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Supporting Information

Total Synthesis of Coibacin D by Using Enantioselective Allylation and Metathesis Reactions

Kristýna Kolská,[a] Mukund Ghavre,[b] Milan Pour,[b] Simona Hybelbauerová,[c] and Martin Kotora*[a]

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I General remarks

The following general procedures were used in all reactions unless otherwise noted. Reaction vessels were dried by heat gun under dry argon pressure. Oxygen and moisture sensitive reactions were carried out under slight argon overpressure and in dry solvents. All commercially available reagents were purchased in the best quality and used without further purification unless otherwise noted. Solvents were purified and dried by distillation as follows: THF, Et_2O, and toluene from sodium/benzophenone and CH_2Cl_2 from CaH_2. All reactions were monitored by using TLC on E. Merck silica gel 60 F_{254} coated aluminium plates. Compounds were detected at long wave UV (254 nm) or visualized using anisaldehyde stain (15 g anisaldehyde, 2.5 mL conc. H_2SO_4 / 250 mL EtOH) and subsequent heating. Column chromatography was performed on Merck Silica gel 60 (0.040-0.063 µm, 240-400 mesh) or Merck PLC Silica gel 60 F_{254}, 0.5 mm. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on Varian UNITY 300 MHz and Bruker AVANCE III 600 MHz spectrometer. Chemical shifts are given in δ scale (ppm units). All NMR spectra were referenced to residual solvent signal of $CDCl_3$ (^{1}H δ 7. 26, ^{13}C δ 77. 0). NMR experiments with internal standard were performed by using mesitylene. Infrared spectra were recorded with Thermo Nicolet AVATAR 370 FT-IR spectrometer on KBr tablets of the compounds via DRIFT method and reported in wave numbers (cm^{-1}). High resolution mass spectra were recorded on VG-Analytical ZAB-SEQ or AT 6530 Accurate-Mass Q-TOF LC/MS. Optical rotations were recorded on AUTOMATIC POLARIMETR, Autopol III are measured with accuracy of ±2 given in (deg·mL)/(g·dm)cm^2 g^{-1} with accuracy ±2 and the mass concentrations (marked as *c* are given in g/100 mL. In this respect it is necessary to note that given the low concentration of some measured samples, the final error in the measurement was rather large.

II Preparation of 1,5-pentadienes 2 and 4

(*E*)-(2-Allylhex-1-enyl)trimethylsilane (4a). The synthesis was based on the previously reported methodology.[1] To a solution of Cp_2ZrCl_2 (5 g, 17.10 mmol) in THF (70 mL) ethylmagnesium bromide (34.2 mL, 34.20 mmol) was added at -78 °C under argon atmosphere and stirred for 30 min at -78 °C and then for 1 h at room temperature. Then 1-trimethylsilylhex-1-yne (5.8 mL, 28.50 mmol) was added. After 1 h of stirring allyloxytrimethysilane (3.0 mL, 17.80mmol) was added and reaction was heated to 60 °C for 3 hs under reflux. The reaction was quenched with 3M HCl (8 mL) and extracted by CH_2Cl_2 (3×15 mL). The organic layer was separated and dried over Na_2SO_4 and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane) gave 2.53 g (90%) of a mixture of **4a** and ***Z*-4a** (97/3) as a colorless viscous liquid.

^1H NMR (400 MHz, $CDCl_3$, 25 ºC) δ 0.04-0.15 (s, 9H), 0.84-1.05 (m, 3H), 1.19-1.51 (m,4H), 2.02-2.23 (m, 2H), 2.82 (dd, *J* = 7.1, 1.5 Hz, 2H), 4.95-5.13 (m, 2H), 5.20 (s, 1H), 5.69-5.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC) δ 0.37 (3C), 14.09, 23.00, 31.25, 35.96, 43.45, 115.95, 124.26, 136.88, 157.95; IR (KBr) ν 3081, 2956, 2926, 2860, 1607, 1467, 1458, 1245, 911, 887, 839, 689 cm^{-1}; MS-EI m/z (% relative intensity) 196.2 (M+, 14), 182.1 (12), 181.1. (62), 155.1 (18), 154.1 (76), 153.1 (14), 140.1 (6), 139.1 (44), 137.1 (6), 125.1 (17), 123.1 (12), 121.1 (8), 111.1 (17), 109.0 (10), 99.1 (60), 97.0 (21), 95.0 (8), 85.0 (16), 80.1 (16), 75.0 (8), 74.0 (18), 73.6 (24), 73.0 (100), 71.0 (7), 59.0 (54); HR-EI calculated for $C_{12}H_{24}Si$ 196.1647, found 196.1649. R_f (hexane) = 0.89.

Characteristic signals of ***Z*-4a** isomer: 2.88 (td, *J* = 7.9, 1.5 Hz, 2H), 5.27 (s, 1H), other peaks were overlapped by the major product.

(*E*)-Trimethyl(2-methylpenta-1,4-dien-1-yl)silane (4b). To a solution of Cp_2ZrCl_2 (7 g, 23.95mmol) in THF (70 mL) ethylmagnesium bromide (48.0 mL, 48.00 mmol) was added at -78 °C under argon atmosphere and stirred for 30 min at -78 °C and then for 1 h at room temperature. Then 1-trimethylsilylprop-1-yne (6 mL, 22.0 mmol) was added. After 1 h of stirring allyloxytrimethysilane (4.2 mL, 24.92mmol) was added and reaction was heated to 60 °C for 3 h under reflux. The reaction was quenched with 3M HCl (5 mL) and extracted by ether (3×10 mL). The organic layer was separated and dried over Na_2SO_4 and decaline was added. Fractional distillation of the mixture containing the product furnished several fractions containg various amounts of **4b**. The collected fractions provided 1.5 g (54 %) of a colorless viscous liquid containing mostly the desired product **4b** (~85%), **(*Z*)-4b** (**4b**/**(*Z*)-4b** 95/5), small amounts of decaline, and other unidentified compounds. The total amount of **4b** in each fraction was determined by ^1H NMR.

^1H NMR (400 MHz, $CDCl_3$, 25 ºC) δ 0.02-0.23 (m, 9H), 1.77-1.83 (m, 3H), 2.80 (dd, *J* = 6.8, 1.2 Hz, 2H), 4.93-5.19 (m, 2H), 5.23 (s, 1H), 5.74-5.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC) δ 0.11, 21.66, 46.88, 115.89, 124.17, 136.60, 153.20. The spectral characteristics were in agreement with the previously reported data.[2]

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[1] (a) Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. *Tetrahedron Lett.* **1994**, *35*, 5685-5688. (b) Takahashi, T.; Suzuki, N.; Kageyama, M.; Kondakov, D. Y.; Hara, R. *Tetrahedron Lett.* **1993**, *34*, 4811-4814.

[2] Fujiwara, M.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 4095-4101.

Characteristic signals of ***Z*-4b** isomer: 2.86 (td, *J* = 7.6, 2.7, 1.4 Hz, 2H), 5.29 (s, 1H), other peaks were overlapped by the major product.

(*E*)-4-(Halogenomethylene)oct-1-ene (2). To a solution of **4** (200 mg, 1.00 mmol) in DMF/MeCN (3 mL) NBS/NCS (362/272 mg, 2.00 mmol) was added at 0 °C under argon atmosphere. The reaction mixture was stirred for 1-3 days at 20 or 45 °C (see Table 1). The reaction was quenched with the saturated solution of $NaHCO_3$ (1 mL) and extracted by hexane (3×2 mL). The combined organic fractions were dried over Na_2SO_4 and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane) provided products as viscous liquids.

(*E*)-4-(Chloromethylene)oct-1-ene (2a) and (*Z*)-4-(chloromethylene)oct-1-ene ((*Z*)-2a). Column chromatography provided 70 mg (43 %) of a mixture of **2a** and **(*Z*)-2a** (88/12) as a yellowish viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 0.79-1.05 (m, 3H), 1.18-1.48 (m, 4H), 2.13-2.41 (m, 2H), 2.78 (dq, *J* = 6.7, 4.1, 1.5 Hz, 2H), 4.96-5.19 (m, 2H), 5.65-5.91 (m, 1H); 5.80 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC) δ 13.93, 22.56, 29.07, 29.98, 39.20, 113.12, 117.03, 135.09, 141.26; IR (KBr) ν 3081, 2956, 2875, 2860, 1640, 1467, 1455, 1251, 991, 919, 893, 842, 797, 764 cm^{-1}; MS-EI m/z (% relative intensity) 160.1 (M+2, 33), 158.1(99), 123.1 (81), 121.1 (23), 116.0 (34), 115.0 (13), 109.1 (15), 107.1 (15), 95.1 (20), 93.1 (17), 82.1 (11), 81.1 (100), 79.1 (25), 67.1 (49); HR-EI calculated for $C_9H_{15}Cl$ 158.0862, found 158.0861. R_f (hexane) = 0.86.

Characteristic signals of **(*Z*)-2a** isomer: 2.92 (td, *J* = 6.3, 2.8, 1.7 Hz, 2H), 5.83 (s, 1H), other peaks were overlapped by the major product.

(*E*)-4-(Bromomethylene)oct-1-ene (Br-2a) and (*Z*)-4-(bromomethylene)oct-1-ene ((*Z*)-Br-2a). Column chromatography provided 107 mg (52 %) of a mixture of **Br-2a** and **(*Z*)-Br-2a** (92/8) as a yellowish viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 0.78-1.02 (m, 3H), 1.19-1.50 (m, 4H), 2.16-2.29 (m, 2H), 2.83 (dq,*J* = 7.0, 3.9, 1.2 Hz, 2H), 4.99-5.17 (m, 2H), 5.66-5.85 (m, 1H), 5.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 13.95, 22.56, 29.06, 32.45, 40.34, 102.37, 117.12, 134.94, 144.11; IR (KBr) ν 3081, 2950, 2932, 2869, 2860, 1637, 1464, 1455, 1251, 994, 914, 845, 779 cm^{-1}; MS-EI m/z (% relative intensity) 204.0 (M+2, 24), 202.0 (24), 161.0 (13), 124.1 (9), 123.1 (69), 121.1 (14), 82.1 (9), 81.1 (100), 79.1 (8), 67.1 (47); HR-EI calculated for $C_9H_{15}Br$202.0357, found 202.0363. R_f (hexane) = 0.83.

Characteristic signals of **(*Z*)-Br-2a** isomer: 2.98 (td, *J* = 6.9, 3.0, 1.4 Hz, 2H), 5.95 (s, 1H), other peaks were overlapped by the major product.

SI-Table 1. Halogenolysis of trimethylsilylpenta-1,4-dienes **4** with NBS and NCS

Entry	NXS	Solvent	T (°C)	t (d)	Yield (%)[a]
1	NBS	DMF	r.t.	1	24
2	NBS	DMF	r.t./45	1/1.5h	35
3	NCS	DMF	r.t.	3	0
4	NCS	DMF	45	3	33
5	NCS	DMF	45	2	43
6	NBS	MeCN	r.t.	1	52
7	NCS	MeCN	r.t.	1	0
8	NCS	MeCN	r.t.	3	0
9	NCS	MeCN	r.t./45	3	11
10	NCS	MeCN	45	1	27

[a] Isolated yields.

III Preparation of racemic and enantioenriched ester 5

Hept-6-enal (7). To the solution of oxalylchloride (7.4 mL, 0.09 mol) in DCM (70 mL) under argon atmosphere cooled to -78 °C DMSO (12.5 mL, 0.18 mol) was added. After 15 min the solution of hept-6-enol (5 g, 0.04 mol) in DCM (5 mL) was added. After another 15 min Et_3N (30.6 mL, 0.22mmol) was added and the reaction mixture was stirred for 10 min at -78 °C and then at 20 °C until the completion of the reaction (monitored by TLC). The reaction mixture was quenched by water (25 mL), extracted by DCM (3×20 ml) and washed with brine. The combined organic fractions were dried over $MgSO_4$ and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane) gave 4.05 g (82 %) of the title compound as a colorless viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 1.34-1.49 (m, 2H), 1.54-1.74 (m, 2H), 1.99-2.20 (m, 2H), 2.43 (td, J = 7.3, 1.8 Hz, 2H), 4.88-5.08 (m, 2H), 5.79 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 9.76 (t, J = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 21.47, 28.30, 33.39, 43.69, 114.81, 138.20, 202.56; IR (KBr) ν 3078, 2926, 2860, 1727, 1712, 1643, 1458, 1437, 1356, 1260, 1132, 1081, 994, 908 cm^{-1}; MS-ESI m/z (% relative intensity) 113.1 (M+, 10), 96.1 (7), 95.1 (100), 69.1 (13), 68.1 (4); HR-ESI calculated for $C_7H_{13}O$ 113.0966, found 113.0963. R_f (hexane) = 0.5.

Deca-1,9-dien-4-ol (6) (Method A). To the solution of **7** (400 mg, 3.57 mmol) in Et_2O (13 mL) allylmagnesium bromide (3.9 ml, 3.92 mmol) was added at 0 °C under argon atmosphere. After 2 h of stirring the saturated solution of NH_4Cl (5 mL) was added and the reaction mixture was extracted by Et_2O (3×3 mL). The combined organic fractions were dried over $MgSO_4$ and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (10/1 hexane/EtOAc) gave 401 mg (73 %) of the title compound as a colorless viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 1.19-1.56 (m, 6H), 1.72 (s, 1H), 1.96-2.18 (m, 3H), 2.18-2.38 (m, 1H), 3.51-3.74 (m, 1H), 4.83-5.05 (m, 2H), 5.05-5.25 (m, 2H), 5.66-5.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 25.13, 28.89, 33.70, 36.62, 41.93, 70.59, 114.37, 118.06, 134.85, 138.86; IR (KBr) ν 3342, 3075, 2977, 2932, 2860, 1640, 1437, 1078, 991, 914, 635 cm^{-1}; MS-ESI m/z (% relative intensity) 155.1 (M+, 6), 137.1 (65), 135.1 (17), 131.1 (87), 109.1 (9), 96.1 (57), 95.7 (100), 95.1 (93), 93.1 (41), 83.1 (70), 81.1 (85), 79.1 (21), 71.0 (59), 69.1 (62), 67.0 (89), 57.0 (28), 55.0 (36); HR-ESI calculated for $C_{10}H_{19}O$ 155.1436, found 155.1437. R_f (10/1 hexane/EtOAc) = 0.43.

(*R*)-Deca-1,9-dien-4-ol ((*R*))-6). *Reaction with allyltrichlorosilane* (Method B). To a solution of (*R,S*)-*N,N'*-dioxide (16 mg, 0.036 mmol) in THF (2 mL) hepten-6-enal **7** (80 mg, 0.71 mmol), diisopropylethylamine (149 μL, 0.86 mmol) and allyltrichlorsilane (123 μL, 0.86 mmol) were added at -78 °C under argon atmosphere. After 1 day of stirring at -78 °C the saturated solution of $NaHCO_3$ (2 mL) was added and the reaction mixture was extracted by Et_2O (3×2 mL). The combined organic fractions were dried over $MgSO_4$ and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (10/1 hexane/EtOAc) gave 28 mg (24 %, 57 % ee) of the title compound as a colorless viscous liquid.

(*R*)-Deca-1,9-dien-4-ol ((*R*))-6). *Reaction with allylboronic acid pinacol ester* (Method C). To a solution of hepten-6-enal **7** (400 mg, 3.57 mmol) and (*S*)-TRIP-PA (67 mg, 0.09 mmol, 2.5 mol %) in toluene (30 mL) cooled to -30°C was added dropwise allylboronic acid pinacol ester (4.28 mmol, 803 µL) over 30 seconds under argon atmosphere. The reaction mixture was stirred at -30°C for 2 days, then volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (10/1 hexane/EtOAc) gave 517 mg (93%, 90 % ee) of the title compound as a colorless viscous liquid.
$[\alpha]_D$ +10.8° (c 0.0093, $CHCl_3$).

(*S*)-Deca-1,9-dien-4-ol ((*S*)-6). *Reaction with allylboronic acid pinacol ester* (Method D). To a solution of hepten-6-enal **7** (1.6 g, 14.29 mmol) and (*R*)-TRIP-PA (269 mg, 0.36 mmol, 2.5 mol %) in toluene (100 mL) cooled to -30°C was added dropwise allylboronic acid pinacol ester (17.15 mmol, 3.2 mL) over 30 seconds under argon atmosphere. The reaction mixture was stirred at -30°C for 2 days, then volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (10/1 hexane/EtOAc) gave 1.98 g (90 %, 96 % ee) of the title compound as a colorless viscous liquid.
$[\alpha]_D$-5.6° (c 0.006, $CHCl_3$).

Deca-1,9-dien-4-yl acrylate (5). To a solution of **6** (0.98 g, 6.40 mmol) v DCM (5 mL) Et_3N (3.1 mL, 22.60 mmol) was added under argon atmosphere. Then a solution of acryloyl chloride (1.02 g, 11.3 mmol) in DCM (1 mL) was addend at 0 °C. After 5 h of stirring the reaction mixture was quenched by brine (5 mL) and extracted by DCM (3×5 mL). The combined organic fractions were dried over $MgSO_4$ and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (15/1 hexane/EtOAc) gave 886 mg (66 %) of the title compound as a colorless viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.11-1.48 (m, 4H), 1.47-1.70 (m, 2H), 1.93-2.14 (m, 2H), 2.19-2.49 (m, 2H), 4.84-5.19 (m, 5H), 5.61-5.93 (m, 3H), 6.10 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.39 (dd, *J* = 17.3, 1.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 24.69, 28.66, 33.37, 33.55, 38.57, 73.48, 114.44, 117.68, 128.84, 130.33, 133.61, 138.68, 165.88; IR (KBr) ν 3075, 2932, 2857, 1724, 1637, 1404, 1293, 1269, 1195, 1048, 985, 961, 914, 812 cm^{-1}; MS-ESI m/z (% relative intensity) 209.2 (M+,19), 167.1 (32), 138.1 (10), 137.1 (76), 135.1 (27), 127.0 (26), 101.1 (70), 95.7 (89), 95.1(58), 94.1 (36), 82.1 (24), 81.6 (64), 81.1 (80), 80.1 (21), 73.0 (54), 67.0 (81), 55.5 (11), 55.1 (19); HR-ESI calculated for $C_{13}H_{21}O_2$ 209.1542, found 209.1539. R_f (20/1 hexane/EtOAc) = 0.61.

(*R*)-Deca-1,9-dien-4-yl acrylate ((*R*)-5). To a solution of (*R*)-**6** (400 mg, 2.59 mmol) v DCM (3 mL) Et_3N (1.3 mL, 9.15 mmol) was added under argon atmosphere. Then a solution of acryloyl chloride (413 mg, 4.56 mmol) in DCM (2 mL) was addend at 0 °C. After 5 h of stirring the reaction mixture was quenched by brine (5 mL) and extracted with DCM (3×5 mL). The combined organic fractions were dried over $MgSO_4$ and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (15/1 hexane/EtOAc) gave 410 mg (76 %, 95 % ee) of the title compound as a colorless viscous liquid.
$[\alpha]_D$ +19.2° (c 0.0068, $CHCl_3$).

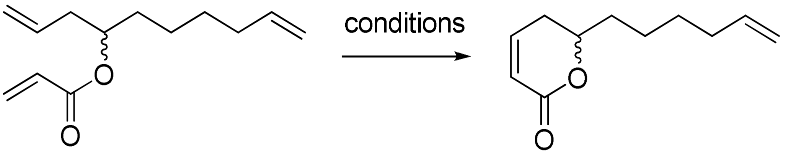
(*S*)-Deca-1,9-dien-4-yl acrylate ((*S*)-5). To a solution of (*S*)-**6** (1 g, 6.48 mmol) v DCM (5 mL) Et_3N (3.2 ml, 22.90 mmol) was added under argon atmosphere. Then a solution of acryloyl chloride (1.04 g, 11.45 mmol) in DCM (1 mL) was added at 0 °C. After 5 h of stirring the reaction mixture was quenched by brine (5 mL) and extracted with DCM (3×5 mL). The combined organic fractions were dried over Na_2SO_4 and volatiles were removed moved under reduced pressure. Column chromatography of the residue on silica gel (20/1 hexane/EtOAc) gave 0.95 g (71 %, 98 % ee) of the title compound as a colorless viscous liquid.
$[\alpha]_D$ -18.2° (c 0.0142, $CHCl_3$).

IV Metathesis reactions

6-(Hex-5-enyl)-5,6-dihydro-2H-pyran-2-one (3). To a solution of the Grubbs 2nd generation catalyst (143 mg, 0.17 mmol) in DCM (200 mL) **5** (350 mg, 1.68 mmol) and CuI (see Table 2) were added at 20 °C under argon atmosphere. After 20 h volatiles were removed under reduced pressure and column chromatography of the residue on silica gel (5/1 hexane/EtOAc) gave the title compound as a brownish viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.30-1.73 (m, 5H), 1.72-1.92 (m, 1H), 1.92-2.16 (m, 2H), 2.16-2.55 (m, 2H), 4.34-4.49 (m, 1H), 4.82-5.14 (m, 2H), 5.64-5.90 (m, 1H), 6.02 (dt, J = 9.4, 1.8 Hz, 1H), 6.88 (ddd, J = 9.7, 5.1, 3.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 24.29, 28.60, 29.39, 33.55, 34.72, 77.91, 114.65, 121.47, 138.55, 144.96, 164.54; IR (KBr) ν 3069, 2932, 2860, 1721, 1643, 1389, 1245, 1039, 958, 914, 818 cm^{-1}; MS-ESI m/z (% relative intensity) 182.1 (M+H$^+$,13), 181.1 (M+, 100), 164.1 (11), 163.1 (82), 145.1 (9), 135.1 (63), 95.1 (23), 81.1 (8); HR-ESI calculated for $C_{11}H_{17}O_2$ 181.1229, found 181.1226. R_f (5/1 hexane/EtOAc) = 0.26.

SI-Table 2. Ring closing metathesis of **5** to **3** under various conditions.



Entry	Cat. (mol%)	Solvent	Aditives	T (°C)	t (d)	Yield (%)[a]
1	5	DCM	-	20	1	34
2	10	DCM	-	20	1	37
3	5	DCM	CuI (6 mol%)	20	1	38
4	10	DCM	CuI (6 mol%)	20	1	40
5	10	DCM	CuI (10 mol%)	20	1	44
6	10	DCM	CuI (20 mol%)	20	1	48
7	7	DCM	CuI (20 mol%)	20	1	52
8	10	Et_2O	CuI (6 mol%)	20	2	0

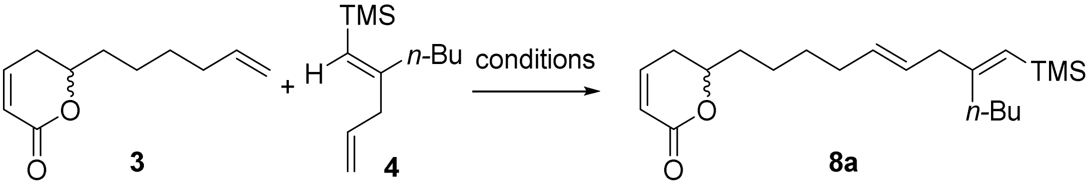
[a] Isolated yields.

General procedure for formation of 6-((5*E*,8*E*)-8-((trimethylsilyl)methylene)dodec-5-en-1-yl)-5,6-dihydro-2*H*-pyran-2-one (8a) and 6-((5*E*,8*Z*)-8-((trimethylsilyl)methylene)dodec-5-en-1-yl)-5,6-dihydro-2*H*-pyran-2-one ((8*Z*)-8a). Cross metathesis of 3 with 4 (see SI-Table 3). To a solution of **3** (50 mg, 0.28mmol) and **4** in DCM (50 mL) the Hoveyda-Grubbs 2nd generation catalyst and additives were added at 20 °C under argon atmosphere. After 20 h volatiles were removed under reduced pressure and column chromatography of the residue on silica gel (5/1 hexane/EtOAc) gave a mixture of **8a** and **(8*Z*)-8a** (78/22) as a brownish viscous liquid.

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ 0.06-0.15 (m, 9H), 0.83-0.98 (m, 4H), 1.22-1.92 (m, 9H), 1.92-2.20 (m, 4H), 2.20-2.42 (m, 2H), 2.77 (d, J = 4.4 Hz, 2H), 4.32-4.48 (m, 1H), 5.19 (s, 1H), 5.31-5.52 (m, 2H), 5.97-6.09 (m, 1H), 6.82-6.92 (m, 1H); ^{13}CNMR (150 MHz, $CDCl_3$, 25 °C) δ 0.42 (3C), 14.11, 23.01, 24.32, 29.22, 29.39, 31.25, 32.35, 34.73, 35.90, 42.26, 77.95, 121.48, 123.61, 128.53, 131.68, 144.94, 158.87, 164.54; IR (KBr) ν 2953, 2929, 2860, 1736, 1721, 1610, 1458, 1392, 1248, 1141, 1069, 1039, 970, 839, 815, 689 cm^{-1}; MS-EI m/z (% relative intensity) 349.3 ($M+H^+$, 4), 348.2 (M+, 10), 334.2 (22), 333.2 (87), 291.2 (8),235.1 (9), 231.2 (9), 216.2 (18), 201.1 (15), 191.2 (95), 187.1 (14), 173.1 (32), 169.1 (100),158.1 (42), 147.1 (33), 142.0 (78), 133.1 (36), 129.0 (34), 121.1 (27), 119.1 (23), 105.1(19), 97.0 (26), 93.1 (32), 91.1 (11), 81.1 (19), 79.1 (22), 75.0 (31), 68.0 (32), 59.0 (31); HR-EI calculated for $C_{21}H_{36}O_2Si$ 348.2485, found 348.2495. R_f (5/1 hexane/EtOAc) = 0.33.

Characteristic signals of **(8*Z*)-8a** isomer: 2.82 (d, *J* = 6.6 Hz, 2H), 5.21 (s, 1H), other peaks were overlapped by the major product.

SI-Table 3. Cross metathesis of **3** with **4** in DCM under various conditions.



3 **4** **8a**

Entry	**4** (eq)	H-G II (mol%)	Additives (mol%)	T (°C)	t (d)	Yield (%)[a]	Comment[a]
1	1	2 × 5	-	20	2	0	SP + SM
2	2	5	-	20	1	0	SP + SM
3	5	5	-	20	1	0	SP + SM
4	15	5	-	20	1	18	SP + SM
5	9	5	CuI (10)	20	4	17	P + SM
6	9	5	CuI(20)	20	7	6	
7	15	5	-	45	1	26	P + SP

[a] Isolated yields. [b] SM = starting material, P = product, SP = unidentified side-products.

General procedure for formation of 6-((5*E*,8*E*)-8-((trimethylsilyl)methylene)dodec-5-en-1-yl)-5,6-dihydro-2*H*-pyran-2-one (8a) and 6-((5*E*,8*Z*)-8-((trimethylsilyl)methylene)dodec-5-en-1-yl)-5,6-dihydro-2*H*-pyran-2-one ((8*Z*)-8a). One-pot metathesis of 5 with 4a. To a solution of **5** (100 mg, 0.48 mmol) in toluene (48 mL) the Hoveyda-Grubbs 2nd generation catalyst (30 mg, 0.048 mmol) was added at 20 °C under argon atmosphere. The reaction mixture was stirred for 24 hours under reflux and then was cooled to the room temperature. Then **4a** (654 mg,, 3.33 mmol) and Grubbs 2nd generation catalyst (20 mg, 0.024 mmol) was added After 24 h of stirring volatiles were removed under reduced pressure and column chromatography of the residue on silica gel (5/1 hexane/EtOAc) gave 27 mg (32%) of a mixture of **8a** and **(8*Z*)-8a** (82/18) as a brownish viscous liquid.

6-((5*E*,8*E*)-8-Methyl-9-(trimethylsilyl)nona-5,8-dien-1-yl)-5,6-dihydro-2*H*-pyran-2-one (8b) 6-((5*E*,8*Z*)-8-methyl-9-(trimethylsilyl)nona-5,8-dien-1-yl)-5,6-dihydro-2*H*-pyran-2-

one ((8*Z*)-8b). To a solution of **dim-3** (60 mg, 0.18 mmol) and **4b** (417 mg, 2.70 mmol) in toluene (20 mL) the Grubbs 2nd generation catalyst (23 mg, 0.03 mmol) was added at 20 °C under argon atmosphere. After 2 days of stirring volatiles were removed under reduced pressure and column chromatography of the residue on silica gel (5/1 hexane/EtOAc) gave 33 mg (60%) of a mixture of **8b** and **(8*Z*)-8b** (82/18) as a brownish viscous liquid. The spectral and other characteristic are listed in section VII.

General procedure for formation of 6-((5*E*,8*E*)-8-Methyl-9-(trimethylsilyl)nona-5,8-dien-1-yl)-5,6-dihydro-2*H*-pyran-2-one (8b) and 6-((5*E*,8*Z*)-8-methyl-9-(trimethylsilyl)nona-5,8-dien-1-yl)-5,6-dihydro-2*H*-pyran-2-one ((8*Z*)-8b). One-pot metathesis of 5 with 4b. To a solution of **5** (100 mg, 0.48 mmol) in toluene (48 mL) the Hoveyda-Grubbs 2nd generation catalyst (30 mg, 0.048 mmol) was added at 20 °C under argon atmosphere. The reaction mixture was stirred for 24 hours under reflux and then was cooled to the room temperature. Then **4b** (695 mg, 4.50 mmol) and Grubbs 2nd generation catalyst (20 mg, 0.024 mmol) was added After 24 h of stirring volatiles were removed under reduced pressure and column chromatography of the residue on silica gel (5/1 hexane/EtOAc) gave 21 mg (28 %) of a mixture of **8b** and **(8*Z*)-8b** (73/27) as a brownish viscous liquid. The spectral and other characteristic are listed in section VII.

V Synthesis of racemic 1

6-((5*E*,8*E*)-8-(Chloromethylene)dodec-5-en-1-yl)-5,6-dihydro-2*H*-pyran-2-one (1a) and 6-((5*E*,8*E*)-8-(chloromethylene)dodec-5-en-1-yl)-5,6-dihydro-2*H*-pyran-2-one ((8*Z*)-1a). To a solution of **8a** (50 mg, 0.14 mmol) in DMF (3 ml) NCS (25 mg, 0.19 mmol) was added at room temperature under argon atmosphere. Reaction mixture was stirred overnight at 45 °C. The reaction was quenched with the saturated solution of $NaHCO_3$ (1 ml) and extracted by hexane (3 × 2 ml). The organic layer was separated and dried over Na_2SO_4 and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (5/1 hexane/EtOAc) provided 34 mg (75%) of a mixture of **1a** and **(8*Z*)-1a** (74/26) as a colorless viscous liquid.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) δ 0.78-1.06 (m, 3H), 1.24-1.97 (m, 10H), 1.97-2.15 (m, 2H), 2.15-2.28 (m, 2H), 2.30-2.47 (m, 2H), 2.75 (d, *J* = 6.7 Hz, 2H), 4.33-4.57 (m, 1H), 5.26-5.65 (m, 2H), 5.80 (s, 1H), 5.98-6.11 (m, 1H), 6.82-6.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC) 13.95, 22.56, 24.35, 29.09 (2C), 29.40, 29.98, 32.26, 34.71, 38.03, 77.89, 112.68, 121.47, 126.77, 132.76, 142.22, 144.95, 164.58; IR (KBr) ν 2954, 2932, 2861, 1720, 1459, 1386, 1248, 1147, 1039, 971, 816 cm^{-1}, compound did not have the molecular peak. R_f (3/1 hexane/EtOAc) = 0.23.

Characteristic signals of **(8*Z*)-1a** isomer: 2.81 (d, *J* = 7.2 Hz, 2H), 5.82 (s, 1H), other peaks were overlapped by the major product.

6-((5*E*,8*E*)-9-Chloro-8-methylnona-5,8-dien-1-yl)-5,6-dihydro-2*H*-pyran-2-one (1b) and 6-((5*E*,8*Z*)-9-chloro-8-methylnona-5,8-dien-1-yl)-5,6-dihydro-2*H*-pyran-2-one ((8*Z*)-1b). To a solution of **8b** (30 mg, 0.10 mmol) in DMF (2 mL) under argon atmosphere NCS (17 mg, 0.13 mmol) was added at 20 °C. The reaction mixture was stirred overnight at 45 °C and then quenched with the saturated solution of $NaHCO_3$ (1 mL), extracted by hexane (3×2 mL). The combined organic fractions were dried over Na_2SO_4 and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (3/1 hexane/EtOAc) provided 9 mg (34%) of a mixture of **1b** and **(8*Z*)-1b** (75/25) as a colorless viscous liquid.

The spectral and other characteristic are listed in chiral section.

VI Decomposition of 8a

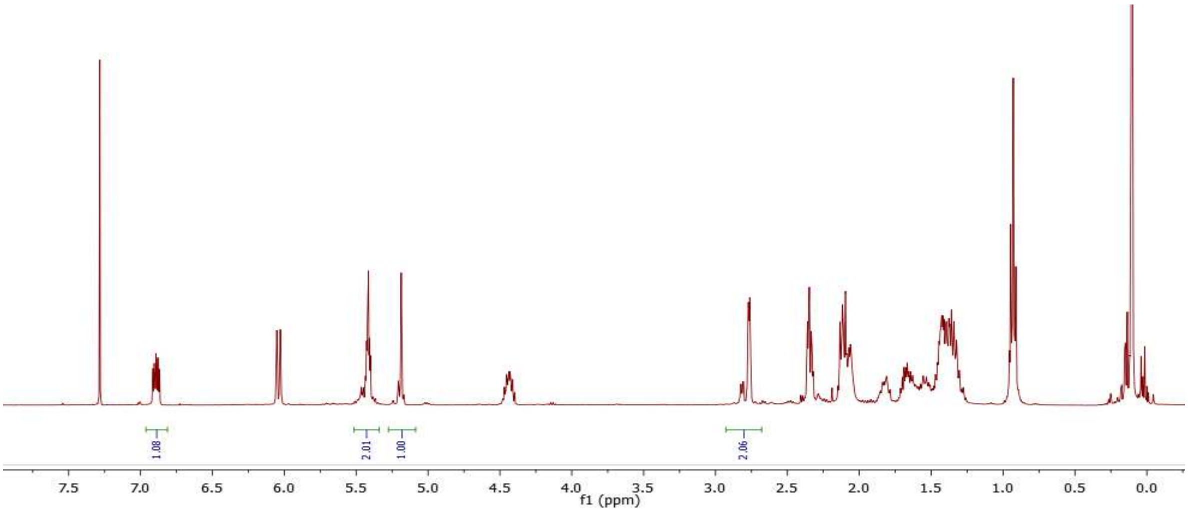


Figure SI-1. Sample of **8a** in $CDCl_3$ (immediately after isolation ~ 10 min).

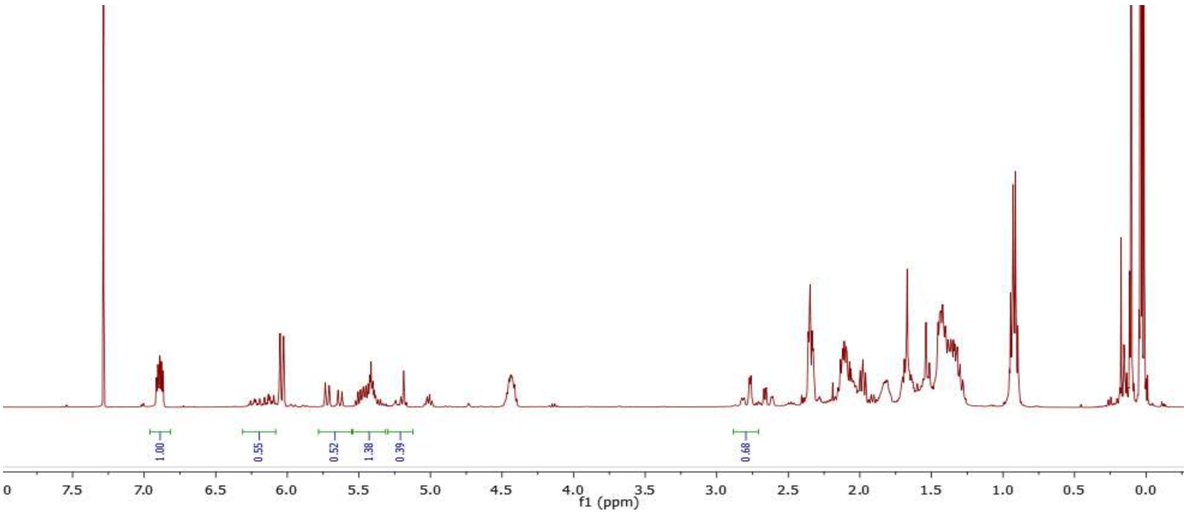


Figure SI-2. Sample of **8a** in $CDCl_3$ (after 5 h).

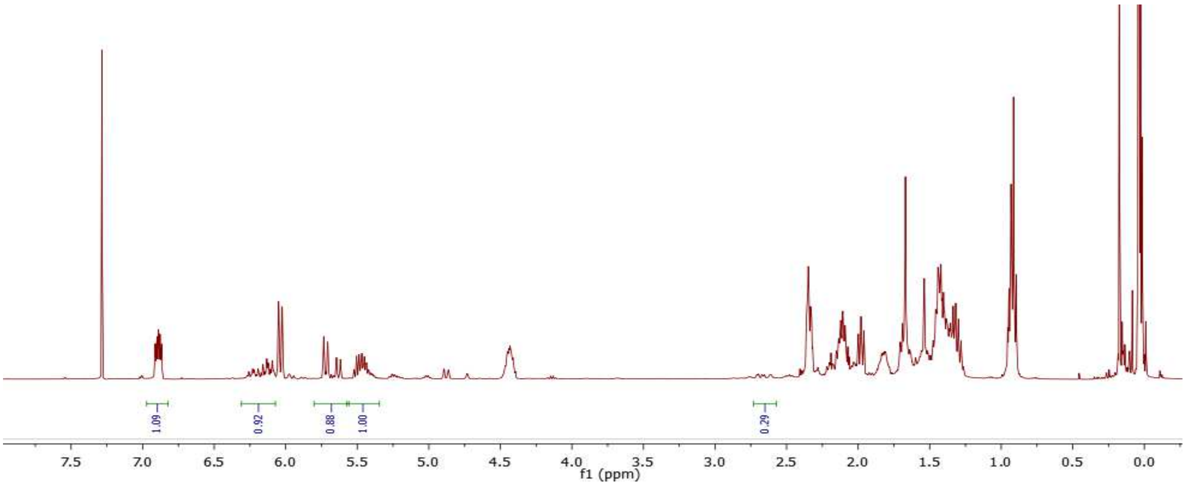


Figure SI-3. Sample of **8a** in $CDCl_3$ (after 22 h).

VII Synthesis of coibacin D

(*S*)-6-(Hex-5-en-1-yl)-5,6-dihydro-2*H*-pyran-2-one ((*S*)-3) and (6*S*,6'*S*)-6,6'-((*E*)-dec-5-ene-1,10-diyl)bis(5,6-dihydro-2*H*-pyran-2-one) ((*S*)-dim-3).

To a solution of the Grubbs 2nd generation catalyst (82 mg, 0.10 mmol) in DCM (100 mL) (*S*)-**5** (200 mg, 0.96 mmol) was added at 20 °C under argon atmosphere. After 24 h of stirring under reflux volatiles were removed under reduced pressure and column chromatography of the residue on silica gel (1/1 hexane/EtOAc) gave (*S*)-**3** (41 mg, 24%, 96% ee) and (*S*)-**dim-3** (83 mg, 52 %) as brownish viscous liquids.

(*S*)-3

$[\alpha]_D$+96.9° (c 0.0075,$CHCl_3$);

(*S*)-Dim-3

$[\alpha]_D$ +96.65° (c 0.0054, $CHCl_3$);

^1H NMR (400 MHz, $CDCl_3$, 25 ºC) δ 1.32-1.73 (m, 5H), 1.75-1.94 (m, 1H), 1.94-2.12 (m, 2H), 2.21-2.50 (m, 2H), 4.343 (ddt, *J* = 10.3, 7.4, 5.2, 1H), 5.27-5.53 (m, 1H), 6.03 (ddd, *J* = 9.7, 2.3, 1.4, 1H), 6.84-6.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC) δ 24.30, 29.25, 29.41, 32.34, 34.74, 77.97, 121.42, 130.25, 145.05, 164.59; IR (KBr) ν 2926, 2857, 1718, 1392, 1251, 1141, 1066, 1039, 970, 818, 665 cm^{-1}; MS-ESI m/z (% relative intensity) 334.2 (18), 333.2 (M+, 100), 316.2 (9), 315.2 (43), 297.2(8); HR-ESI calculated for $C_{20}H_{29}O_4$ 332.2066, found 332.2063. R_f (1/1 hexane/EtOAc) = 0.24.

(*S*)-6-((5*E*,8*E*)-8-Methyl-9-(trimethylsilyl)nona-5,8-dien-1-yl)-5,6-dihydro-2*H*-pyran-2-one ((*S*)-8b) and (*S*)-6-((5*E*,8*E*)-8-methyl-9-(trimethylsilyl)nona-5,8-dien-1-yl)-5,6-dihydro-2*H*-pyran-2-one ((8*Z*)-(*S*)-8b).

To a solution of **dim-3** (59 mg, 0.18 mmol) and **4b** in toluene (20 mL) the Grubbs 2nd generation catalyst (23 mg, 0.03 mmol) was added at 20 °C under argon atmosphere. After 2 days of stirring volatiles were removed under reduced pressure and column chromatography of the residue on silica gel (5/1 hexane/EtOAc) gave 24 mg (44 %) of a mixture of **(*S*)-8b** and **(8*Z*)-(*S*)-8b** (82/18) as a brownish viscous liquid.

$[\alpha]_D$ +48.6° (c 0.0058,$CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 25 ºC) δ 0.06-0.27 (m, 9H),1.29-1.52 (m, 3H), 1.52-1.74 (m, 2H), 1.74-1.93 (m, 4H), 1.93-2.25 (m, 2H), 2.25-2.52 (m, 2H), 2.75 (d, *J* = 4.2 Hz, 2H), 4.36-4.56 (m, 1H), 5.22 (d, *J* = 1.0 Hz, 1H 5.33-5.54 (m, 2H), 6.04 (ddd, *J* = 9.8, 2.3, 1.4 Hz, 1H), 6.80-7.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC) δ 0.10 (3C), 21.59, 24.31, 29.19, 29.39, 32.34, 34.72, 45.76, 77.95, 121.46, 123.53, 128.22, 131.78, 144.96, 154.13, 164.55; IR (KBr) ν 2944, 2857, 1718, 1613, 1440, 1386, 1245, 1144, 1039, 970, 869, 836, 815, 773, 682 cm^{-1}; HR-ESI calculated for $C_{18}H_{31}O_2Si$ 307.2093, found 307.2085. R_f (5/1 hexane/EtOAc) = 0.31.

Characteristic signals of **(8*Z*)-(*S*)-8b** isomer: 2.81 (d, *J* = 6.7 Hz, 2H), 5.24 (d, *J* = 1.0 Hz, 1H) other peaks were overlapped by the major product.

(*S*)-6-((5*E*,8*E*)-9-Chloro-8-methylnona-5,8-dien-1-yl)-5,6-dihydro-2*H*-pyran-2-one (1b) and (*S*)-6-((5*E*,8*Z*)-9-chloro-8-methylnona-5,8-dien-1-yl)-5,6-dihydro-2*H*-pyran-2-one ((8*Z*)-(*S*)-1b). To a solution of **8b** (24 mg, 0.08 mmol) in DMF (2 mL) under argon atmosphere

NCS (14 mg, 0.10 mmol) was added at 20 °C. The reaction mixture was stirred overnight at 45 °C and then quenched with the saturated solution of $NaHCO_3$ (1 mL), extracted by hexane (3×2 mL). The combined organic fractions were dried over Na_2SO_4 and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (3/1 hexane/EtOAc) provided 9 mg (44%) of a mixture of **1b** and **(8*Z*)-(*S*)-1b** (73/27) as a colorless viscous liquid.

[[α]$_D$ +56.6° (c 0.0032, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) δ 1.34-1.95 (m, 9H), 1.98-2.15 (m, 2H), 2.23-2.50 (m, 2H), 2.74 (d, *J* = 6.7 Hz, 2H), 4.36-4.52 (m, 1H), 5.26-5.44 (m, 1H), 5.49 (ddt, *J* = 14.3, 6.5, 1.2 Hz, 1H), 5.83 (q, *J* =1.5, 2.8 Hz, 1H), 6.04 (ddt, *J* = 9.7, 2.4, 1.2 Hz, 1H), 6.90 (ddd, *J* = 9.6, 5.6, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC) δ 16.59, 24.33, 29.08, 29.40, 32.25, 34.71, 40.19, 77.89, 112.57, 121.47, 126.59, 132.82, 137.91, 144.96, 164.53. R_f (3/1 hexane/EtOAc) = 0.34. The spectral characteristics were in agreement with previously reported data.[3]

Characteristic signals of **(8*Z*)-(*S*)-1b** isomer: 2.81 (d, *J* = 7.5 Hz, 2H), 5.81 (t, *J* = 0.7, 1H), other peaks were overlapped by the major product.

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[3] Balunas, M.J.; Grosso, M.F.; Villa, F.A.; Engene, N.; McPhail, K.L.; Tidgewell, K.; Pineda, L.M.; Gerwick, L.; Spadafora, C.; Kyle, D.E.; Gerwick, W.H. *Org.Lett.* **2012,***14,* 3878-3881.

VIII Determination of *ee* and absolute configuration of products

General procedure for the preparation of Mosher´s esters. To a solution of an alcohol (0.04 mmol) and DMAP (0.2 mmol, 24 mg) in CH_2Cl_2 (2 mL) (*R*)-(-)-α-methoxy-α-(trifluoromethyl)phenylacetic chloride (0.04 mmol, 10.1 mg) was added under argon atmosphere at 20 °C and the reaction mixture was stirred overnight. The reaction mixture was quenched with the saturated aqueous solution of NH_4Cl (5 mL), washed with the saturated aqueous solution of $NaHCO_3$ (4 mL), and extracted by ether (3×5 mL). The combined organic fractions were dried over $MgSO_4$ and volatiles were removed under reduced pressure. The crude product was used for determination of the diastereoisomeric ratio without further purification to avoid possible amplification of the ee.

Preparation from 6 (Method A). The final mixture of diastereoisomeric Mosher’s esters (*R*)-(-)-MTPA-(*S*)-**11** a (*R*)-(-)-MTPA-(*R*)-**11** was obtained in 13 mg (86 %) as a colorless viscous liquid.

^{19}F NMR (300 MHz, C_6D_6, 25 ºC) δ -71.20 (50 %), -71.29 (50 %).

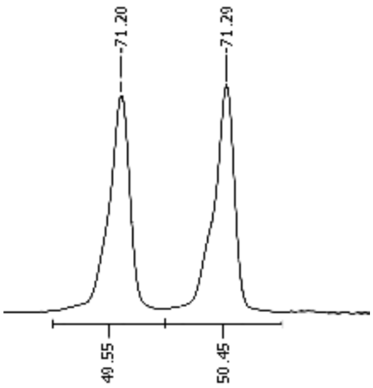


Figure SI-4. ^{19}F NMR (*R*)-(-)-MTPA-(*S*)-**11** a (*R*)-(-)-MTPA-(*R*)-**11** (from racemic **6**).

Preparation from (*R*)-6 (Method B). The final mixture of diastereoisomeric Mosher’s esters (*R*)-(-)-MTPA-(*S*)-**11** a (*R*)-(-)-MTPA-(*R*)-**11** was obtained in 12 mg (81 %) as a colorless viscous liquid.

ee 57%, ^{19}F NMR (300 MHz, C_6D_6, 25 ºC) δ -71.19 (21.5 %), -71.28 (78.5 %).

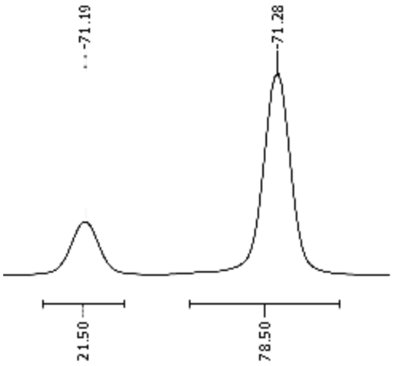


Figure SI-5. ^{19}F NMR of (*R*)-(-)-MTPA-(*S*)-**11** a (*R*)-(-)-MTPA-(*R*)-**11** (from (*R*)-**6**).

Preparation from (*R*)-6 (Method C). The final mixture of diastereoisomeric Mosher's esters (*R*)-(-)-MTPA-(*S*)-**11** a (*R*)-(-)-MTPA-(*R*)-**11** was obtained in 12 mg (81 %) as a colorless viscous liquid.
ee 90 %, ^{19}F NMR (300 MHz, C_6D_6, 25 ºC) δ -71.19 (5 %), -71.27 (95 %).

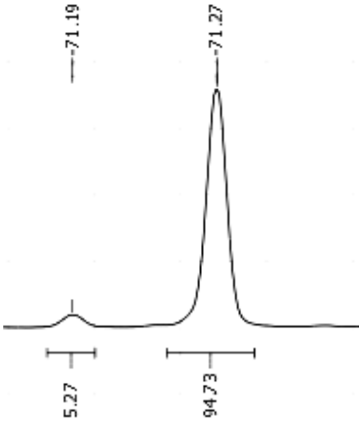


Figure SI-6. ^{19}F NMR of (*R*)-(-)-MTPA-(*S*)-**11** a (*R*)-(-)-MTPA-(*R*)-**11** (from (*R*)-**6**).

Preparation from (*S*)-6 (Method D). The final mixture of diastereoisomeric Mosher's esters (*R*)-(-)-MTPA-(*S*)-**11** a (*R*)-(-)-MTPA-(*R*)-**11** was obtained in 12 mg (81 %) as a colorless viscous liquid.
ee 96 %, ^{19}F NMR (300 MHz, C_6D_6, 25 ºC) δ -71.19 (98 %), -71.27 (2 %).

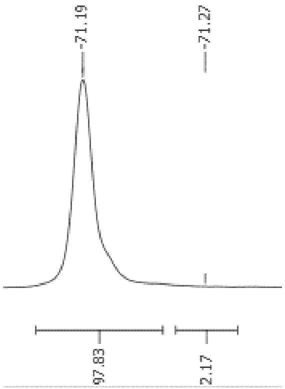
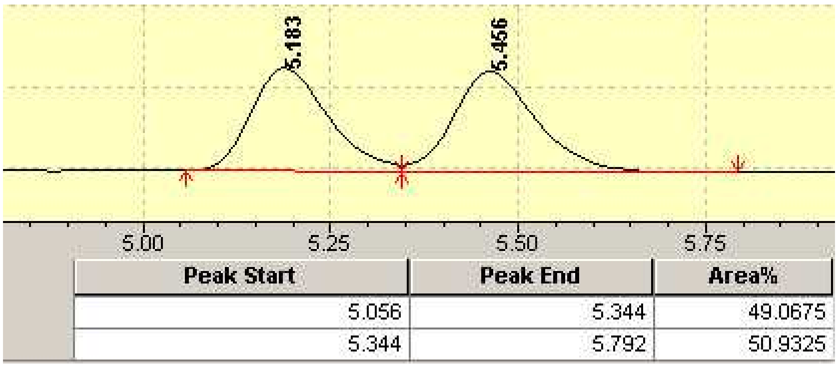


Figure SI-7. ^{19}F NMR of (*R*)-(-)-MTPA-(*S*)-**11** a (*R*)-(-)-MTPA-(*R*)-**11** (from (*S*)-**6**).

For compound (*R*)-**5** (ee 92 %*) enantiomeric excess was determined by HPLC equipped with Chiralpak IC column (t_S = 5.18 min, t_R = 5.41 min, *i*-PrOH/heptane 0.1/99.9, flow rate 1 mL/min, 35°C).

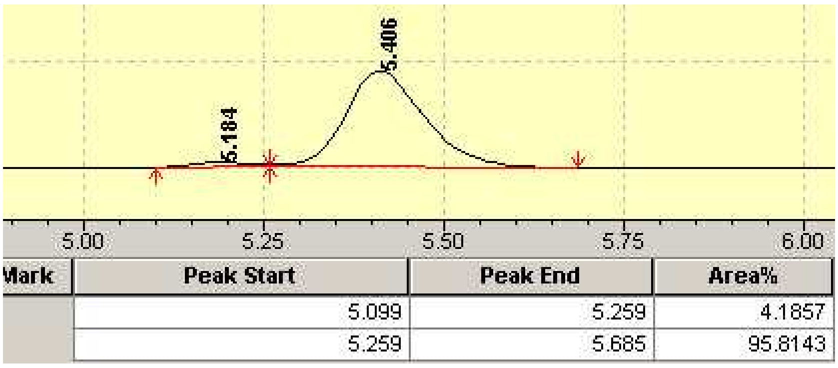
* (Taking into the account non-optimal resolution of enantiomers, the real ee could be higher.)

For compound (*S*)-**5** (ee 98 %) enantiomeric excess was determined by HPLC equipped with Chiralpak IC column (t_S = 5.11 min, t_R= 5.32 min, *i*-PrOH/heptane 0.1/99.9, flow rate 1 mL/min, 35°C).



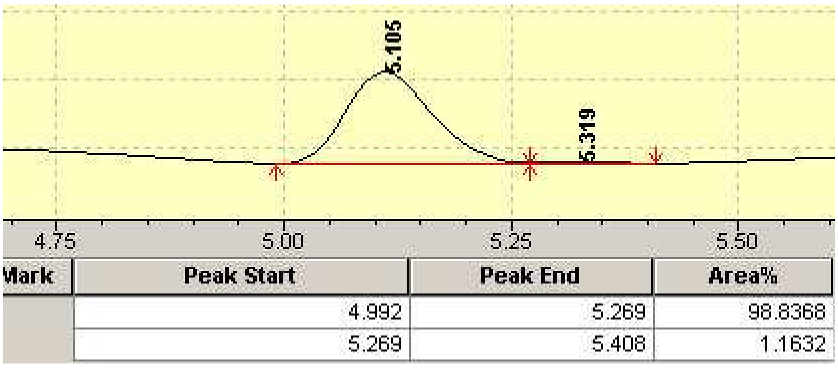
	Peak Start	Peak End	Area%
	5.056	5.344	49.0675
	5.344	5.792	50.9325

Figure SI-8. HPLC of racemic **5**.



Mark	Peak Start	Peak End	Area%
	5.099	5.259	4.1857
	5.259	5.685	95.8143

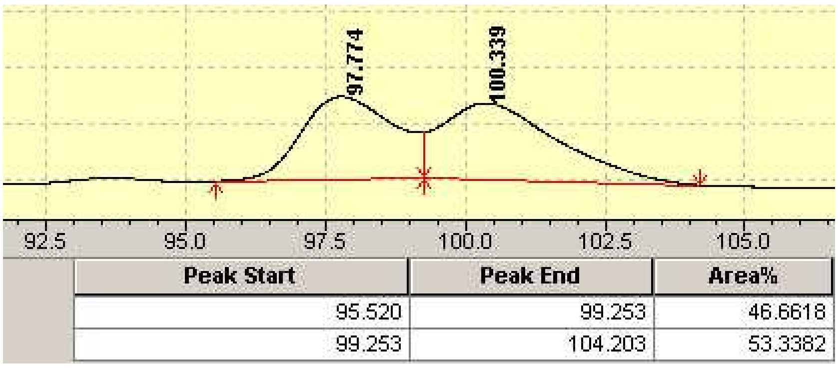
Figure SI-9. HPLC of (*R*)-**5**.



Mark	Peak Start	Peak End	Area%
	4.992	5.269	98.8368
	5.269	5.408	1.1632

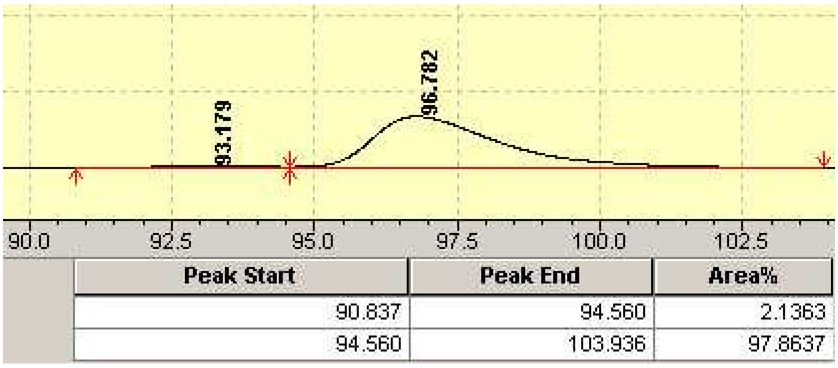
Figure SI-10. HPLC of (*S*)-**5**.

For compound (*S*)-**3** (ee 96 %) enantiomeric excesses were determined by HPLC equipped with Chiralpak IC column (t_R = 93.18 min, t_S = 96.78 min, *i*-PrOH/heptane 1.0/99.0, flow rate 1 mL/min, 35°C).



	Peak Start	Peak End	Area%
	95.520	99.253	46.6618
	99.253	104.203	53.3382

Figure SI-11. HPLC of racemic **3**.



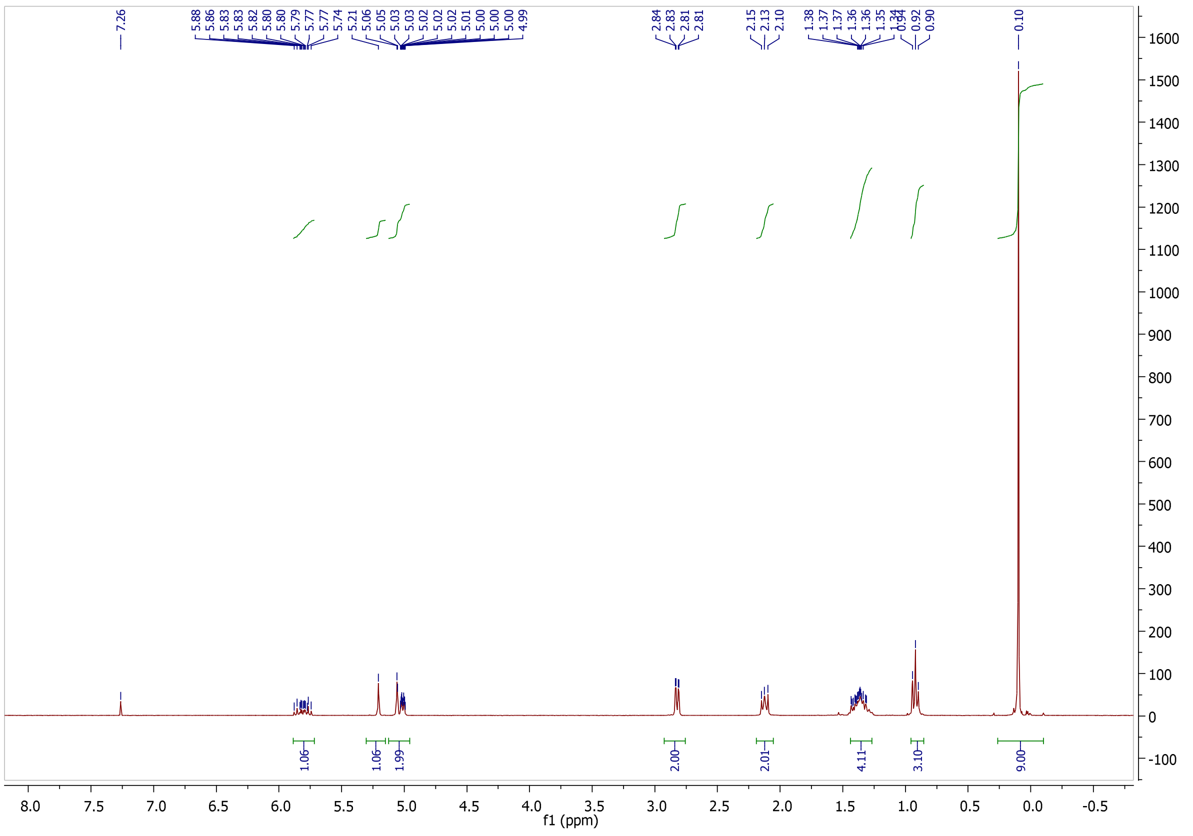
	Peak Start	Peak End	Area%
	90.837	94.560	2.1363
	94.560	103.936	97.8637

Figure SI-12. HPLC of racemic (*S*)-**3**.

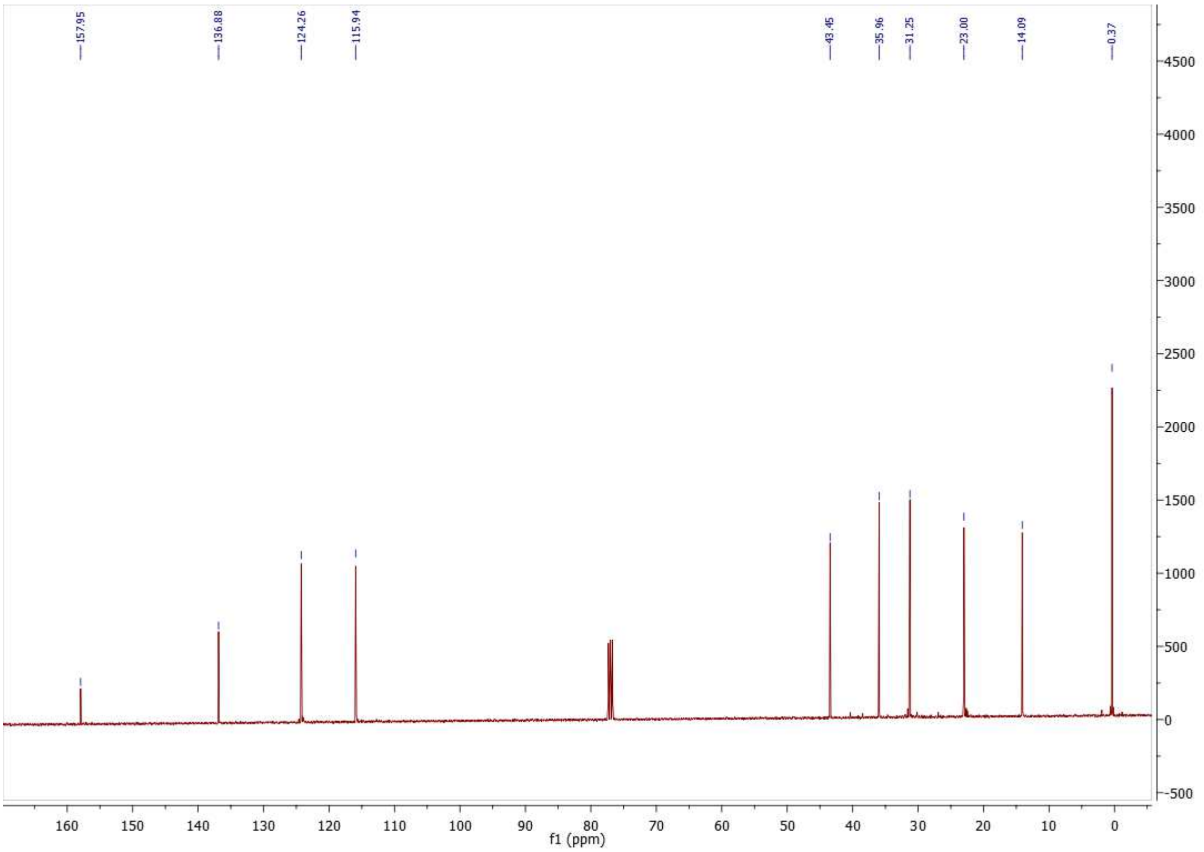
For compound (*S*)-**dim-3** could not be found suitable conditions.

IX Copies of ^{1}H and ^{13}C NMR spectra

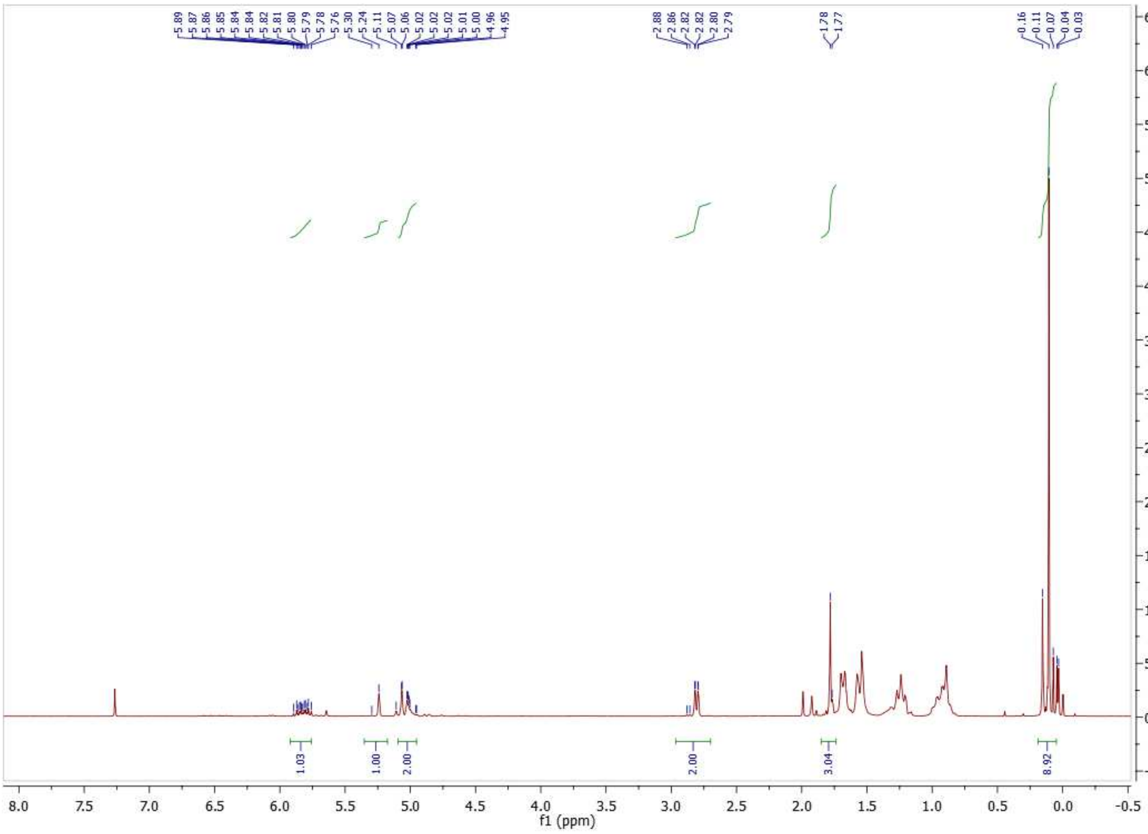
4a – ^{1}H NMR spectrum



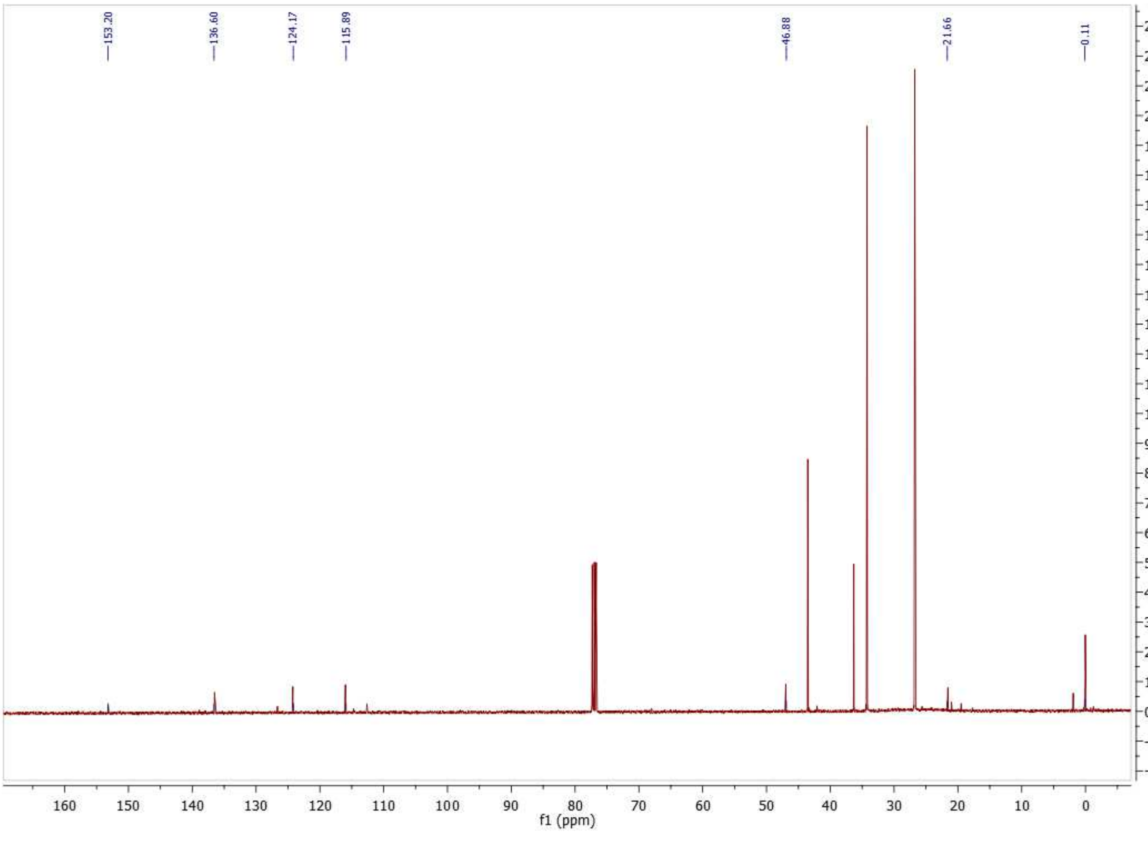
4a – ^{13}C NMR spectrum



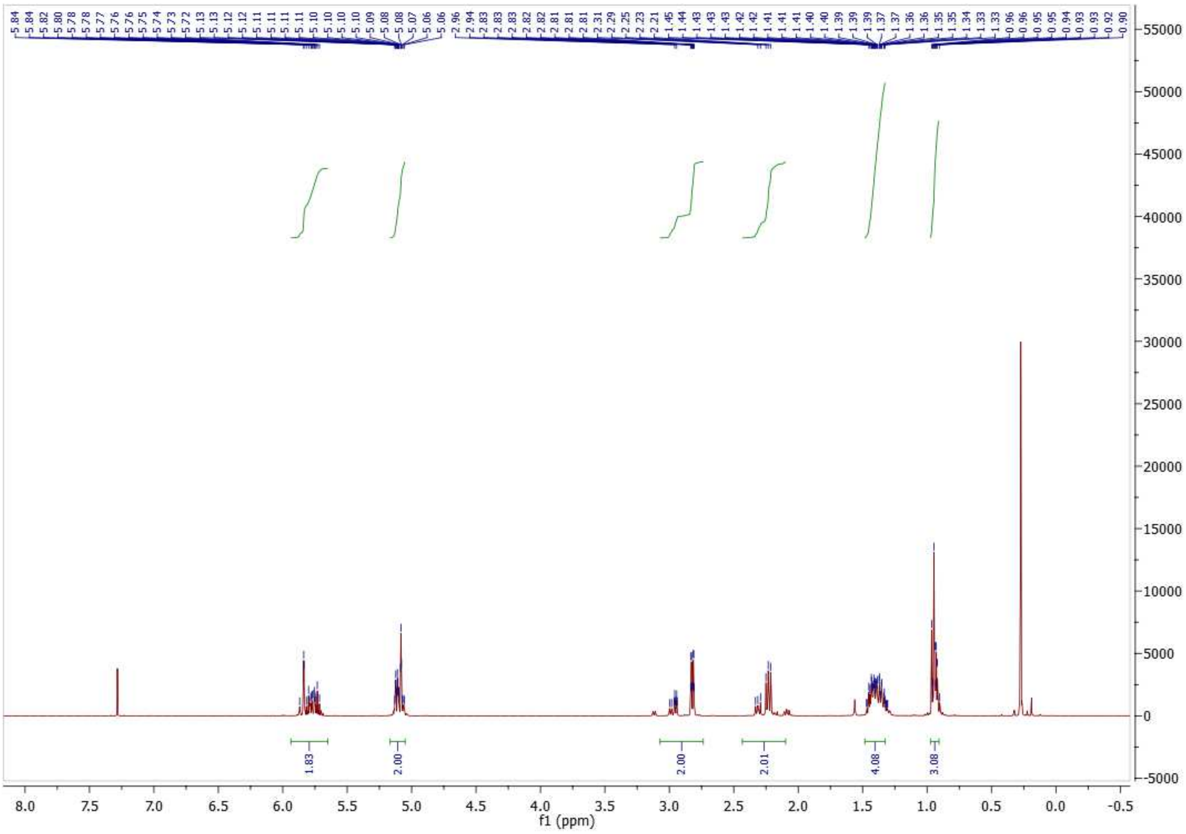
4b – ^{1}H NMR spectrum



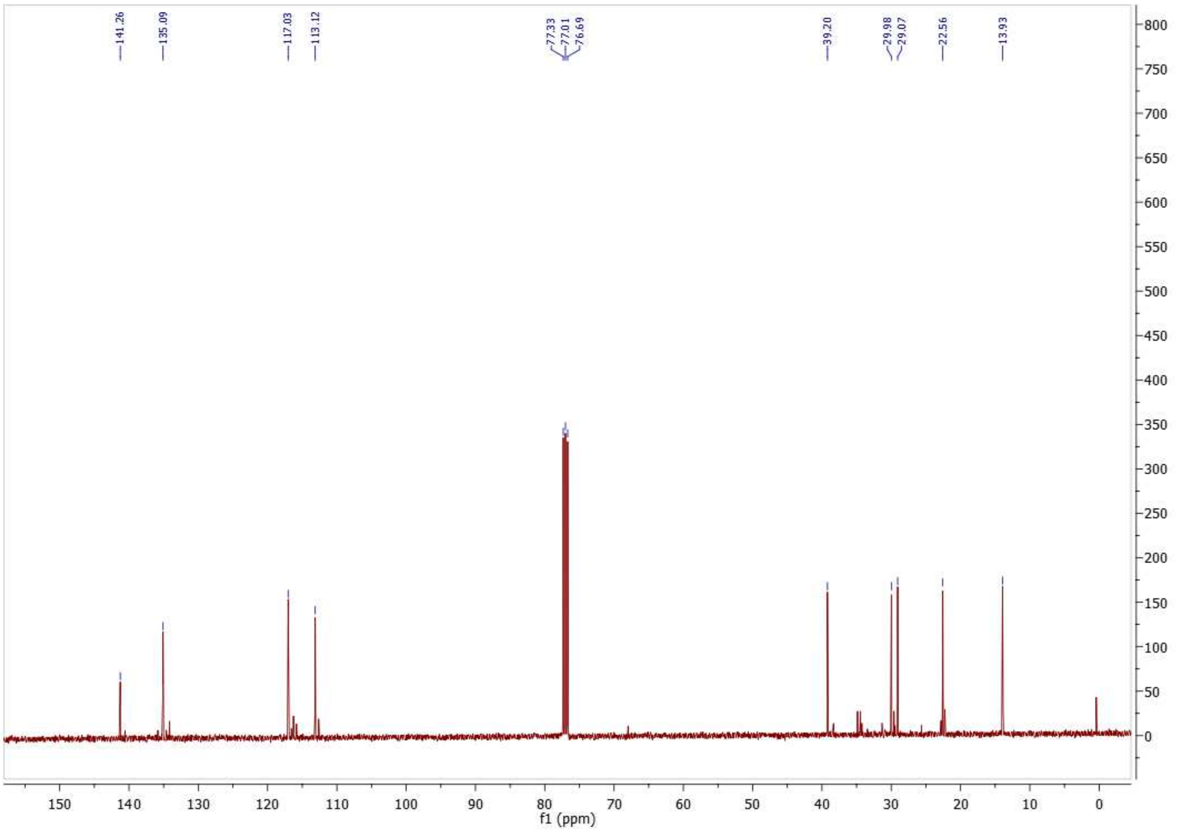
4b – ^{13}C NMR spectrum



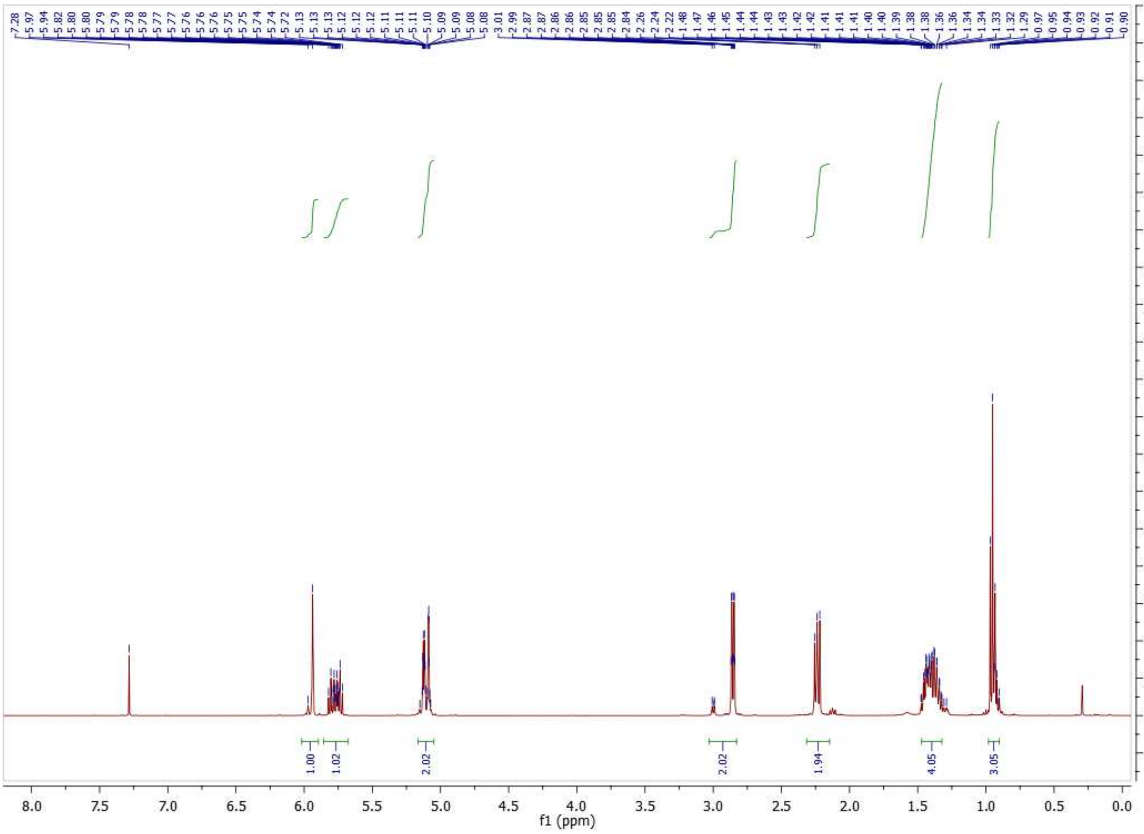
2-Cl – ^{1}H NMR spectrum



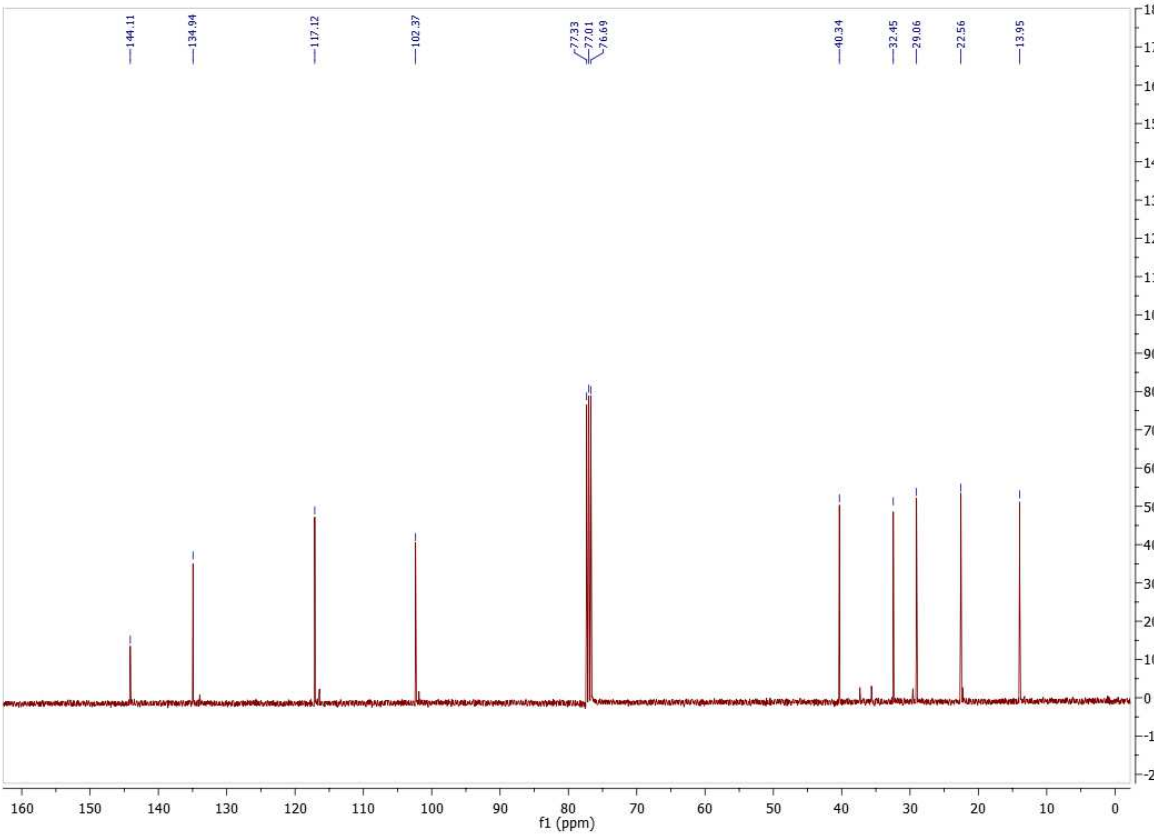
2-Cl – ^{13}C NMR spectrum



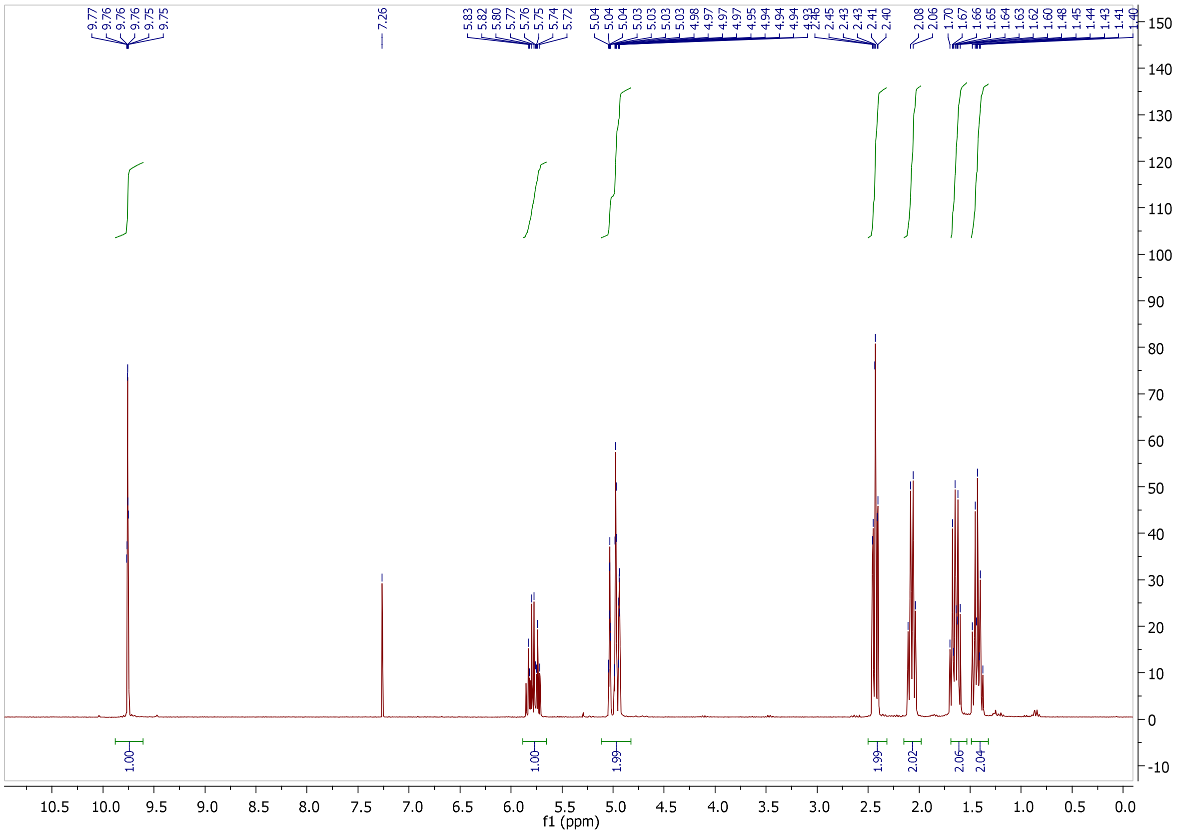
2-Br – ^{1}H NMR spectrum



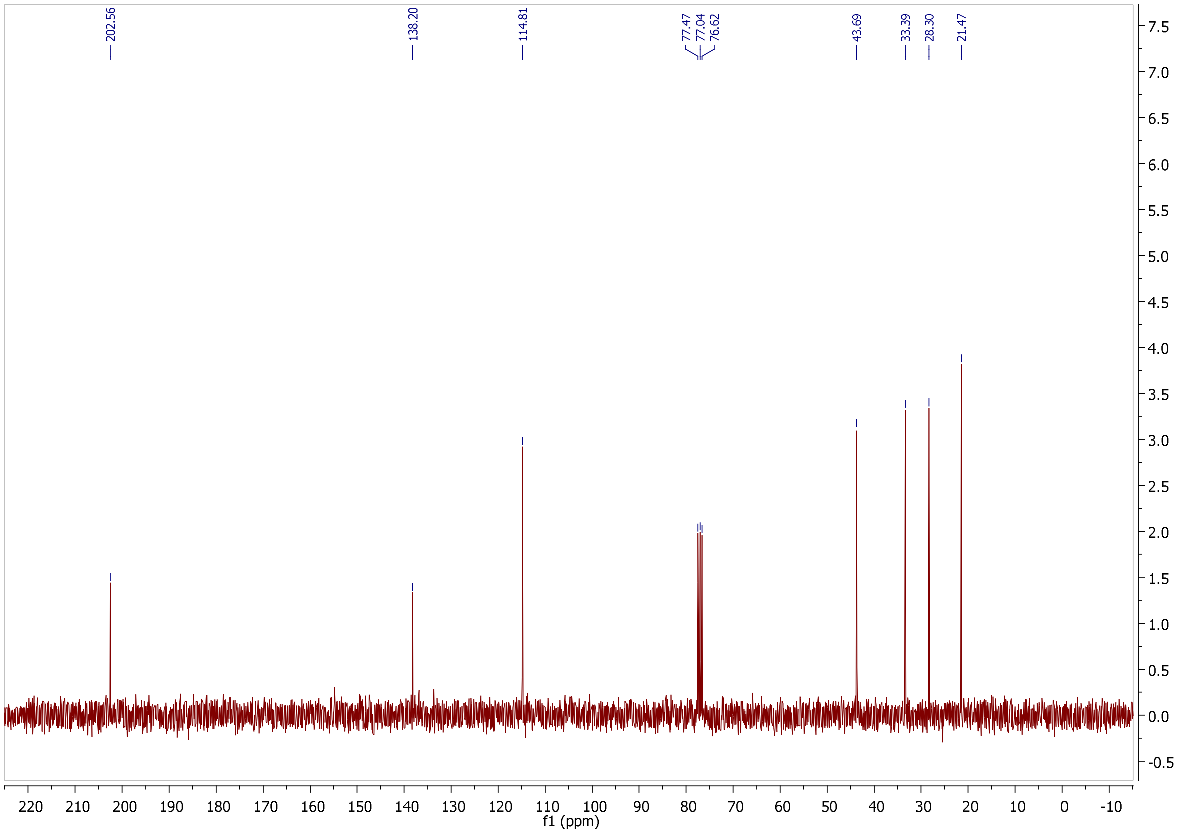
2-Br – ^{13}C NMR spectrum



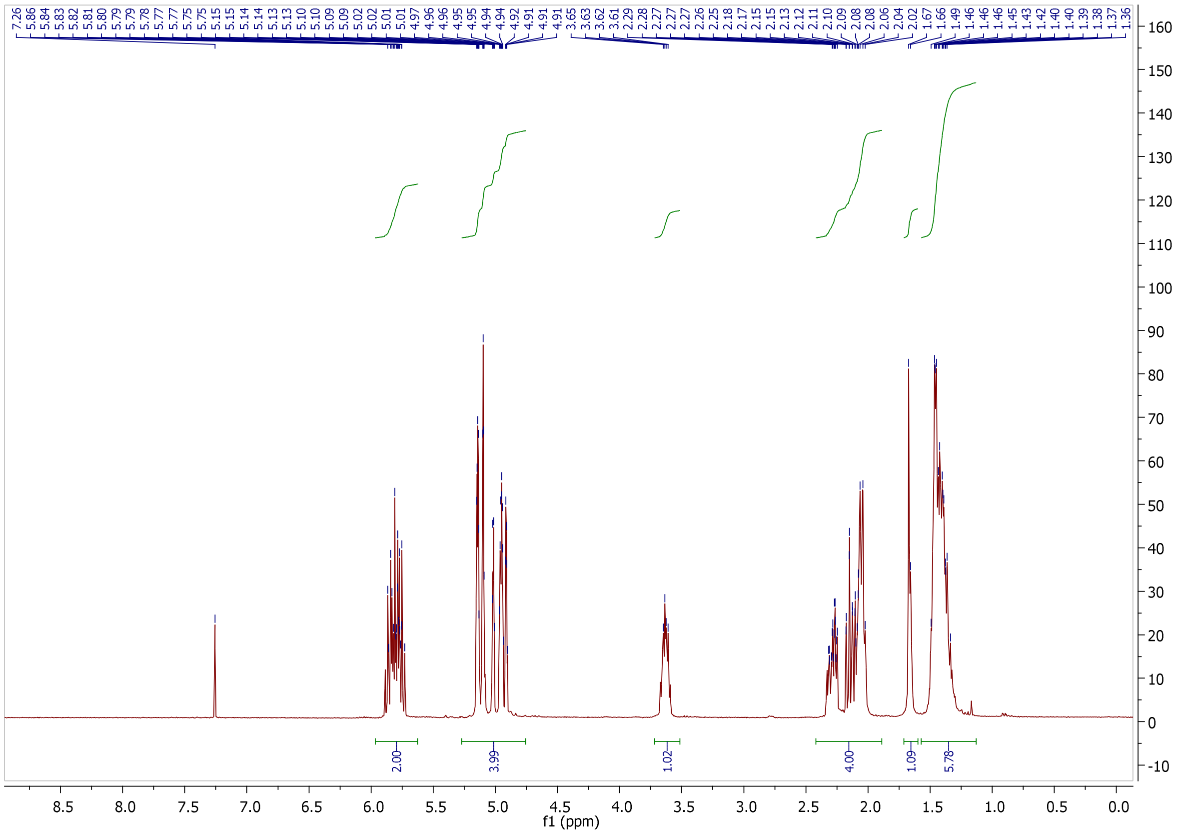
7 – ^{1}H NMR spectrum



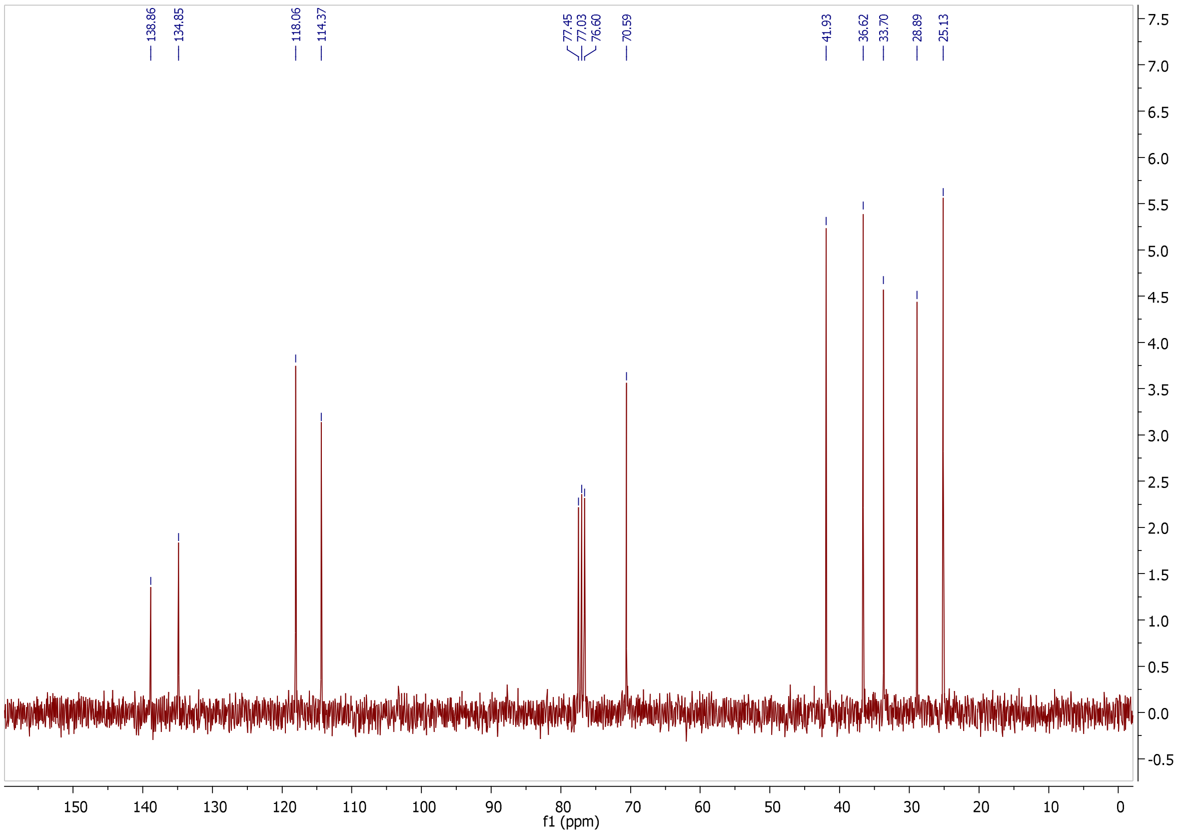
7 – ^{13}C NMR spectrum



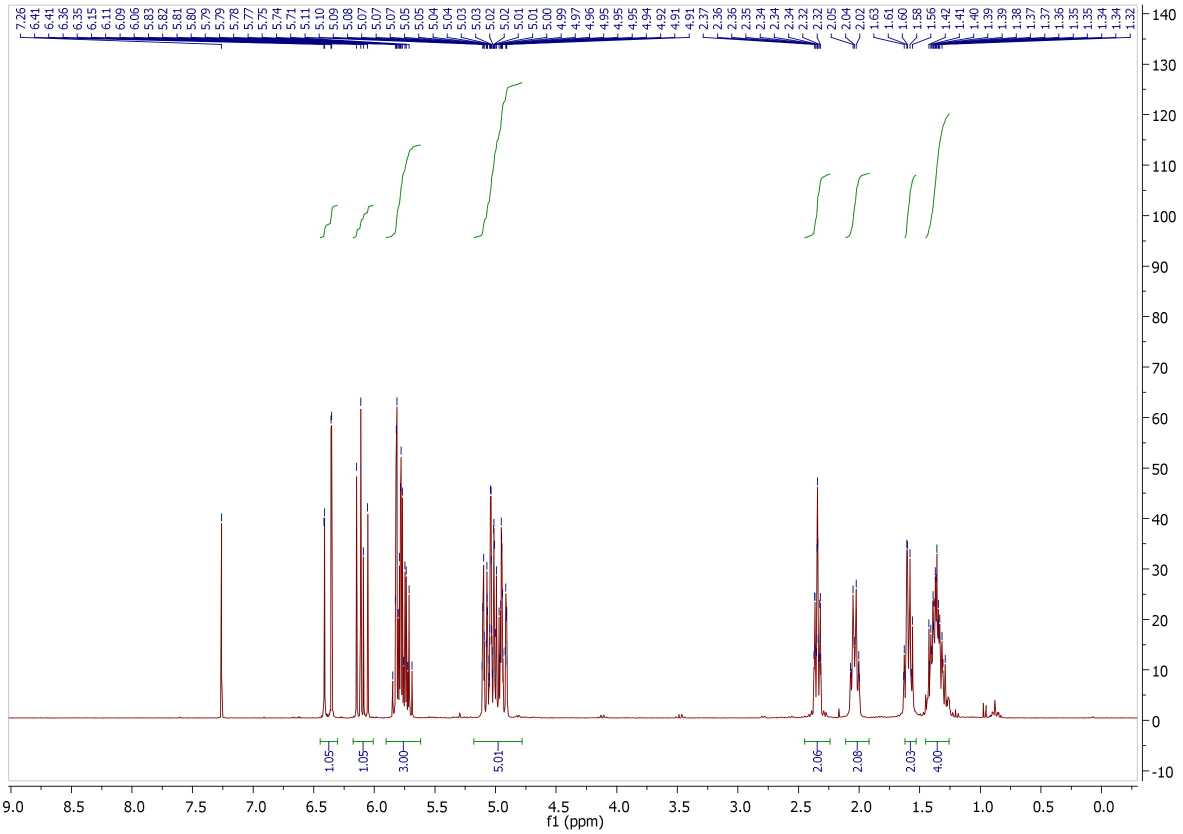
6 – ^{1}H NMR spectrum



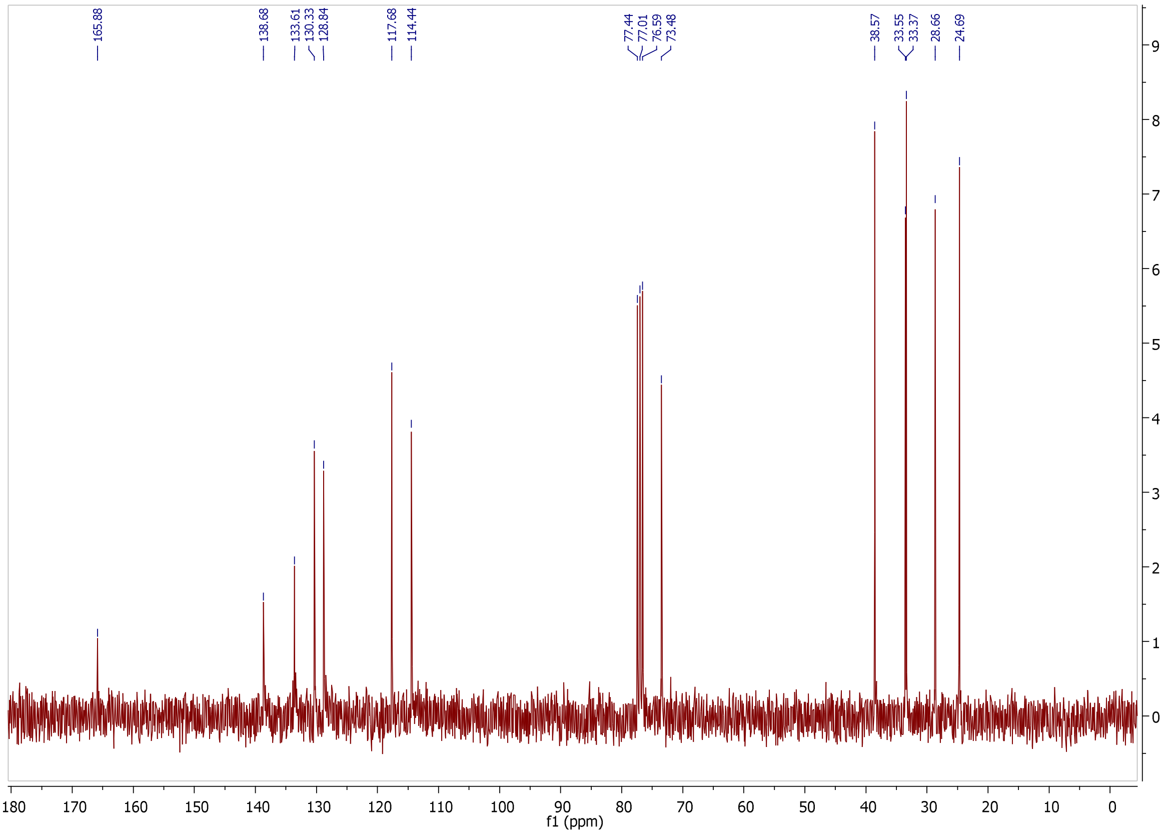
6 – ^{13}C NMR spectrum



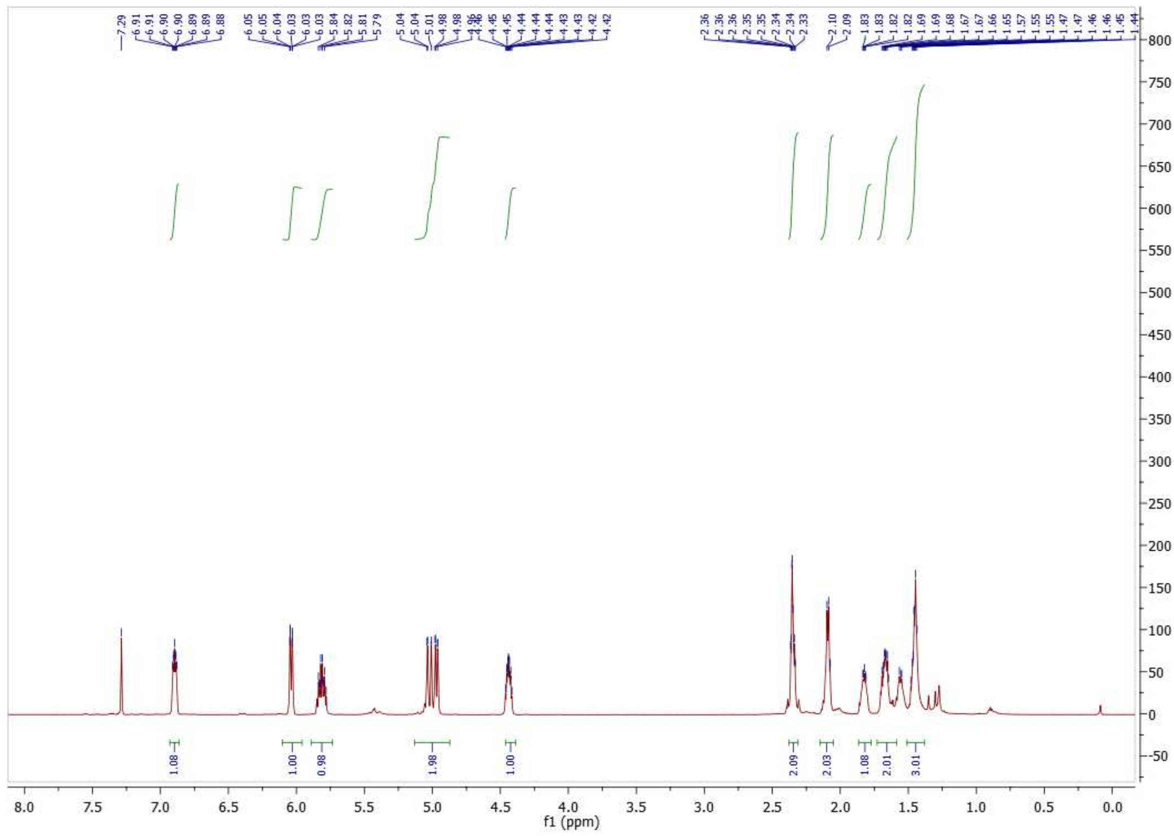
5 – ^{1}H NMR spectrum



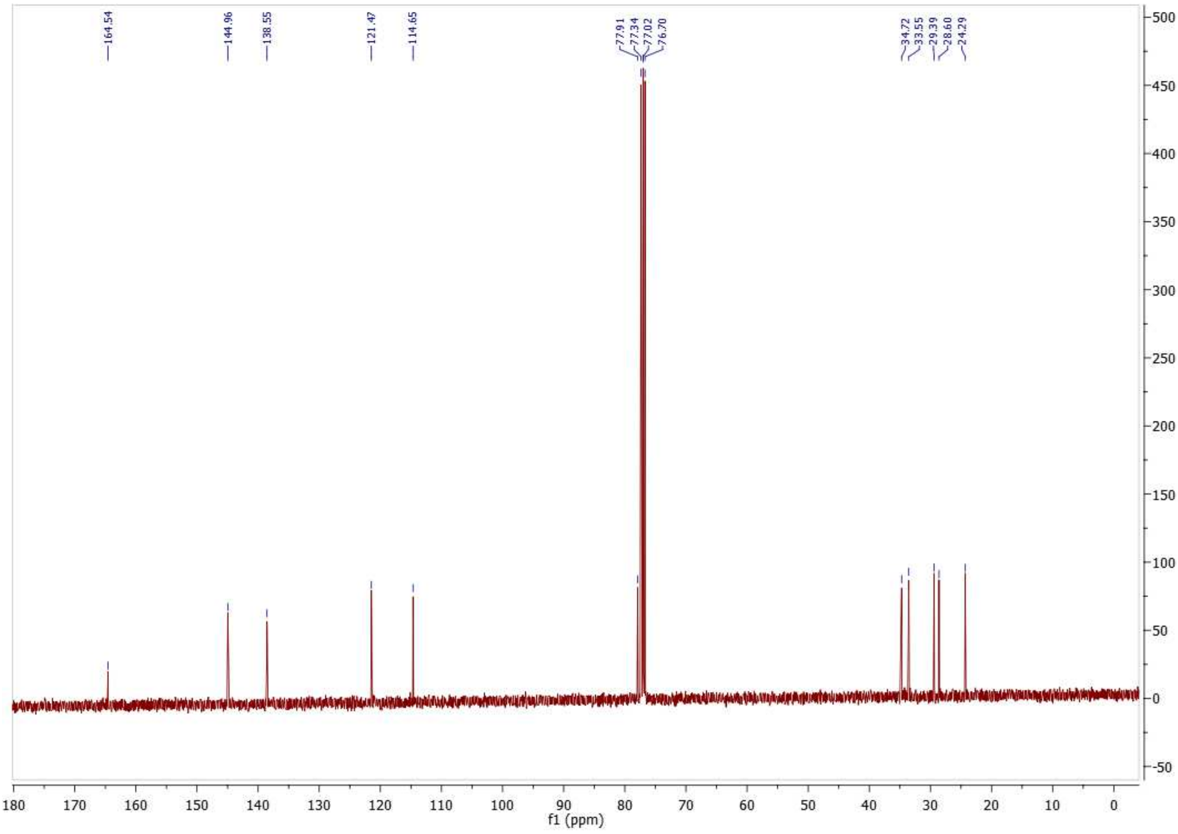
5 – ^{13}C NMR spectrum



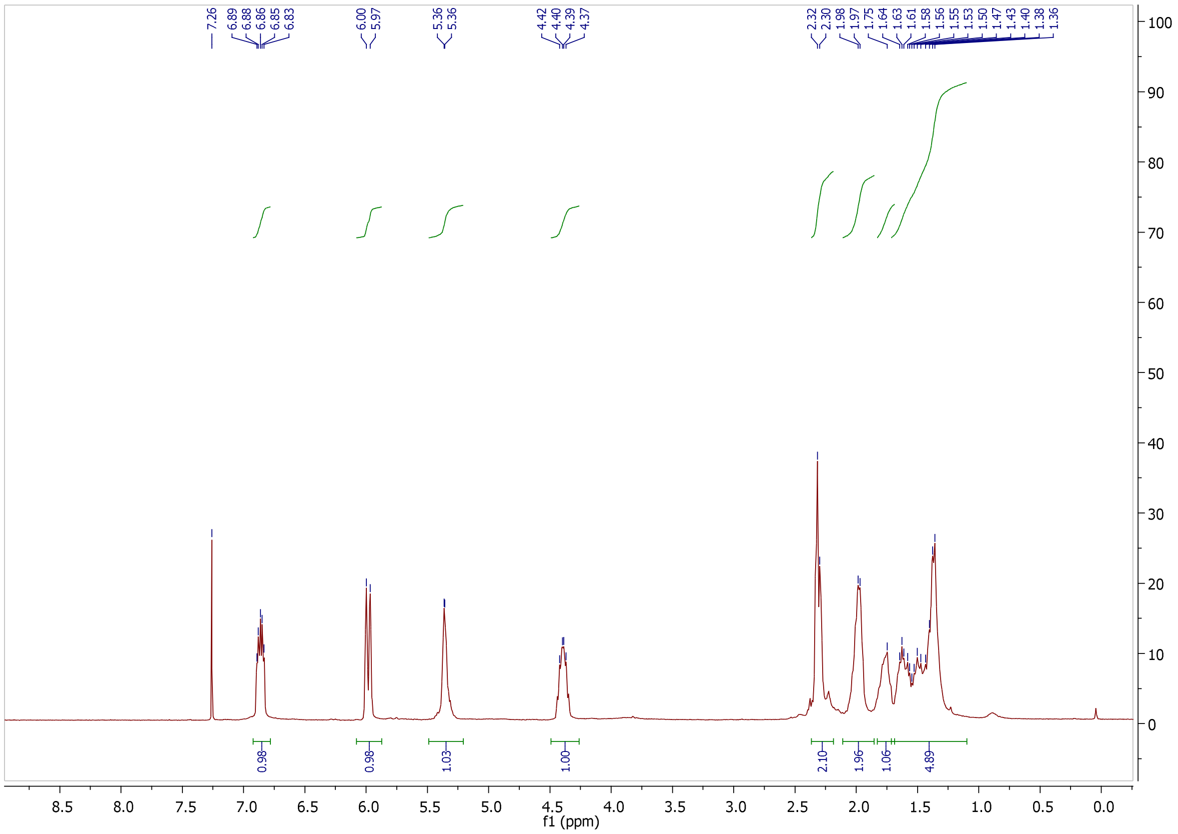
mon-3 – ^{1}H NMR spectrum



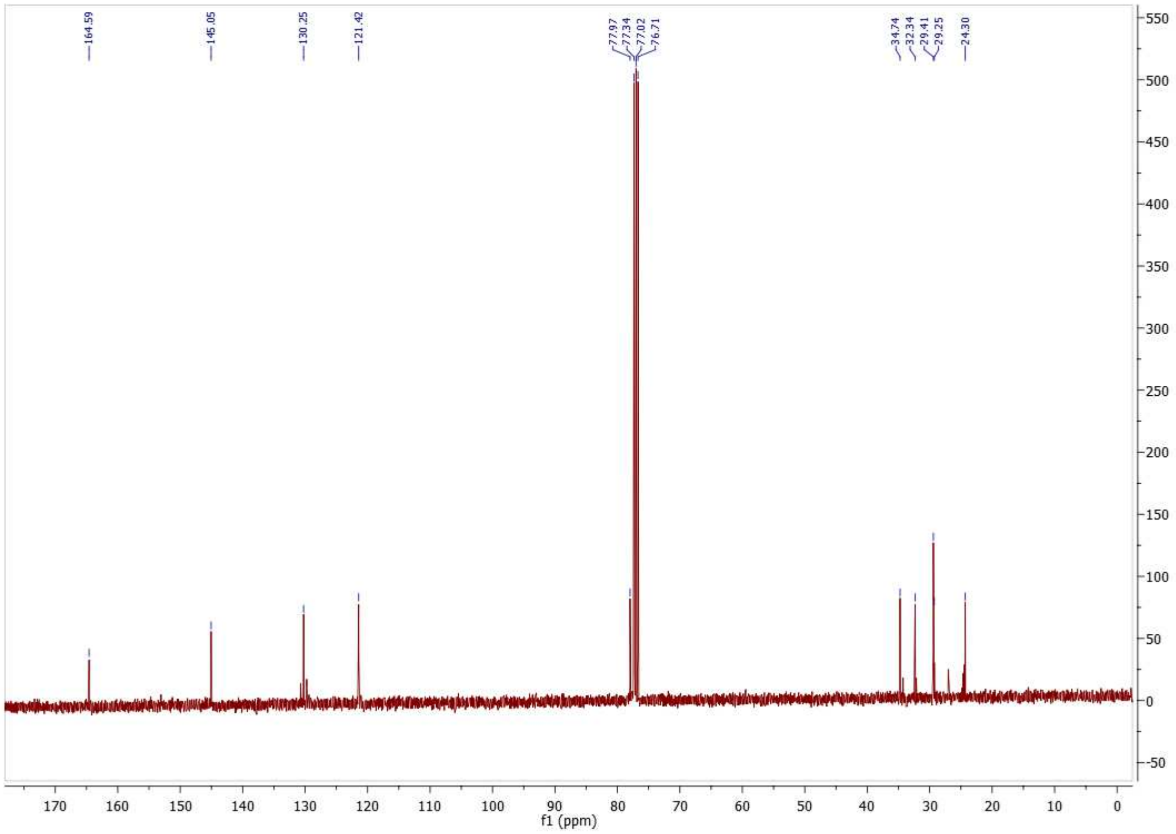
mon-3 – ^{13}C NMR spectrum



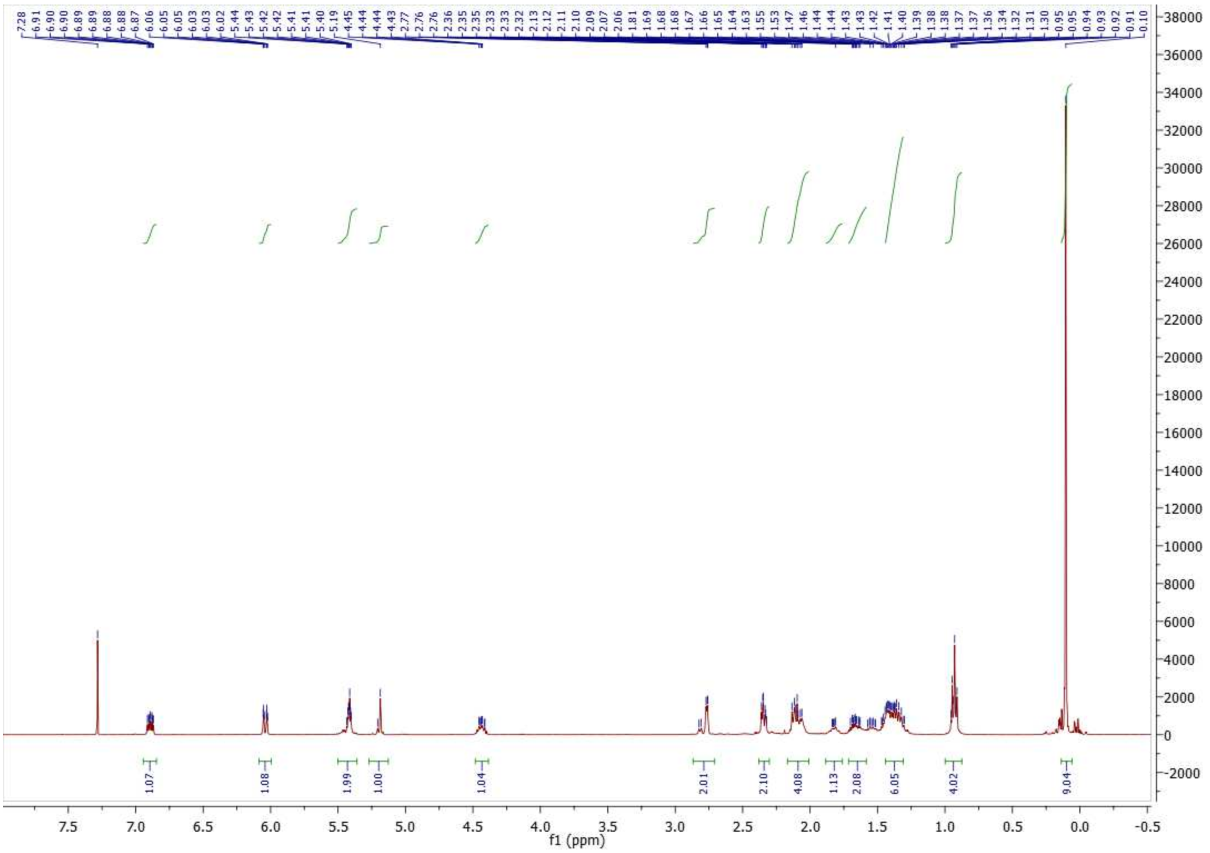
Dim-3 – ^{1}H NMR spectrum



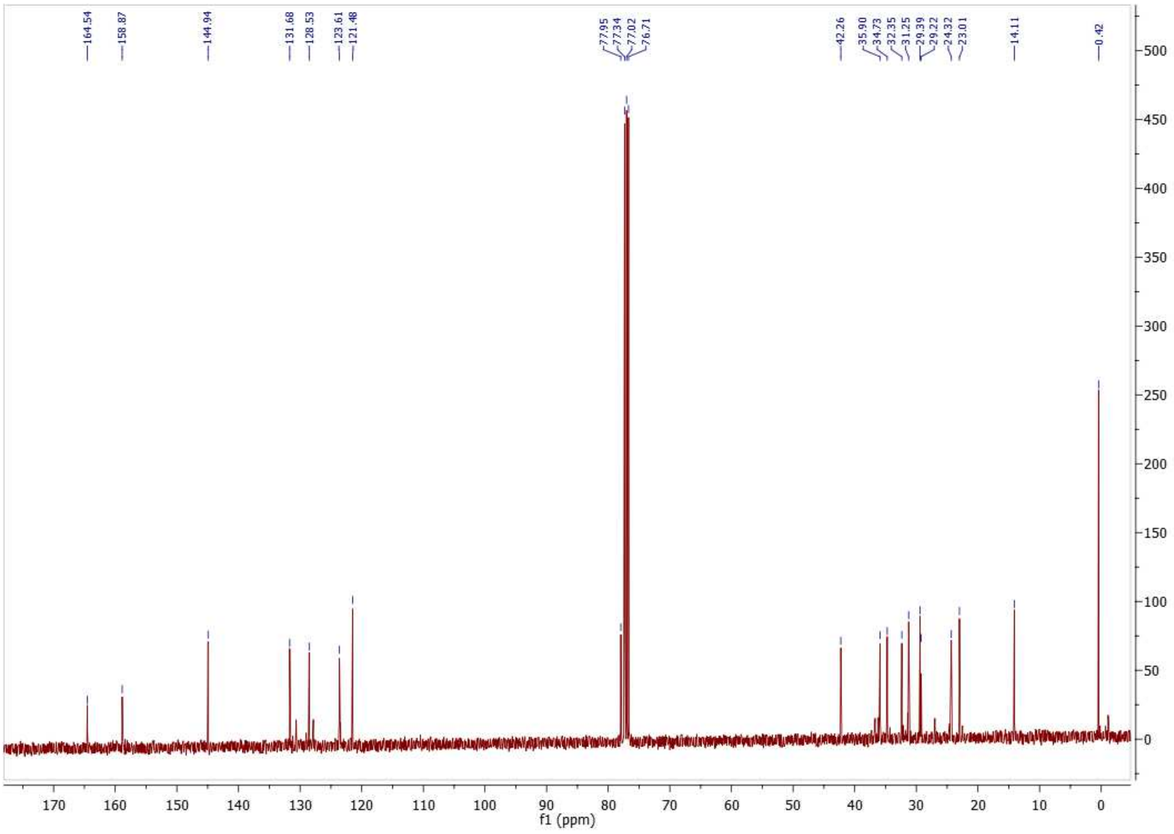
Dim-3 – ^{13}C NMR spectrum



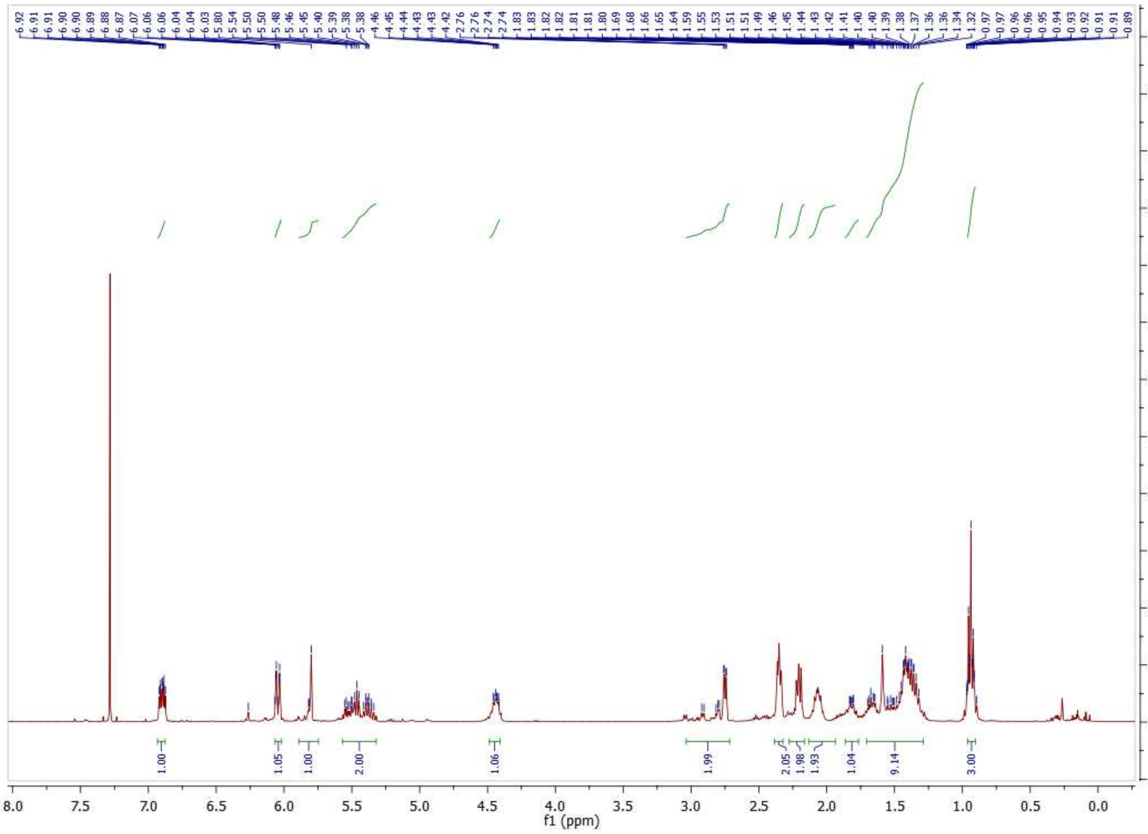
8a – ^{1}H NMR spectrum



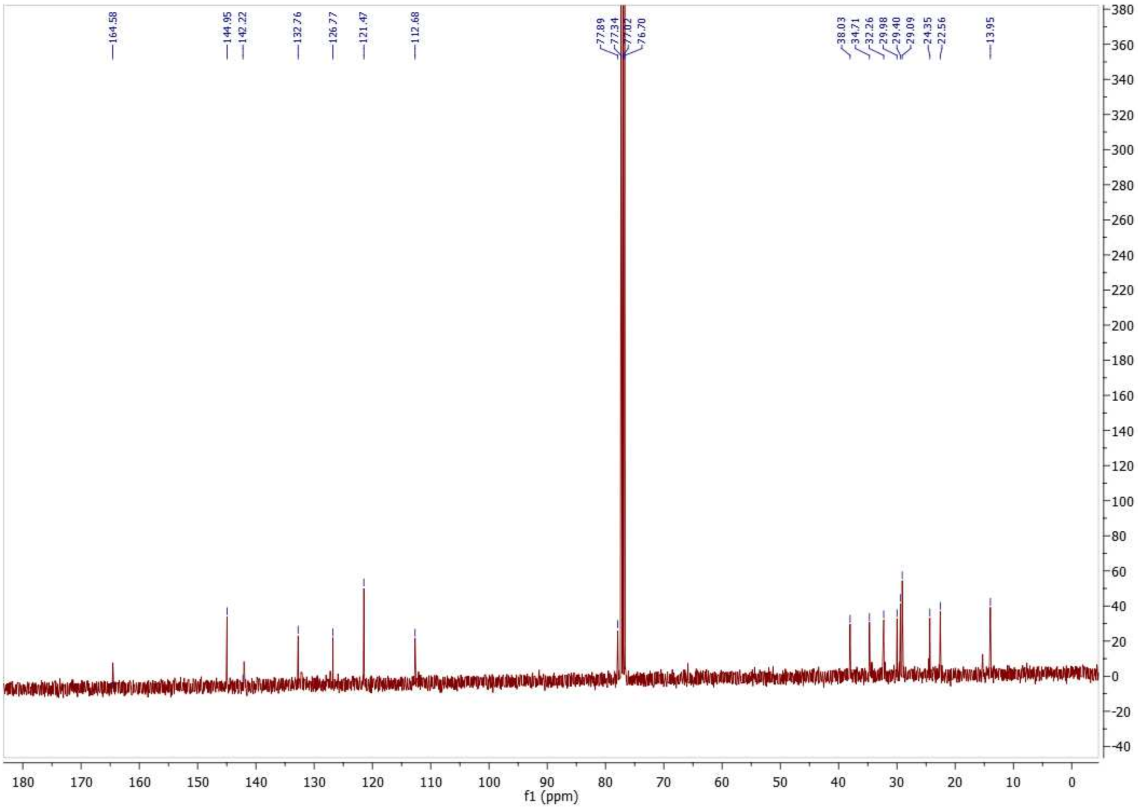
8a – ^{13}C NMR spectrum



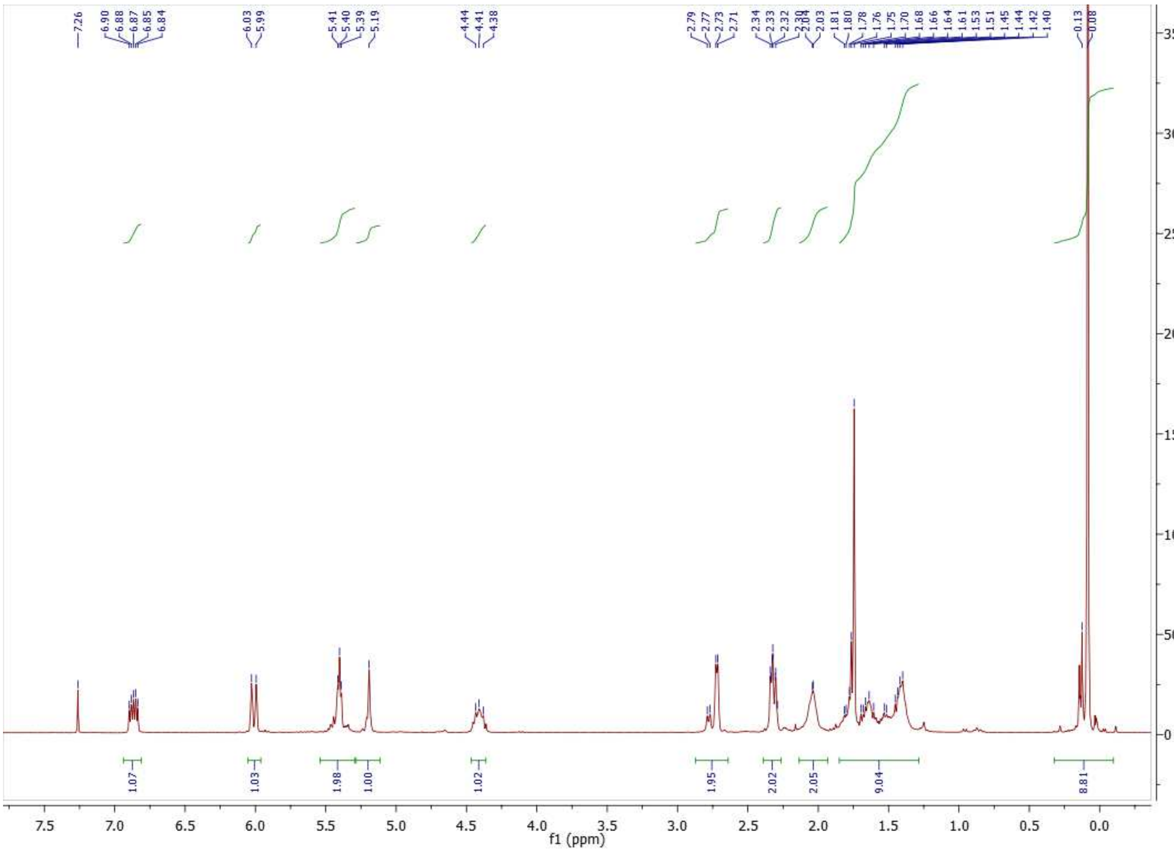
1a – ^{1}H NMR spectrum



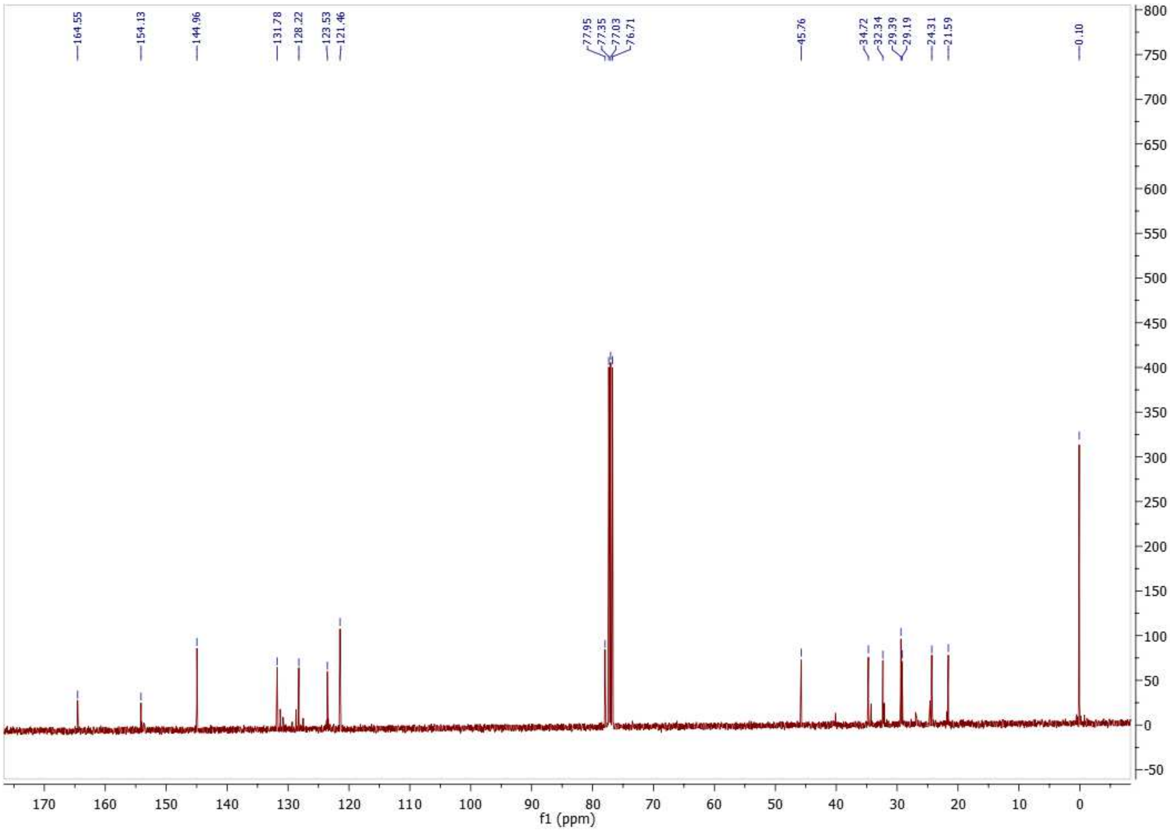
1a – ^{13}C NMR spectrum



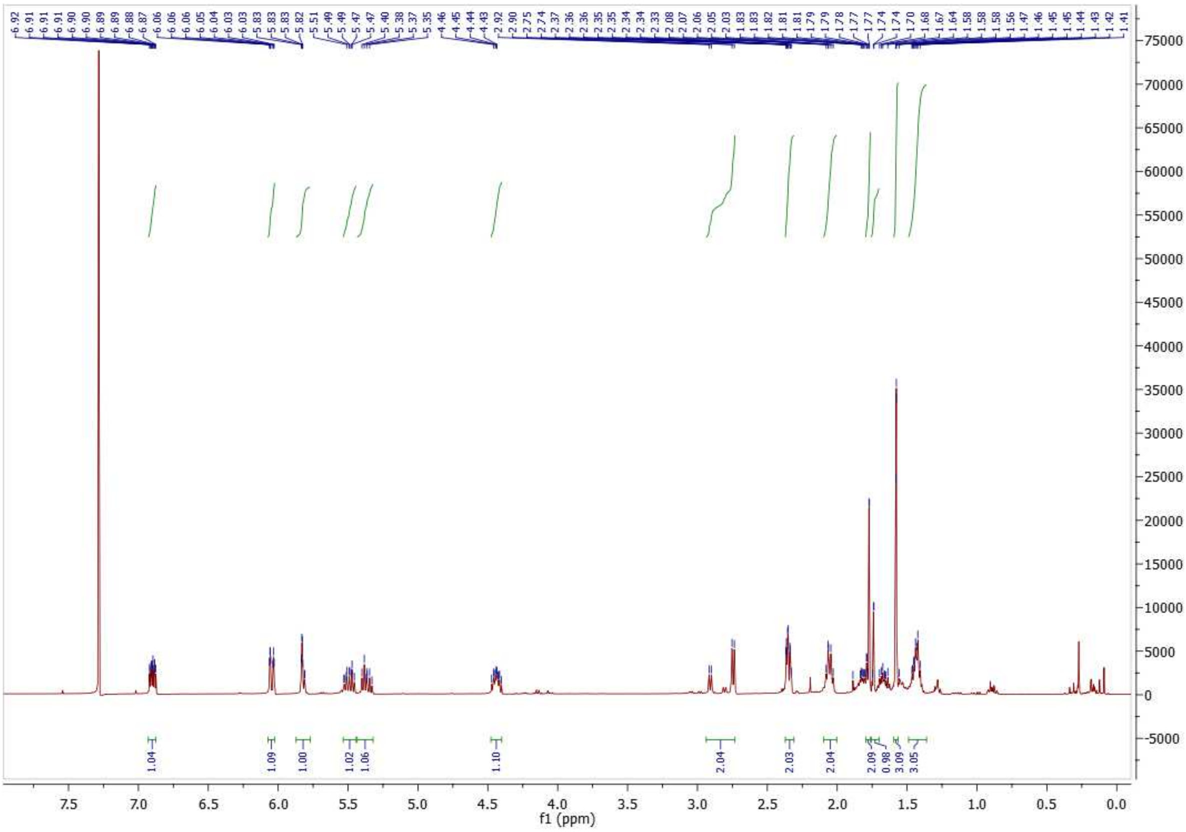
8b – ^{1}H NMR spectrum



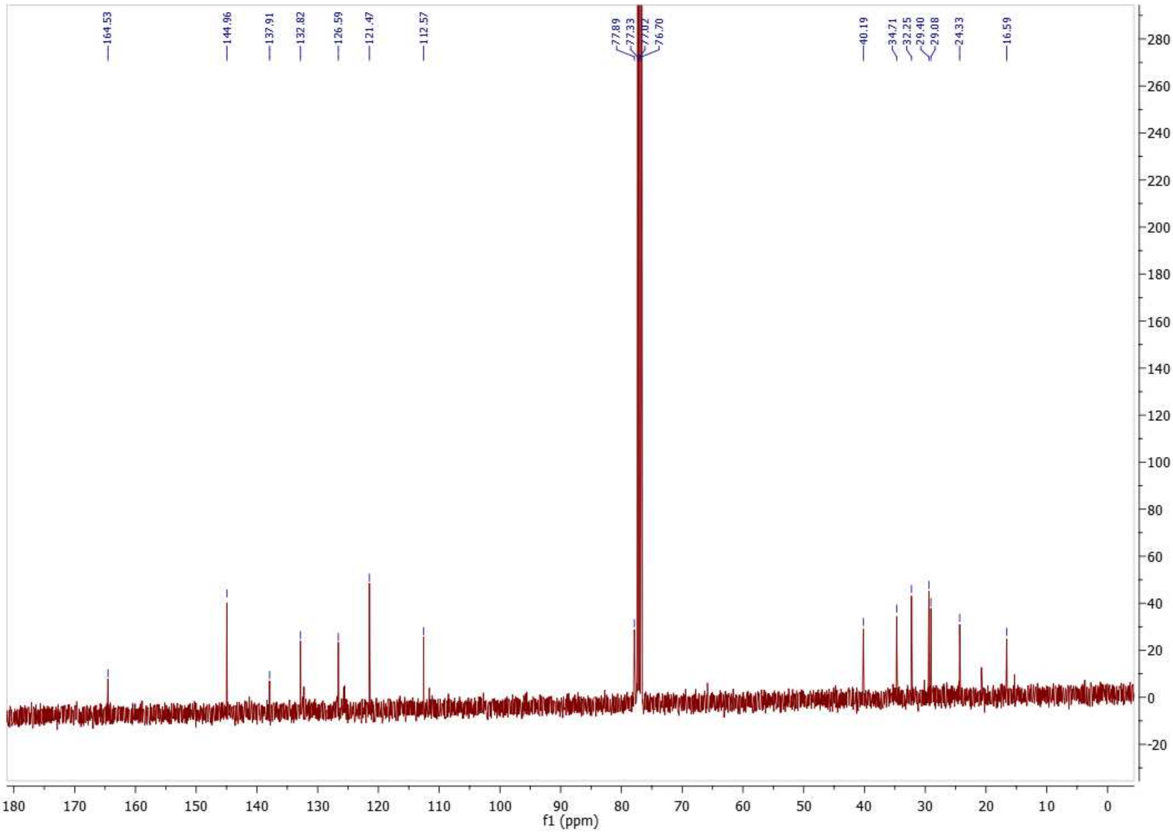
8b – ^{13}HCNMR spectrum



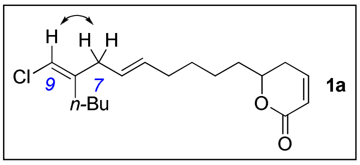
1b – ^{1}H NMR spectrum



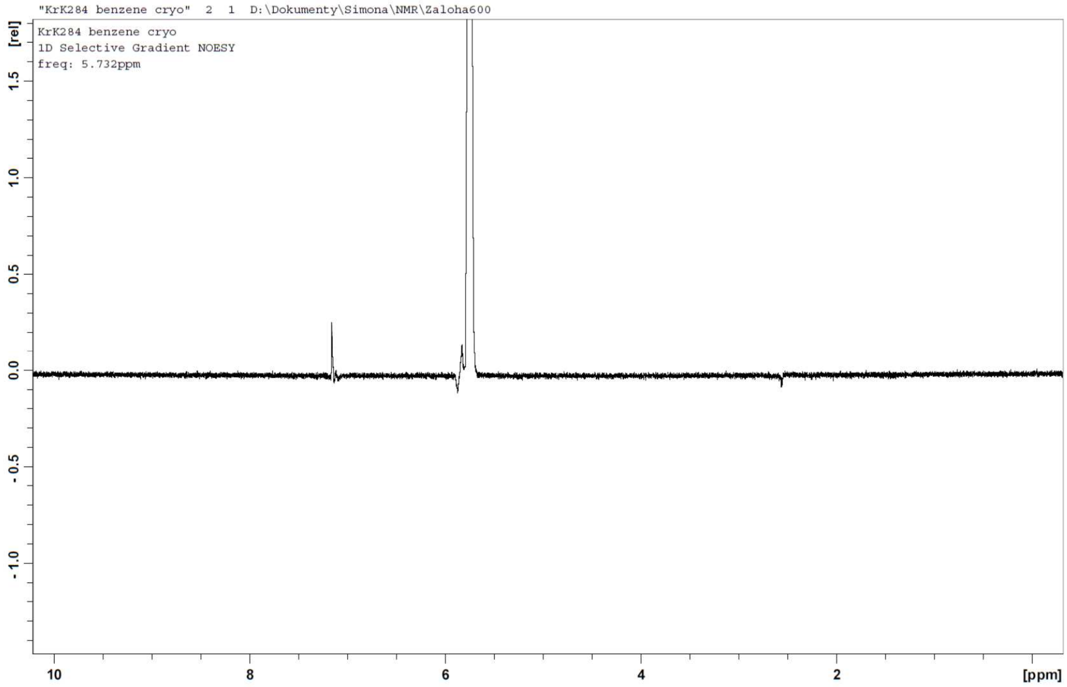
1b – ^{13}CNMR spectrum



1D-NOESY of **1a**



Irradiation of the hydrogen atom in the position 9 (5.80 ppm) having a cross peak with the hydrogen atoms in the position 7 (2.30-2.47 ppm).



Irradiation of the hydrogen atoms in the position 7 having a cross peak with the hydrogen atom in the position 9