Photocatalytic ATRA Reaction Promoted by Iodo-Bodipy and Sodium Ascorbate

Electronic Supplementary Information

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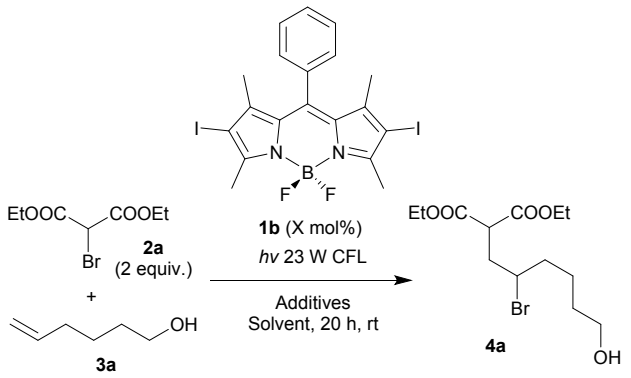
General methods. ^{1}H NMR spectra were recorded on Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: δ = 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = duplet, t = triplet, q = quartet, dd = double duplet, dt = double triplet, bs = broad signal, m = multiplet), coupling constants (Hz). ^{13}C NMR spectra were recorded on Varian MR400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: δ = 77.0 ppm). The elemental composition of the compounds was determined by using an elemental analyzer (Thermo Scientific, Flash 2000, Organic Elemental Analyzer) by means of the flash combustion technique. Chromatographic purification was done with 240-400 mesh silica gel. Purification on preparative thin layer chromatography was done on Merck TLC silica gel 60 F_{254}.

All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques. Synthesis grade solvents were used as purchased and the reaction mixtures were degassed by three cycles of freeze-pump-thaw.

Materials. If not otherwise stated, all reactions were carried out in flame dried glassware under nitrogen atmosphere. Anhydrous solvents were supplied by Aldrich in Sureseal® bottles and were used as received avoiding further purification. Bodipy **1b** was synthetized following reported procedure.[1] Precursor 1,3,5,7-tetramethyl-8-phenyl-dipyrromethane was prepared using the procedure reported by Zoli and Cozzi.[2]

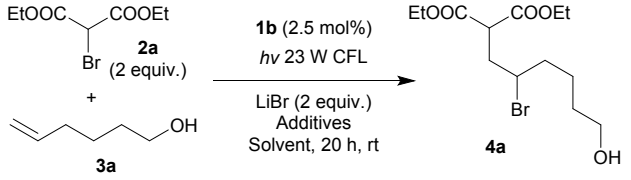
Compound **3b**[3] and **3d**[4] were prepared according to literature procedures.

Photocatalytic ATRA reaction: optimization



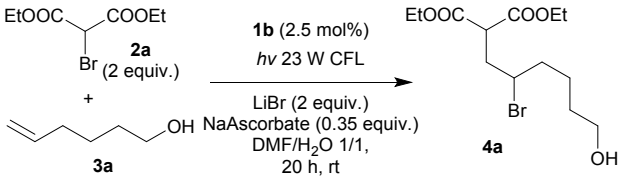
Entry[a]	1b (mol%)	LiBr	Additive	Solvent	Product 4a[b]
1	5	-	2,6-lutidine (1 equiv.)	CH_3CN	✘
2	2.5	2 equiv.	-	DMF/H_2O 1/4	✘
3	2.5	2 equiv.	-	DMF	✘
4	5	2 equiv.	TEA (2 equiv.)	DMF	✘
5	2.5	2 equiv.	TEA (0.35 equiv.)	DMF	✘

Table S1. a) The reactions were performed using **2a** (0.2 mmol), **3a** (0.1 mmol) and **1b** in the reported amount, in 200 µL of solvent; b) Determined by ^{1}H-NMR and TLC of the crude.



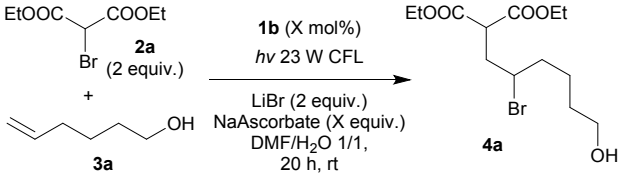
Entry[a]	Additive	Solvent	Product 4a[b]
1	TEA (0.35 equiv.)	DMF	✘
2	NaAscorbate (0.35 equiv.)	DMF/H_2O 4/1	✓ (42%)
3	Hantzsch ester[c] (0.35 equiv.)	DMF	✘
4	NaAscorbate (1 equiv.) 2,6-lutidine (2 equiv.)	DMF/H_2O 4/1	✘
5	NaAscorbate (1 equiv.)	DMF/H_2O 1/1	✓ (97%)

Table S2. a) The reactions were performed using **2a** (0.2 mmol), **3a** (0.1 mmol), LiBr (0.25 mmol), the additives and **1b** (0.0025 mmol) in 200 µL of solvent; b) Determined by ^{1}H-NMR and TLC of the crude, conversion inside brackets; c) Diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate.



Entry[a]	1b	LiBr	NaAscorbate	*hv*	Air	Product 4a[b]
1	Yes	Yes	Yes	Yes	No	✓ (97%)
2	No	Yes	Yes	Yes	No	✗
3	Yes	No	Yes	Yes	No	✓ (56%)
4	Yes	Yes	No	Yes	No	✗
5	Yes	Yes	Yes	No	No	✗
5	Yes	Yes	Yes	Yes	Yes	✗

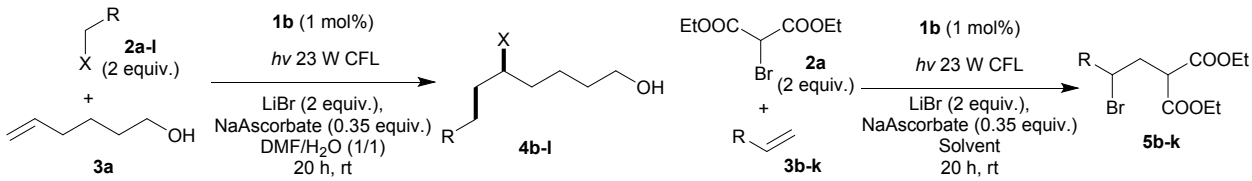
Table S3. a) The reactions were performed using **2a** (0.2 mmol), **3a** (0.1 mmol), LiBr (0.25 mmol), sodium ascorbate (0.035 mmol) and **1b** (0.0025 mmol) in 200 µL of solvent; b) Determined by ^{1}H-NMR and TLC of the crude, conversion inside brackets.



Entry[a]	mol% 1b	Eq. NaAscorbate	Yield (%)[b]
1	2.5	1	92
2	2.5	0.35	92
3	1	0.35	94

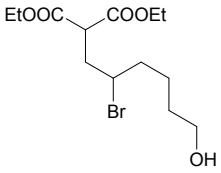
Table S4. a) The reactions were performed using **2a** (0.2 mmol), **3a** (0.1 mmol), LiBr (0.25 mmol), sodium ascorbate and **1b** in 200 µL of solvent; b) After column chromatography.

General procedure for the photocatalytic ATRA reaction:

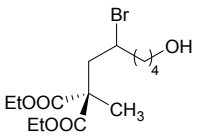


A dry 10 mL Schlenk tube, equipped with a Rotaflo Stopcock, magnetic stirring bar and an argon supply tube, was charged in order and under argon with the photocatalyst **1b** (1 mol%, 0.002 mmol, 1.2 mg), sodium ascorbate (0.35 equiv., 0.07 mmol, 14 mg), LiBr (2 equiv., 0.4 mmol, 35 mg), DMF (200 µL or if

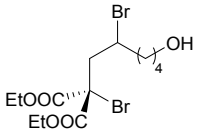
specified CH_3CN), alkyl halide (0.4 mmol, 2 equiv.), olefin (0.2 mmol, 1 equiv.) and water (200 µL, or MeOH if specified). The reaction mixture was degassed *via* freeze pump thaw (x3), and the vessel refilled with argon. The reaction mixture was positioned approximately 10 cm away from the light source (23 W CFL lamp). After vigorous stirring for 20 h, the mixture was transferred in a separator funnel and extracted with AcOEt (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give the crude products. The residue was purified by flash column chromatography (SiO_2) to afford the title compounds in the stated yields.



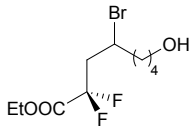
4a: 94% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2a** (0.4 mmol, 68 µL), **3a** (0.2 mmol, 24 µL) and H_2O (200 µL). Purification by flash column chromatography (7:3 cyclohexane:AcOEt) afforded the title compound **4a** (94% yield, 64 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_{13}H_{23}BrNaO_5^+$ $[M+Na]^+$ 361.0621, found 361.0625.



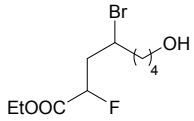
4b: 42% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2b** (0.4 mmol, 76 µL), **3a** (0.2 mmol, 24 µL) and H_2O (200 µL). Purification by flash column chromatography (7:3 cyclohexane:AcOEt) afforded the title compound **4b** (42% yield, 30 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_{14}H_{25}BrNaO_5^+$ $[M+Na]^+$ 375.0778, found 375.0782.



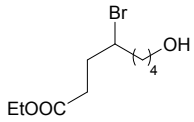
4c: 54% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2c** (0.4 mmol, 76 µL), **3a** (0.2 mmol, 24 µL) and H_2O (200 µL). Purification by flash column chromatography (8:2 cyclohexane:AcOEt) afforded the title compound **4c** (54% yield, 45 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_{13}H_{22}Br_2NaO_5^+$ $[M+Na]^+$ 438.9726, found 438.9734.



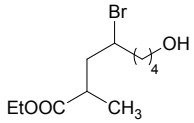
4d: 34% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2d** (0.4 mmol, 76 µL), **3a** (0.2 mmol, 24 µL) and H_2O (200 µL). Purification by flash column chromatography (8:2 cyclohexane:AcOEt) afforded the title compound **4d** (34% yield, 21 mg) as a colourless oil. Spectral properties were according to the literature.[6] HRMS (ESI): calculated for $C_{10}H_{17}BrF_2NaO_3^+$ $[M+Na]^+$ 325.0221, found 325.0230.



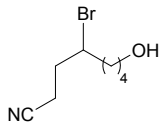
4e: 89% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2e** (0.4 mmol, 47 µL), **3a** (0.2 mmol, 24 µL) and H_2O (200 µL). Purification by flash column chromatography (7:3 cyclohexane:AcOEt) afforded the title compound **4e** (89% yield, 52 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_{10}H_{18}BrFNaO_3^+$ $[M+Na]^+$ 307.0316, found 307.0312.



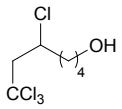
4f: 72% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2f** (0.4 mmol, 44 µL), **3a** (0.2 mmol, 24 µL) and H_2O (200 µL). Purification by flash column chromatography (7:3 cyclohexane:AcOEt) afforded the title compound **4f** (72% yield, 53 mg) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.15 (q, *J*=7.1, 2H), 4.12 – 4.04 (m, 1H), 3.68 (t, *J*=6.1, 2H), 2.66 – 2.43 (m, 2H), 2.26 – 2.15 (m, 1H), 2.14 – 2.00 (m, 1H), 1.94 – 1.80 (m, 2H), 1.73 – 1.57 (m, 4H), 1.28 (t, *J*=7.1, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 172.8, 62.6, 60.6, 56.9, 38.9, 33.9, 32.3, 32.0, 23.9, 14.2; HRMS (ESI): calculated for $C_{10}H_{19}BrNaO_3^+$ $[M+Na]^+$ 289.0410, found 289.0417.



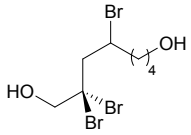
4g: 65% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2g** (0.4 mmol, 55 µL), **3a** (0.2 mmol, 24 µL) and H_2O (200 µL). Purification by flash column chromatography (gradient eluent from 8:2 to 6:4 cyclohexane:AcOEt) afforded the title compound **4g** (65% yield, 37 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_{11}H_{21}BrNaO_3^+$ $[M+Na]^+$ 303.0566, found 303.0556.



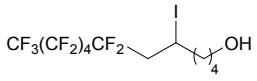
4h: 94% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2h** (0.4 mmol, 28 µL), **3a** (0.2 mmol, 24 µL) and H_2O (200 µL). Purification by flash column chromatography (7:3 cyclohexane:AcOEt) afforded the title compound **4h** (94 % yield, 41 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_8H_{15}BrNO^+$ $[M+H]^+$ 220.0332, found 220.0322.



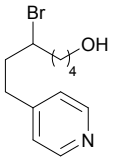
4i: 68% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiCl (0.4 mmol, 17 mg), DMF (200 µL), **2k** (0.4 mmol, 40 µL), **3a** (0.2 mmol, 24 µL) and H_2O (200 µL). Purification by flash column chromatography (7:3 cyclohexane:AcOEt) afforded the title compound **4k** (68% yield, 34 mg) as a colourless oil. Spectral properties were according to the literature.[5] Elemental Analysis: Found C, 33.8; H, 4.9%. Calc. for $C_7H_{12}Cl_4O$; C, 33.1; H, 4.8%.



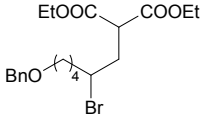
4j: 63% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2j** (0.4 mmol, 113 mg), **3a** (0.2 mmol, 24 µL) and H_2O (200 µL). Purification by flash column chromatography (6:4 cyclohexane:AcOEt) afforded the title compound **4j** (63% yield, 48 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_8H_{15}Br_3NaO_2^+$ $[M+Na]^+$ 402.8514, found 402.8519.



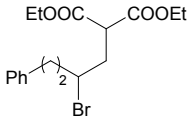
4k: 35% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2k** (0.4 mmol, 40 µL), **3a** (0.2 mmol, 24 µL) and H_2O (200 µL). Purification by flash column chromatography (gradient eluent from 8:2 to 6:4 cyclohexane:AcOEt) afforded the title compound **4k** (35% yield, 38 mg) as a colourless oil. Spectral properties were according to the literature.[5] Elemental Analysis: Found C, 26.2; H, 2.1%; Calc. for $C_{12}H_{12}F_{13}IO$; C, 26.4; H, 2.2%.



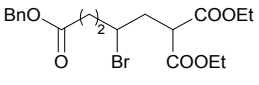
4l: 56% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (400 µL), **2l** (0.4 mmol, 101 mg), **3a** (0.2 mmol, 24 µL) and H_2O (400 µL). After stirring for 20 h, the crude mixture was diluted with DCM (15 mL) and NaOH 0.1 N (15 mL) were added. The phases were separated and the organic layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product. The final mixture was purified by flash column chromatography (8:2 AcOEt:cyclohexane) to afford the title compound **4l** (56% yield, 30 mg) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.49 (bs, 2H), 7.14 (d, *J*=5.2, 2H), 4.01 – 3.86 (m, 1H), 3.65 (t, *J*=5.6, 2H), 2.96 – 2.85 (m, 1H), 2.74-2.69 (m, 1H), 2.21 – 1.97 (m, 2H), 1.97 – 1.78 (m, 2H), 1.73 – 1.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ 150.0, 149.6 (2C), 124.0 (2C), 62.3, 56.7, 39.4, 38.9, 33.1, 32.0, 23.9; HRMS (ESI): calculated for $C_{12}H_{19}BrNO^+$ $[M+H]^+$ 272.0645, found 272.0636.



5b: 77% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2a** (0.4 mmol, 68 µL), **3b** (0.2 mmol, 41 µL) and H_2O (200 µL). Purification by flash column chromatography (95:5 cyclohexane:AcOEt) afforded the title compound **5b** (77% yield, 66 mg) as a colourless oil. Spectral properties were according to the literature.[6] HRMS (ESI): calculated for $C_{20}H_{29}BrNaO_5^+$ $[M+Na]^+$ 451.1091, found 451.1083.

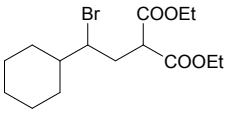


5c: 62% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), CH_3CN (200 µL), **2a** (0.4 mmol, 68 µL), **3c** (0.2 mmol, 30 µL) and MeOH (200 µL). Purification by flash column chromatography (95:5 cyclohexane:AcOEt) afforded the title compound **5c** (62% yield, 46 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_{17}H_{23}BrNaO_4^+$ $[M+Na]^+$ 393.0672, found 393.0679.

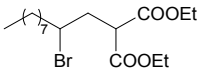


5d: 46% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2a** (0.4 mmol, 68 µL), **3d** (0.2 mmol, 41 µL) and H_2O (200 µL). Purification by flash column chromatography (95:5 cyclohexane:AcOEt) afforded the title compound **5d** (46% yield, 40

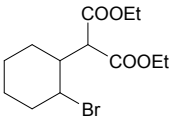
mg) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.40 – 7.32 (m, 5H), 5.10 (s, 2H), 4.28 – 4.14 (m, 4H), 4.13 – 3.99 (m, 1H), 3.77 (dd, *J*=10.0, 4.4, 1H), 2.75 – 2.62 (m, 1H), 2.62 – 2.54 (m, 1H), 2.54 – 2.42 (m, 1H), 2.37 – 2.20 (m, 2H), 2.18 – 2.06 (m, 1H), 1.31 – 1.25 (m, 6H); ^{13}C NMR (100 MHz ,$CDCl_3$, 25 °C): 172.2, 168.8, 168.5, 135.7, 128.5 (2C), 128.3, 128.2 (2C), 66.4, 61.7, 61.7, 53.4, 50.4, 37.8, 34.1, 32.2, 14.0, 14.0; HRMS (ESI): calculated for $C_{19}H_{25}BrNaO_6^+$ [M+Na]$^+$ 451.0727, found 451.0720.



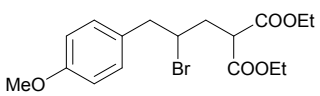
5e: 64% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), CH_3CN (200 µL), **2a** (0.4 mmol, 68 µL), **3e** (0.2 mmol, 27 µL) and MeOH (200 µL). Purification by flash column chromatography (20:1 cyclohexane:AcOEt) afforded the title compound **5e** (64% yield, 45 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_{15}H_{25}BrNaO_4^+$ [M+Na]$^+$ 371.0828, found 371.0832.



5f: 49% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), CH_3CN (200 µL), **2a** (0.4 mmol, 68 µL), **3f** (0.2 mmol, 38 µL) and MeOH (200 µL). Purification by flash column chromatography (20:1 cyclohexane:AcOEt) afforded the title compound **5f** (49% yield, 37 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_{17}H_{31}BrNaO_4^+$ [M+Na]$^+$ 401.1298, found 401.1308.

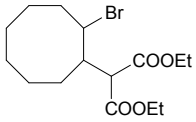


5g: 68% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2a** (0.4 mmol, 68 µL), **3g** (0.2 mmol, 20 µL) and H_2O (200 µL). Purification by flash column chromatography (20:1 cyclohexane:AcOEt) afforded the title compound **5g** (64% yield, 43 mg) as a colourless oil. Spectral properties were according to literature.[5] HRMS (ESI): calculated for $C_{13}H_{21}BrNaO_4^+$ [M+Na]$^+$ 343.0515, found 343.0522.

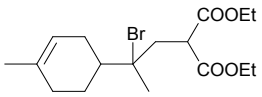


5h: 58% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2a** (0.4 mmol, 68 µL), **3h** (0.2 mmol, 31 µL) and H_2O (200 µL).

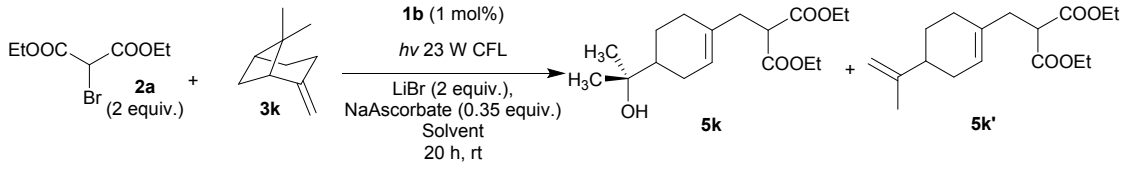
Purification by flash column chromatography (95:5 cyclohexane:acetone) afforded the title compound **5h** (58% yield, 44 mg) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.17 – 7.10 (m, 2H), 6.89 – 6.81 (m, 2H), 4.27 – 4.08 (m, 5H), 3.81-3.74 (m, 1H), 3.77 (s, 3H), 3.24 – 3.07 (m, 2H), 2.50 (tdd, *J*=19.4, 13.5, 5.8, 1H), 2.23 (ddd, *J*=14.9, 11.0, 4.0, 1H), 1.32 – 1.18 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 168.9, 168.8, 158.5, 130.2 (2C), 129.8, 113.8 (2C), 61.7, 61.6, 55.2, 54.6, 50.6, 44.9, 37.0, 14.0 (2C); HRMS (ESI): calculated for $C_{17}H_{23}BrNaO_5^+$ [M+Na]$^+$ 409.0621, found 409.0616.



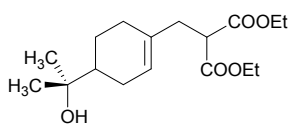
5i: 45% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), CH_3CN (200 µL), **2a** (0.4 mmol, 68 µL), **3i** (0.2 mmol, 26 µL) and MeOH (200 µL). Purification by flash column chromatography (30:1 cyclohexane:AcOEt) afforded the title compound **5i** (45% yield, 31 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_{15}H_{25}BrNaO_4^+$ [M+Na]$^+$ 371.0828, found 371.0834.



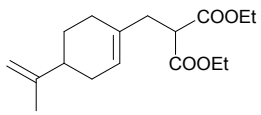
5j: 47% yield; the reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2a** (0.4 mmol, 68 µL), **3j** (0.2 mmol, 32 µL) and H_2O (200 µL). Purification by flash column chromatography (9:1 cyclohexane:acetone) afforded the title compound **5j** (47% yield, 35 mg) as a colourless oil. Spectral properties were according to the literature.[5] HRMS (ESI): calculated for $C_{17}H_{27}BrNaO_4^+$ [M+Na]$^+$ 397.0985, found 397.0990.



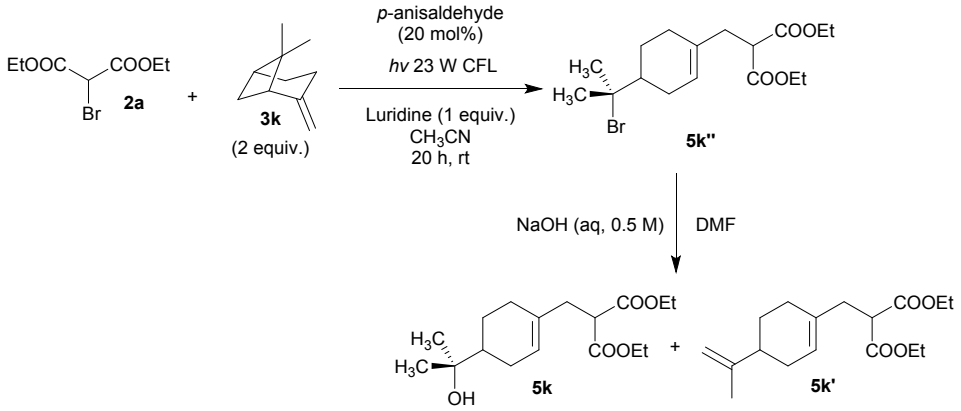
The reaction was performed following the general procedure using the photocatalyst **1b** (1% mol, 1.2 mg), sodium ascorbate (0.07 mmol, 14 mg), LiBr (0.4 mmol, 35 mg), DMF (200 µL), **2a** (0.4 mmol, 68 µL), **3k** (1S)-(-)-β-pinene (0.2 mmol, 32 µL) and H_2O (200 µL). Purification by flash column chromatography (95:5 to 50:50 cyclohexane:AcOEt) afforded the title compounds **5k** (29% yield) and **5k'** (18% yield) as colourless oils.



(**5k**): ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 5.47 – 5.36 (m, 1H), 4.15 (q, *J*=7.1, 4H), 3.50 (t, *J*=7.9, 1H), 2.52 (d, *J*=7.8, 2H), 2.13 – 1.92 (m, 3H), 1.91 – 1.82 (m, 1H), 1.82 – 1.68 (m, 1H), 1.51 – 1.39 (m, 1H), 1.25 – 1.20 (m, 7H), 1.15 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ =169.3, 169.2, 133.7, 123.2, 72.6, 61.3 (2C), 50.7, 44.8, 36.4, 28.9, 27.4, 26.8, 26.3, 23.8, 14.1 (2C); HRMS (ESI): calculated for $C_{17}H_{29}O_5^+$ $[M+H]^+$ 313.2010, found 313.2004.

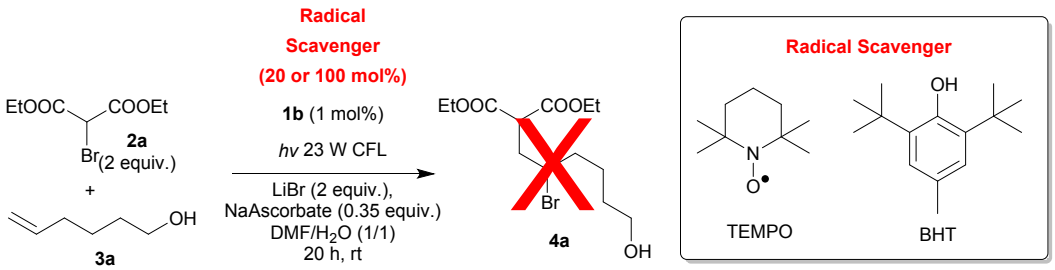


(**5k'**): ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 5.50 – 5.46 (m, 1H), 4.74 – 4.66 (m, 2H), 4.19 (q, *J*=7.1, 4H), 3.54 (t, *J*=7.9, 1H), 2.56 (d, *J*=7.8, 2H), 2.18-1.95 (m, 4H), 1.95 – 1.85 (m, 1H), 1.85 – 1.76 (m, 1H), 1.72 (s, 3H), 1.44 (tdd, *J*=13.3, 11.4, 5.8, 1H), 1.29 – 1.23 (m, 6H);^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.3 (2C), 149.8, 133.4, 123.2, 108.6, 61.3 (2C), 50.7, 40.9, 36.5, 30.7, 28.4, 27.7, 20.8, 14.1 (2C).



Structures of compounds **5k** and **5k'** were confirmed by chemical correlation and NMR spectroscopy (^{1}H, ^{13}C, COSY, HSQC NMR experiments). Compound **5k''** was prepared following the procedure reported by Melchiorre[5] (0.1 mmol of (-)-β-pinene). Then the reaction crude was dissolved in DMF (2 mL) and treated with an aqueous solution of NaOH (0.5 M, 2 mL). After 3 hours the mixture was transferred in a separator funnel and extracted with AcOEt (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give a mixture of **5k** and **5k'** in 36:64 ratio with complete conversion of **5k''**.

Evidences of radical mechanism



Evidence of a possible radical mechanism was highlighted performing the reaction in presence of radical scavengers. The experiments were performed using general procedure in the presence of catalytic (20 mol%) and stoichiometric amount of TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) or BHT (3,5-di-*tert*-butylhydroxytoluene). In both cases no formation of the desired product or adducts between TEMPO and reaction intermediates were observed.

Photophysical measurements

Photochemical experiments were carried out at room temperature in deaerated solutions. All absorption spectra were recorded in a quartz cuvette (optical pathlength 0.1 cm) with a UV/VIS spectrophotometer Perkin Elmer Lambda 650. Luminescence spectra were performed with a PerkinElmer LS-55. Lifetimes of **1b** with increasing amount of NaAscorbate were measured by Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution) with a PicoQuant pulsed diode laser 340 ± 20 nm.

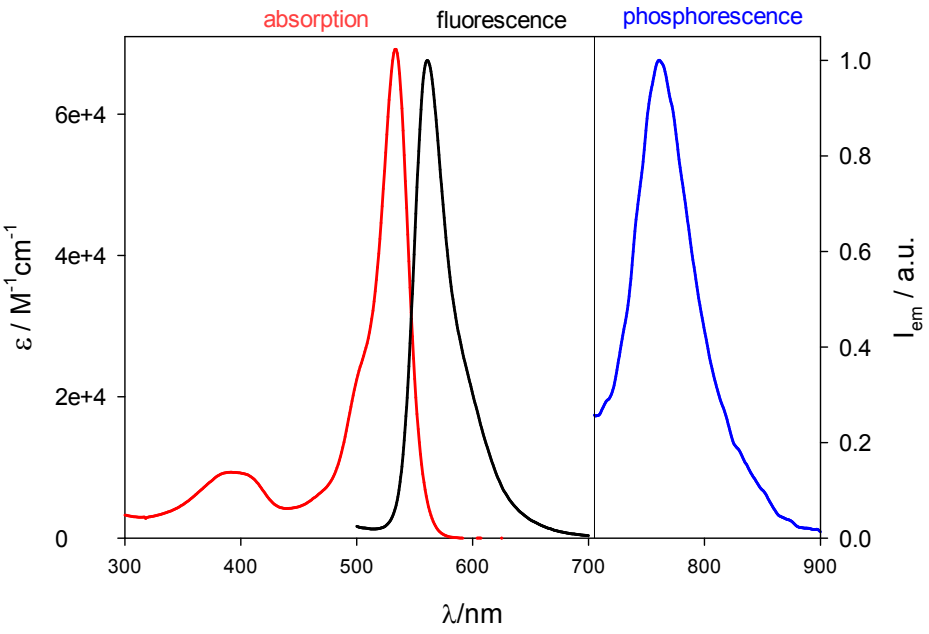


Figure S1. Absorption (red solid line) and fluorescence emission (black solid line, λ_{ex} 405 nm) spectra of **1b** in DMF Uvasol® at 298 K. The phosphorescence emission spectrum (blue solid lines) was obtained after 5 freeze-pump cycles (λ_{ex} 525 nm).

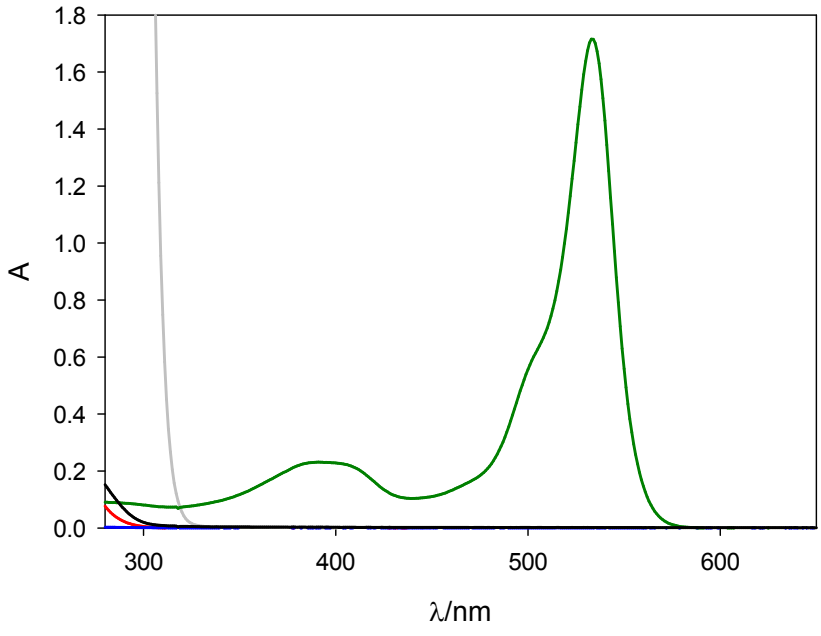


Figure S2. Absorption spectra of 5-hexenol 0.25 M (blue solid line), diethyl 2-bromo-malonate 0.5 M (red solid line), sodium ascorbate 0.088 M (grey solid line), lithium bromide 0.5 M (black solid line) and **1b** 2.5 ×

10^{-4} M (dark green solid line) in DMF Uvasol®:H_2O ratio 1:1. The amount of the species in solution is the same used in reaction mixture condition, a part from **1b**, that is ten times more diluted.

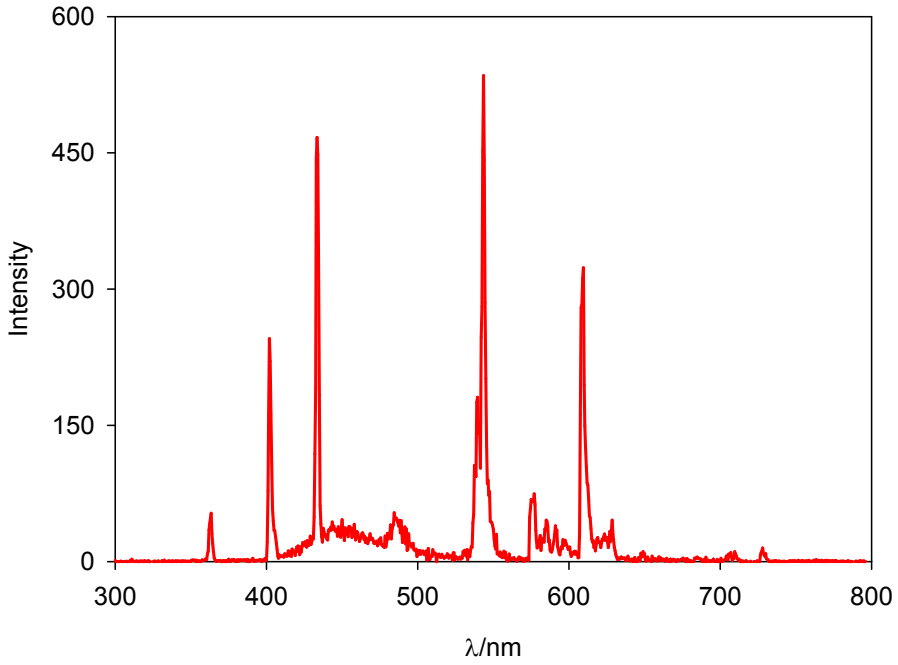


Figure S3. Emission profile of the 23W Compact Fluorescent lamp used to irradiate the solutions.

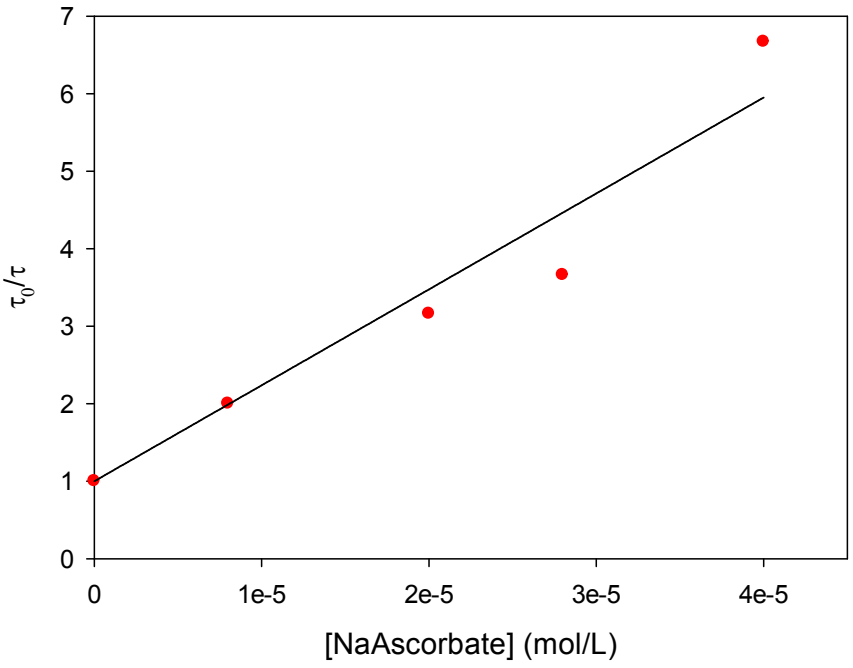


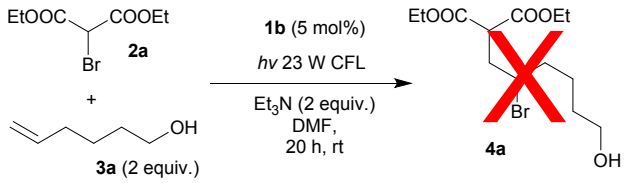
Figure S4. Stern-Volmer quenching plot. After every addition of NaAscorbate, the solution undergoes 5 freeze-pump cycles, before collecting the phosphorescence lifetime.

The Stern-Volmer plot shows a linear correlation between the amounts of NaAscorbate and the ratio τ_0/τ. On the basis of the Stern-Volmer equation (1), it is possible to calculate the quenching constant:

(1) $\tau_0/\tau = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q]$

We calculated a quenching constant k_q of 5.5 x 10^8 $M^{-1}s^{-1}$. The estimated value of k_q is high and close to the diffusion limit.

Reaction in presence of triethylamine



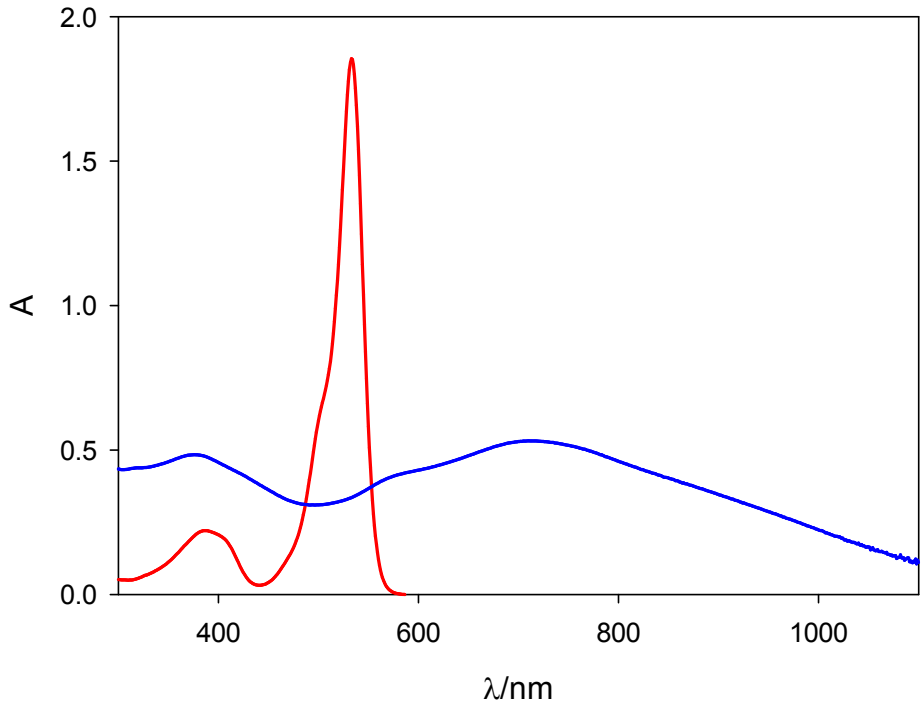


Figure S5. Absorption spectra of reaction mixture containing **3a** 0.01 M, **2a** 0.005 M, **1f** 2.5 × 10^{-4} M (red solid line), and upon addition of Et_3N 0.01 M and irradiation with 23W Compact Fluorescent lamp (blue solid line) in DMF Uvasol®. The amount of the species in solution is a hundred times more diluted respect to the reaction mixture.

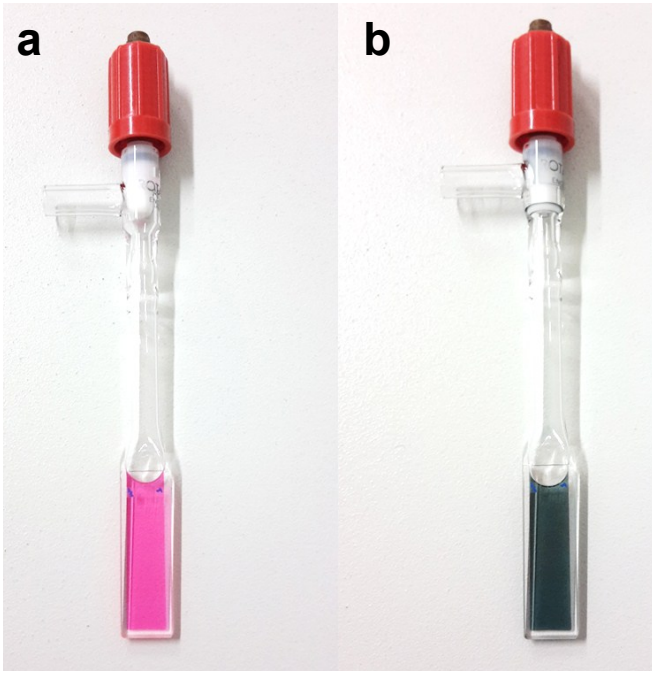


Figure S6. Reaction mixture without Et_3N (cuvette on the left) and after addition of the amine and 30 minutes of irradiation with 23W Compact Fluorescent lamp (cuvette on the right).

References:

[1] C. Zhang, J. Zhao, S. Wu, Z. Wang, W. Wu, J. Ma, S. Guo and L. Huang, *J. Am. Chem. Soc.* 2013, **135**, 10566-10578.

[2] L. Zoli and P. G. Cozzi, *ChemSusChem* 2009, **2**, 218-220.

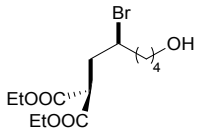
[3] I. Taisuk, M. Takumi, S. Yohei and K. Motomu *Chem.—Eur. J.* 2015, **21**, 15955-15959.

[4] A. Palani, J. Su, D. Xiao, X. Huang, A. U. Rao, X. Chen, H. Tang, J. Qin, Y. R. Huang, R. G. Aslanian, B. A. Mckittrick and S. Degrado, U.S. Pat. Appl. Publ. 238 pp., 2008, US 20080019978 A1.

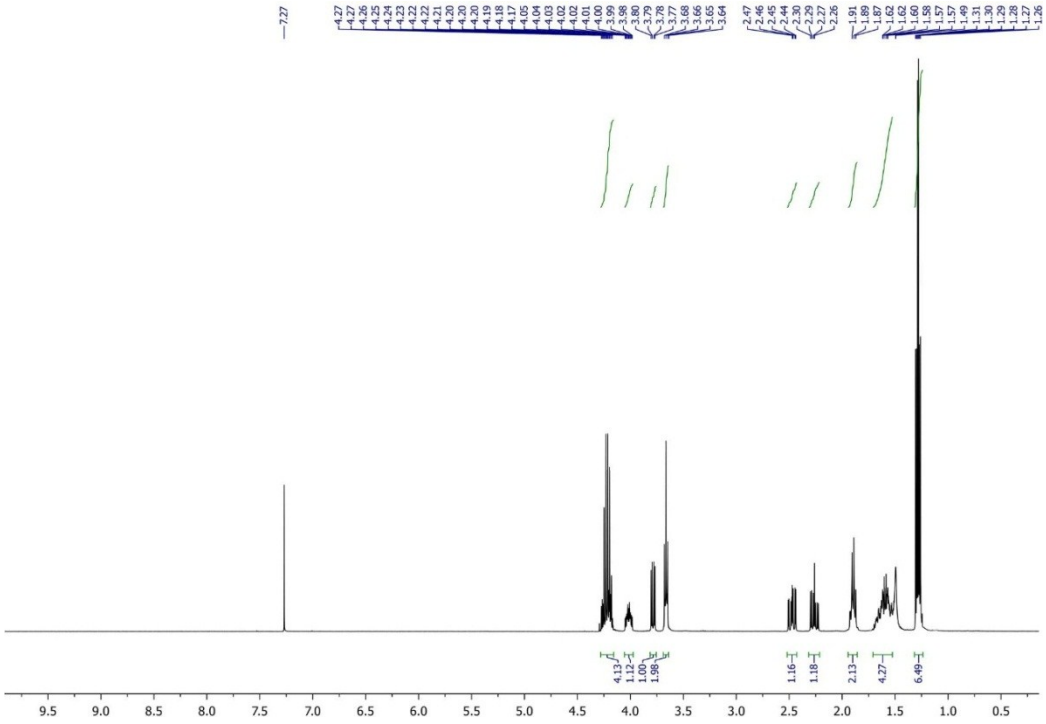
[5] E. Arceo, E. Montroni and P. Melchiorre *Angew. Chem. Int. Ed.* 2014, **53**, 12064 –12068.

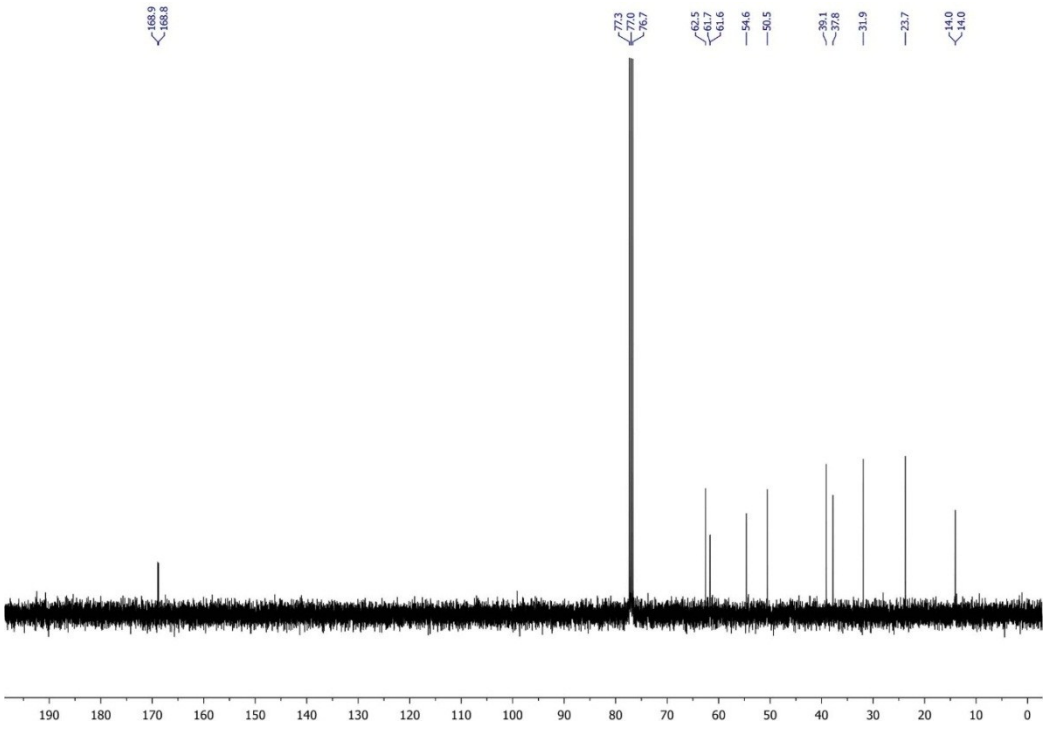
[6] J. D. Nguyen, J.W. Tucker, M. D. Konieczynska and C. R. J. Stephenson, *J. Am. Chem. Soc.* 2011, **133**, 4160-4163.

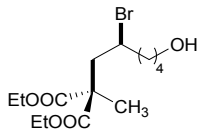
Copies of NMR spectra



4a



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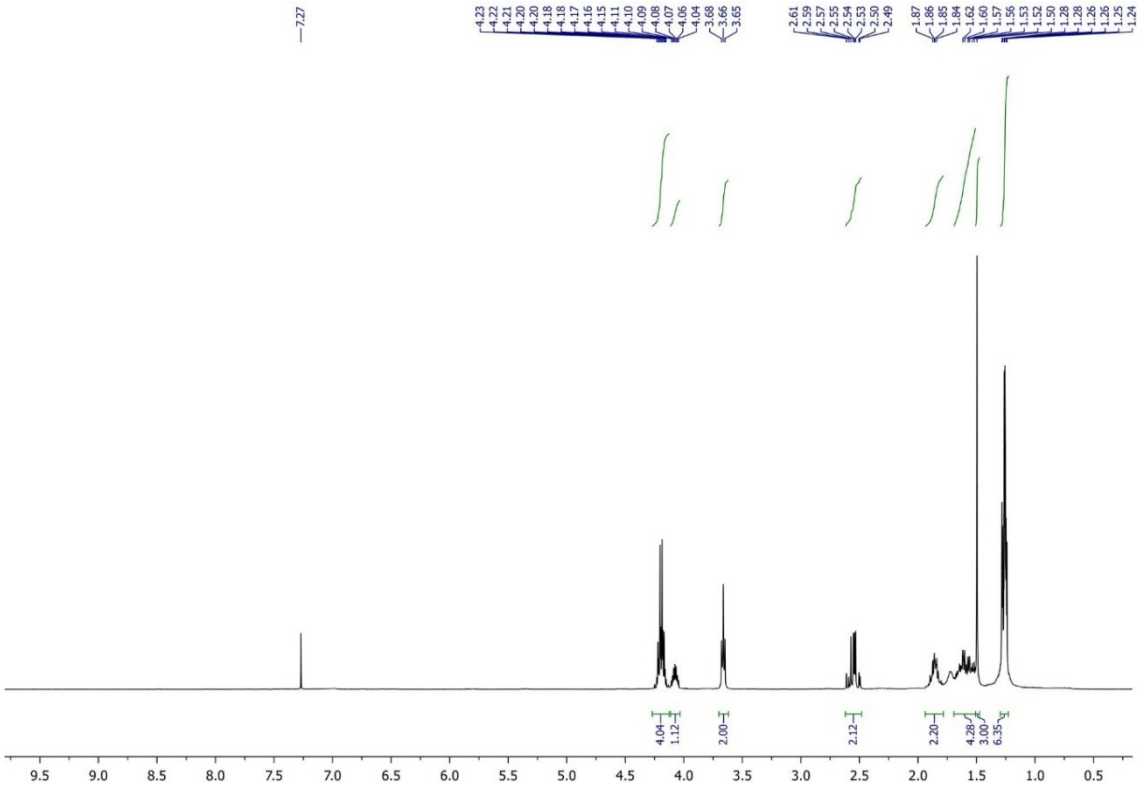
EtOOC
CH3
EtOOC

4b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4.16
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4.09
4.08
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1.25
1.24
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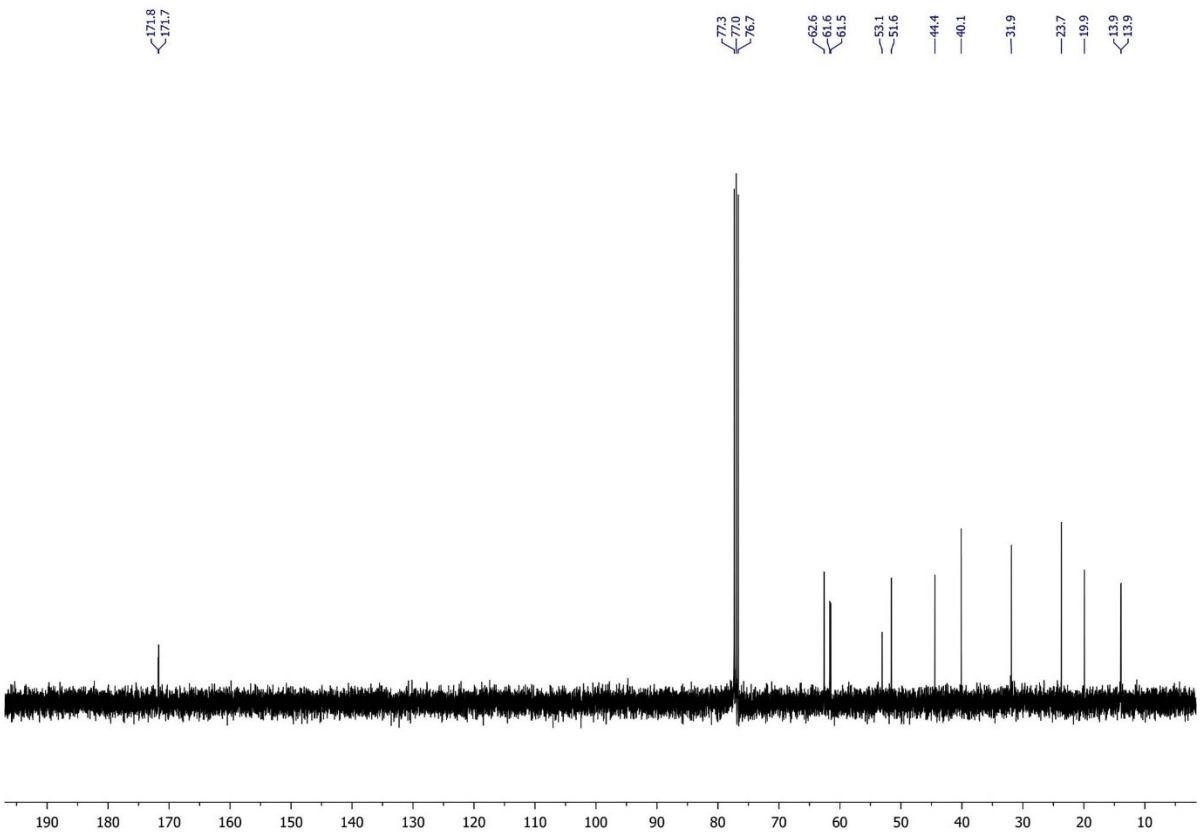
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13.9
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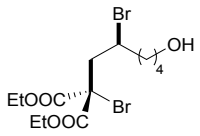
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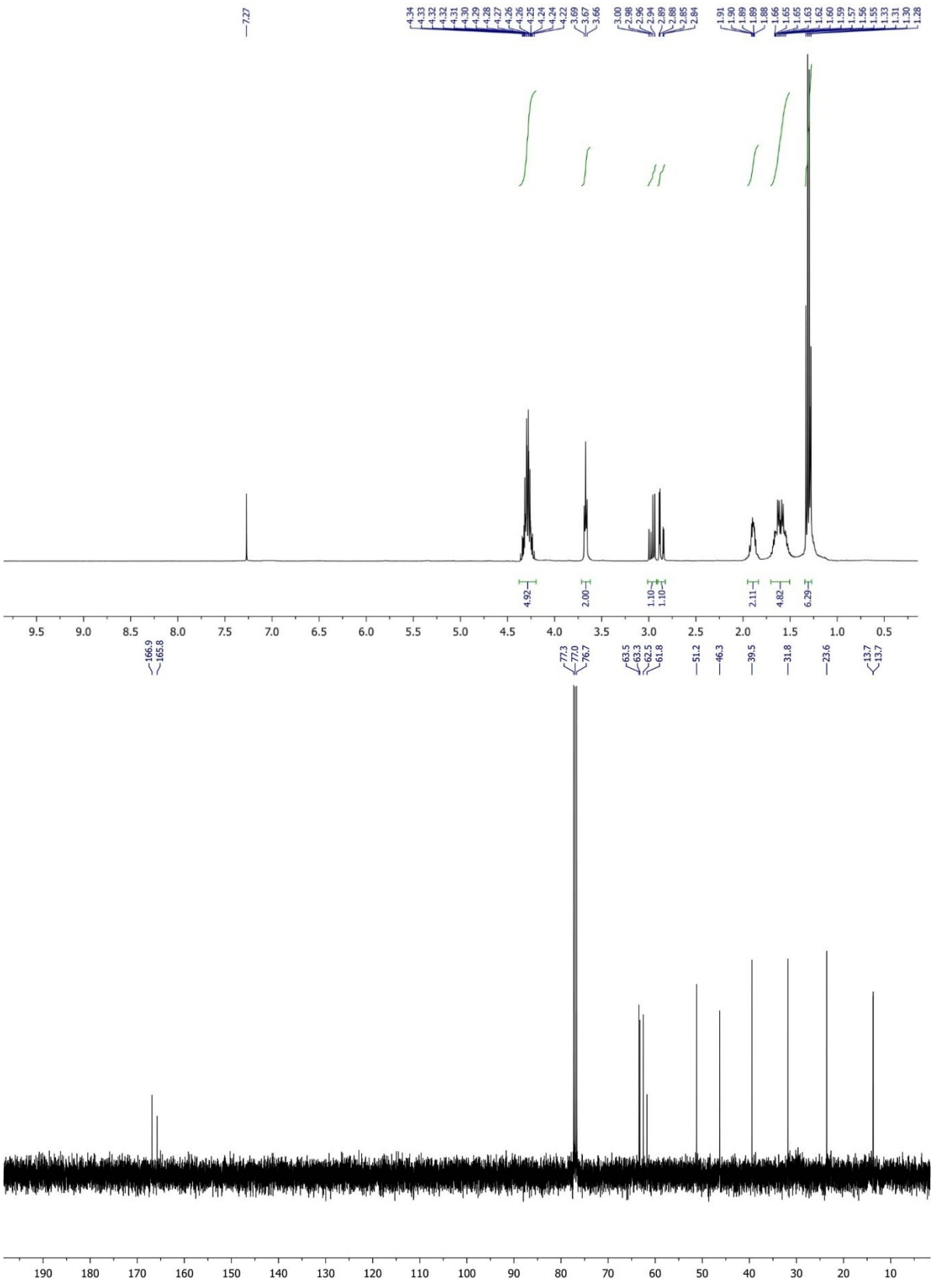
Br
EtOOC

4c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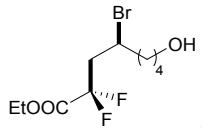
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F

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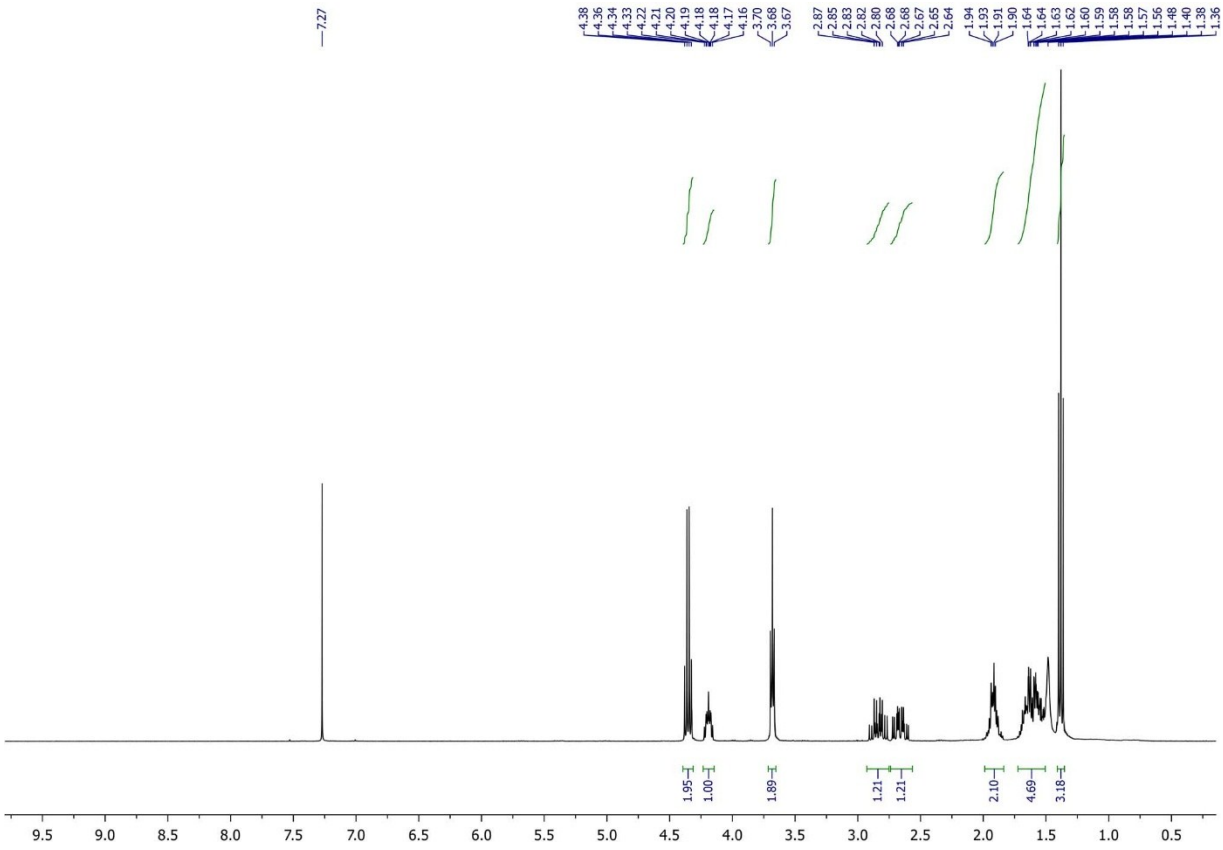
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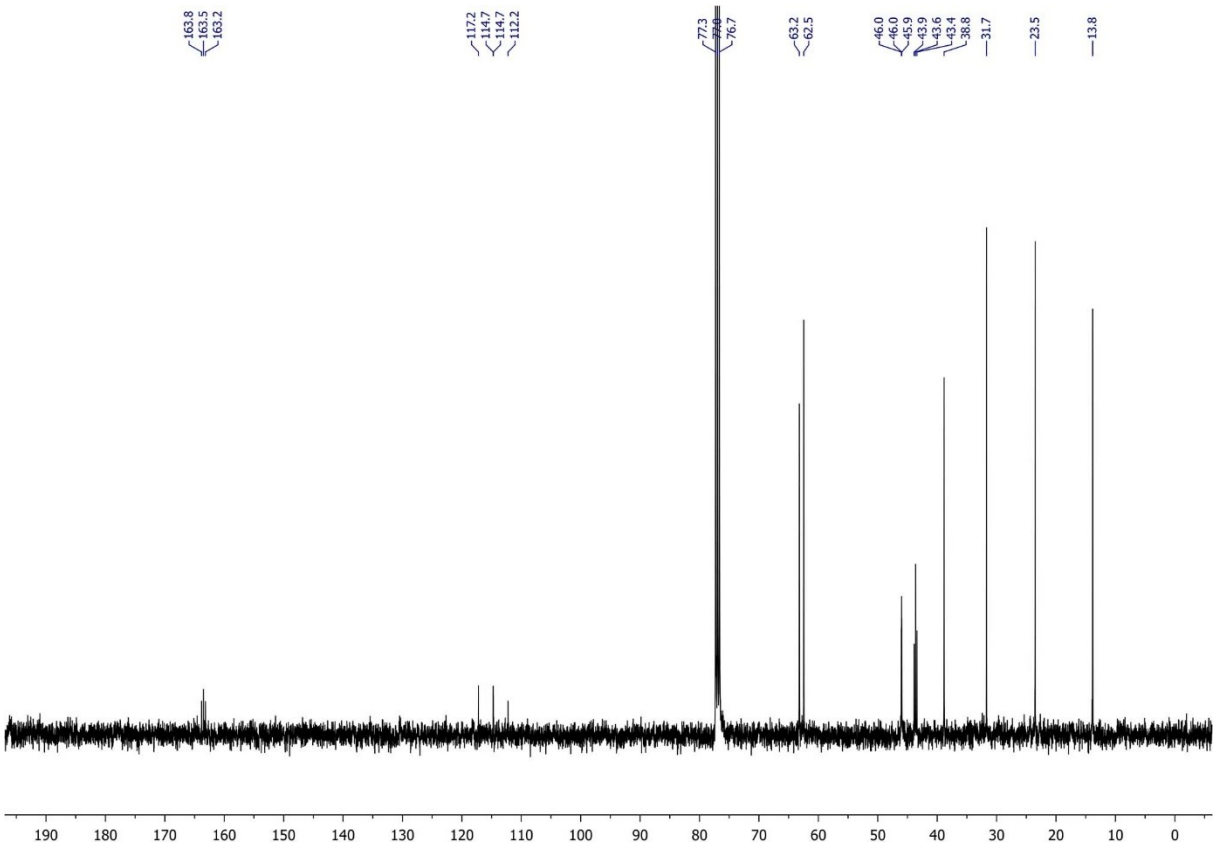
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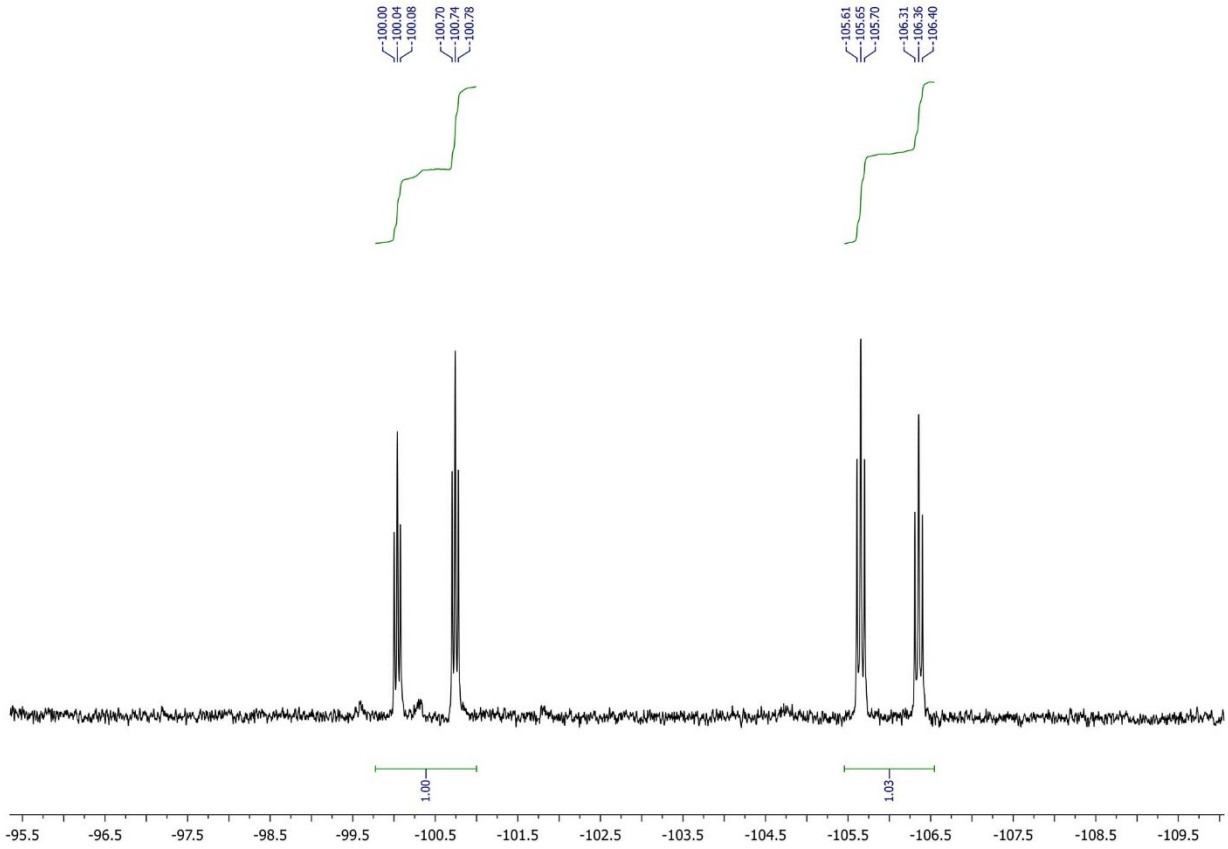
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1.03
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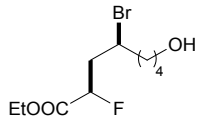
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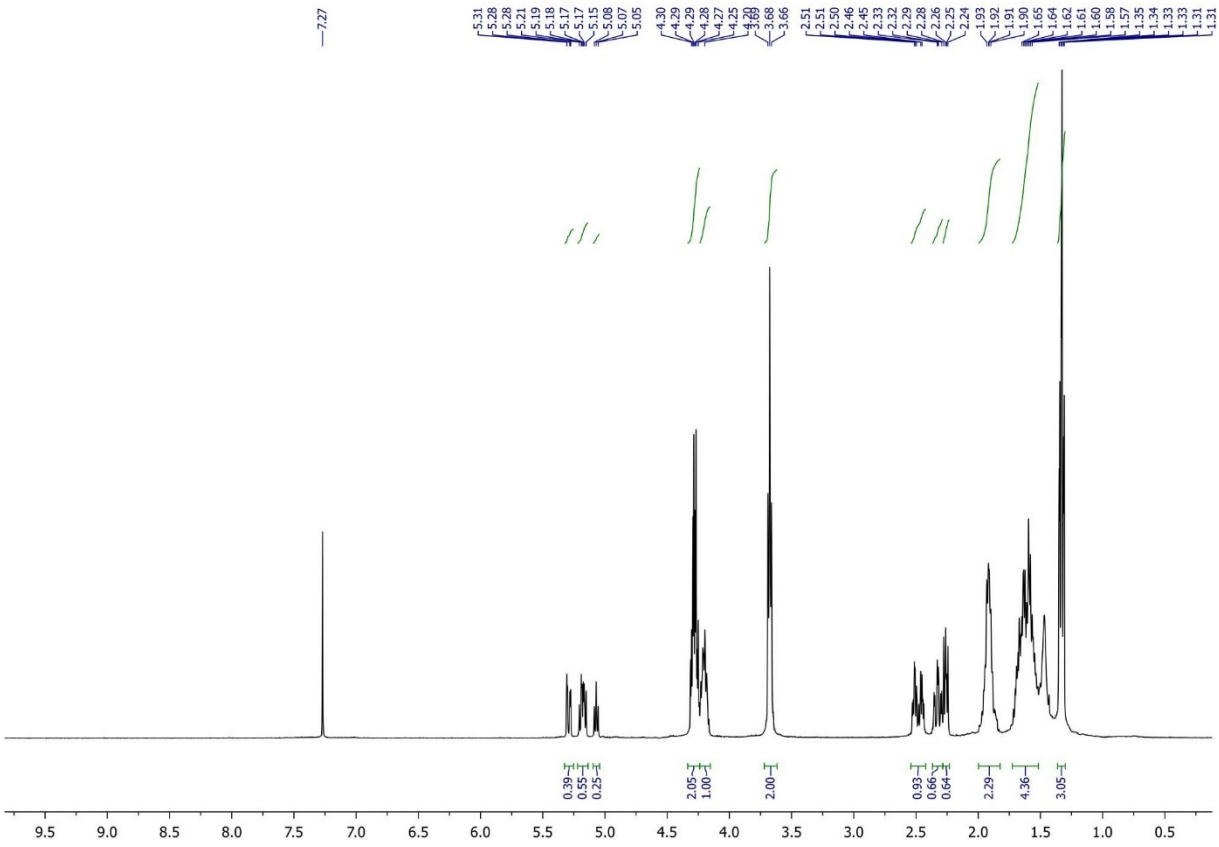
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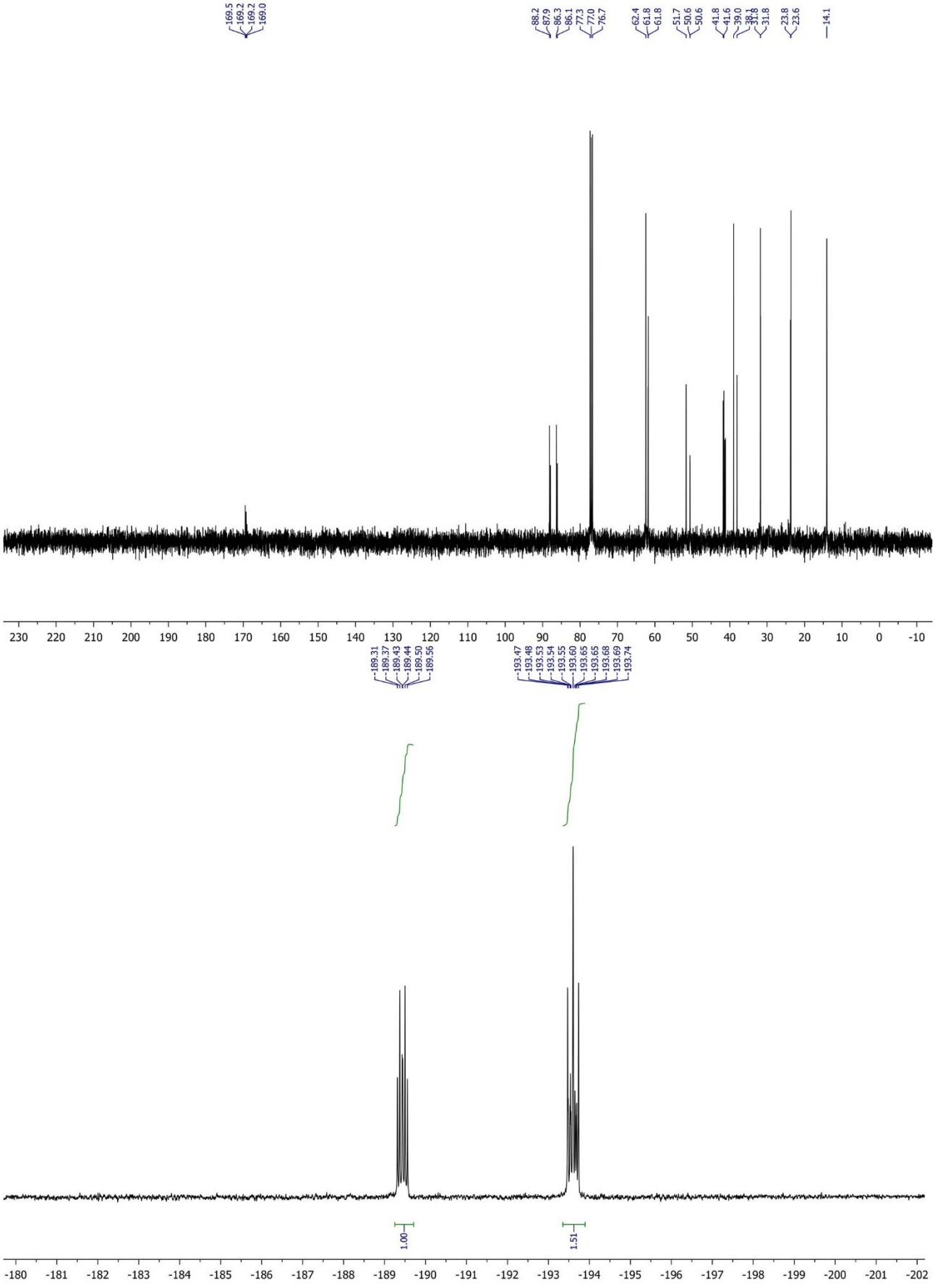
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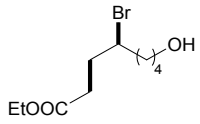
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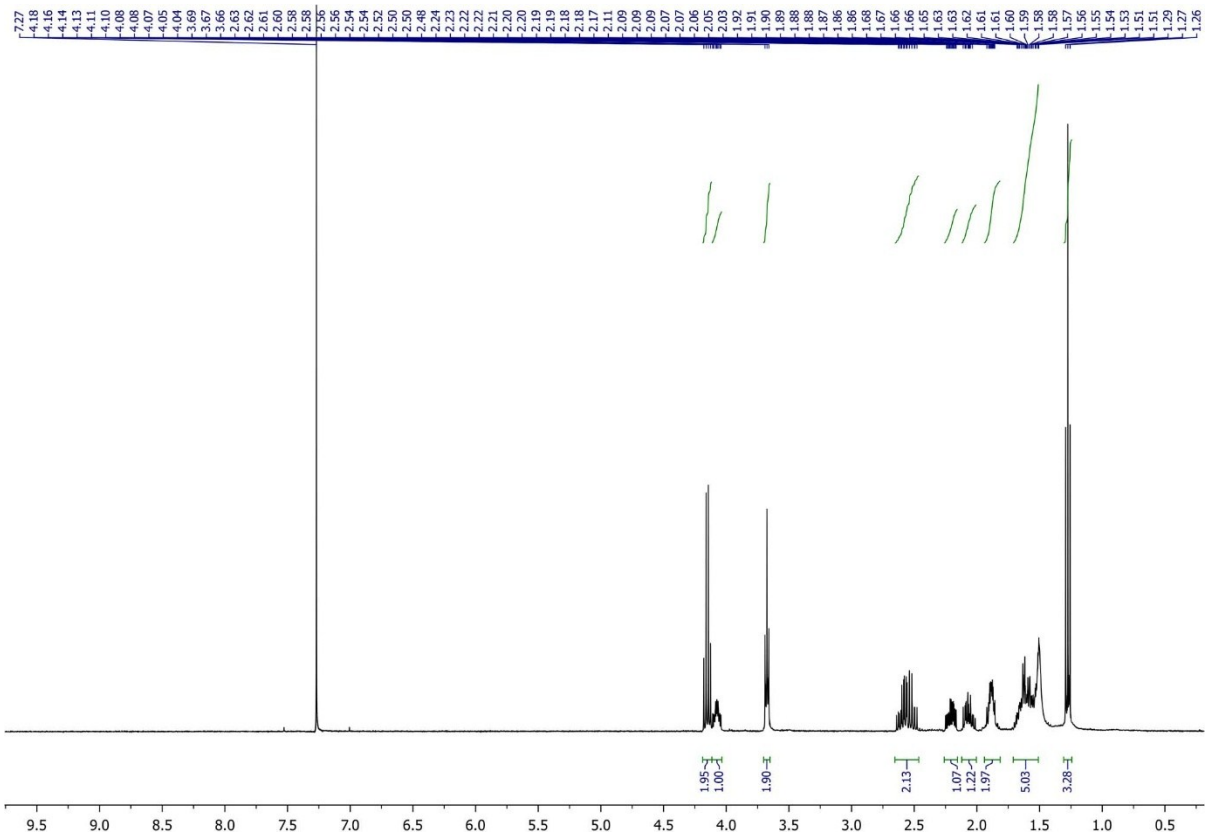
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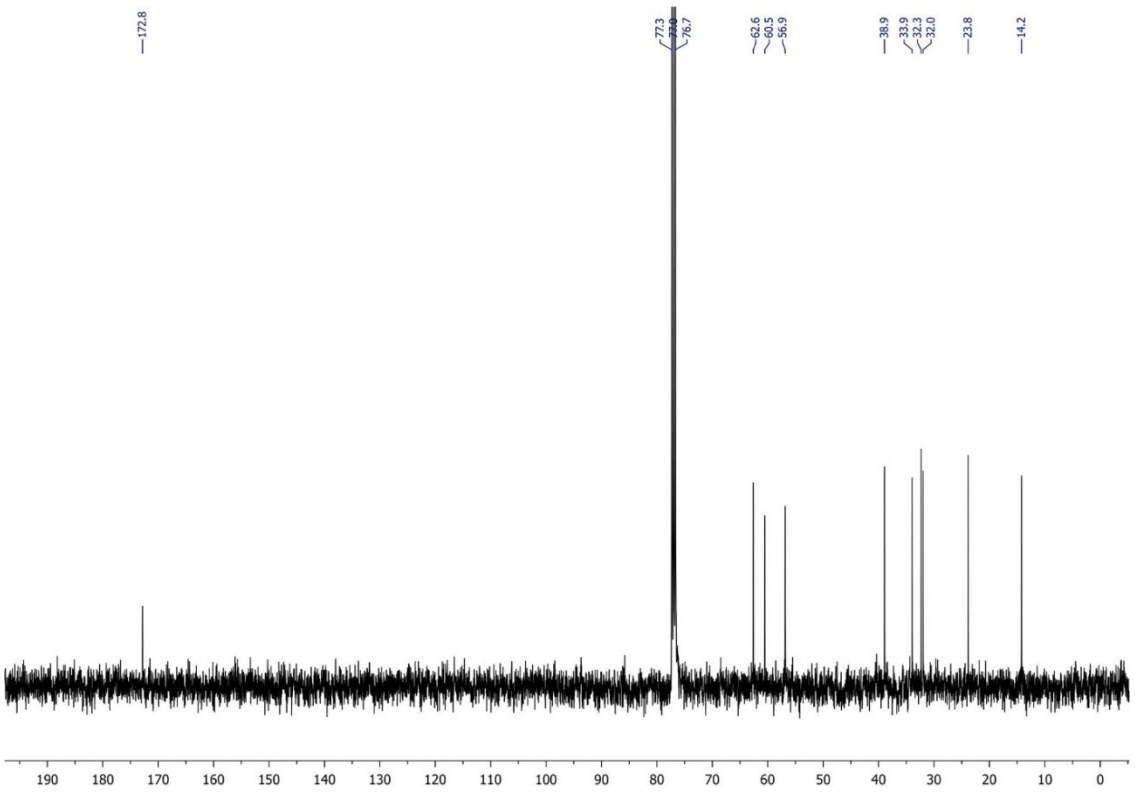
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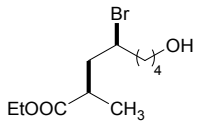
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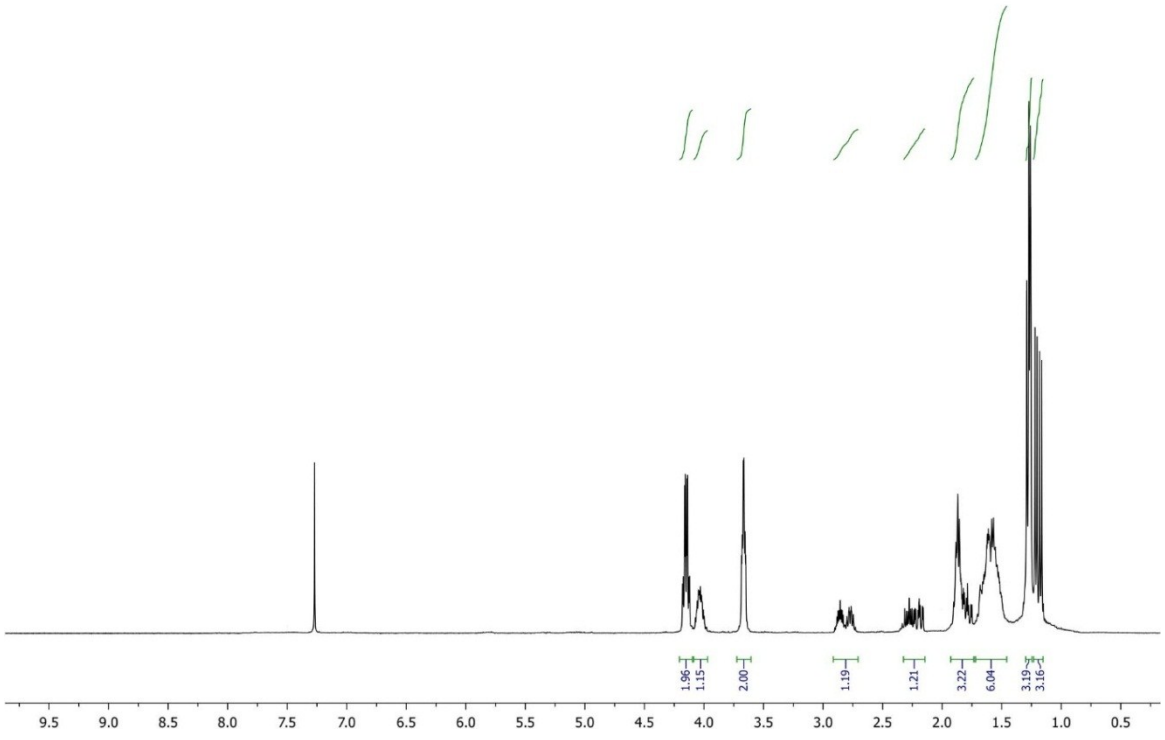
CH3

4g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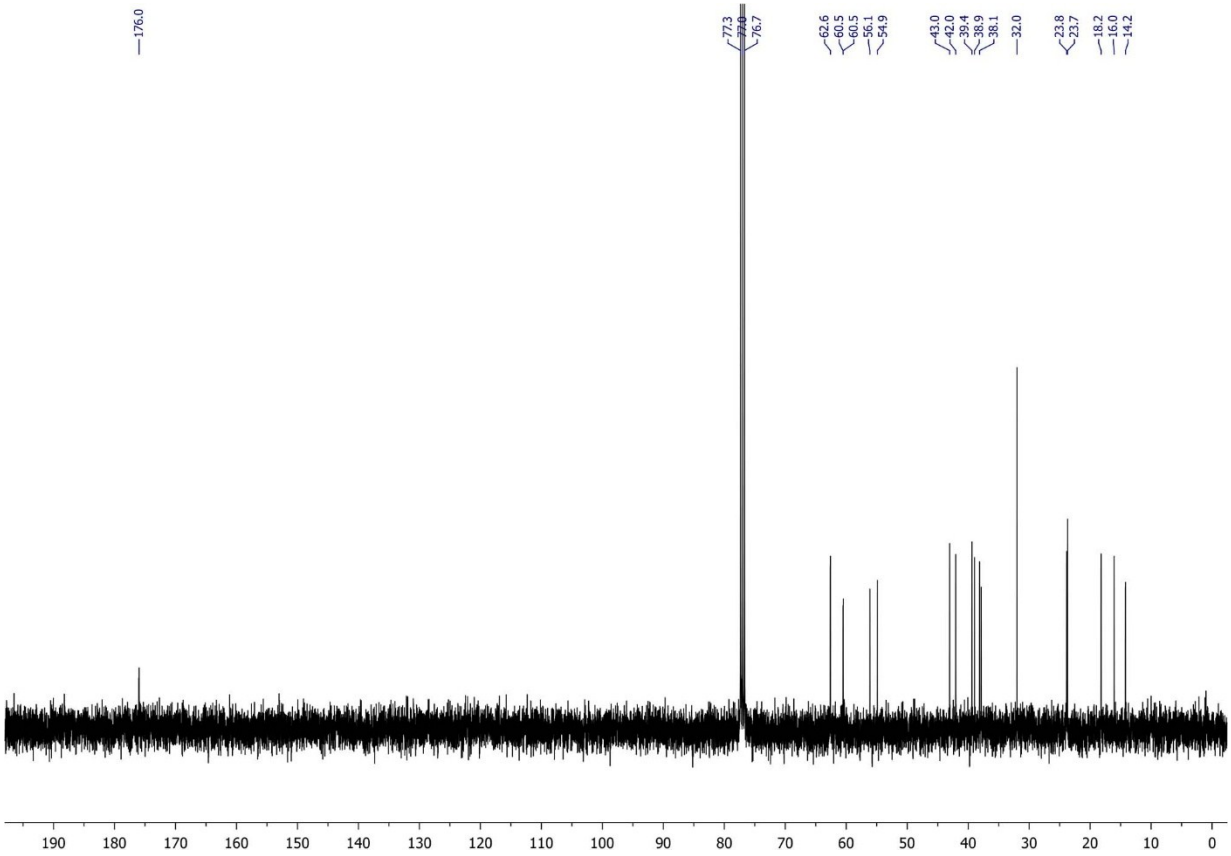
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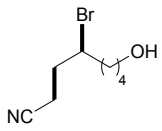
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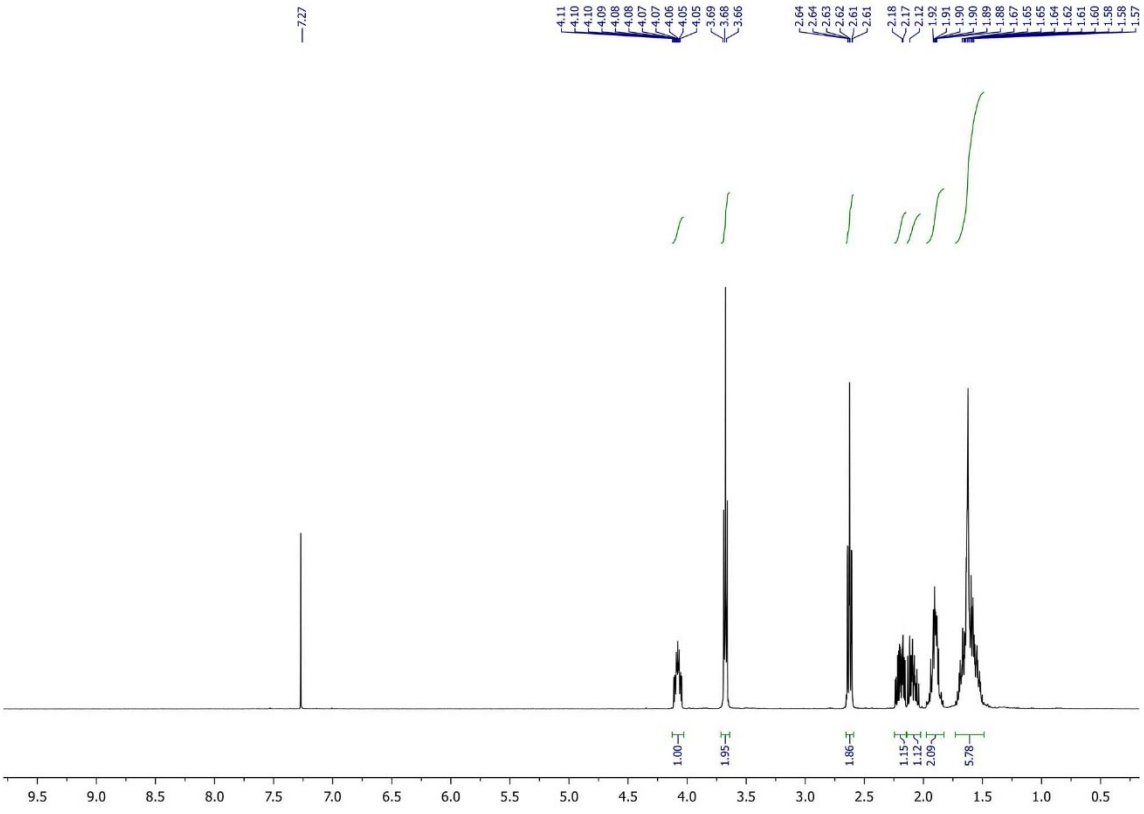
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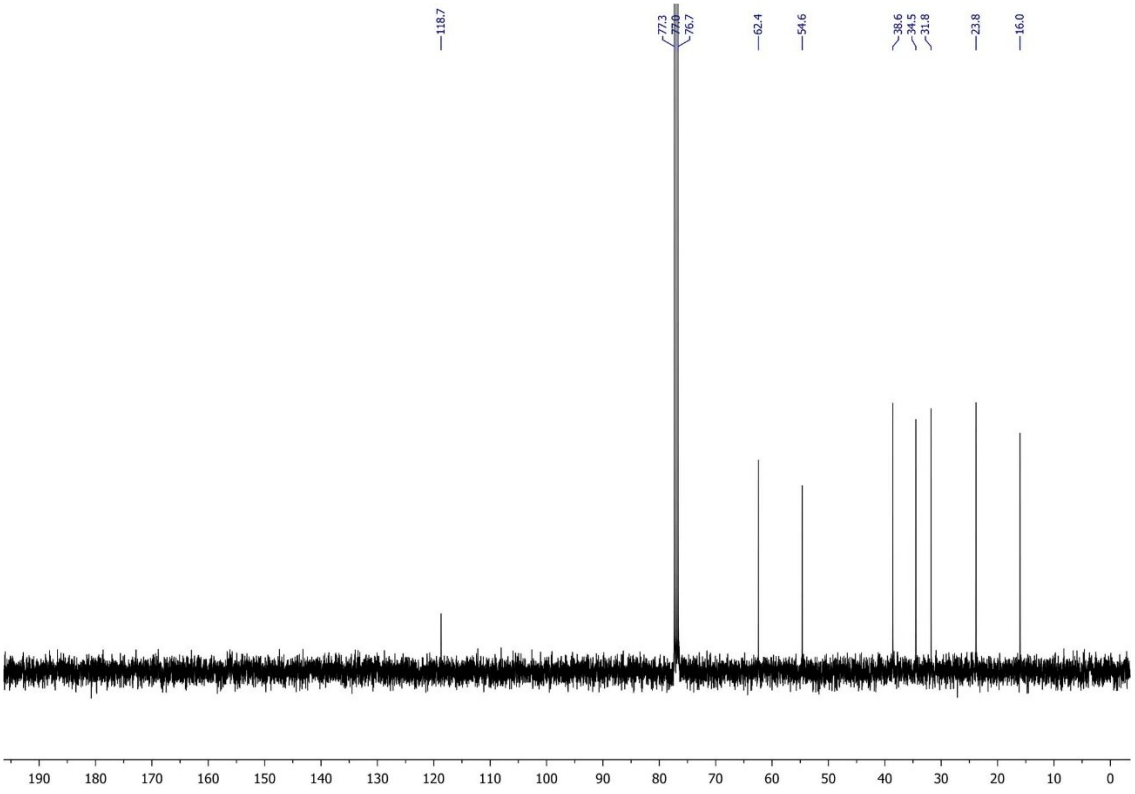
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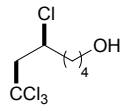
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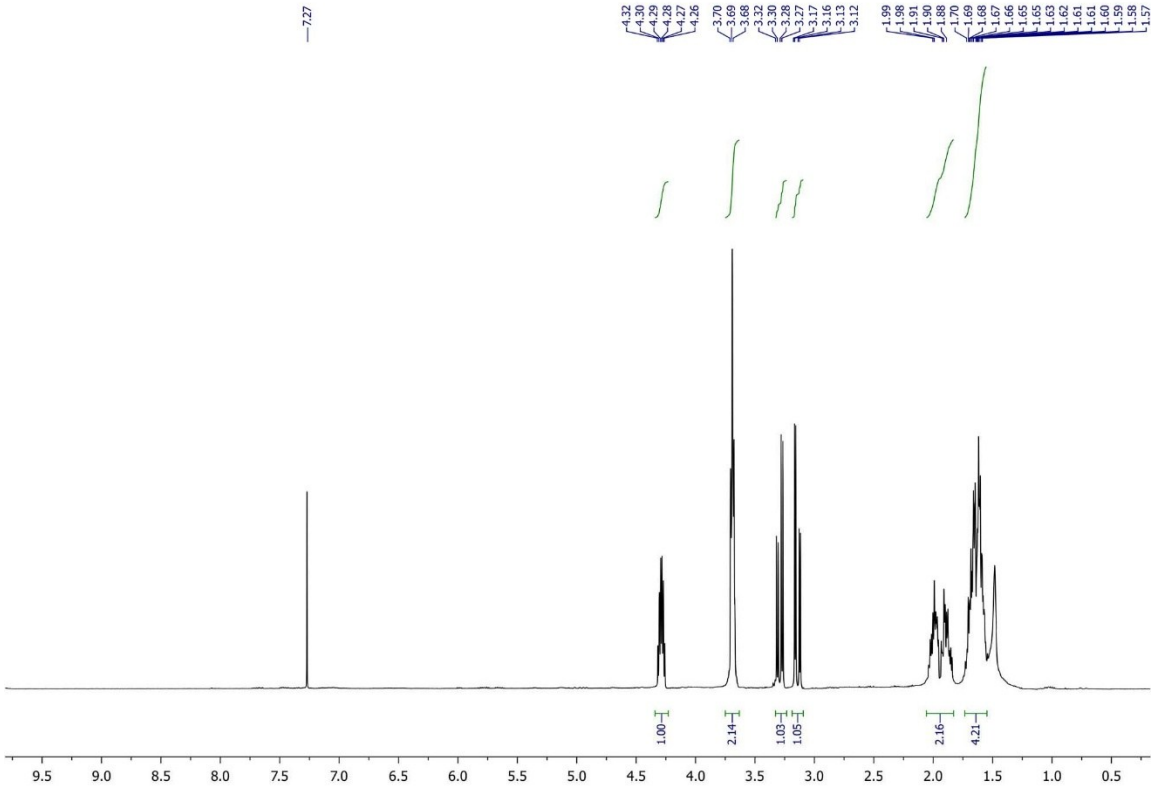
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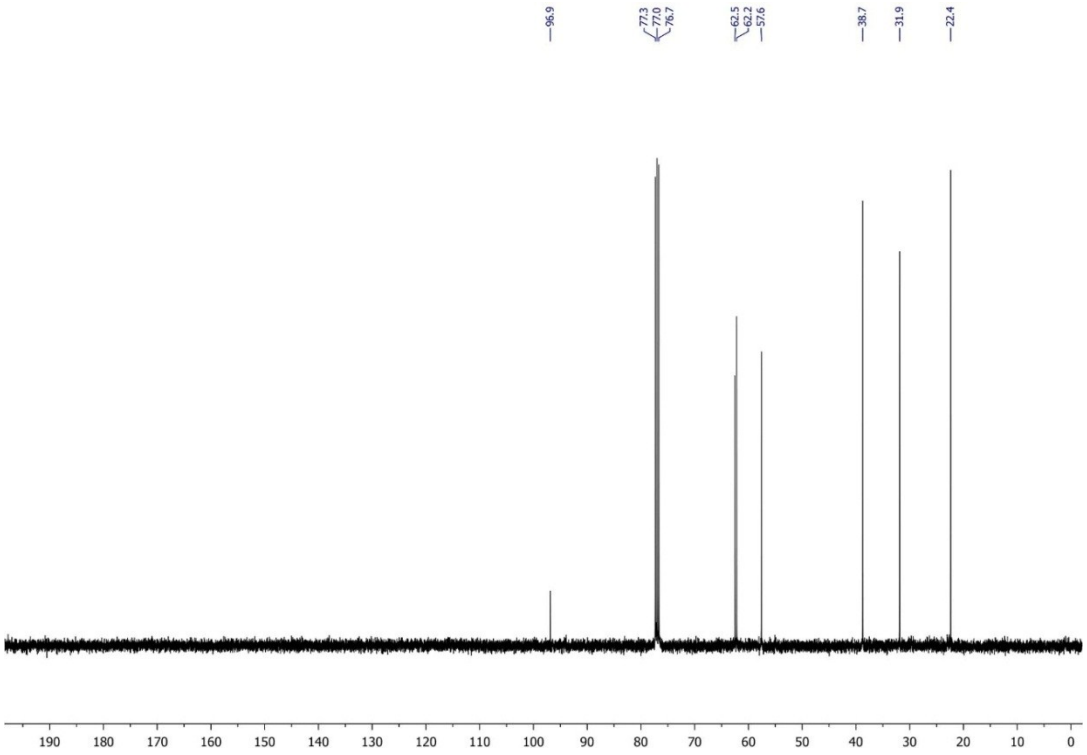
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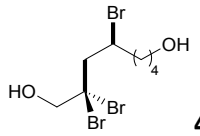
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HO
Br
Br

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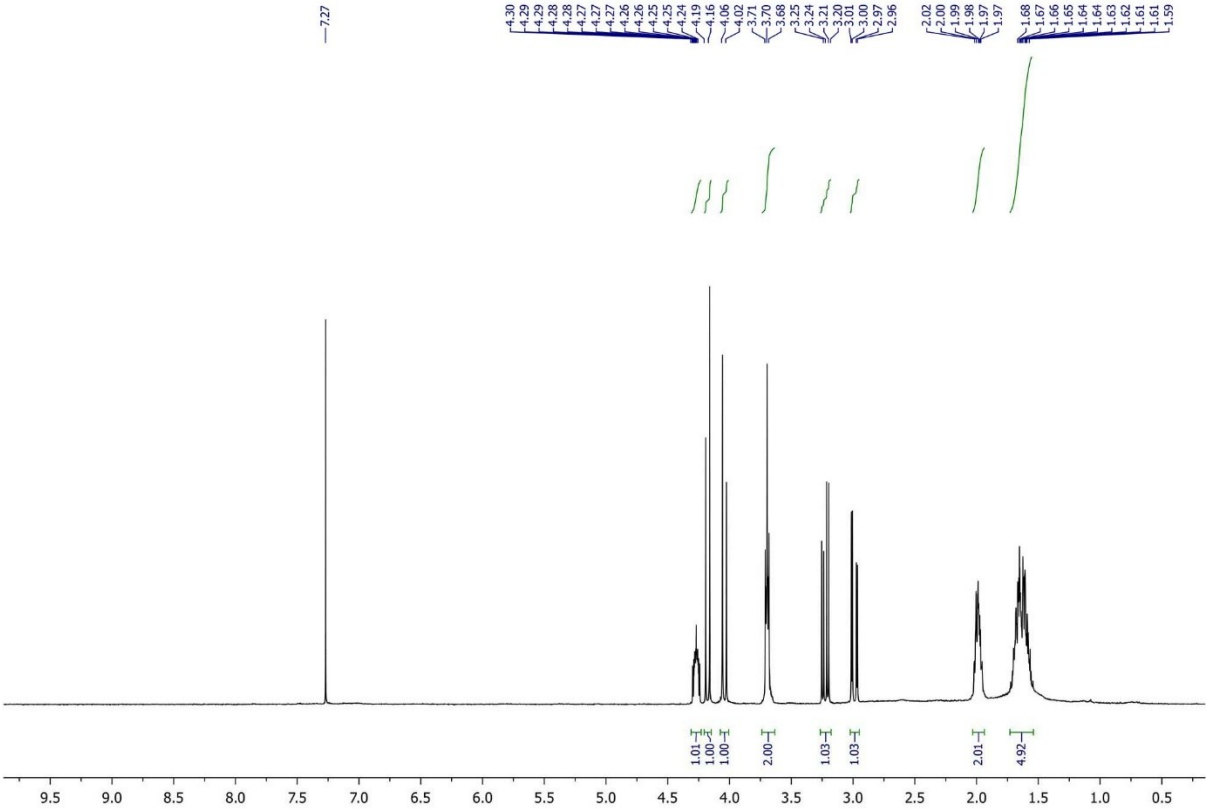
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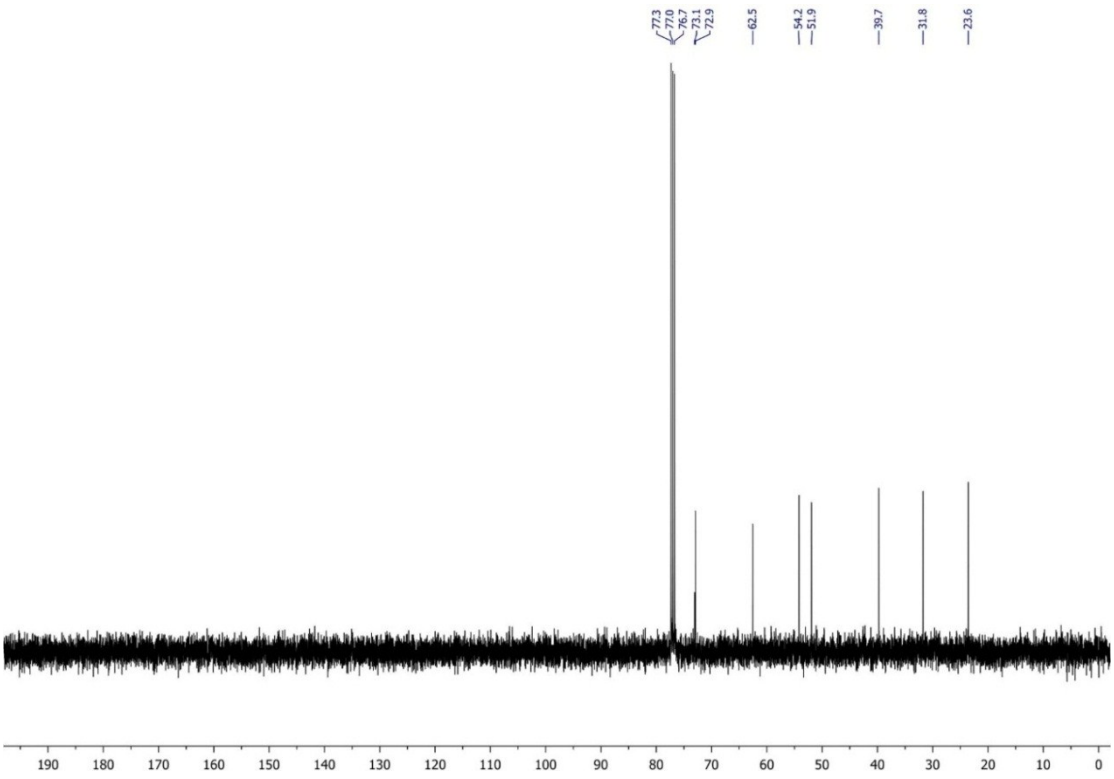
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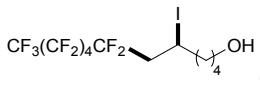
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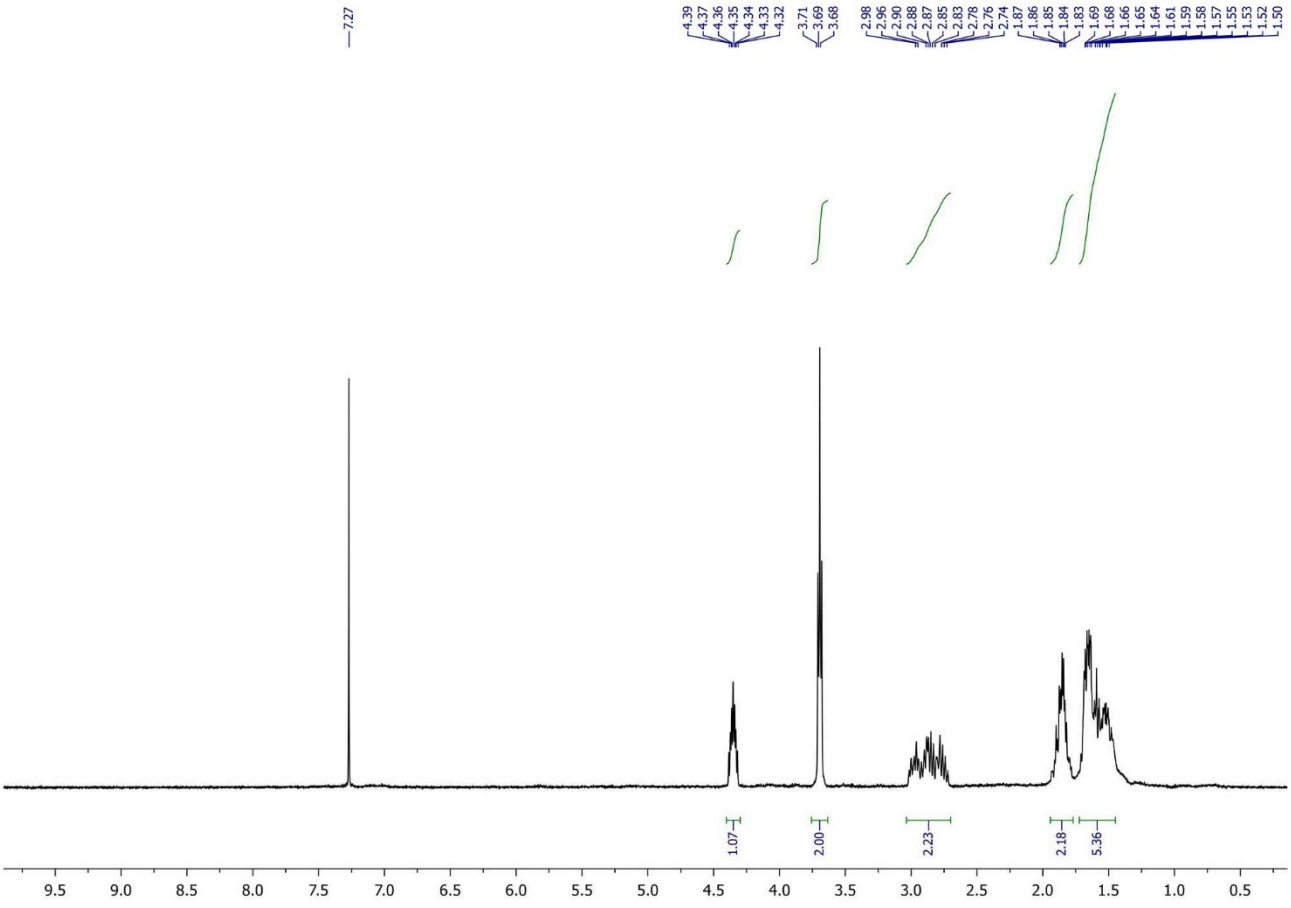
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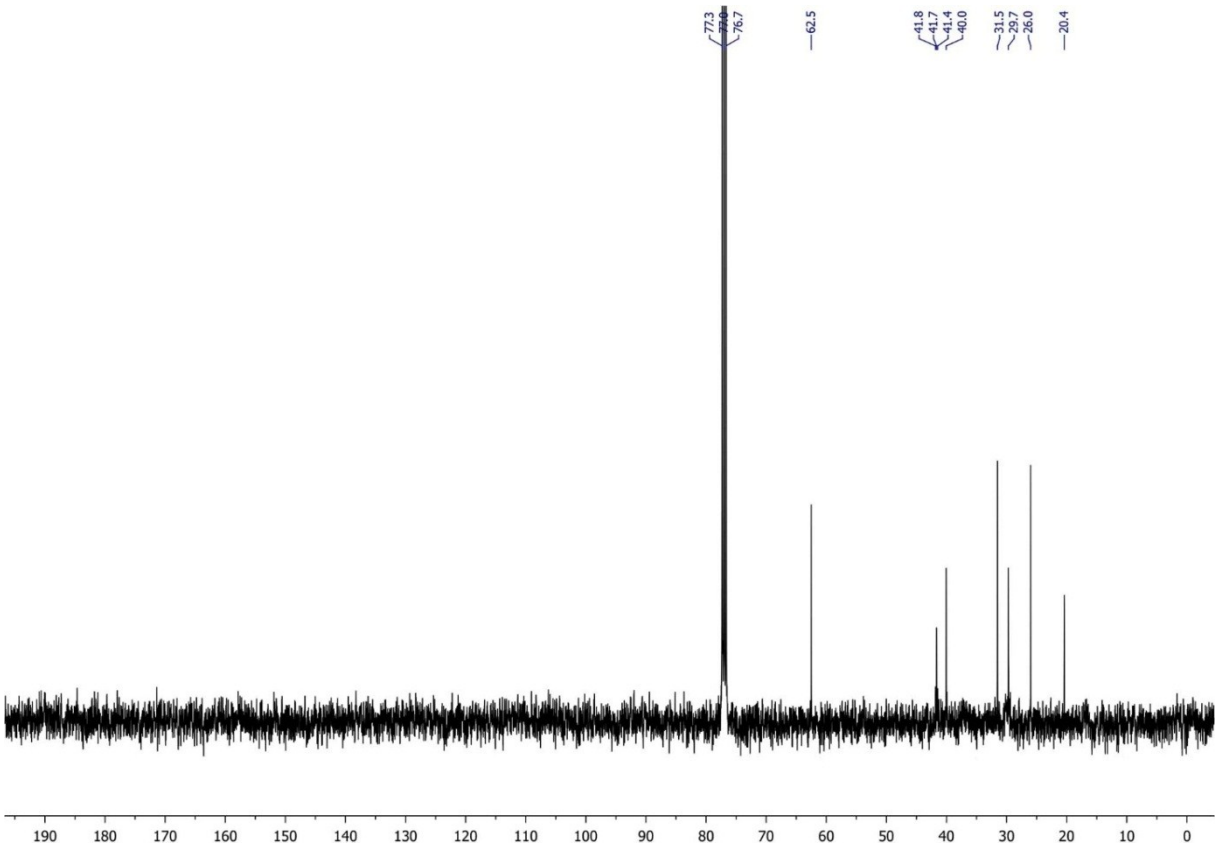
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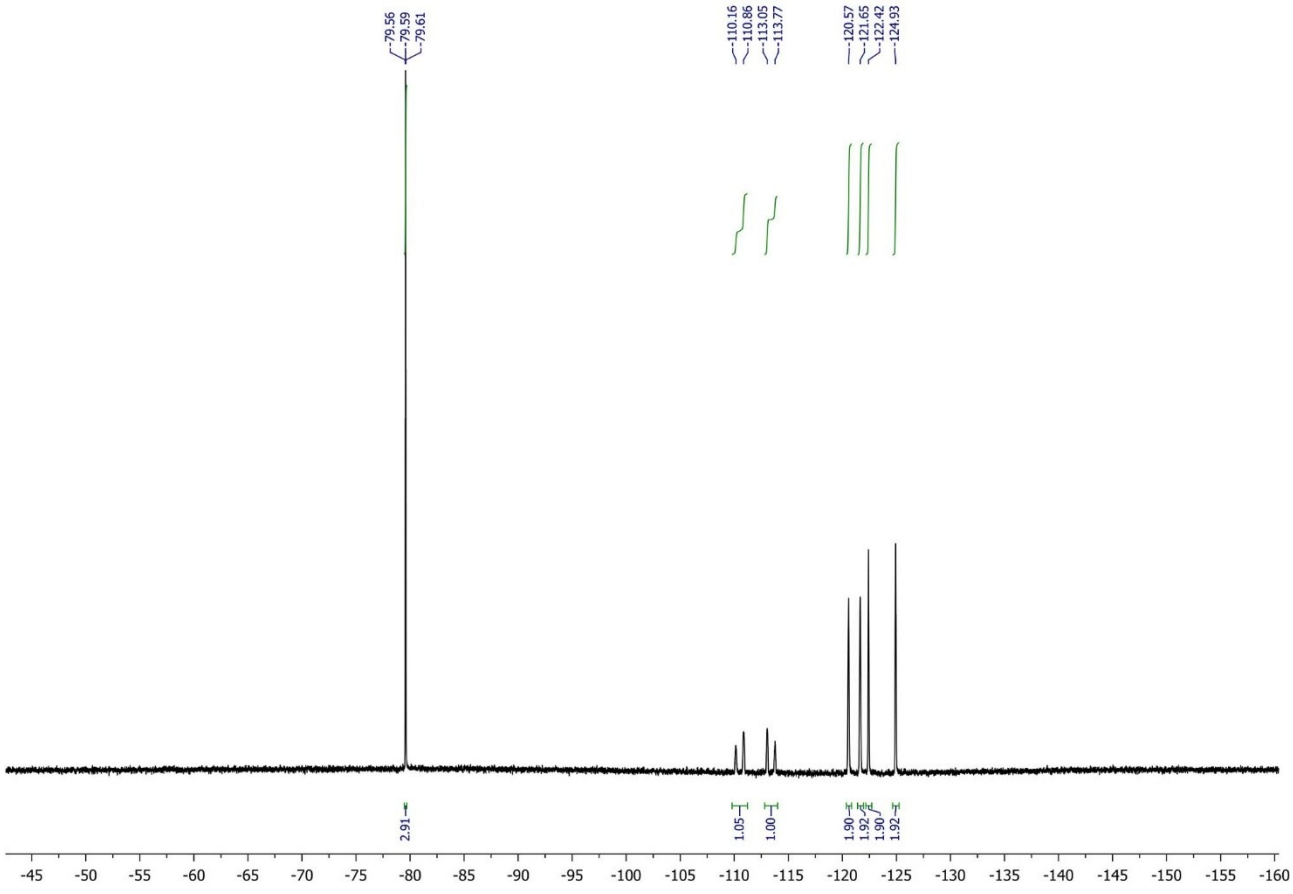
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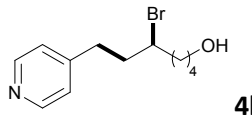
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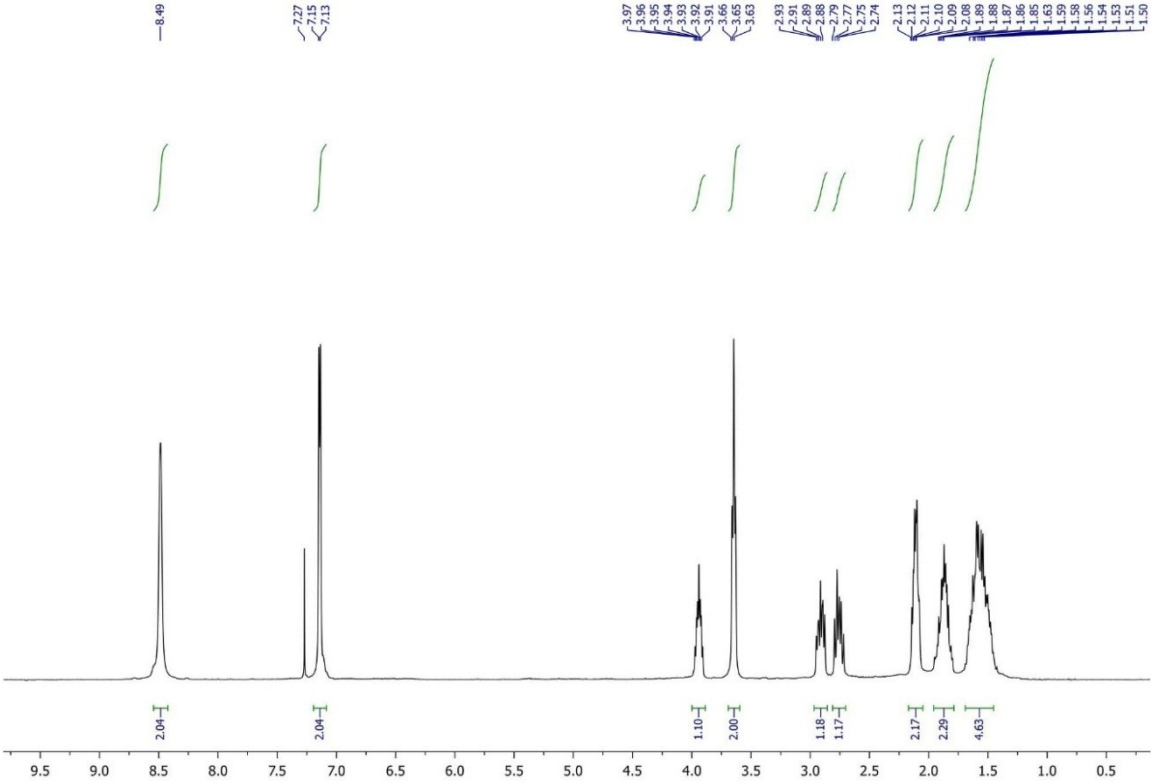
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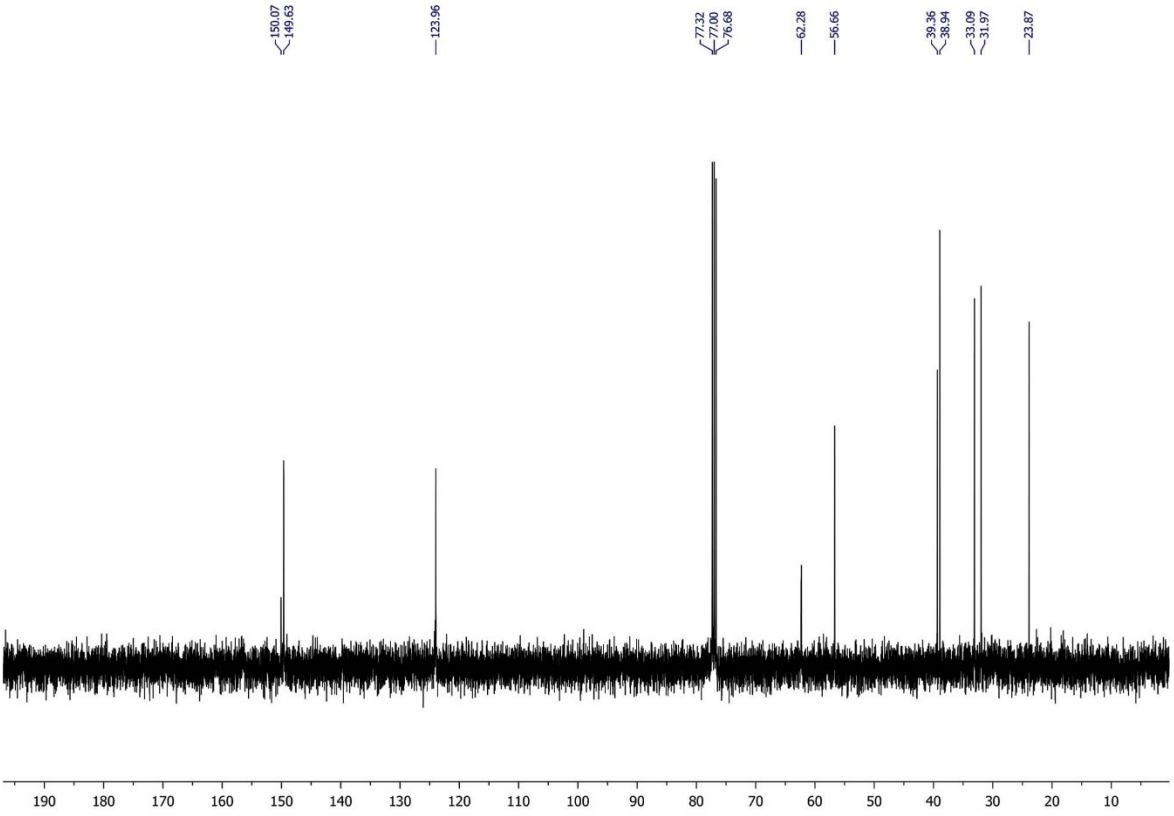
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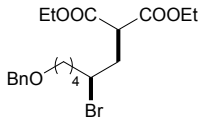
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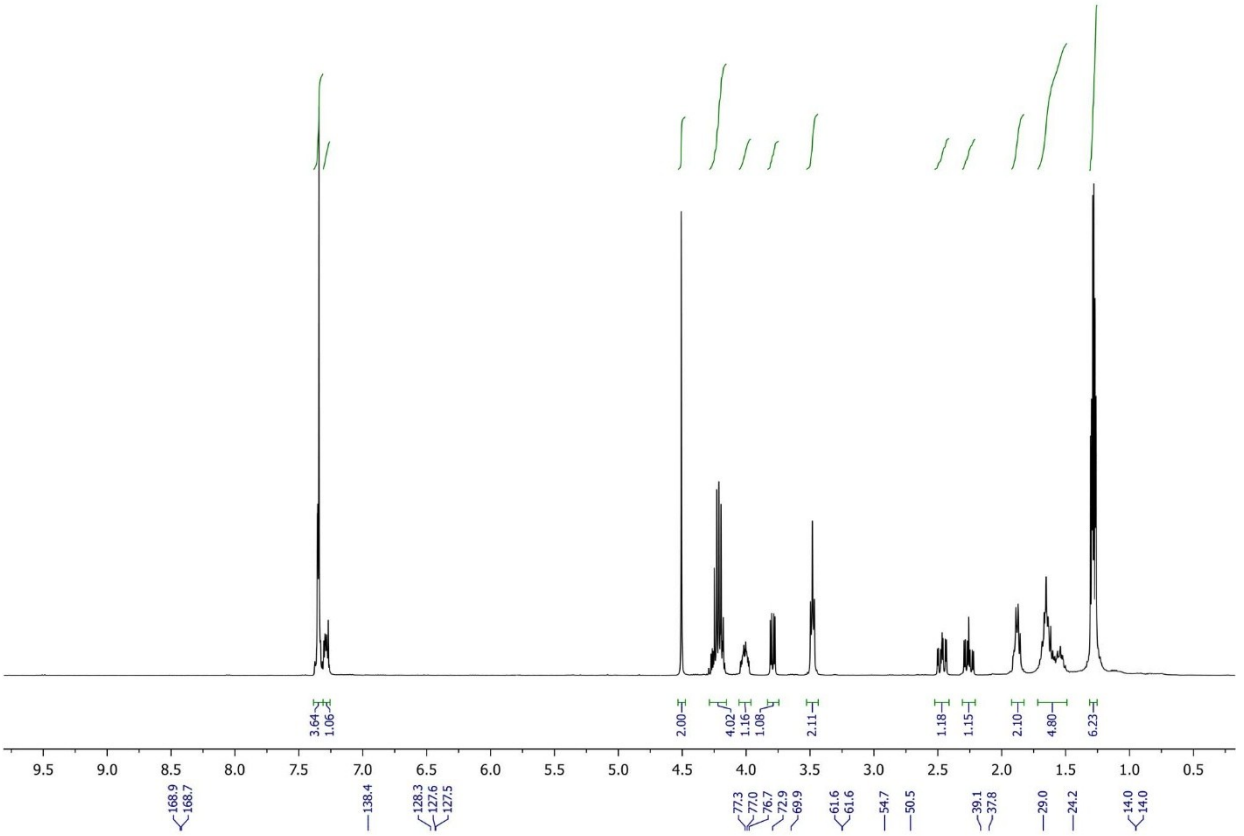
COOEt
BnO
4
Br

5b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2.10
4.80
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168.7
138.4
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127.6
127.5
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77.0
76.7
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50.5
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37.8
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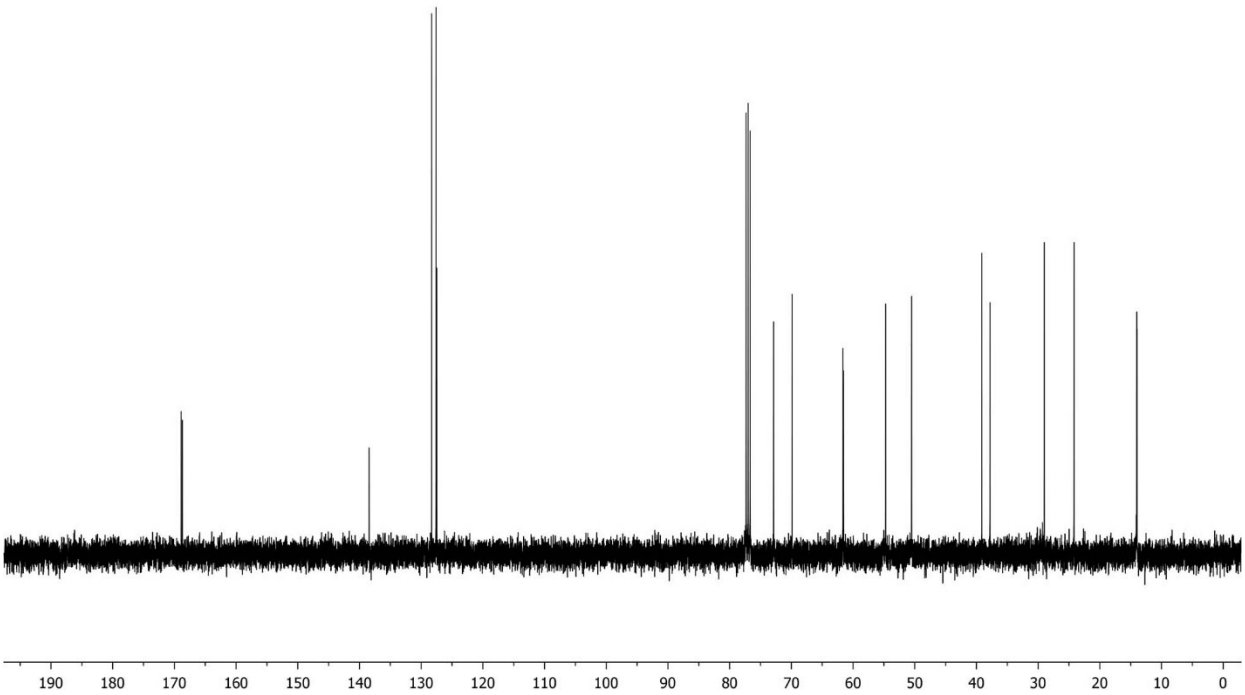
14.0
14.0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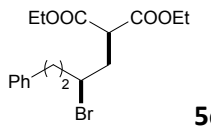
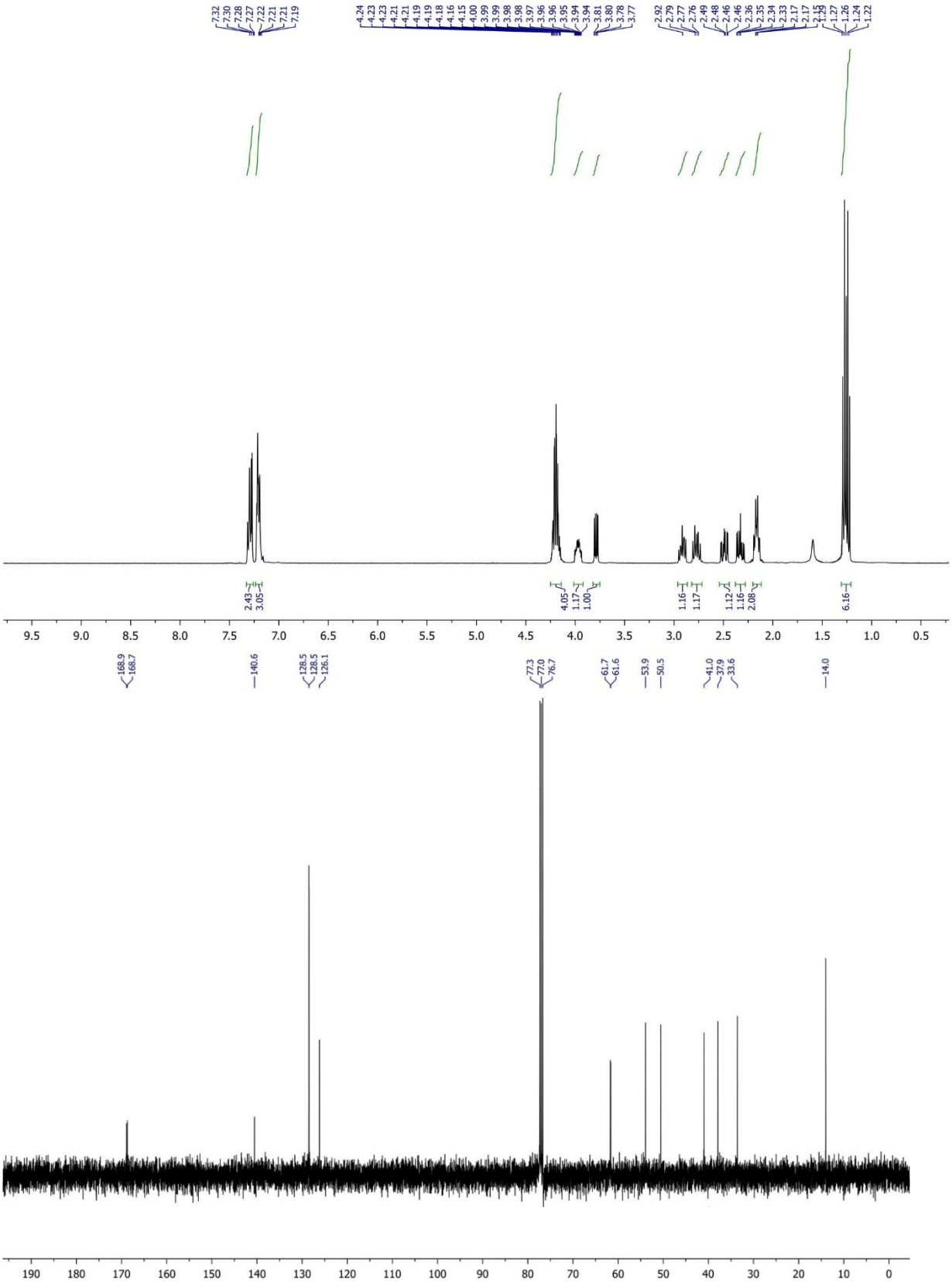
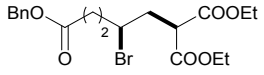
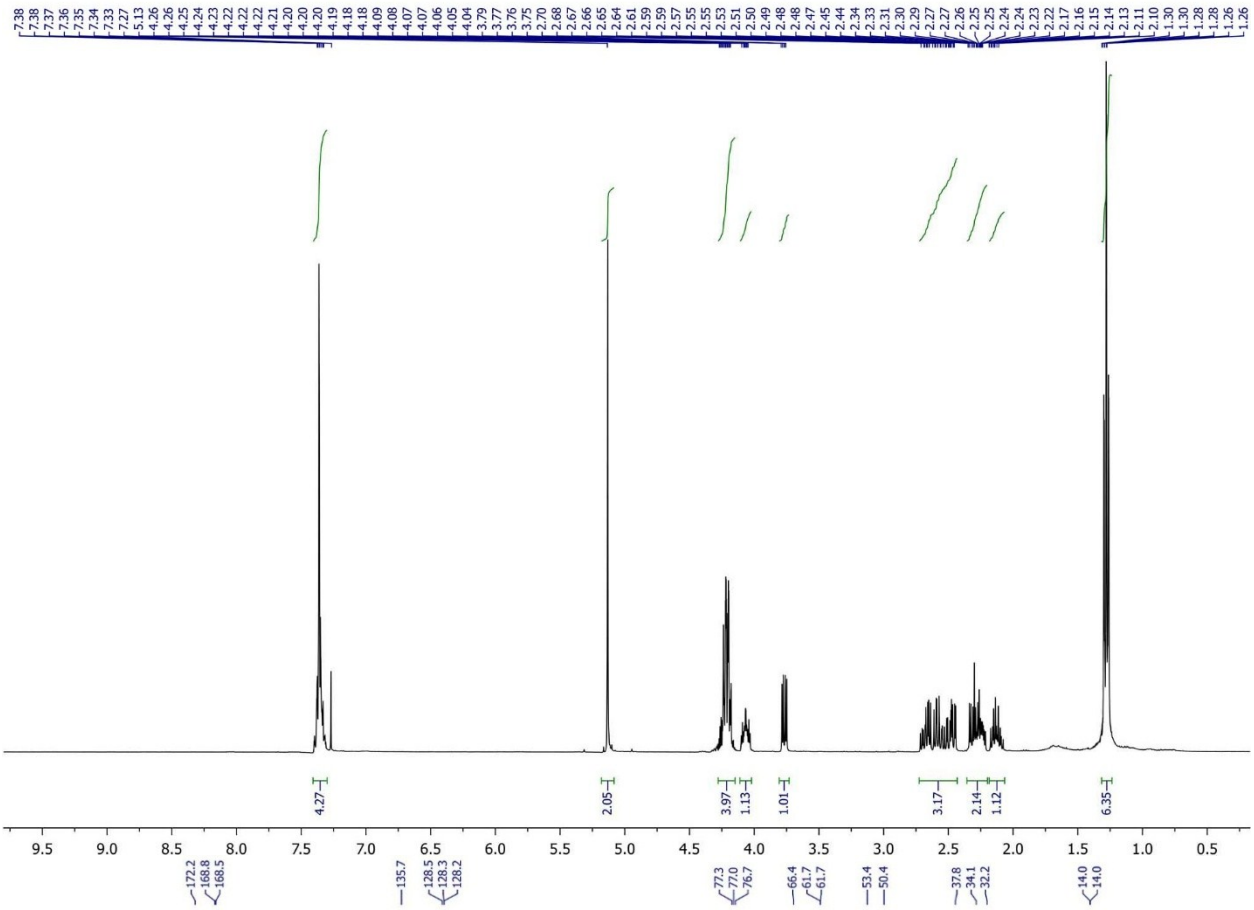


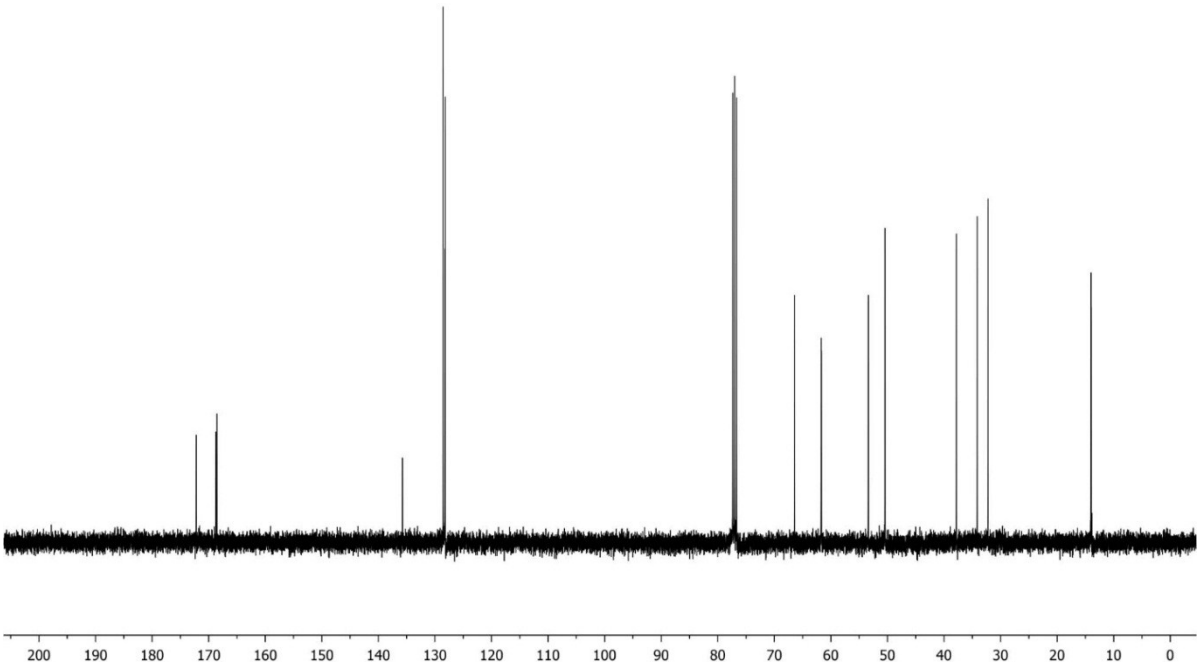
5c

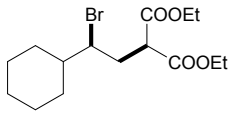




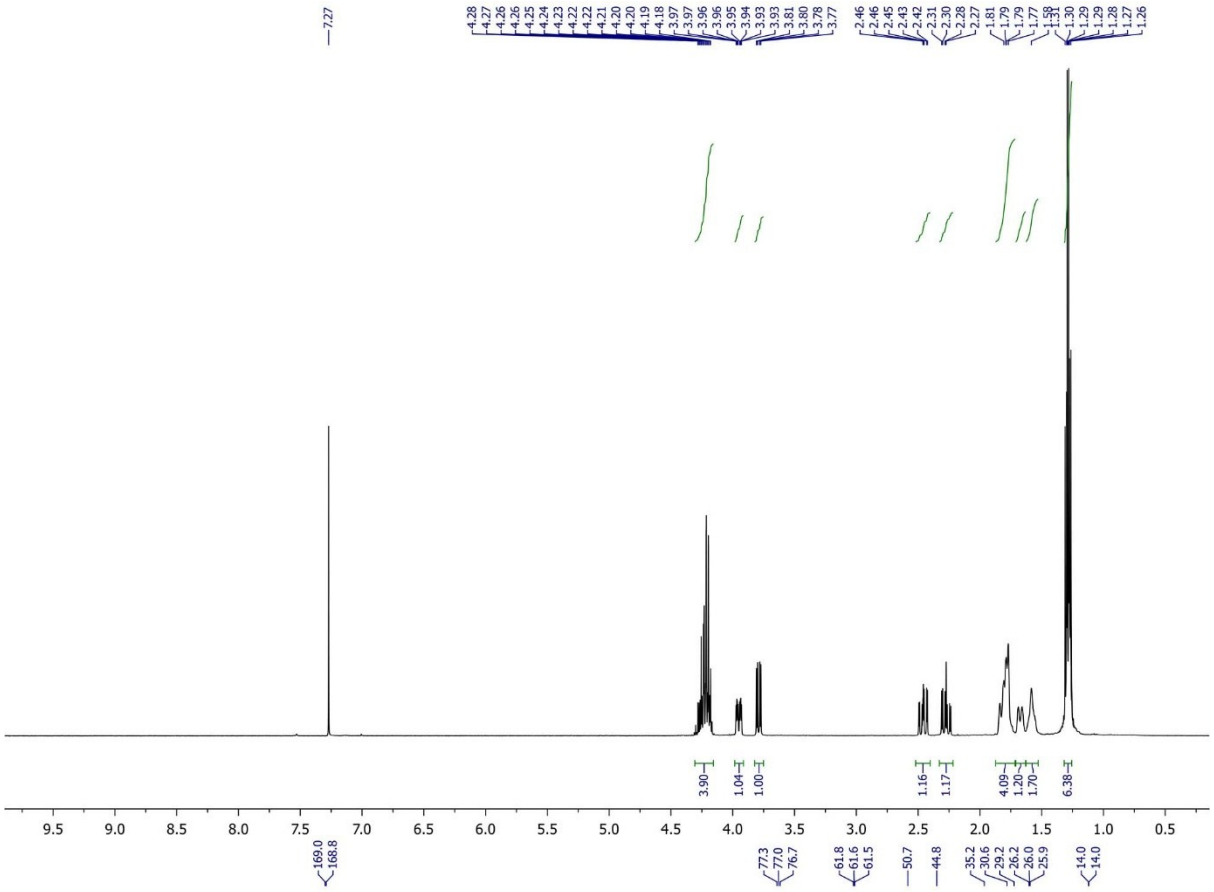
5d






Br
COOEt
COOEt

5e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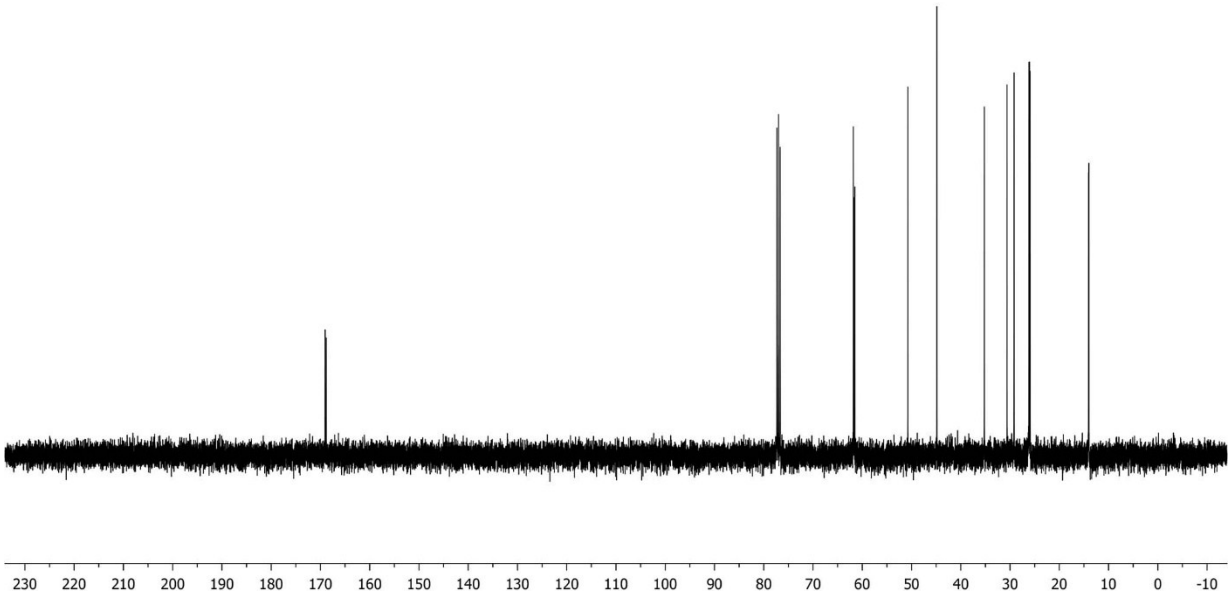
4.28 4.27 4.26 4.26 4.25 4.24 4.23 4.22 4.22 4.21 4.20 4.20 4.19 4.18 3.97 3.97 3.96 3.96 3.95 3.94 3.93 3.93 3.81 3.80 3.78 3.77
2.46 2.46 2.45 2.43 2.42 2.31 2.30 2.28 2.27 1.81 1.79 1.79 1.77 1.58 1.31 1.30 1.29 1.28 1.27 1.26
3.90 1.04 1.00 1.16 1.17 4.09 1.20 1.70 6.38
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
169.0 168.8
77.3 77.0 76.7
61.8 61.6 61.5
50.7
44.8
35.2 30.6 29.2 26.2 26.0 25.9
14.0 14.0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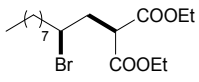
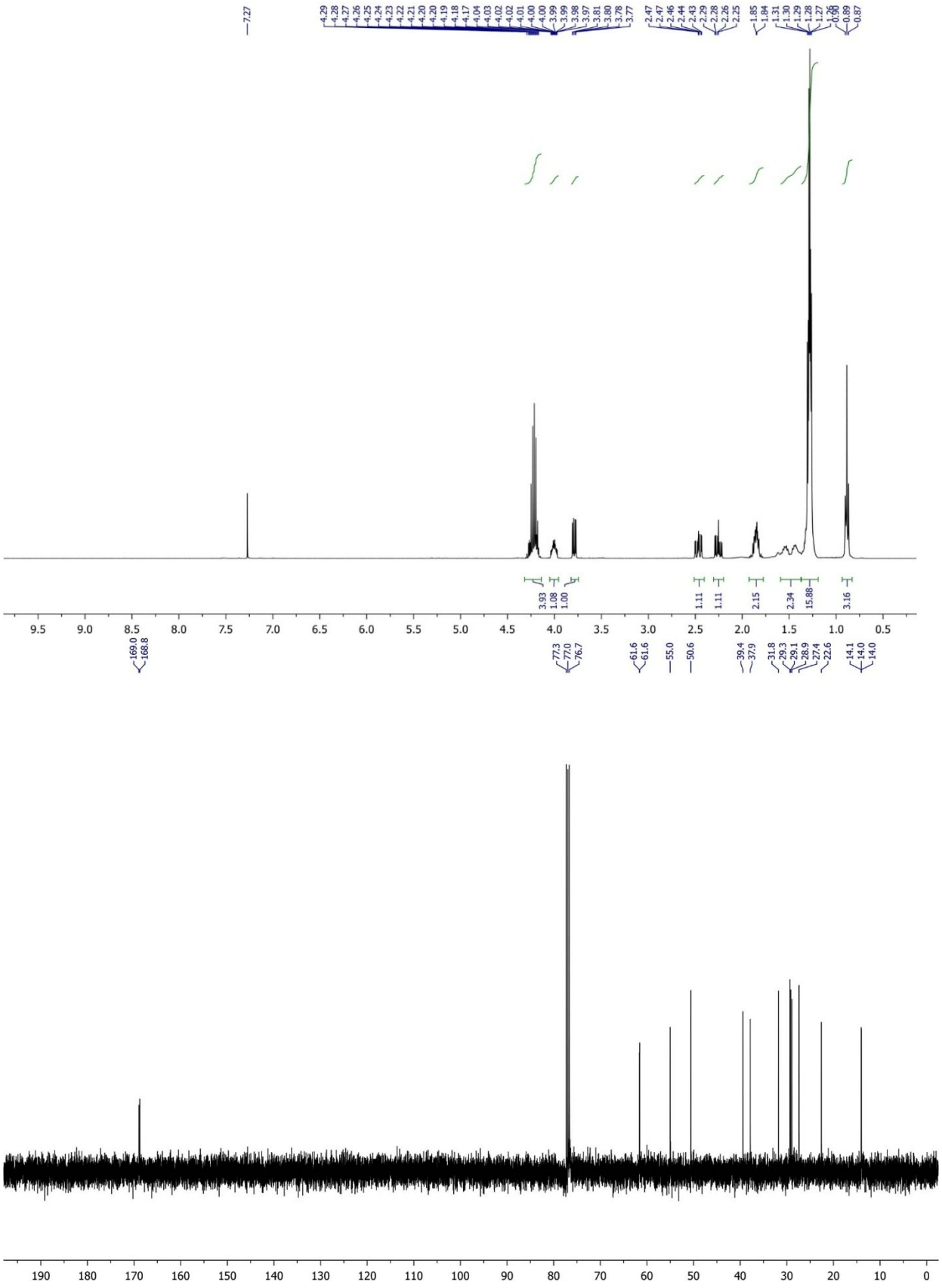

COOEt
7
Br
COOEt

5f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4.23
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4.19
4.18
4.17
4.04
4.03
4.02
4.02
4.01
4.00
4.00
3.99
3.99
3.98
3.97
3.81
3.80
3.78
3.77
2.47
2.47
2.46
2.44
2.43
2.29
2.28
2.26
2.25
1.85
1.84
1.31
1.30
1.29
1.28
1.27
0.89
0.87
3.93
1.08
1.00
1.11
1.11
2.15
2.34
15.88
3.16
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
169.0
168.8
77.3
77.0
76.7
61.6
61.6
55.0
50.6
39.4
37.9
31.8
29.3
29.1
28.9
27.4
22.6
14.1
14.0
14.0
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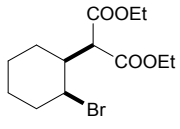
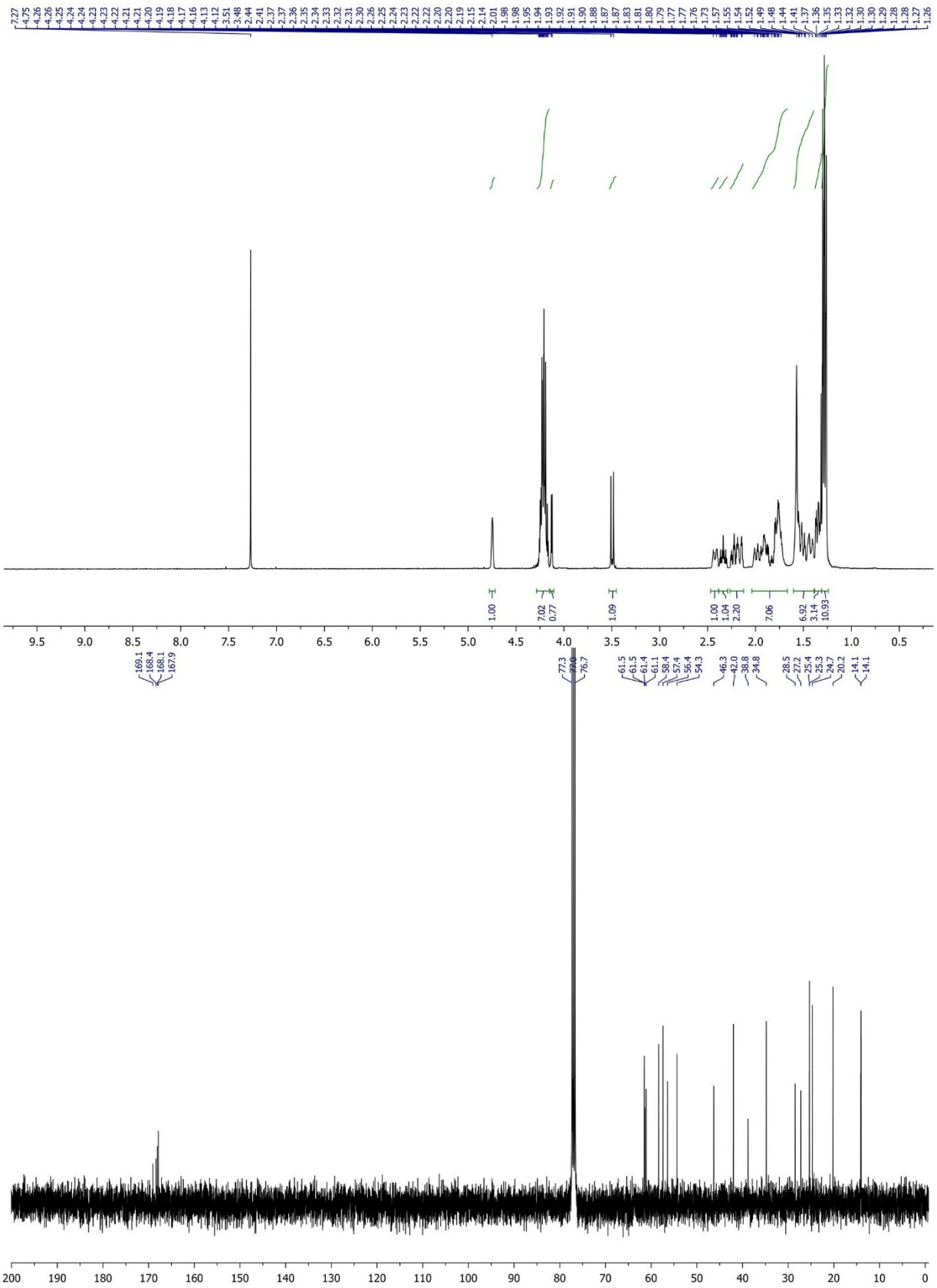
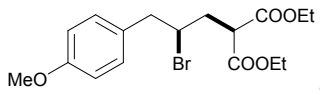
30
20
10
0

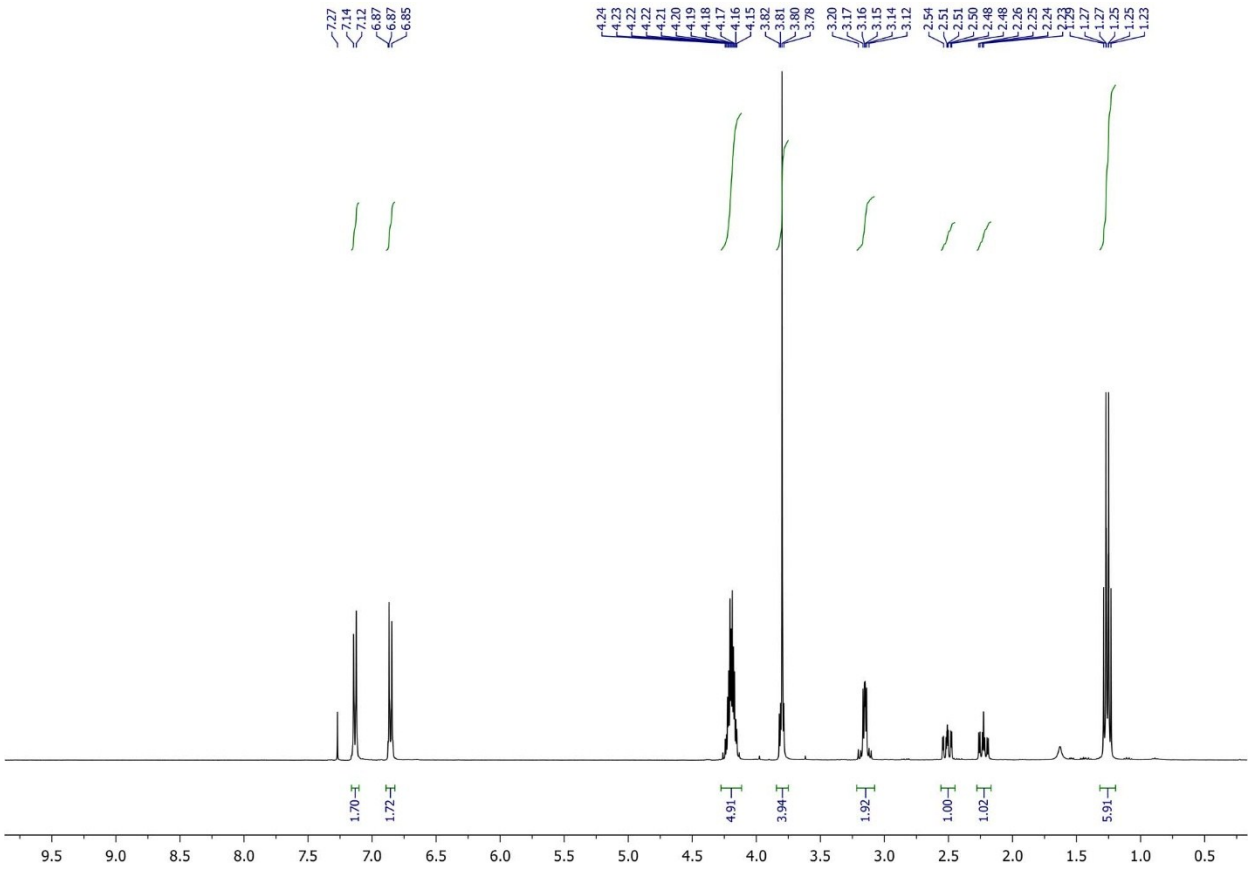


5g




COOEt
Br
COOEt
MeO

5h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6.87
6.85
4.24
4.23
4.22
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
3.82
3.81
3.80
3.78
3.20
3.17
3.16
3.15
3.14
3.12
2.54
2.51
2.51
2.50
2.48
2.26
2.25
2.24
1.27
1.27
1.25
1.25
1.23
1.70
1.72
4.91
3.94
1.92
1.00
1.02
5.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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4.5
4.0
3.5
3.0
2.5
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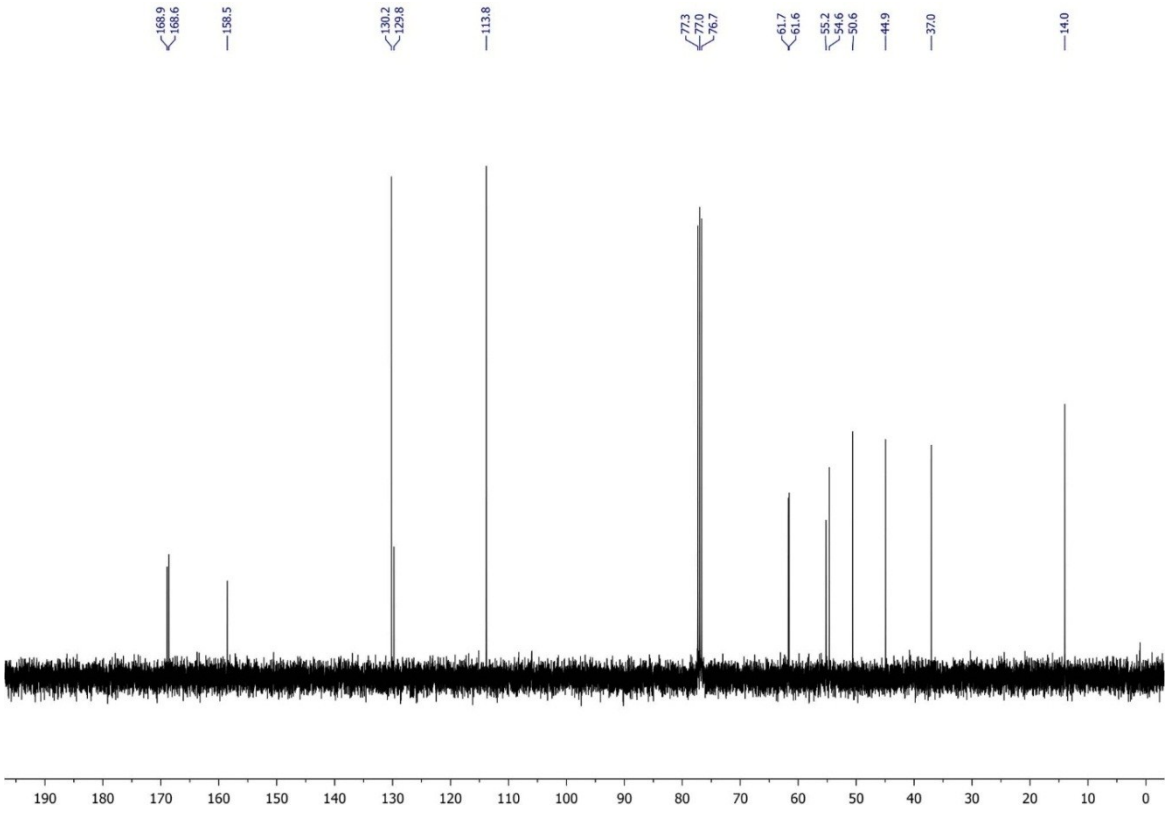
1.0
0.5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168.6
158.5
130.2
129.8
113.8
77.3
77.0
76.7
61.7
61.6
55.2
54.6
50.6
44.9
37.0
14.0
190
180
170
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150
140
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120
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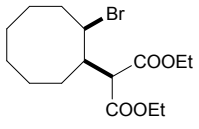
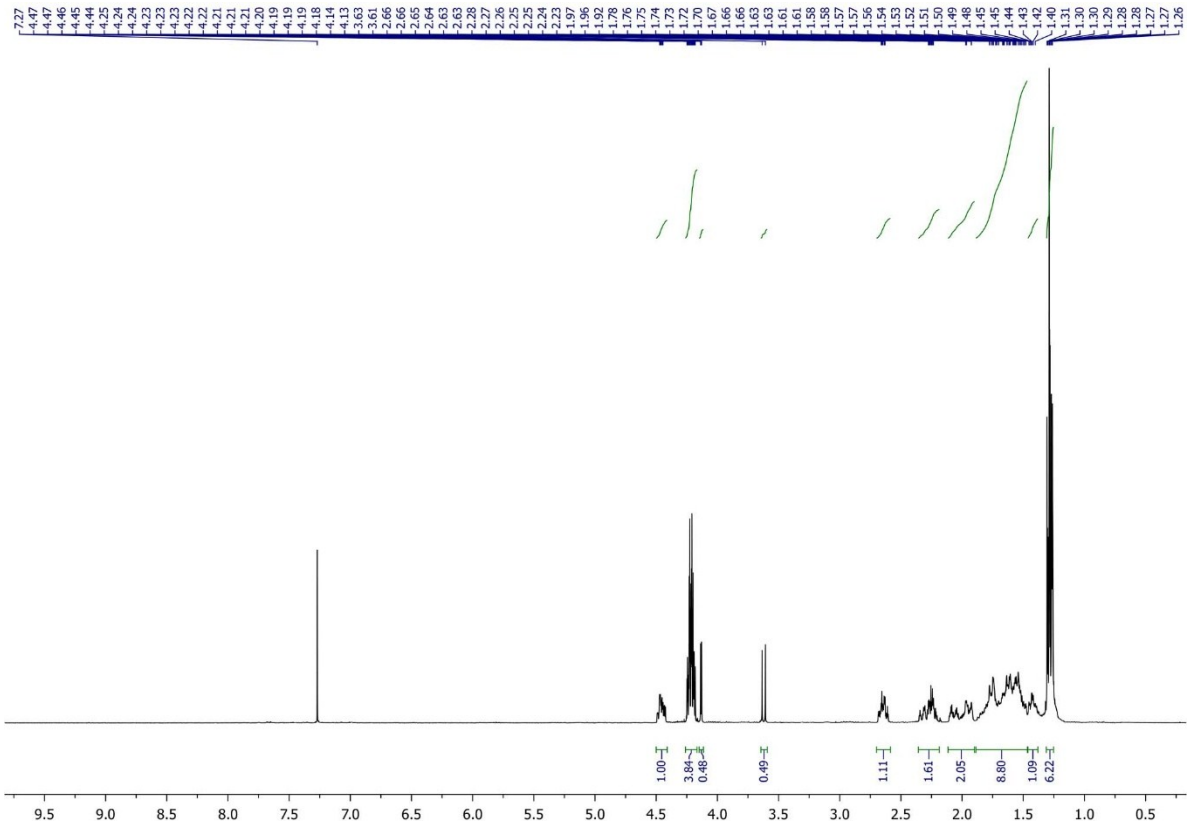
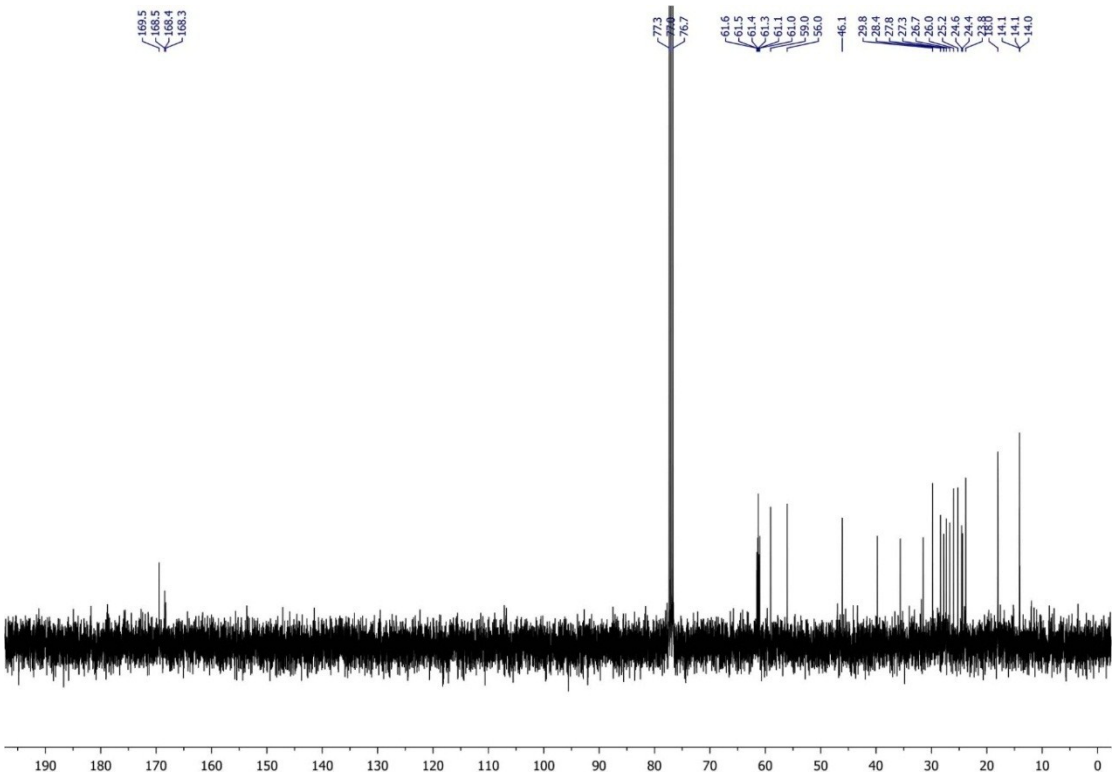
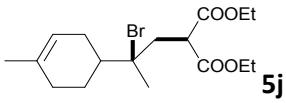
10
0



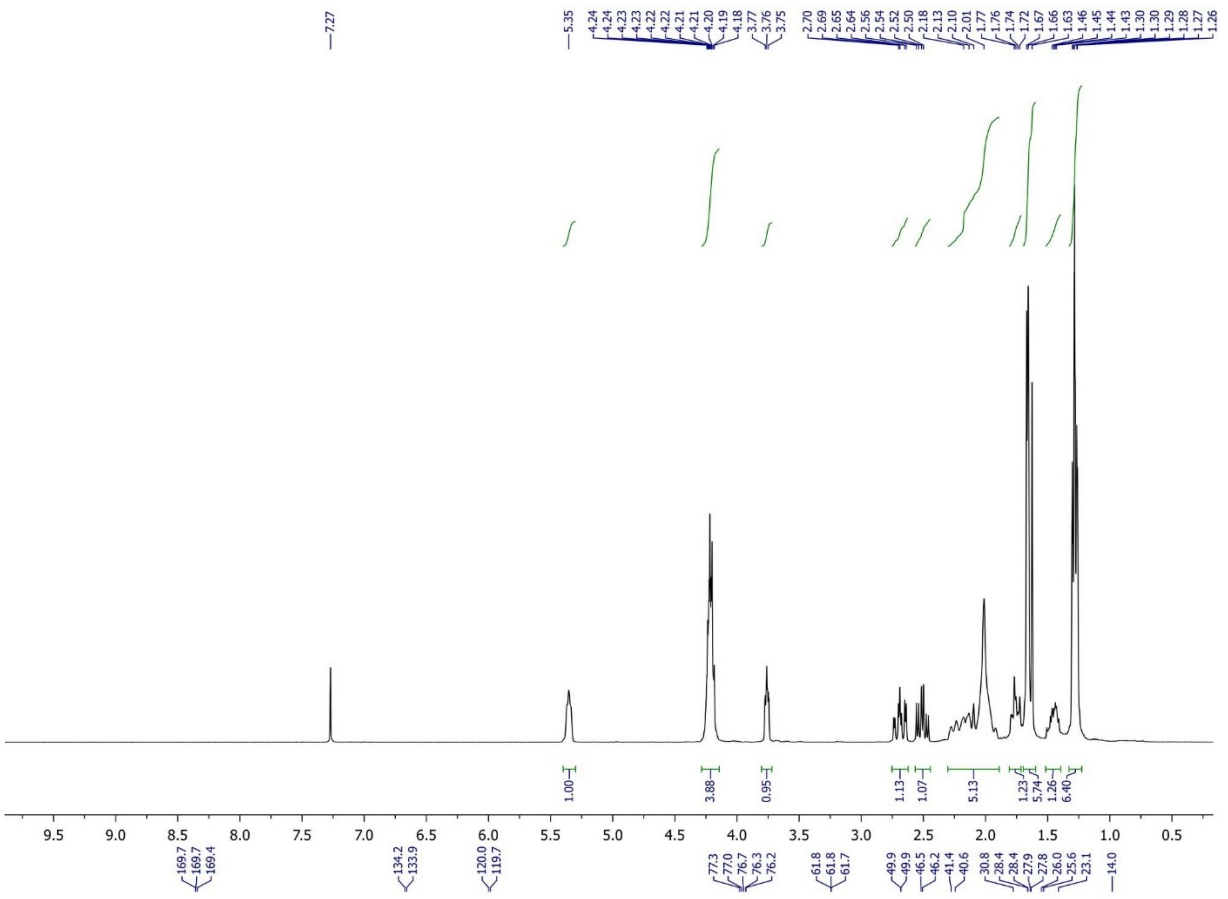
5i

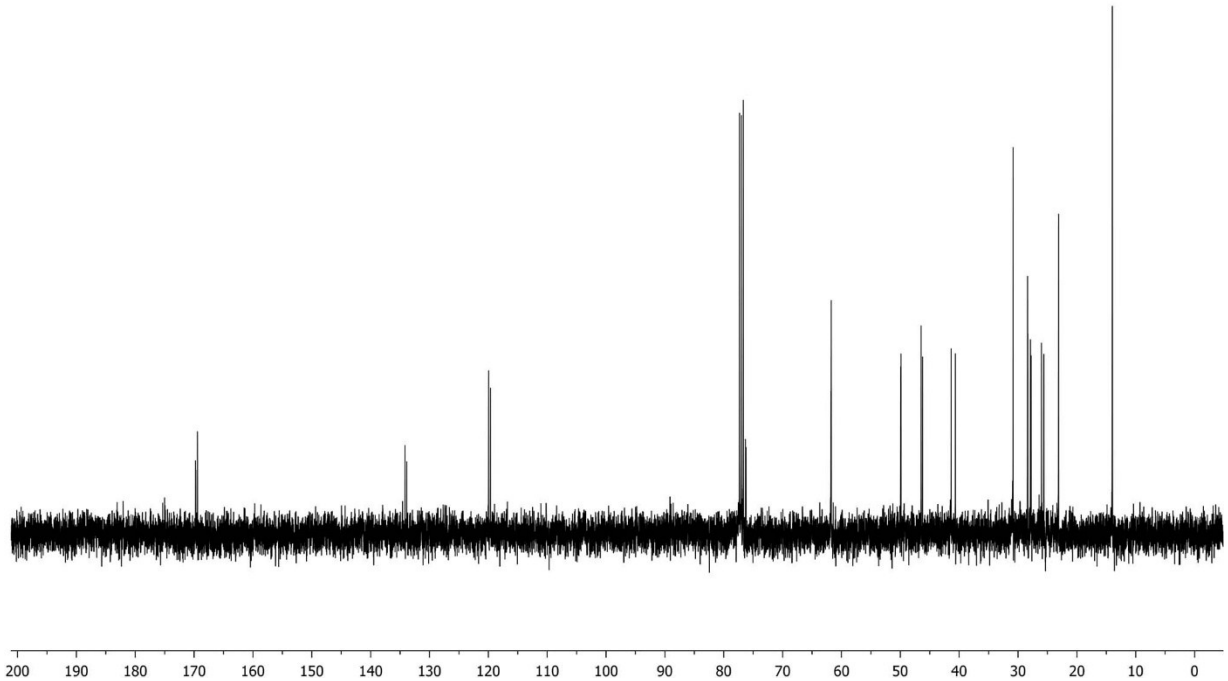


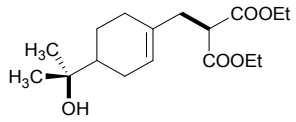




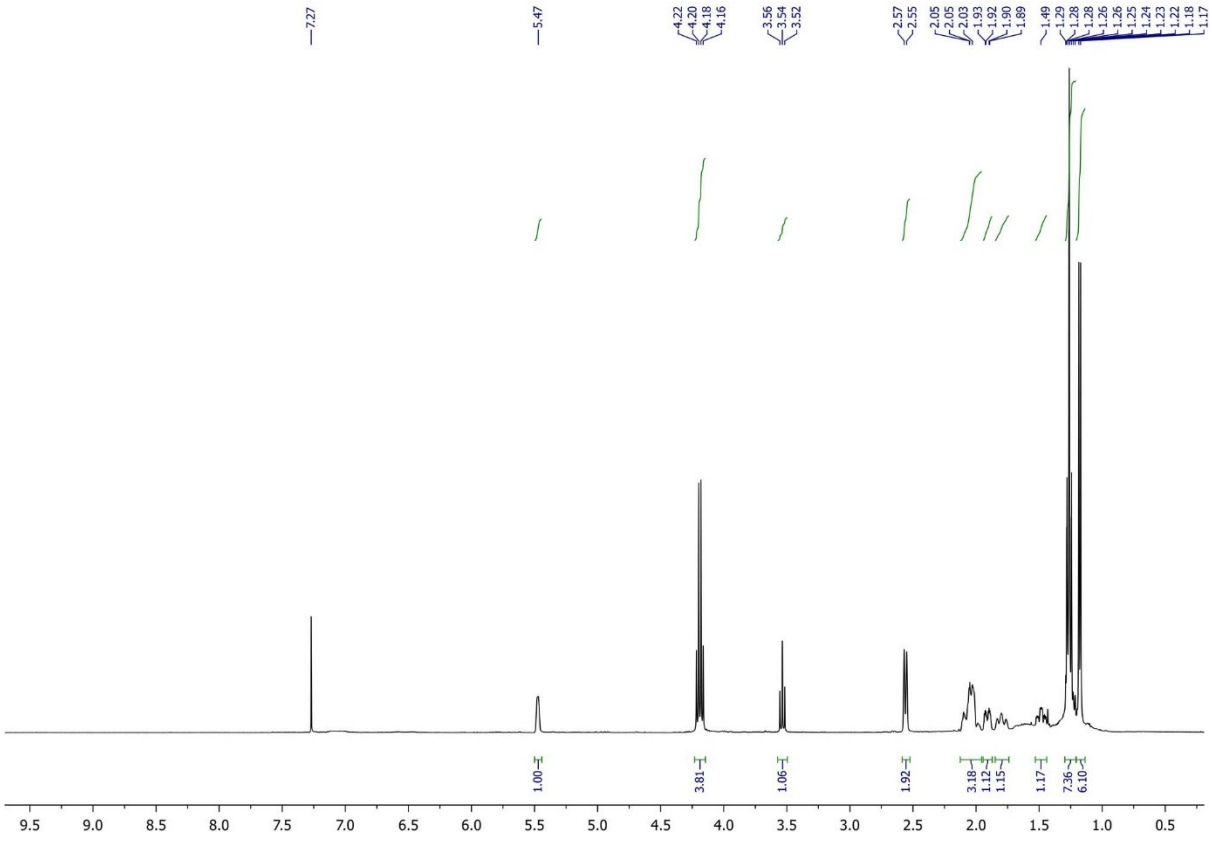
5j






COOEt
COOEt
H3C
H3C
OH

5k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2.57
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2.05
2.05
2.03
1.93
1.92
1.90
1.89
1.49
1.29
1.28
1.28
1.26
1.26
1.25
1.24
1.23
1.22
1.18
1.17
1.00
3.81
1.06
1.92
3.18
1.12
1.15
1.17
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9.5
9.0
8.5
8.0
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7.0
6.5
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2.5
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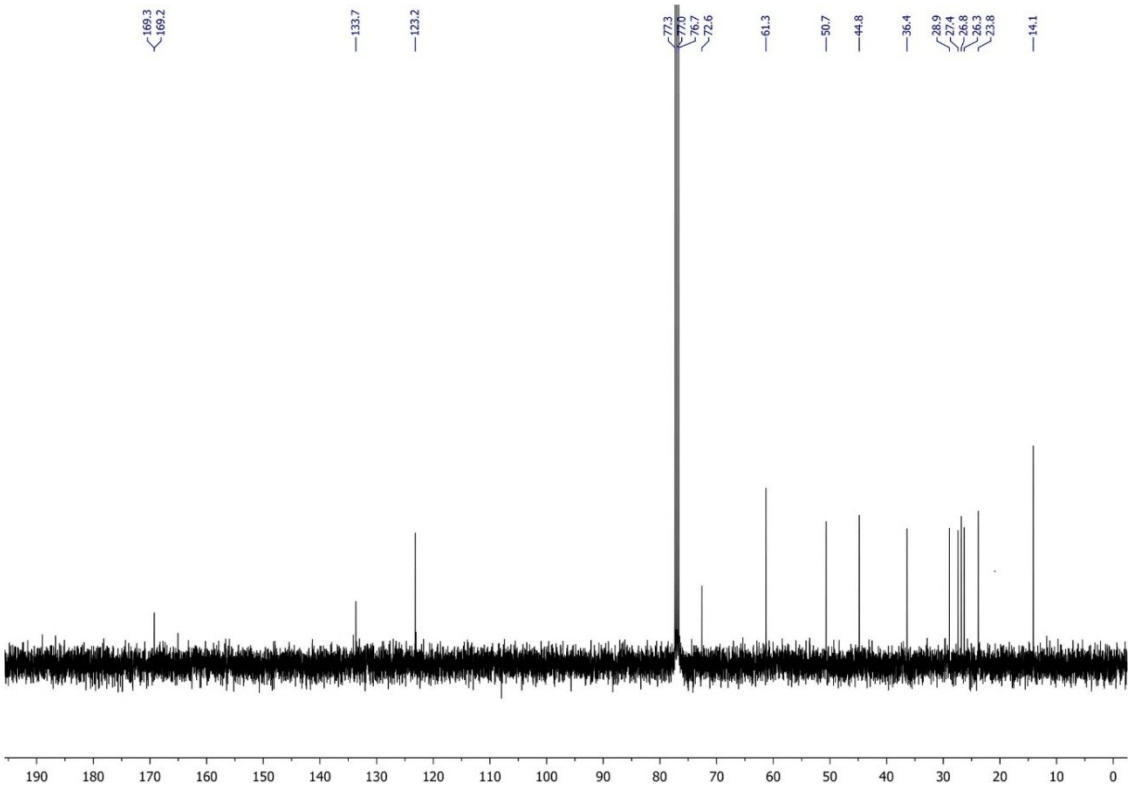
0.5


169.3
169.2
133.7
123.2
77.3
77.0
76.7
72.6
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50.7
44.8
36.4
28.9
27.4
26.8
26.3
23.8
14.1
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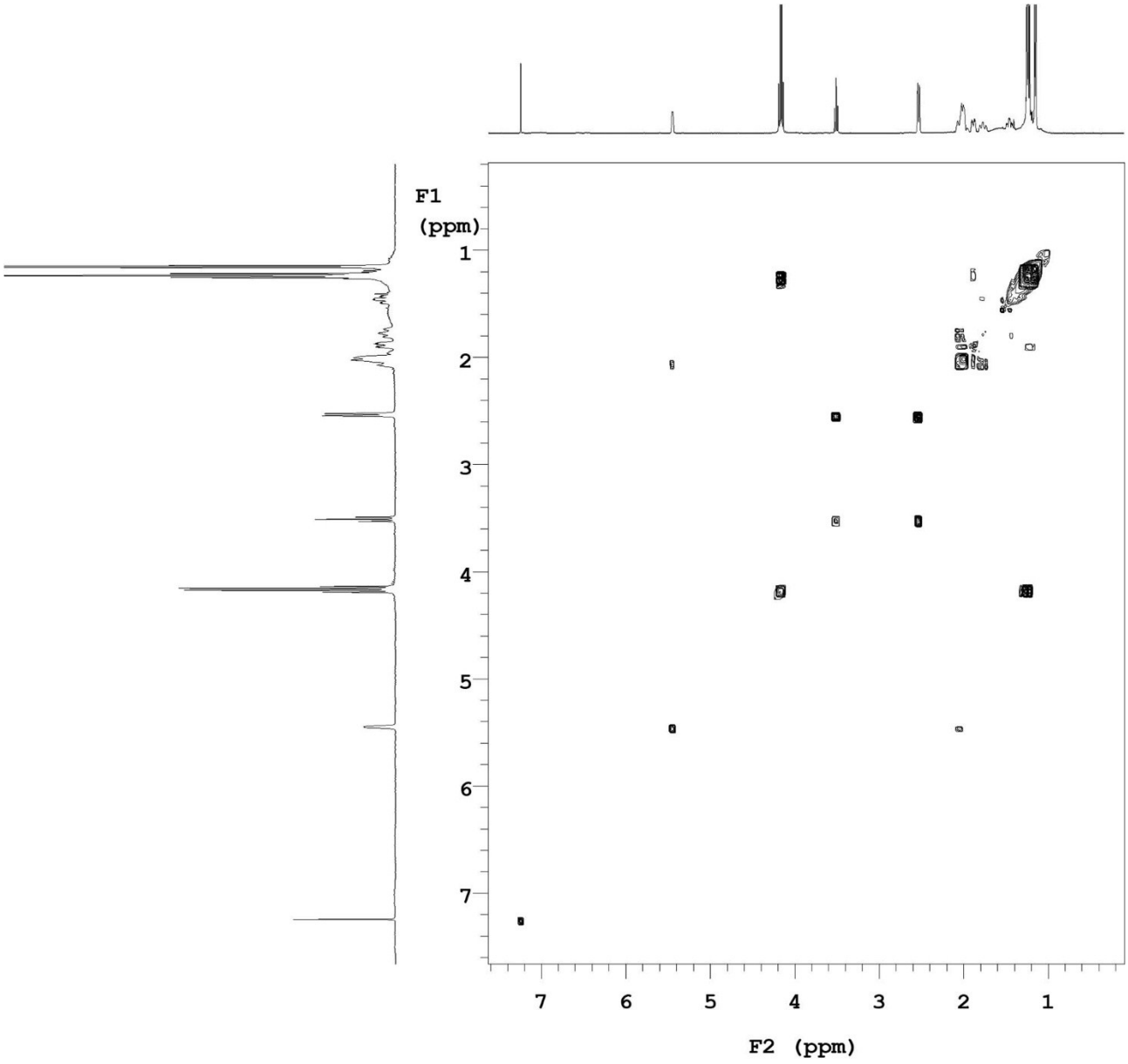
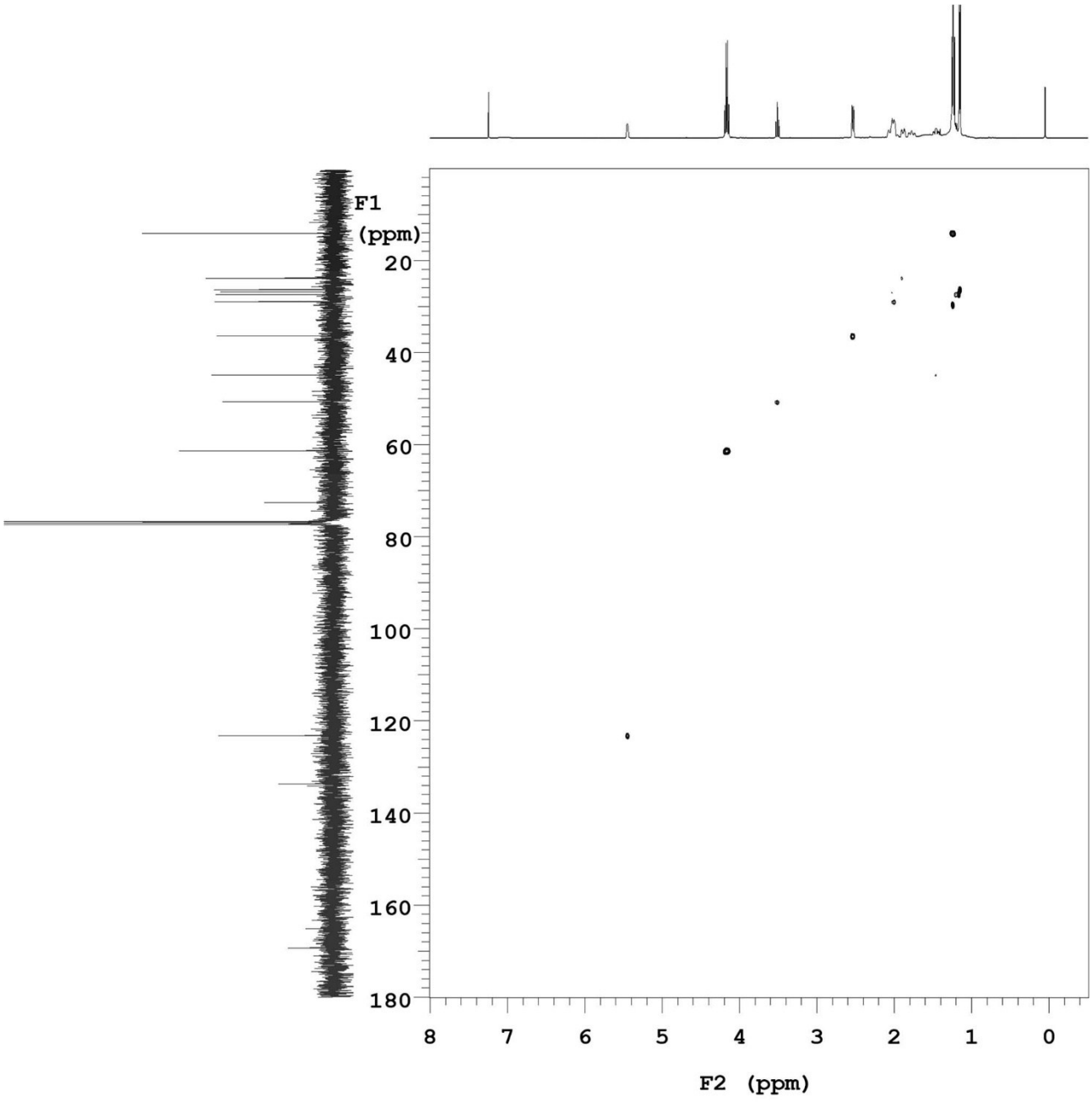
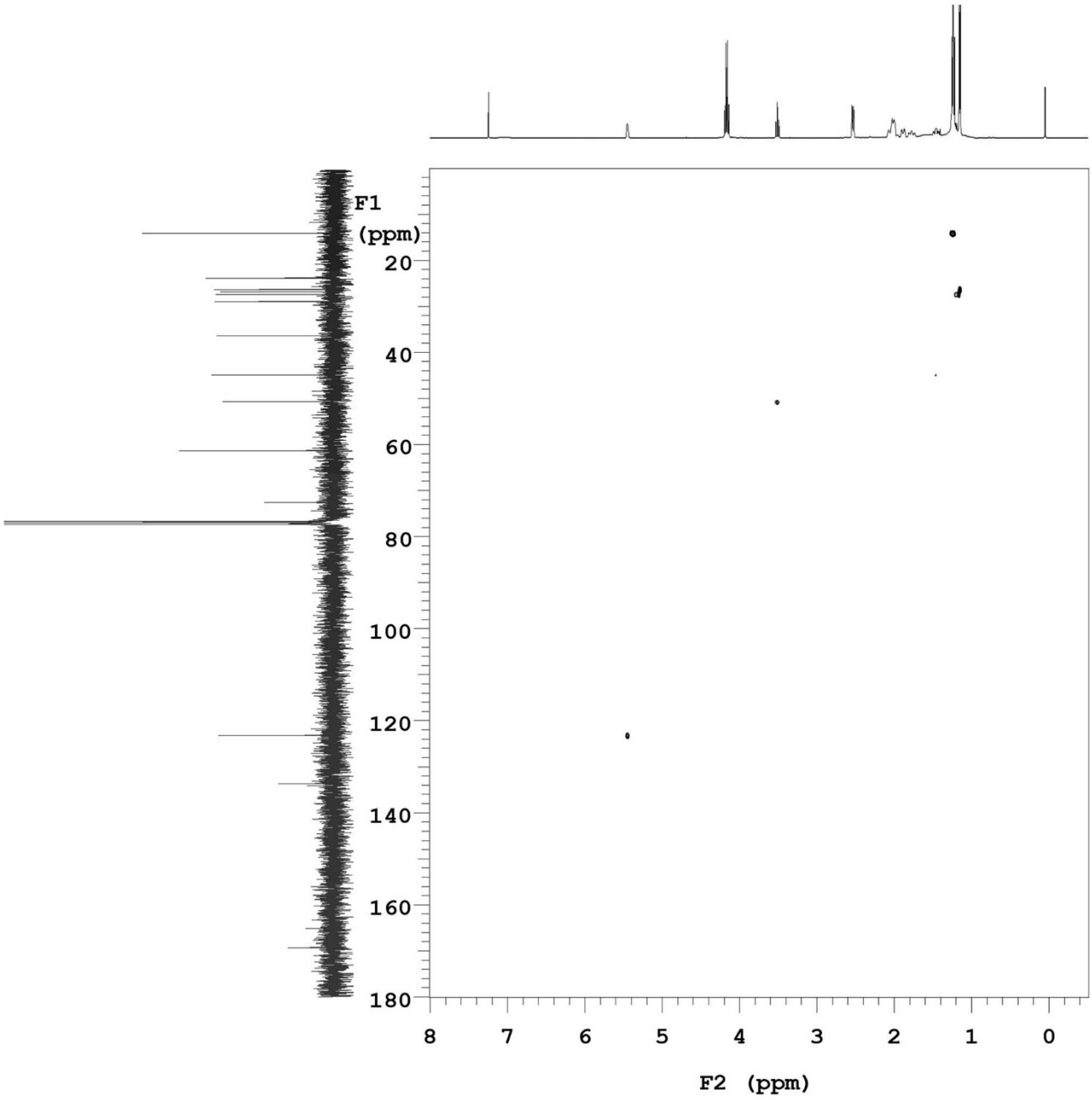


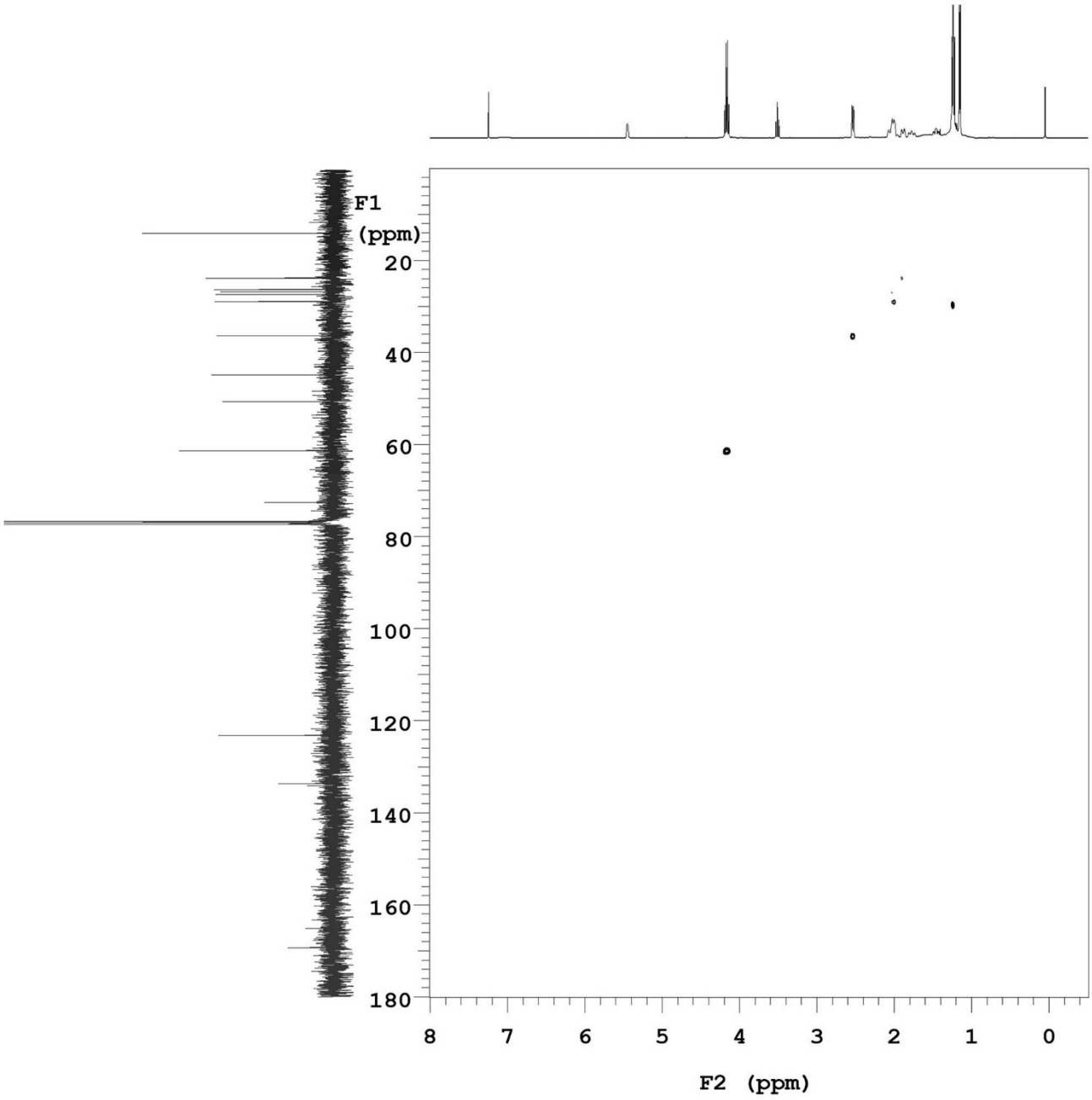
g-COSY of **5k**.



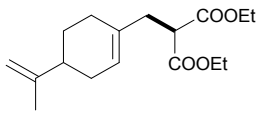
g-HSQC of **5k**. Positive and negative contours are shown.



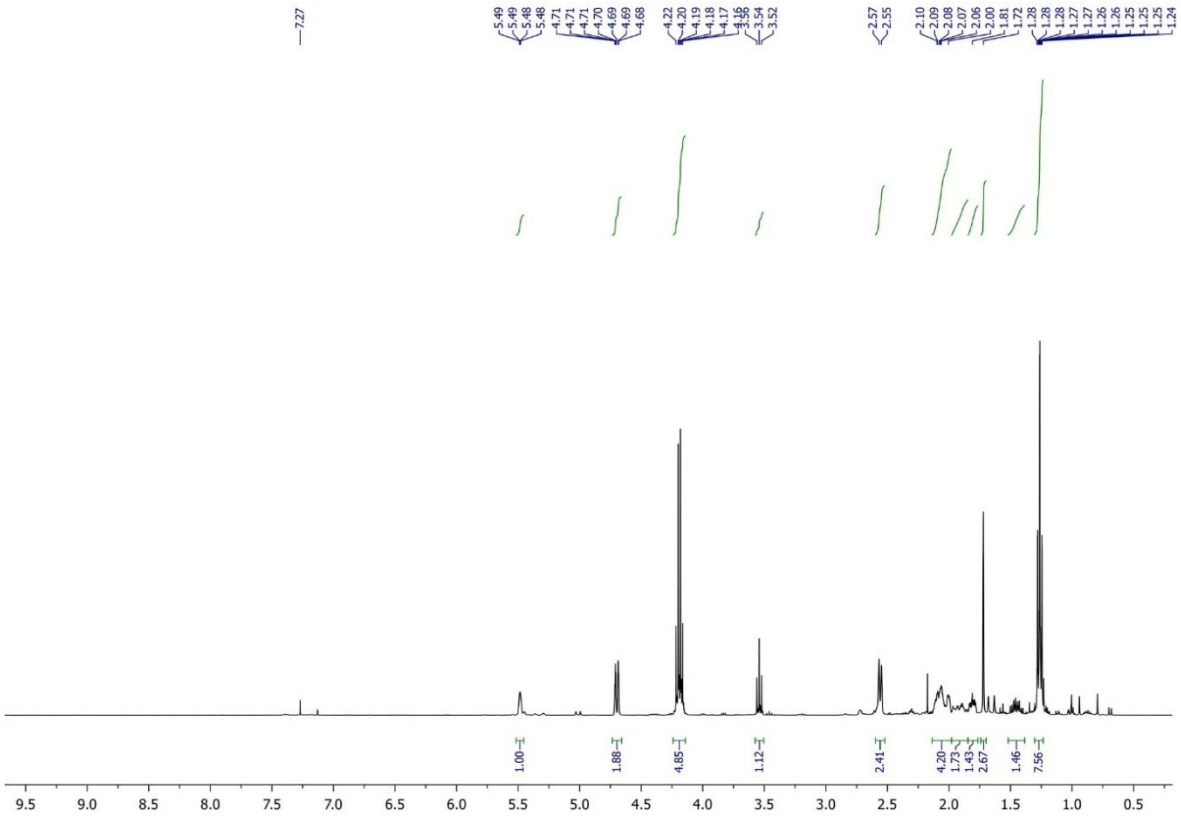
g-HSQC of **5k**. Positive contours (CH and CH_3) are shown.



g-HSQC of **5k**. Negative contours (CH_2) are shown.


COOEt
COOEt

5k'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4.71
4.71
4.71
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4.69
4.69
4.68
4.22
4.20
4.19
4.18
4.17
3.56
3.54
3.52
2.57
2.55
2.10
2.09
2.08
2.07
2.06
2.00
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1.72
1.28
1.28
1.28
1.27
1.26
1.26
1.25
1.25
1.25
1.24
1.00
1.88
4.85
1.12
2.41
4.20
1.73
1.43
2.67
1.46
7.56
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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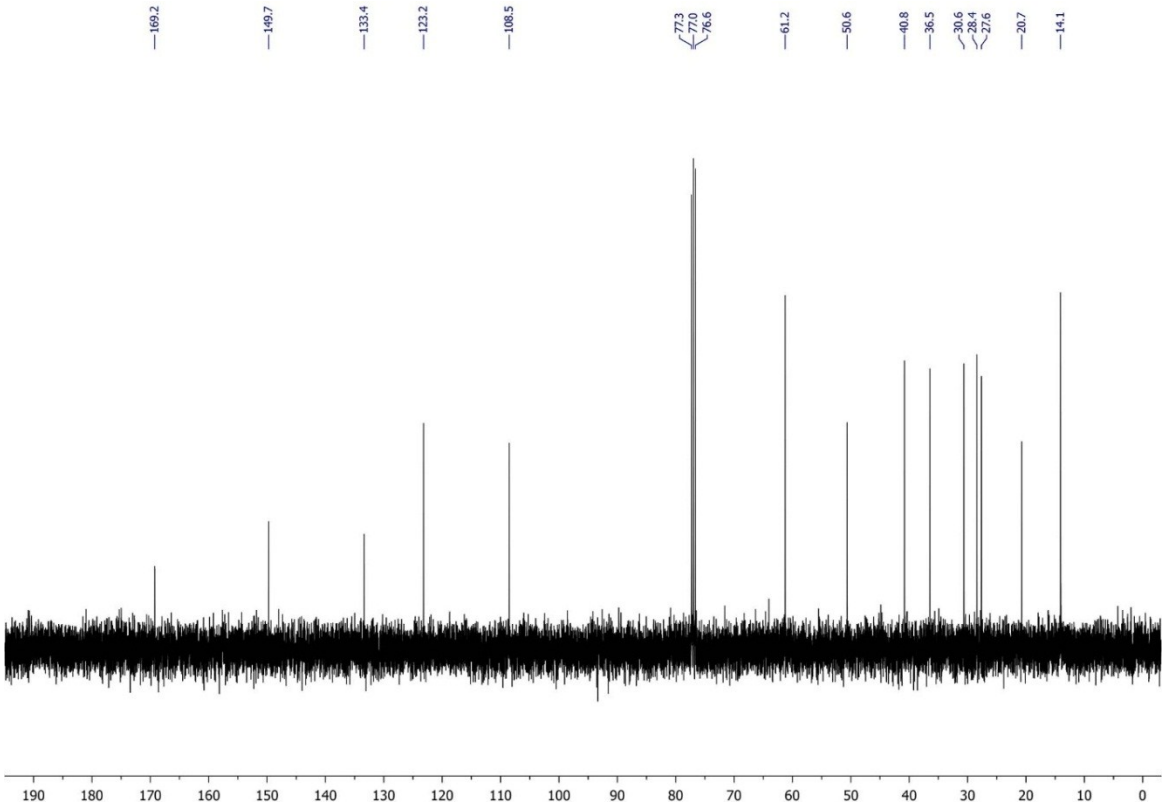
0.5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123.2
108.5
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77.0
76.6
61.2
50.6
40.8
36.5
30.6
28.4
27.6
20.7
14.1
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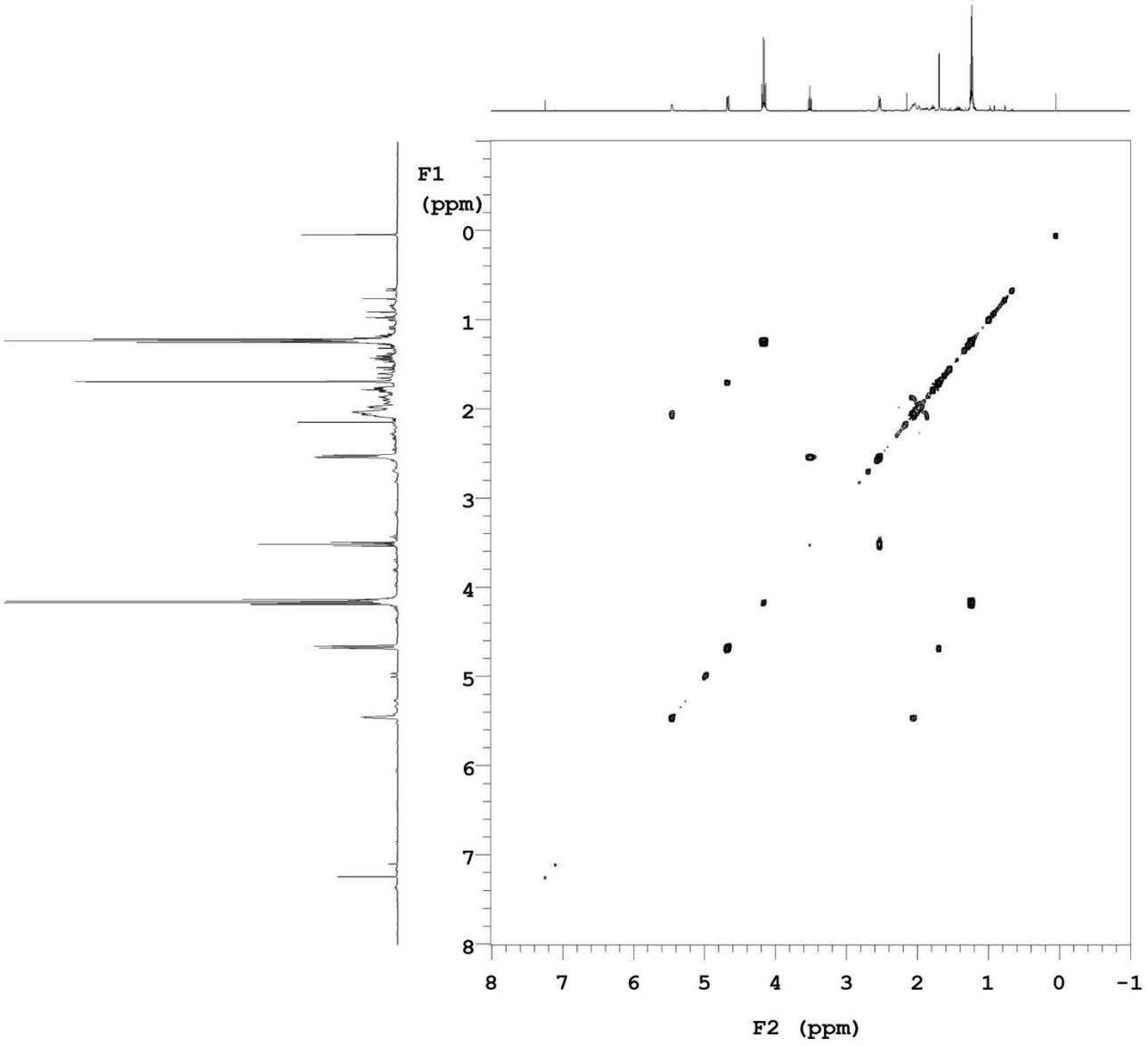
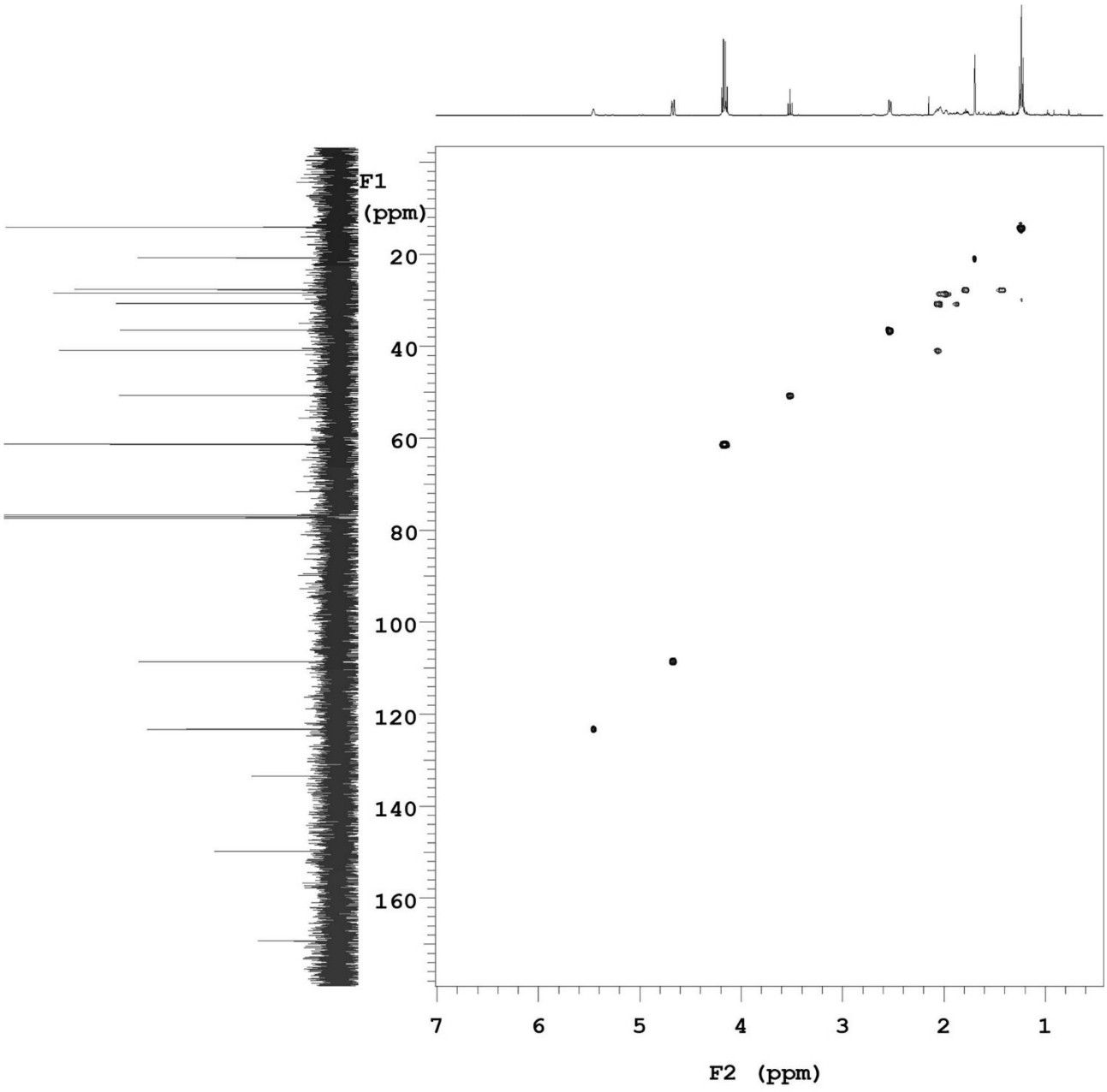
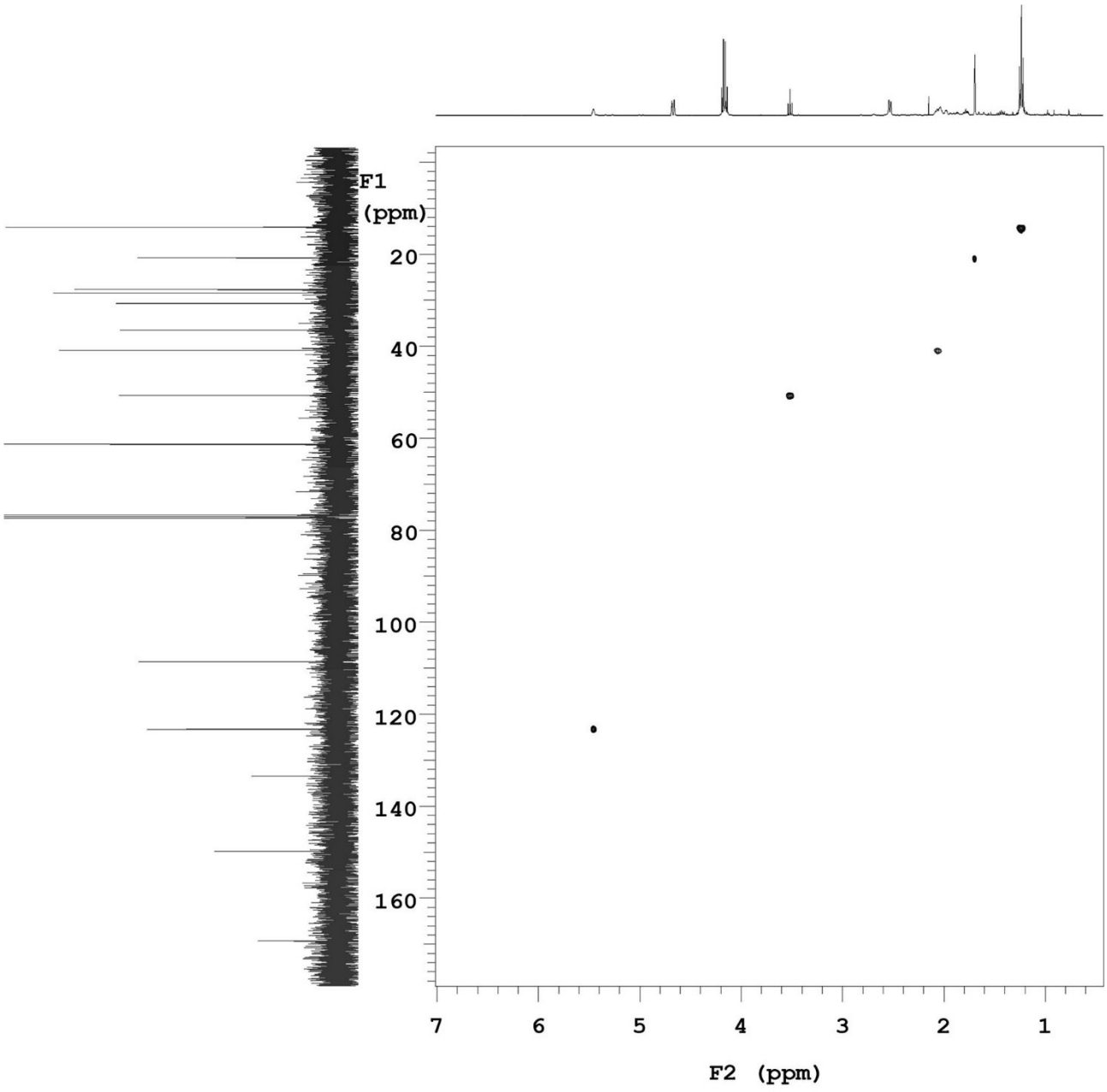


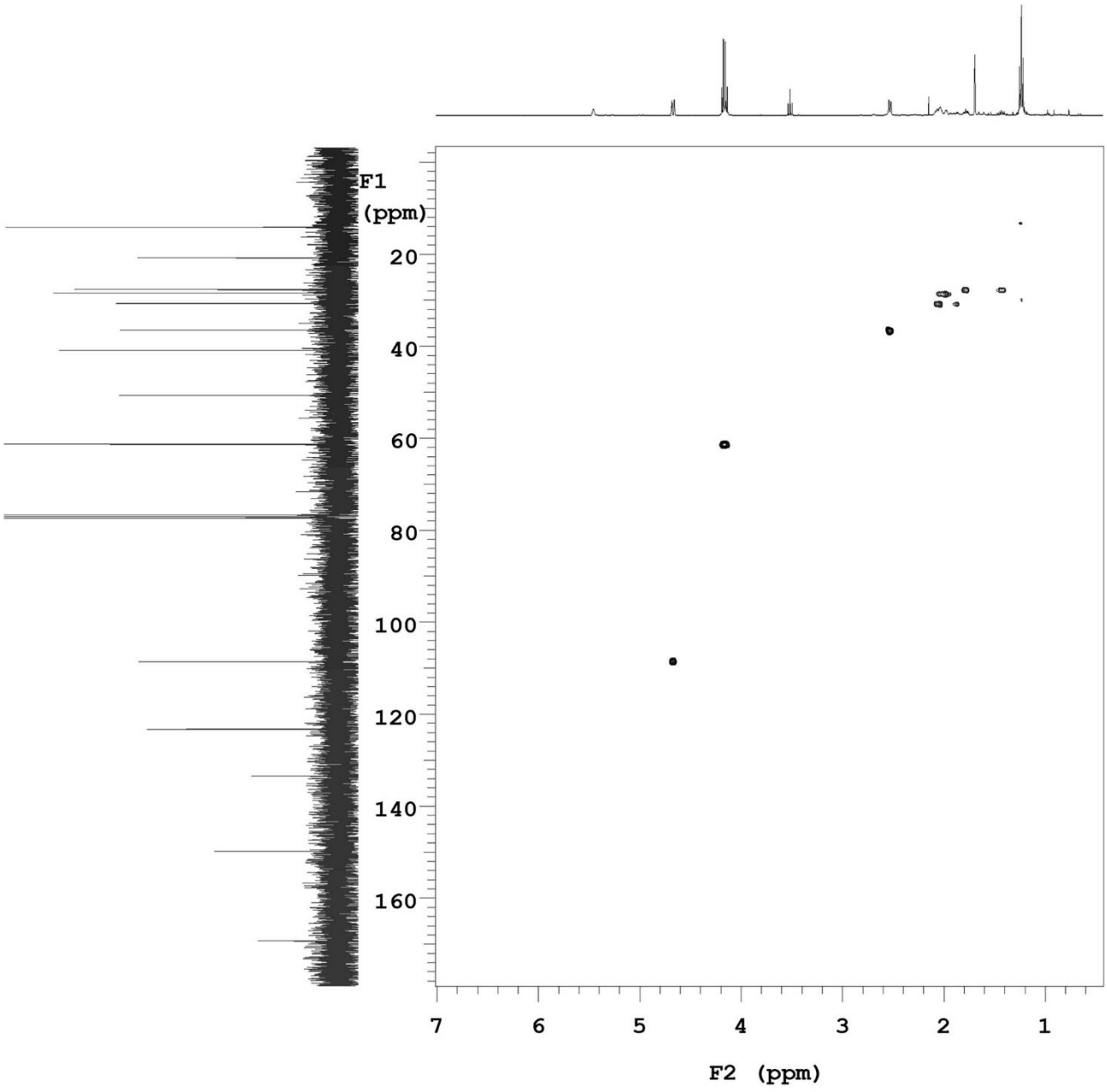
g-COSY of **5k'**.



g-HSQC of **5k'**. Positive and negative contours are shown.



g-HSQC of **5k'**. Positive contours (CH and CH_3) are shown.



g-HSQC of **5k'**. Negative contours (CH_2) are shown.