Electronic Supplementary Material (ESI) for Chemical Science.

# Photoredox Radical Conjugate Addition of Dithiane-2-carboxylate Promoted by an Iridium(III) Phenyl-tetrazole Complex: a Formal Radical Methylation of Michael Acceptors

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# Electronic Supplementary Information

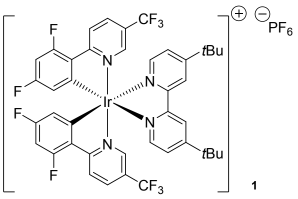
**Table of contents:**

**General methods and materials.** $^1$H NMR spectra were recorded on Varian Gemini 200, Varian Mercury 400. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: $\delta$ = 7.24 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 Gemini 200, Varian MR400 spectrometers. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: $\delta$ = 77.0 ppm). GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. LC-electrospray ionization mass spectra (ESI-MS) were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. They are reported as: *m/z* (rel. intense). IR spectra were recorded using Bruker Alpha FTIR spectrometer equipped with single reflection diamond ATR accessory. Chromatographic purification was done with 240-400 mesh silica gel. Purification on preparative thin layer chromatography was done on Merck TLC silica gel 60 $F_{254}$.

**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.

Reagents were purchased from Aldrich and AlfaAesar, and used without further purification unless otherwise stated. Compounds **3e**, **3f**, **3h**, **3i**, **3l**, **3m**, **3o**, **3p**, **3q** and **25** were commercially available. 1,3-dithianecarboxylic acid **4a** was prepared according reported procedure.[1] Iridium complexes **1**,[2] **2**,[3] **19-20**,[4] **21**,[3] **22**,[2] and **23-24**[4] were prepared according to described procedures.

## Optimization of radical conjugate addition of dithiane-2-carboxylate



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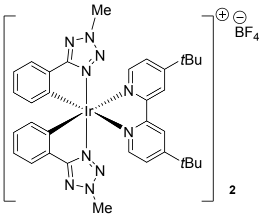

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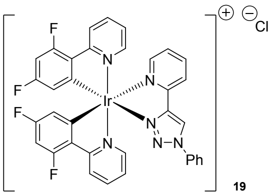

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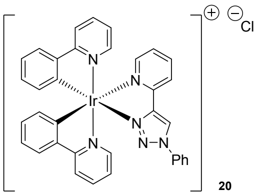

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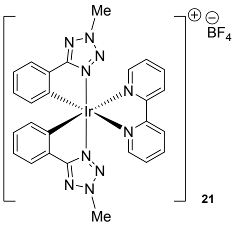

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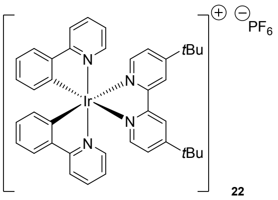

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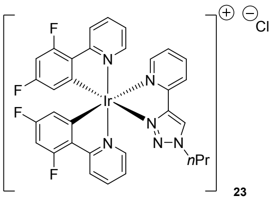

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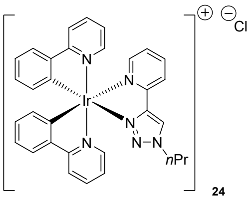

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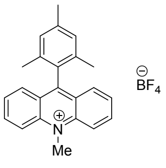


**25**

**Table S1.** Iridium catalyst screening.[a]

| Entry | Catalyst | Conversion (%)[b] |
|---|---|---|
| 1 | **1** | 93 |
| 2 | **2** | 97 |
| 3 | **19** | 18 |
| 4 | **20** | 17 |
| 5 | **21** | 72 |
| 6 | **22** | 47 |
| 7 | **23** | 13 |
| 8 | **24** | 13 |
| 9 | **25** | 0 |

[a] The reactions were performed at r.t. with 0.1 mmol of **4a**, 2 equiv of malonate (**3a**) and 1 equiv of $K_2HPO_4$, in the presence of 1 mol% of photocatalyst and in DMSO (0.2 M), and stopped after 16 h. [b] Determined by $^1$H NMR using internal standard.

**Table S2.** Solvent screening.[a]

| Entry | Solvent | Conversion (%)[b] |
|---|---|---|
| 1 | DMSO | 97 |
| 2 | DMF | 53 |
| 3 | DCE | 11 |
| 4 | EtOH | 34 |
| 5 | EtOH:$H_2O$ (8:2) | 45 |

[a] The reactions were performed at r.t. with 0.1 mmol of **4a**, 2 equiv of malonate (**3a**) and 1 equiv of $K_2HPO_4$, in the presence of 1 mol% of iridium complex **2** and in reported solvent (0.2 M), and stopped after 16 h. [b] Determined by $^1$H NMR using internal standard.

**Table S3.** Base screening.[a]

| Entry | Base (equiv.) | Solvent | Conversion (%)[b] |
|---|---|---|---|
| 1 | Lutidine (1) | DMSO | 65 |
| 2 | Lutidine (0.5) | DMSO | 35 |
| 3 | - | DMSO | 2 |
| 4 | $K_2HPO_4$ (1.5) | DMSO | 75 |
| 5 | $K_2HPO_4$ (1) | DMSO | 97 |
| 6 | $CsCO_3$ (1) | DMSO | 0 |
| 7 | DBU (1) | DMSO | 45 |
| 8 | $CsCO_3$ (1) | DMF | 0 |
| 9 | DBU (1) | DMF | 30 |

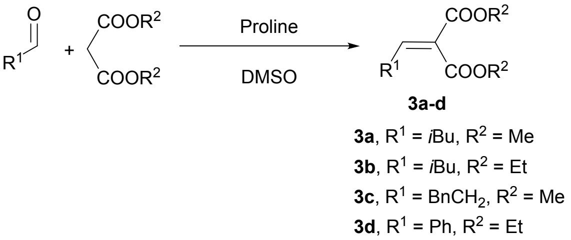
[a] The reactions were performed at r.t. with 0.1 mmol of **4a**, 2 equiv of malonate (**3a**) and base, in the presence of 1 mol% of iridium complex **2** and in reported solvent (0.2 M), and stopped after 16 h. [b] Determined by $^1$H NMR using internal standard.

**Table S4**

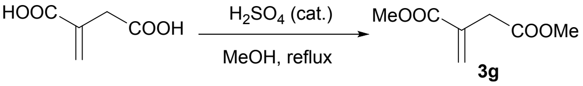
| Entry | Conversion (%)[b] | Variation from standard conditions |
|---|---|---|
| 1 | 97 | - |
| 2 | 0 | No Light |
| 3 | 0 | No iridium complex |
| 4 | 37 | **4a**:**3a** 1.5:1 |
| 5 | 42 | **4a**:**3a** 1:1 |
| 6 | 60 | **4a**:**3a** 1:1.5 |
| 7 | 94 | Temperature controlled at 25±3°C |

[a] Standard conditions: 0.1 mmol of **4a**, 2 equiv of malonate (**3a**) and 1 equiv of $K_2HPO_4$, in the presence of 1 mol% of iridium complex **2** and in DMSO (0.2 M), and stopped after 16 h. [b] Determined by $^1H$ NMR using internal standard.

## Preparation of starting Michael acceptors

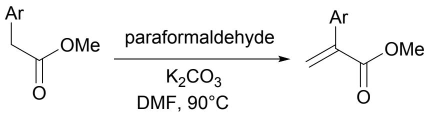


Compounds **3a-d** were prepared following reported procedure.[5] To a solution of proline (1 mmol, 0.115 g) in DMSO (3.3 mL) aldehyde (10 mmol) was added. After 10 min. malonate (10 mmol) was slowly added and the reaction stirred overnight. The reaction mixture was diluted with $Et_2O$ (30 mL) and washed with water (20 mL), $NaHCO_3$ sat. sln. (20 mL) and brine (20 mL). The organic phase was concentrated under reduced pressure and the residue was purified by column chromatography on silica (cyclohexane:ethyl acetate from 95:5 to 90:10) to give pure **3a-d** as white oils (65-84% yields). Spectroscopic data were according to the literature.[6]



To a solution of itaconic acid (3.9 mmol, 0.500 g) in MeOH (10 mL) some drops of concentrated sulfuric acid were added. The reaction was refluxed for 8 hours, cooled at room temperature and the solvent was evaporated under reduced pressure. The residue was dissolved in $Et_2O$ (30 mL) and washed with $NaHCO_3$ sat. sln. (2 x 10 mL) and brine (20 mL). The organic phase was concentrated under reduced pressure to give **3g** (94%, 3.7 mmol, 0.576 g) as colorless oil. The product was used in the next step without purification.

$^1H$ NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 6.27 (s, 1H), 5.67 (s, 1H), 3.71 (s, 3H), 3.64 (s, 3H), 3.29 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ =171.0, 166.5, 133.6, 128.4, 52.0, 51.9, 37.4.

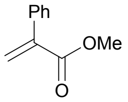


**3j,k**

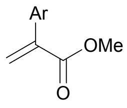
**3j**, Ar = Ph

**3k**, Ar = 4-Me-$C_6H_4$

Compounds **3j,k** were prepared following reported procedure.[7] A mixture of ester (7.0 mmol, 1.044 g, 1 mL), paraformaldehyde (10.5 mmol, 0.313 g) and $K_2CO_3$ (7.0 mmol, 0.960 g) in DMF (5 mL) was heated at 100°C for 6h. The mixture was cooled at room temperature, water (20 mL) and $Et_2O$ (30 mL) were added and the organic layer was separated. The aqueous layer was extracted with $Et_2O$ (2 x 20 mL). The collected organic layers were washed with brine (10 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure to give the crude products. Column chromatography on silica (cyclohexane:$Et_2O$ from 100:0 to 90:5) afforded pure **3j,k** as colorless oils.

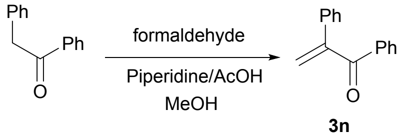


**3j**: colorless oil; 73% yield; $^1$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 7.45 – 7.28 (m, 5H), 6.36 (d, $J$=1.2, 1H), 5.88 (d, $J$=1.2, 1H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 167.2, 141.3, 136.6, 128.2 (2C), 128.1, 128.0 (2C), 126.8, 52.1.



Ar = 4-Me-$C_6H_4$

**3k**: colorless oil, 85% yield; $^1$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 7.33 – 7.28 (m, 2H), 7.19 – 7.14 (m, 2H), 6.31 (d, $J$=1.3, 1H), 5.86 (d, $J$=1.3, 1H), 3.81 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 167.4, 141.1, 138.0, 133.8, 128.8 (2C), 128.1 (2C), 126.0, 52.1, 21.1.



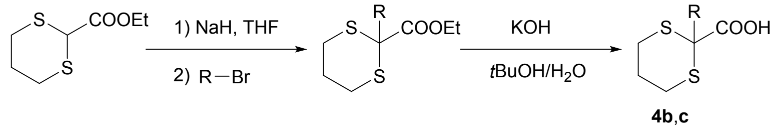
**3n**

Compounds **3n** were prepared following reported procedure.[8] A mixture of deoxibenzoin (5.1 mmol, 1.0 g), formaldehyde (38% in water, 1.8 mL), piperidine (0.66 mmol, 65 μL) and acetic acid (1.1 mmol, 63 μL) in MeOH (13 mL) was refluxed for 6h. The mixture was cooled at room temperature and the volatiles were evaporated under reduced pressure. The residue was dissolved in ethyl acetate (30 mL) and washed with 1 M HCl (10 mL), $NaHCO_3$ sat. sln. (10 mL) and brine (20 mL). The organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure to give the crude product. Column chromatography on silica (cyclohexane:ethyl acetate from 95:5 to 80:20) afforded pure **3n** as colorless oil (94%, 4.8 mmol, 1.0 g).

(**3n**): $^1$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 7.95 – 7.87 (m, 2H), 7.58 – 7.47 (m, 1H), 7.47 – 7.41 (m, 4H), 7.41 – 7.24 (m, 3H), 6.06 (s, 1H), 5.63 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ =

241.8, 216.7, 167.4, 156.2, 156.2, 152.2, 149.1 (2C), 147.8 (2C), 147.6 (2C), 146.2 (2C), 140.0.

## Preparation of 2-substituted 1,3-dithiane-2-carboxylate 4b,c

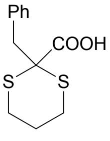


**4b**,**c**

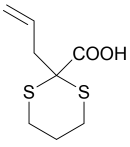
**4b**, R = Bn, 86%
**4c**, R = allyl, 78%

To a solution of 1,3-dithiane-2carboxylate (0.95 mmol, 0.183 g, 154 μL) in THF (3 mL), NaH (60% suspension in mineral oil, 1.9 mmol, 0.076 g) was slowly added at 0°C. The reaction mixture was gently heated at 70°C for 20 min. and cooled at room temperature. Alkylating agent (1.4 mmol) was added and the reaction mixture was stirred overnight. After that, the reaction was cooled at 0°C, water (10 mL) and ethyl acetate (20 mL) were added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (2 x 20 mL). The collected organic layers were washed with brine (10 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure to give the crude ester product.

The residue was dissolved in *t*BuOH (4 mL) and 1M KOH aq. (4 mL) was added. After 24 hours volatiles were evaporated under reduced pressure, water (10 mL) and $Et_2O$ (20 mL) were added and the organic layer was separated. The aqueous layer was extracted with $Et_2O$ (2 x 10 mL). 5 M HCl aq. was slowly added to aqueous layer until pH = 1, and they were extracted with DCM (4 x 20 mL). The collected organic layers were washed with brine (10 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure to give pure compounds as white solids, that were used in the photocatalytic reaction without further purification.



**4b**: White solid, 87% yield (two steps); m.p. = 79°C; $^1$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 7.39 – 7.32 (m, 2H), 7.31 – 7.25 (m, 3H), 3.42 – 3.31 (s, 2H), 3.26 (ddd, *J*=14.8, 12.8, 2.6, 2H), 2.76 – 2.63 (m, 2H), 2.18 – 2.08 (m, 1H), 1.91 – 1.76 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 176.7, 134.0, 130.8 (2C), 128.0 (2C), 127.5, 53.2, 44.3, 29.6, 28.0, 24.1; HRMS calcd for $C_{12}H_{14}O_2S_2$: 254.0435; found: 254.0430.

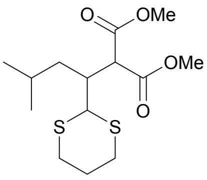


**4c**: White solid, 83% yield (two steps); m.p. = 56°C;$^1$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$= 11.57 (bs, 1H), 5.95 – 5.78 (m, 1H), 5.26 – 5.10 (m, 2H), 3.33 (ddd, *J*=14.1, 12.9, 2.6, 2H), 2.73 (d, *J*=7.1, 2H), 2.63 (ddd, *J*=14.2, 4.2, 3.1, 2H), 2.26 – 2.00 (m, 1H), 1.91 – 1.70 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$= 177.2, 131.1, 119.9, 50.2, 42.7, 27.6 (2C), 24.1; HRMS calcd for $C_8H_{12}O_2S_2$: 204.0279; found: 204.0274.

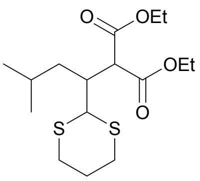
## Photoredox radical conjugate addition of carboxylates

**General procedure on 0.2 mmol scale:** In a Schlenk tube with rotaflo stopcock under argon atmosphere at r.t., catalyst **2** (1.7 mg, 0.002 mmol), 1,3-dithiane-2-carboxylic acid **4a** (0.2 mmol, 0.032g) and $K_2HPO_4$ (0.2 mmol, 0.034 g), were dissolved in 400 μL DMSO. After 2 min, Michael acceptor (0.4 mmol) was added. The reaction mixture was carefully degassed via freeze-pump thaw (three times), and the vessel refilled with argon. The Schlenk tube was stirred and irradiated with a blu LED positioned approximately at 10 cm distance from the reaction vessel. After 16 h of irradiation, $NaHCO_3$ sat. sln. (2 mL) was added and the mixture was extracted with ethyl acetate (4 x 5 mL). The collected organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to give crude products. Column chromatography on silica (cyclohexane:ethyl acetate or cyclohexane:$Et_2O$) afforded pure compounds.

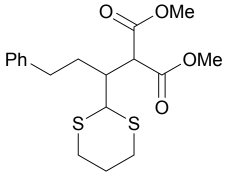
**General procedure on 2.4 mmol scale:** The reaction was conducted applying the same protocol used for 0.2 mmol scale but using: catalyst **2** (10.4 mg, 0.012 mmol), 1,3-dithiane-2-carboxylic acid **4a** (2.4 mmol, 0.393 g) and $K_2HPO_4$ (2.4 mmol, 0.417 g) and Michael acceptor **5a** (4.8 mmol, 0.960 g), were dissolved in 4.8 mL DMSO. Product **5a** was obtained in 84% yield.



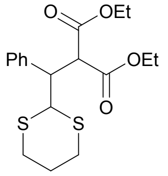
**5a**: colorless oil, 86% yield; $^1H$ NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 4.31 (d, *J*=4.4, 1H), 3.77 (d, *J*=7.0, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 2.94 – 2.71 (m, 4H), 2.71 – 2.55 (m, 1H), 2.14 – 1.98 (m, 1H), 1.93 – 1.75 (m, 1H), 1.68 (ddd, *J*=14.0, 7.3, 5.7, 1H), 1.59 (dt, *J*=13.4, 6.6, 1H), 1.36 – 1.26 (m, 1H), 0.90 (d, *J*=6.5, 3H), 0.87 (d, *J*=6.5, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 169.0, 168.9, 53.6, 52.6, 52.4, 52.2, 41.1, 38.5, 31.0, 30.5, 26.5, 25.9, 22.5, 22.4.; HRMS calcd for $C_{14}H_{24}O_4S_2$: 320.1116; found: 320.1108.



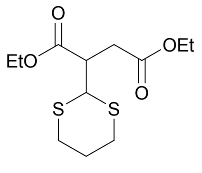
**5b**: colorless oil, 87% yield; $^1H$ NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 4.33 (d, *J*=4.3, 1H), 4.25 – 4.11 (m, 4H), 3.72 (d, *J*=7.0, 1H), 2.93 – 2.72 (m, 4H), 2.68 – 2.57 (m, 1H), 2.11 – 2.00 (m, 1H), 1.89 – 1.73 (m, 1H), 1.73 – 1.55 (m, 3H), 1.26 (t, *J*=7.2, 6H), 0.88 (dd, *J*=10.0, 6.4, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 168.7, 168.5, 61.5, 61.4, 54.1, 52.4, 40.9, 38.6, 31.1, 30.6, 26.5, 26.0, 22.6, 22.5, 14.0 (2C); EI-MS: *m/z* = 347 (2), 303 (10, M-OEt), 257 (26), 188 (76), 145 (100), 119 (65); HRMS calcd for $C_{16}H_{28}O_4S_2$: 348.1429; found: 348.1422.



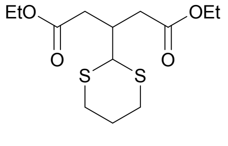
**5c**: colorless oil, 85% yield; $^{1}$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 7.30 – 7.22 (m, 2H), 7.21 – 7.08 (m, 3H), 4.31 (d, $J$=5.3, 1H), 3.86 (d, $J$=6.8, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 2.87 – 2.77 (m, 4H), 2.76 – 2.63 (m, 3H), 2.17 – 1.99 (m, 2H), 1.94 – 1.74 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 169.0, 168.8, 141.7, 128.4 (2C), 128.3 (2C), 125.9, 53.4, 52.7, 52.5, 51.5, 42.7, 34.9, 31.8, 30.7, 30.3, 25.9; EI-MS: $m/z$ = 236 (56), 145 (100), 119 (65), 91 (45); HRMS calcd for $C_{18}H_{24}O_4S_2$: 368.1116; found: 368.119.



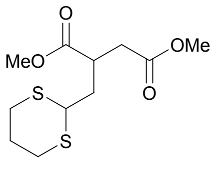
**5d**: white solid; m.p. = 77 °C, 84% yield; $^{1}$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 7.60 – 6.97 (m, 5H), 4.57 (d, $J$=6.1, 1H), 4.21 (q, $J$=6.9, 2H), 4.17 (d, $J$=10.7, 1H), 3.90 (dd, $J$=10.7, 6.1, 1H), 3.84 (q, $J$=7.2, 2H), 2.91 – 2.67 (m, 4H), 1.98 (m, 1H), 1.76 (m, 1H), 1.25 (t, $J$=6.9, 3H), 0.89 (t, $J$=7.1, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 167.9, 167.4, 136.7, 129.4 (2C), 127.9 (2C), 127.8, 61.7, 61.3, 54.9, 51.3, 49.4, 30.5, 30.4, 25.6, 14.0, 13.6; HRMS calcd for $C_{18}H_{24}O_4S_2$: 368.1116; found: 368.1109.



**5e**: colorless oil, 91% yield; $^{1}$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 4.26 – 4.15 (m, 3H), 4.15 – 4.08 (m, 2H), 3.37 (dddd, $J$=9.5, 7.1, 4.8, 0.9, 1H), 3.01 – 2.70 (m, 6H), 2.13 – 1.99 (m, 1H), 1.88 (m, 1H), 1.25 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 171.6, 171.5, 61.3, 60.8, 47.6, 46.1, 34.1, 29.3, 29.1, 25.3, 14.1, 14.0; ESI-MS: $m/z$ = 292 (53), 263 (2, M-Et), 218 (43), 158 (34), 145 (36), 119 (100); HRMS calcd for $C_{12}H_{20}O_4S_2$: 292.0803; found: 292.0796.

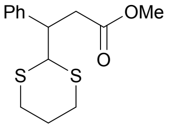


**5f**: yellowish oil, 49% yield; $^{1}$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 4.29 (d, $J$=5.3, 1H), 4.15 – 4.08 (m, 4H), 2.89 – 2.79 (m, 6H), 2.74 (dd, $J$=16.5, 5.7, 1H), 2.55 (dd, $J$=12.4, 6.4, 1H), 2.48 (dd, $J$=16.5, 7.3, 1H), 2.11 – 2.02 (m, 1H), 1.89 – 1.77 (m, 1H), 1.33 – 1.16 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 172.0 (2C), 60.6 (2C), 51.1 (2C), 39.8, 36.0 (2C), 29.9, 25.9, 14.2 (2C); EI-MS: $m/z$ = 306 (36), 261 (43) 218 (47), 145 874), 119 (100); HRMS calcd for $C_{13}H_{22}O_4S_2$: 306.0960; found: 306.0955.

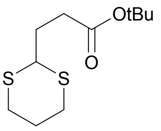


**5g**: colorless oil, 90% yield; $^{1}$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 3.99 (dd, $J$=8.0, 6.9, 1H), 3.68 (s, 3H), 3.64 (s, 3H), 3.18 – 3.08 (m, 1H), 2.86 – 2.75 (m, 4H), 2.68 (dd, $J$=16.5, 8.2, 1H), 2.54 (dd, $J$=16.5, 5.7, 1H), 2.19 (ddd, $J$=14.4, 7.7, 6.9, 1H), 2.05 (m, 1H), 1.89 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 174.2, 171.6, 52.1, 51.8, 44.4, 38.4, 36.7, 35.6, 29.7, 29.6, 25.7; HRMS calcd for $C_{11}H_{18}O_4S_2$: 278.0647; found:

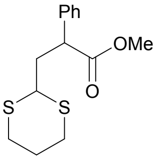
278.0639.



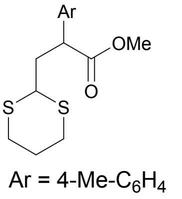
**5h**: yellowish oil, 79% yield; $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 7.29 – 7.11 (m, 5H), 4.12 (d, *J*=8.7, 1H), 3.56 (s, 3H), 3.24 (dd, *J*=13.4, 4.2, 1H), 3.12 (m, 1H), 2.97 – 2.87 (m, 3H), 2.86 – 2.73 (m, 2H), 2.17 – 2.01 (m, 1H), 2.00 – 1.86 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 172.6, 138.6, 128.8 (2C), 128.4 (2C), 126.5, 52.6, 51.7, 47.6, 36.4, 29.7, 28.9, 25.6; EI-MS: *m/z* = 282 (42), 191 (35), 159 (29), 119 (100), 91 (87); HRMS calcd for $C_{14}H_{18}O_2S_2$: 282.0748; found: 282.0741.



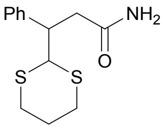
**5i**: colorless oil, 39% yield; $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 4.03 (t, *J*=7.0, 1H), 2.88 – 2.73 (m, 4H), 2.43 (dd, *J*=8.0, 7.1, 2H), 2.11 – 1.97 (m, 3H), 1.92 – 1.81 (m, 1H), 1.43 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 172.8, 77.2, 46.4, 32.5, 30.5, 29.9 (2C), 28.1 (3C), 25.8; HRMS calcd for $C_{11}H_{20}O_2S_2$: 248.0905; found: 248.0901.



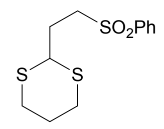
**5j**: yellowish oil; 90% yield; $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 7.36 – 7.21 (m, 5H), 3.96 (t, *J*=7.6, 1H), 3.75 (dd, *J*=8.7, 6.3, 1H), 3.64 (s, 3H), 2.87 – 2.73 (m, 4H), 2.55 (ddd, *J*=14.2, 8.7, 7.6, 1H), 2.21 (ddd, *J*=14.2, 8.0, 7.6, 1H), 2.05 (m, 1H), 1.86 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 173.6, 137.9, 128.8 (2C), 128.0 (2C), 127.5, 52.1, 48.1, 44.3, 38.4, 29.6, 29.4, 25.8; ESI-MS: *m/z* = 251.0 [M-OMe]$^+$, 283.0 [M+H]$^+$, 305.0 [M+Na]$^+$; HRMS calcd for $C_{14}H_{18}O_2S_2$: 282.0748; found: 282.0741.



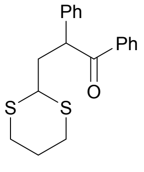
**5k**: yellowish oil, 88% yield; $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ =7.21 – 7.15 (m, 2H), 7.15 – 7.09 (m, 2H), 3.92 (t, *J*=7.6, 1H), 3.75 (dd, *J*=8.7, 6.2, 1H), 3.64 (s, 3H), 2.90 – 2.65 (m, 4H), 2.52 (ddd, *J*=14.1, 8.7, 7.1, 1H), 2.19 (ddd, *J*=14.1, 8.1, 6.2, 1H), 2.31 (s, 3H), 2.12 – 1.97 (m, 1H), 1.94 – 1.78 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 173.7, 137.2, 134.9, 129.5 (2C), 127.8 (2C), 52.1, 47.7, 44.3, 38.4, 29.6, 29.3, 25.8, 21.0; HRMS calcd for $C_{15}H_{20}O_2S_2$: 296.0905; found: 296.0899.



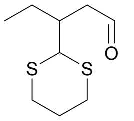
**5l**: sticky solid, 45% yield; $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 7.31 – 7.15 (m, 5H), 5.32 (bs, 1H), 5.24 (bs, 1H), 4.27 (d, *J*=8.4, 1H), 3.24 (dd, *J*=13.5, 4.8, 1H), 2.99 – 2.82 (m, 5H), 2.68 (ddd, *J*=13.5, 8.5, 4.7, 1H), 2.18 – 2.07 (m, 1H), 1.97 – 1.82 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 173.2, 138.8, 129.0 (2C), 128.6 (2C), 126.6, 54.0, 48.3, 36.3, 30.3, 29.7, 25.8; HRMS calcd for $C_{13}H_{17}NOS_2$: 267.0752; found: 267.0745.



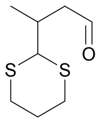
**5m**: sticky solid, 75% yield; $^{1}$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 7.94 – 7.86 (m, 2H), 7.71 – 7.61 (m, 1H), 7.61 – 7.52 (m, 2H), 4.00 (t, $J$=7.0, 1H), 3.37 – 3.21 (m, 2H), 2.90 – 2.72 (m, 4H), 2.28 – 2.12 (m, 2H), 2.14 – 1.97 (m, 1H), 1.91 – 1.74 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 138.8, 133.8, 129.4 (2C), 128.0 (2C), 53.3, 44.9, 29.5 (2C), 28.4, 25.5; EI-MS: $m/z$ = 288 (64), 146 (100), 119 (76), 77 (87); HRMS calcd for $C_{12}H_{16}O_2S_3$: 288.0312; found: 288.0306.



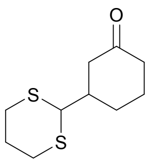
**5n**: colorless oil, 85% yield; $^{1}$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 8.18 – 7.88 (m, 2H), 7.63 – 6.99 (m, 8H), 4.98 (t, $J$=7.2, 1H), 3.83 (dd, $J$=8.2, 6.9, 1H), 2.97 – 2.57 (m, 5H), 2.24 (dt, $J$=14.1, 7.2, 1H), 2.13 – 1.94 (m, 1H), 1.94 – 1.74 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 198.6, 138.4, 136.4, 132.9, 129.0 (2C), 128.8 (2C), 128.5 (2C), 128.3 (2C), 127.3, 50.0, 44.7, 38.8, 29.6, 29.5, 25.9; ESI-MS: $m/z$ = 329.2 [M+H]$^+$, 351.0 [M+Na]$^+$; HRMS calcd for $C_{19}H_{20}OS_2$: 328.0956; found: 328.0947.



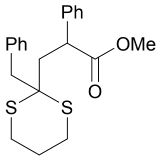
**5o**: colorless oil, 76% yield; $^{1}$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 9.72 (s, 1H), 4.13 (d, $J$=4.4, 1H), 2.88 – 2.66 (m, 4H), 2.40 (dd, $J$=17.6, 7.0, 1H), 2.35 – 2.21 (m, 1H), 2.12 – 1.93 (m, 1H), 1.86 – 1.70 (m, 1H), 1.69 – 1.52 (m, 1H), 1.52 – 1.44 (m, 1H), 1.43 – 1.29 (m, 1H), 0.86 (t, $J$=7.5, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 201.1, 52.0, 45.6, 39.5, 30.5, 30.4, 26.0, 24.7, 11.6; HRMS calcd for $C_9H_{16}OS_2$: 204.0643; found: 204.0638.



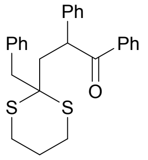
**5p**: colorless oil, 93% yield; $^{1}$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 9.75 (t, $J$=1.5, 1H), 4.08 (d, $J$=4.9, 1H), 2.87 – 2.82 (m, 4H), 2.80 (d, $J$=4.9, 1H), 2.63 – 2.50 (m, 1H), 2.44 (ddd, $J$=17.2, 8.0, 1.9, 1H), 2.17 – 2.00 (m, 1H), 1.93 – 1.71 (m, 1H), 1.13 (d, $J$=6.8, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 200.9, 53.9, 48.0, 33.1, 30.5, 30.3, 26.0, 17.8; HRMS calcd for $C_8H_{14}OS_2$: 190.0486; found: 150.0481.



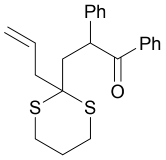
**5q**: colorless oil, 85% yield; $^{1}$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 4.07 (d, $J$=5.0, 1H), 2.97 – 2.75 (m, 4H), 2.54 (ddt, $J$=14.2, 4.2, 2.0, 1H), 2.48 – 2.32 (m, 2H), 2.30 – 2.03 (m, 5H), 1.92 – 1.76 (m, 1H), 1.74 – 1.51 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 210.4, 53.5, 45.2, 43.5, 41.1, 30.7, 30.7, 28.4, 26.1, 24.8; HRMS calcd for $C_{10}H_{16}OS_2$: 216.0643; found: 216.0638.



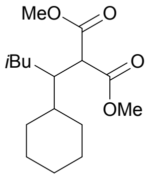
**5r**: The product was obtained using general procedure with **4b** instead of **4a**; yellowish oil, 89% yield; $^{1}$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 7.49 – 6.93 (m, 10H), 3.98 (dd, *J*=9.1, 2.4, 1H), 3.63 (s, 3H), 3.24 (dd, *J*=14.5, 8.7, 1H), 3.19 (d, *J*=12.8, 1H), 3.14 (d, *J*=14.2, 1H), 2.99 (ddd, *J*=14.5, 10.3, 2.9, 1H), 2.87 (ddd, *J*=14.2, 10.2, 3.0, 1H), 2.77 – 2.63 (m, 2H), 2.06 (dd, *J*=15.0, 2.4, 1H), 1.98 (m, 1H), 1.83 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 174.5, 139.8, 135.1, 131.0 (2C), 128.7 (2C), 127.9 (2C), 127.8 (2C), 127.2, 127.0, 53.2, 52.3, 48.2, 45.9, 41.6, 26.9, 26.2, 24.4; HRMS calcd for $C_{21}H_{24}O_2S_2$: 372.1218; found: 372.1210.



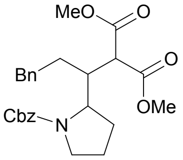
**5s**: The product was obtained using general procedure with **4b** instead of **4a**; colorless oil, 87% yield; $^1$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 8.03 – 7.91 (m, 2H), 7.57 – 7.43 (m, 1H), 7.41 – 7.34 (dd, *J*=8.3, 6.8, 2H), 7.31 – 7.20 (m, 9H), 7.17 – 7.10 (m, 1H), 5.03 (dd, *J*=9.1, 1.7, 1H), 3.61 (dd, *J*=14.9, 9.1, 1H), 3.32 (d, *J*=14.0, 1H), 3.29 (d, *J*=14.0, 1H), 3.02 – 2.82 (m, 2H), 2.87 (ddd, *J*=14.4, 6.9, 3.1, 1H), 2.63 (ddd, *J*=14.4, 6.8, 3.2, 1H), 2.10 (dd, *J*=14.9, 1.7, 1H), 2.02 – 1.87 (m, 1H), 1.9 – 1.78 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 198.7, 139.7, 137.1, 135.4, 132.5, 131.1 (2C), 128.9 (2C), 128.8 (2C), 128.4 (2C), 128.3 (2C), 127.9 (2C), 127.0, 126.9, 53.6, 49.8, 46.8, 42.2, 26.9, 26.3, 24.5; HRMS calcd for $C_{26}H_{26}OS_2$: 418.1425; found: 418.1416.



**5t**: The product was obtained using general procedure with **4c** instead of **4a**; yellowish oil, 86% yield; $^1$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 8.03 – 7.93 (m, 2H), 7.51 – 7.43 (m, 1H), 7.42 – 7.34 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.20 (m, 2H), 7.20 – 7.11 (m, 1H), 5.97 – 5.79 (m, 1H), 5.18 – 5.12 (m, 1H), 5.12 – 5.07 (m, 1H), 4.99 (dd, *J*=8.9, 1.9, 1H), 3.54 (dd, *J*=14.9, 8.9, 1H), 2.87-2.81 (m, 2H), 2.78 – 2.67 (m, 1H), 2.67 – 2.55 (m, 3H), 2.10 (dd, *J*=14.9, 1.9, 1H), 1.96-1.93 (m, 1H), 1.91 – 1.78 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 198.6, 140.0, 137.1, 132.6, 132.4, 129.0 (2C), 128.7 (2C), 128.4 (2C), 128.2 (2C), 127.0, 118.8, 52.6, 49.7, 44.3, 42.2, 26.5, 26.0, 24.7; HRMS calcd for $C_{22}H_{24}OS_2$: 368.1269; found: 368.1260.



**14**: The product was obtained using general procedure with cyclohexylcarboxylic acid instead of **4a** and catalyst **1** replaced **2**; colorless oil, 46% yield; $^1$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 3.69 (d, *J*=5.9, 6H), 3.45 (d, *J*=7.5, 1H), 2.14 – 2.07 (m, 1H), 1.76 – 1.56 (m, 5H), 1.38 – 1.25 (m, 3H), 1.21 – 1.01 (m, 6H), 0.85 (d, *J*=4.0, 3H), 0.83 (d, *J*=4.0, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ =170.0, 169.9, 54.4, 52.3, 52.1, 41.7, 40.7, 38.2, 30.5, 29.20, 26.9, 26.8, 26.6, 26.5, 22.8, 22.6.

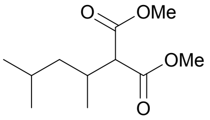


**16**: The product was obtained using general procedure with *rac*-Cbz-proline instead of **4a**; sticky solid, 87% yield; The molecules present different diastereoisomer and different conformers, NMR signal appears very broad and some $^{13}$C NMR signals were missed. $^1$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 7.56 – 6.76 (m, 10H), 5.11 (bs, 2H), 4.22 – 3.91 (m, 1H), 3.75 – 3.50 (m, 9H), 3.19 (m, 1H), 3.09 (dq, *J*=8.5, 4.3, 1H), 2.80 – 2.37 (m, 3H), 2.07 – 1.90 (m, 1H), 1.90 – 1.59 (m, 3H); $^{13}$CNMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 169.2, 155.6, 141.8, 136.6, 128.4 (2C), 128.3 (2C) 128.2 (2C), 128.1, (2C), 127.9 (2C), 125.8, 66.8, 60.3, 58.7, 52.3, 48.2, 46.9, 40.6, 31.9, 29.7, 27.0; ESI-MS: *m/z* = 454.2 $[M+H]^+$, 476.2 $[M+Na]^+$.

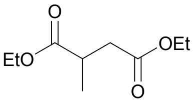
**Reductive removal of the dithiane moiety**

**General Procedure**: To a solution of **5a** (0.1 mmol, 0.032 g) in methanol (2 mL), Ni-Raney (0.450 g, slurry in water) was added and the reaction was keep under $H_2$ atmosphere (1 atm). After 3h the reaction mixture was filtered through a Celite® pad washed with DCM and the organic solvent was removed under reduce pressure. The residue was diluted with ethyl acetate (10 mL), the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2 x 5 mL). The collected organic layers were washed with brine (5 mL), dried over $Na_2SO_4$ and concentrated under reduce pressure.

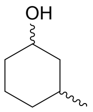
Flash chromatography (cyclohexane:diethyl ether, 95:5) of the residue give **6** in 91% yield (0.091 mmol, 0.02 g).



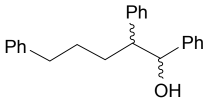
**6**: yellowish oil, 90% yield; $^1$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 3.71 (s, 6H), 3.22 (d, *J*=7.8, 1H), 2.35 – 2.24 (m, 1H), 1.61 (m, 1H), 1.15 – 1.05 (m, 2H), 0.94 (d, *J*=6.7, 3H), 0.87 (d, *J*=6.5, 3H), 0.85 (d, *J*=6.5, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 169.3 (2C), 57.8, 52.2, 52.1, 31.4, 29.7, 25.2, 23.7, 21.3, 16.9; EI-MS: *m/z* = 201 (6, M-Me), 185 (10, M-OMe), 132 (100), 100 (56), 83 (45), 69 (50); HRMS calcd for $C_{11}H_{20}O_4$: 216.1362; found: 216.1351.



**7**: yellowish oil, 84% yield; Spectral proprieties were in according with literature.[9] $^1$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta$ = 4.24 – 4.04 (m, 4H), 2.95 – 2.81 (m, 1H), 2.70 (dd, *J*=16.4, 8.1, 1H), 2.37 (dd, *J*=16.4, 6.1, 1H), 1.26 – 1.21 (m, 6H), 1.20 (d, *J*=7.1, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta$ = 175.2, 171.8, 60.5, 60.4, 37.7, 35.8, 16.9, 14.1, 14.0.

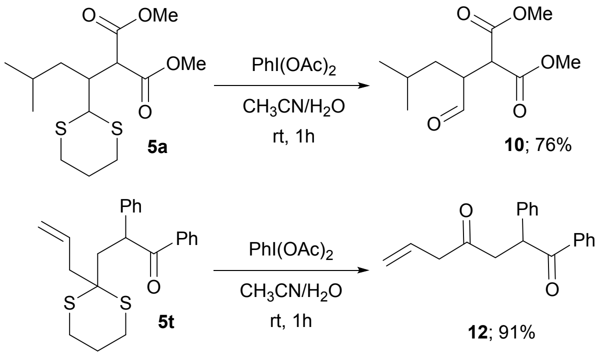


**8**: yellowish oil, 88% yield; Spectral proprieties were in according with literature.[10]

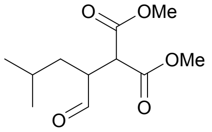


**9**: yellowish oil, 90% yield; $^{1}$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 7.38 - 7.23$ (m, 4H), 7.27 – 7.09 (m, 6H), 7.13 – 7.02 (m, 3H), 7.05 – 6.91 (m, 2H), 4.68 (d, $J$=8.4, 1H), 2.97 – 2.80 (m, 1H), 2.47 (ddd, $J$=14.5, 8.6, 6.4, 1H), 2.34 (ddd, $J$=14.5, 8.8, 6.9, 1H), 1.67 – 1.53 (m, 1H), 1.49 – 1.24 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C): $\delta = 142.7$, 142.2, 141.1, 128.8 (2C), 128.6 (2C), 128.3 (2C), 128.2 (2C), 128.1 (2C), 127.8, 127.0, 126.9 (2C), 126.4, 125.5, 78.8, 54.2, 35.6, 29.1; ESI-MS: $m/z = 317.1$ $[M+H]^+$, 339.2 $[M+Na]^+$; HRMS calcd for $C_{23}H_{24}O$: 316.1827; found: 316.1821.

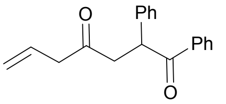
**Hydrolysis of the dithiane moiety**



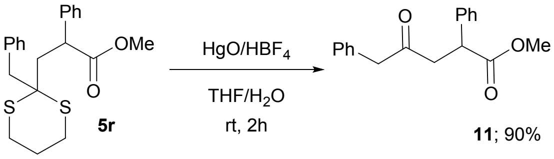
**PhI(OAc)$_2$ method**:[11] Bis(trifluoroacetoxy)iodobenzene (52 mg, 0.16 mmol) was added at 0°C to a stirred solution of **5a** or **5t** (0.1 mmol), water (1 mL) and $CH_3CN$ (9 mL). After it was stirred at room temperature for 30 min, the reaction was quenched with $NaHCO_3$ sat. sln. (10 ml) and the volatiles were evaporated. The residue was dissolved in ethyl acetate (20 mL) and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The collected organic layers were washed with brine (10 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure to give the crude product. Column chromatography on silica (cyclohexane:ethyl acetate from 95:5 to 80:20) afforded pure products.



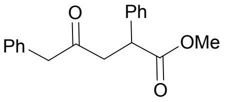
**10**: yellowish oil, 76% yield; $^{1}$H NMR (400 MHz, $CDCl_3$, 25°C): $\delta = 9.77$ (d, $J$=1.2, 1H), 3.75 (s, 3H), 3.73 (d, $J$=7.8, 1H), 3.72 (s, 3H), 3.17 – 3.01 (m, 1H), 1.62 – 1.64 (m, 1H), 1.37 – 1.20 (m, 2H), 0.94 (d, $J$=6.3, 3H), 0.91 (d, $J$=6.2, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$, 25°C): $\delta = 198.0$, 168.5 (2C), 52.8, 52.1, 48.3, 36.5, 29.7, 25.9, 22.9, 22.1; HRMS calcd for $C_{11}H_{18}O_5$: 230.1154; found: 230.1149.



**12**: yellowish oil, 91% yield; $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 8.08 – 7.76 (m, 2H), 7.47 – 7.42 (m, 1H), 7.39 – 7.31 (m, 2H), 7.30 – 7.21 (m, 4H), 7.21 – 7.15 (m, 1H), 5.89 (m, 1H), 5.16 (m, 2H), 5.13 – 5.06 (m, 1H), 3.59 (dd, *J*=18.0, 10.0, 1H), 3.27 – 3.13 (m, 2H), 2.76 (dd, *J*=18.0, 4.0, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 206.7, 198.8, 138.5, 136.3, 132.9, 130.2, 129.1 (2C), 128.9 (2C), 128.4 (2C), 128.1 (2C), 127.3, 119.0, 48.7, 47.7, 46.8; ESI-MS: *m/z* = 279.0 [M+H]$^+$, 301.0 [M+Na]$^+$; HRMS calcd for $C_{19}H_{18}O_2$: 278.1307; found: 278.1302.

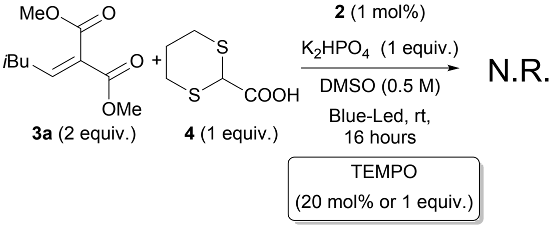


**HgO/HBF$_4$ method:** To a suspension of HgO (0.18 mmol, 0.039 g) in HBF$_4$ (48% in water, 0.2 mL) and THF (1 mL) a solution of **5r** (0.09 mmol, 0.034 g) in THF (1 mL) was added. After 2 hours the reaction was quenched adding 10 mL of NaHCO$_3$ sat. sln. until basic pH. The mixture was filtered through a Celite® pad washing with ethyl acetate. Water (10 mL) was added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The collected organic layers were washed with brine (10 mL), dried over Na$_2$SO$_4$ and concentrated under reduced pressure to give the crude product. Column chromatography on silica (cyclohexane:ethyl acetate from 95:5 to 90:10) afforded pure product **11** (90%, 0.08 mmol, 0.021 g) as yellowish oil.



**11**: $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 7.49 – 6.86 (m, 10H), 4.07 (dd, *J*=10.2, 4.5, 1H), 3.70 (s, 2H), 3.62 (s, 3H), 3.36 (dd, *J*=18.0, 10.2, 1H), 2.71 (dd, *J*=18.0, 4.5, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 205.9, 173.6, 138.0, 133.7, 129.4 (2C), 128.8 (2C), 128.7 (2C), 127.7 (2C), 127.5, 127.1, 52.3, 50.1, 46.2, 45.5; HRMS calcd for $C_{18}H_{18}O_3$: 282.1256; found: 282.1251.

## Reaction in presence of TEMPO



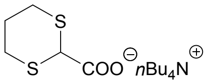
Evidence of a possible radical mechanism was determinate by performing the reaction in the presence of radical scavengers like TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl).

Two different experiments were conducted in the presence of a catalytic (20 mol%) and stoichiometric amount of TEMPO. In both cases no formation of product or adduct between TEMPO and reaction intermediates were observed.

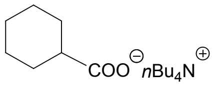
## Preparation of ammonium salts 17, 18, 19

$$\mathrm{R{-}COOH} \xrightarrow[\mathrm{H_2O}]{n\mathrm{Bu_4N^{\oplus}}\ {}^{\ominus}\mathrm{OH}} \mathrm{R{-}COO^{\ominus}}\ n\mathrm{Bu_4N^{\oplus}}$$

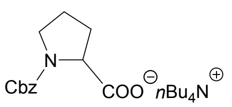
**General procedure:**[12] To a solution of **4a** (0.3 mmol, 0.05g) in water (5 mL) *n*Bu$_4$NOH*30H$_2$O (0.3 mmol, 0.240 g) was added and the reaction mixture was heated at 60°C for 2 hours. Water was evaporated under reduced pressure and the residue was dried under high vacuum for 2 hours to give pure **17** (96%, 0,29 mmol, 0.117 g) as white solid.



**17**: sticky solid, quantitative; $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 4.70 (s, 1H), 3.45 – 3.23 (m, 8H), 2.99 (ddd, $J$=14.0, 6.3, 3.0, 2H), 2.75 (ddd, $J$=13.7, 10.5, 2.7, 2H), 2.08 – 1.94 (m, 1H), 1.90 – 1.76 (m, 1H), 1.68 – 1.55 (m, 8H), 1.53 – 1.33 (m, 8H), 0.99 (t, $J$=7.3, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 170.6, 58.5 (4C), 52.9, 30.2 (2C), 26.2, 23.9 (4C), 19.6 (4C), 13.6 (4C).

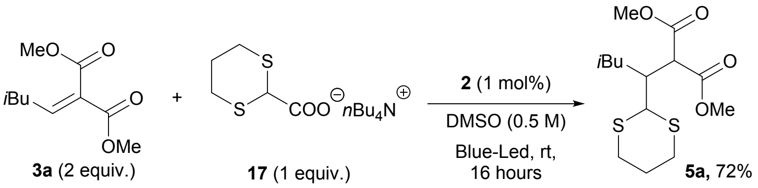


**18**: sticky solid, quantitative; $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 3.46 – 3.17 (m, 8H), 2.90 (bs, 1H), 2.11 – 2.00 (m, 1H), 1.95 – 1.85 (m, 2H), 1.77 – 1.54 (m, 10H), 1.51 – 1.30 (m, 10H), 1.31 – 1.10 (m, 3H), 0.97 (t, $J$=7.3, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ = 58.9 (4C), 48.0, 31.0 (2C), 26.6 (2C), 24.2 (4C), 19.9, 19.8 (4C), 13.7 (4C), carboxylic carbon was not detected also using long acquisition time with 4s delay.



**19**: sticky solid, quantitative; The compound is present as two different conformers (A and B). $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ = 7.42 – 7.01 (m, 10H, A+B), 5.20 (d, *J*=13.2, 1H), 5.11 (d, *J*=12.7, 1H, B), 4.99 (d, *J*=13.0, 1H, B), 4.27 (t, *J*=5.9, 1H, A), 4.15 (dd, *J*=7.8, 3.1, 2H, A), 3.74 – 3.58 (m, 2H, B), 3.42 (td, *J*=17.5, 8.1, 2H, A), 3.35 – 3.16 (m, 8H, A+B), 2.26 – 2.00 (m, 2H, A+B), 1.81 – 1.67 (m, 2H, A+B), 1.68 – 1.54 (m, 8H, A+B), 1.47 – 1.27 (m, 8H, A+B), 0.96 (t, *J*=7.3, 12H, A+B); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C): $\delta$ =171.2 (A), 171.1 (B), 154.7 (A+B), 128.4 (B, 2C), 128.3 (A, 2C), 127.9 (A, 2C), 127.6 (B, 2C), 127.4 (A), 127.2 (B), 66.9 (A), 66.5 (B), 58.8 (A+B, 4C), 46.8 (A), 46.4 (B), 30.6 (B), 29.6 (A), 24.4 (A), 24.1 (B), 24.0 (A+B, 4C), 23.3 (A), 23.2 (B), 23.1 (C), 19.6 (A+B, 4C), 13.6 (A+B, 4C), carboxylic carbon was not detected also using long acquisition time with 4s delay.

## Photoredox radical conjugate addition of salt 17



To determinate if tetrabutylammonium salt **17** is a suitable substrate for the photoredox radical conjugate addition we tested it in the reaction using general procedure without the presence of K$_2$HPO$_4$ as base. Product **5a** was obtained in 72% of yield, demonstrating the possibility to use tetrabutylammonium carboxylate as substrate.

## Photostability of Ir(III) complex 2

In order to test its photostability during the reaction, complex **2** was dissolved in degassed deuterated DMSO and was irradiated using blue light LED for 24 hours in order to replicate the reaction conditions. Any possible photolysis was monitored by $^1$H NMR spectroscopy. As reported in Figure S1, less than 5% of complex **2** undergoes to photochemical decomposition after 24 hours of irradiation, revealing its good photostability under reaction conditions, differently from complex **1**.[13]

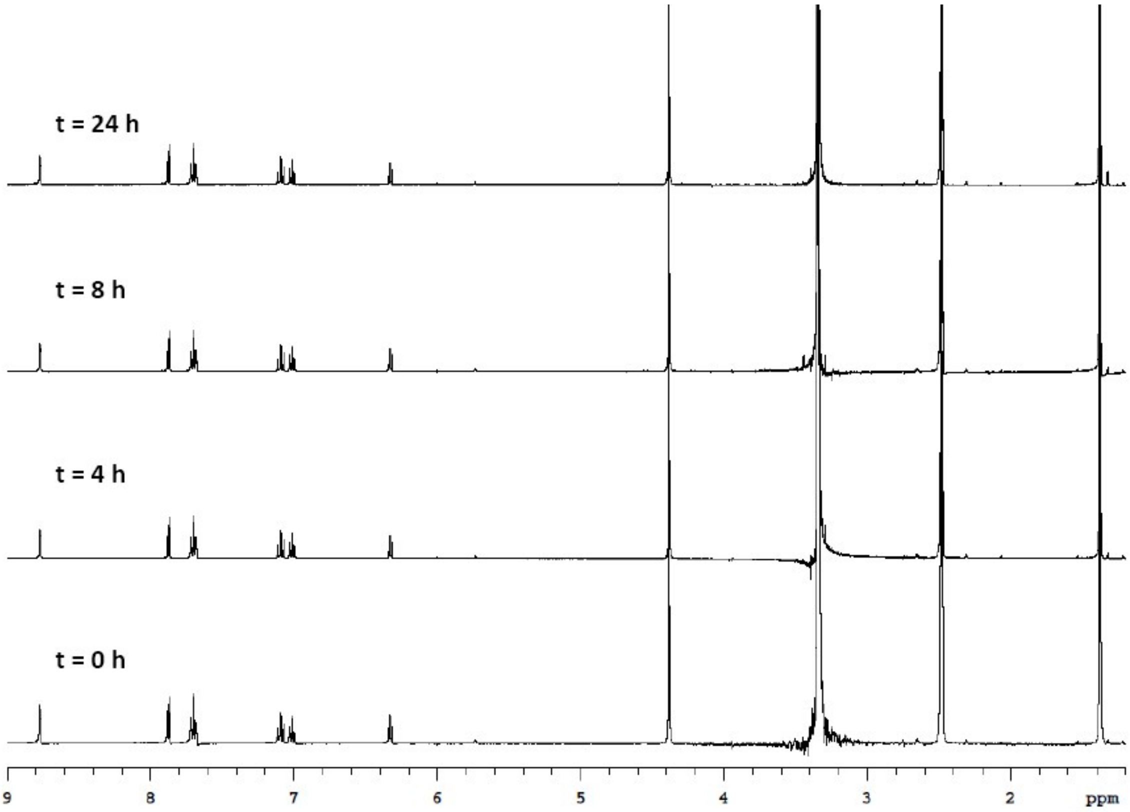


**Figure S1.** $^{1}$H NMR spectra for complex **2** in deuterated DMSO solution irradiated with blue light LED for increasing times. The solution was degassed by nitrogen gas for 15 minutes.

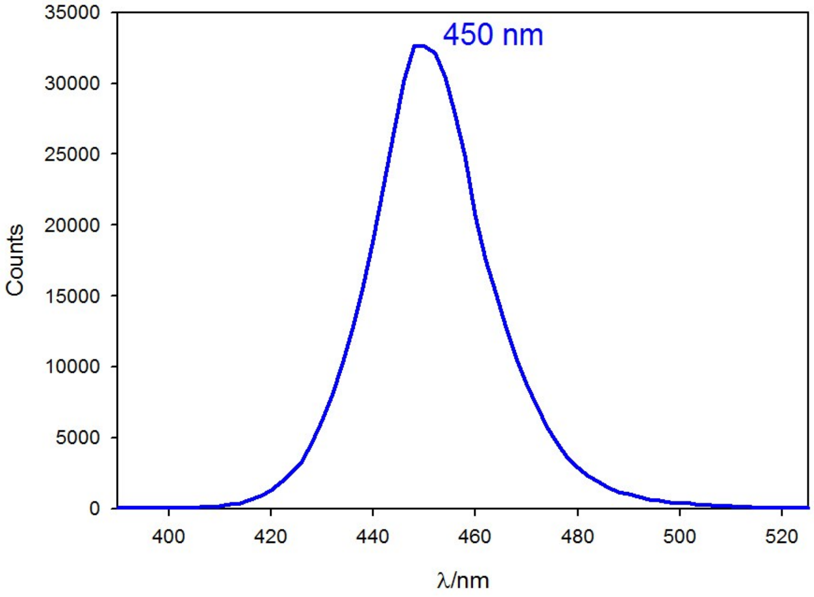


**Figure S2.** Emission profile of the 24W Blue LED strip used to irradiate the solutions.

## Photophysical and electrochemical data

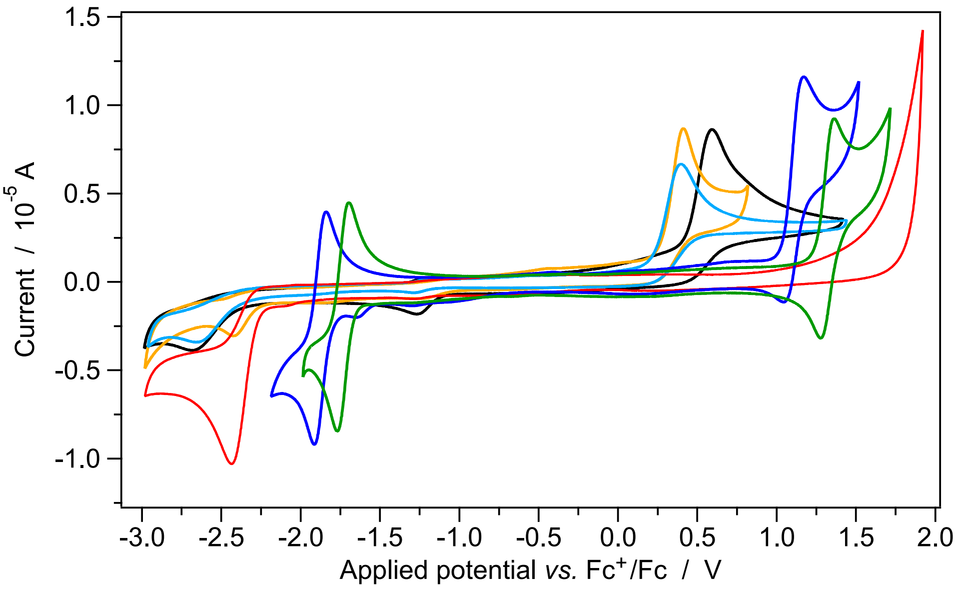


**Figure S3.** Cyclic voltammograms of the **17** (orange), **18** (black) and **19** (light blue) substrates, together with the one of the Michael acceptor **3a** (red) and of the iridium(III) photocatalysts **1** (green) and **2** (dark blue). The voltammograms are recorded at a scan rate of 200 mV $s^{-1}$ in room-temperature acetonitrile in the presence of $TBAPF_6$ 0.1 M as supporting electrolyte.

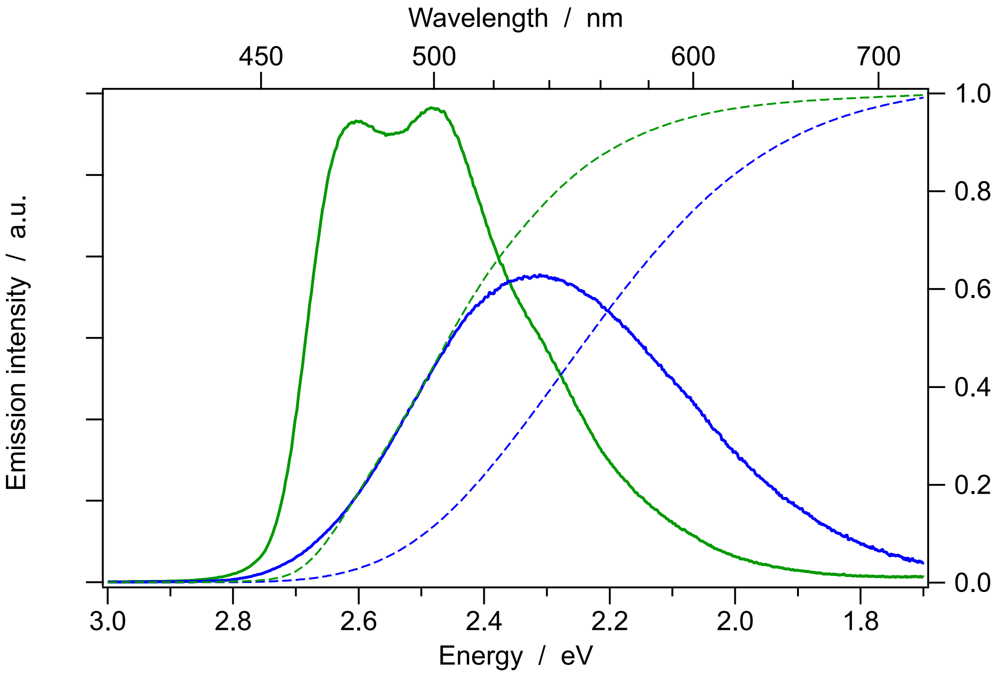


**Figure S4.** Full lines: corrected and normalized emission spectra of photocatalyst **1** (green) and **2** (dark blue) in room-temperature acetonitrile solution, reported in relative quanta per energy interval. Dashed lines: integrals of the spectra; the mean photon energy is calculated as the value at which the integral is 50%.

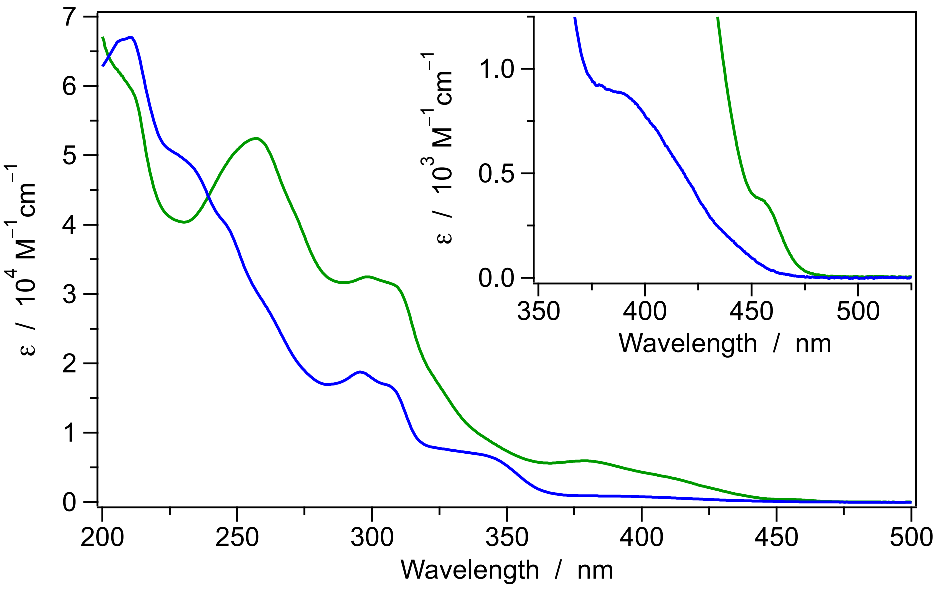


**Figure S5.** Absorption spectra of photocatalyst **1** (green) and **2** (dark blue) in room-temperature acetonitrile solution. The lowest-energy electronic transition, attributed to the direct population of the emitting state, is magnified in the inset for each of the two iridium(III) photocatalysts.

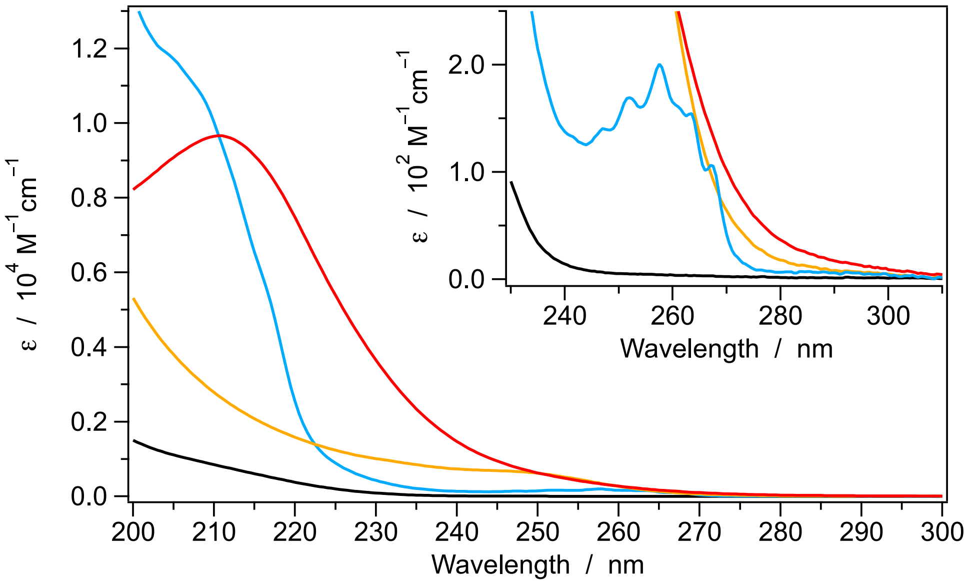
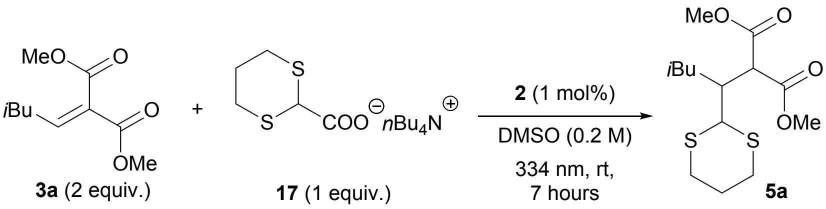


**Figure S6.** Absorption spectra of the **17** (orange), **18** (black) and **19** (light blue) substrates, together with the one of the Michael acceptor **3a** (red), in room-temperature acetonitrile solution. The lowest-energy transitions are magnified in the inset for the sake of clarity.

## Determination of quantum yield



The reaction was carried out in spectrofluorimetric grade DMSO and placed in a Suprasil® quartz cuvette with a 2.00 mm path length. The cuvette was charged with the ammonium carboxylate **17** (81 mg, 0.20 mmol, 1 equiv), the Michael acceptor **3a** (80 mg, 0.40 mmol, 2 equiv), the iridium photocatalyst **2** (1.7 mg, 0.0020 mmol), and 500 µl of DMSO. Before irradiating the sample, dissolved oxygen was removed from the cuvette by argon bubbling for 15 minutes. The reaction mixture was excited at 334 nm for exactly 7 hours, using a 100 W Hg lamp equipped with an appropriate dichroic filter. During this process, the solution was stirred and kept at constant temperature.

The photon flux coming from the lamp to the sample in the cuvette was estimated using the ferrioxalate actinometer (photon flux: 1.97 nmol/s).[14] This experimental value was also confirmed by using a calibrated silicon diode (light power: 0.6 mW, corresponding to a photon flux of 2 nmol/s at 334 nm). In our experimental conditions, all the incident light is quantitatively absorbed by the iridium photocatalyst (A > 3 at 334 nm).

The product formation was determined by $^1$H-NMR based on the relative conversion of the carboxylate derivative.

After irradiation, the estimated conversion was 7%, corresponding to 14 µmol of product formed.

$$\Phi = \frac{moles\ of\ product\ formed}{moles\ of\ photons\ absorbed} = \frac{14\ \cdot 10^{-6} mol}{1.97 \cdot 10^{-9}\frac{mol}{s}\ \cdot\ 2.5 \cdot 10^{4}\, s} =\ 0.28 \pm 0.05$$

## References

[1] E. Massolo, M. Benaglia, A. Genoni, R. Annunziata, G. Celentano and N. Gaggero, *Org. Biomol. Chem.*, 2015, **13**, 5591-5596.

[2] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal Jr., G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, **17**, 5712-5719.

[3] F. Monti, A. Baschieri, I. Gualandi, J. J. Serrano-Pérez, J. M. Junquera-Hernández, D. Tonelli, A. Mazzanti, S. Muzzioli, S. Stagni, C. Roldan-Carmona, A. Pertegás, H. J. Bolink, E. Ortí, L. Sambri and N. Armaroli, *Inorg. Chem.*, 2014, **53**, 7709-7721.

[4] M. Felici, P. Contreras-Carballada, Y. Vida, J. M. M. Smits, R. J. M. Nolte, L. De Cola, R. M. Williams, M. C. Feiters, *Chem. Eur. J.*, 2009, **15**, 13124–13134.

[5] G. Cardillo, S. Fabbroni, L. Gentilucci, M. Gianotti and A. Tolomelli, *Synth. Comm.* 2003, **33**, 1587-1594.

[6] a) G. Cardillo, L. Gentilucci, M. Gianotti, R. Perciaccante and A. Tolomelli, *J. Org. Chem.* 2001, **66**, 8657-8660; b) P. Ramesh, B. Shalini and N. W. Fadnavis, *RSC Adv.,* 2014, **4**, 7368-7373

[7] a) M. J. Lavecchia, R. Puig de la Bellacasa, J. I. Borrell and C. N. Cavasotto, *Biorg. Med. Chem.*, 2016, **24**, 768-778; b) J. Pietruszka and M. Schölzel, *Adv. Synth. Catal.*, 2012, **354**, 751-756.

[8] V. Gembus, J.-J. Bonnet, F. Janin, P. Bohn, V. Levacher and J.-F. Briere, *Org. Biomol. Chem.*, 2010, **8**, 3287-3293.

[9] Y. Chen, E. Kervio and J. Retey, *Helv. Chim. Acta*, 2002, **85**, 552-558.

[10] K. Kamata, K. Yonehara, Y. Nakagawa, K. Uehara and N. Mizuno, *Nature Chemistry* 2010, **2**, 478–483.

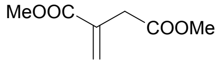
[11] Z. Meng and S. Danishefsky, *Angew. Chem. Int. Ed.*, 2005, **44**, 1511-1513.

[12] C. R. Allen, P. L. Richard, A. J. Ward, L. G. A. van de Water, A. F. Masters and T. Maschmeyer, *Tetrahedron Letters*, 2006, **47**, 7367-7370

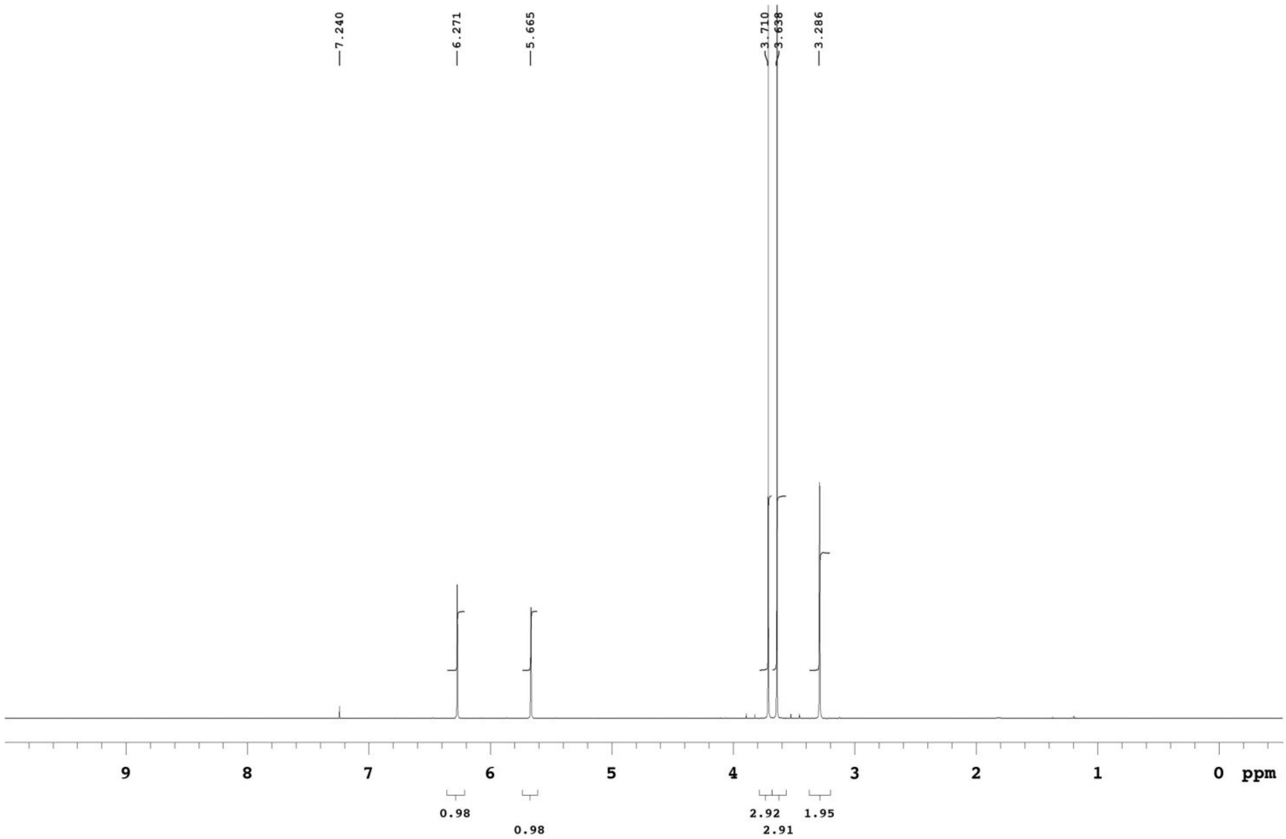
[13] C. Yang, F. Mehmood, T. L. Lam, S. L.-F. Chan, Y. Wu, C.-S. Yeung, X. Guan, K. Li, C. Y.-S. Chung, C.-Y. Zhou, T. Zou, and C.-M. Che, *Chem. Sci.* **2016**, *7*, 3123-3136.

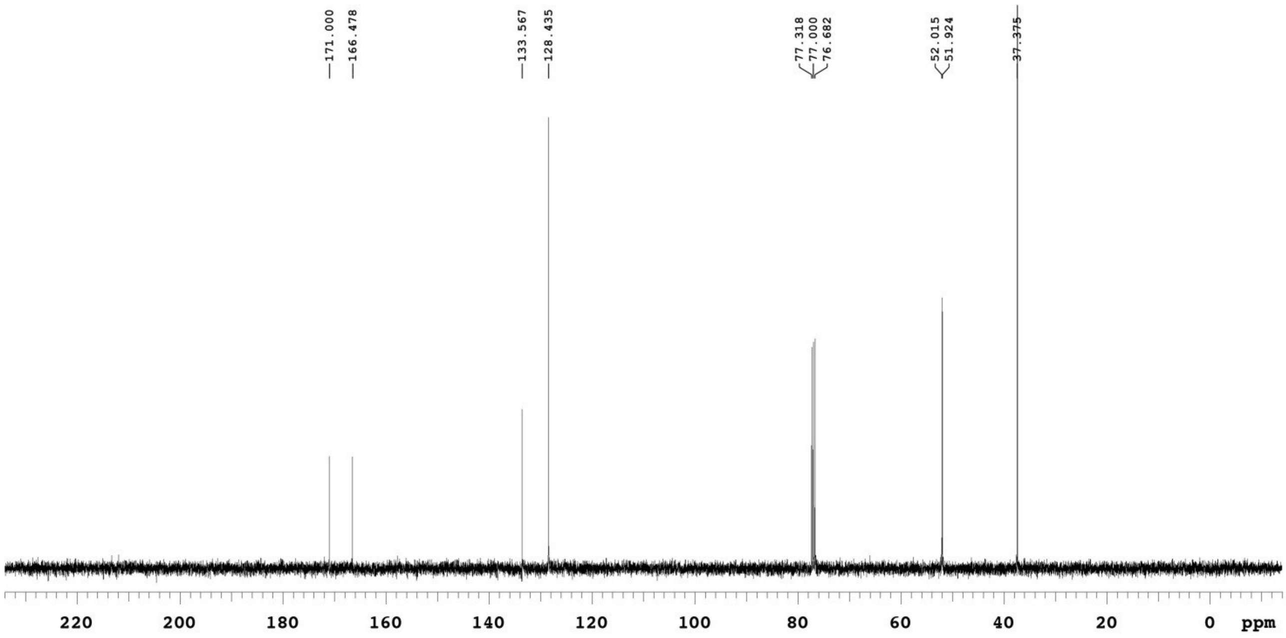
[14] M. Montalti, A. Credi, L. Prodi , and M. T. Gandolfi, Handbook of Photochemistry, Third Edition, CRC Press, 2006, chapter 12.

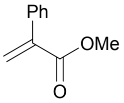
## Copies of NMR spectra



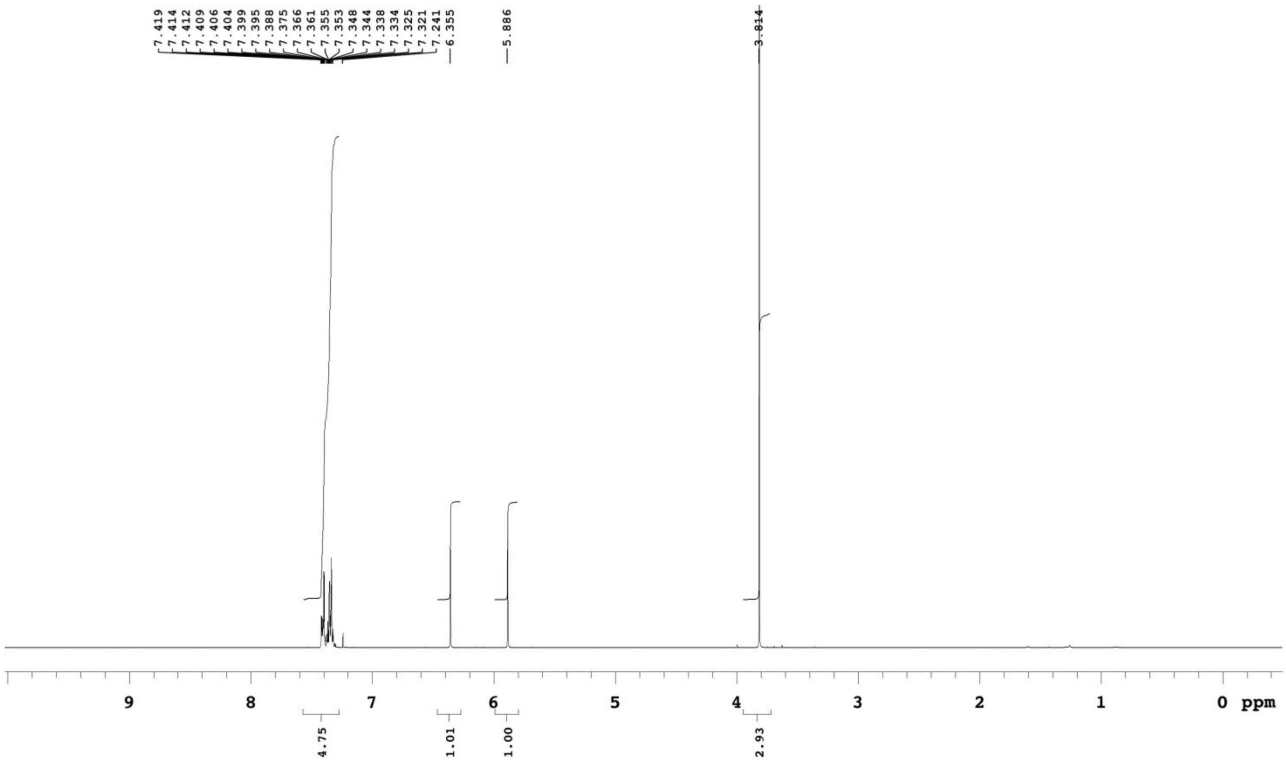
**3g**






Ph
OMe
O

**3j**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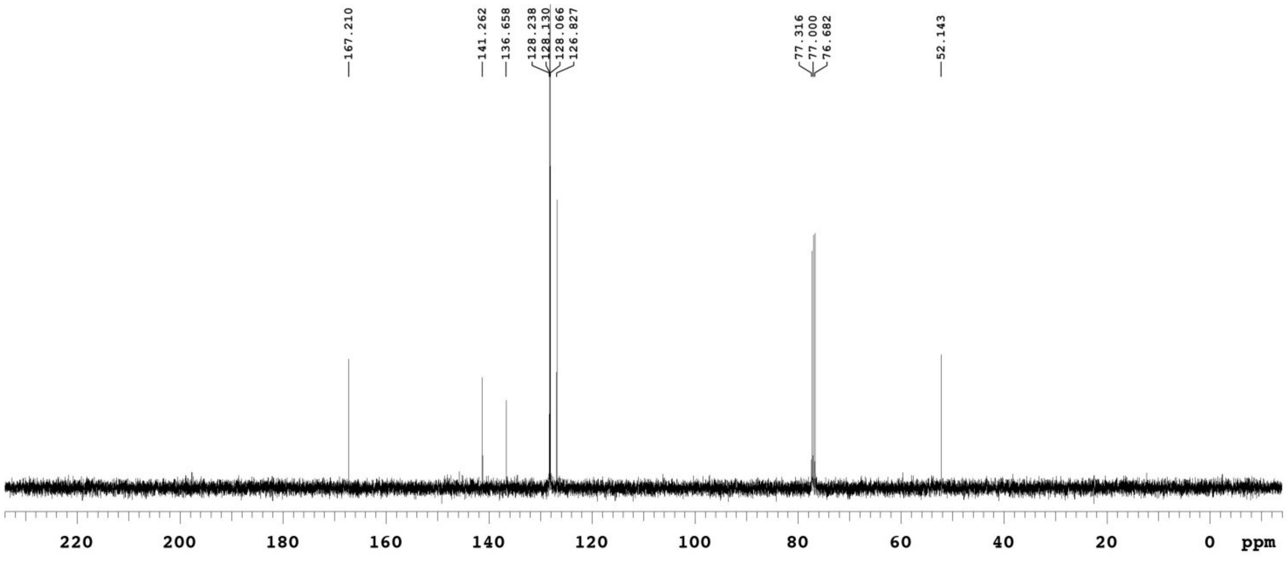
7.355
7.353
7.348
7.344
7.338
7.334
7.325
7.321
7.241
6.355
5.886
3.814
9
8
7
6
5
4
3
2
1
0 ppm
4.75
1.01
1.00
2.93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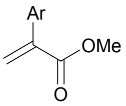
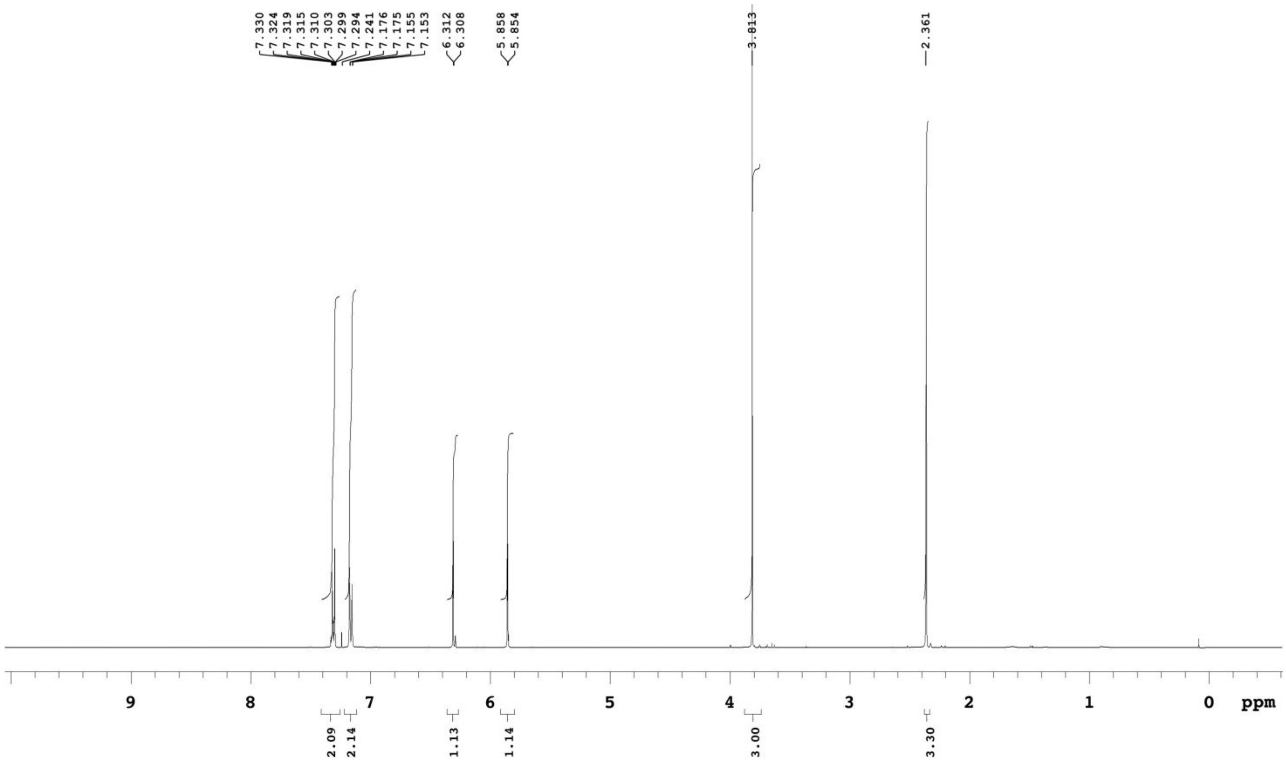
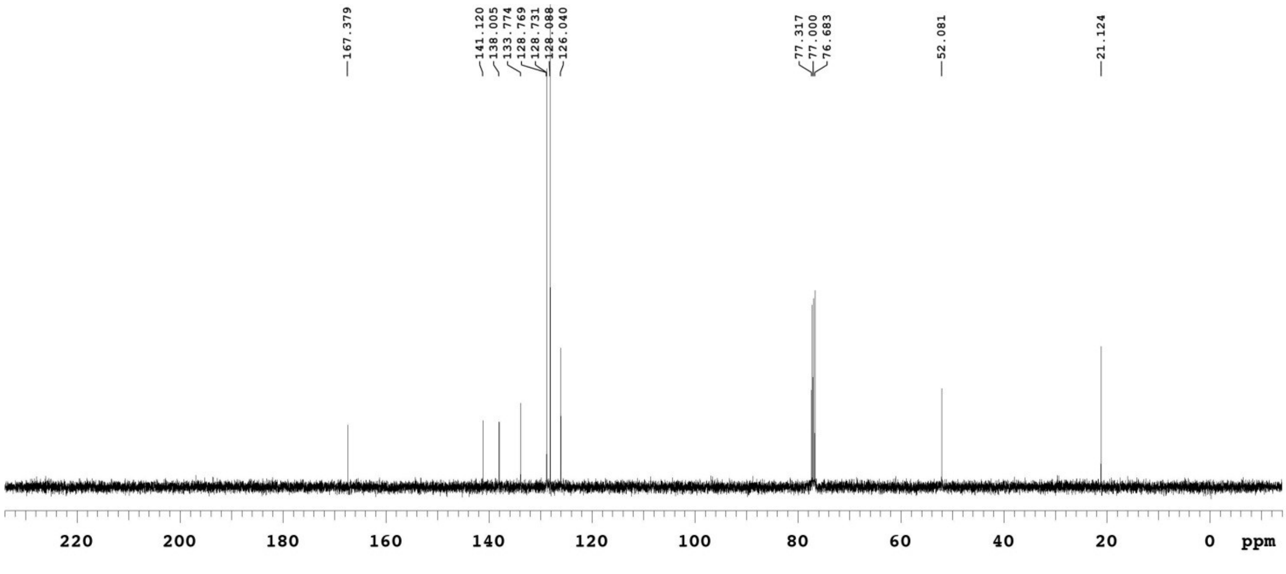
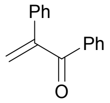
180
160
140
120
100
80
60
40
20
0 ppm



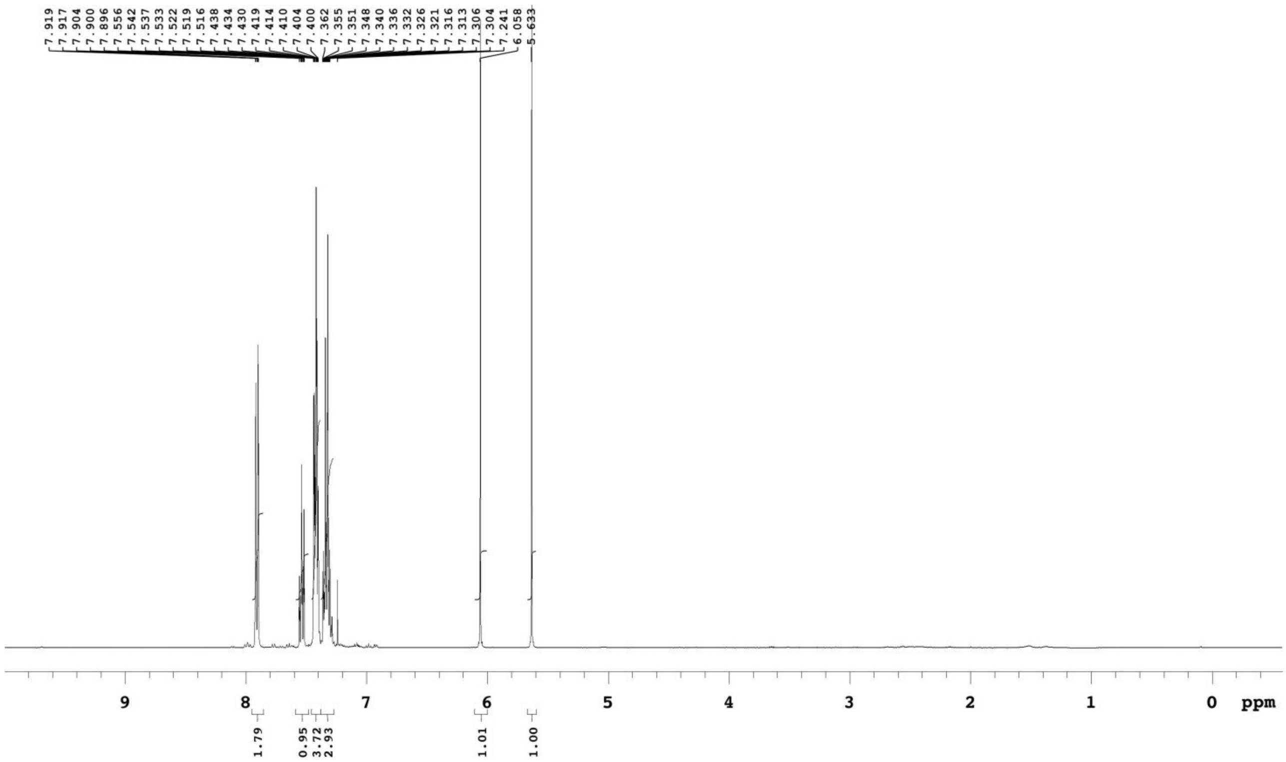
Ar = 4-Me-$C_6H_4$ **3k**






Ph
Ph
O

**3n**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7.516
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7.434
7.430
7.419
7.414
7.410
7.404
7.400
7.362
7.355
7.351
7.348
7.340
7.336
7.332
7.326
7.321
7.316
7.313
7.306
7.304
7.241
6.058
5.633
9
8
7
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5
4
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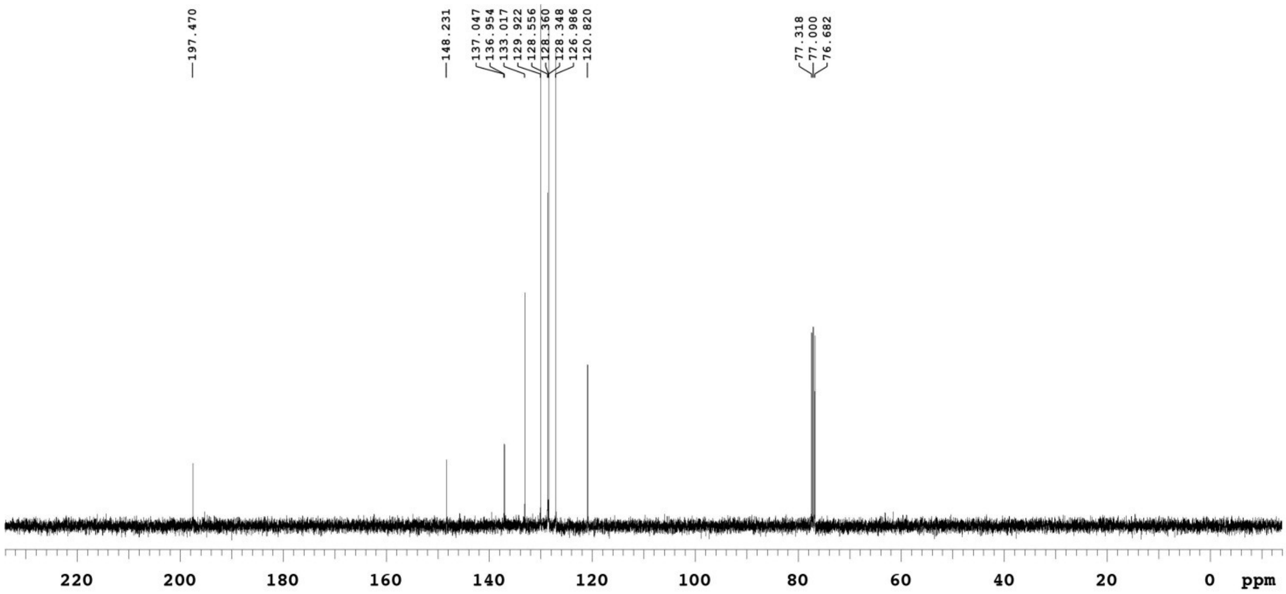
1.00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77.000
76.682
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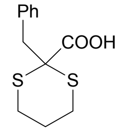
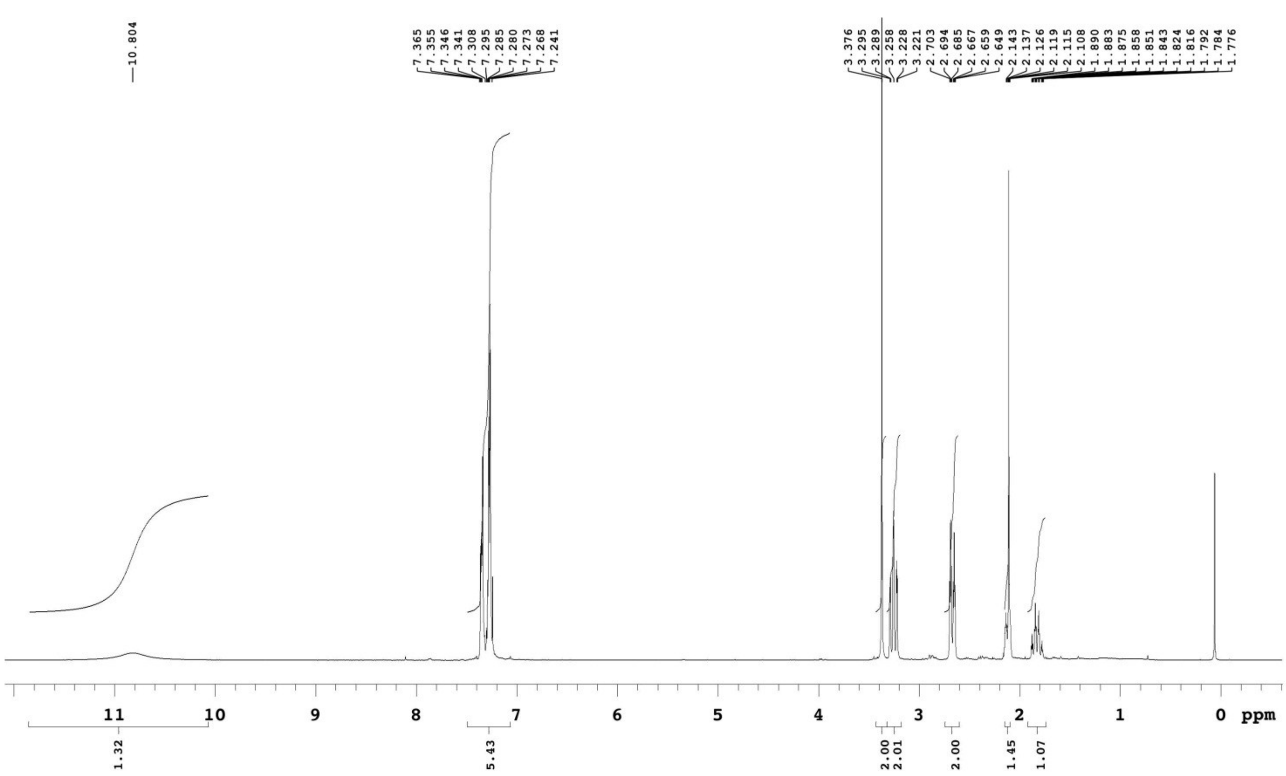
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
COOH
S
S

**4b**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7.295
7.285
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7.273
7.268
7.241
3.376
3.295
3.289
3.258
3.228
3.221
2.703
2.694
2.685
2.667
2.659
2.649
2.143
2.137
2.126
2.119
2.115
2.108
1.890
1.883
1.875
1.858
1.851
1.843
1.824
1.816
1.792
1.784
1.776
11
10
9
8
7
6
5
4
3
2
1
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2.00
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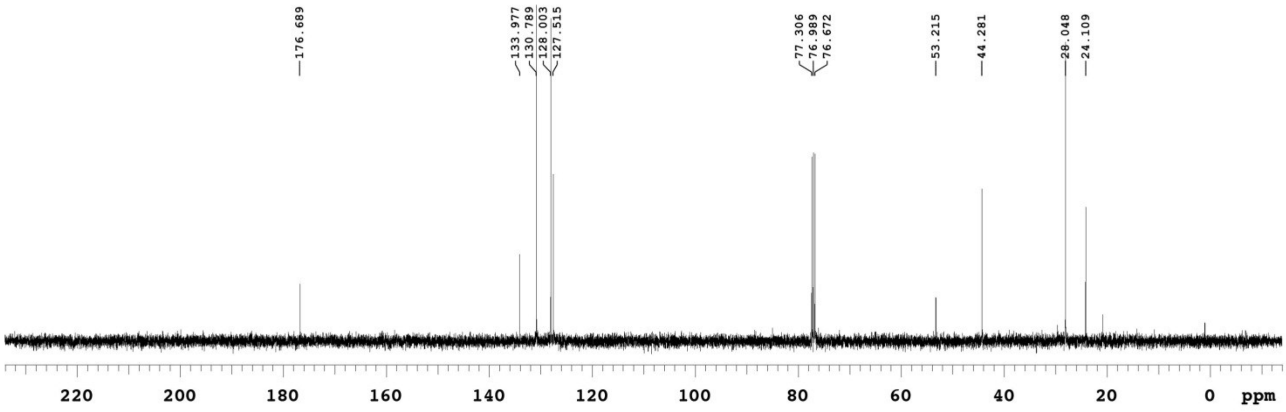
2.00
1.45
1.07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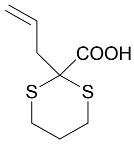
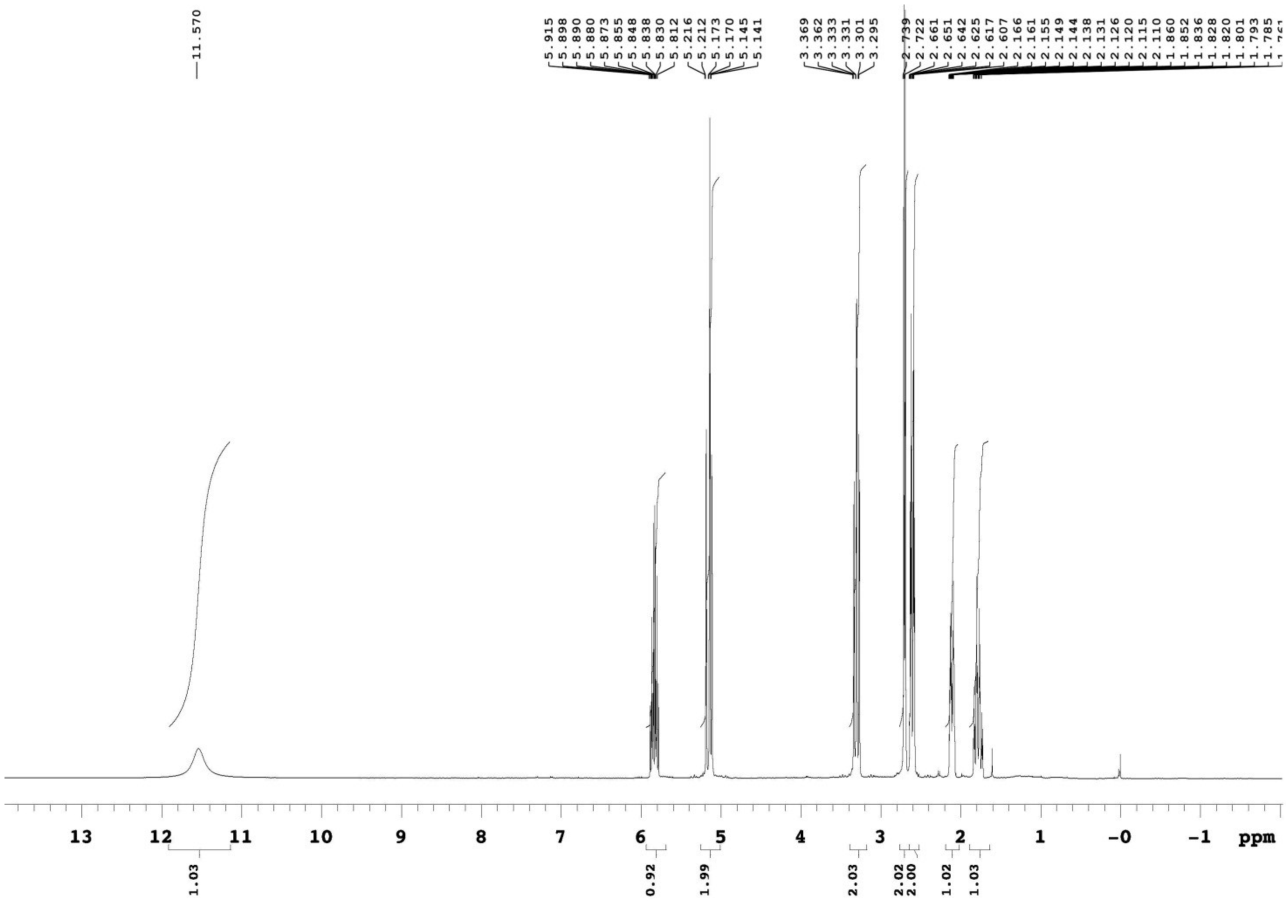
200
180
160
140
120
100
80
60
40
20
0 ppm


COOH
S
S

**4c**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5.212
5.173
5.170
5.145
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3.333
3.331
3.301
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2.739
2.722
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2.642
2.625
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2.144
2.138
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1.820
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1.785
13
12
11
10
9
8
7
6
5
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-1
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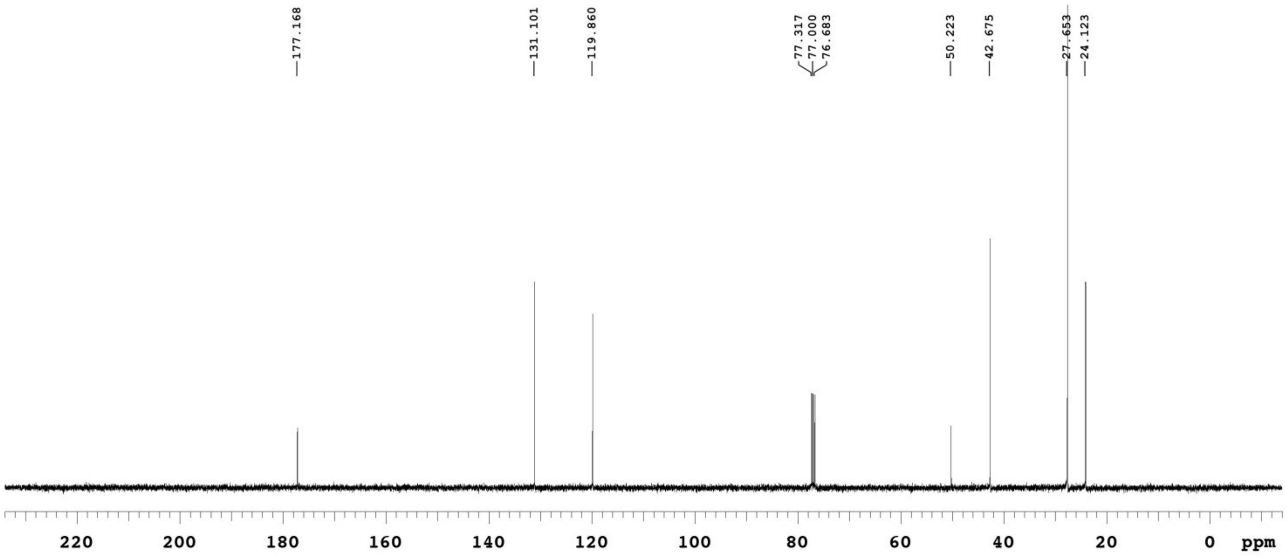
2.00
1.02
1.03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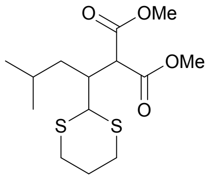
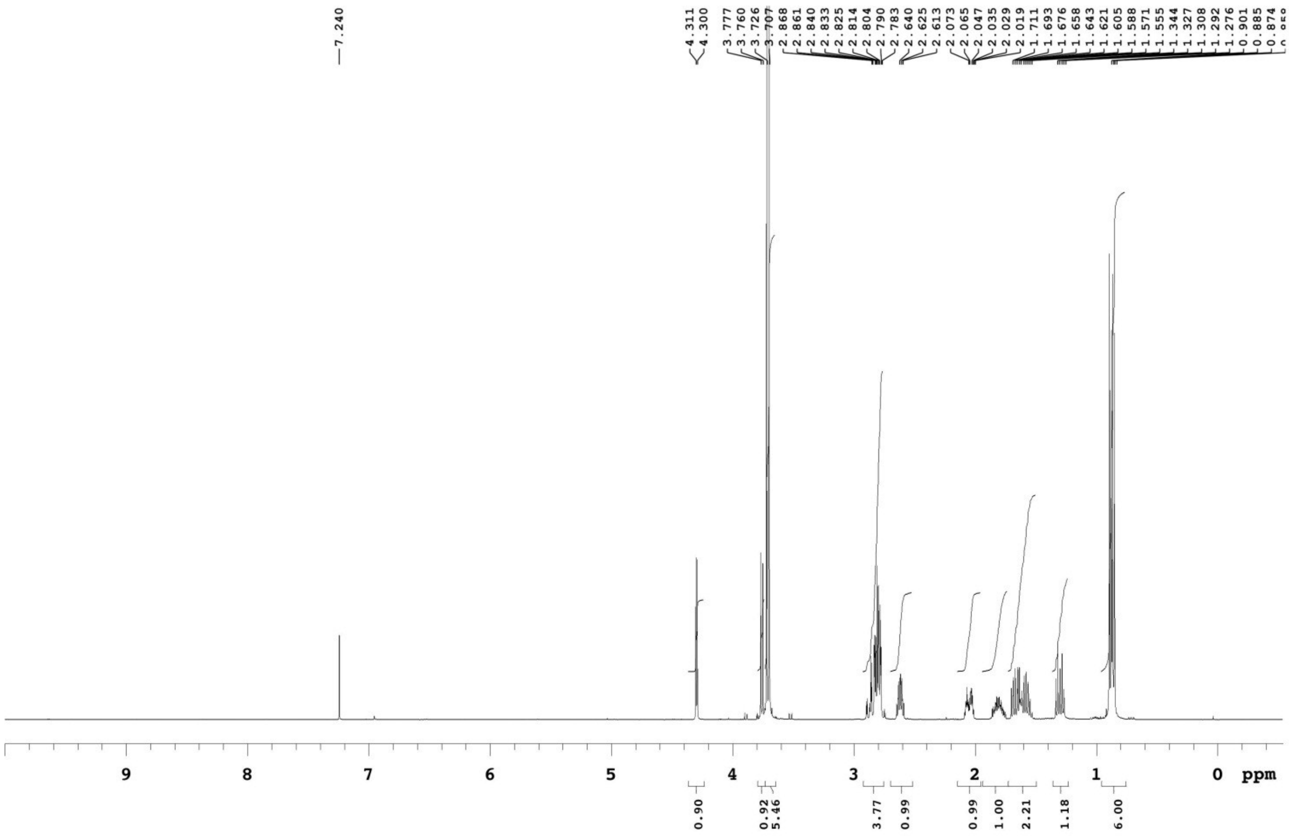
160
140
120
100
80
60
40
20
0
ppm


O
OMe
OMe
O
S
S

**5a**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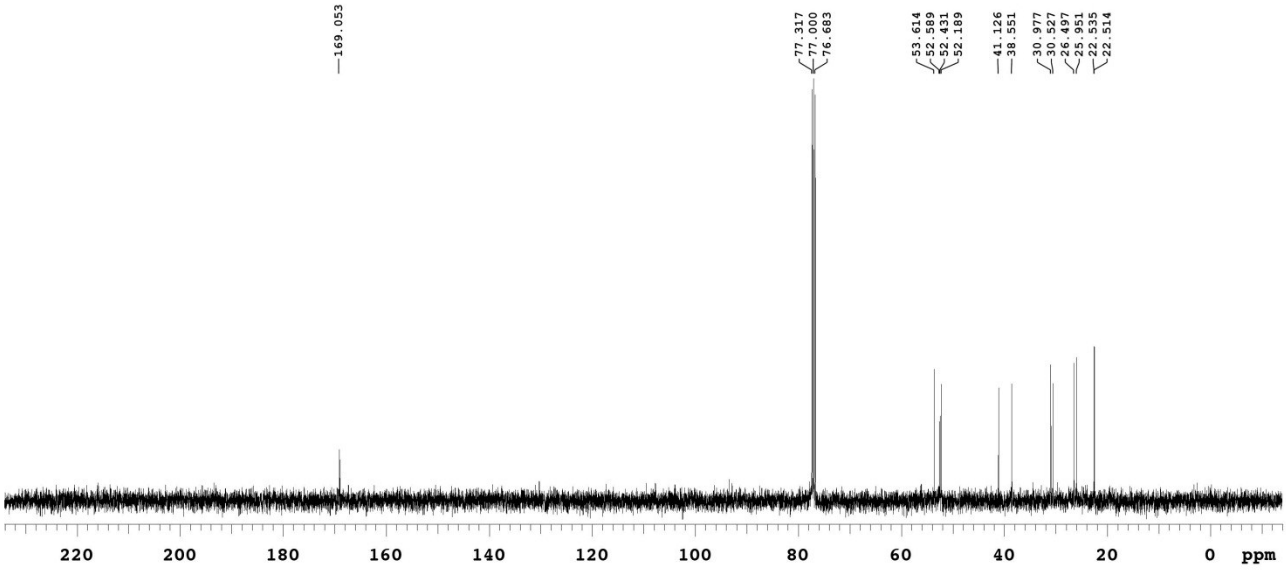
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30.527
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22.535
22.514
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140
120
100
80
60
40
20
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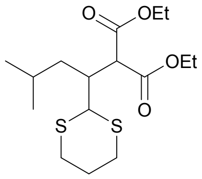
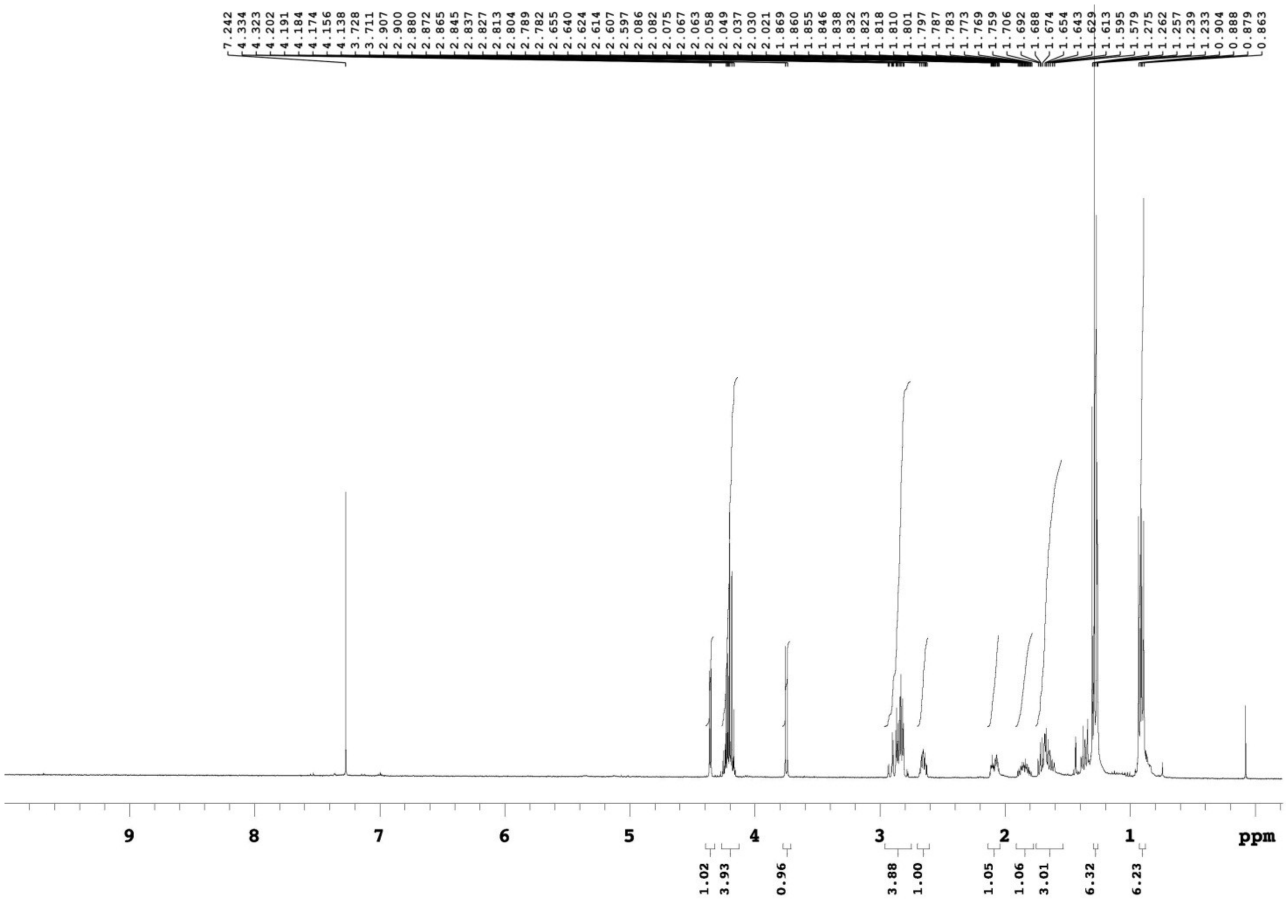
ppm


O
OEt
OEt
O
S
S

**5b**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2.900
2.880
2.872
2.865
2.845
2.837
2.827
2.813
2.804
2.789
2.782
2.655
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2.624
2.614
2.607
2.597
2.086
2.082
2.075
2.067
2.063
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2.049
2.037
2.030
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1.855
1.846
1.838
1.832
1.823
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1.810
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1.759
1.706
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1.674
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1.233
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9
8
7
6
5
4
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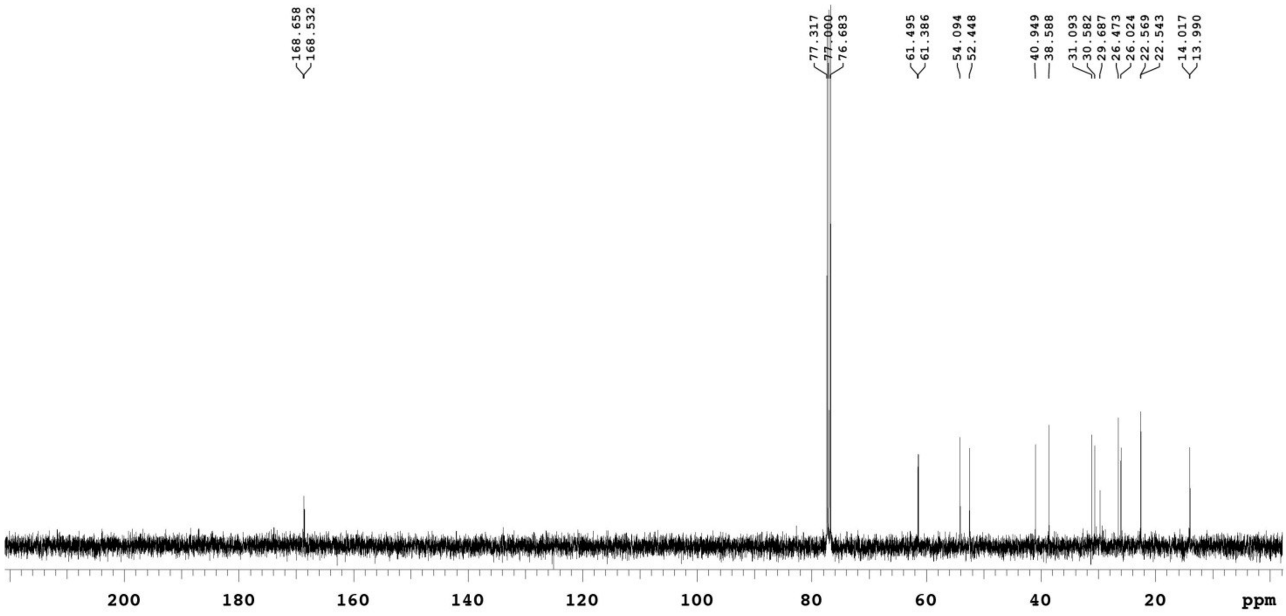
6.23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29.687
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22.543
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20
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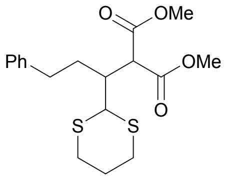
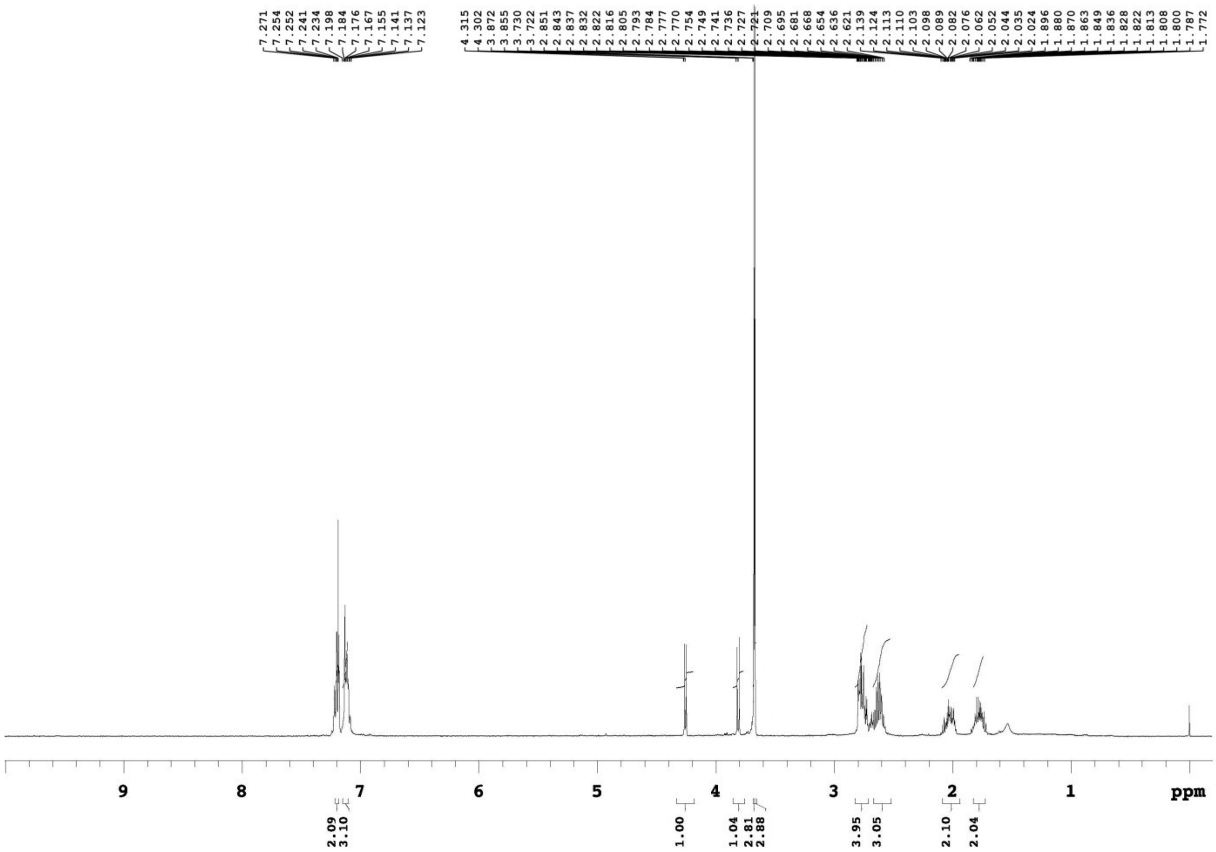

O
OMe
Ph
OMe
O
S
S

**5c**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2.062
2.052
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2.035
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1.822
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1.808
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1.787
1.772
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8
7
6
5
4
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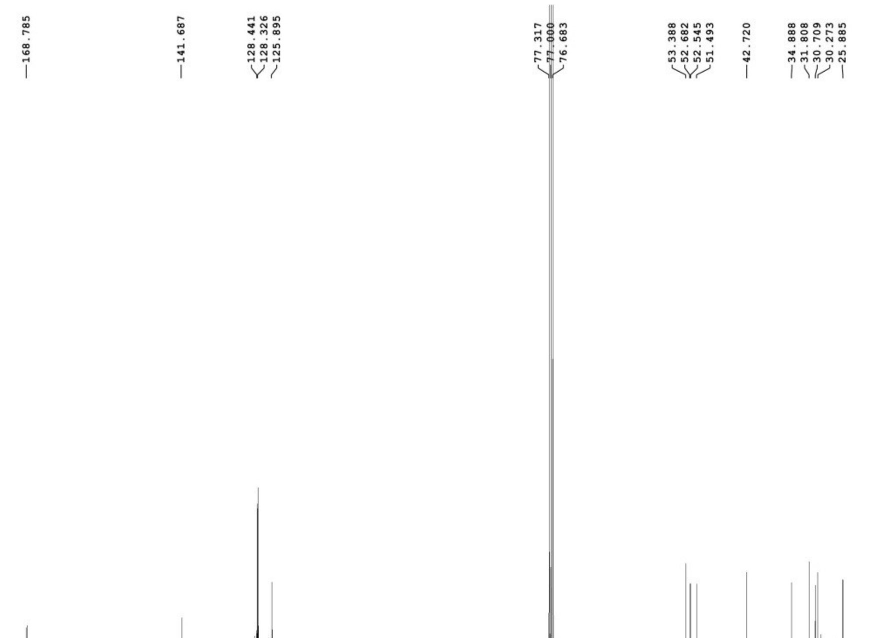
3.05
2.10
2.04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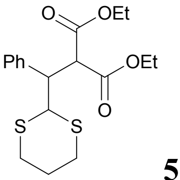
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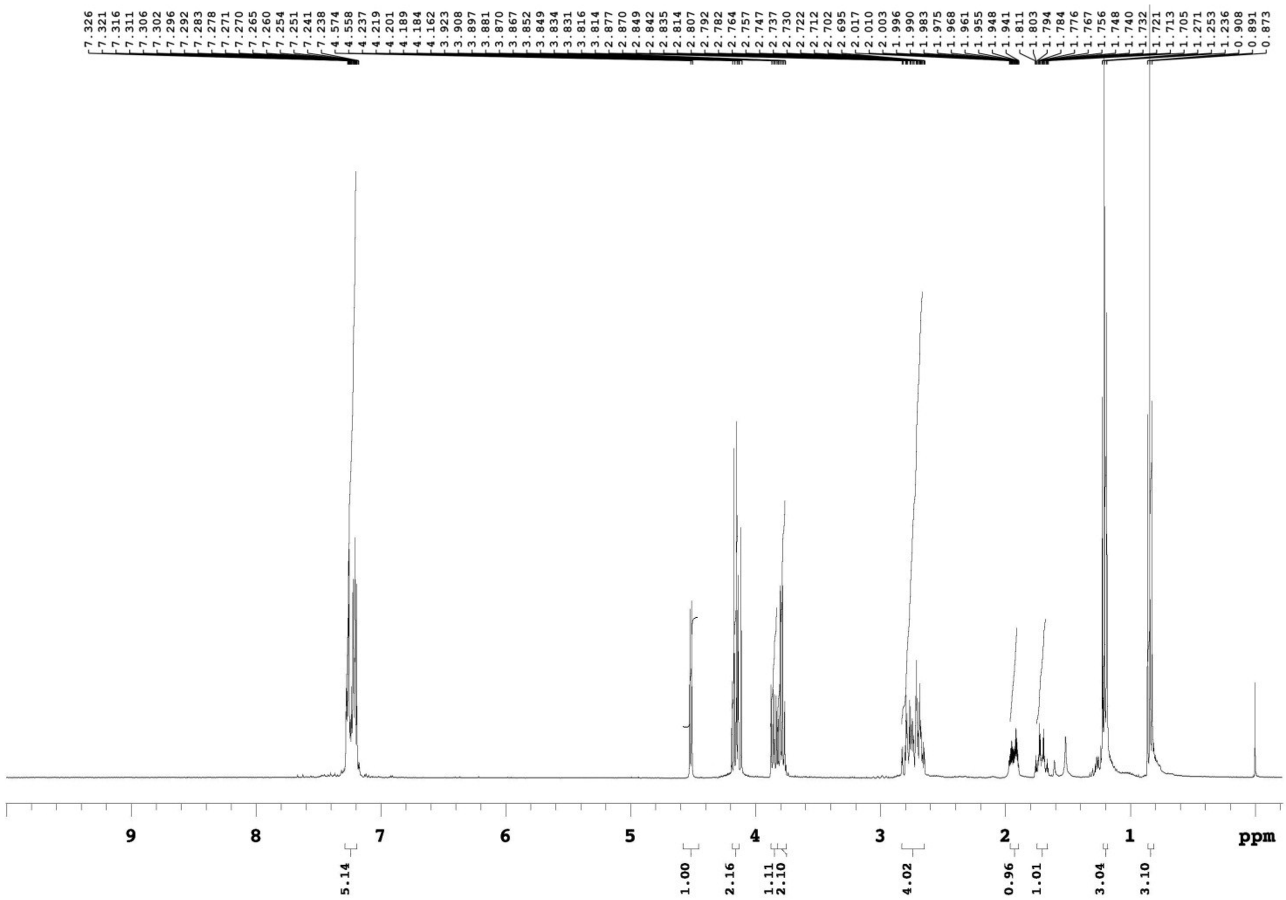
OEt
Ph
OEt
O
S
S

**5d**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7.251
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4.189
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1.236
0.908
0.891
0.873
9
8
7
6
5
4
3
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4.02
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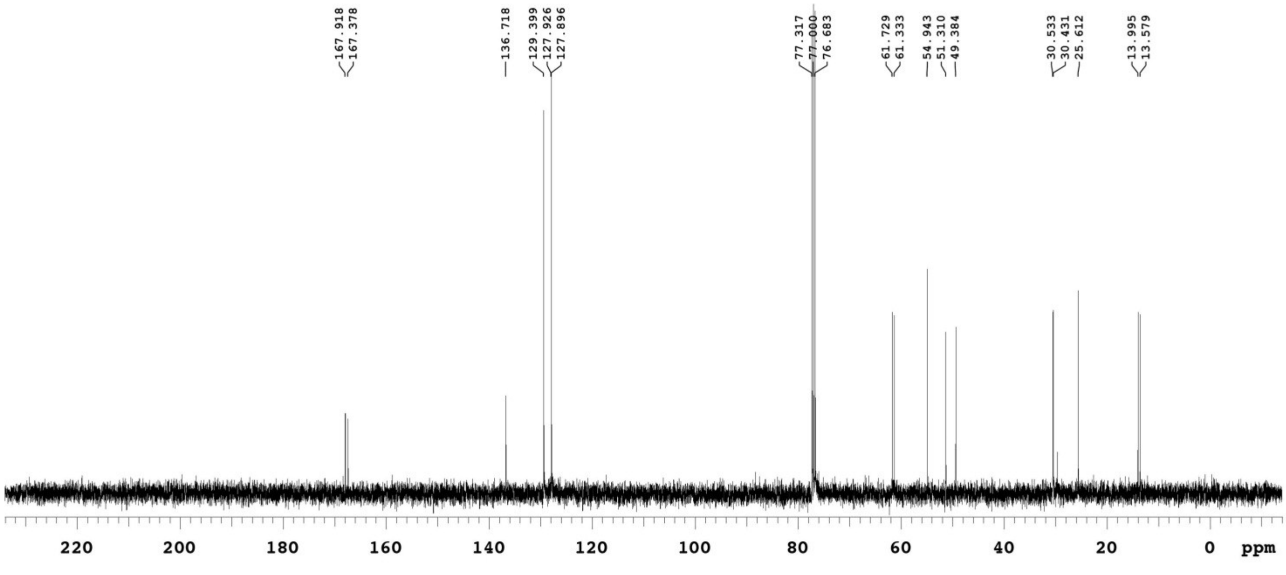
3.04
3.10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51.310
49.384
30.533
30.431
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13.995
13.579
220
200
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120
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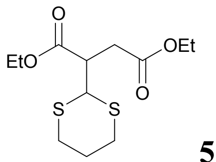
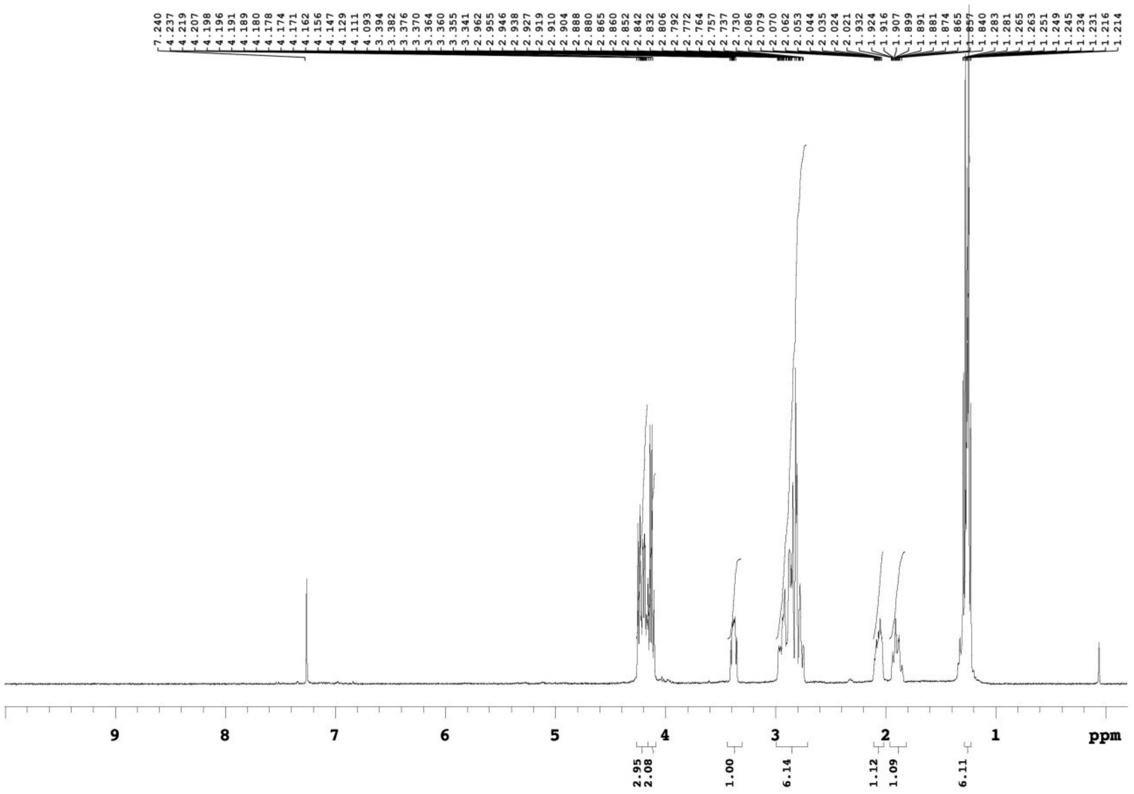
60
40
20
0
ppm


O
EtO
OEt
O
S
S

**5e**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4.189
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4.174
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4.156
4.147
4.129
4.111
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3.394
3.382
3.376
3.370
3.364
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2.044
2.035
2.024
2.021
1.932
1.924
1.916
1.907
1.899
1.891
1.881
1.874
1.865
1.857
1.840
1.283
1.281
1.265
1.263
1.251
1.249
1.245
1.234
1.231
1.216
1.214
9
8
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6
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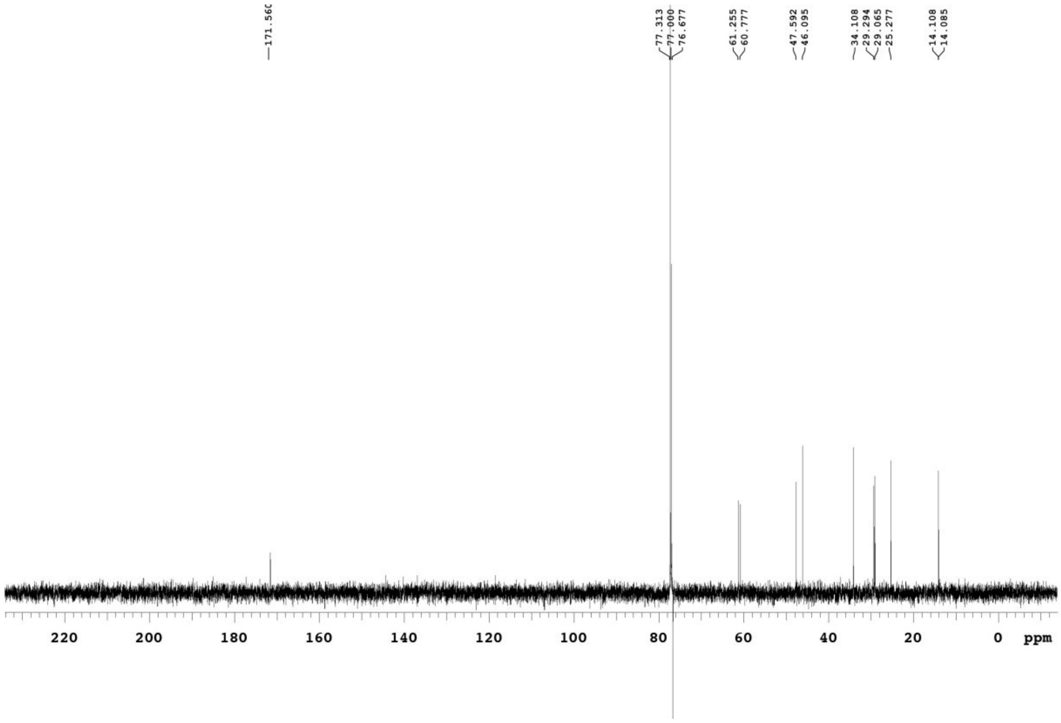
4
3
2
1
ppm
2.95
2.08
1.00
6.14
1.12
1.09
6.11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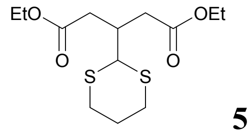
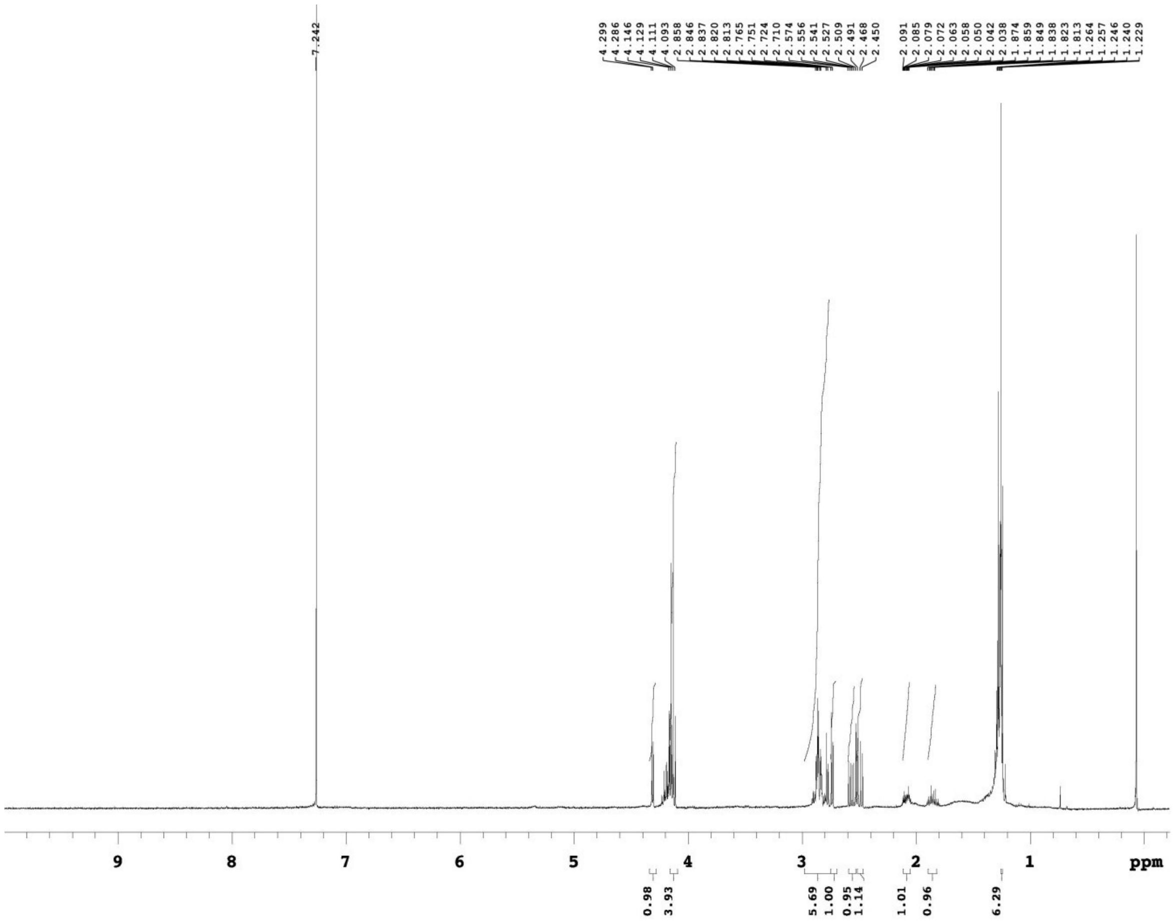
76.677
61.255
60.777
47.592
46.095
34.108
29.294
29.065
25.277
14.108
14.085
220
200
180
160
140
120
100
80
60
40
20
0
ppm



**5f**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4.286
4.146
4.129
4.111
4.093
2.858
2.846
2.837
2.820
2.813
2.765
2.751
2.724
2.710
2.574
2.556
2.541
2.527
2.509
2.491
2.468
2.450
2.091
2.085
2.079
2.072
2.063
2.058
2.050
2.042
2.038
1.874
1.859
1.849
1.838
1.823
1.813
1.264
1.257
1.246
1.240
1.229
9
8
7
6
5
4
3
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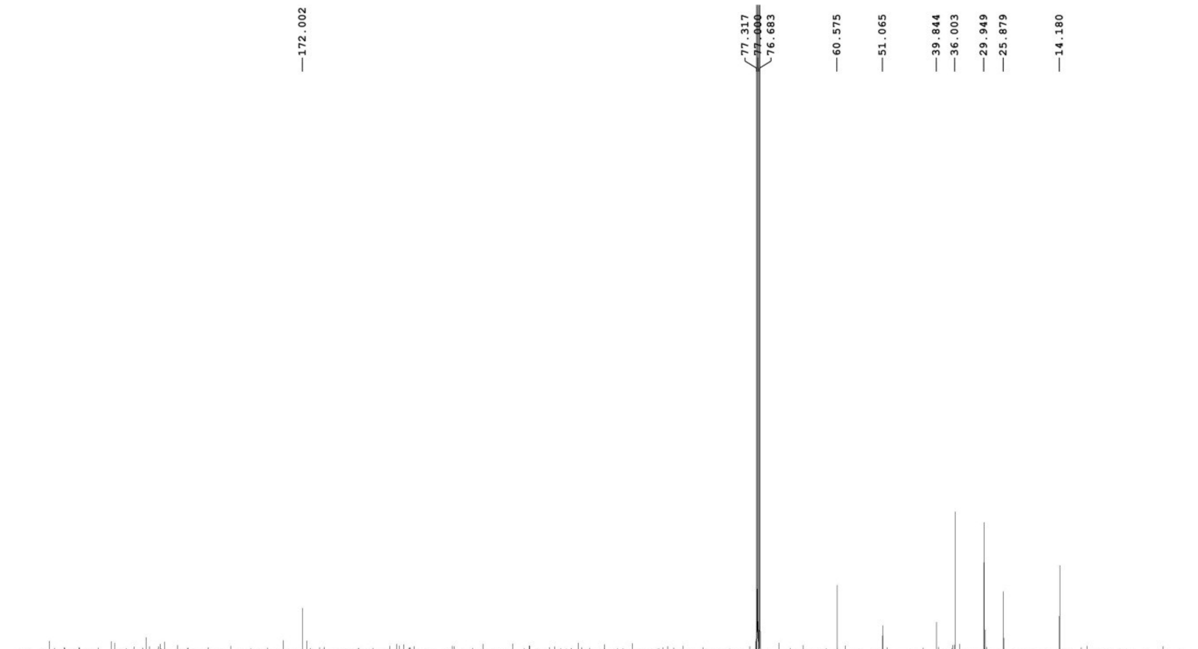
1
ppm
0.98
3.93
5.69
1.00
0.95
1.14
1.01
0.96
6.29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51.065
39.844
36.003
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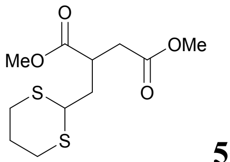
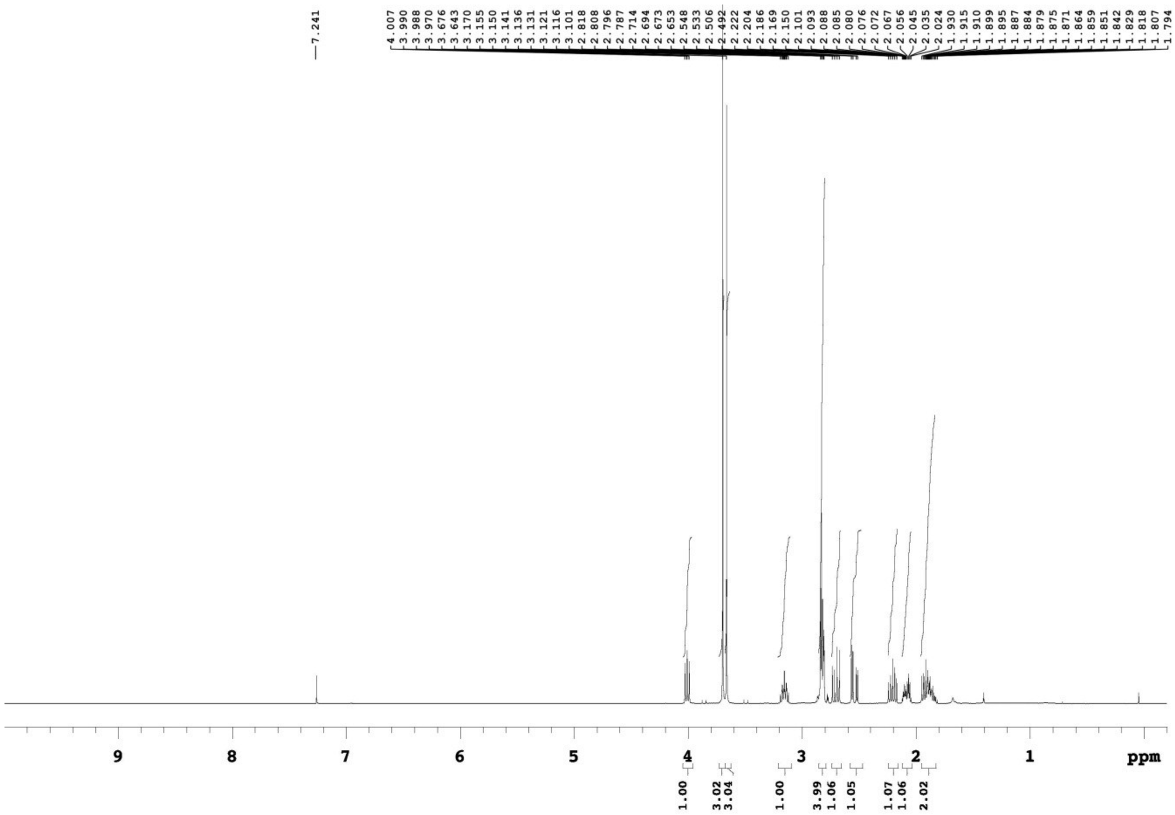
25.879
14.180
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
MeO
OMe
O
S
S

**5g**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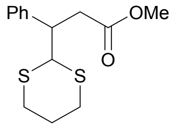
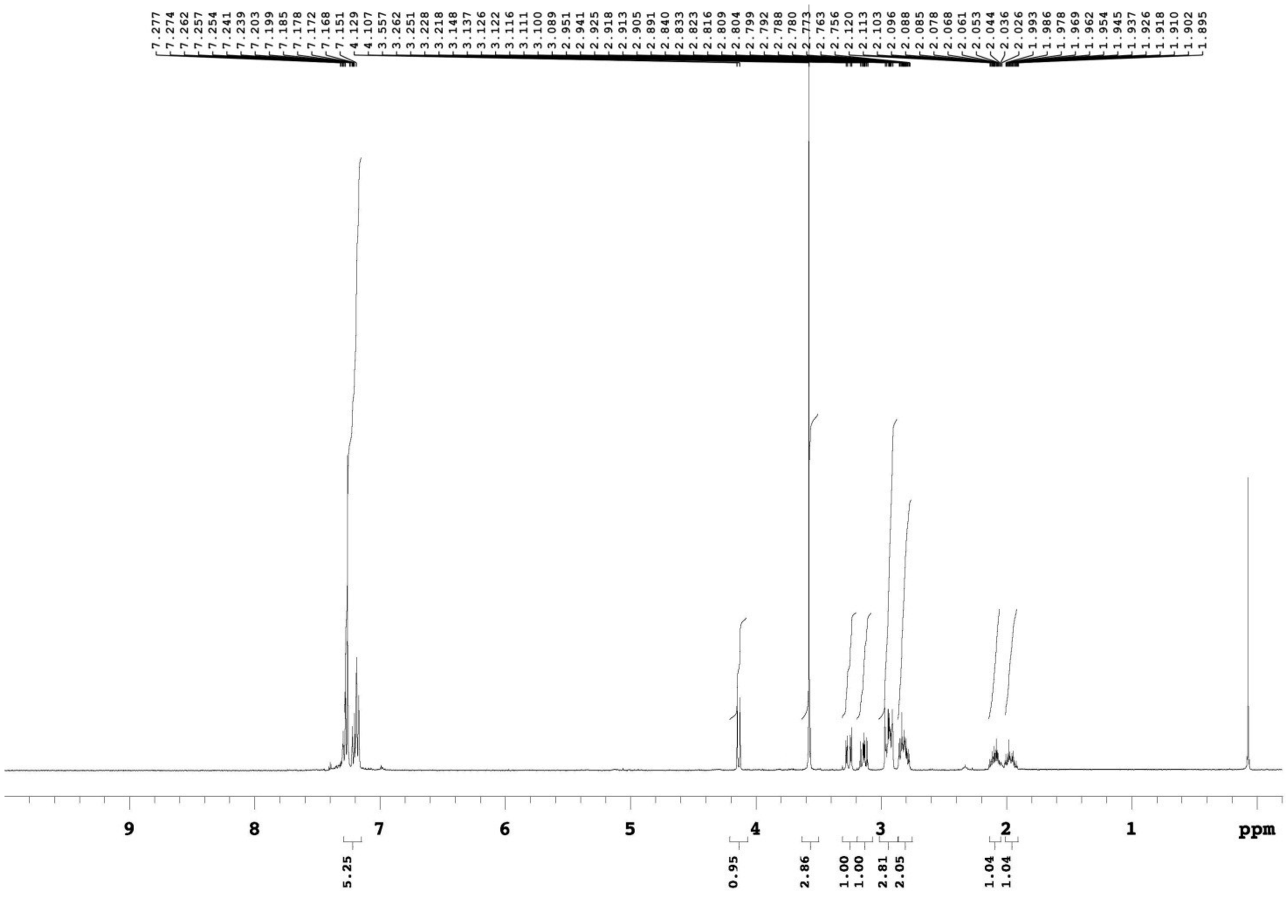
3.170
3.155
3.150
3.141
3.136
3.131
3.121
3.116
3.101
2.818
2.808
2.796
2.787
2.714
2.694
2.673
2.653
2.548
2.533
2.506
2.492
2.222
2.204
2.186
2.169
2.150
2.101
2.093
2.088
2.085
2.080
2.076
2.072
2.067
2.056
2.045
2.035
2.024
1.930
1.915
1.910
1.899
1.895
1.887
1.884
1.879
1.875
1.871
1.864
1.859
1.851
1.842
1.829
1.818
1.807
1.794
9
8
7
6
5
4
3
2
1
ppm
1.00
3.02
3.04
1.00
3.99
1.06
1.05
1.07
1.06
2.02


Ph
OMe
O
S
S

**5h**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7.262
7.257
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7.241
7.239
7.203
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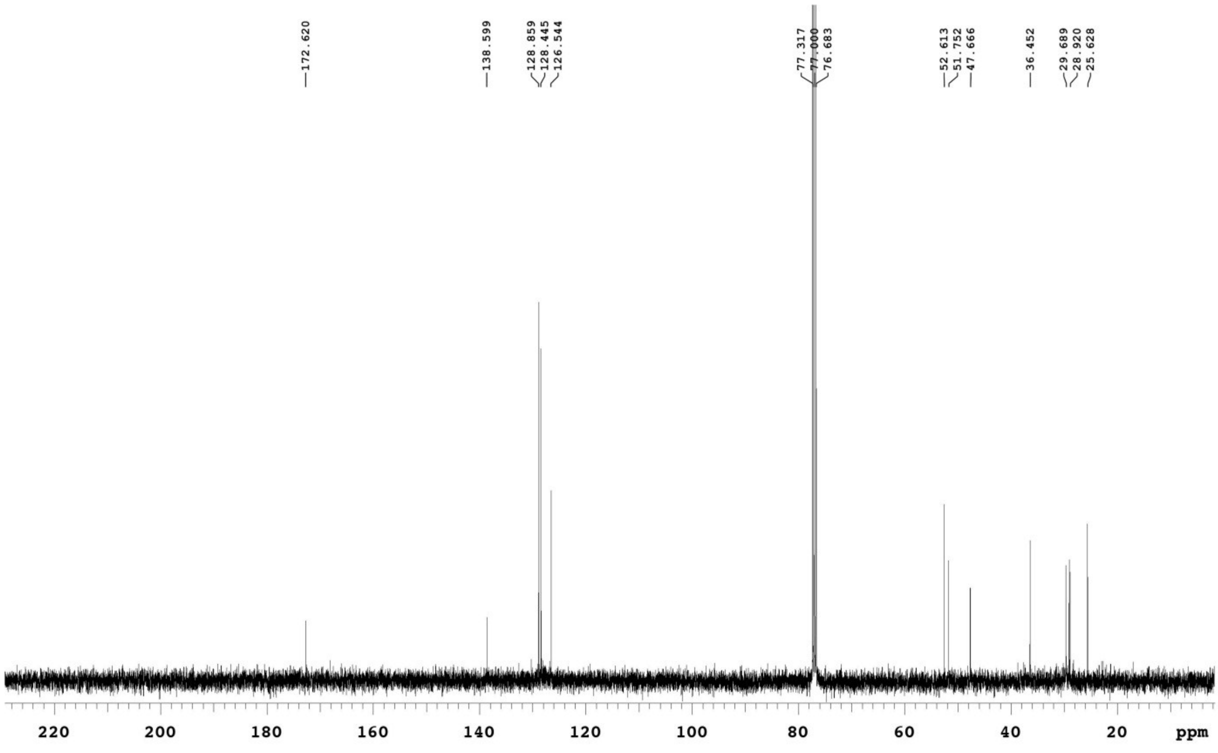
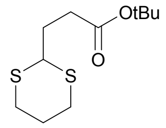
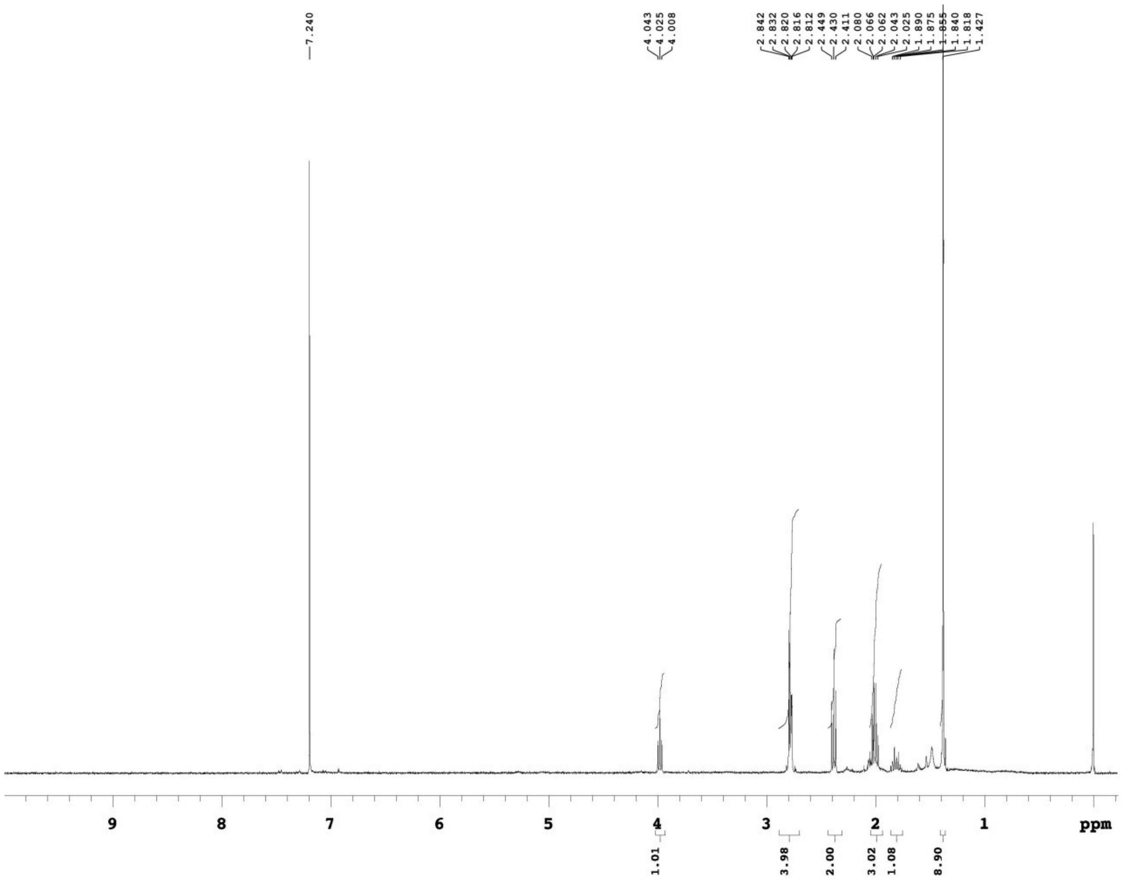
7.185
7.178
7.172
7.168
7.151
4.129
4.107
3.557
3.262
3.251
3.228
3.218
3.148
3.137
3.126
3.122
3.116
3.111
3.100
3.089
2.951
2.941
2.925
2.918
2.913
2.905
2.891
2.840
2.833
2.823
2.816
2.809
2.804
2.799
2.792
2.788
2.780
2.773
2.763
2.756
2.120
2.113
2.103
2.096
2.088
2.085
2.078
2.068
2.061
2.053
2.044
2.036
2.026
1.993
1.986
1.978
1.969
1.962
1.954
1.945
1.937
1.926
1.918
1.910
1.902
1.895
9
8
7
6
5
4
3
2
1
ppm
5.25
0.95
2.86
1.00
1.00
2.81
2.05
1.04
1.04


172.620
138.599
128.859
128.445
126.544
77.317
77.000
76.683
52.613
51.752
47.666
36.452
29.689
28.920
25.628
220
200
180
160
140
120
100
80
60
40
20
ppm


OtBu
O
S
S

**5i**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4.025
4.008
2.842
2.832
2.820
2.816
2.812
2.449
2.430
2.411
2.080
2.066
2.062
2.043
2.025
1.890
1.875
1.855
1.840
1.818
1.427
9
8
7
6
5
4
3
2
1
ppm
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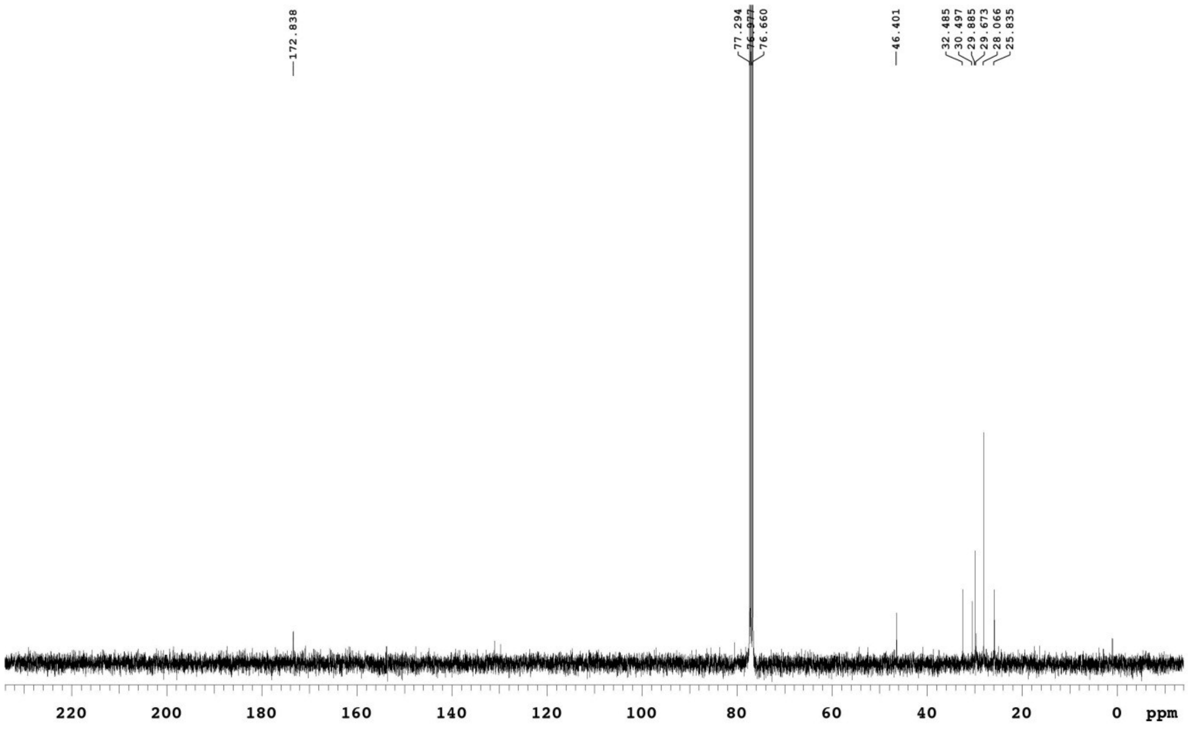
2.00
3.02
1.08
8.90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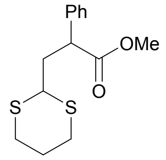
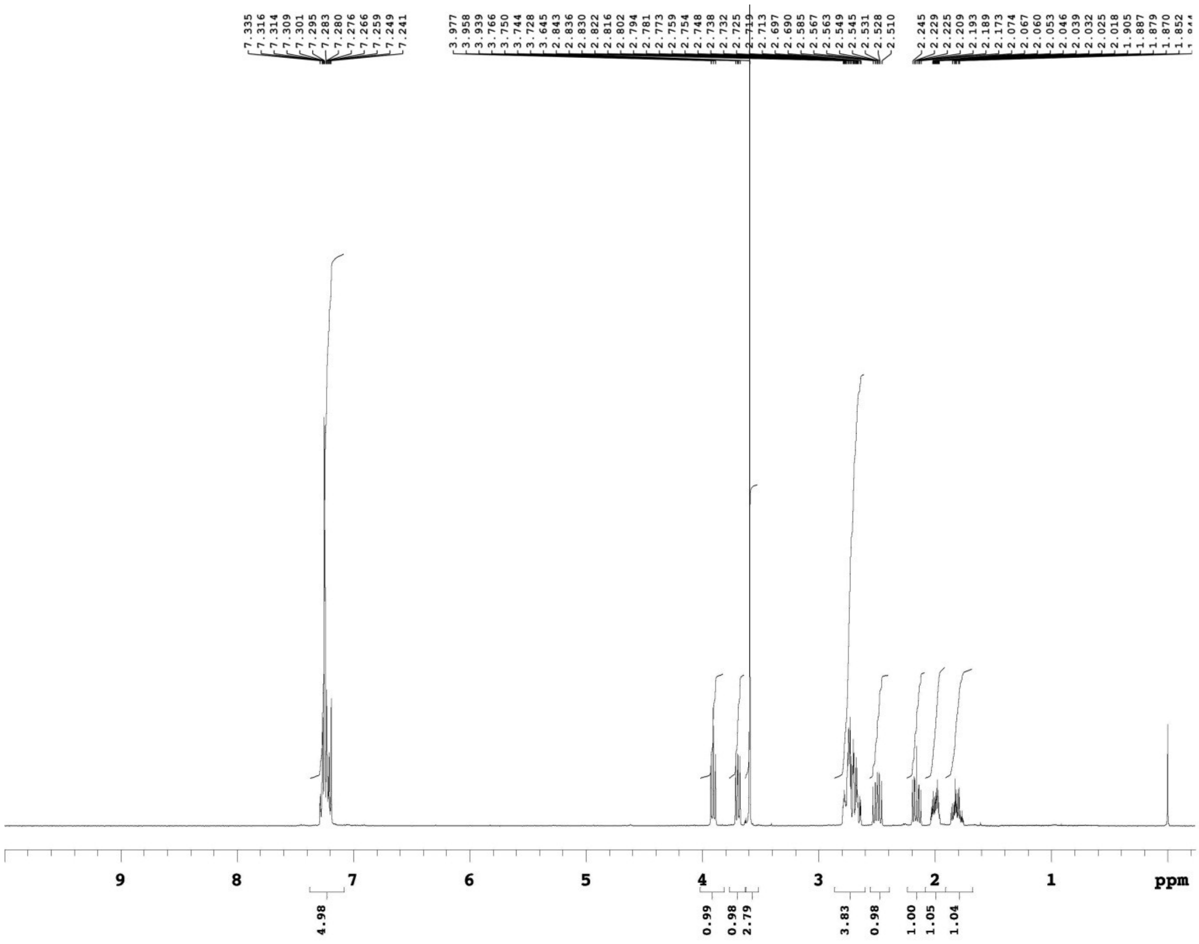
77.294
76.977
76.660
46.401
32.485
30.497
29.885
29.673
28.066
25.835
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
OMe
O
S
S

**5j**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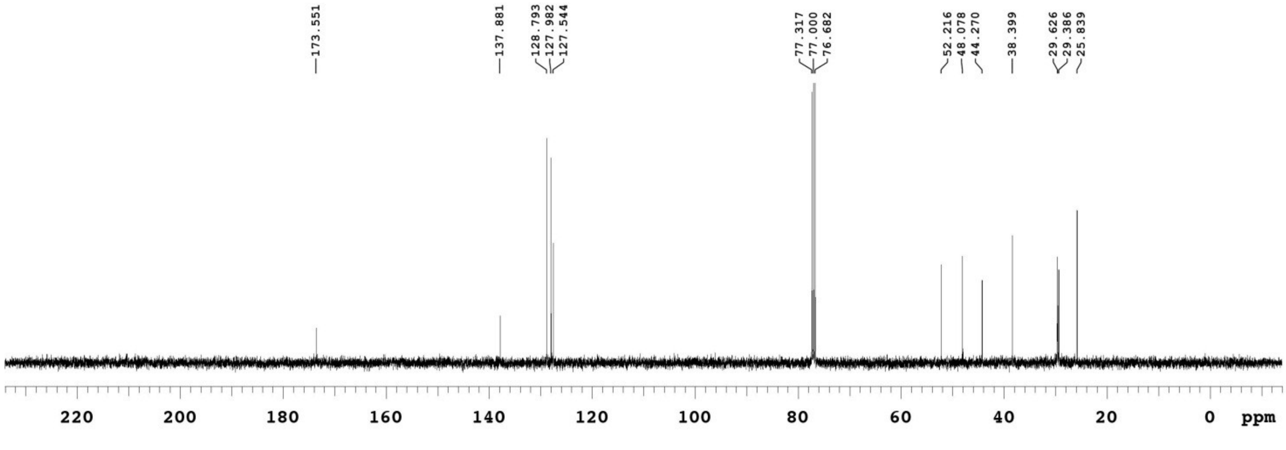
7.314
7.309
7.301
7.295
7.283
7.280
7.276
7.266
7.259
7.249
7.241
3.977
3.958
3.939
3.766
3.750
3.744
3.728
3.645
2.843
2.836
2.830
2.822
2.816
2.802
2.794
2.781
2.773
2.759
2.754
2.748
2.738
2.732
2.725
2.719
2.713
2.697
2.690
2.585
2.567
2.563
2.549
2.545
2.531
2.528
2.510
2.245
2.229
2.225
2.209
2.193
2.189
2.173
2.074
2.067
2.060
2.053
2.046
2.039
2.032
2.025
2.018
1.905
1.887
1.879
1.870
1.852
9
8
7
6
5
4
3
2
1
ppm
4.98
0.99
0.98
2.79
3.83
0.98
1.00
1.05
1.04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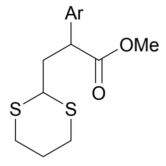
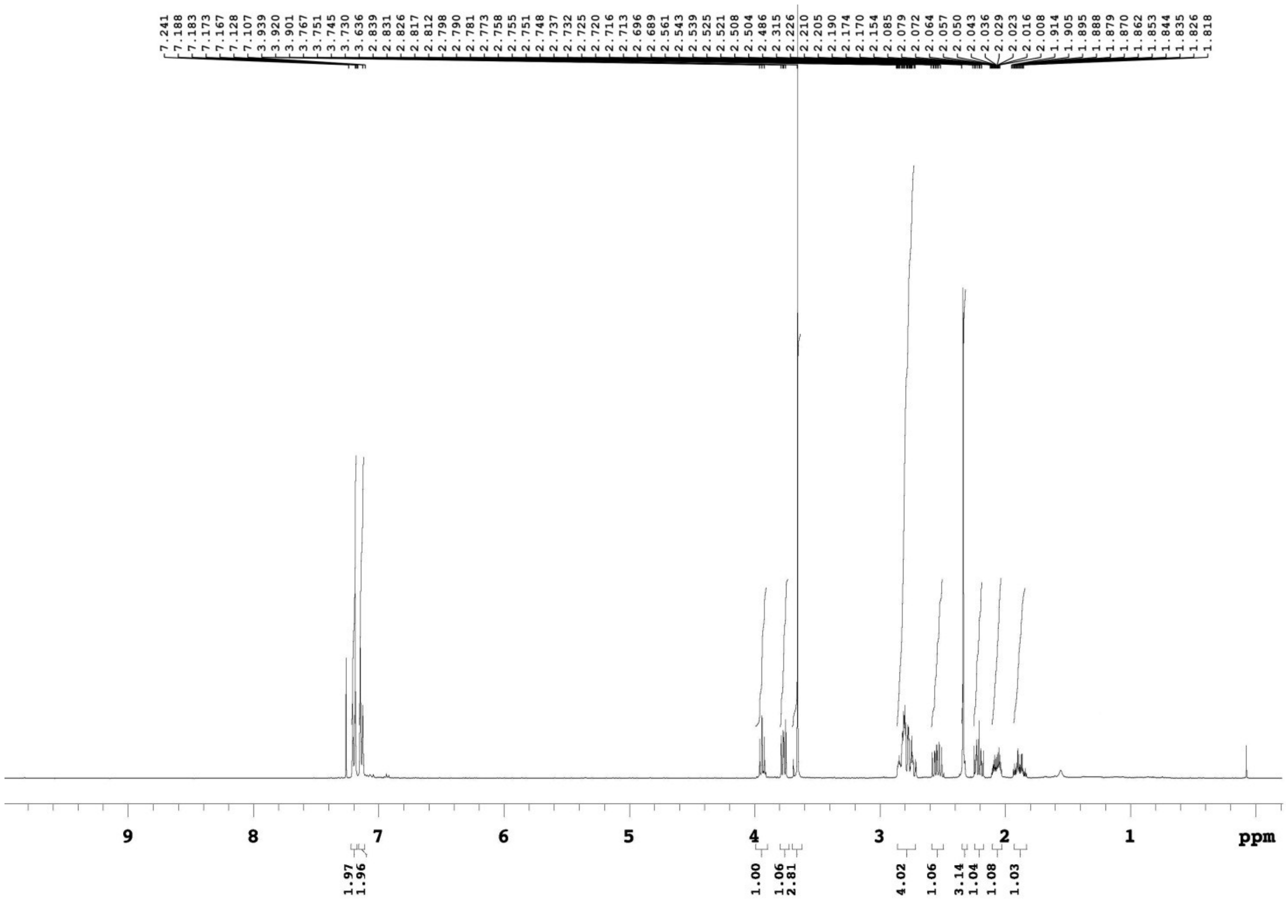
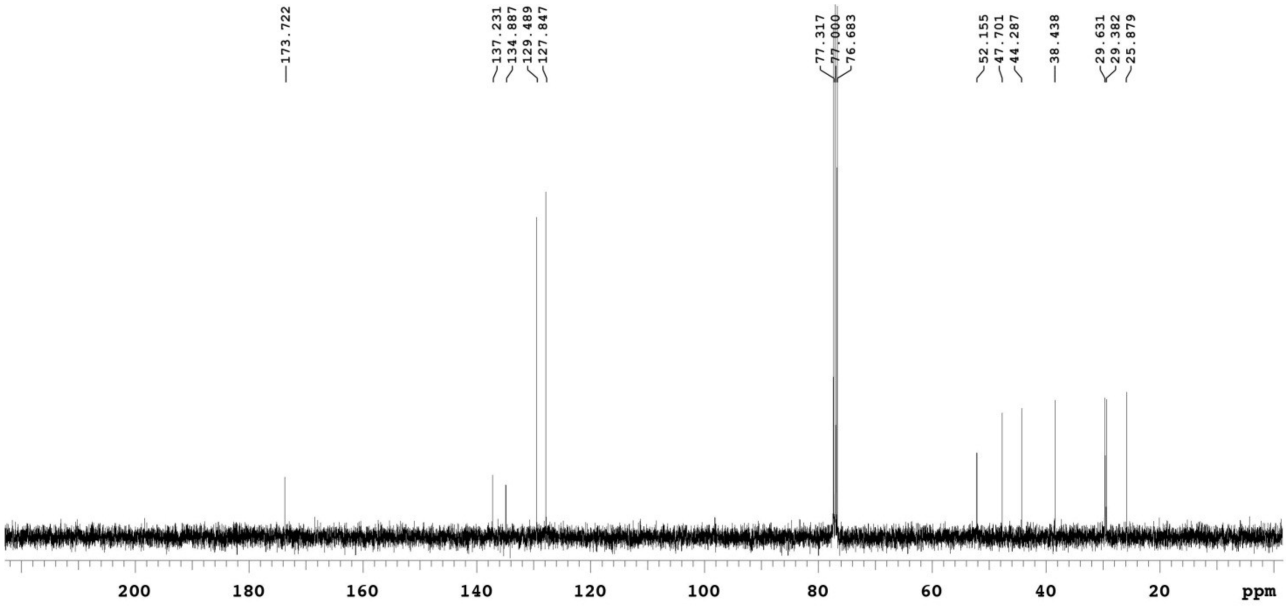
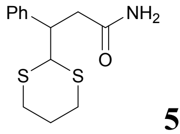
137.881
128.793
127.982
127.544
77.317
77.000
76.682
52.216
48.078
44.270
38.399
29.626
29.386
25.839
220
200
180
160
140
120
100
80
60
40
20
0
ppm



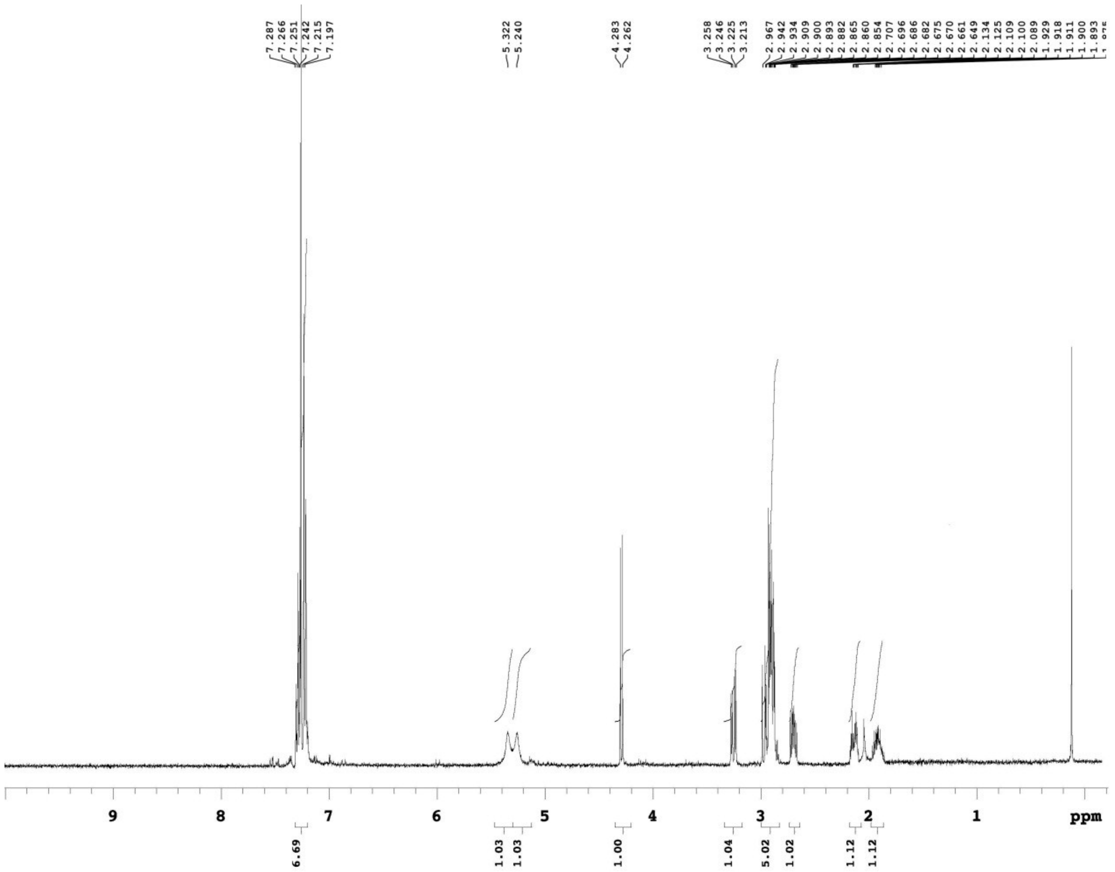
Ar = 4-Me-$C_6H_4$ **5k**






Ph
NH2
O
S
S

**5l**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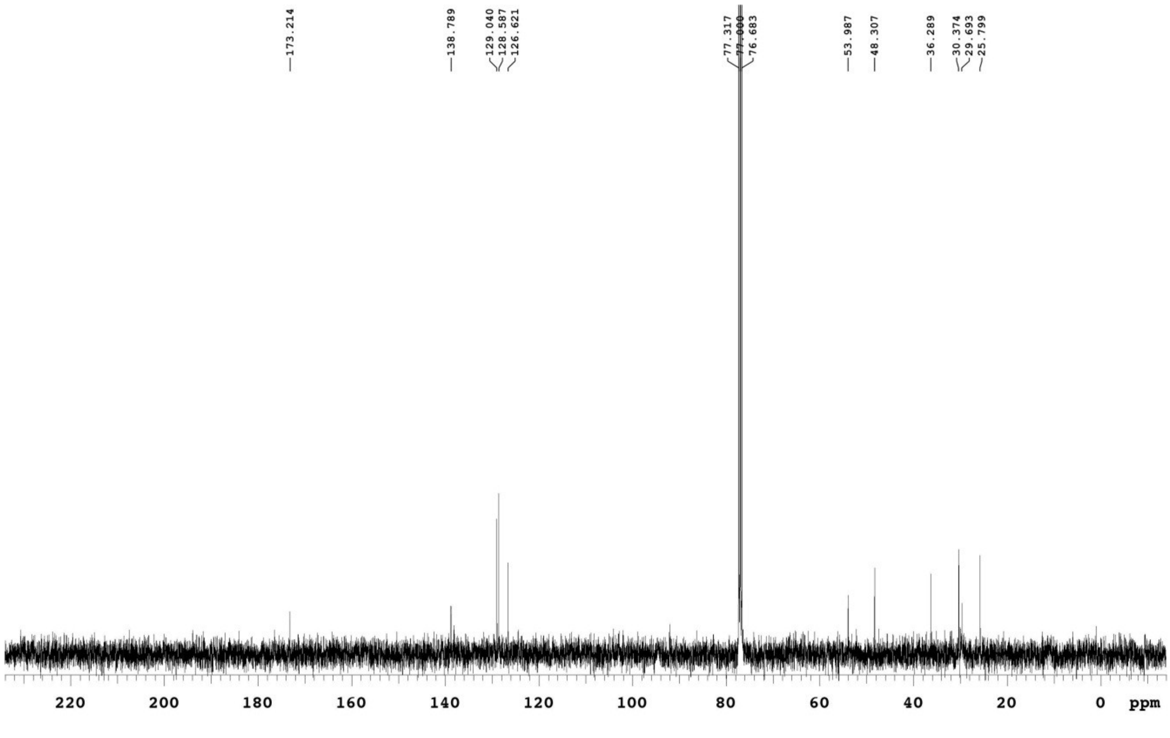
7.197
5.322
5.240
4.283
4.262
3.258
3.246
3.225
3.213
2.967
2.942
2.934
2.909
2.900
2.893
2.882
2.865
2.860
2.854
2.707
2.696
2.686
2.682
2.675
2.670
2.661
2.649
2.134
2.125
2.109
2.100
2.089
1.929
1.918
1.911
1.900
1.893
9
8
7
6
5
4
3
2
1
ppm
6.69
1.03
1.03
1.00
1.04
5.02
1.02
1.12
1.12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126.621
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77.000
76.683
53.987
48.307
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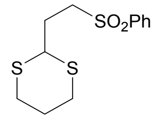
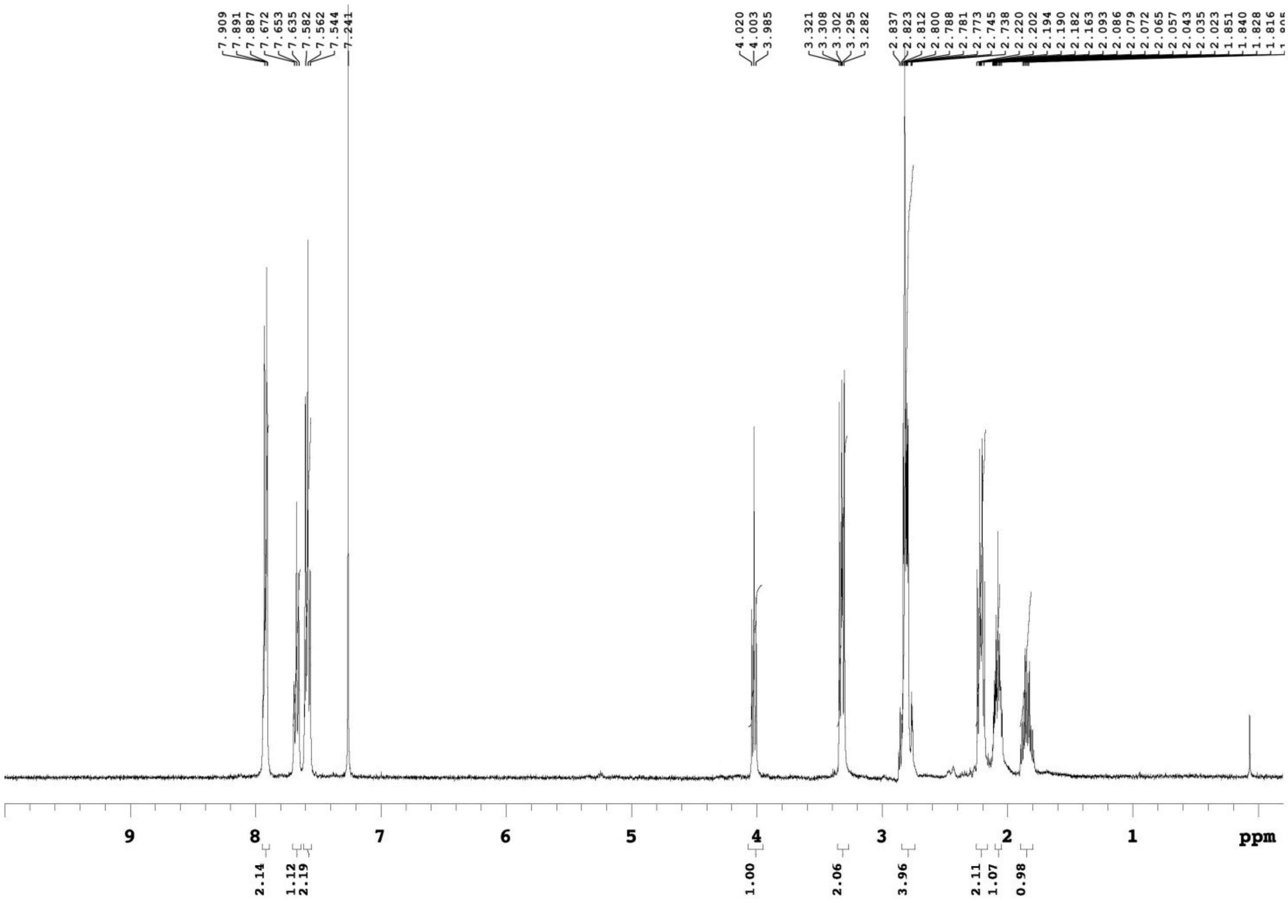
30.374
29.693
25.799
220
200
180
160
140
120
100
80
60
40
20
0
ppm


SO2Ph
S
S

**5m**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7.891
7.887
7.672
7.653
7.635
7.582
7.562
7.544
7.241
4.020
4.003
3.985
3.321
3.308
3.302
3.295
3.282
2.837
2.823
2.812
2.800
2.788
2.781
2.773
2.745
2.738
2.220
2.202
2.194
2.190
2.182
2.163
2.093
2.086
2.079
2.072
2.065
2.057
2.043
2.035
2.023
1.851
1.840
1.828
1.816
9
8
7
6
5
4
3
2
1
ppm
2.14
1.12
2.19
1.00
2.06
3.96
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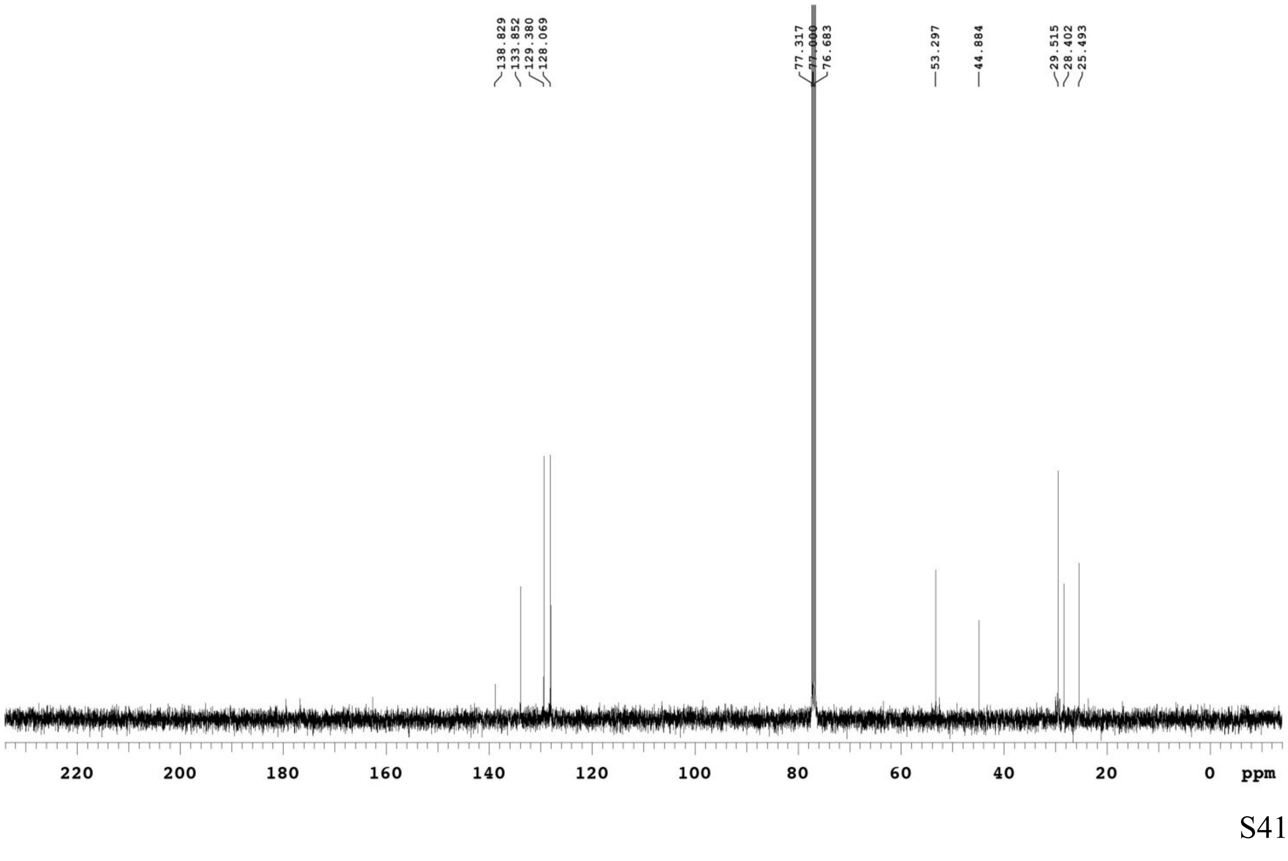
1.07
0.98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133.852
129.380
128.069
77.317
77.000
76.683
53.297
44.884
29.515
28.402
25.493
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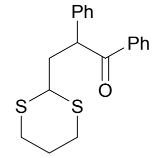
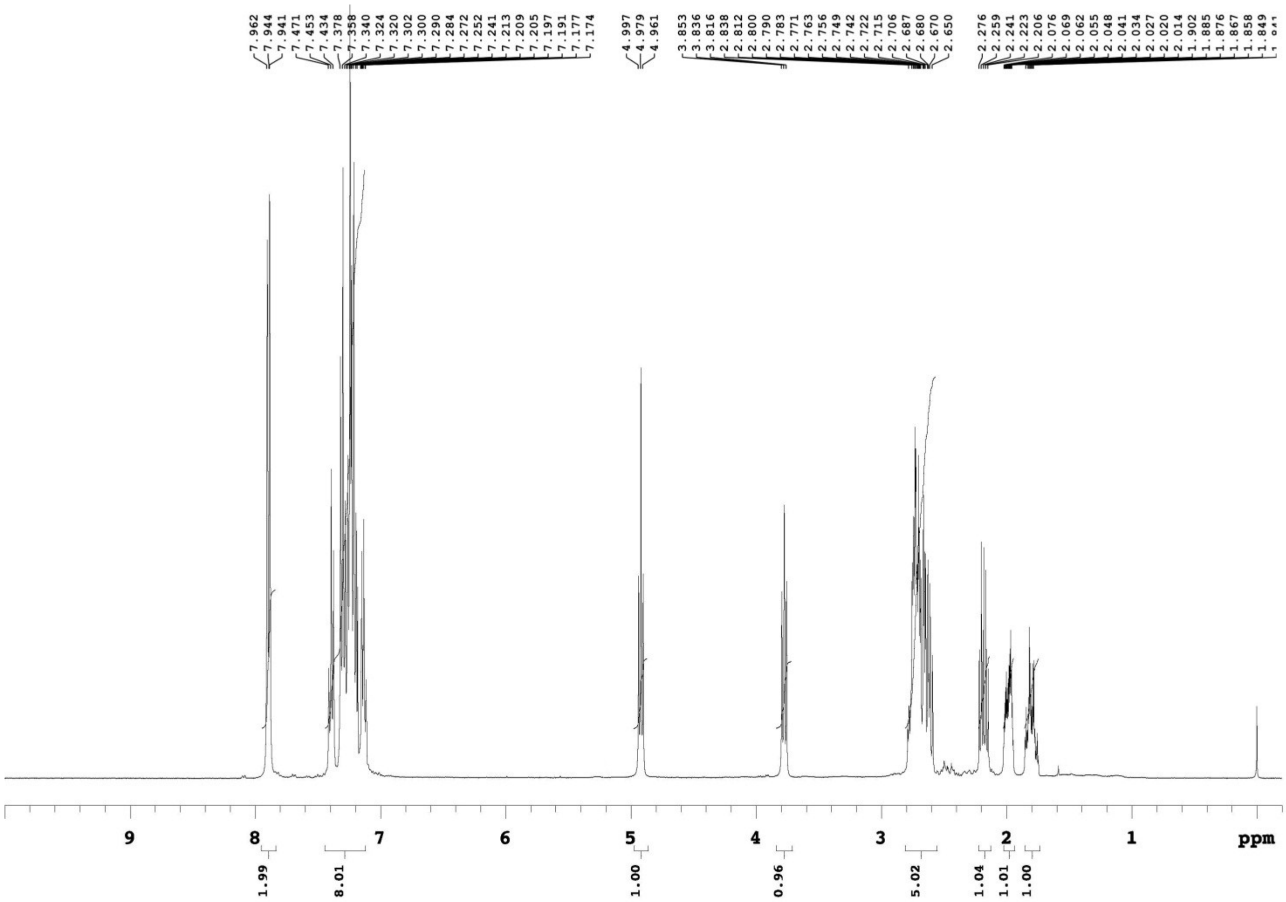
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
Ph
O
S
S

**5n**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7.941
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7.434
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7.358
7.340
7.324
7.320
7.302
7.300
7.290
7.284
7.272
7.252
7.241
7.213
7.209
7.205
7.197
7.191
7.177
7.174
4.997
4.979
4.961
3.853
3.836
3.816
2.838
2.812
2.800
2.790
2.783
2.771
2.763
2.756
2.749
2.742
2.722
2.715
2.706
2.687
2.680
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2.650
2.276
2.259
2.241
2.223
2.206
2.076
2.069
2.062
2.055
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2.041
2.034
2.027
2.020
2.014
1.902
1.885
1.876
1.867
1.858
1.849
9
8
7
6
5
4
3
2
1
ppm
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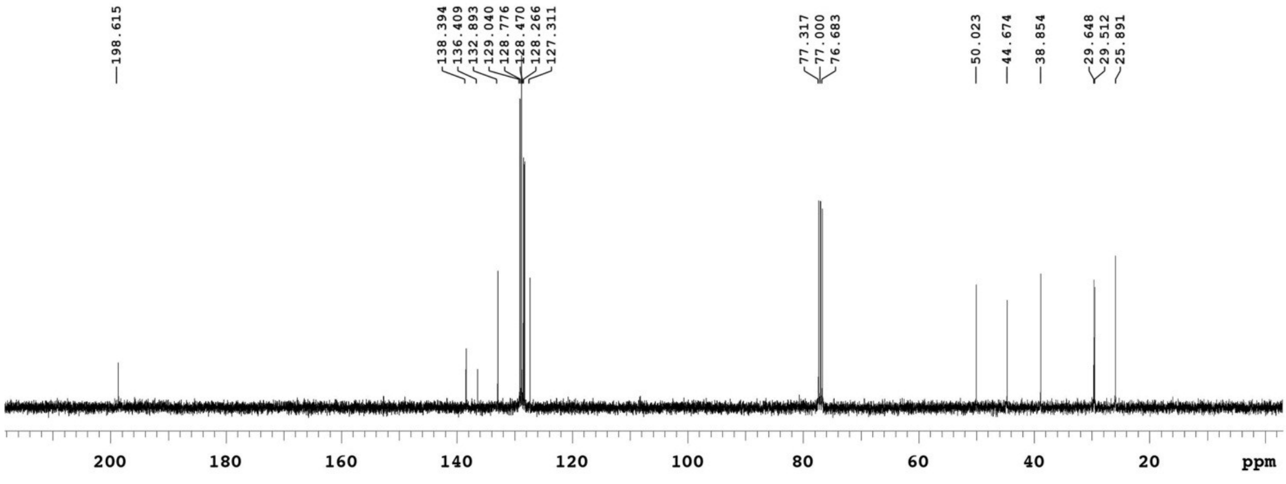
8.01
1.00
0.96
5.02
1.04
1.01
1.00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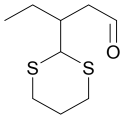
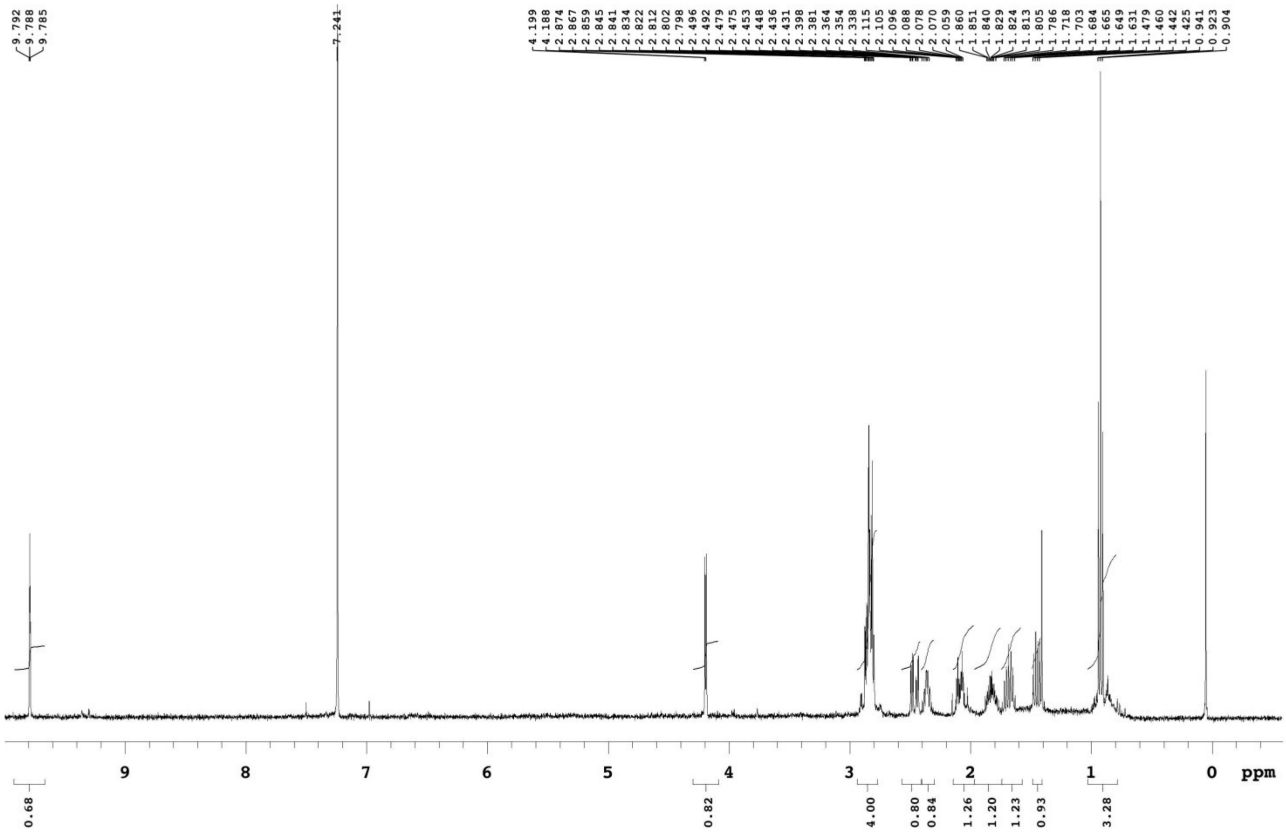
132.893
129.040
128.776
128.470
128.266
127.311
77.317
77.000
76.683
50.023
44.674
38.854
29.648
29.512
25.891
200
180
160
140
120
100
80
60
40
20
ppm



S
S
O

**5o**



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4.188
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2.867
2.859
2.845
2.841
2.834
2.822
2.812
2.802
2.798
2.496
2.492
2.479
2.475
2.453
2.448
2.436
2.431
2.398
2.381
2.364
2.354
2.338
2.115
2.105
2.096
2.088
2.078
2.070
2.059
1.860
1.851
1.840
1.829
1.824
1.813
1.805
1.786
1.718
1.703
1.684
1.665
1.649
1.631
1.479
1.460
1.442
1.425
0.941
0.923
0.904
9
8
7
6
5
4
3
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1.26
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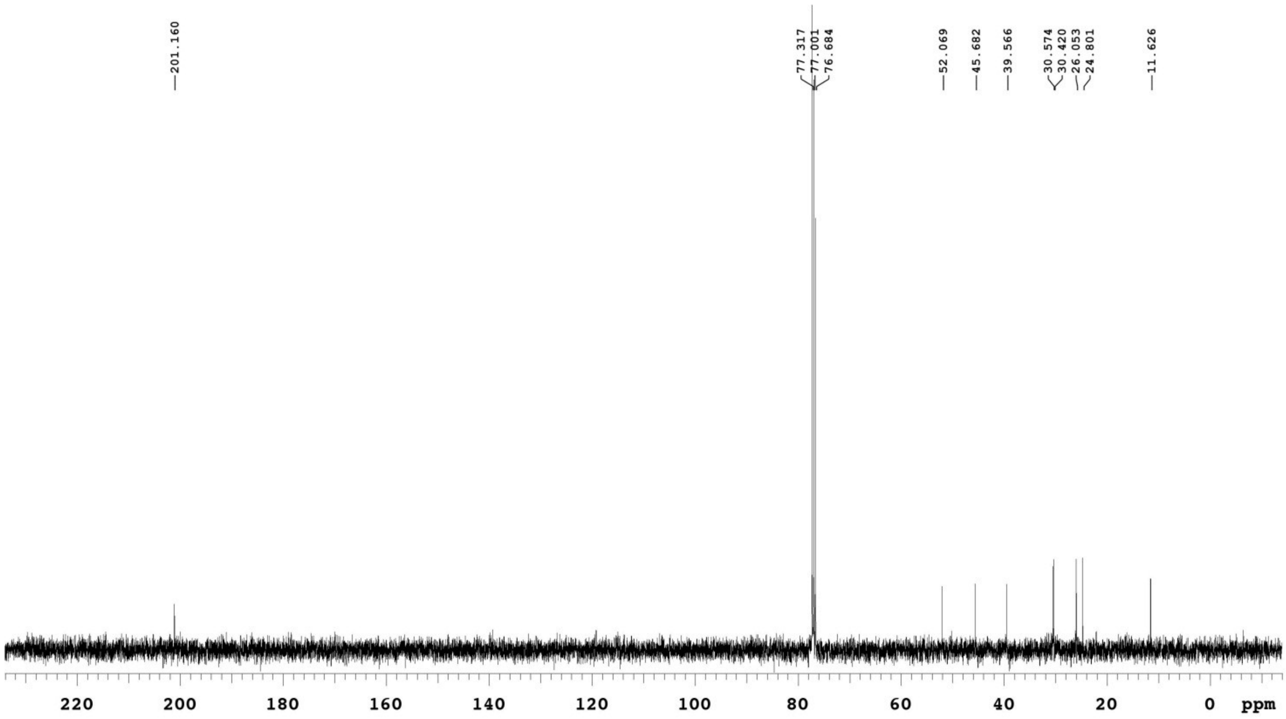
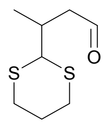
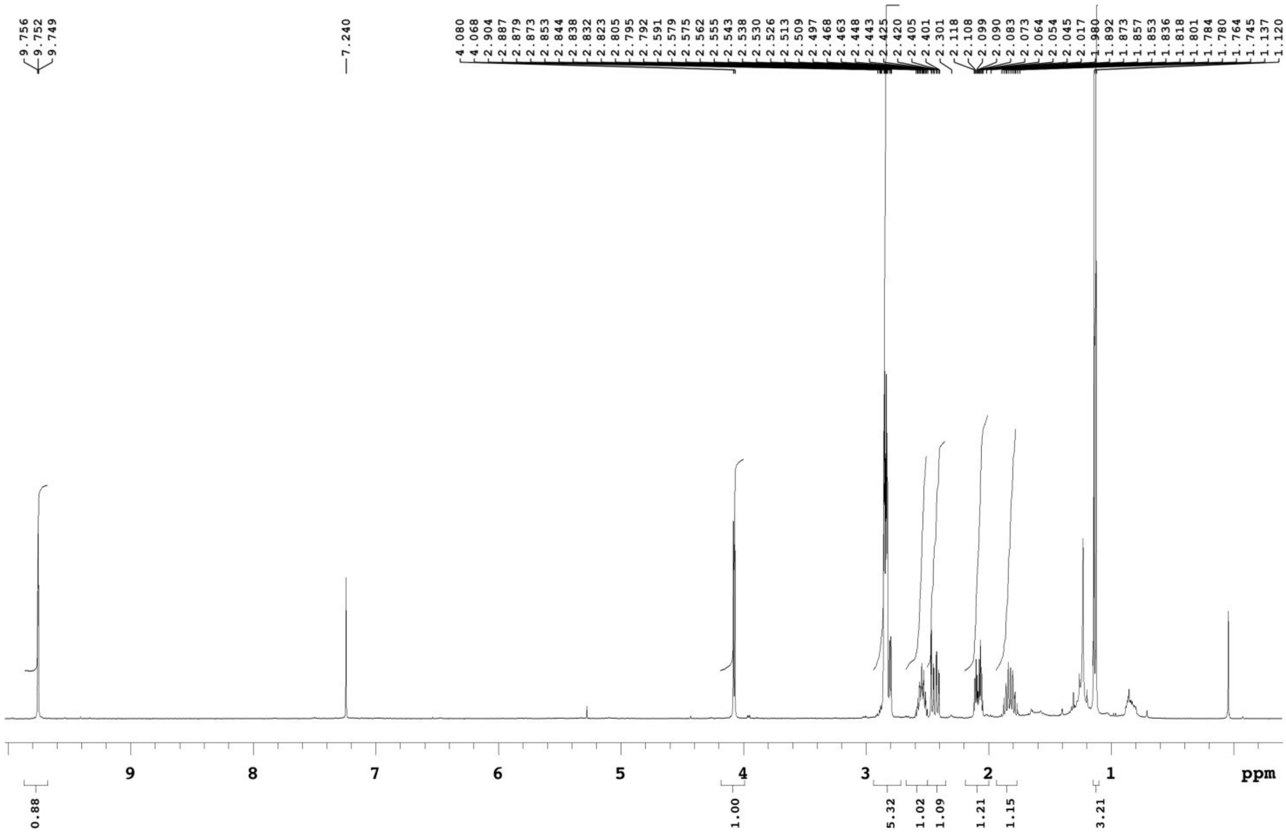
1.23
0.93
3.28



201.160
77.317
77.001
76.684
52.069
45.682
39.566
30.574
30.420
26.053
24.801
11.626
220
200
180
160
140
120
100
80
60
40
20
0
ppm


S
S
O

**5p**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9.752
9.749
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4.068
2.904
2.887
2.879
2.873
2.853
2.844
2.838
2.832
2.823
2.805
2.795
2.792
2.591
2.579
2.575
2.562
2.555
2.543
2.538
2.530
2.526
2.513
2.509
2.497
2.468
2.463
2.448
2.443
2.425
2.420
2.405
2.401
2.301
2.118
2.108
2.099
2.090
2.083
2.073
2.064
2.054
2.045
2.017
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1.873
1.857
1.853
1.836
1.818
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1.780
1.764
1.745
1.137
1.120
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7
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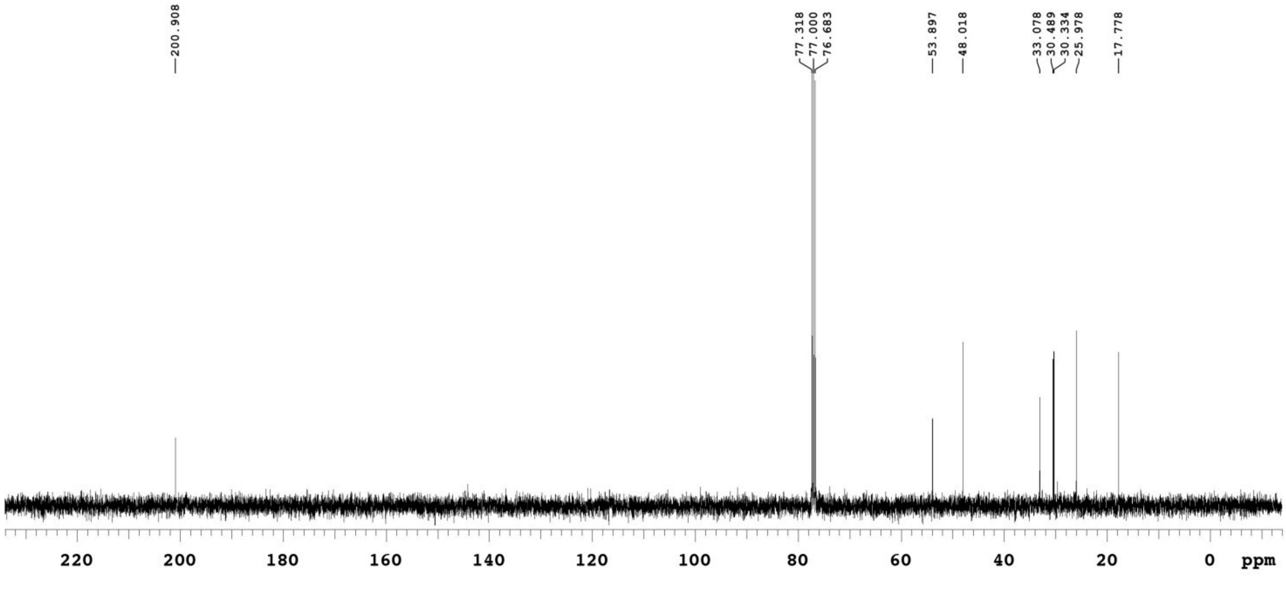
1.15
3.21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120
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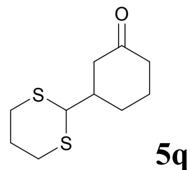
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S
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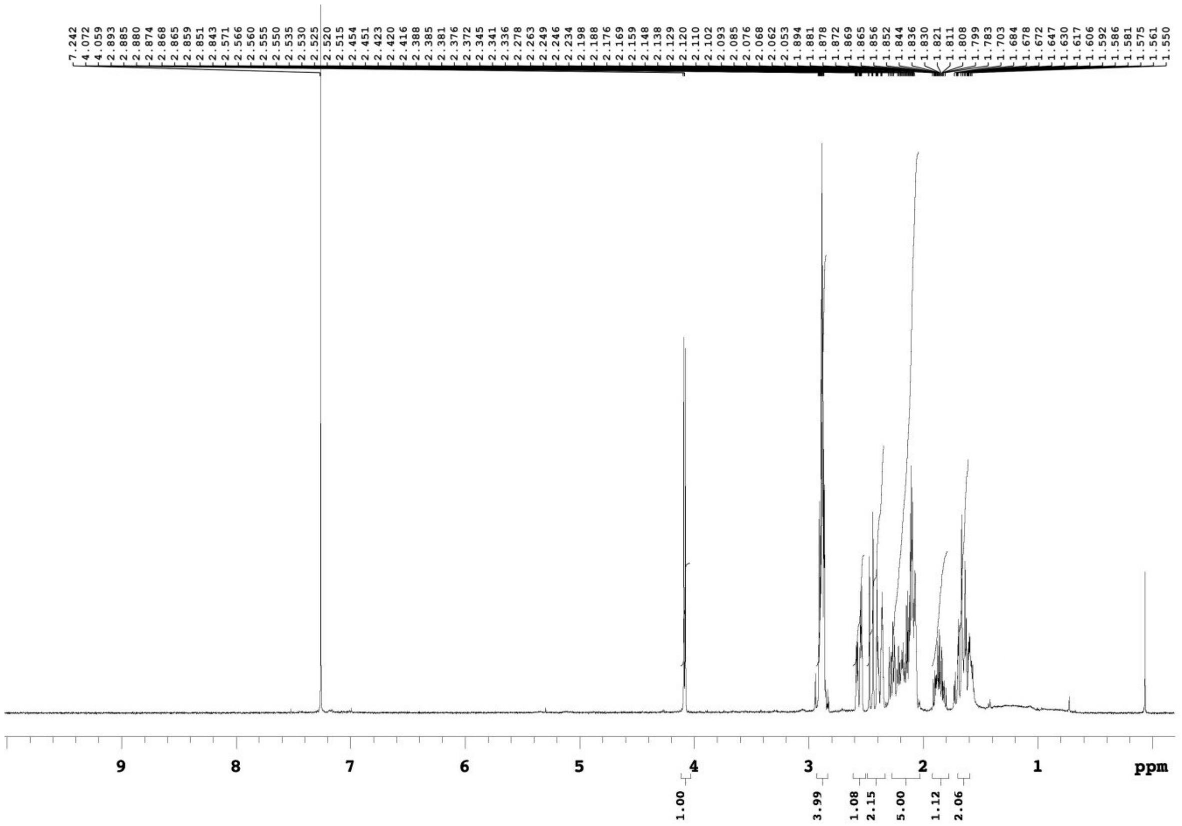
**5q**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2.560
2.555
2.550
2.535
2.530
2.525
2.520
2.515
2.454
2.451
2.423
2.420
2.416
2.388
2.385
2.381
2.376
2.372
2.345
2.341
2.336
2.278
2.263
2.249
2.246
2.234
2.198
2.188
2.176
2.169
2.159
2.148
2.138
2.129
2.120
2.110
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2.068
2.062
2.053
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1.844
1.836
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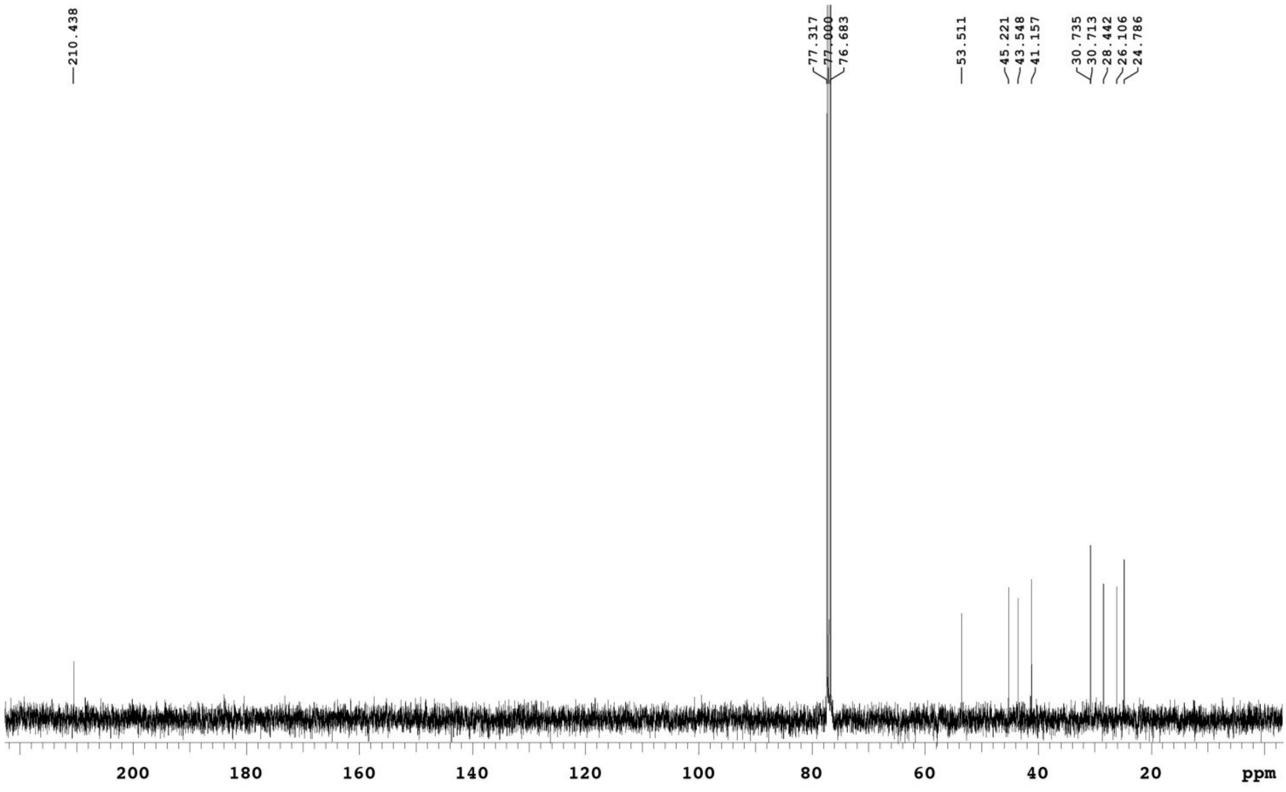
2.06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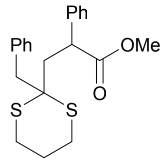
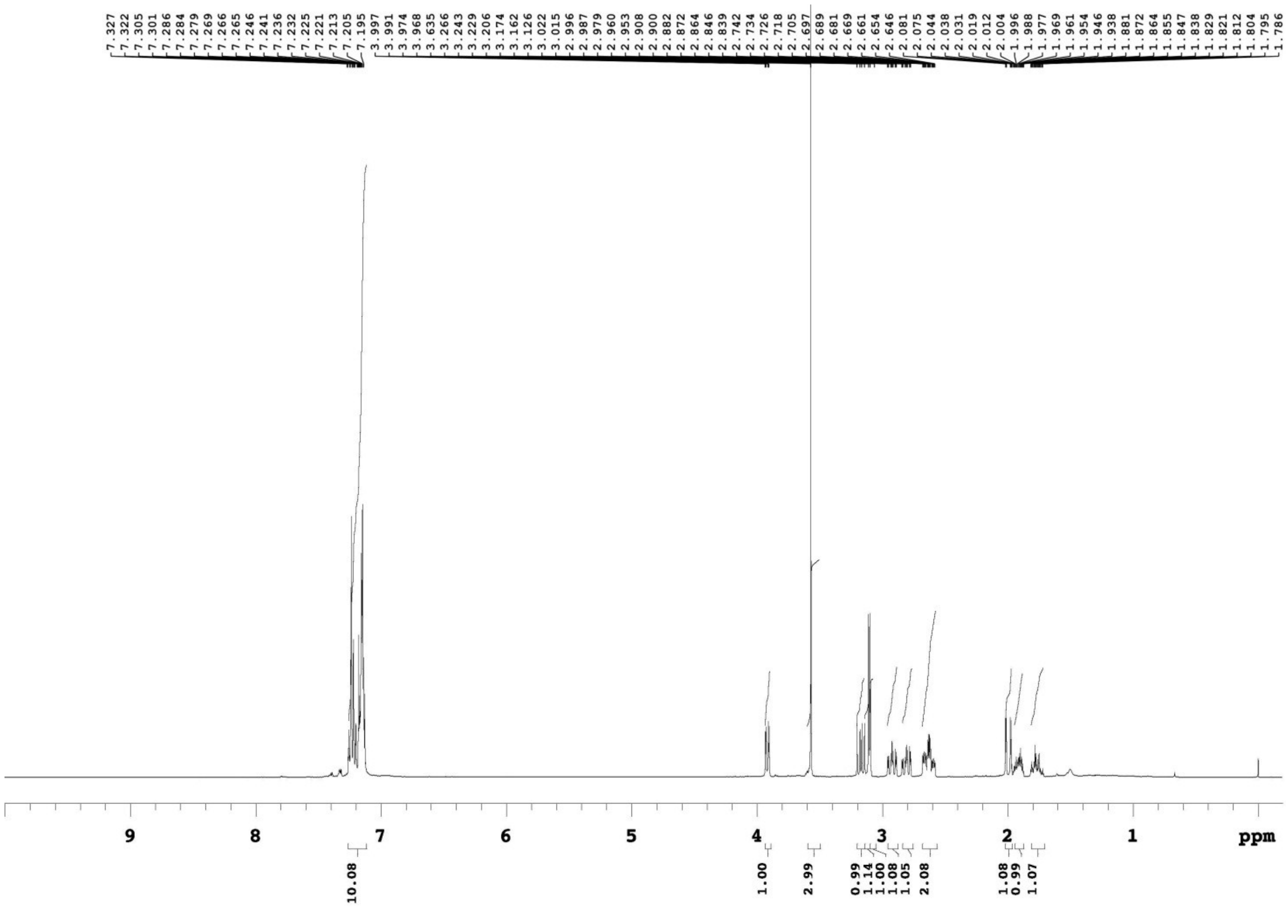
ppm


Ph
Ph
OMe
O
S
S

**5r**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7.266
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7.236
7.232
7.225
7.221
7.213
7.205
7.195
3.997
3.991
3.974
3.968
3.635
3.266
3.243
3.229
3.206
3.174
3.162
3.126
3.022
3.015
2.996
2.987
2.979
2.960
2.953
2.908
2.900
2.882
2.872
2.864
2.846
2.839
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2.734
2.726
2.718
2.705
2.697
2.689
2.681
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2.654
2.646
2.081
2.075
2.044
2.038
2.031
2.019
2.012
2.004
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1.954
1.946
1.938
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1.847
1.838
1.829
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1.786
9
8
7
6
5
4
3
2
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0.99
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1.05
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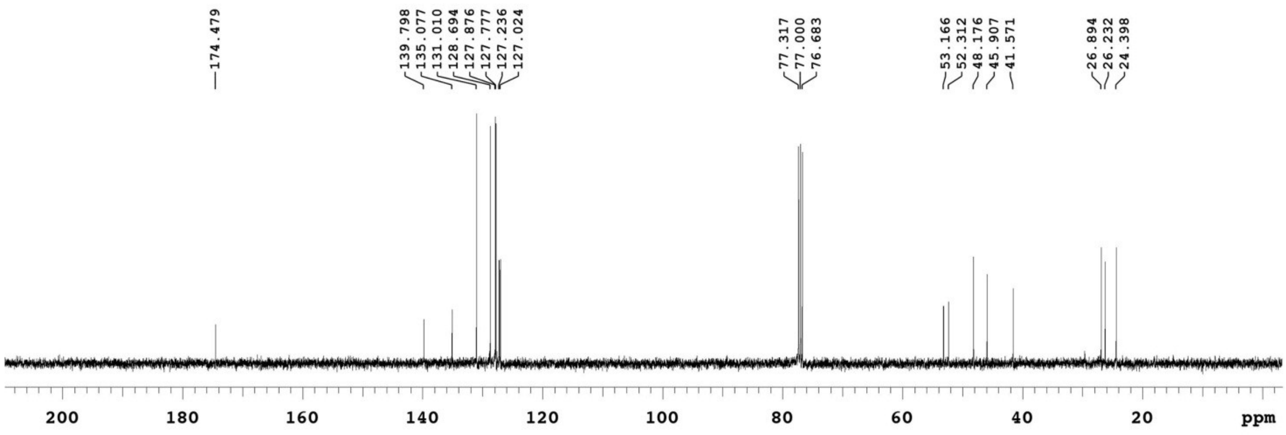
0.99
1.07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76.683
53.166
52.312
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26.894
26.232
24.398
200
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140
120
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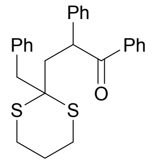
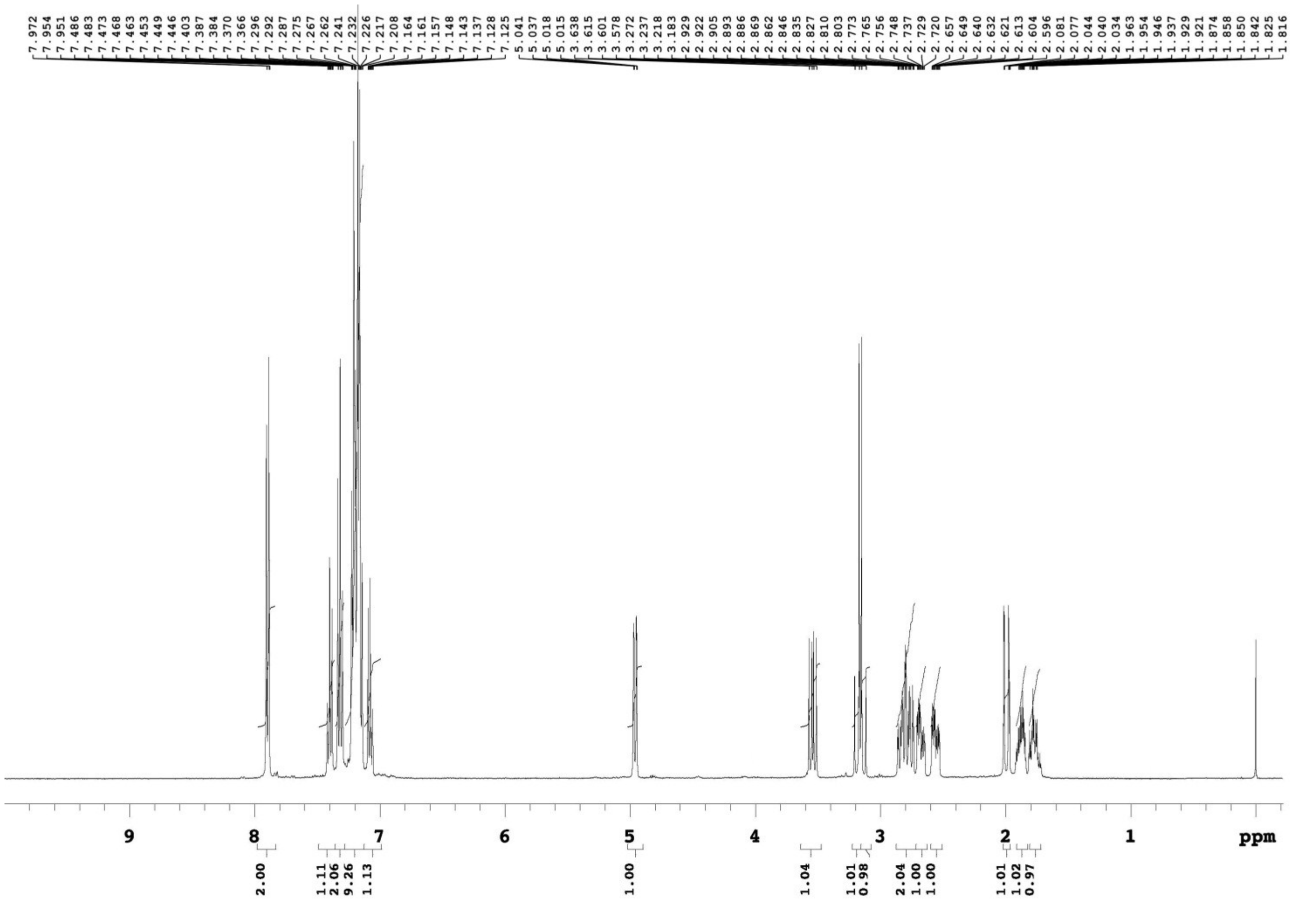
80
60
40
20
ppm


Ph
Ph
Ph
O
S
S

**5s**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7.463
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7.446
7.403
7.387
7.384
7.370
7.366
7.296
7.292
7.287
7.275
7.267
7.262
7.241
7.232
7.226
7.217
7.208
7.164
7.161
7.157
7.148
7.143
7.137
7.128
7.125
5.041
5.037
5.018
5.015
3.638
3.615
3.601
3.578
3.272
3.237
3.218
3.183
2.929
2.922
2.905
2.893
2.886
2.869
2.862
2.846
2.835
2.827
2.810
2.803
2.773
2.765
2.756
2.748
2.737
2.729
2.720
2.657
2.649
2.640
2.632
2.621
2.613
2.604
2.596
2.081
2.077
2.044
2.040
2.034
1.963
1.954
1.946
1.937
1.929
1.921
1.874
1.858
1.850
1.842
1.825
1.816
9
8
7
6
5
4
3
2
1
ppm
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1.11
2.06
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1.04
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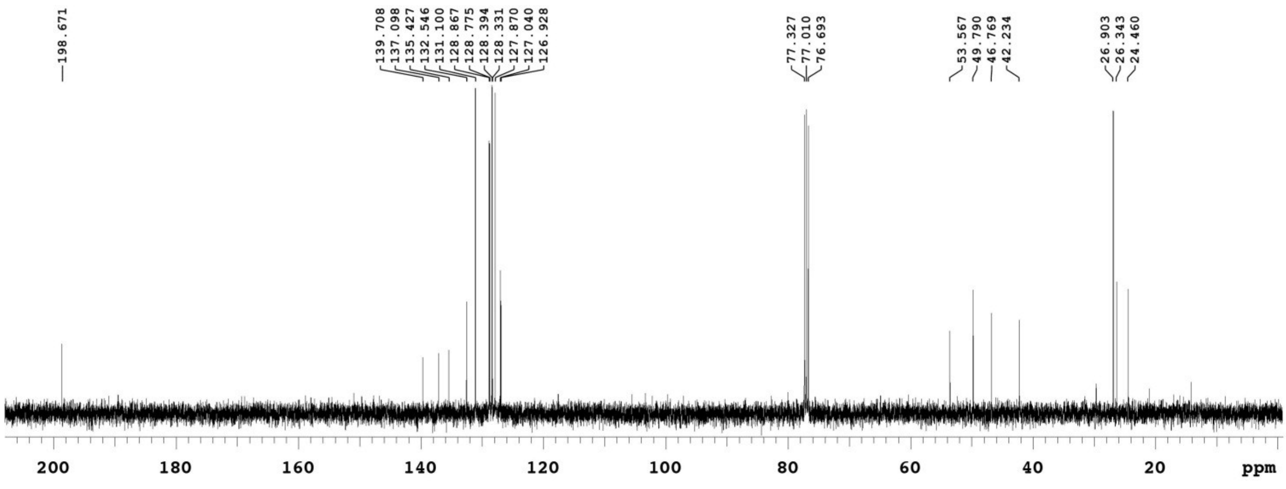
1.00
1.00
1.01
1.02
0.97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128.775
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127.870
127.040
126.928
77.327
77.010
76.693
53.567
49.790
46.769
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26.903
26.343
24.460
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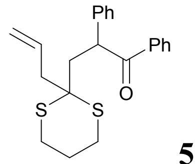
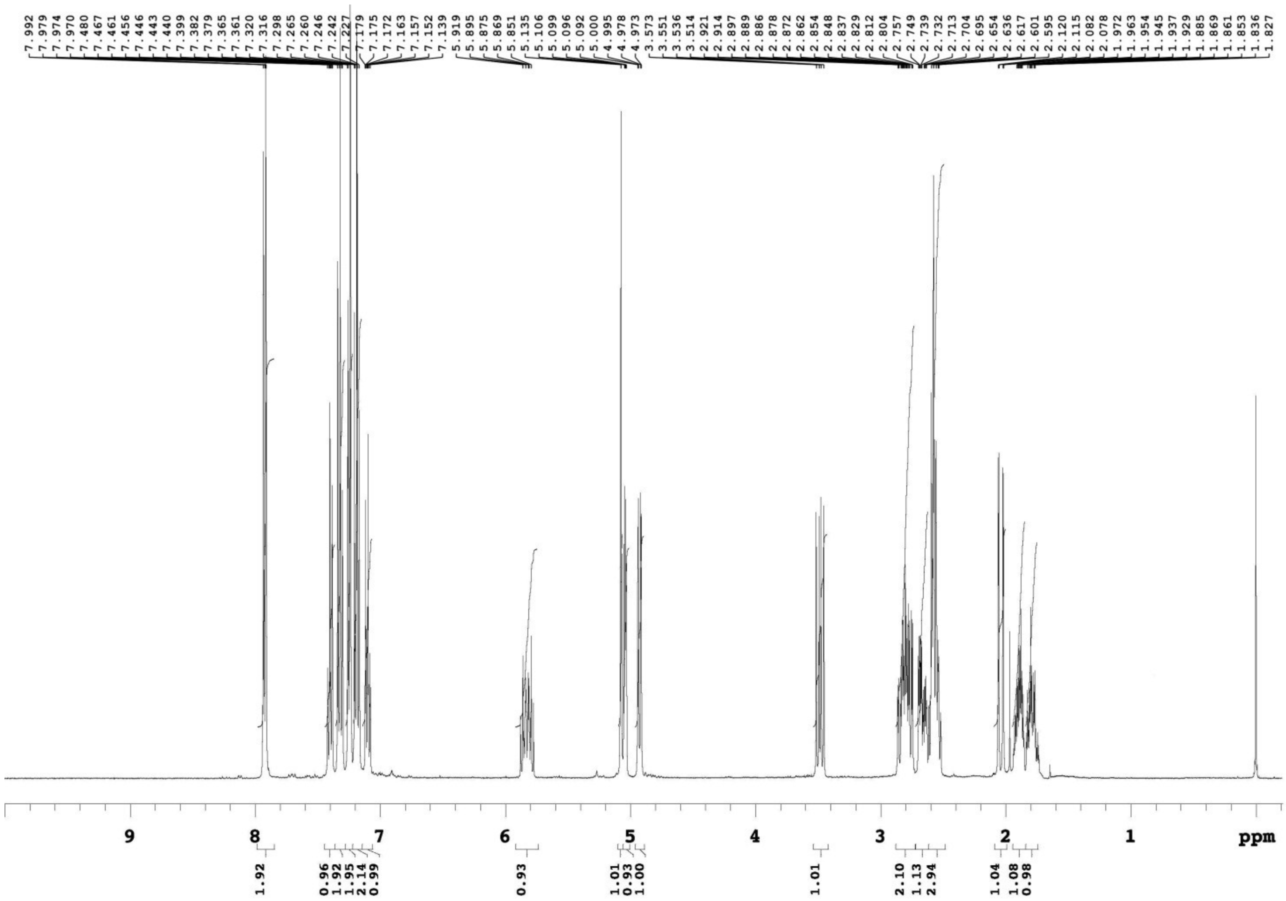
180
160
140
120
100
80
60
40
20
ppm


Ph
Ph
O
S
S

**5t**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7.456
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7.443
7.440
7.399
7.382
7.379
7.365
7.361
7.320
7.316
7.298
7.265
7.260
7.246
7.242
7.227
7.179
7.175
7.172
7.163
7.157
7.152
7.139
5.919
5.895
5.875
5.869
5.851
5.135
5.106
5.099
5.096
5.092
5.000
4.995
4.978
4.973
3.573
3.551
3.536
3.514
2.921
2.914
2.897
2.889
2.886
2.878
2.872
2.862
2.854
2.848
2.837
2.829
2.812
2.804
2.757
2.749
2.739
2.732
2.713
2.704
2.695
2.654
2.636
2.617
2.601
2.595
2.120
2.115
2.082
2.078
1.972
1.963
1.954
1.945
1.937
1.929
1.885
1.869
1.861
1.853
1.836
1.827
9
8
7
6
5
4
3
2
1
ppm
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0.96
1.92
1.95
2.14
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0.93
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0.93
1.00
1.01
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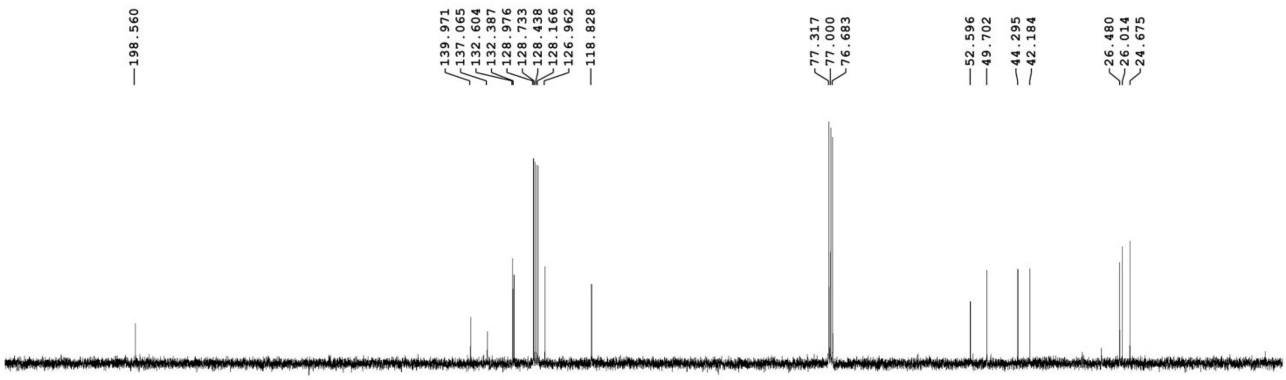
2.94
1.04
1.08
0.98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77.000
76.683
52.596
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26.480
26.014
24.675
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140
120
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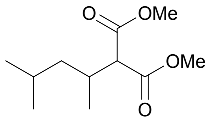
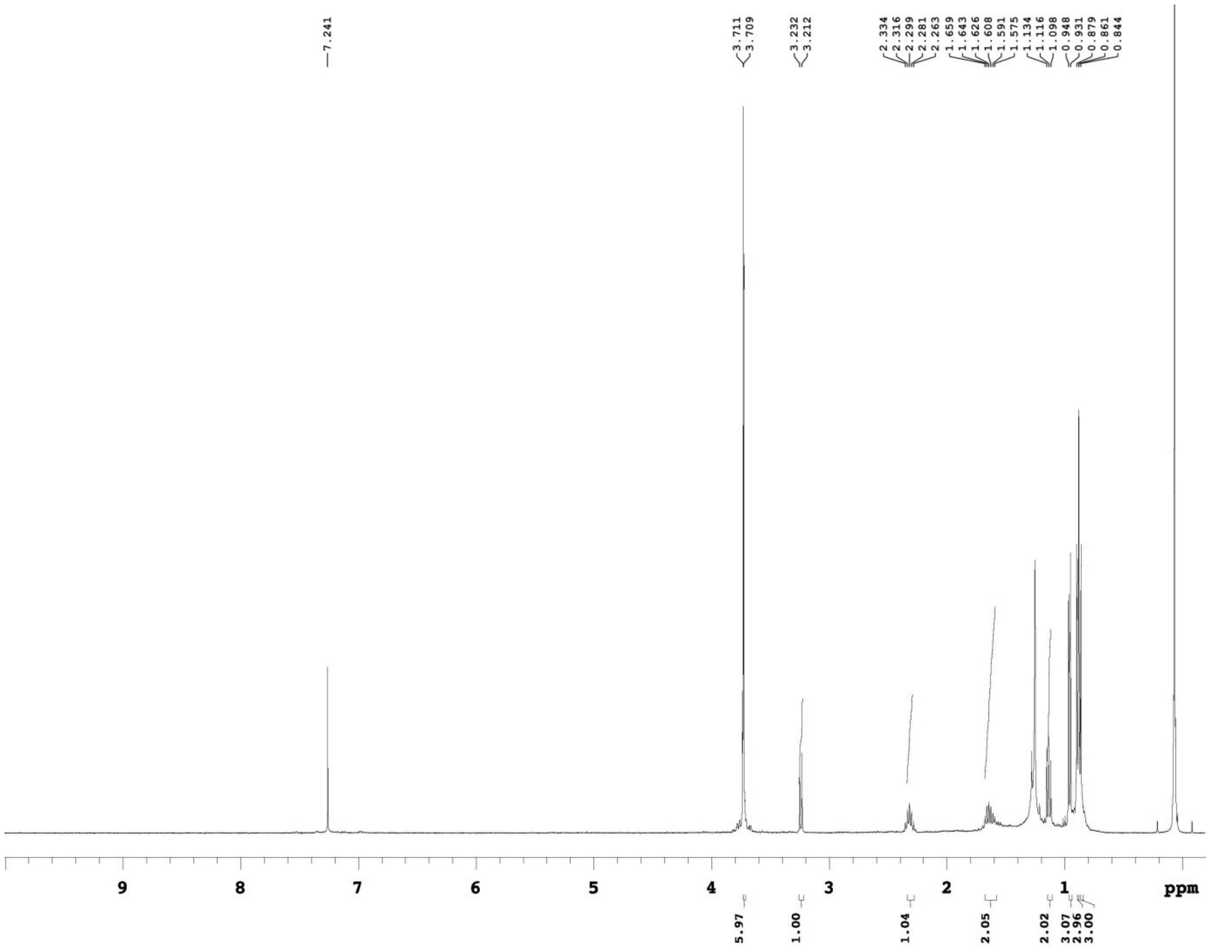
80
60
40
20
ppm


O
OMe
OMe
O

**6**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3.232
3.212
2.334
2.316
2.299
2.281
2.263
1.659
1.643
1.626
1.608
1.591
1.575
1.134
1.116
1.098
0.948
0.931
0.879
0.861
0.844
9
8
7
6
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4
3
2
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ppm
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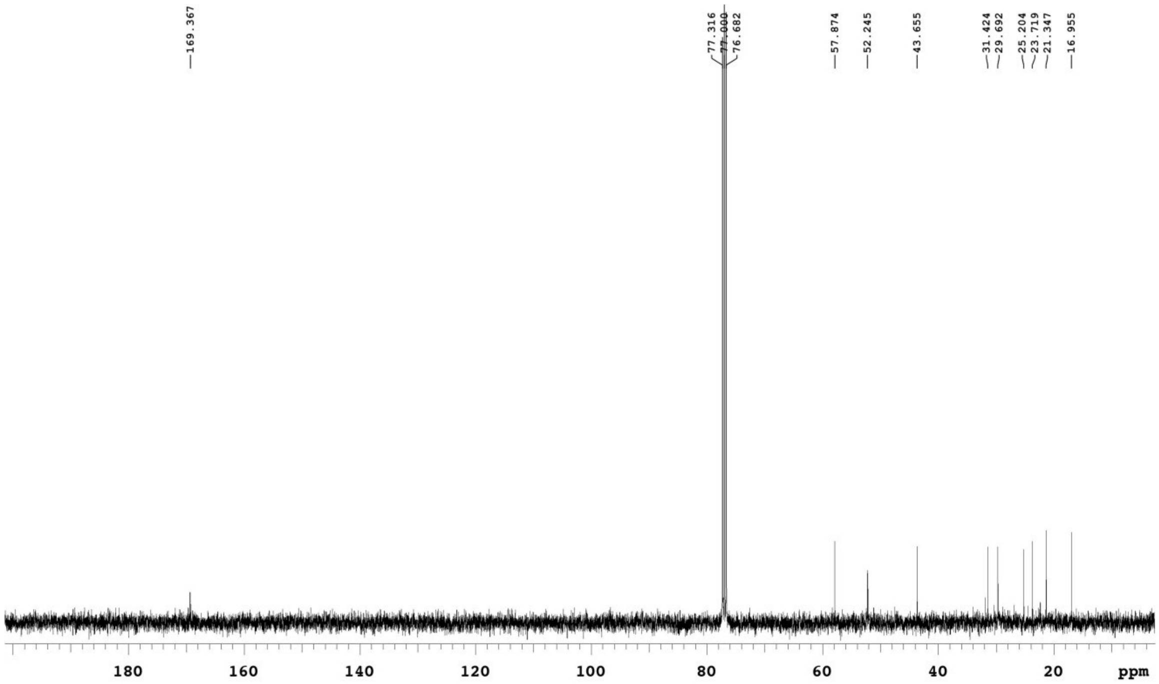
2.05
2.02
3.07
2.96
3.00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16.955
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140
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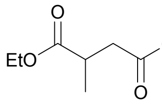
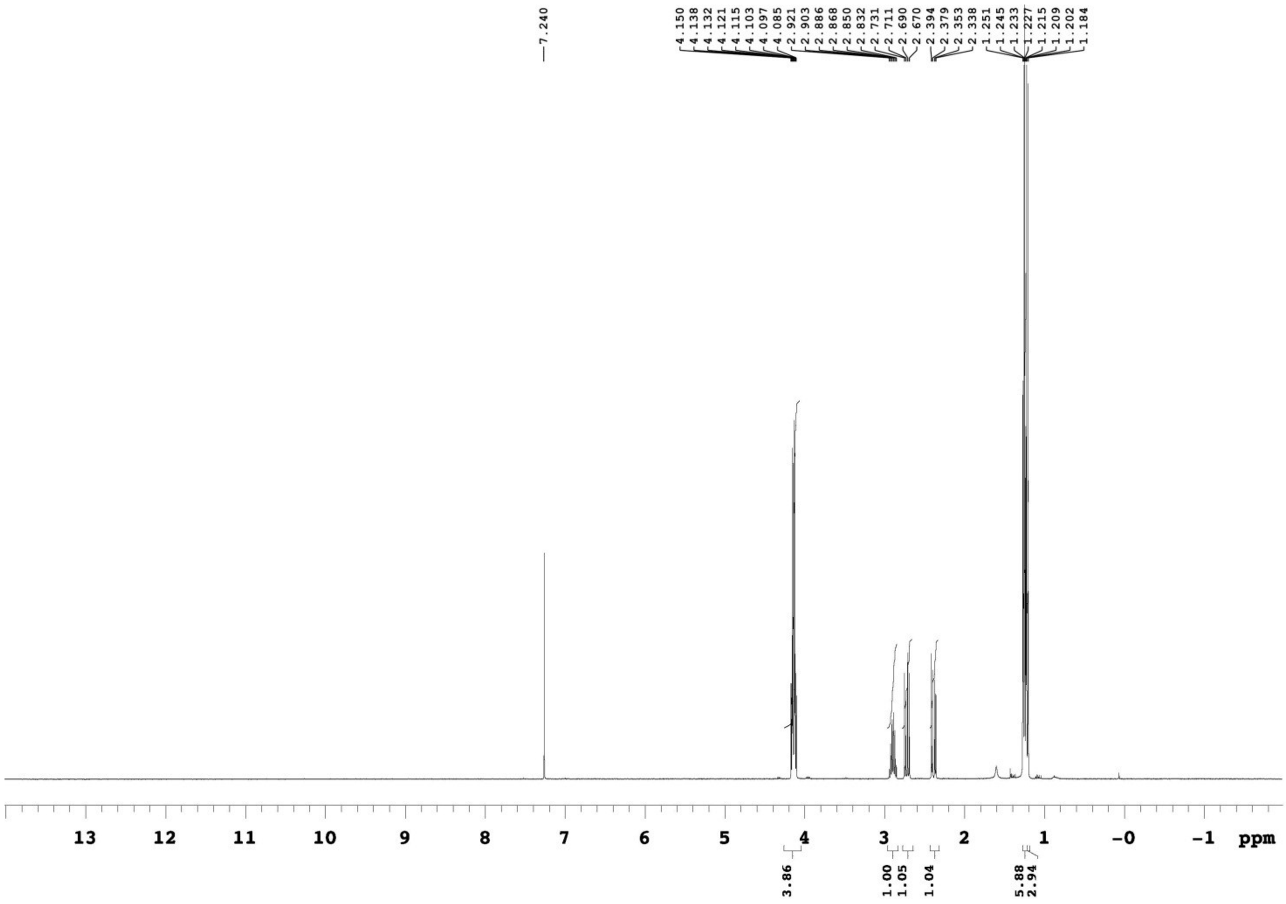
60
40
20
ppm


O
EtO
OEt
O

**7**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4.115
4.103
4.097
4.085
2.921
2.903
2.886
2.868
2.850
2.832
2.731
2.711
2.690
2.670
2.394
2.379
2.353
2.338
1.251
1.245
1.233
1.227
1.215
1.209
1.202
1.184
13
12
11
10
9
8
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-1
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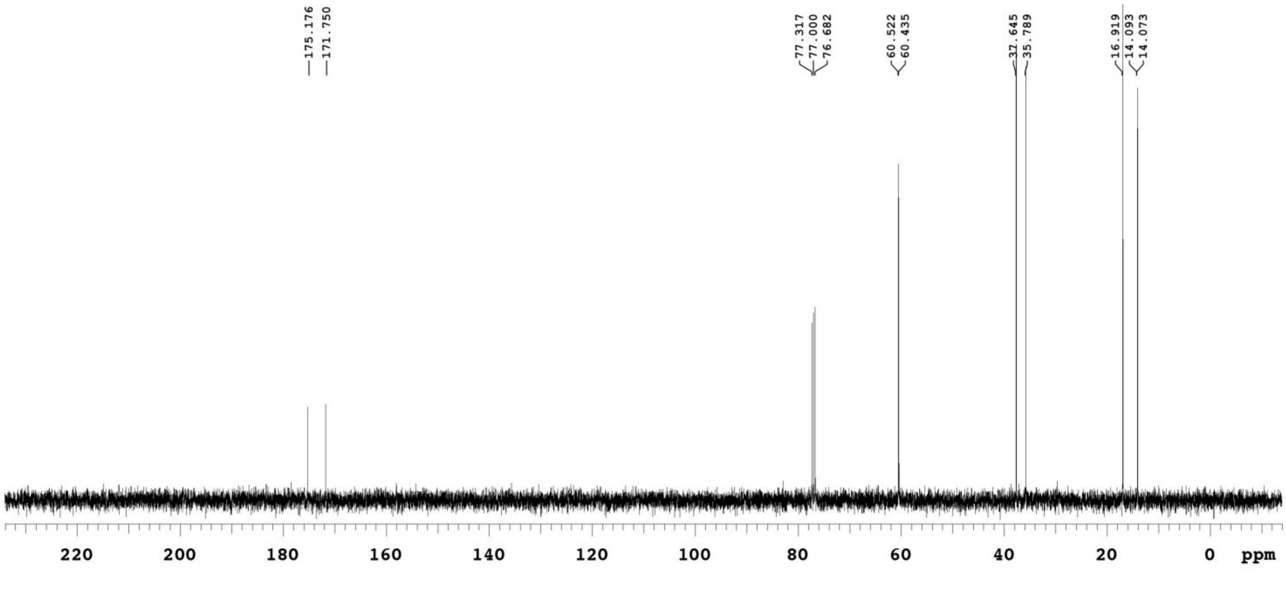
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200
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120
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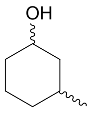
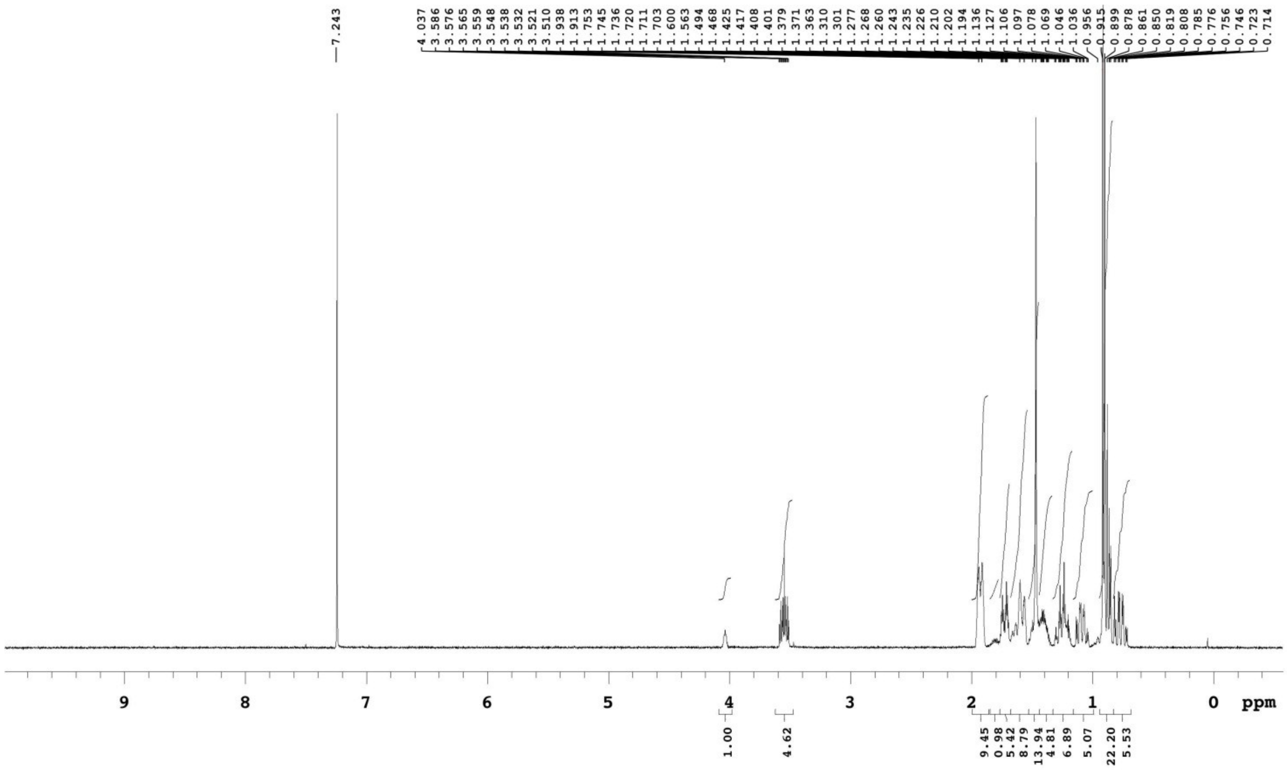
40
20
0
ppm


OH

**8**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3.538
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3.521
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1.913
1.753
1.745
1.736
1.720
1.711
1.703
1.600
1.563
1.494
1.468
1.425
1.417
1.408
1.401
1.379
1.371
1.363
1.310
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1.136
1.127
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1.097
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1.036
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0.915
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0.878
0.861
0.850
0.819
0.808
0.785
0.776
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0.746
0.723
0.714
9
8
7
6
5
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3
2
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0
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4.81
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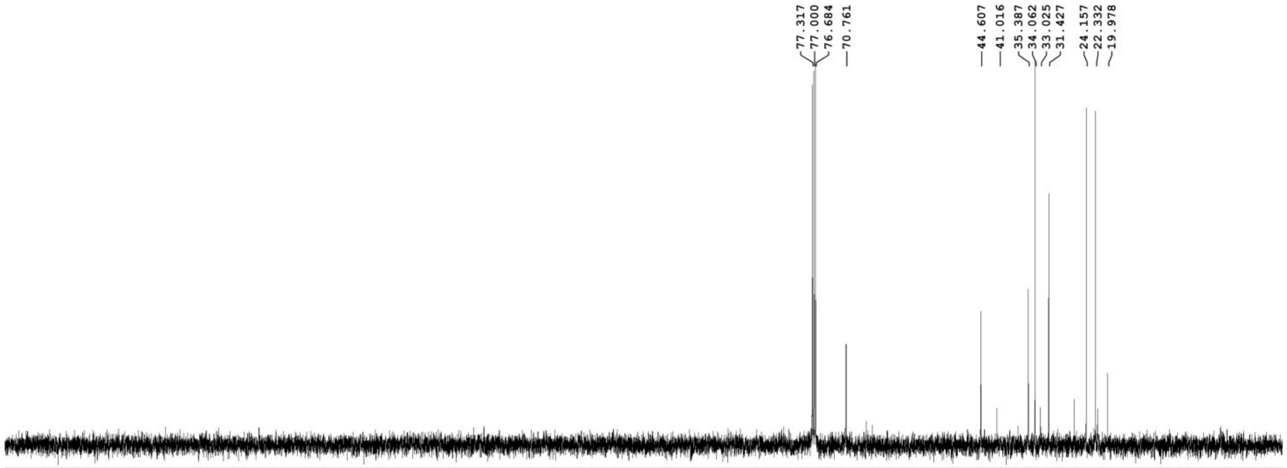
22.20
5.53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33.025
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19.978
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200
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120
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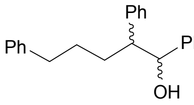
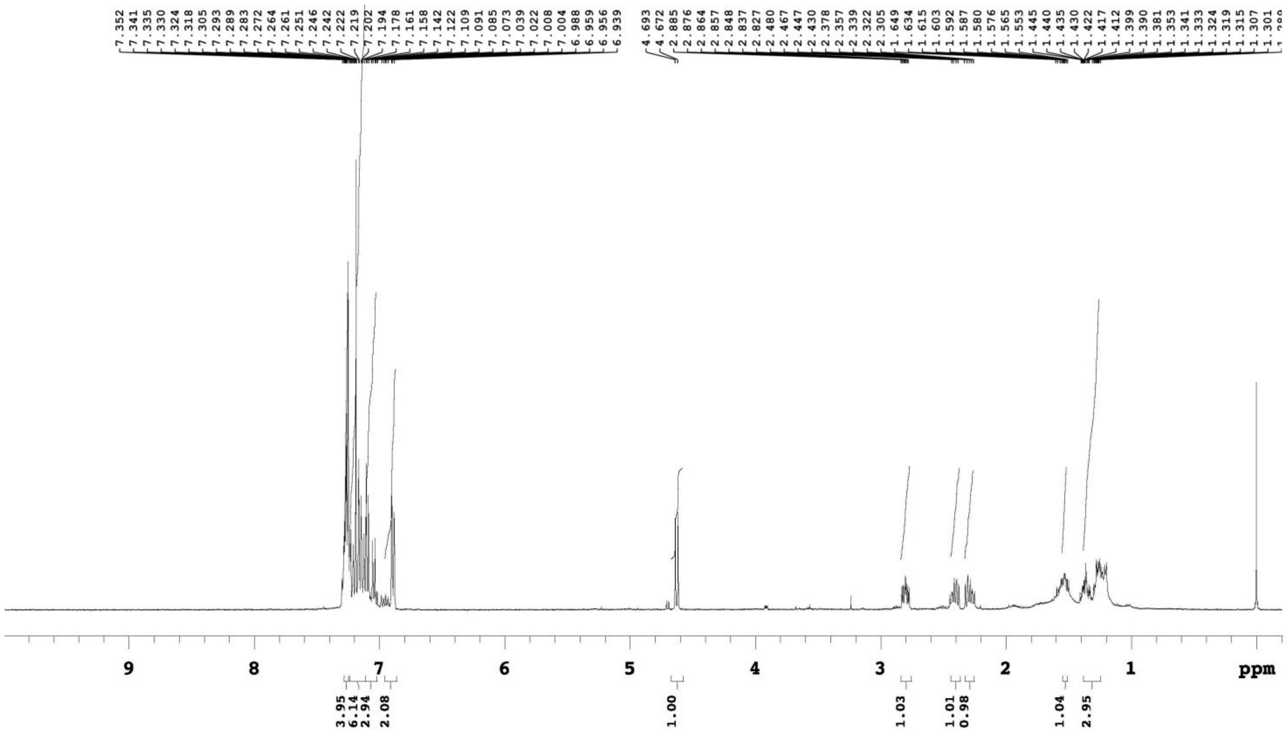
ppm


Ph
Ph
Ph
OH

**9**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7.242
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7.178
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7.122
7.109
7.091
7.085
7.073
7.039
7.022
7.008
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4.672
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2.876
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2.857
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2.430
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1.615
1.603
1.592
1.587
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1.435
1.430
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1.417
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1.324
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1.307
1.301
9
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5
4
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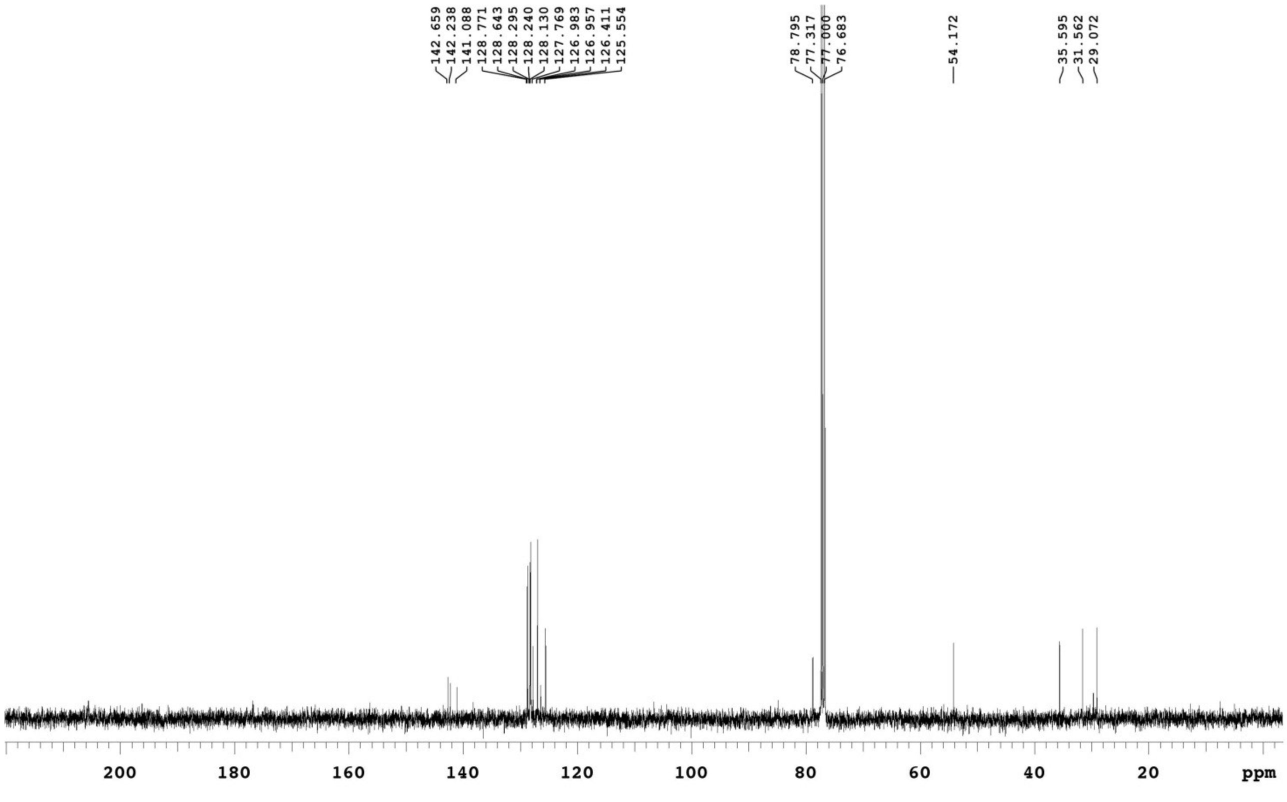
2.95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127.769
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126.411
125.554
78.795
77.317
77.000
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120
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60
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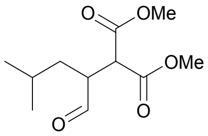
20
ppm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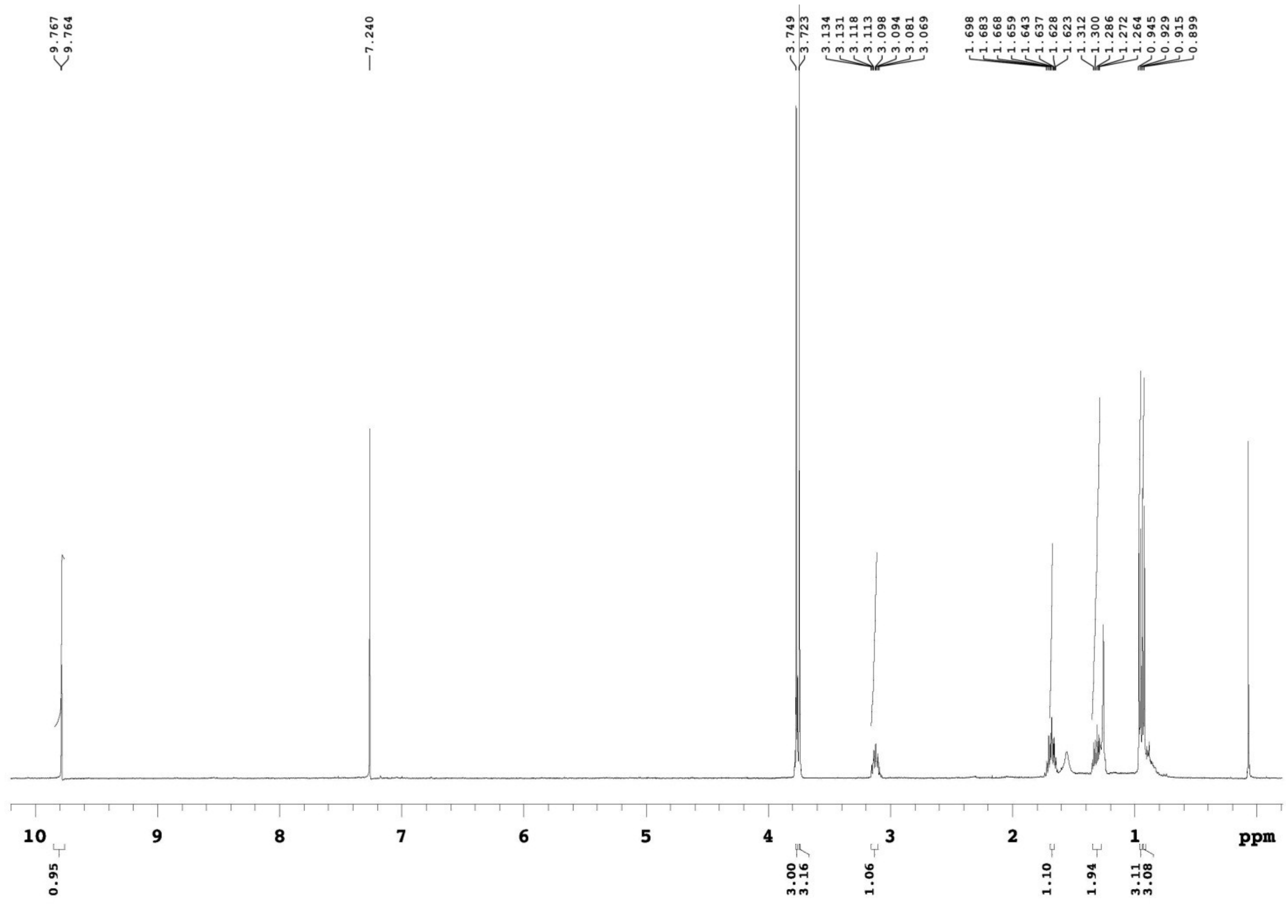
OMe
OMe
O
O

**10**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3.098
3.094
3.081
3.069
1.698
1.683
1.668
1.659
1.643
1.637
1.628
1.623
1.312
1.300
1.286
1.272
1.264
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0.929
0.915
0.899
10
9
8
7
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4
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ppm
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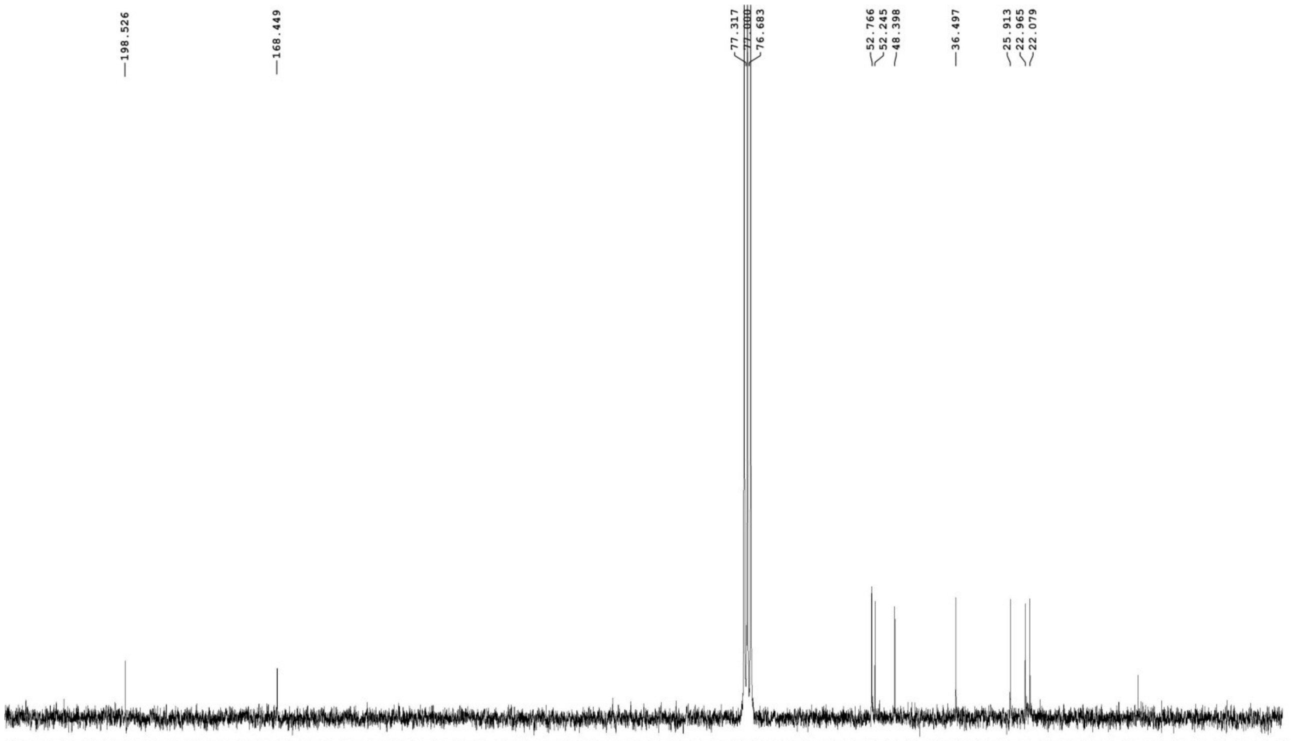
1.06
1.10
1.94
3.11
3.08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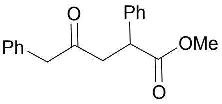
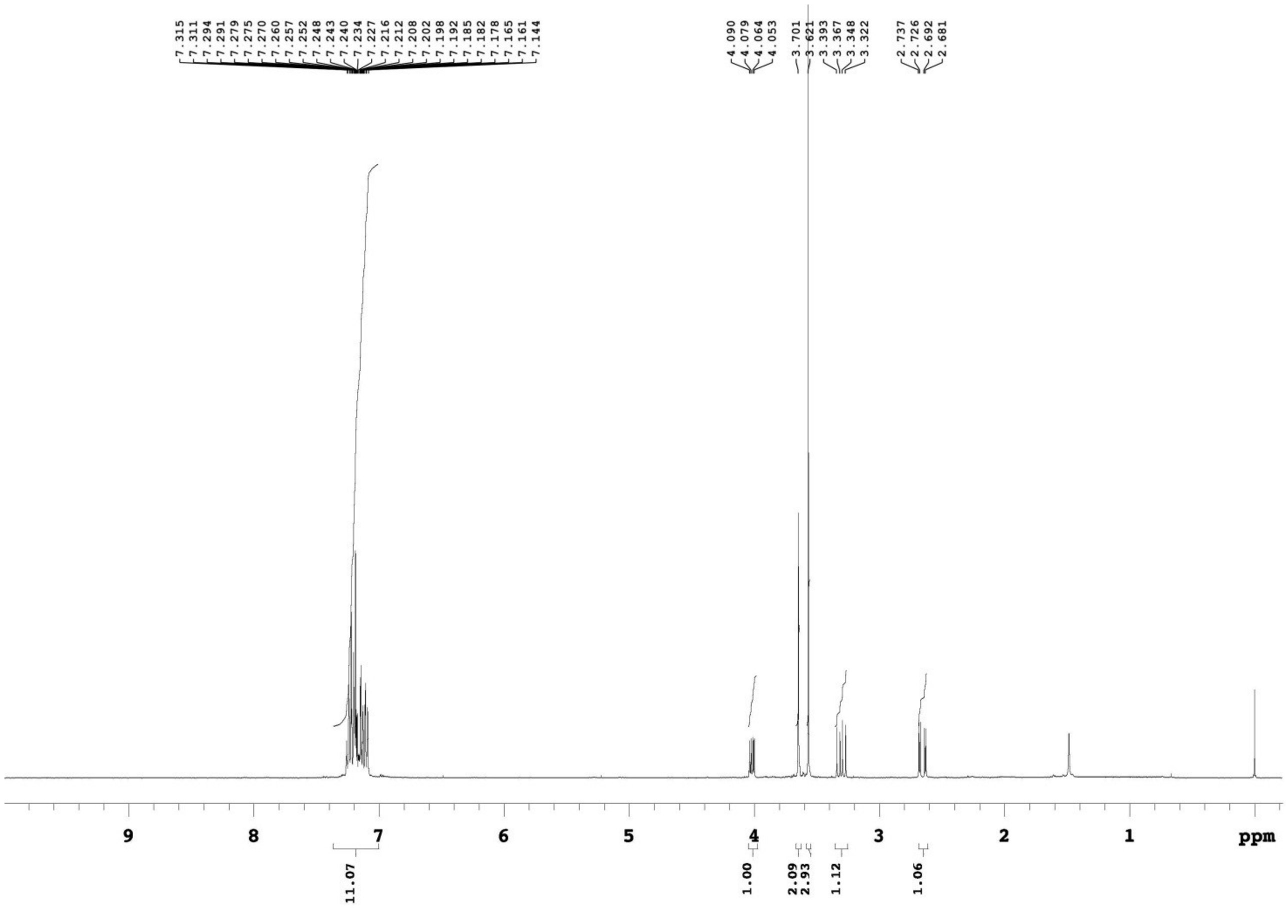
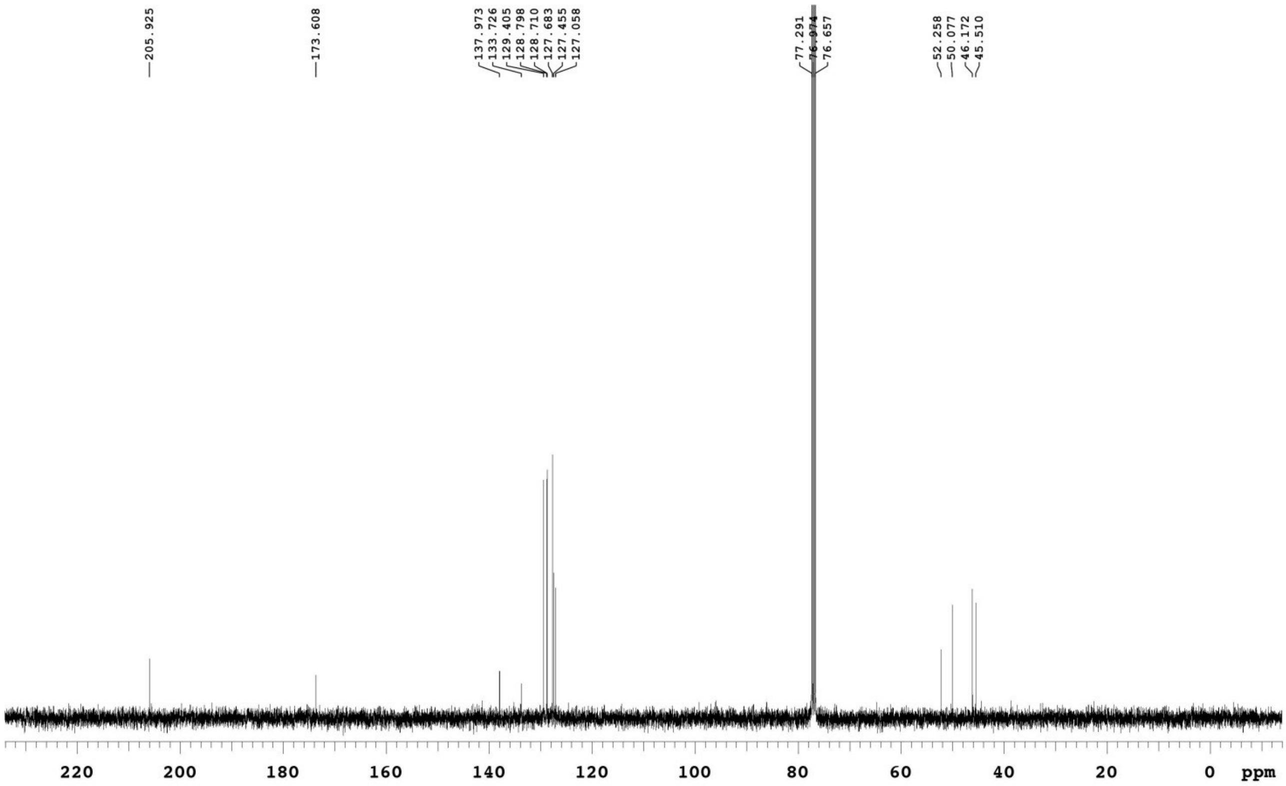
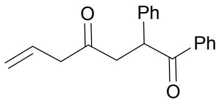
48.398
36.497
25.913
22.965
22.079
200
180
160
140
120
100
80
60
40
20
0
ppm


O
Ph
Ph
OMe
O

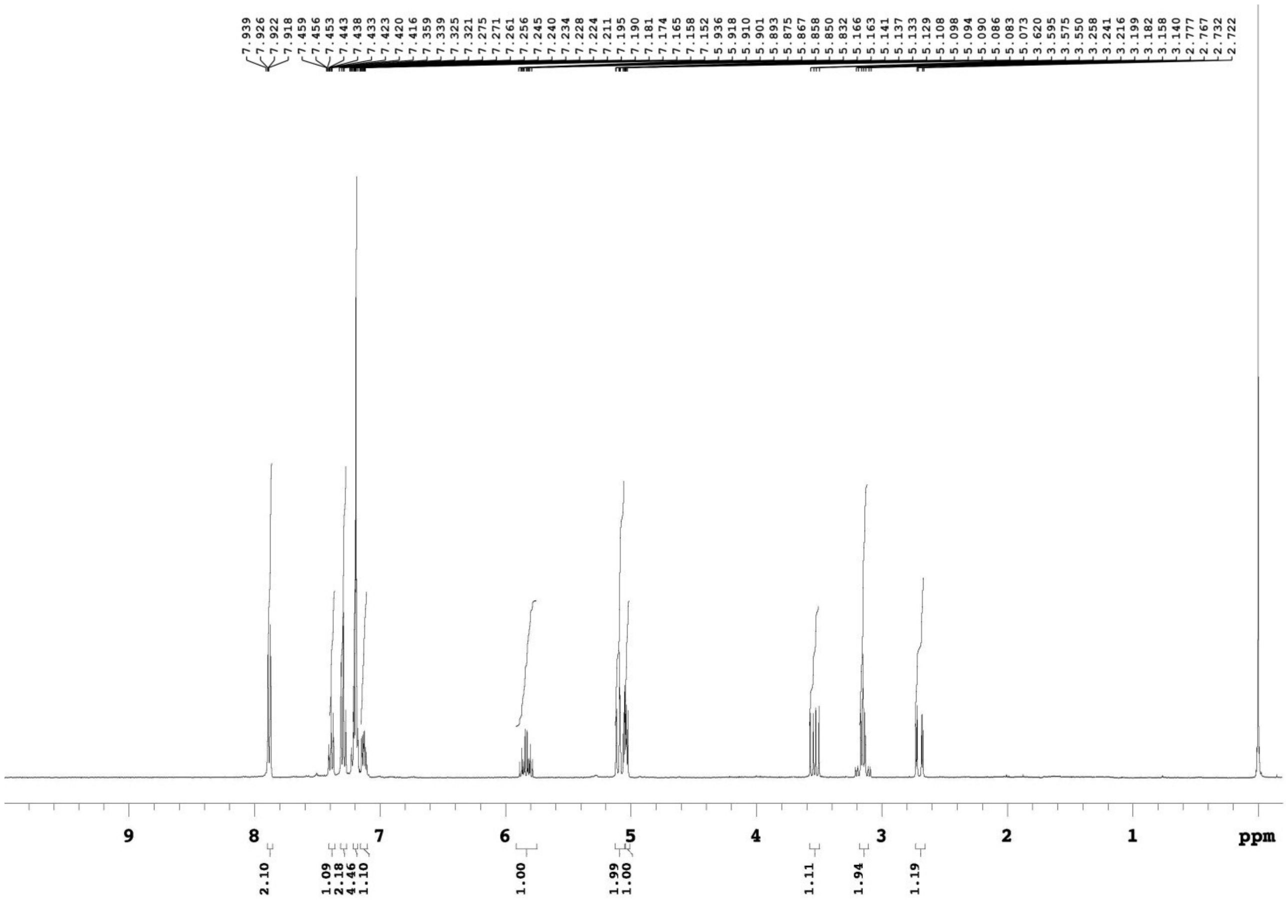
**11**

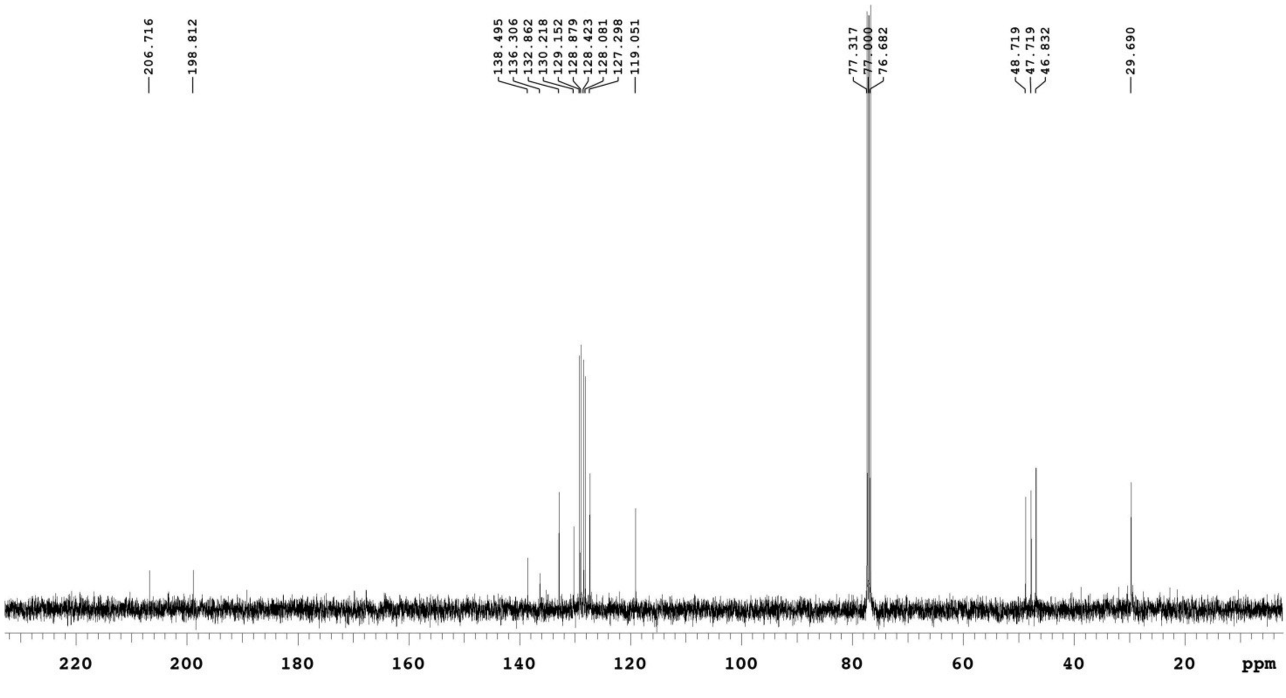

7.315
7.311
7.294
7.291
7.279
7.275
7.270
7.260
7.257
7.252
7.248
7.243
7.240
7.234
7.227
7.216
7.212
7.208
7.202
7.198
7.192
7.185
7.182
7.178
7.165
7.161
7.144
4.090
4.079
4.064
4.053
3.701
3.621
3.393
3.367
3.348
3.322
2.737
2.726
2.692
2.681
9
8
7
6
5
4
3
2
1
ppm
11.07
1.00
2.09
2.93
1.12
1.06

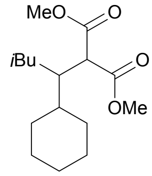

205.925
173.608
137.973
133.726
129.405
128.798
128.710
127.683
127.455
127.058
77.291
76.974
76.657
52.258
50.077
46.172
45.510
220
200
180
160
140
120
100
80
60
40
20
0
ppm



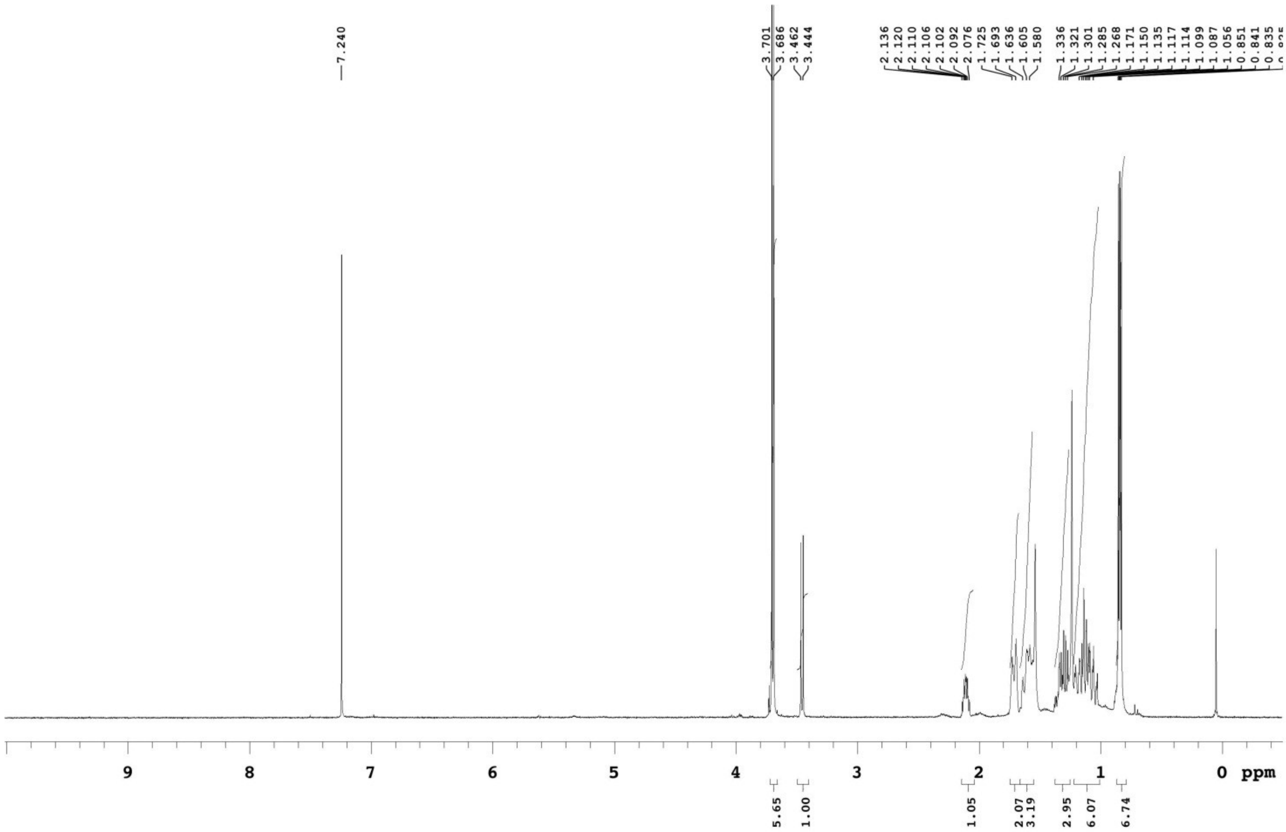
**12**

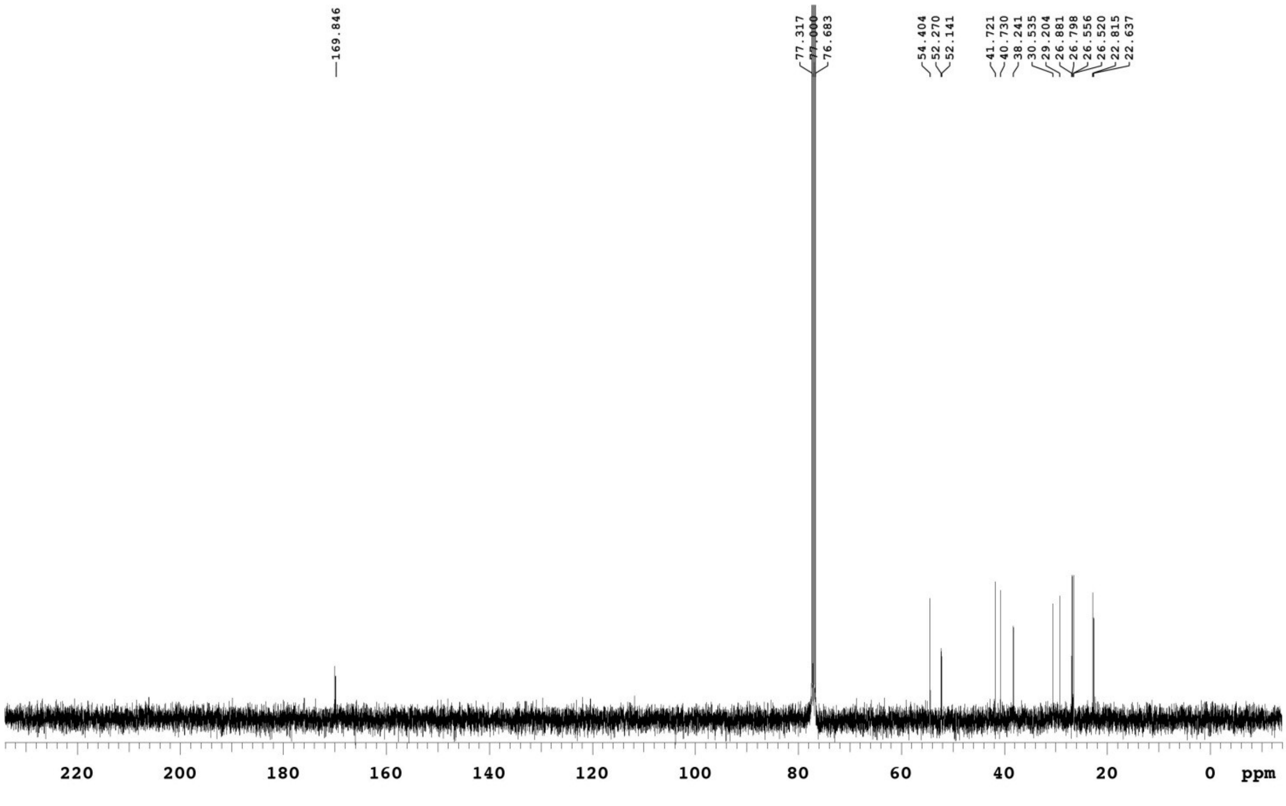

7.939
7.926
7.922
7.918
7.459
7.456
7.453
7.443
7.438
7.433
7.433
7.423
7.420
7.416
7.359
7.339
7.325
7.321
7.275
7.271
7.261
7.256
7.245
7.240
7.234
7.228
7.224
7.211
7.195
7.190
7.181
7.174
7.165
7.158
7.152
5.936
5.918
5.910
5.901
5.893
5.875
5.867
5.858
5.850
5.832
5.166
5.163
5.141
5.137
5.133
5.129
5.108
5.098
5.094
5.090
5.086
5.083
5.073
3.620
3.595
3.575
3.550
3.258
3.241
3.216
3.199
3.182
3.158
3.140
2.777
2.767
2.732
2.722
9
8
7
6
5
4
3
2
1
ppm
2.10
1.09
2.18
4.46
1.10
1.00
1.99
1.00
1.11
1.94
1.19

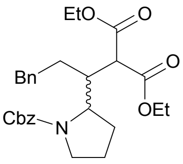

206.716
198.812
138.495
136.306
132.862
130.218
129.152
128.879
128.423
128.081
127.298
119.051
77.317
77.000
76.682
48.719
47.719
46.832
29.690
220
200
180
160
140
120
100
80
60
40
20
ppm


MeO
O
iBu
O
OMe

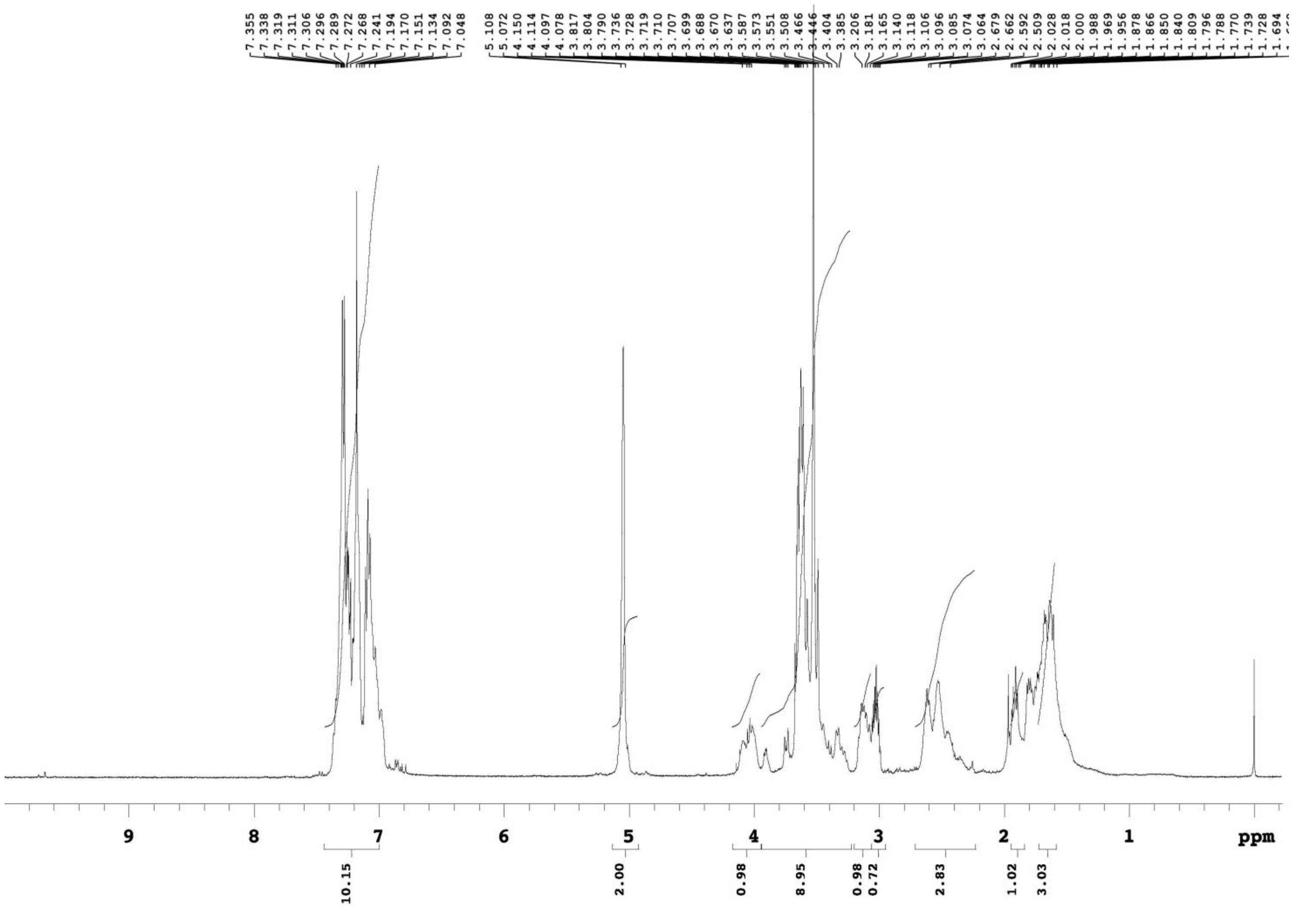
**14**

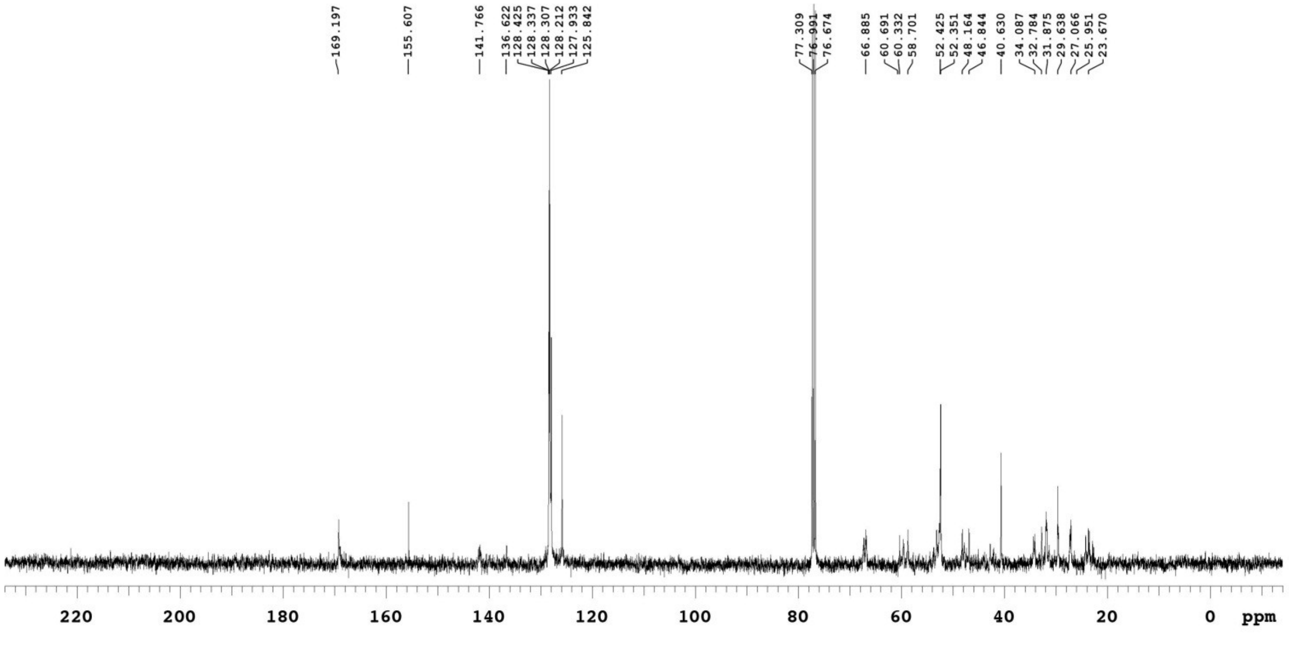

7.240
3.701
3.686
3.462
3.444
2.136
2.120
2.110
2.106
2.102
2.092
2.076
1.725
1.693
1.636
1.605
1.580
1.336
1.321
1.301
1.285
1.268
1.171
1.150
1.135
1.117
1.114
1.099
1.087
1.056
0.851
0.841
0.835
9
8
7
6
5
4
3
2
1
0 ppm
5.65
1.00
1.05
2.07
3.19
2.95
6.07
6.74

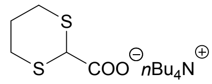

169.846
77.317
77.000
76.683
54.404
52.270
52.141
41.721
40.730
38.241
30.535
29.204
26.881
26.798
26.556
26.520
22.815
22.637
220
200
180
160
140
120
100
80
60
40
20
0 ppm


EtO
O
Bn
O
OEt
Cbz
N

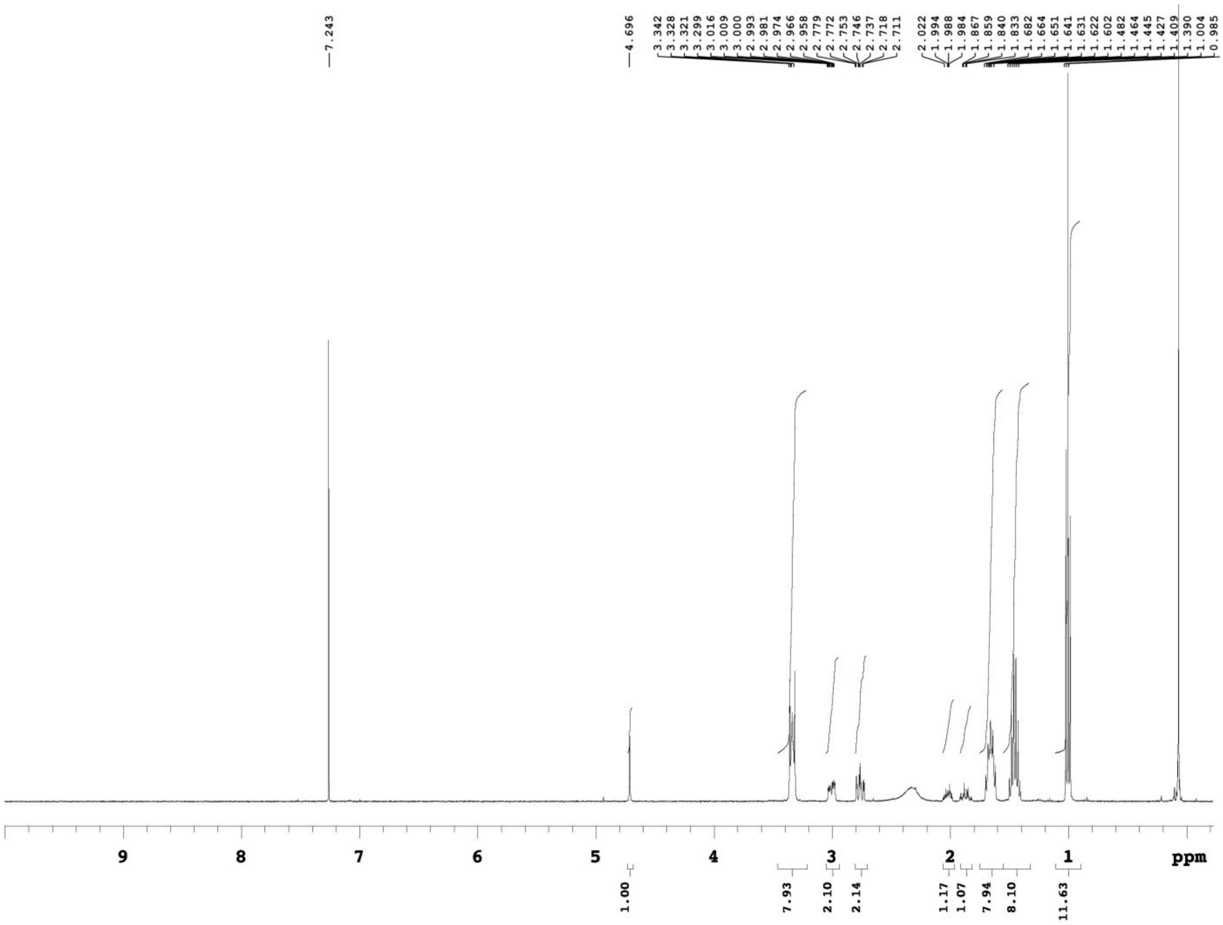
**16**

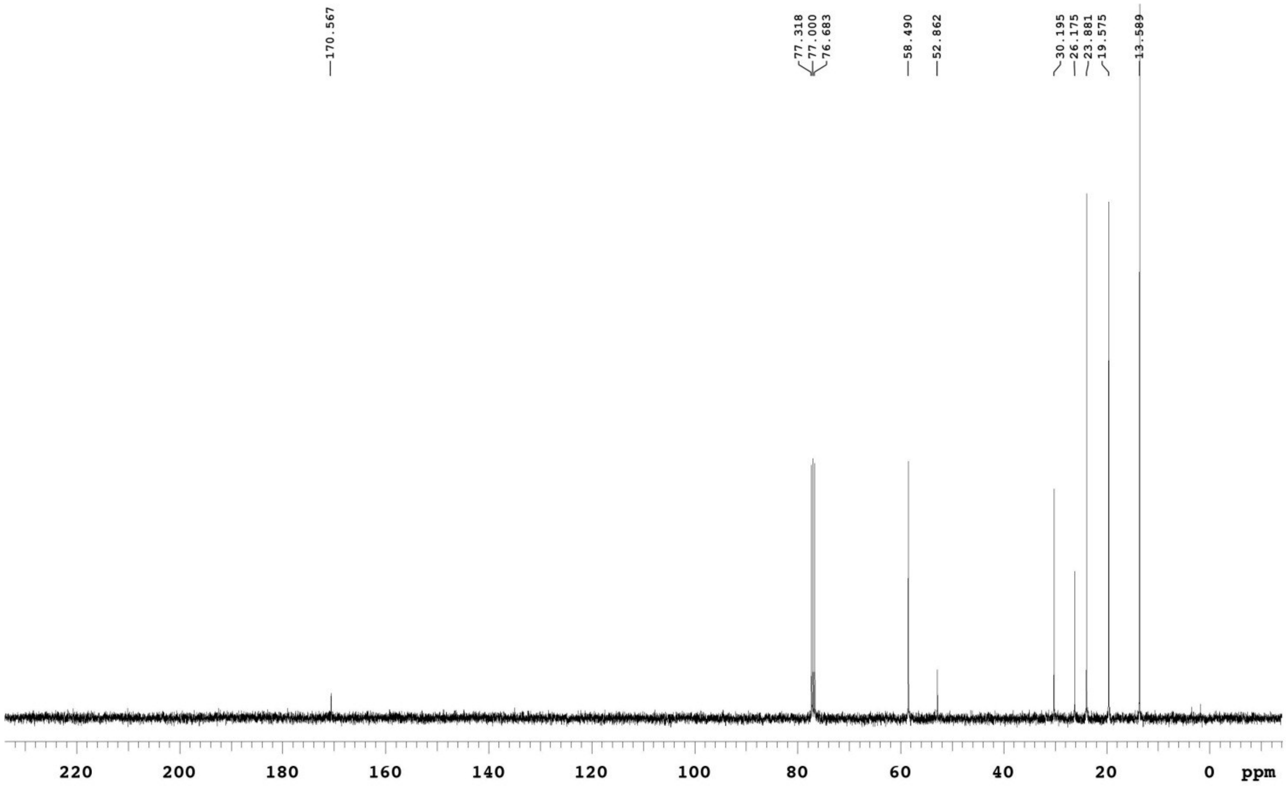

7.355
7.338
7.319
7.311
7.306
7.296
7.289
7.272
7.268
7.241
7.194
7.170
7.151
7.134
7.092
7.048
5.108
5.072
4.150
4.114
4.097
4.078
3.817
3.804
3.790
3.736
3.728
3.719
3.710
3.707
3.699
3.688
3.670
3.637
3.587
3.573
3.551
3.508
3.466
3.446
3.404
3.385
3.206
3.181
3.165
3.140
3.118
3.106
3.096
3.085
3.074
3.064
2.679
2.662
2.592
2.509
2.028
2.018
2.000
1.988
1.969
1.956
1.878
1.866
1.850
1.840
1.809
1.796
1.788
1.770
1.739
1.728
1.694
9
8
7
6
5
4
3
2
1
ppm
10.15
2.00
0.98
8.95
0.98
0.72
2.83
1.02
3.03

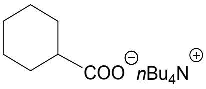

169.197
155.607
141.766
136.622
128.425
128.337
128.307
128.212
127.933
125.842
77.309
76.991
76.674
66.885
60.691
60.332
58.701
52.425
52.351
48.164
46.844
40.630
34.087
32.784
31.875
29.638
27.066
25.951
23.670
220
200
180
160
140
120
100
80
60
40
20
0
ppm


S
S
COO⊖nBu4N⊕

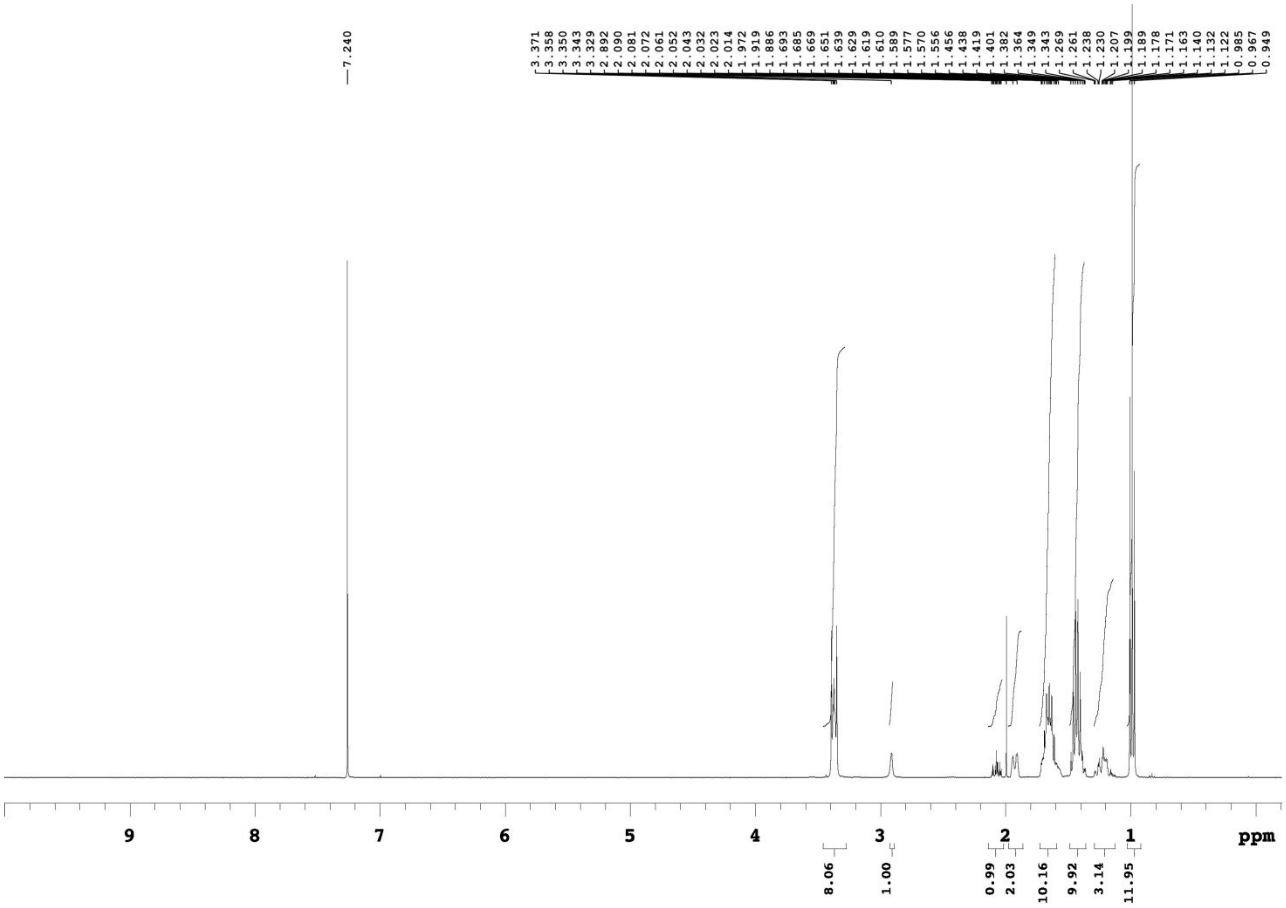
**17**

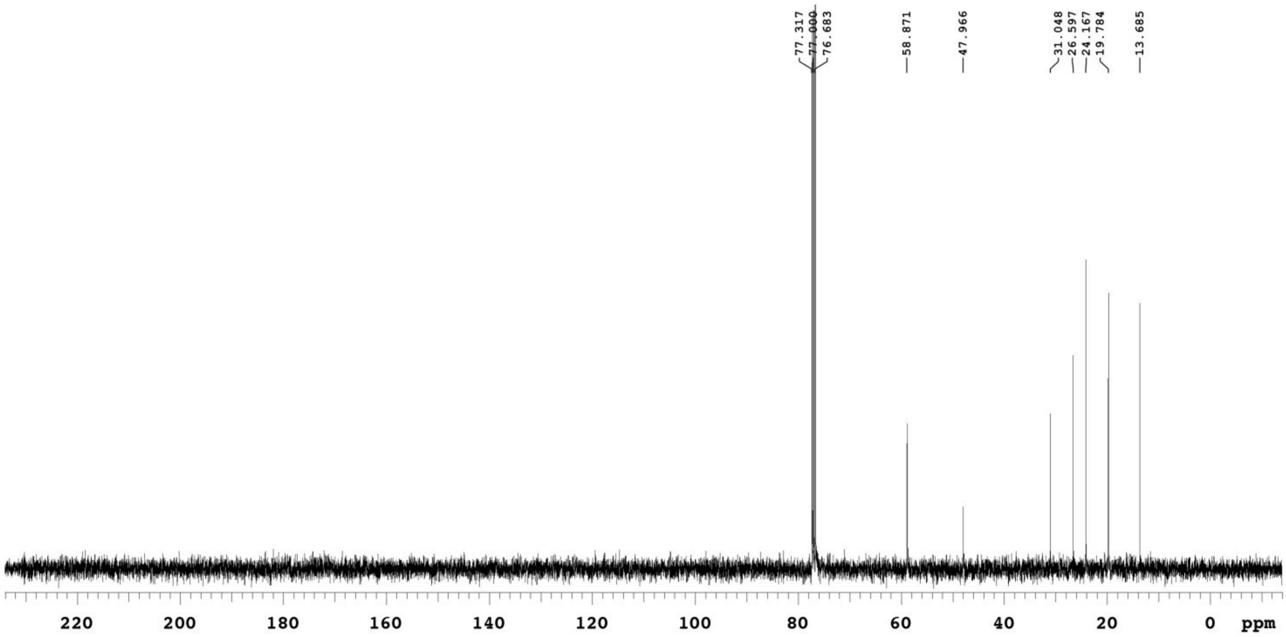

7.243
4.696
3.342
3.328
3.321
3.299
3.016
3.009
3.000
2.993
2.981
2.974
2.966
2.958
2.779
2.772
2.753
2.746
2.737
2.718
2.711
2.022
1.994
1.988
1.984
1.867
1.859
1.840
1.833
1.682
1.664
1.651
1.641
1.631
1.622
1.602
1.482
1.464
1.445
1.427
1.409
1.390
1.004
0.985
9
8
7
6
5
4
3
2
1
ppm
1.00
7.93
2.10
2.14
1.17
1.07
7.94
8.10
11.63

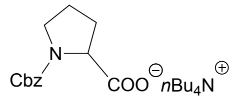

170.567
77.318
77.000
76.683
58.490
52.862
30.195
26.175
23.881
19.575
13.589
220
200
180
160
140
120
100
80
60
40
20
0
ppm


COO⊖ nBu4N⊕

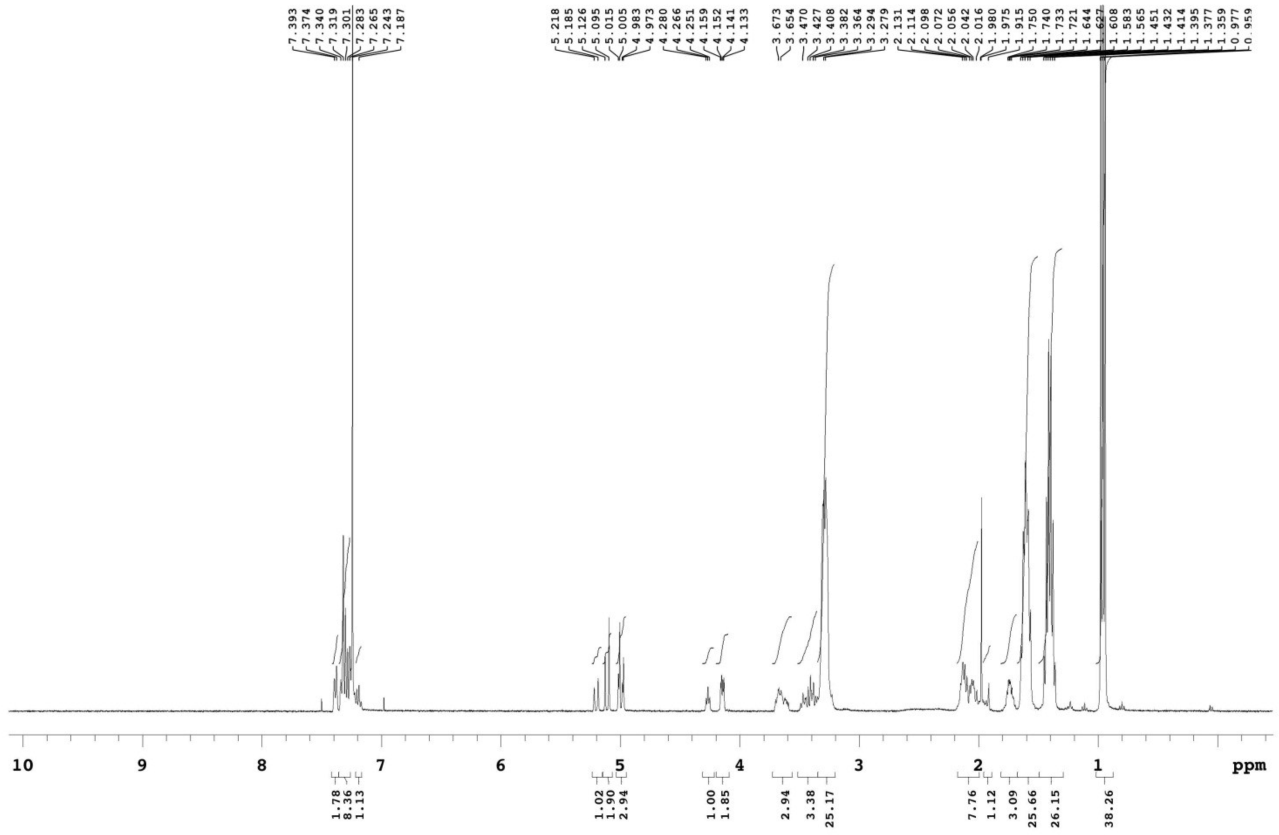
**18**

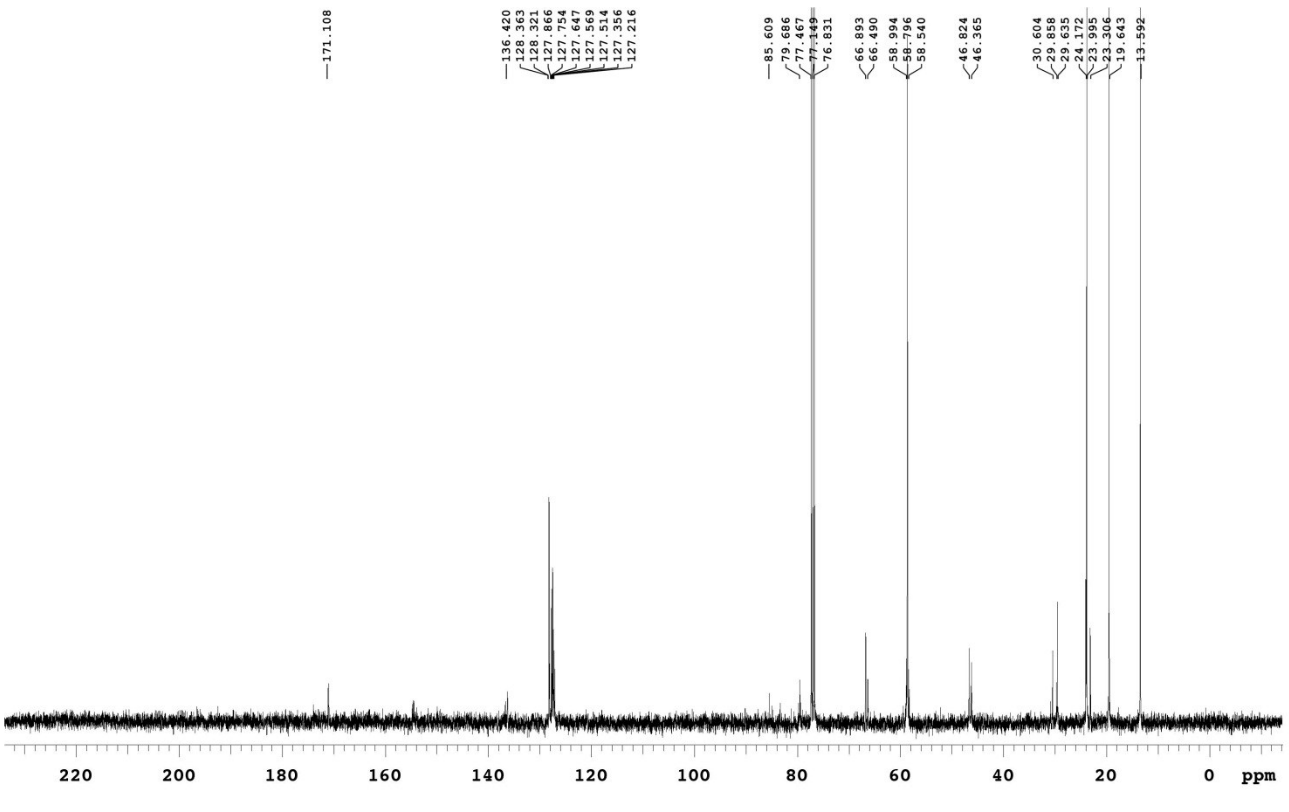

7.240
3.371
3.358
3.350
3.343
3.329
2.892
2.090
2.081
2.072
2.061
2.052
2.043
2.032
2.023
2.014
1.972
1.919
1.886
1.693
1.685
1.669
1.651
1.639
1.629
1.619
1.610
1.589
1.577
1.570
1.556
1.456
1.438
1.419
1.401
1.382
1.364
1.349
1.343
1.269
1.261
1.238
1.230
1.207
1.199
1.189
1.178
1.171
1.163
1.140
1.132
1.122
0.985
0.967
0.949
9
8
7
6
5
4
3
2
1
ppm
8.06
1.00
0.99
2.03
10.16
9.92
3.14
11.95


77.317
77.000
76.683
58.871
47.966
31.048
26.597
24.167
19.784
13.685
220
200
180
160
140
120
100
80
60
40
20
0
ppm

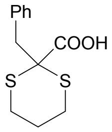

N
Cbz
COO⊖ nBu4N⊕

**19**

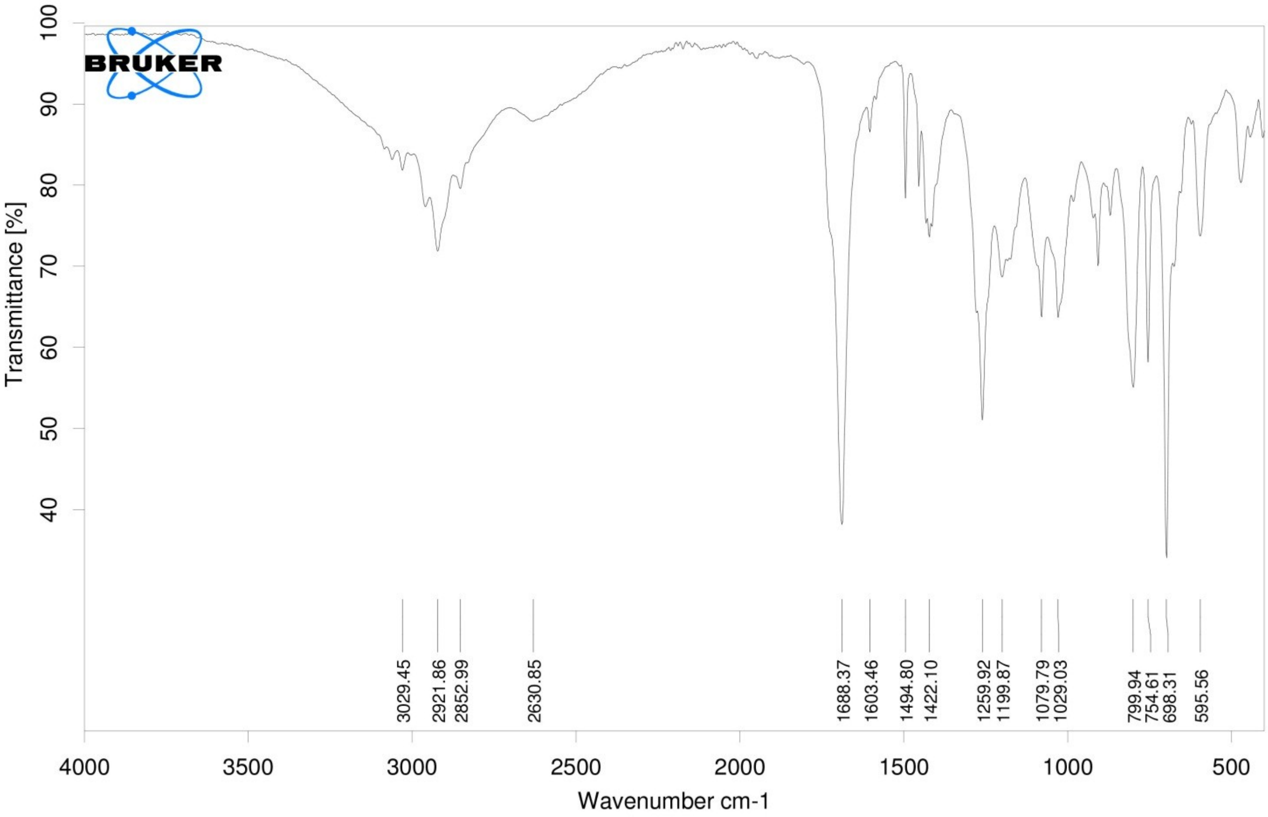

7.393
7.374
7.340
7.319
7.301
7.283
7.265
7.243
7.187
5.218
5.185
5.126
5.095
5.015
5.005
4.983
4.973
4.280
4.266
4.251
4.159
4.152
4.141
4.133
3.673
3.654
3.470
3.427
3.408
3.382
3.364
3.294
3.279
2.131
2.114
2.098
2.072
2.056
2.042
2.016
1.980
1.975
1.915
1.750
1.740
1.733
1.721
1.644
1.627
1.608
1.583
1.565
1.451
1.432
1.414
1.395
1.377
1.359
0.977
0.959
10
9
8
7
6
5
4
3
2
1
ppm
1.78
8.36
1.13
1.02
1.90
2.94
1.00
1.85
2.94
3.38
25.17
7.76
1.12
3.09
25.66
26.15
38.26

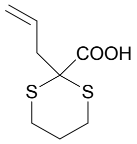

171.108
136.420
128.363
128.321
127.866
127.754
127.647
127.569
127.514
127.356
127.216
85.609
79.686
77.467
77.149
76.831
66.893
66.490
58.994
58.796
58.540
46.824
46.365
30.604
29.858
29.635
24.172
23.995
23.306
19.643
13.592
220
200
180
160
140
120
100
80
60
40
20
0
ppm

**Copies of IR spectra** (all spectra were recorded neat)

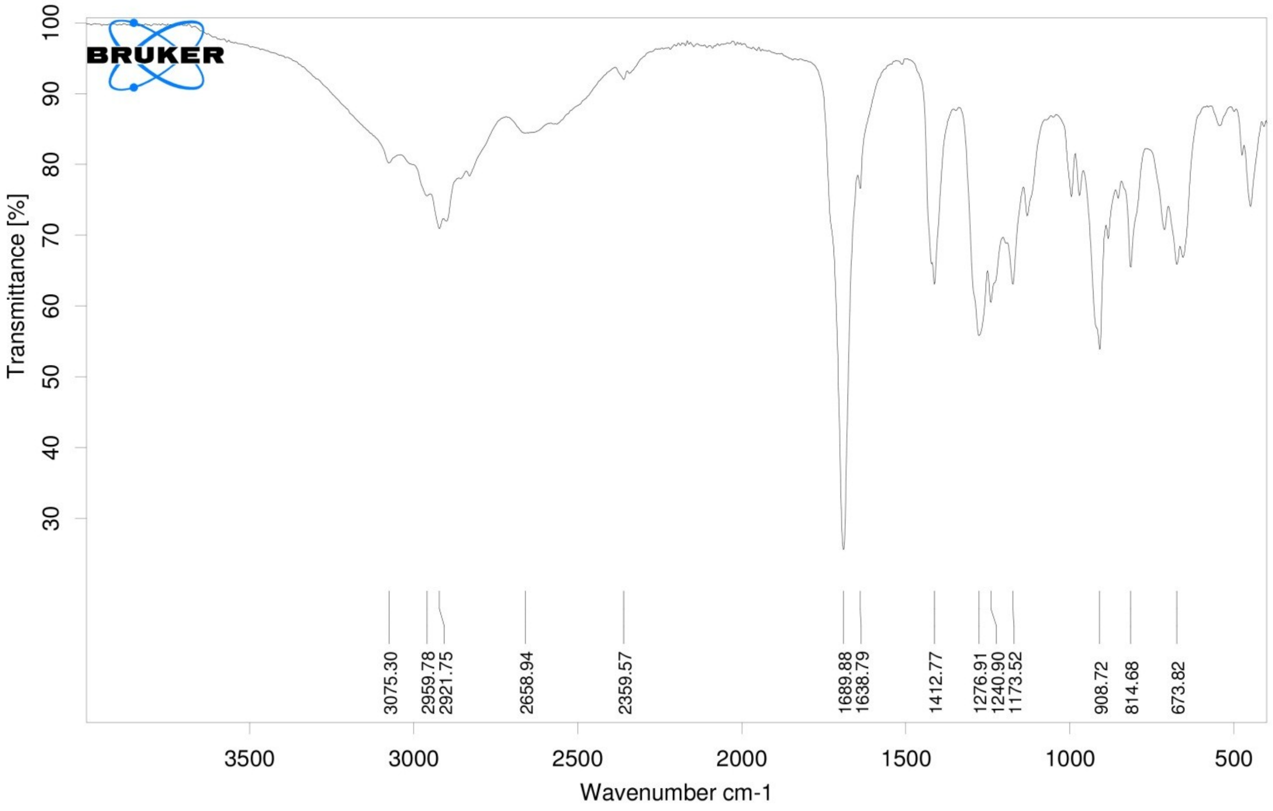


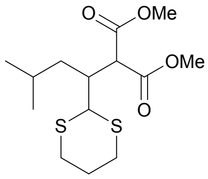
**4b**



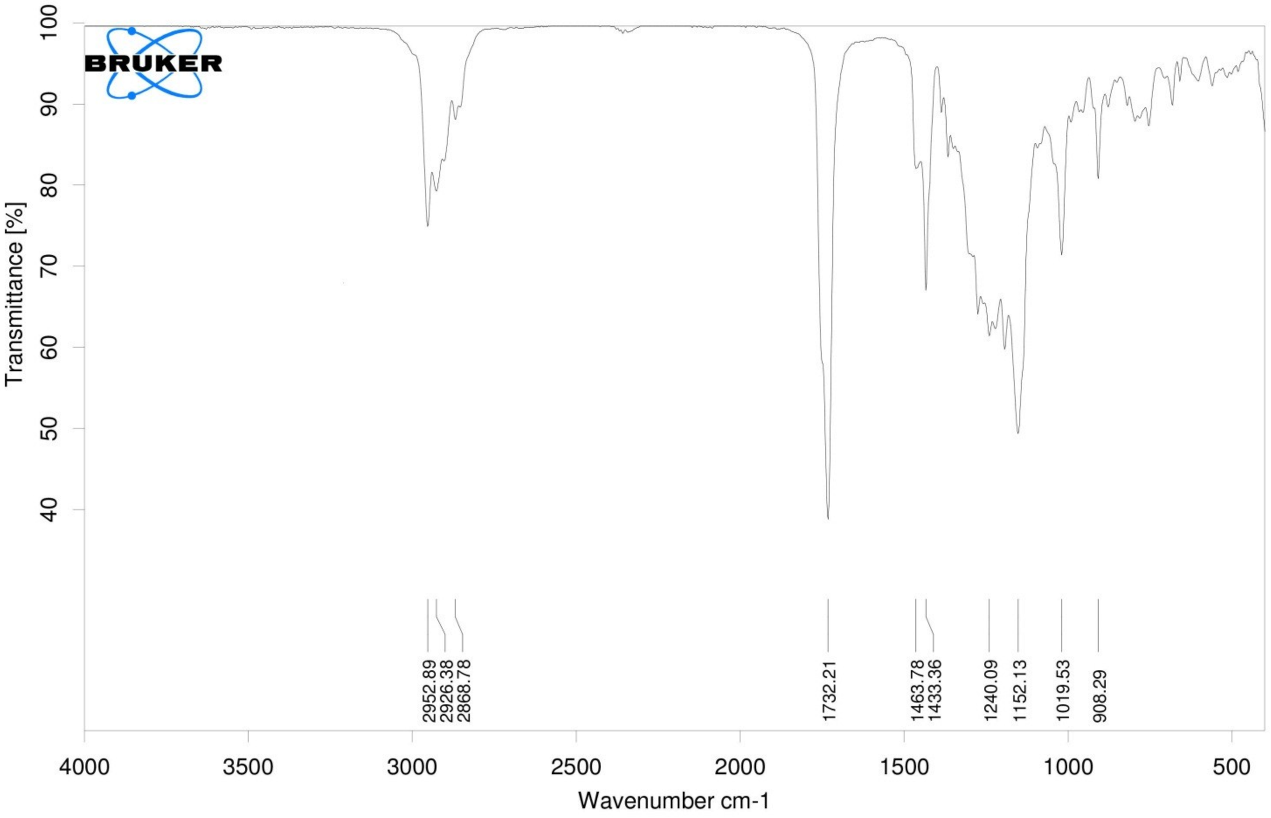

COOH
S
S

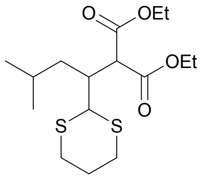
**4c**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
3075.30
2959.78
2921.75
2658.94
2359.57
1689.88
1638.79
1412.77
1276.91
1240.90
1173.52
908.72
814.68
673.82
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

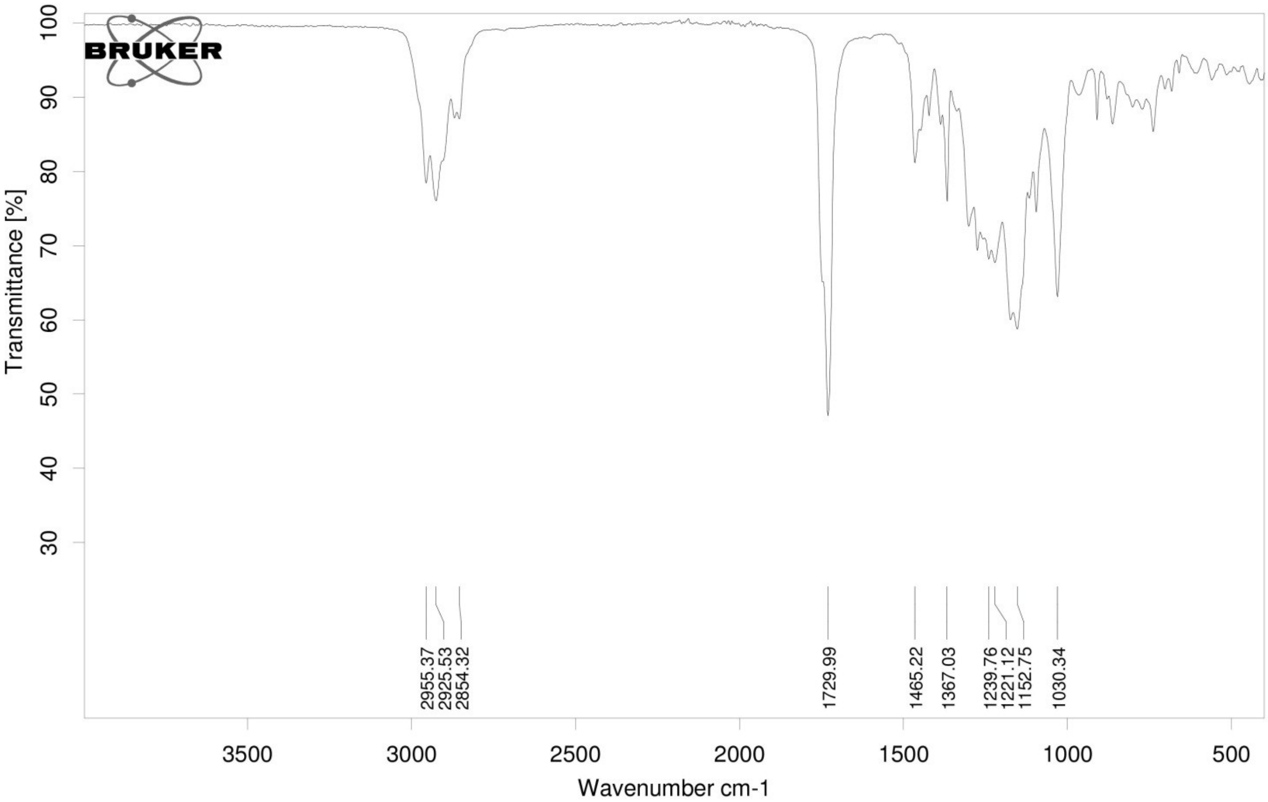

O
OMe
OMe
O
S
S

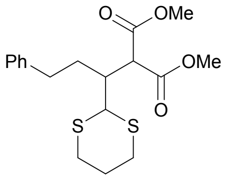
**5a**


Transmittance [%]
100
90
80
70
60
50
40
2952.89
2926.38
2868.78
1732.21
1463.78
1433.36
1240.09
1152.13
1019.53
908.29
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

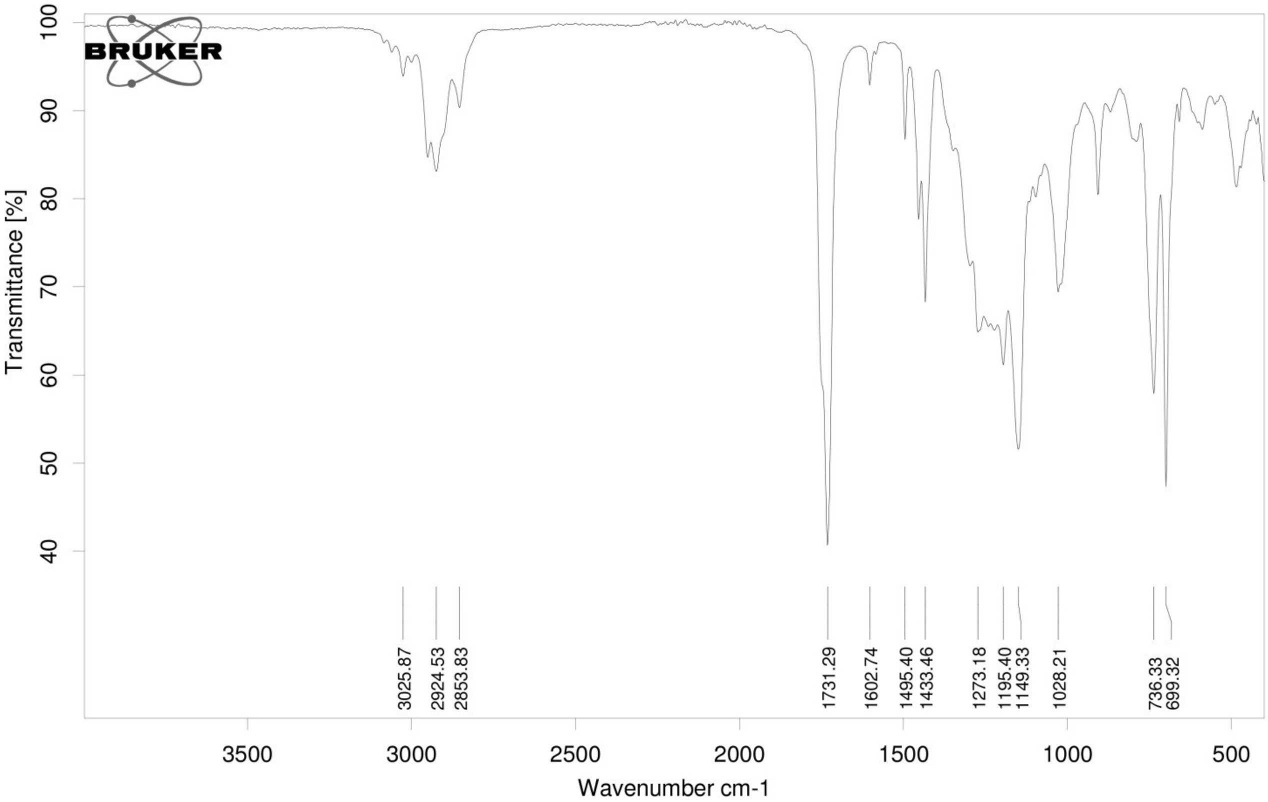

O
OEt
OEt
O
S
S

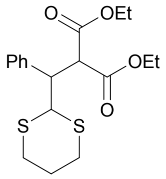
**5b**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
2955.37
2925.53
2854.32
1729.99
1465.22
1367.03
1239.76
1221.12
1152.75
1030.34
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

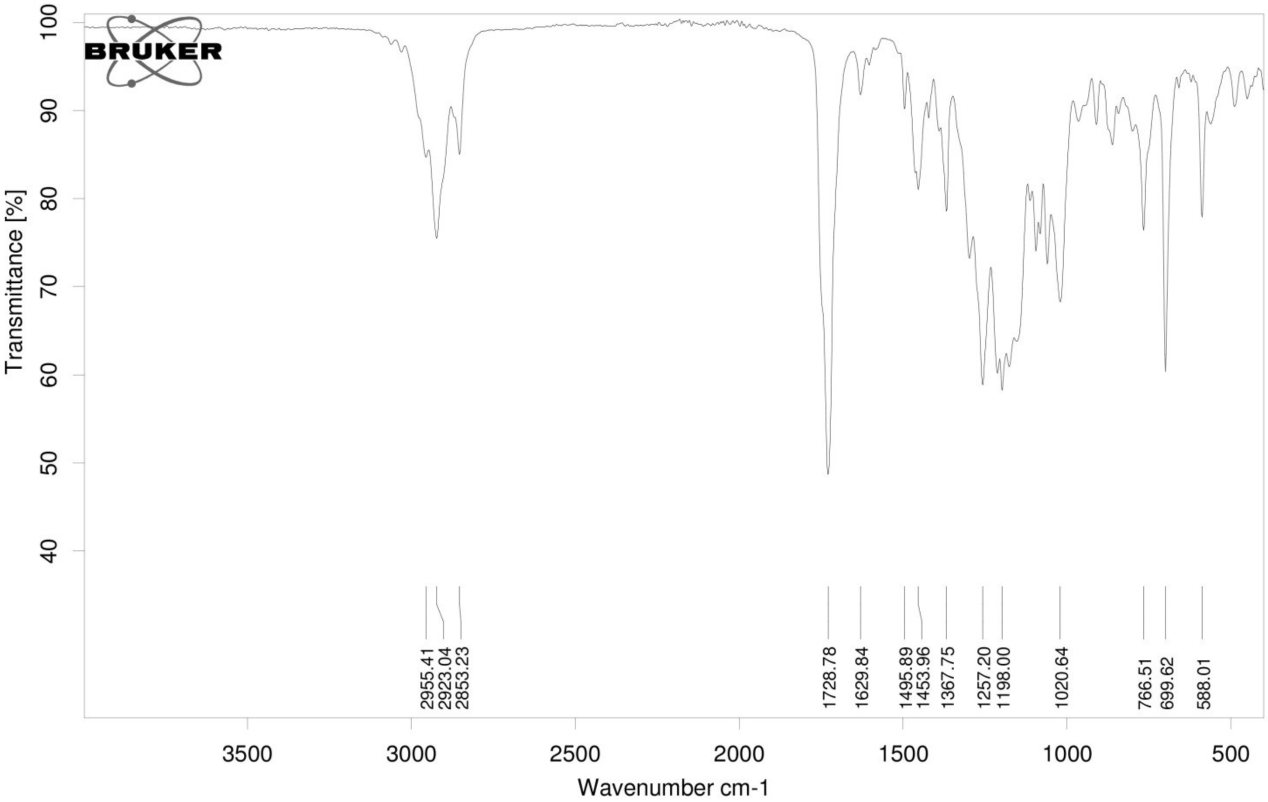

O
OMe
Ph
OMe
O
S
S

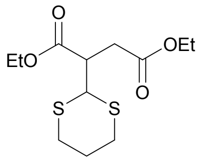
**5c**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
3025.87
2924.53
2853.83
1731.29
1602.74
1495.40
1433.46
1273.18
1195.40
1149.33
1028.21
736.33
699.32
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

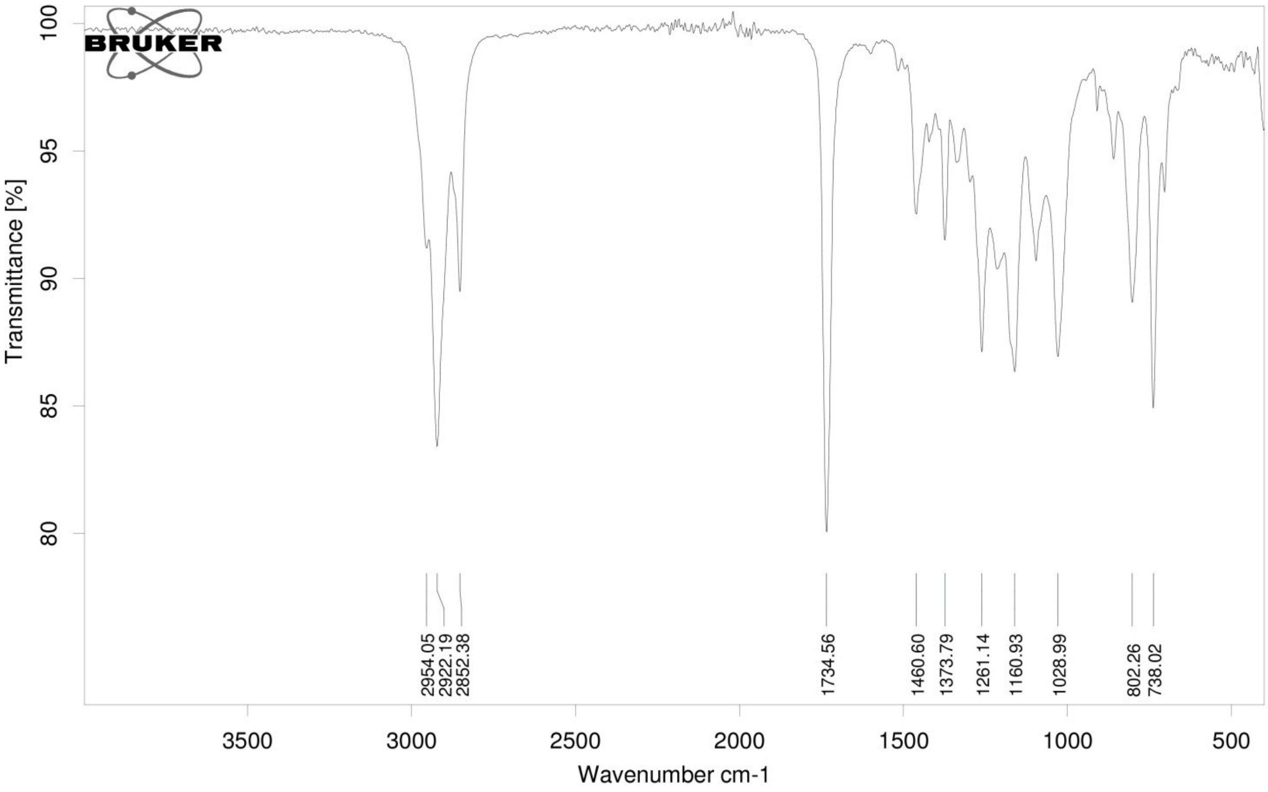

O
OEt
Ph
OEt
O
S
S

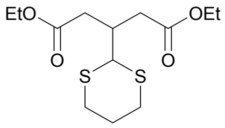
**5d**


Transmittance [%]
100
90
80
70
60
50
40
2955.41
2923.04
2853.23
1728.78
1629.84
1495.89
1453.96
1367.75
1257.20
1198.00
1020.64
766.51
699.62
588.01
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

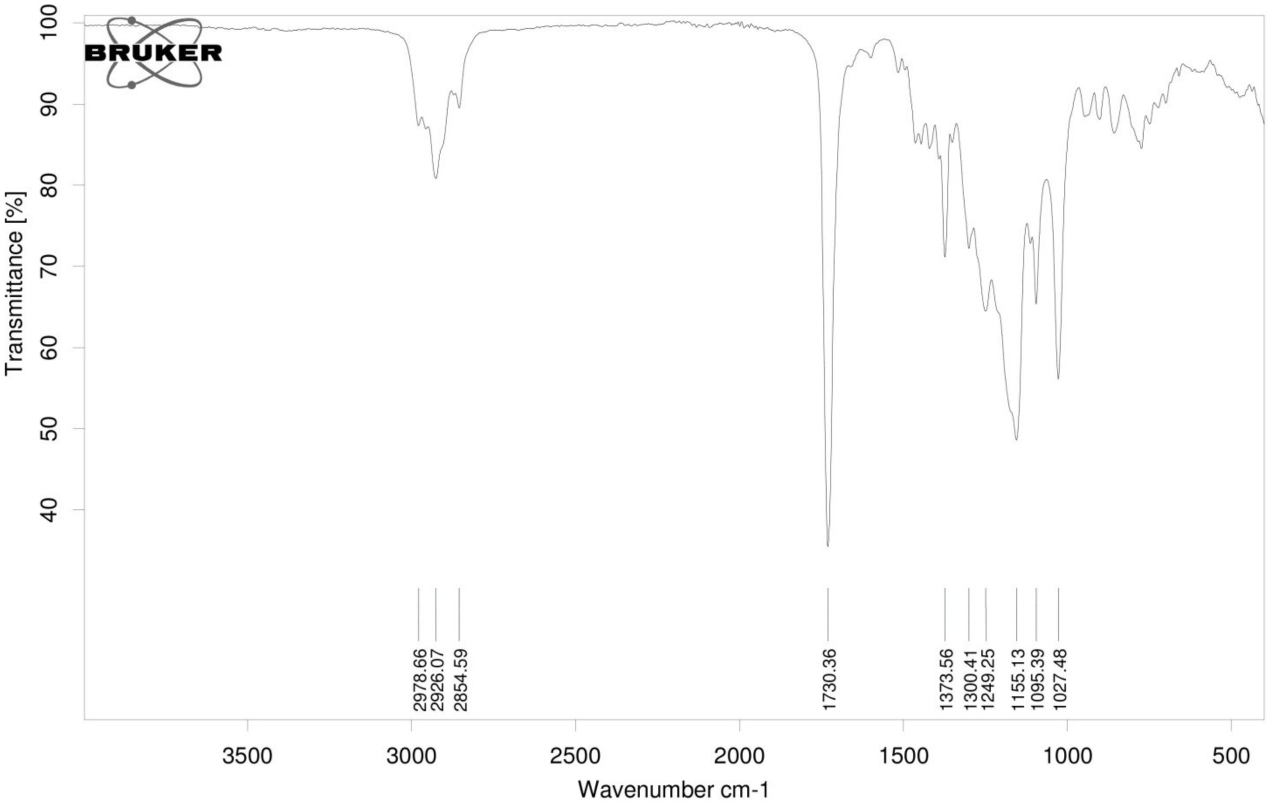

O
EtO
OEt
O
S
S

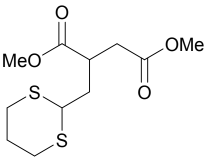
**5e**


BRUKER
Transmittance [%]
100
95
90
85
80
2954.05
2922.19
2852.38
1734.56
1460.60
1373.79
1261.14
1160.93
1028.99
802.26
738.02
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

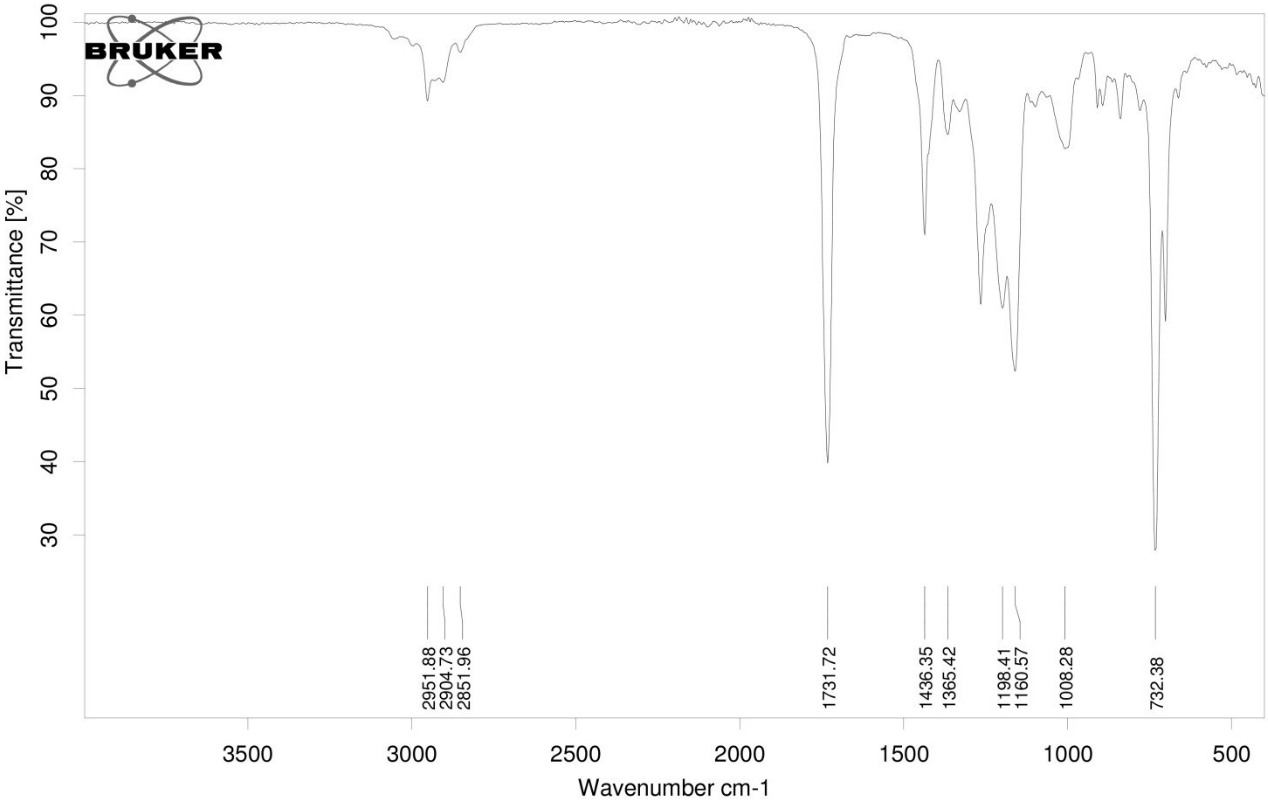

EtO
OEt
O
O
S
S

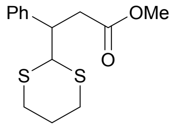
**5f**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
2978.66
2926.07
2854.59
1730.36
1373.56
1300.41
1249.25
1155.13
1095.39
1027.48
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

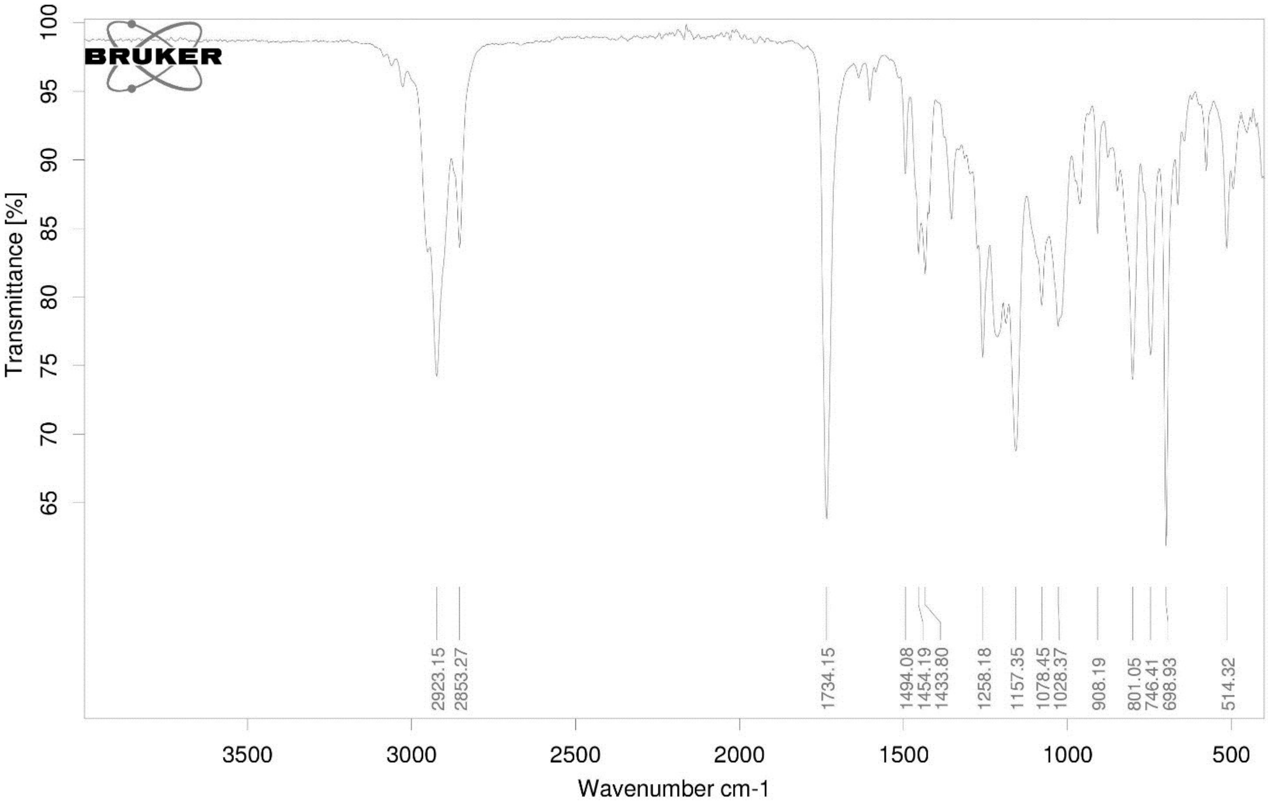

O
MeO
OMe
O
S
S

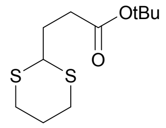
**5g**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
2951.88
2904.73
2851.96
1731.72
1436.35
1365.42
1198.41
1160.57
1008.28
732.38
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

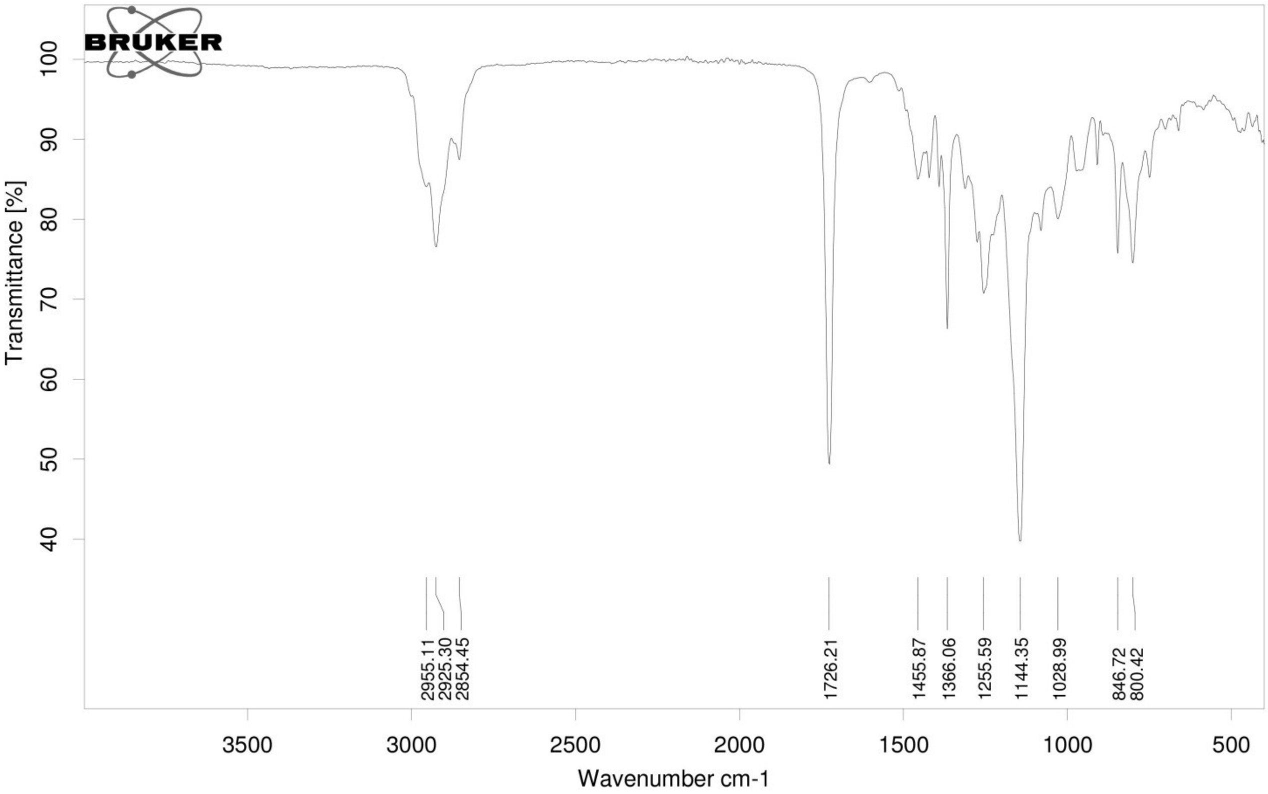

Ph
OMe
O
S
S

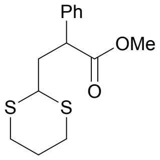
**5h**


BRUKER
Transmittance [%]
100
95
90
85
80
75
70
65
2923.15
2853.27
1734.15
1494.08
1454.19
1433.80
1258.18
1157.35
1078.45
1028.37
908.19
801.05
746.41
698.93
514.32
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

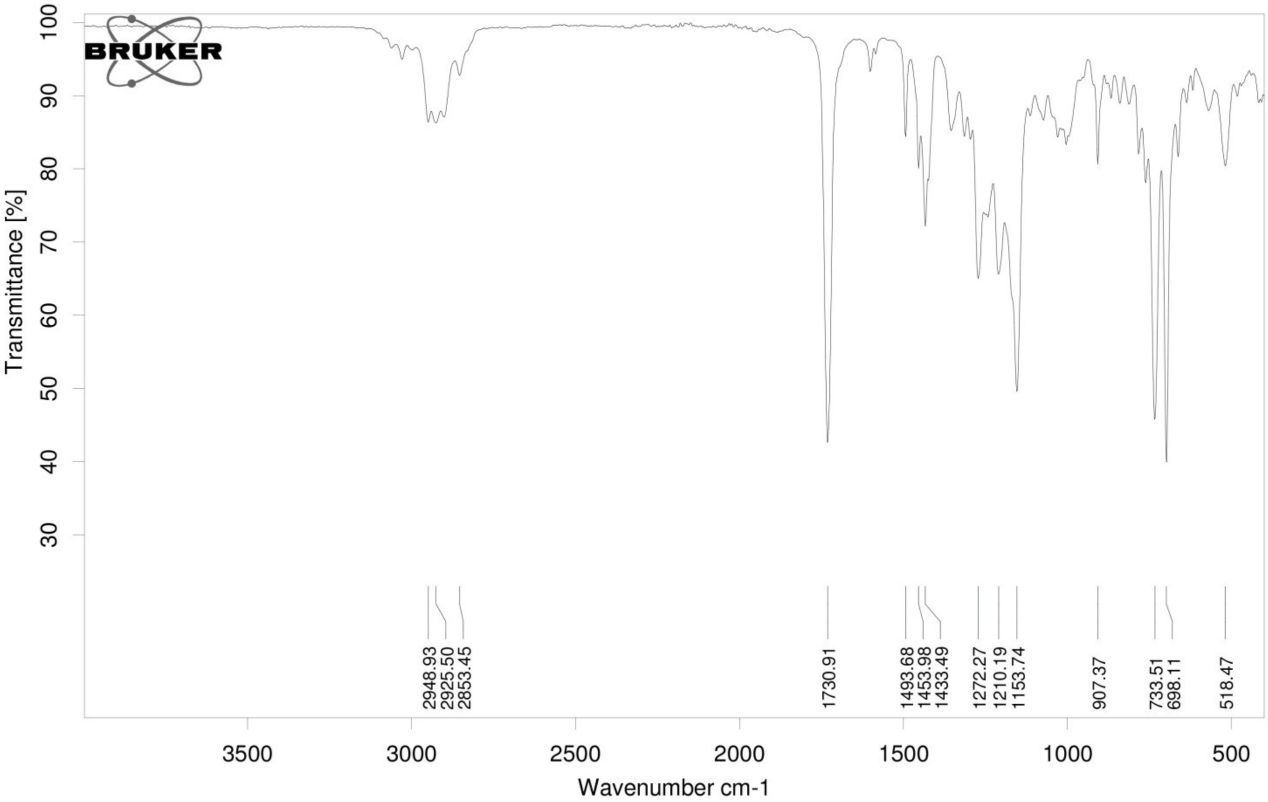

OtBu
O
S
S

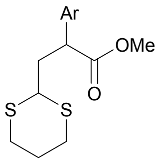
**5i**


Transmittance [%]
100
90
80
70
60
50
40
2955.11
2925.30
2854.45
1726.21
1455.87
1366.06
1255.59
1144.35
1028.99
846.72
800.42
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

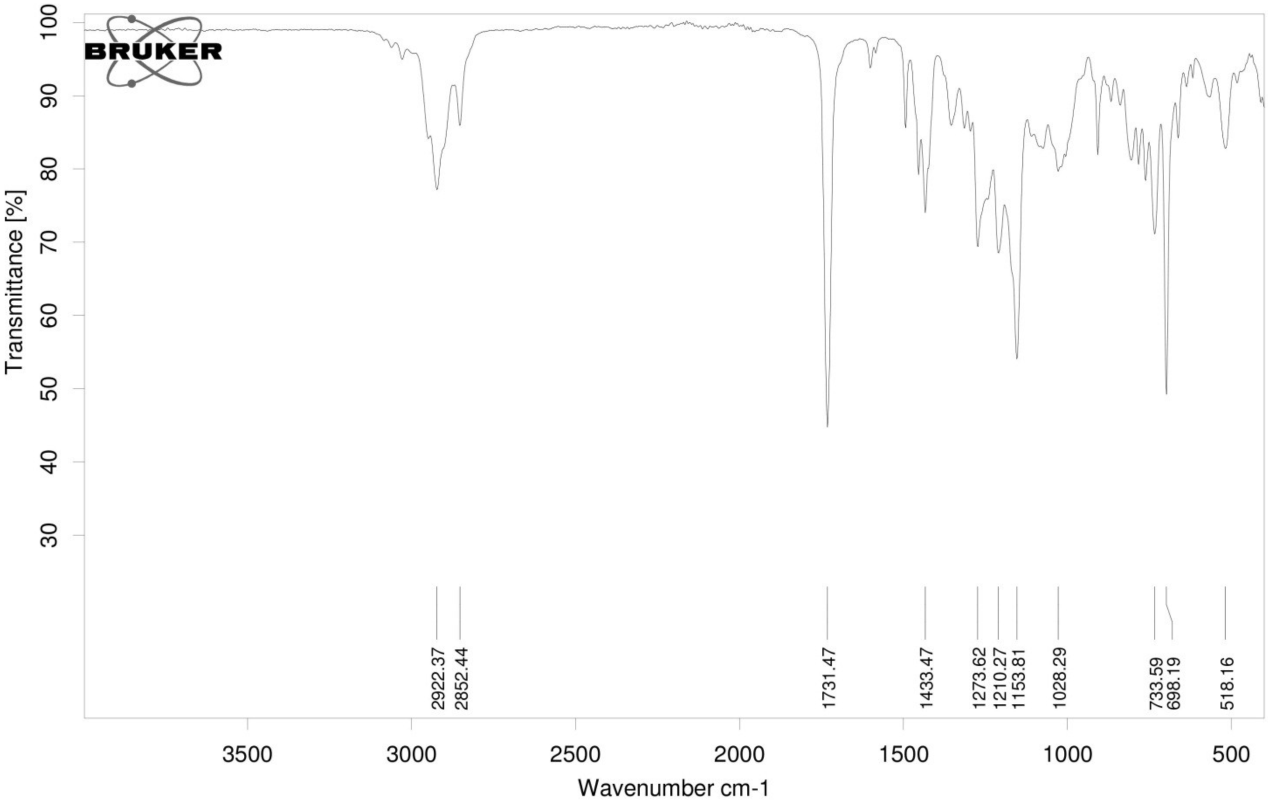

Ph
OMe
O
S
S

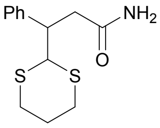
**5j**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
2948.93
2925.50
2853.45
1730.91
1493.68
1453.98
1433.49
1272.27
1210.19
1153.74
907.37
733.51
698.11
518.47
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

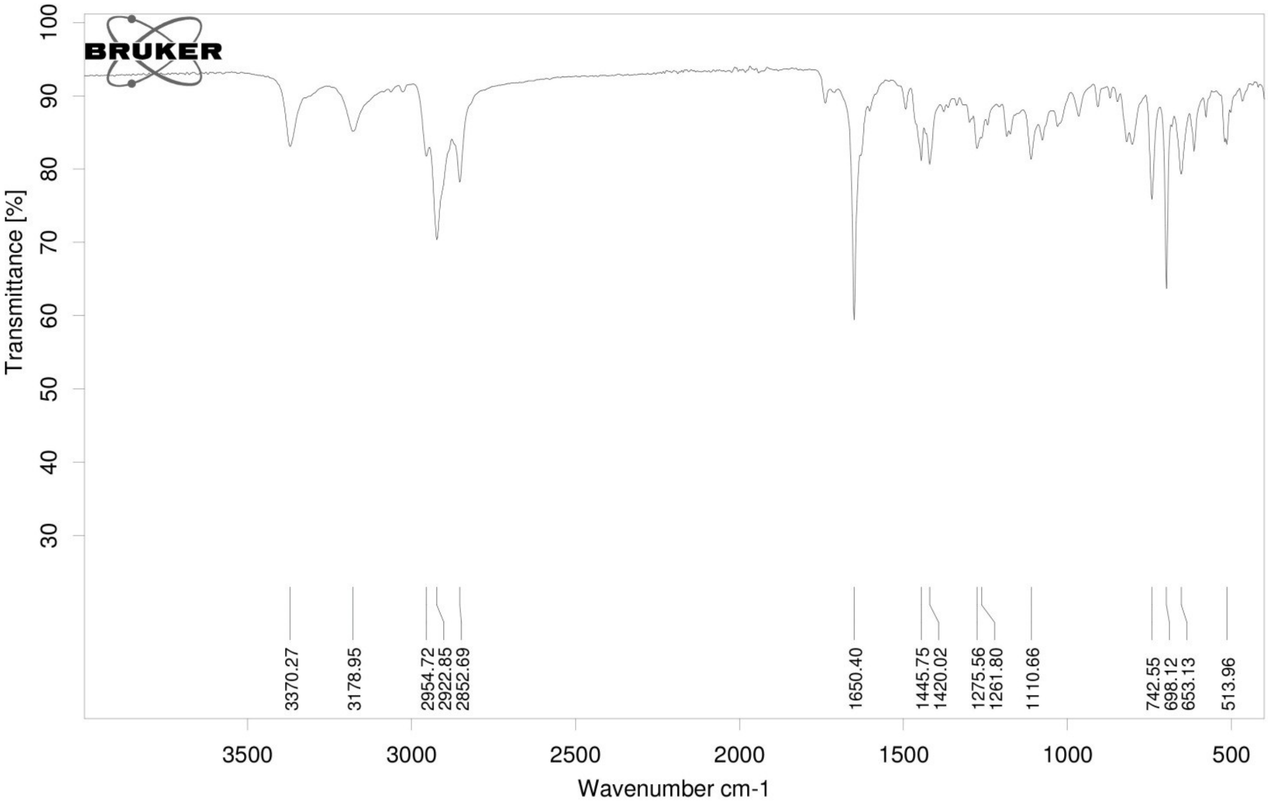


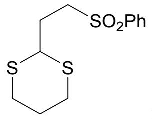
Ar = 4-Me-$C_6H_4$ **5k**



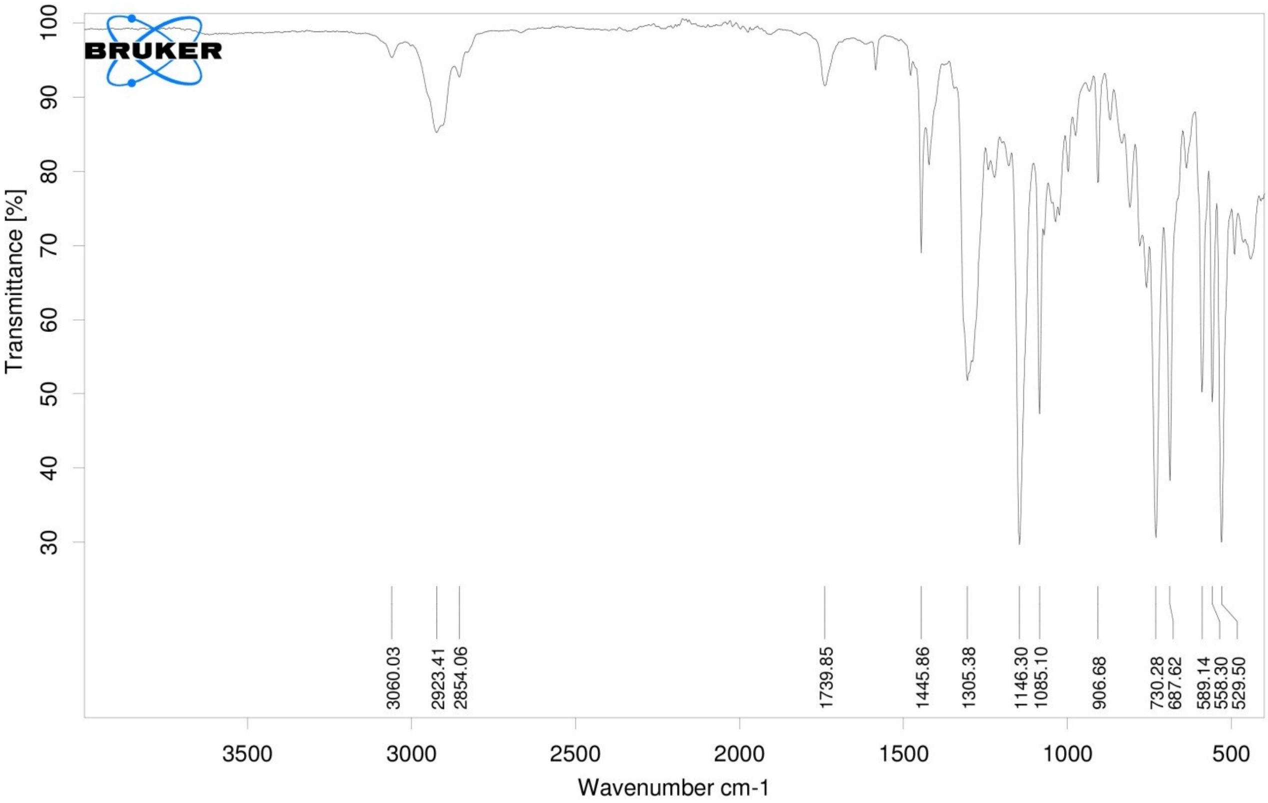

Ph
NH$_2$
O
S
S

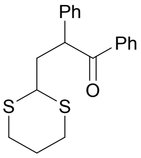
**5l**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
3370.27
3178.95
2954.72
2922.85
2852.69
1650.40
1445.75
1420.02
1275.56
1261.80
1110.66
742.55
698.12
653.13
513.96
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

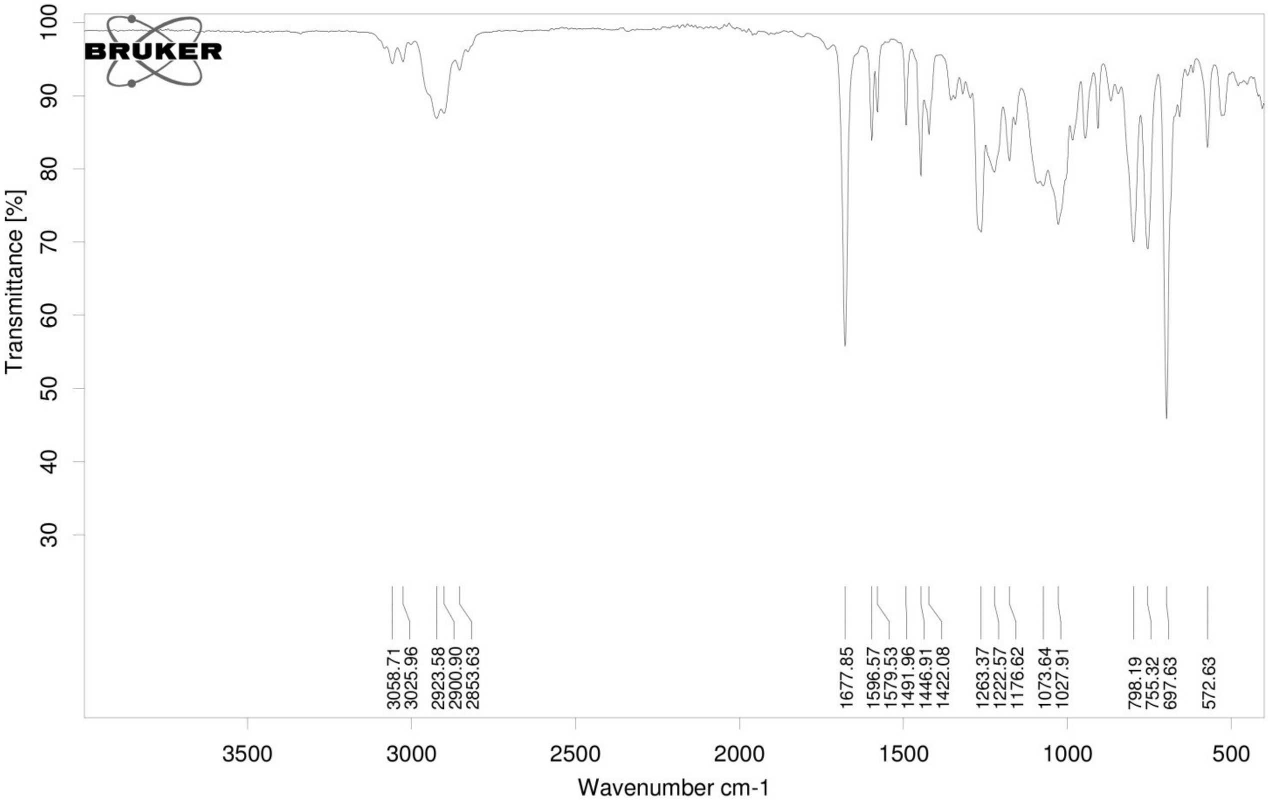

SO2Ph
S
S

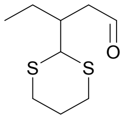
**5m**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
3060.03
2923.41
2854.06
1739.85
1445.86
1305.38
1146.30
1085.10
906.68
730.28
687.62
589.14
558.30
529.50
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

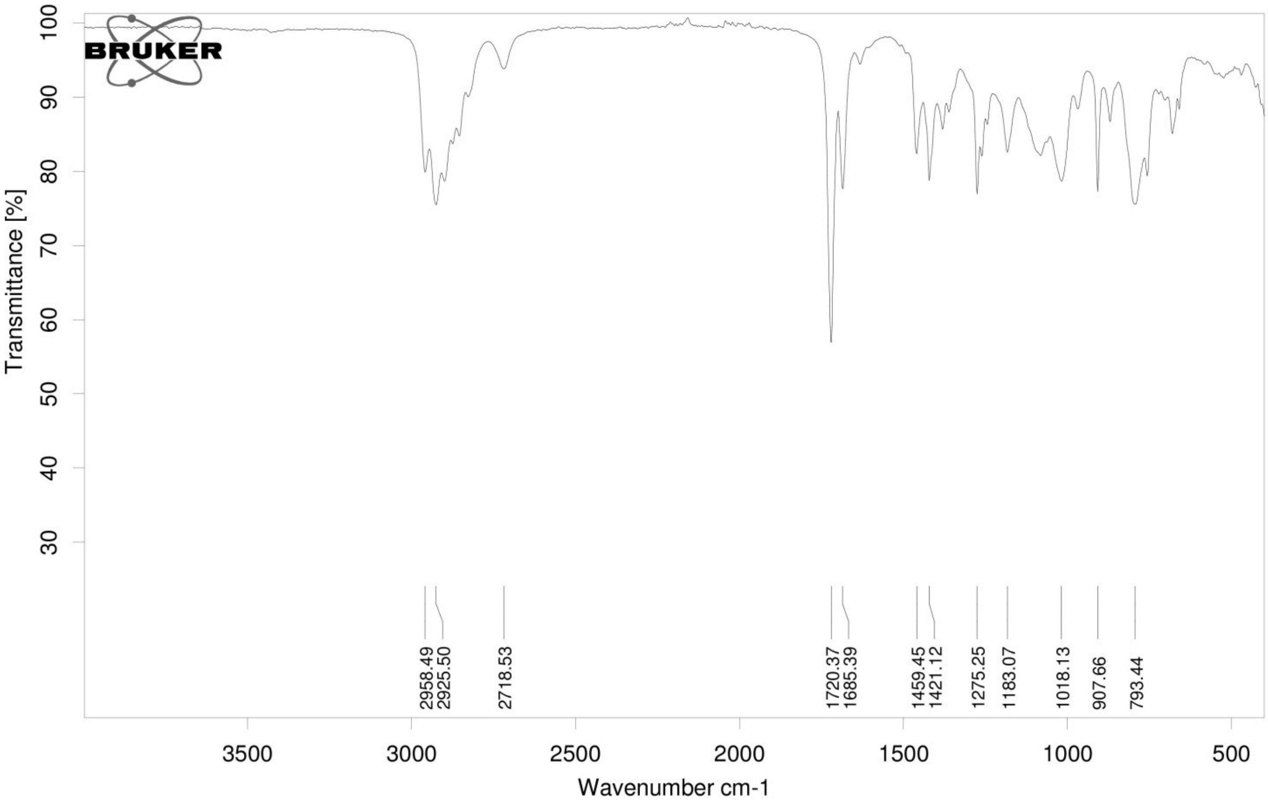

Ph
Ph
O
S
S

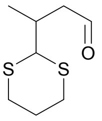
**5n**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
Wavenumber cm-1
3500
3000
2500
2000
1500
1000
500
3058.71
3025.96
2923.58
2900.90
2853.63
1677.85
1596.57
1579.53
1491.96
1446.91
1422.08
1263.37
1222.57
1176.62
1073.64
1027.91
798.19
755.32
697.63
572.63

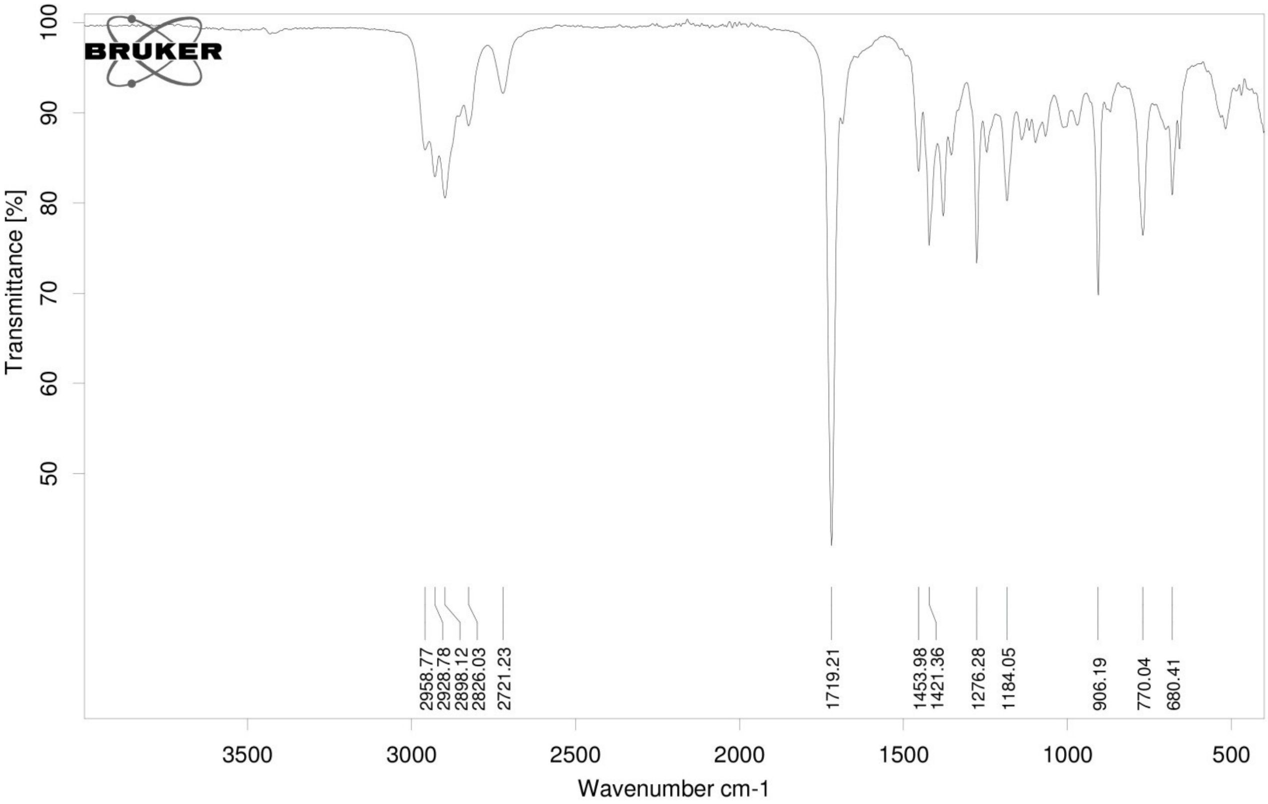


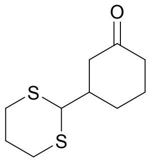
**5o**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
2958.49
2925.50
2718.53
1720.37
1685.39
1459.45
1421.12
1275.25
1183.07
1018.13
907.66
793.44
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

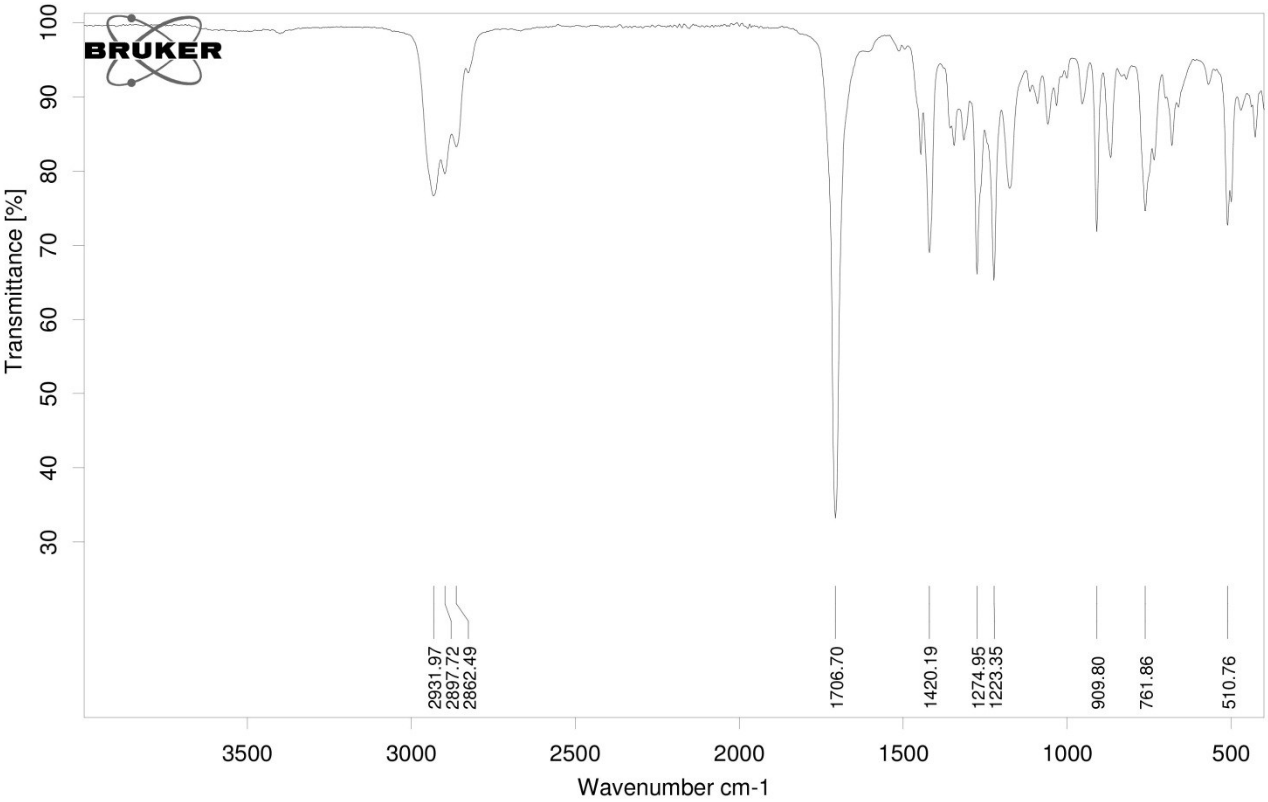

S
S
O

**5p**

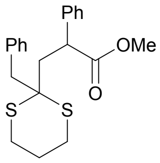

BRUKER
Transmittance [%]
100
90
80
70
60
50
2958.77
2928.78
2898.12
2826.03
2721.23
1719.21
1453.98
1421.36
1276.28
1184.05
906.19
770.04
680.41
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1



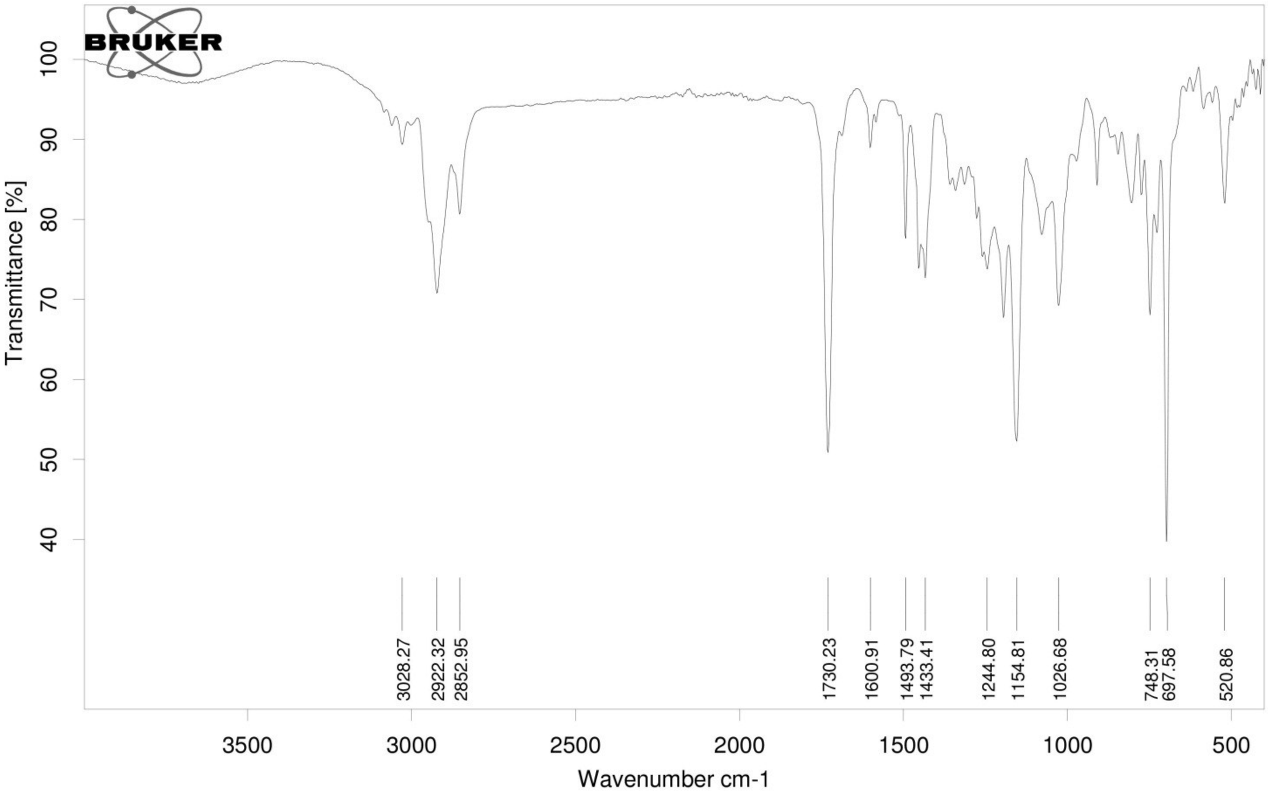
**5q**

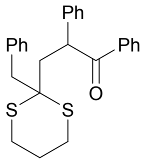


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
2931.97
2897.72
2862.49
1706.70
1420.19
1274.95
1223.35
909.80
761.86
510.76
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

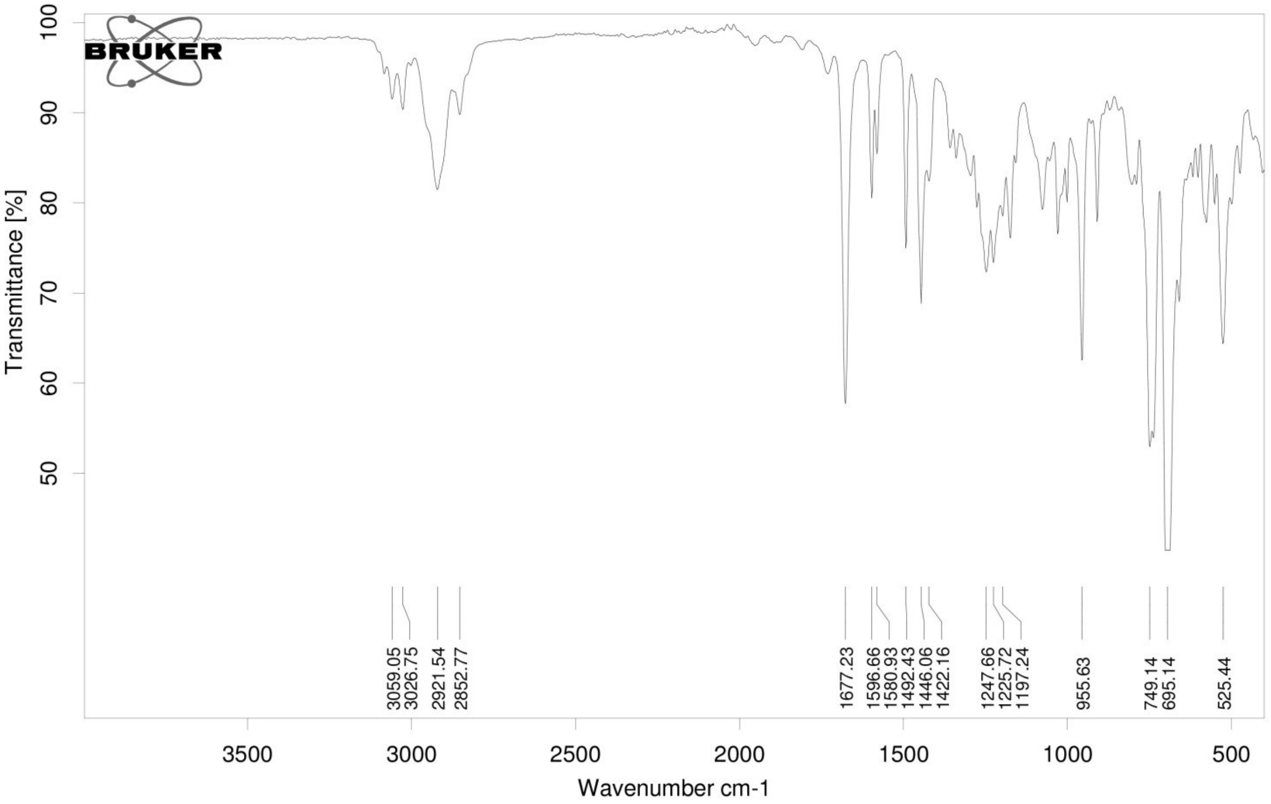

Ph
Ph
OMe
O
S
S

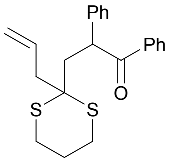
**5r**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
3028.27
2922.32
2852.95
1730.23
1600.91
1493.79
1433.41
1244.80
1154.81
1026.68
748.31
697.58
520.86
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

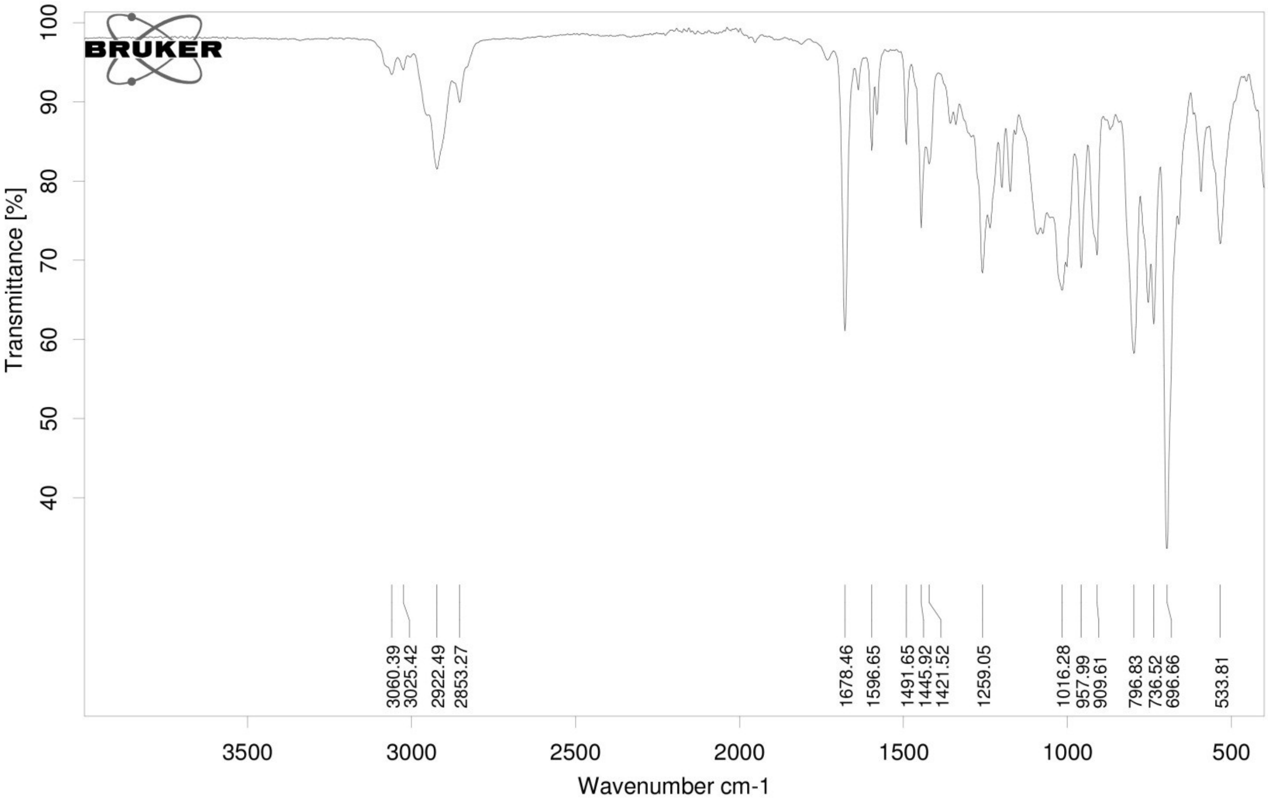

Ph
Ph
Ph
O
S
S

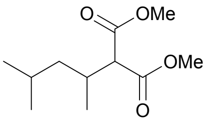
**5s**


BRUKER
Transmittance [%]
100
90
80
70
60
50
3059.05
3026.75
2921.54
2852.77
1677.23
1596.66
1580.93
1492.43
1446.06
1422.16
1247.66
1225.72
1197.24
955.63
749.14
695.14
525.44
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

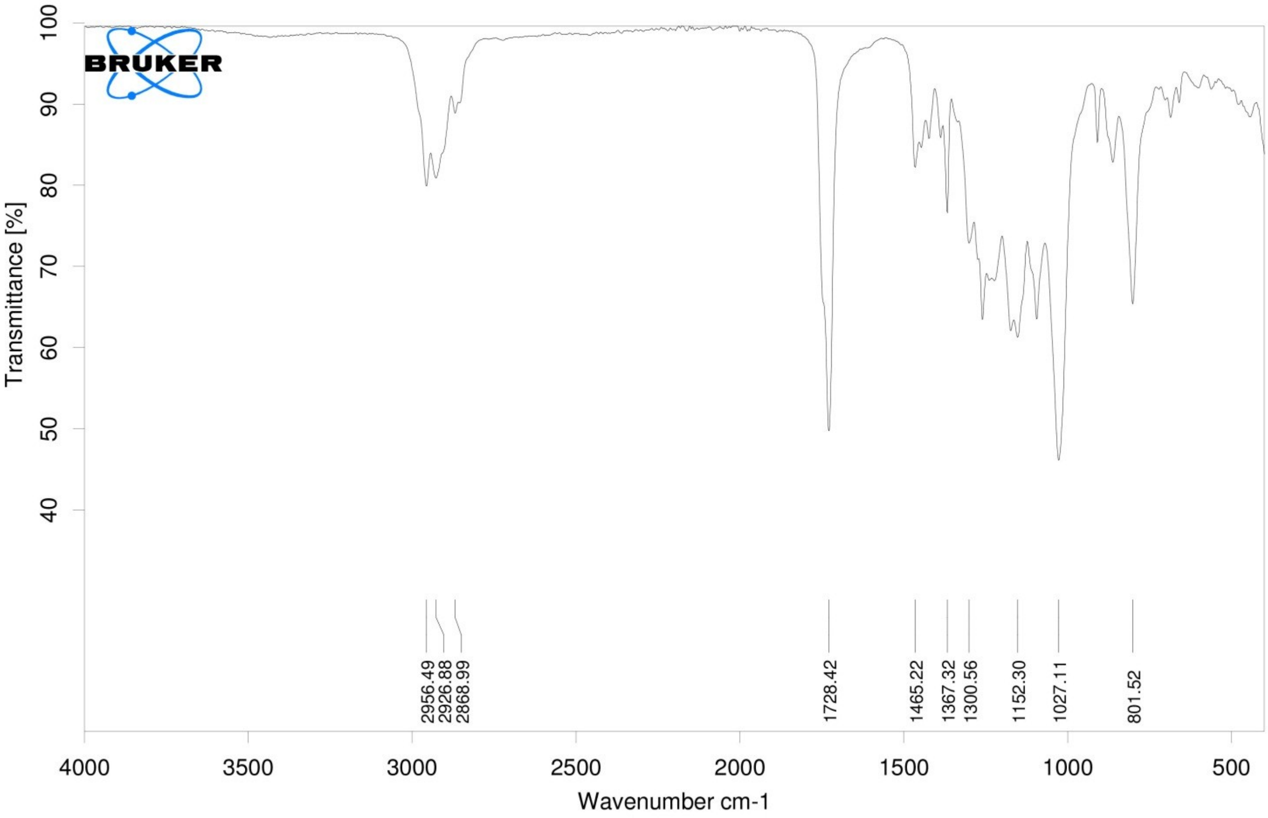

Ph
Ph
O
S
S

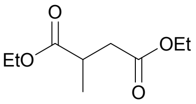
**5t**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
3060.39
3025.42
2922.49
2853.27
1678.46
1596.65
1491.65
1445.92
1421.52
1259.05
1016.28
957.99
909.61
796.83
736.52
696.66
533.81
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

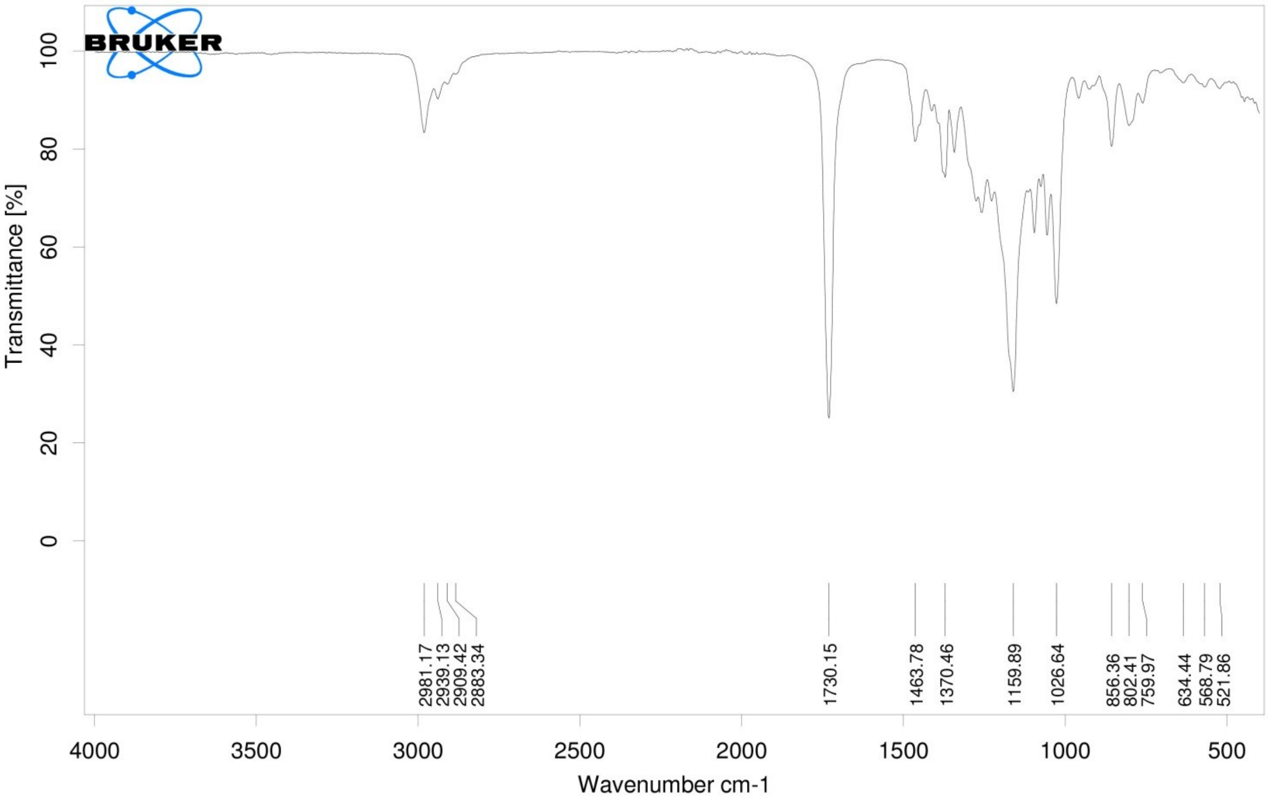

O
OMe
OMe
O

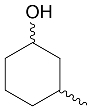
**6**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
2956.49
2926.88
2868.99
1728.42
1465.22
1367.32
1300.56
1152.30
1027.11
801.52
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

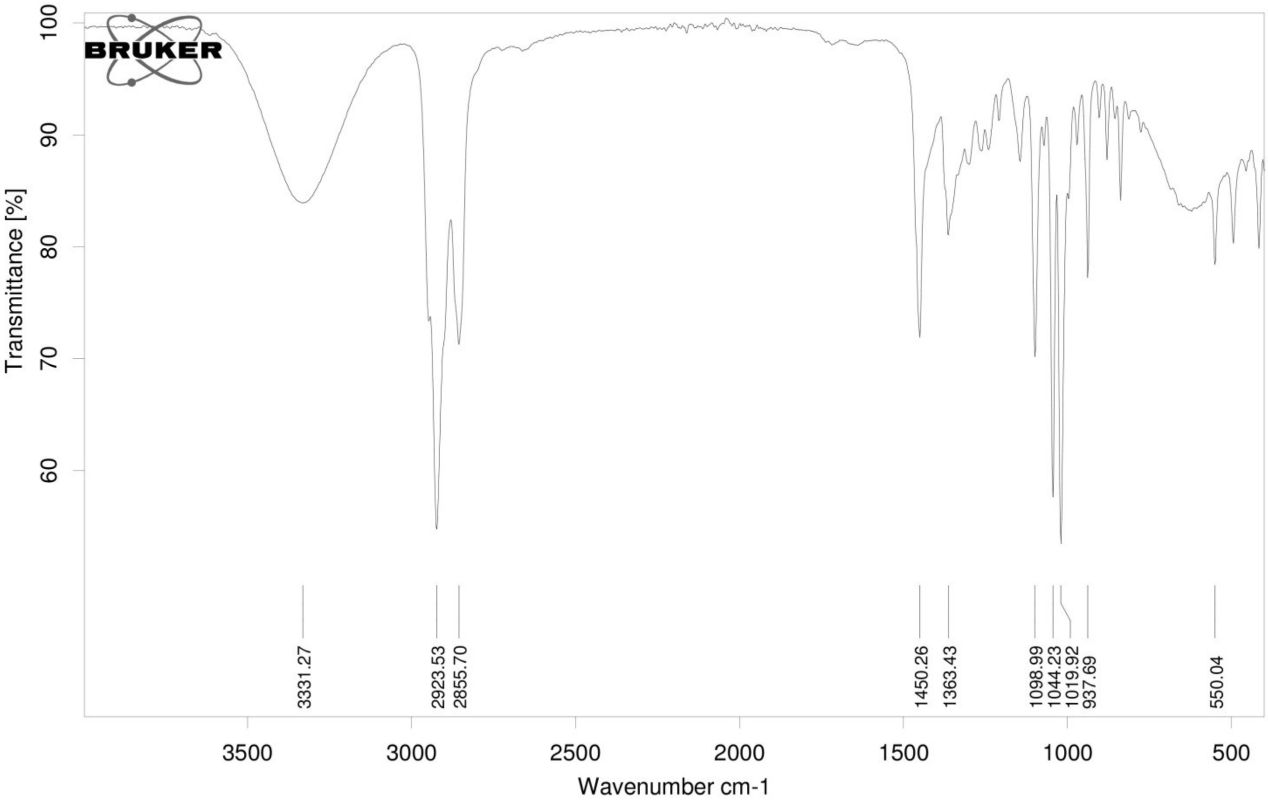

O
EtO
OEt
O

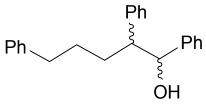
**7**


BRUKER
Transmittance [%]
100
80
60
40
20
0
2981.17
2939.13
2909.42
2883.34
1730.15
1463.78
1370.46
1159.89
1026.64
856.36
802.41
759.97
634.44
568.79
521.86
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

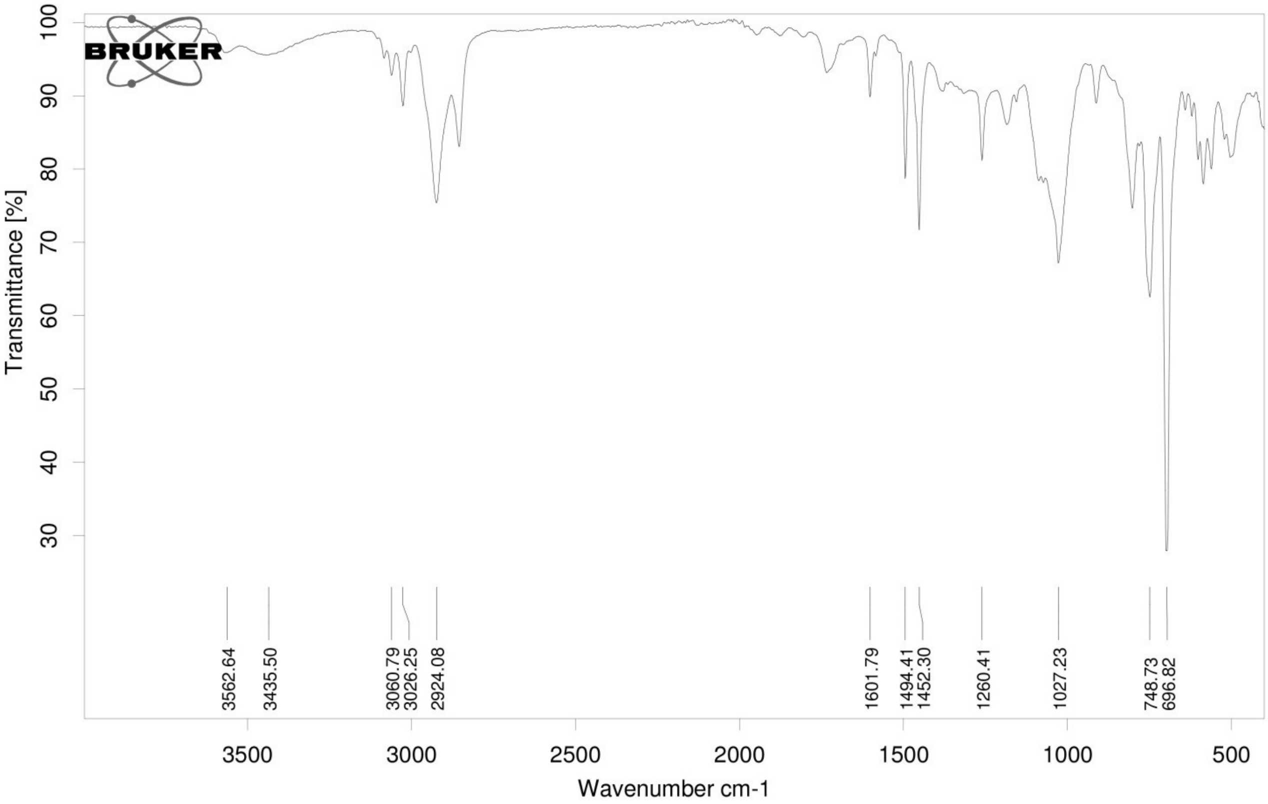

OH

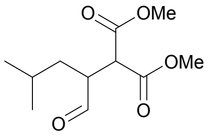
**8**


BRUKER
Transmittance [%]
100
90
80
70
60
3331.27
2923.53
2855.70
1450.26
1363.43
1098.99
1044.23
1019.92
937.69
550.04
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

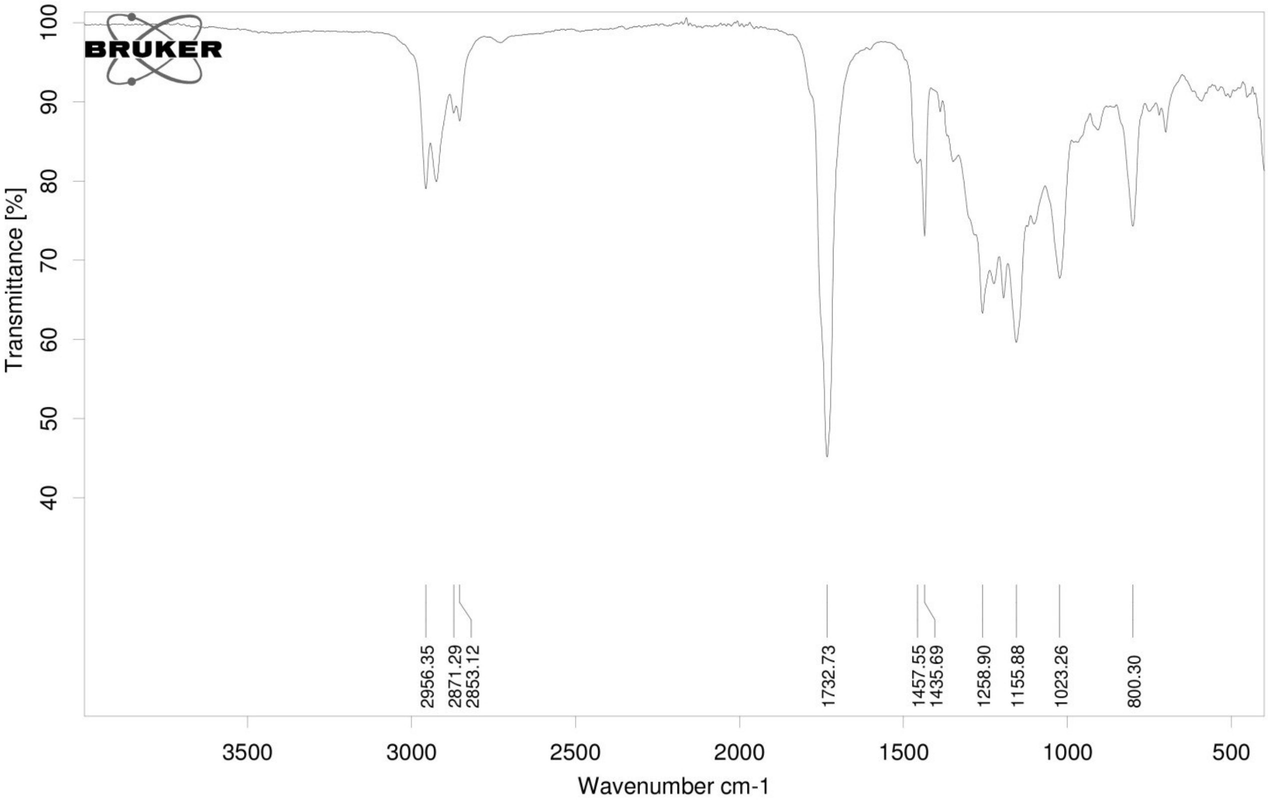

Ph
Ph
Ph
OH

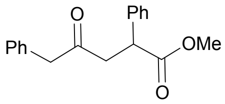
**9**


Transmittance [%]
100
90
80
70
60
50
40
30
3562.64
3435.50
3060.79
3026.25
2924.08
1601.79
1494.41
1452.30
1260.41
1027.23
748.73
696.82
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

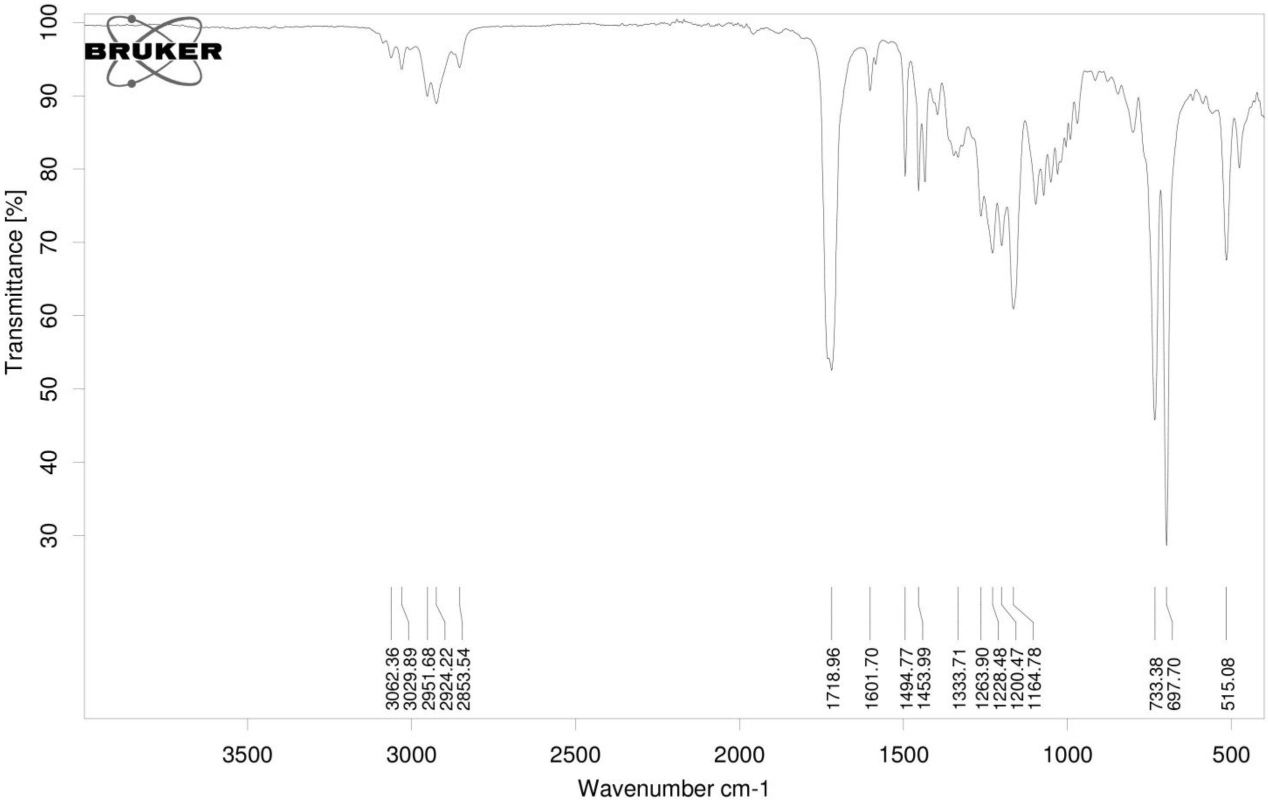

O
OMe
OMe
O
O

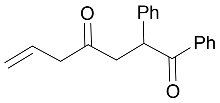
**10**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
2956.35
2871.29
2853.12
1732.73
1457.55
1435.69
1258.90
1155.88
1023.26
800.30
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

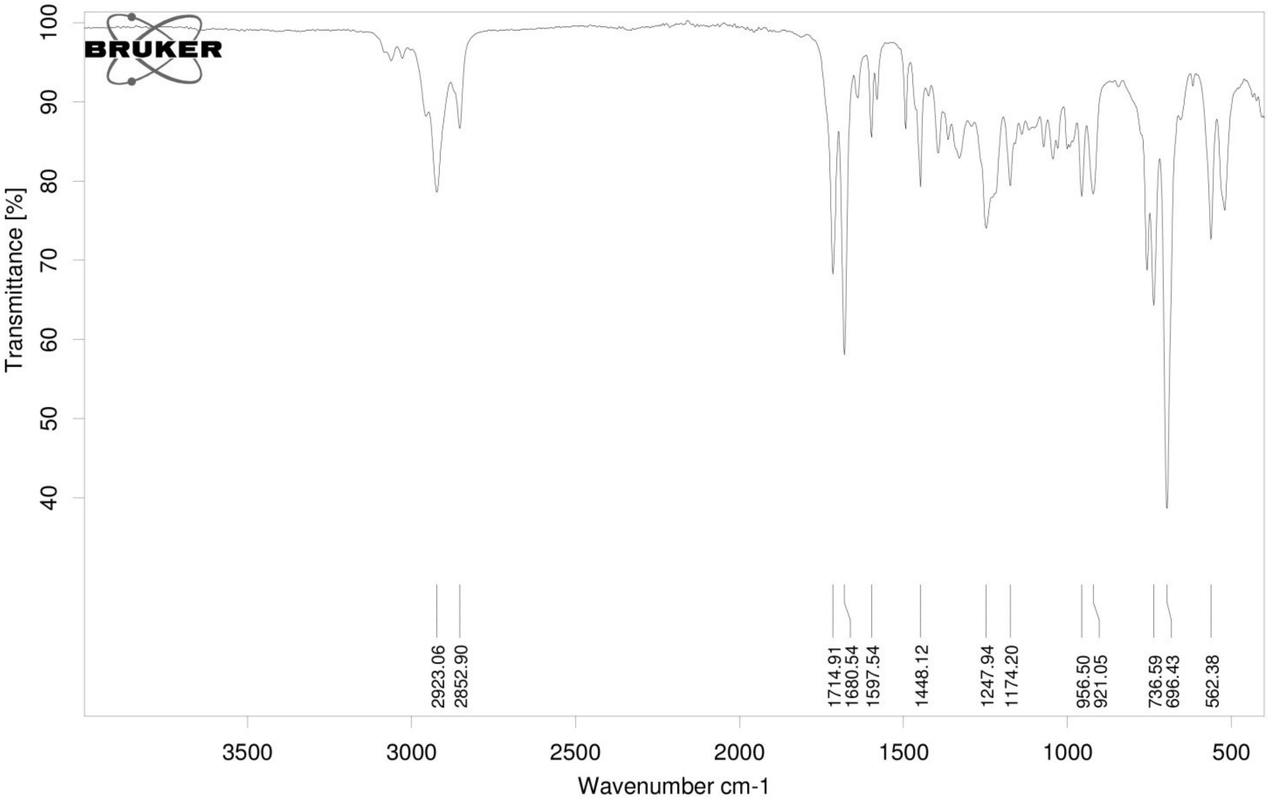

O
Ph
Ph
OMe
O

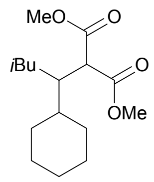
**11**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
3062.36
3029.89
2951.68
2924.22
2853.54
1718.96
1601.70
1494.77
1453.99
1333.71
1263.90
1228.48
1200.47
1164.78
733.38
697.70
515.08
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

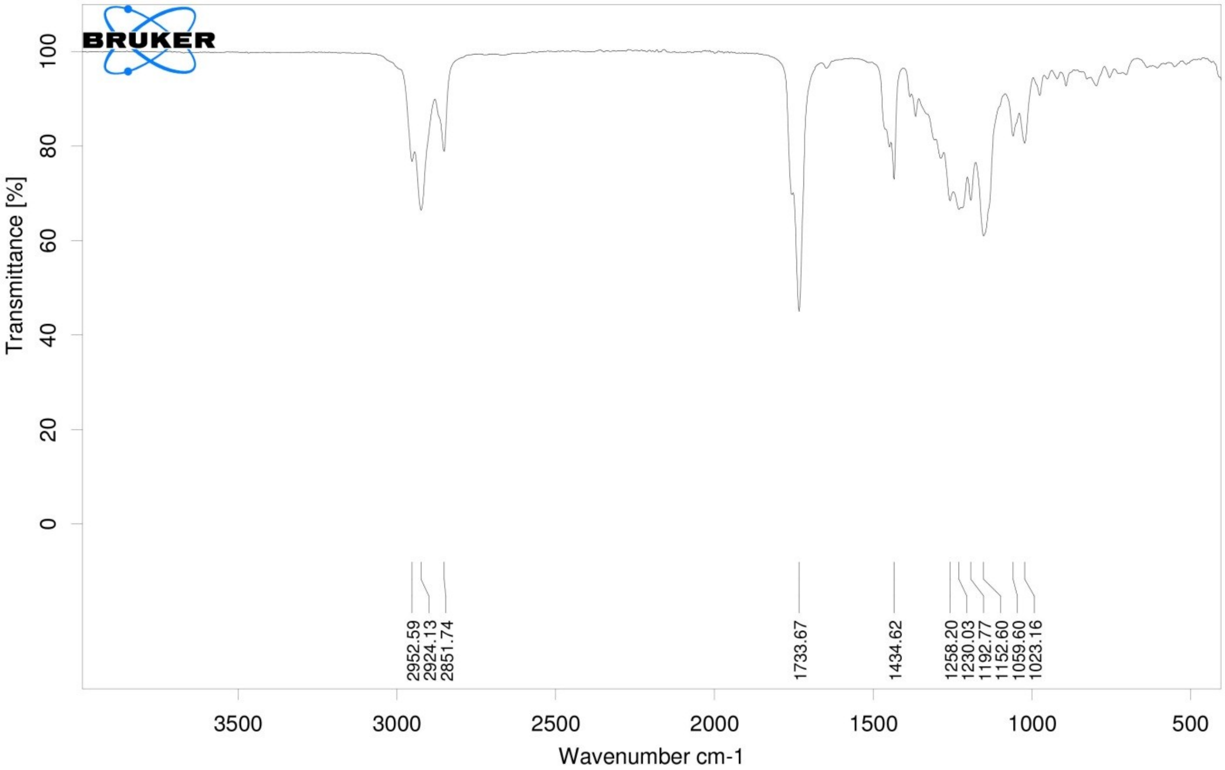

O
Ph
Ph
O

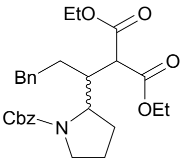
**12**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
2923.06
2852.90
1714.91
1680.54
1597.54
1448.12
1247.94
1174.20
956.50
921.05
736.59
696.43
562.38
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

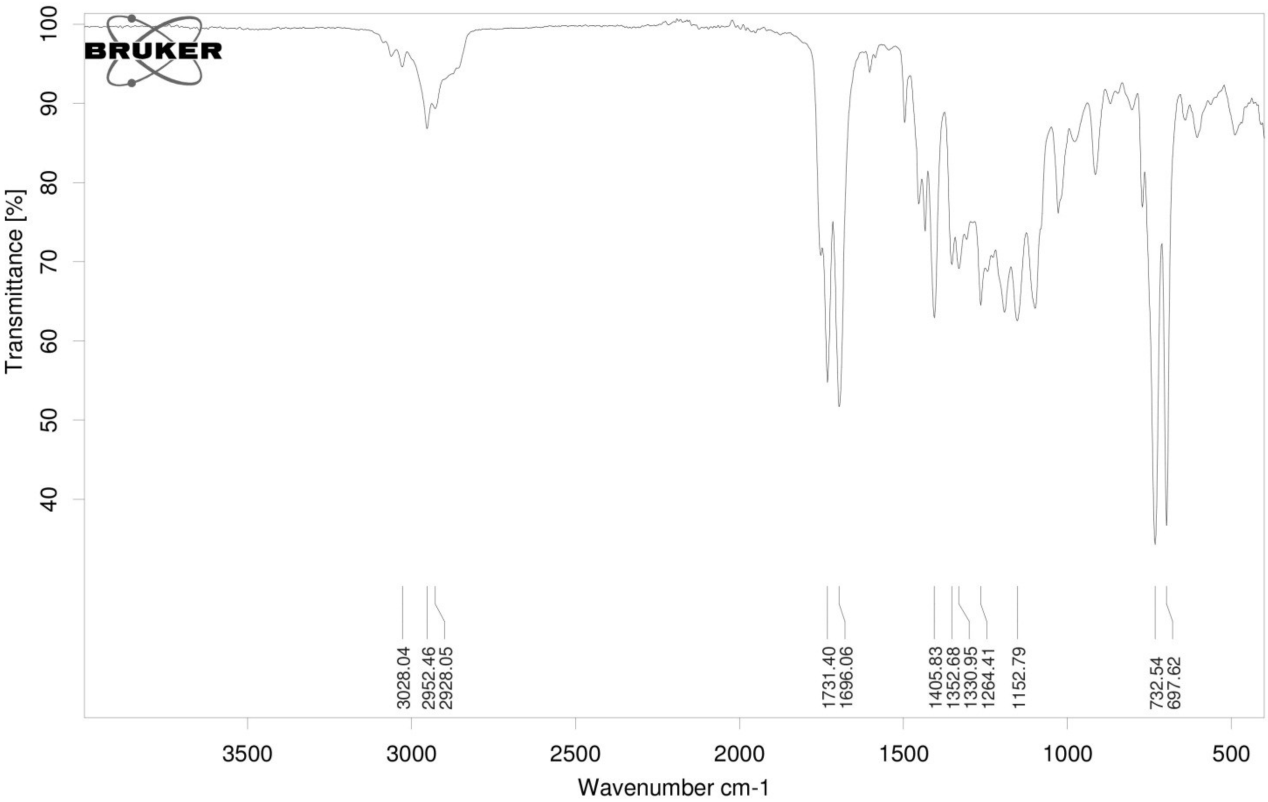

MeO
O
iBu
O
OMe

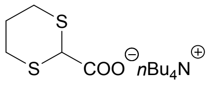
**14**


BRUKER
Transmittance [%]
100
80
60
40
20
0
2952.59
2924.13
2851.74
1733.67
1434.62
1258.20
1230.03
1192.77
1152.60
1059.60
1023.16
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

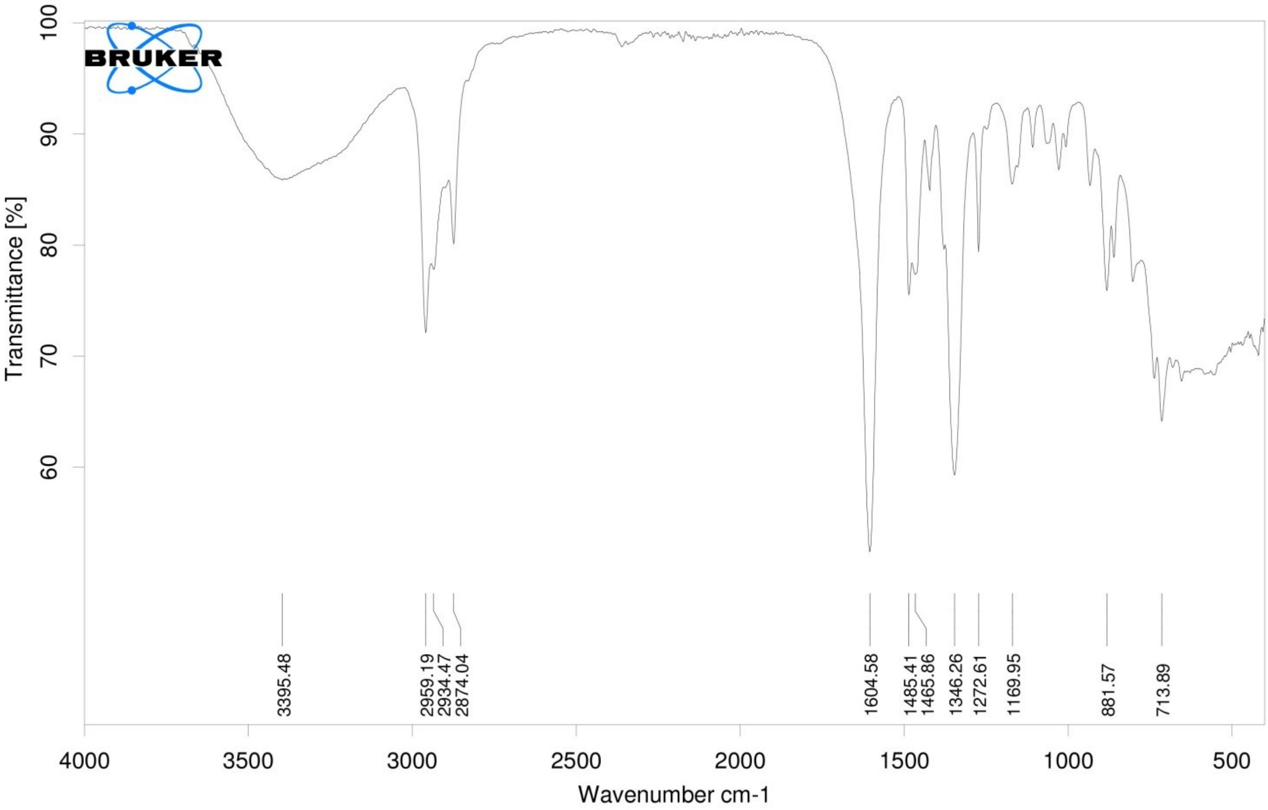

EtO
O
O
Bn
OEt
Cbz
N

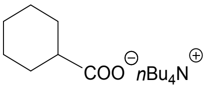
**16**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
3028.04
2952.46
2928.05
1731.40
1696.06
1405.83
1352.68
1330.95
1264.41
1152.79
732.54
697.62
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

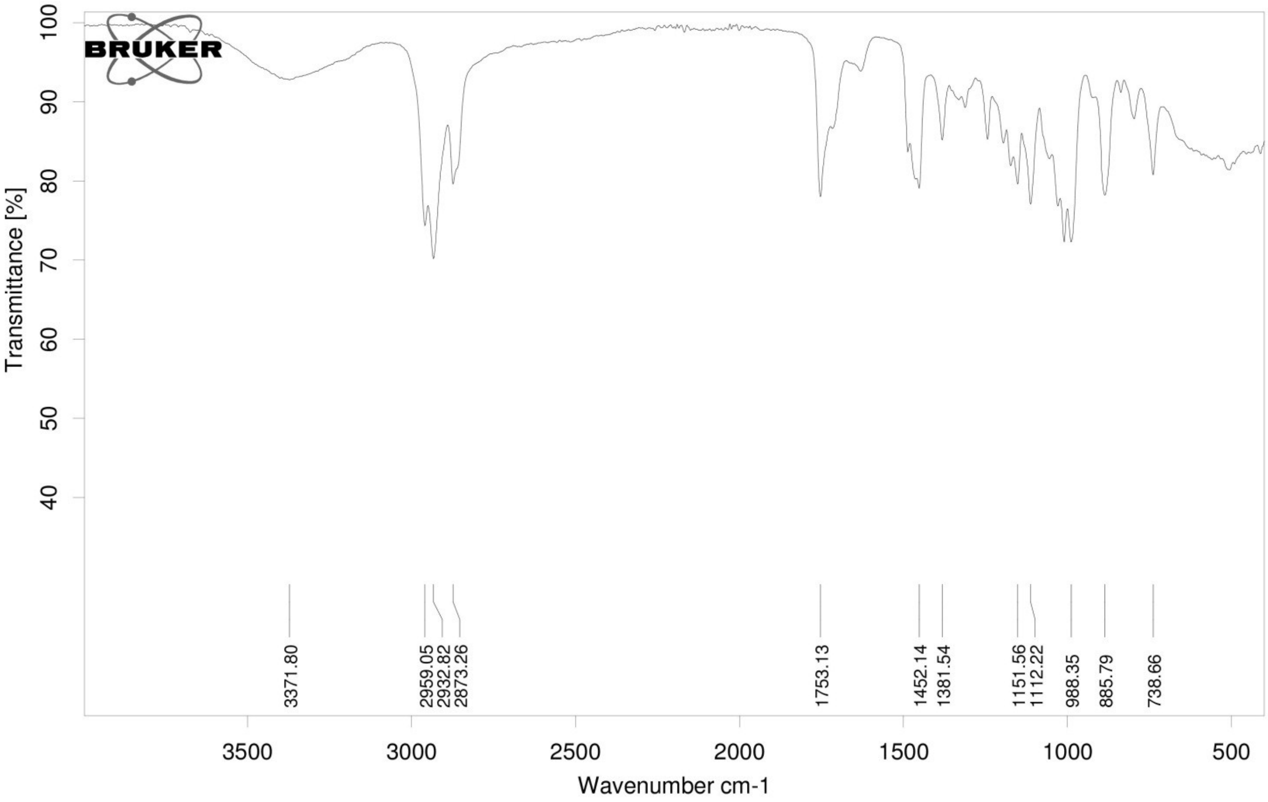

S
S
COO⊖ nBu4N⊕

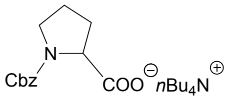
**17**


BRUKER
Transmittance [%]
100
90
80
70
60
3395.48
2959.19
2934.47
2874.04
1604.58
1485.41
1465.86
1346.26
1272.61
1169.95
881.57
713.89
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


COO⊖ *n*Bu4N⊕

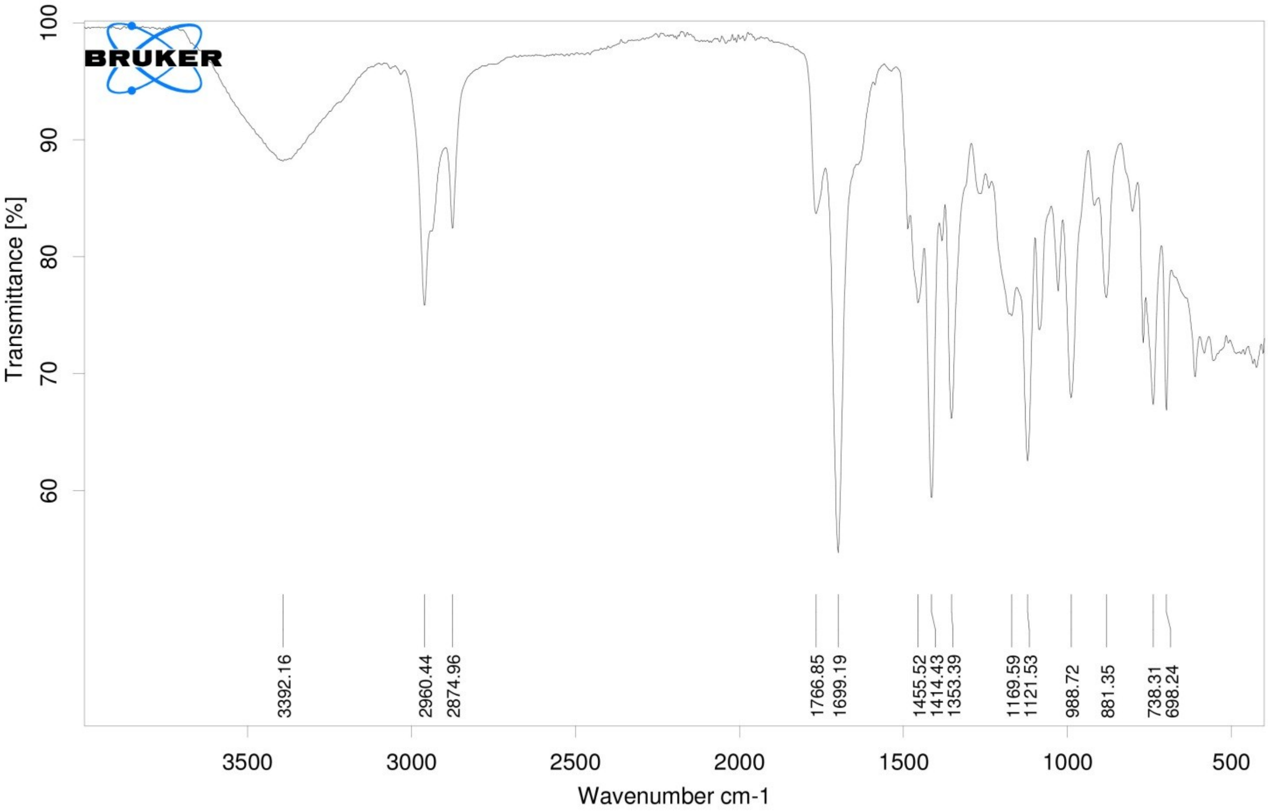
**18**


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
3371.80
2959.05
2932.82
2873.26
1753.13
1452.14
1381.54
1151.56
1112.22
988.35
885.79
738.66
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1



N
Cbz
COO⊖ nBu4N⊕

**19**



BRUKER
Transmittance [%]
100
90
80
70
60
3392.16
2960.44
2874.96
1766.85
1699.19
1455.52
1414.43
1353.39
1169.59
1121.53
988.72
881.35
738.31
698.24
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1