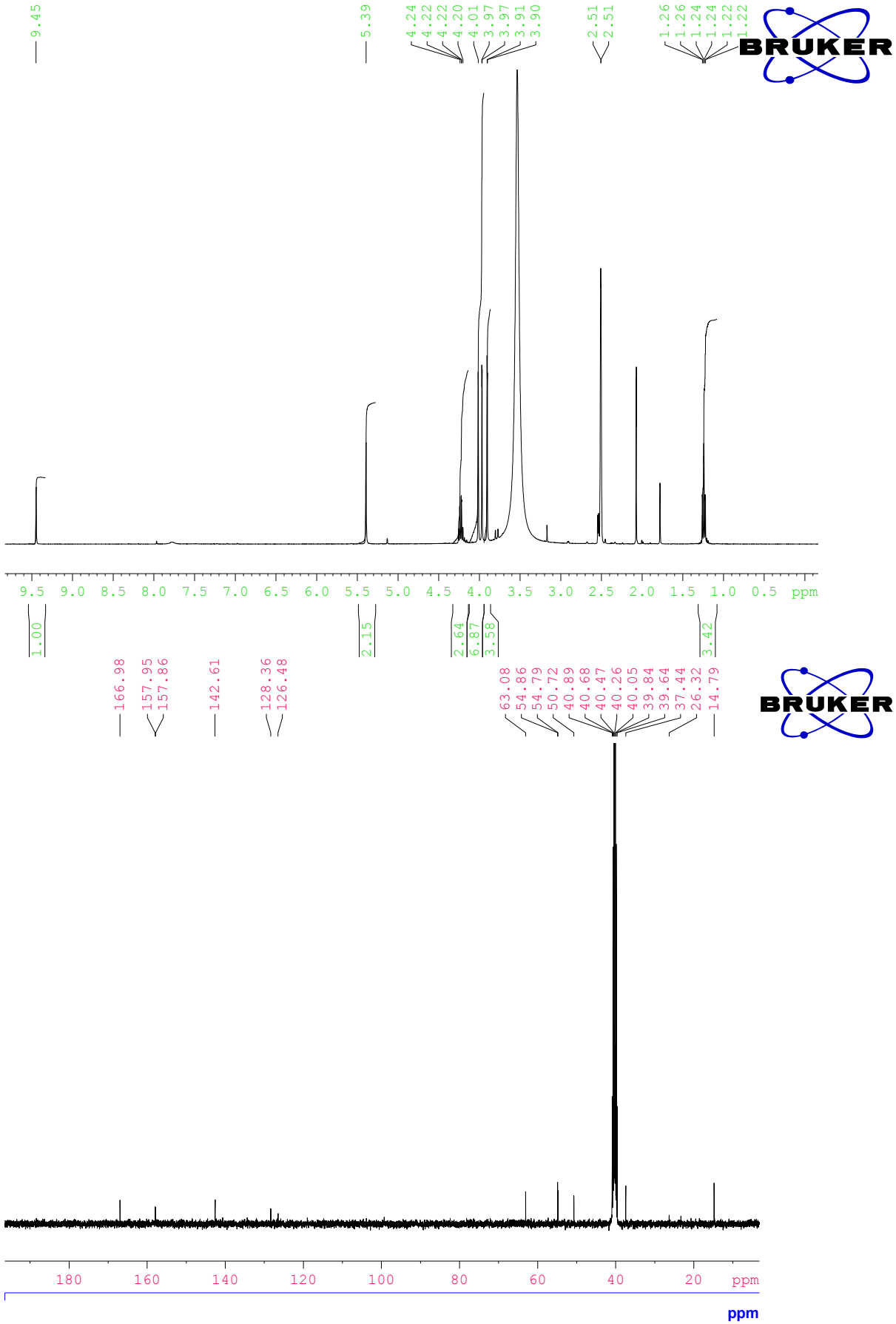


Compound 22

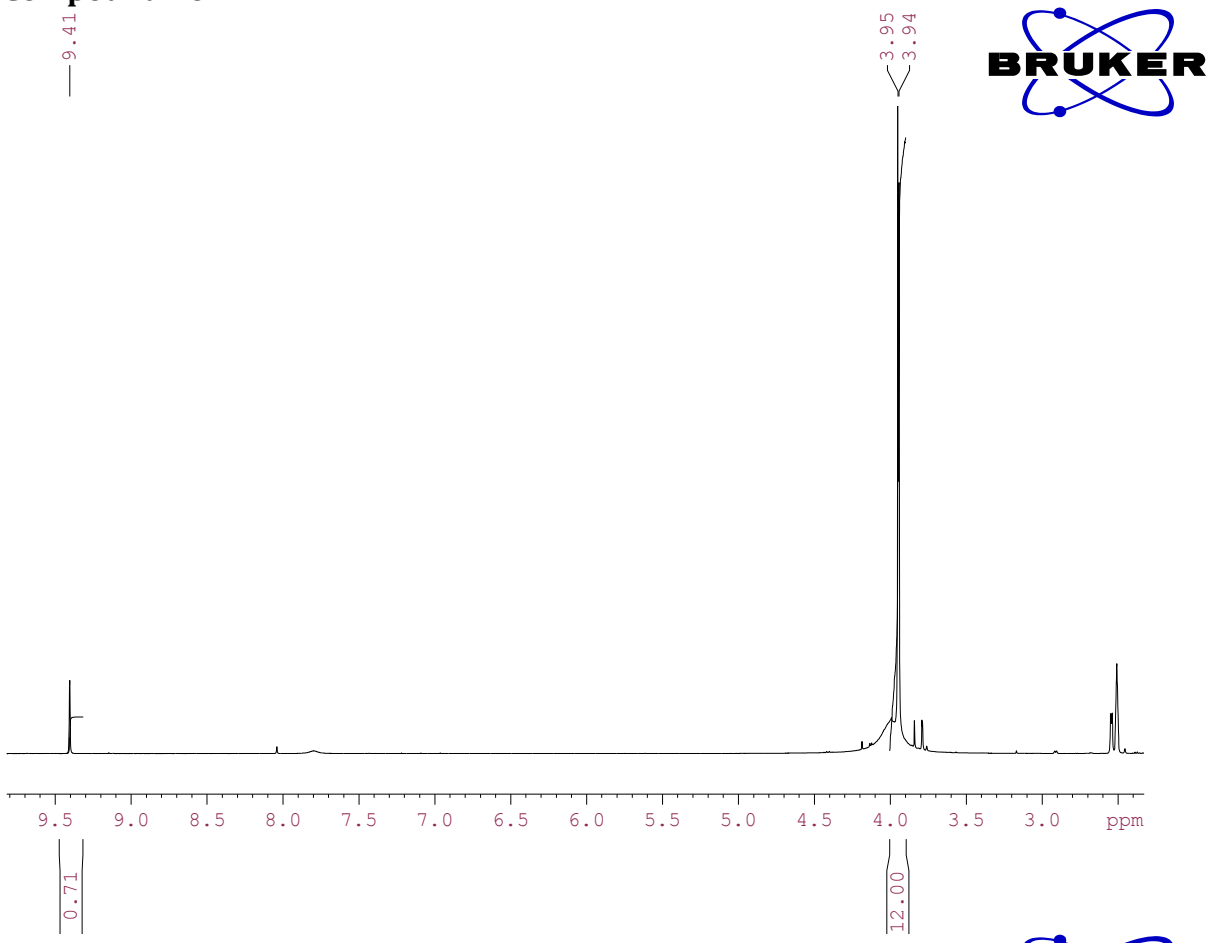


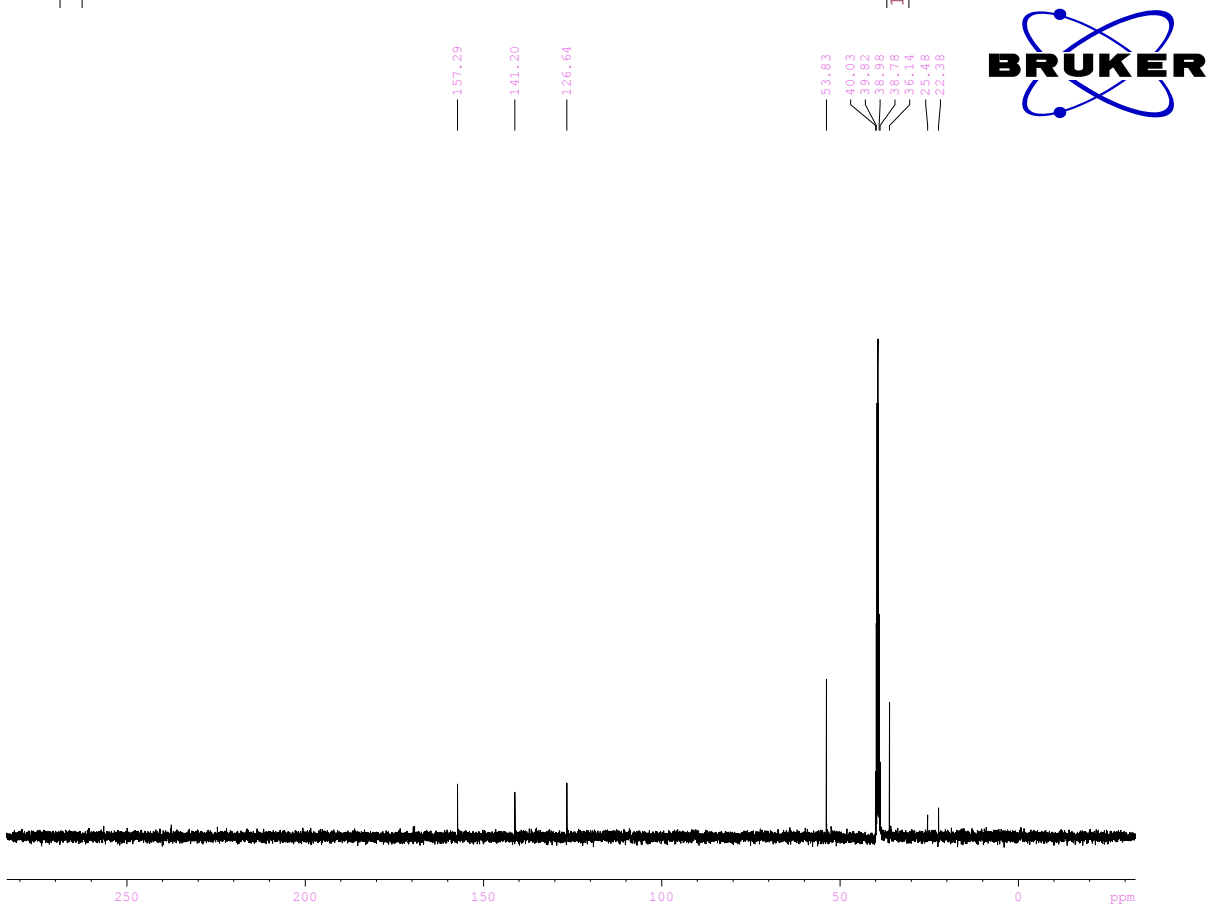


Compound 23

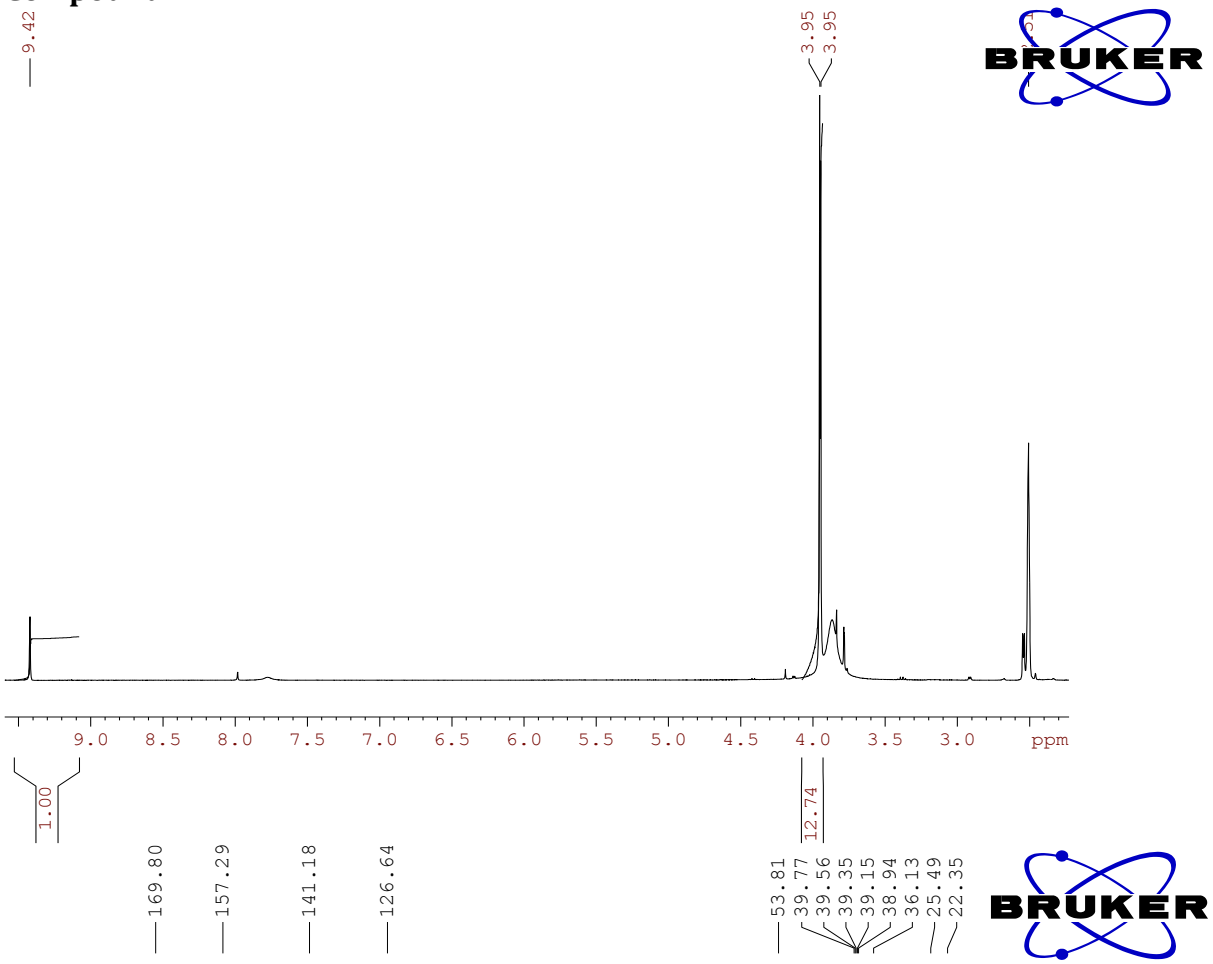

9.45
5.39
4.24
4.22
4.22
4.20
4.01
3.97
3.97
3.91
3.90
2.51
2.51
1.26
1.26
1.24
1.24
1.22
1.22
BRUKER
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.15
2.64
6.87
3.58
3.42
166.98
157.95
157.86
142.61
128.36
126.48
63.08
54.86
54.79
50.72
40.89
40.68
40.47
40.26
40.05
39.84
39.64
37.44
26.32
14.79
BRUKER
180 160 140 120 100 80 60 40 20 ppm
ppm

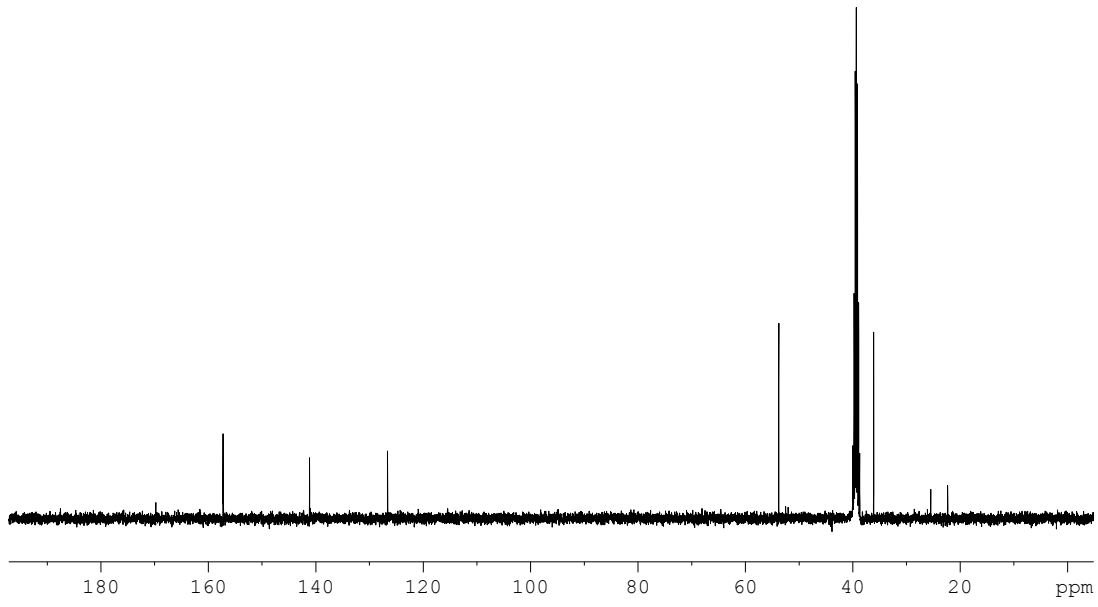
Compound 26



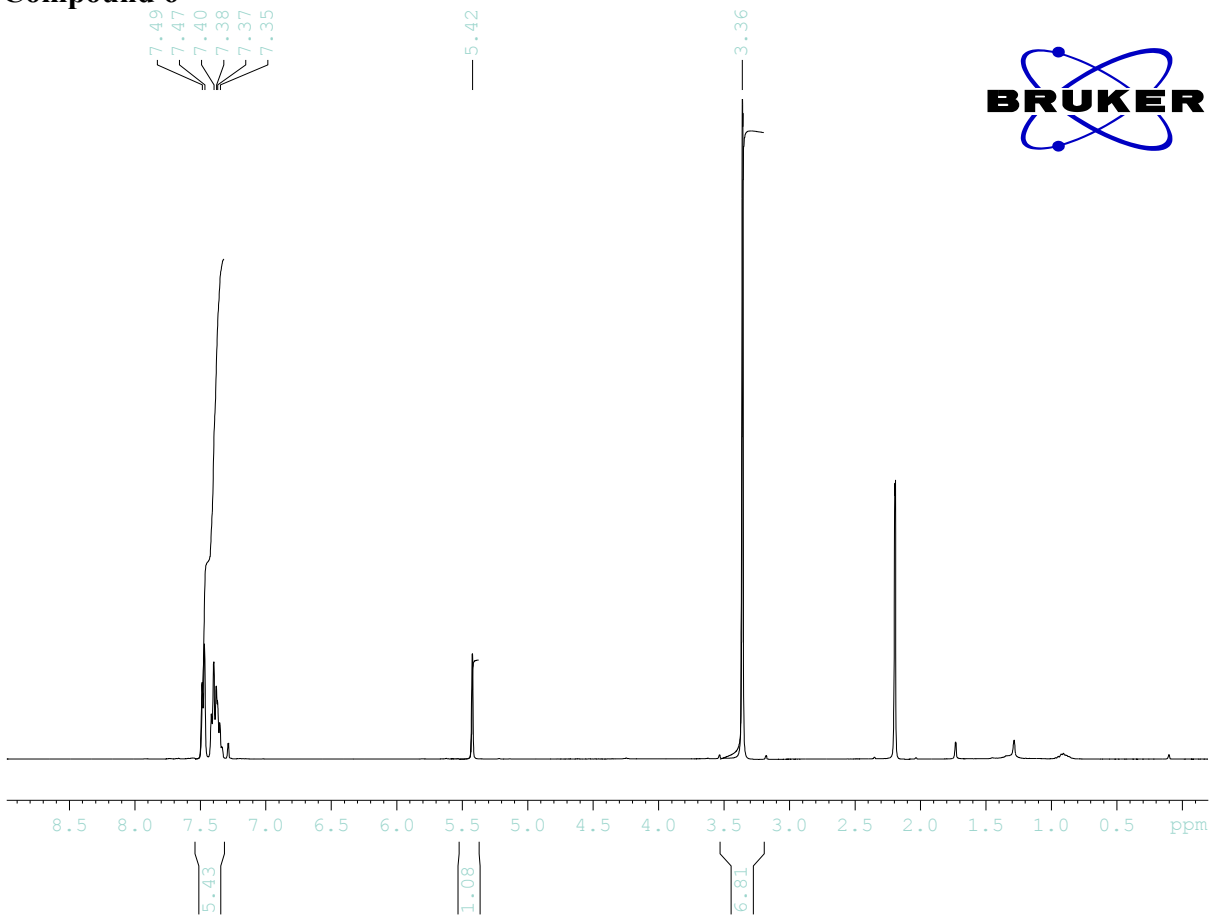


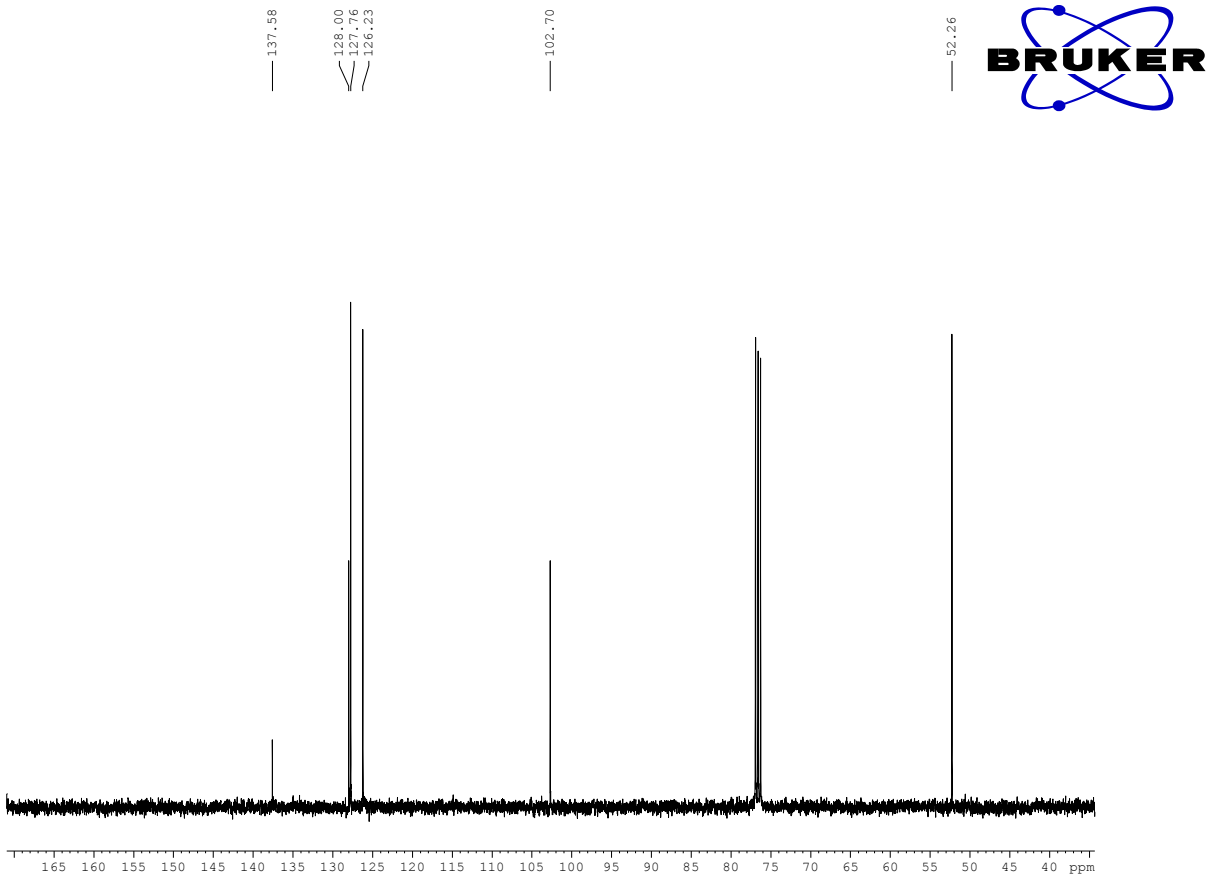
Compound 27



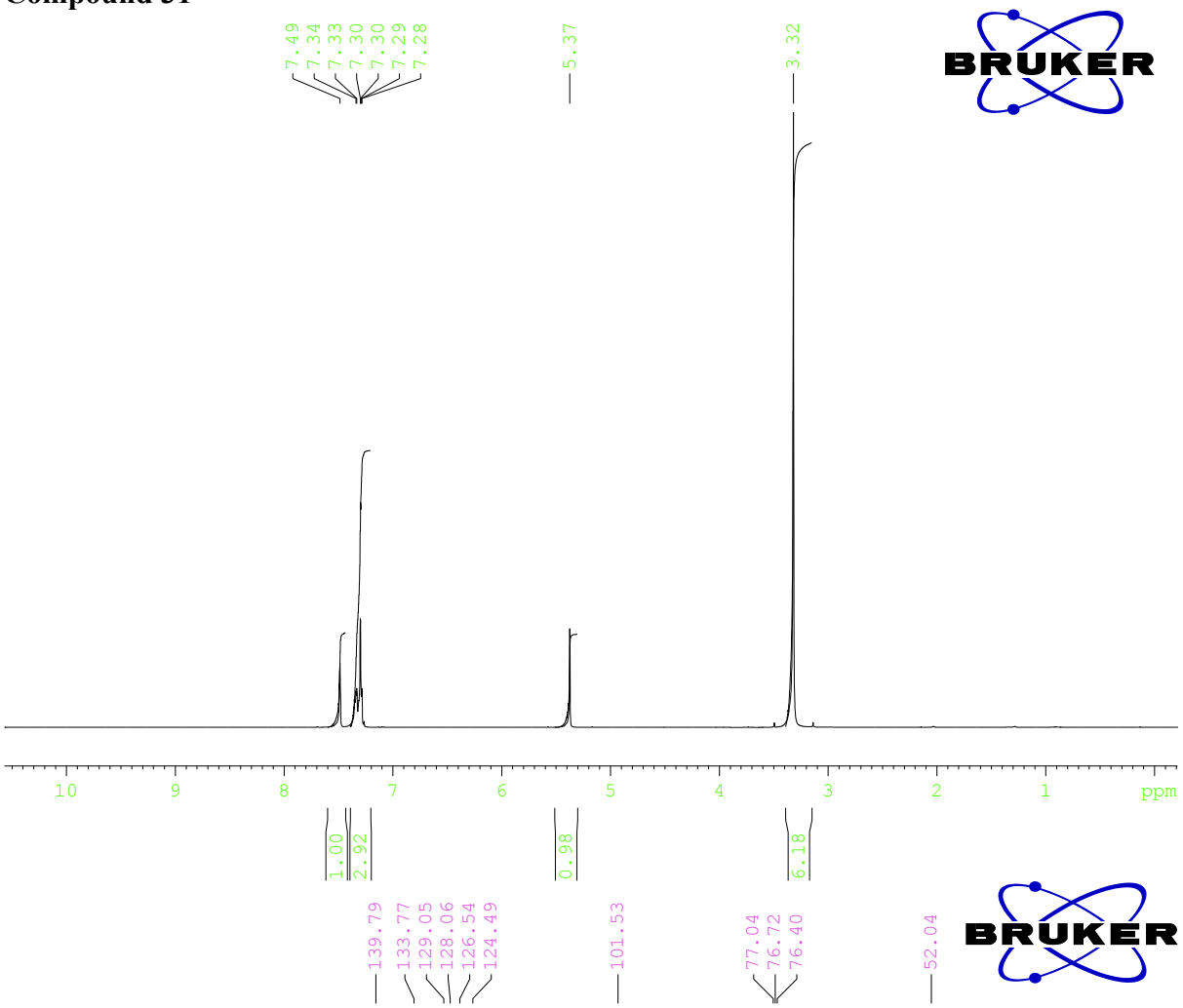


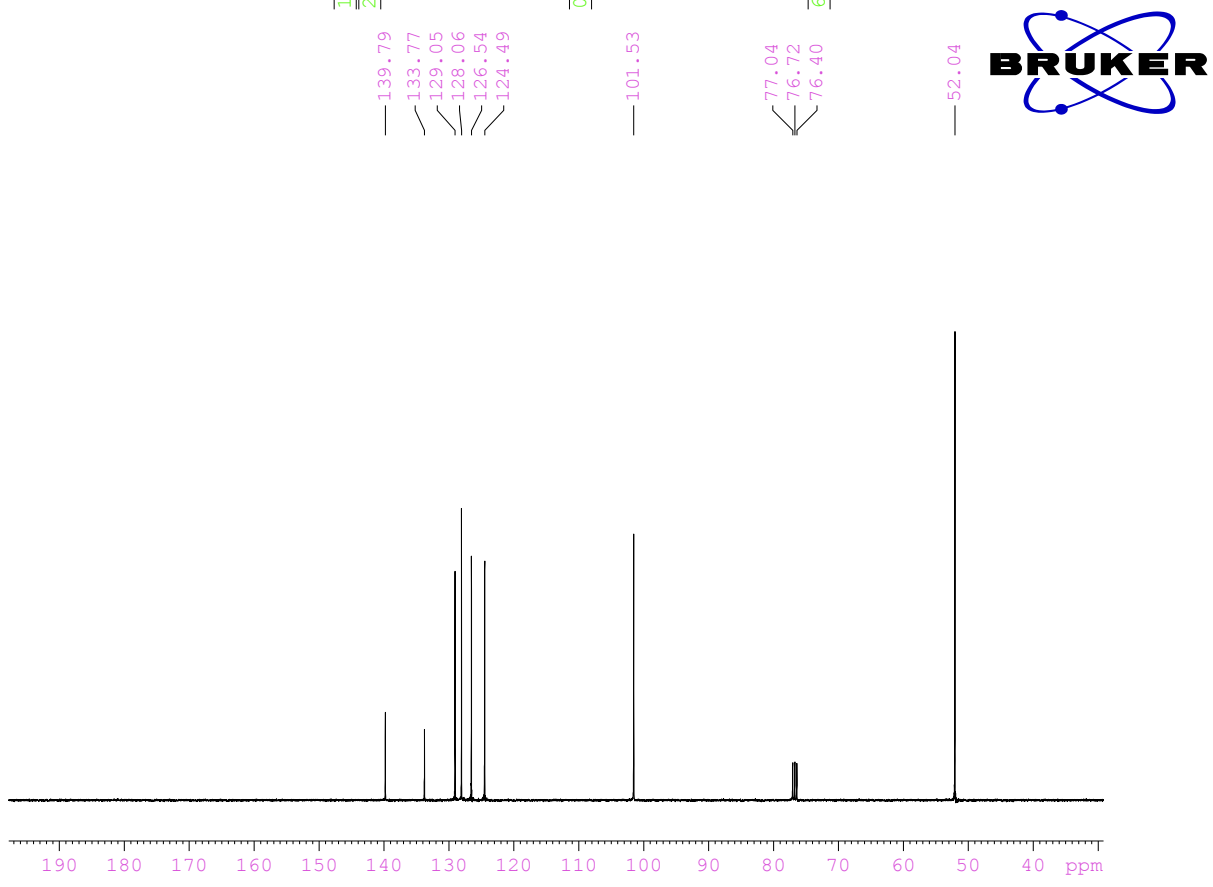
Compound 6



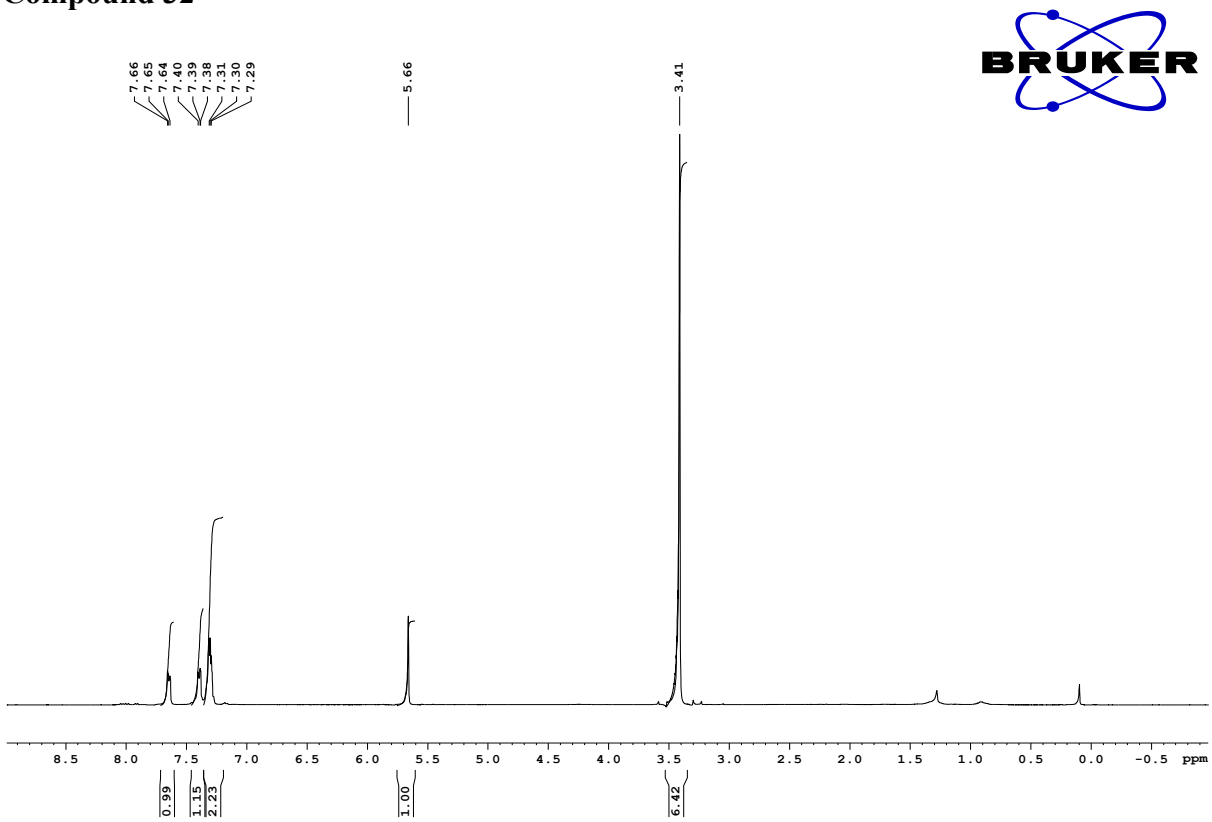


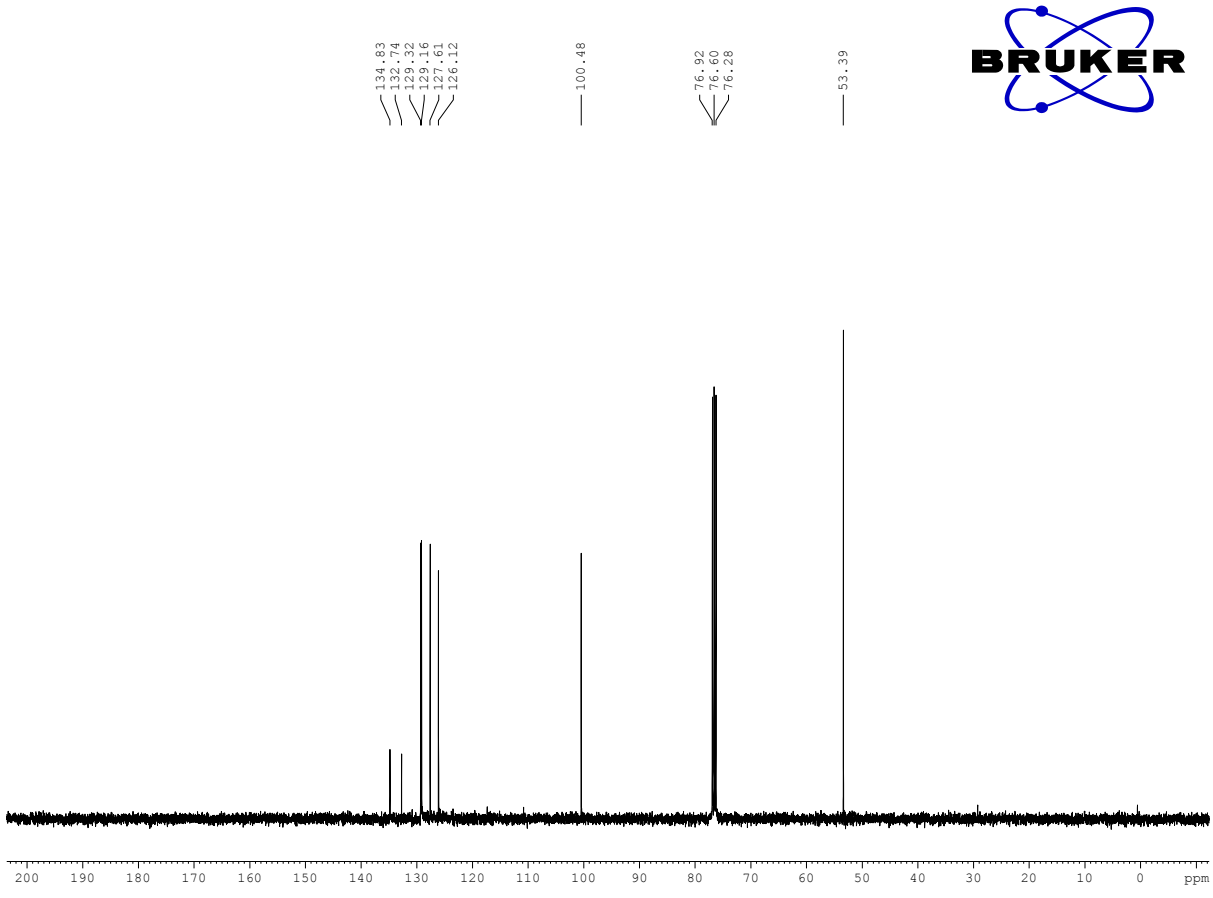
Compound 31



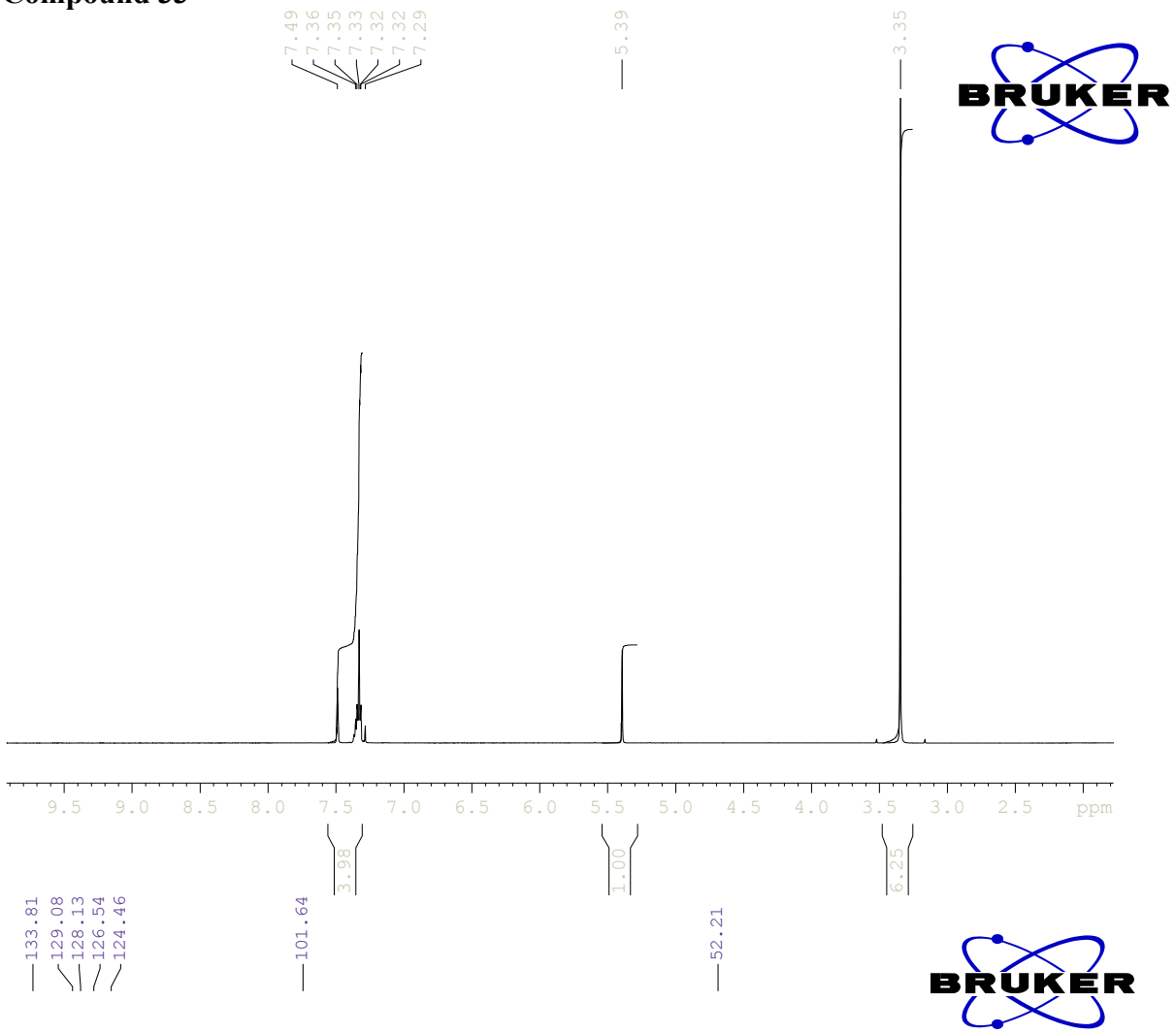


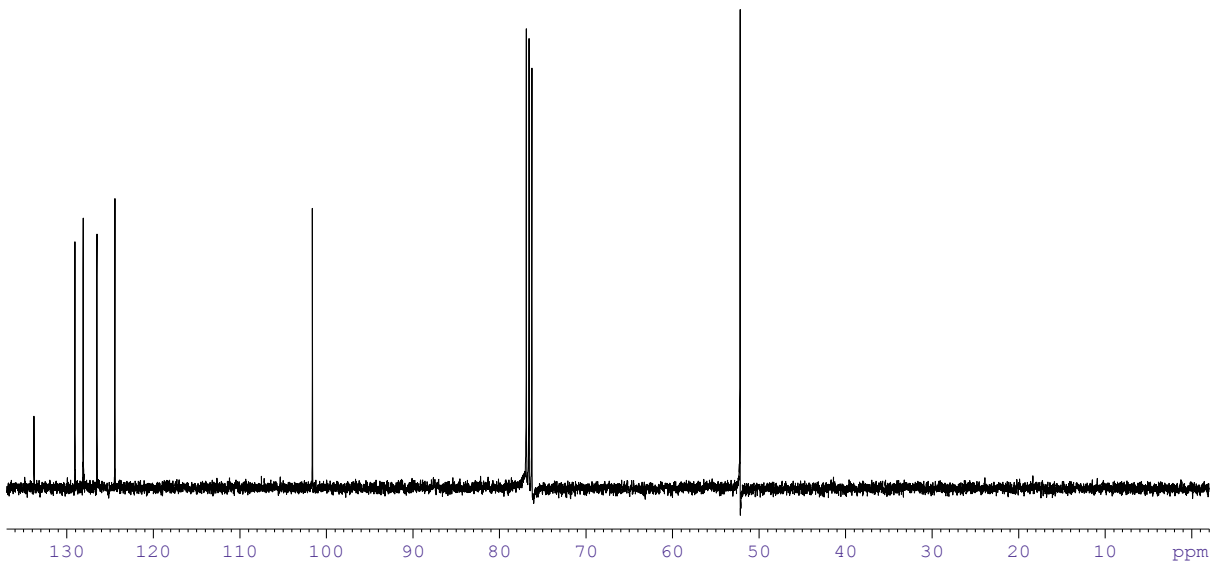
Compound 32


7.66
7.65
7.64
7.40
7.39
7.38
7.31
7.30
7.29
5.66
3.41
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
0.99
1.15
2.23
1.00
6.42

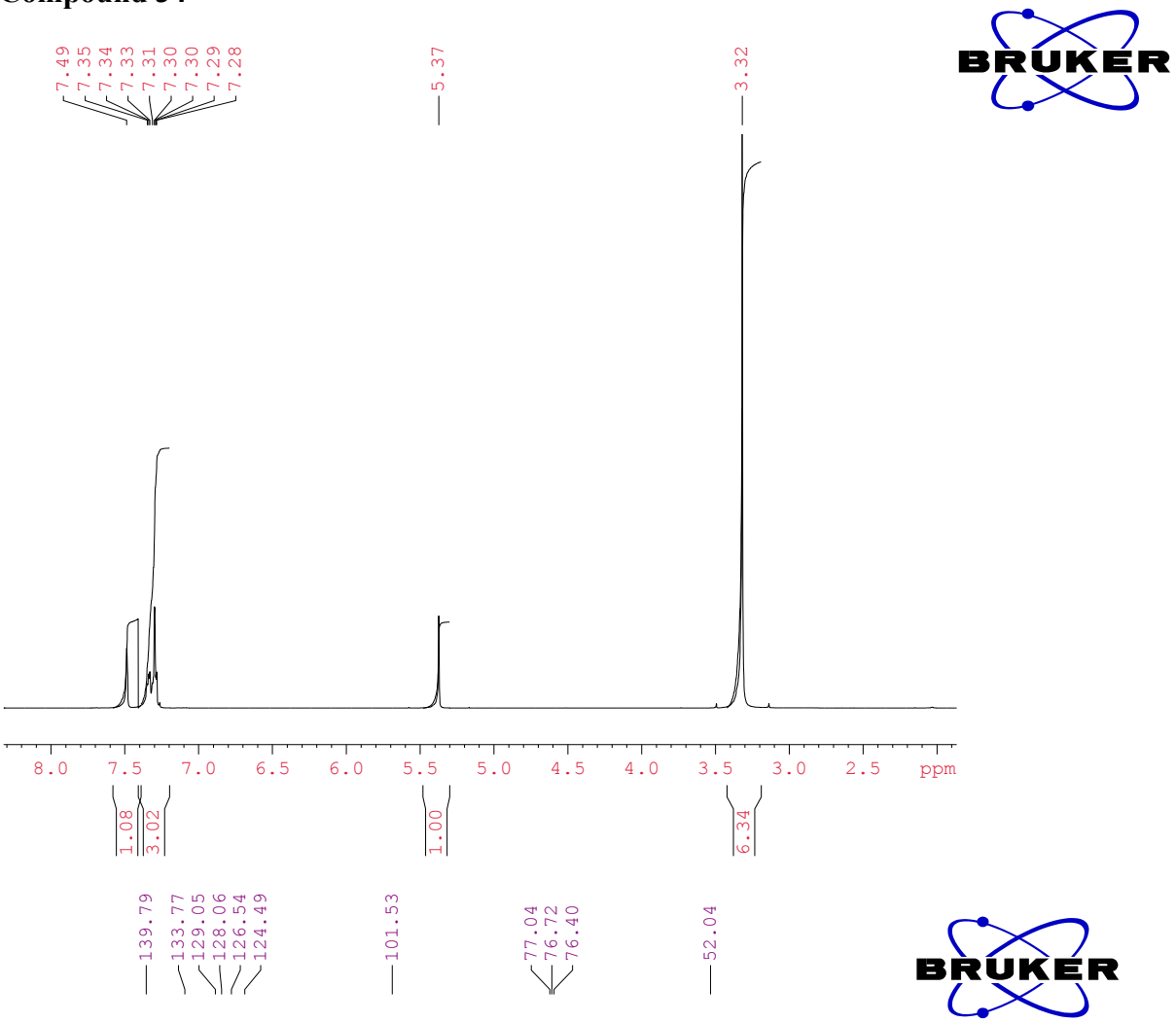

134.83
132.74
129.32
129.16
127.61
126.12
100.48
76.92
76.60
76.28
53.39
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

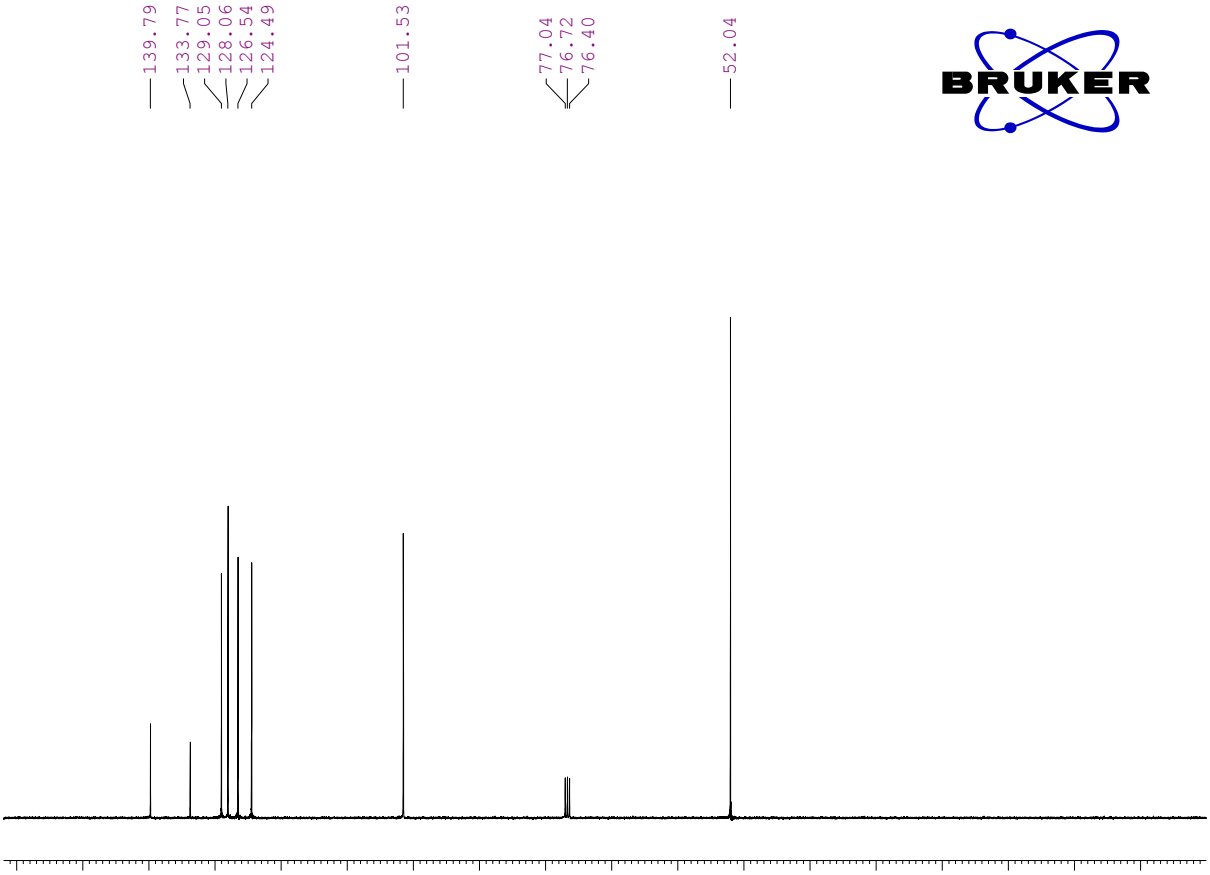
Compound 33



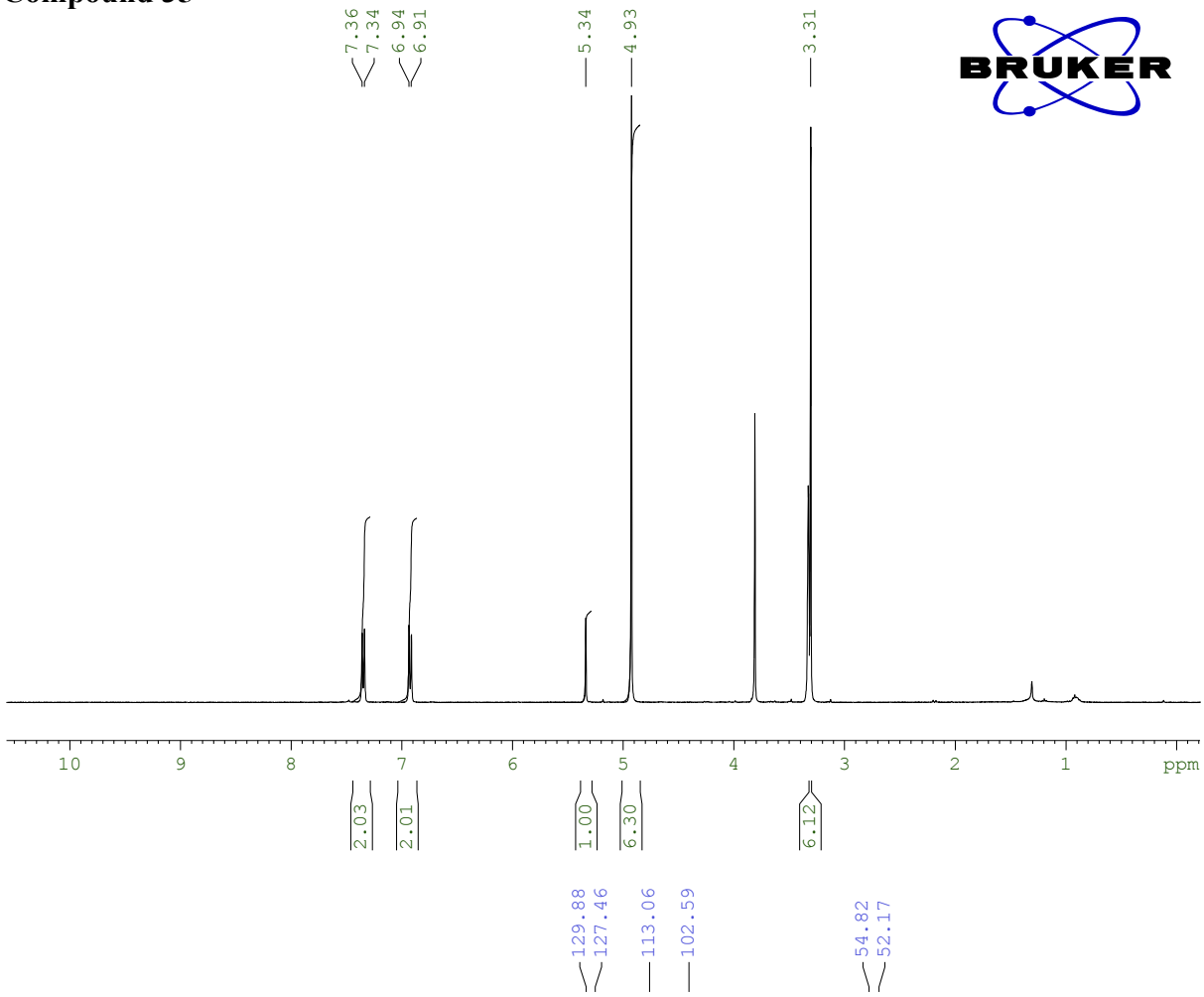


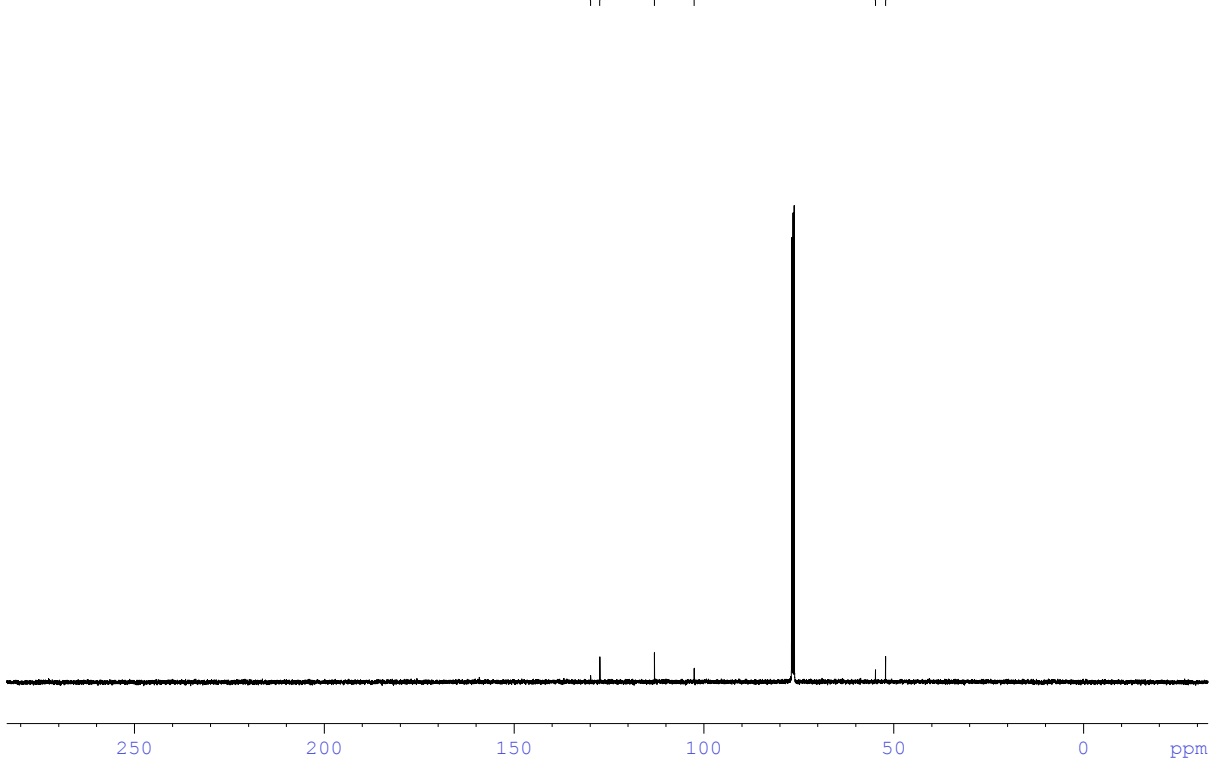
Compound 34



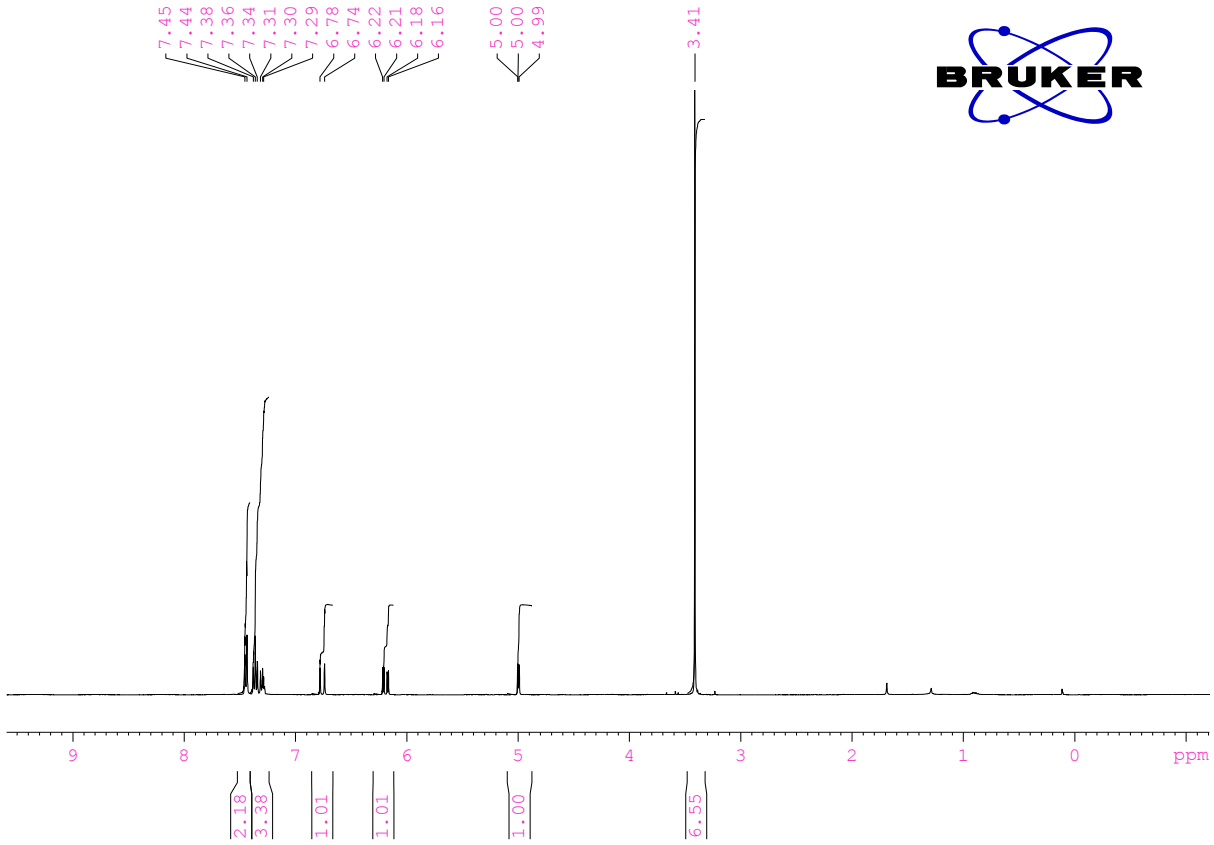


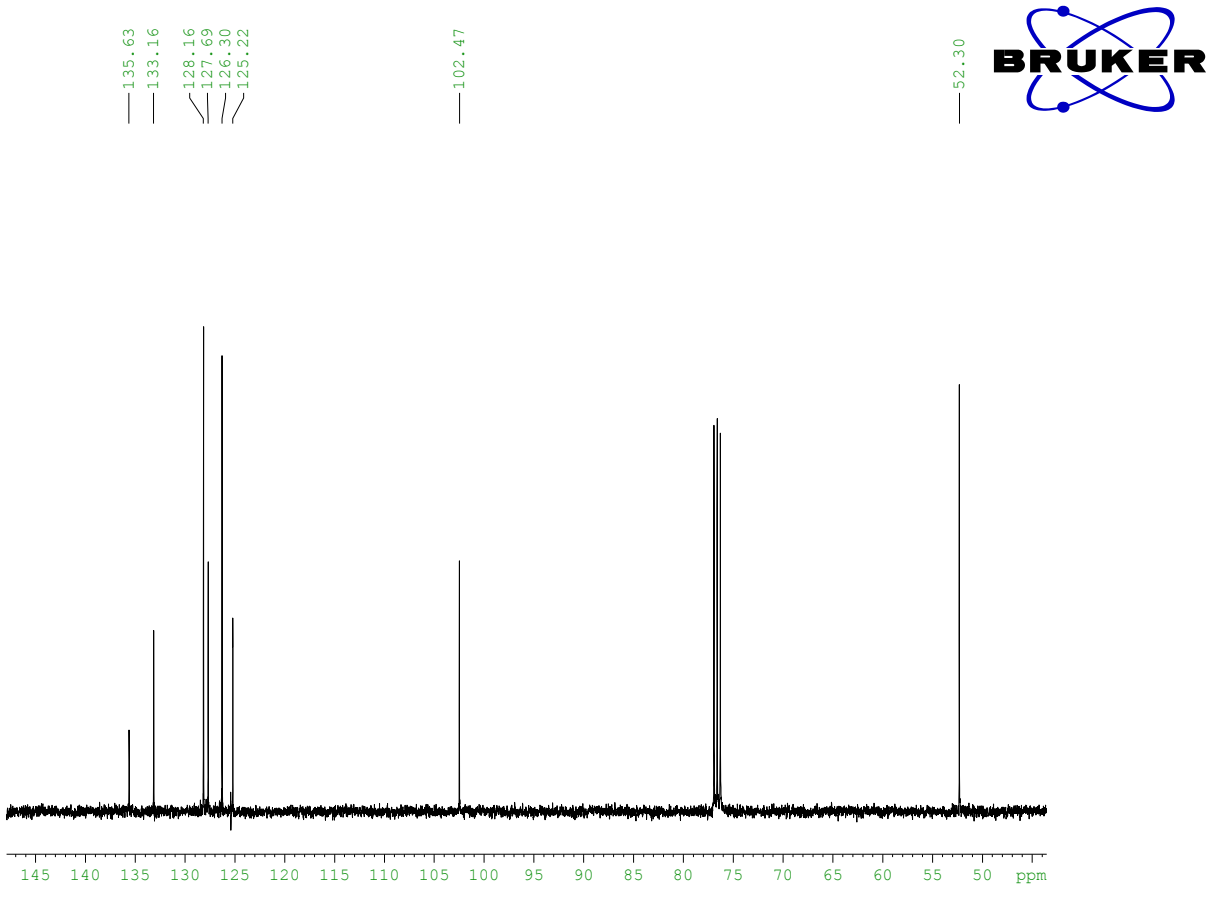
Compound 35



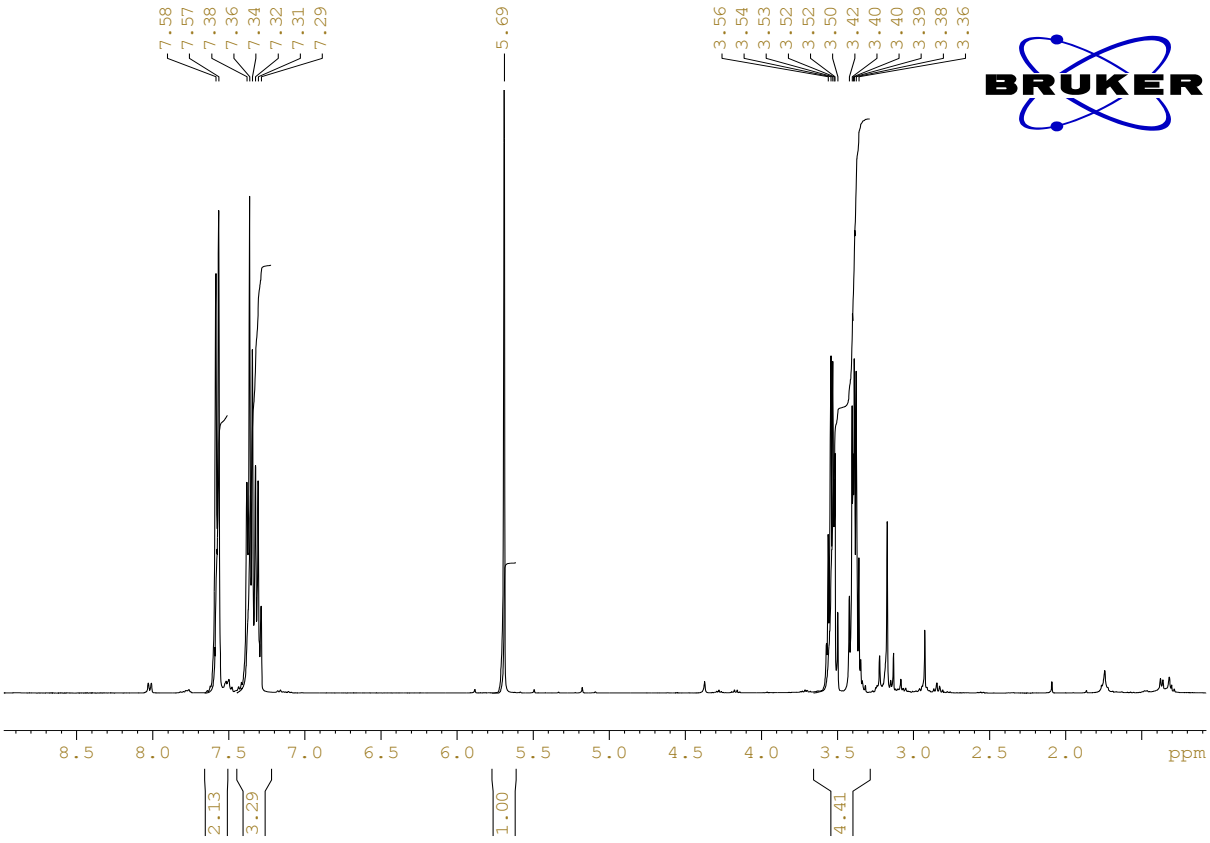


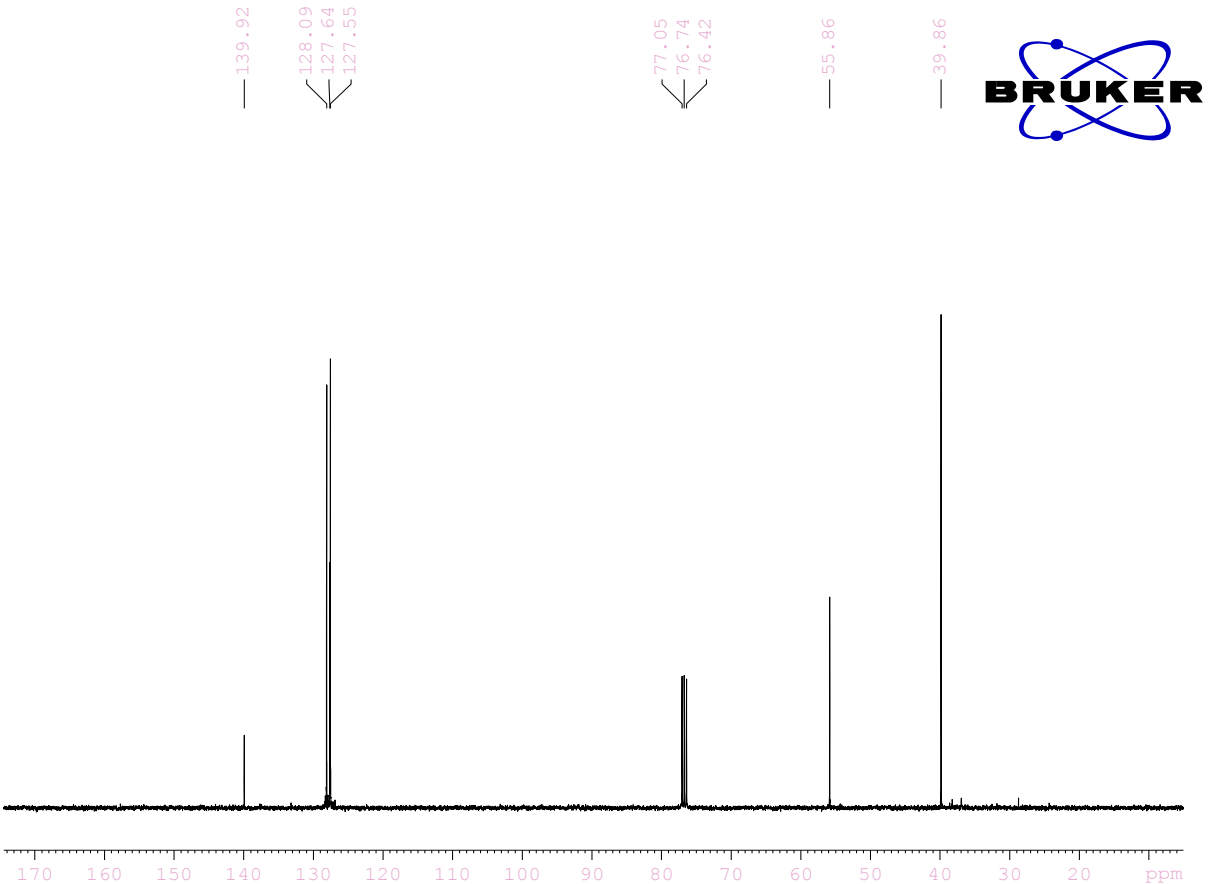
Compound 37



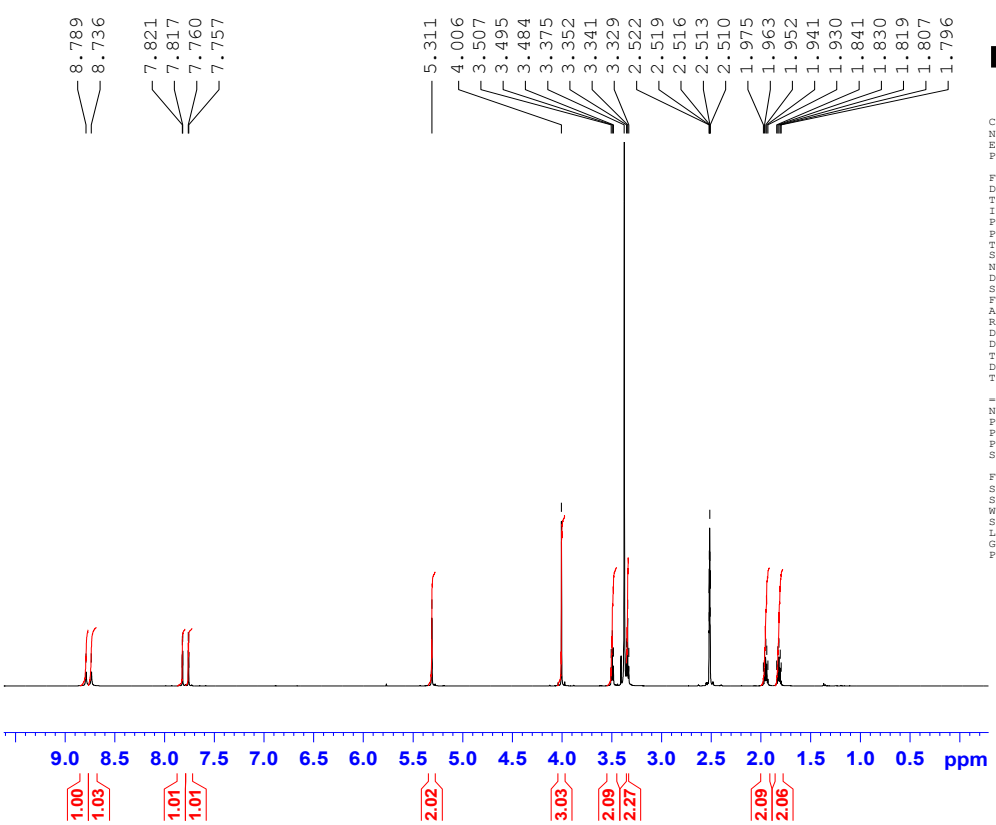


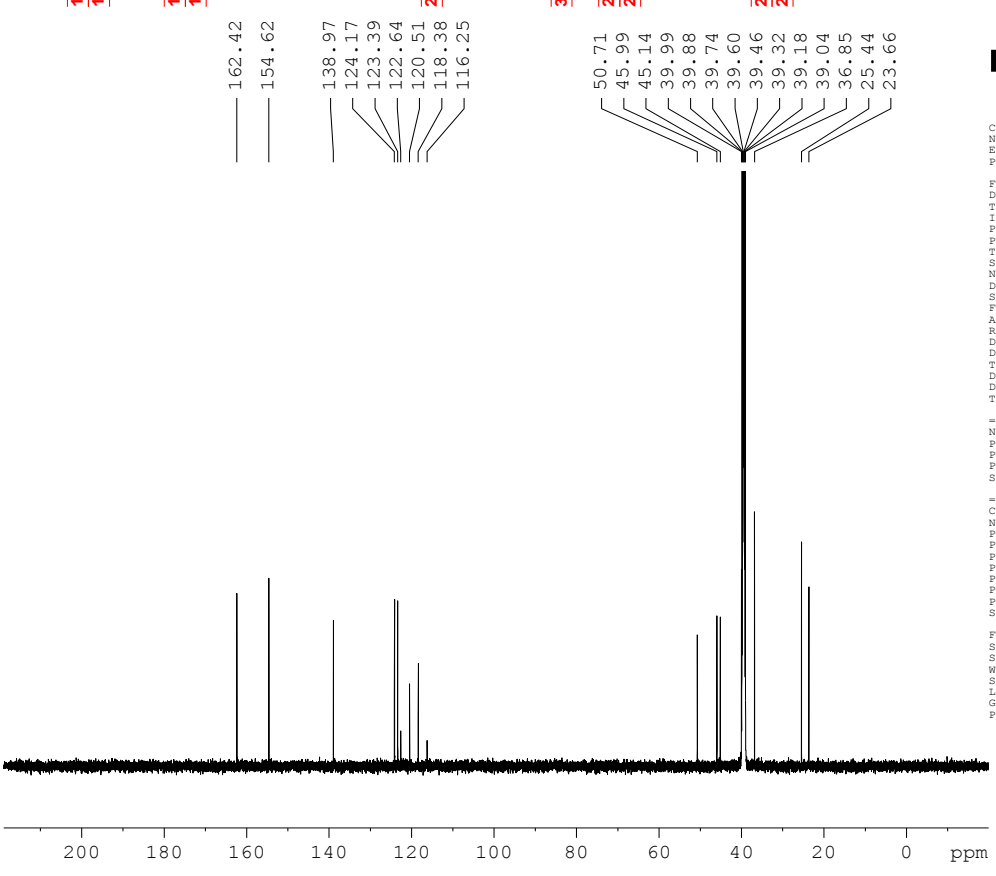
Compound 39





Compound 41





```
Current Data Parameters
NAME                  Feb05-2010
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20100205
Time                       17.41
INSTRUM                    spect
PROBHD  5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                    DMSO
NS                          512
DS                            2
SWH                   12335.526 Hz
FIDRES                0.188225 Hz
AQ                    2.6564426 sec
RG                          181
DW                       40.533 usec
DE                       10.55 usec
TE                       292.7 K
D1                  1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        12.50 usec
PL1                       -5.30 dB
PL1W                25.53414154 W
SFO1               600.3267072 MHz

F2 - Processing parameters
SI                        32768
SF                 600.3230000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

```
Current Data Parameters
NAME                  Feb05-2010
EXPNO                         11
PROCNO                         1

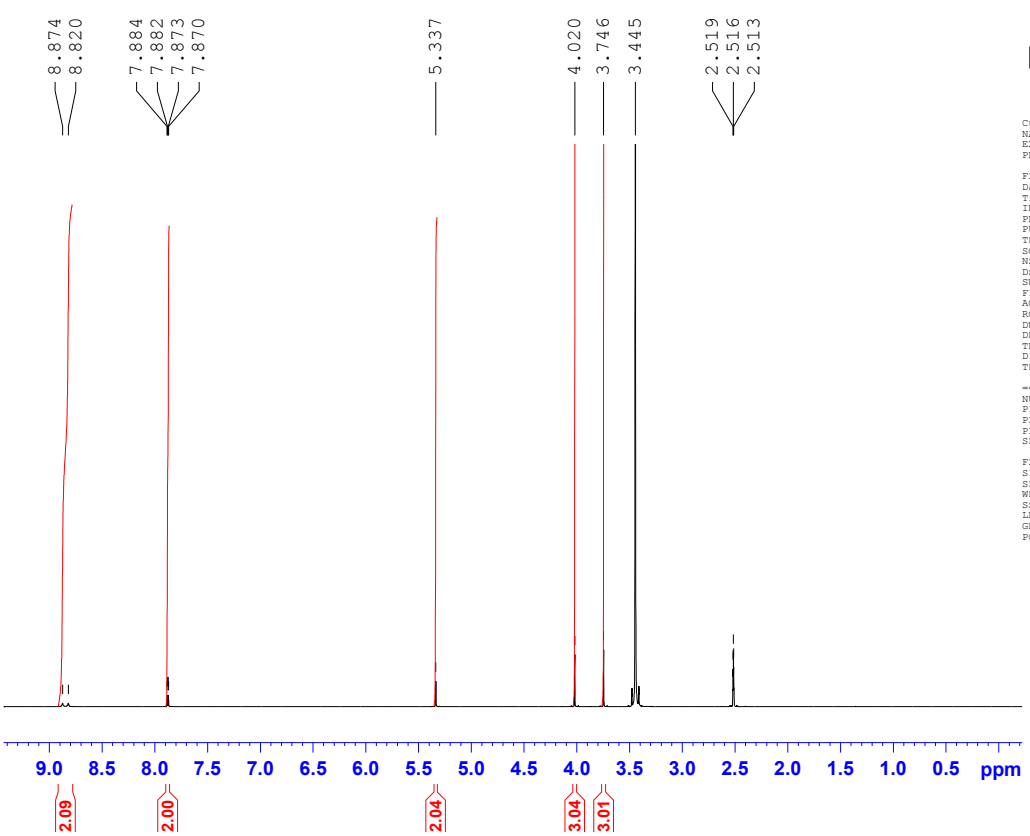
F2 - Acquisition Parameters
Date_                   20100205
Time                       21.05
INSTRUM                    spect
PROBHD  5 mm PABBO BB-
PULPROG                  zgpg30
TD                        65536
SOLVENT                    DMSO
NS                          4096
DS                            4
SWH                   36057.691 Hz
FIDRES                0.550197 Hz
AQ                    0.9088159 sec
RG                         2050
DW                       13.867 usec
DE                        6.50 usec
TE                       293.7 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                         8.00 usec
PL1                        1.50 dB
PL1W                78.77777863 W
SFO1               150.9664335 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                     70.00 usec
PL2                       -5.30 dB
PL12                      10.02 dB
PL13                     120.00 dB
PL2W                25.53414154 W
PL12W                0.75010353 W
PL13W                0.00000000 W
SFO2               600.3254013 MHz

F2 - Processing parameters
SI                        32768
SF                 150.9514145 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

Compound 42



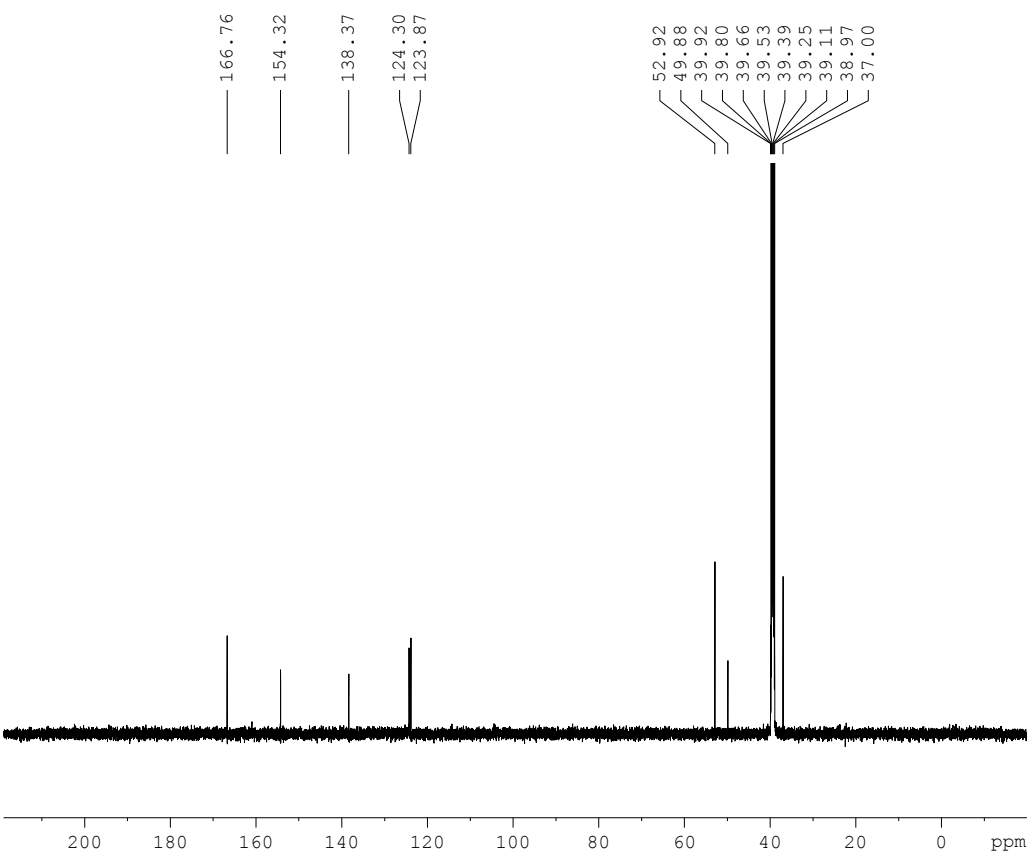
BRUKER

```
Current Data Parameters
NAME                  Dec04-2009
EXPNO                         20
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20091204
Time                       13.47
INSTRUM                    spect
PROBHD  5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                    DMSO
NS                           16
DS                            2
SWH                   12335.526 Hz
FIDRES                0.188225 Hz
AQ                    2.6564426 sec
RG                          101
DW                     40.533 usec
DE                      10.55 usec
TE                        292.5 K
D1                  1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         1H
P1                       12.50 usec
PL1                      -5.30 dB
PL1W                 25.53414154 W
SFO1                600.3267072 MHz

F2 - Processing parameters
SI                         32768
SF                  600.3230000 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```



BRUKER

```
Current Data Parameters
NAME                  Dec04-2009
EXPNO                         21
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20091204
Time                       15.02
INSTRUM                    spect
PROBHD  5 mm PABBO BB-
PULPROG                  zgpg30
TD                        65536
SOLVENT                    DMSO
NS                          1024
DS                             4
SWH                   36057.691 Hz
FIDRES                0.550197 Hz
AQ                    0.9088159 sec
RG                          2050
DW                     13.867 usec
DE                       6.50 usec
TE                        294.2 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                        13C
P1                        8.00 usec
PL1                       1.50 dB
PL1W                78.77777863 W
SFO1               150.9664335 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                    70.00 usec
PL2                      -5.30 dB
PL12                     10.02 dB
PL13                    120.00 dB
PL2W                25.53414154 W
PL12W                0.75010353 W
PL13W                0.00000000 W
SFO2               600.3254013 MHz

F2 - Processing parameters
SI                         32768
SF                 150.9514145 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

7.0 References

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