Electronic Supplementary Information for

An odorless thia-Michael addition using bunte salts as thiol surrogates

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1 Experimental

1.1 General

All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are identified by appropriate technique such as MS, ^{1}H NMR, and compared with previously reported data. All unknown compounds are characterized by ^{1}H NMR, ^{13}C NMR, MS and elemental analyses. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Finnigan TSQ Quantum-MS instrument in the electrospray ionization (ESI) mode. ^{1}H NMR and ^{13}C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in $CDCl_3$, respectively, and chemical shifts are reported in ppm. Elemental analyses are performed on a Yanagimoto MT3CHN recorder. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H_2, FID detection. GC/MS data was recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies).

1.2 Experimental Procedure

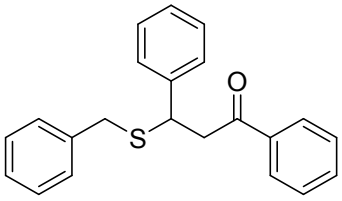
General procedures for the synthesis of bunte salts[10]: A flask was charged with organic halides (50 mmol), sodium thiosulfate pentahydrate (60 mmol), water (10.0 mL) and MeOH (50 mL). The reaction mixture is stirred and heated to 65 ^{o}C. After 16 h at 65 ^{o}C, the reaction mixture is cooled to rt, and then concentrated on a rotovap at a bath temperature of 60 ^{o}C to remove the MeOH and water. The resultant solid is treated with MeOH (100 mL), heated to 50 ^{o}C (most solid dissolves), and filtered to remove excess sodium thiosulfate and sodium bromide. The filtrate is concentrated to a white solid, following trituration of this solid with hexanes, filtration, and drying under vacuum at 50 ^{o}C to afford the corresponding bunte salts.

General procedures for thia-Michael additions with bunte salts and α,β-unsaturated ketones: A mixture of bunte salts **1** 0.60 mmol, α,β-unsaturated ketones **2** 0.50 mmol, TsOH 0.10 mmol in MeOH (1.0 mL) is stirred at 80 ^{o}C for 6 h. Upon completion, the reaction mixture is diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite, The volatiles are removed in *vacuo* to afford the crude product. Further column chromatography on silica gel affords the pure desired product **3**.

General procedures for thia-Michael additions *via* a one-pot process from benzyl chloride, $Na_2S_2O_3$ and α,β-unsaturated ketones: A mixture of benzyl chloride 1.5 mmol and $Na_2S_2O_3$ 2.0 mmol in MeOH (1.0 mL) is stirred at 80 ^{o}C for 2 h. Then, α,β-unsaturated ketones 0.50 mmol and TsOH 0.10 mmol are added to the mixture. The reaction proceeds at the same temperature for additionally 6 h. Upon completion, the

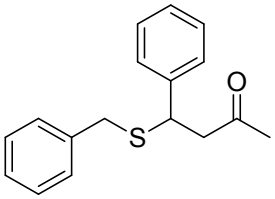
reaction mixture is diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite, The volatiles are removed in *vacuo* to afford the crude product. Further column chromatography on silica gel affords the pure desired product.

2. Characterization Data



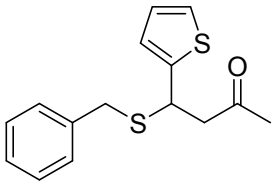
Mass: 332.12

3-(Benzylthio)-1,3-diphenylpropan-1-one **3a**.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.50-3.64 (m, 4H), 4.51-4.54 (t, *J* = 7.0 Hz, 1H), 7.25-7.38 (m, 8H), 7.44-7.46 (t, *J* = 7.5 Hz, 4H), 7.55-7.58 (t, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 36.0 (1C, SCH_2), 44.3 (1C, CH), 45.4 (1C, **C**H_2C=O), 127.2 (1C, Ar-C), 127.5 (1C, Ar-C), 128.2 (4C, Ar-C), 128.6 (2C, Ar-C), 128.7 (4C, Ar-C), 129.1 (2C, Ar-C), 133.3 (1C, Ar-C), 136.9 (1C, Ar-C), 138.0 (1C, Ar-C), 141.9 (1C, Ar-C), 196.9 (1C, C=O). MS (ESI) *m/z*: 332.34 $[M+H]^+$.



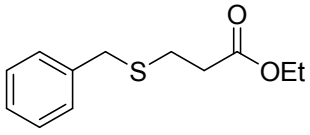
Mass: 270.11

4-(Benzylthio)-4-phenylbutan-2-one **3b**.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95 (s, 3H), 2.83-2.92 (m, 2H), 3.39 (d, *J* = 13.5 Hz, 1H), 3.47 (d, *J* =13.5 Hz, 1H), 4.14-4.17 (t, *J* = 7.0 Hz, 1H), 7.14-7.27 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.1 (1C, CH_3), 35.9 (1C, SCH_2), 44.0 (1C, CH), 50.1 (1C, **C**H_2C=O), 127.1 (1C, Ar-C), 127.5 (1C, Ar-C), 127.9 (2C, Ar-C), 128.6 (1C, Ar-C), 128.7 (1C, Ar-C), 129.0 (1C, Ar-C), 137.9 (1C, Ar-C), 141.6 (1C, Ar-C), 205.4. MS (ESI) *m/z*: 270.05 $[M+H]^+$.



Mass: 276.06

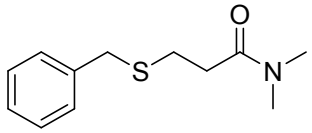
4-(Benzylthio)-4-(thiophen-2-yl)butan-2-one **3c**.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.91-3.03 (m, 2H), 3.58-3.66 (m, 2H), 4.51-4.54 (t, *J* = 7.0 Hz, 1H), 6.91-6.93 (m, 2H), 7.22-7.32 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.6 (1C, CH_3), 36.1 (1C, SCH_2), 39.3 (1C, CH), 50.9 (1C, **C**H_2C=O), 125.0 (1C, Ar-C), 125.9 (1C, Ar-C), 126.6 (1C, Ar-C), 127.3 (1C, Ar-C), 128.6 (2C, Ar-C), 129.1 (2C, Ar-C), 137.8 (1C, Ar-C), 146.5 (1C, Ar-C), 204.9 (1C, C=O). MS (ESI) *m/z*: 275.91 $[M+H]^+$.



Mass: 224.09

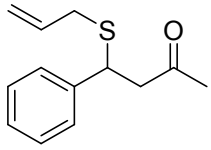
Ethyl 3-(benzylthio)propanoate **3d**.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24-1.27 (t, *J* = 7.0 Hz, 3H),

2.53-2.56 (t, J = 7.5 Hz, 2H), 2.68-2.71 (t, J = 7.5 Hz, 2H), 3.74 (s, 2H), 4.12-4.17 (q, J = 7.0 Hz, 2H), 7.24-7.32 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3 (1C, CH_3), 26.4 (1C, SCH_2), 34.6 (1C, **C**H_2C=O), 36.4 (1C, Ph-**C**H_2S), 60.7 (1C, O=C**C**H_2-Me), 127.2 (1C, Ar-C), 128.7 (2C, Ar-C), 129.0 (2C, Ar-C), 138.2 (1C, Ar-C), 172.0 (1C, C=O). MS (ESI) *m/z*: 224.28 $[M+H]^+$.



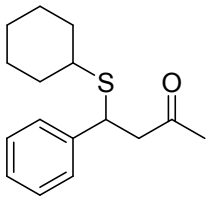
Mass: 223.10

3-(Benzylthio)-*N*,*N*-dimethylpropanamide **3e**.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.47-2.50 (t, J = 7.5 Hz, 2H), 2.74-2.77 (t, J = 7.5 Hz, 2H), 2.91 (s, 3H), 2.92 (s, 3H), 3.74 (s, 2H), 7.21-7.33 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.1 (1C, SCH_2), 33.7 (1C, **C**H_2C=O), 35.5 (1C, Ph-**C**H_2S), 37.0 (1C, NCH_3), 37.2 (1C, NCH_3), 127.1 (1C, Ar-C), 128.6 (2C, Ar-C), 128.9 (2C, Ar-C), 138.7 (1C, Ar-C), 171.3 (1C, C=O). MS (ESI) *m/z*: 223.13 $[M+H]^+$.



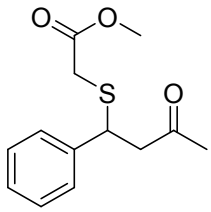
Mass: 220.09

4-(Allylthio)-4-phenylbutan-2-one **3f**.[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.83-2.97 (m, 4H), 4.26-4.29 (t, J = 7.5 Hz, 1H), 5.00-5.08 (m, 2H), 5.68-5.77 (m, 1H), 7.19-7.32 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.8 (1C, CH_3), 34.3 (1C, CH_2S), 43.3 (1C, SCH), 50.1 (1C, CH_2C=O), 117.5 (1C, CH_2=), 127.5 (1C, Ar-C), 128.0 (2C, Ar-C), 128.7 (2C, Ar-C), 134.2 (1C, =CH), 141.8 (1C, Ar-C), 205.5 (1C, C=O). MS (ESI) *m/z*: 220.29 $[M+H]^+$.



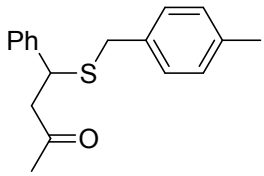
Mass: 262.14

4-(Cyclohexylthio)-4-phenylbutan-2-one **3g**.[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28-1.34 (m, 6H), 1.51-1.53 (m, 1H), 1.61-1.72 (m, 2H), 1.97-2.00 (m, 1H), 2.07 (s, 3H), 2.35-2.40 (m, 1H), 2.93 (d, J = 7.0 Hz, 2H), 4.38-4.41 (t, J = 7.5 Hz, 1H), 7.20-7.36 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.9 (1C, Cy-C), 26.0 (2C, Cy-C), 30.9 (1C, CH_3), 33.3 (1C, Cy-C), 33.7 (1C, Cy-C), 42.8 (1C, SCH), 43.2 (1C, Cy-C), 50.7 (1C, **C**H_2C=O), 127.3 (1C, Ar-C), 127.7 (2C, Ar-C), 128.6 (2C, Ar-C), 142.7 (1C, Ar-C), 205.8 (1C, C=O). MS (ESI) *m/z*: 262.11 $[M+H]^+$.



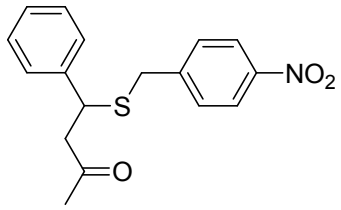
Mass: 252.08

Methyl 2-((3-oxo-1-phenylbutyl)thio)acetate **3h**.[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.09 (s, 3H), 2.94-3.06 (m, 4H), 3.67 (s, 3H), 4.49-4.52 (t, J = 7.5 Hz, 1H), 7.22-7.26 (m, 1H), 7.29 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.6 (1C, O=C**C**H_3), 32.8 (1C, SCH), 44.5 (1C, SCH_2), 49.6 (1C, OCH_3), 52.5 (1C, CH**C**H_2C=O), 127.8 (1C, Ar-C), 128.1 (2C, Ar-C), 128.8 (2C, Ar-C), 140.6 (1C, Ar-C), 170.7 (1C, O-C=O), 204.9 (1C, CH_3**C**=O). MS (ESI) *m/z*: 251.92 $[M+H]^+$.



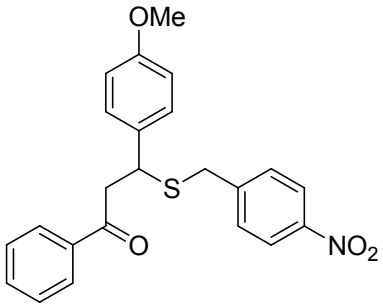
Chemical Formula: $C_{18}H_{20}OS$
Mass: 284.12
Elemental Analysis: C, 76.01; H, 7.09;
O, 5.63; S, 11.27

4-((4-Methylbenzyl)thio)-4-phenylbutan-2-one **3i**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.02 (s, 3H), 2.33 (s, 3H), 2.92-2.94 (m, 2H), 3.41-3.51 (dd, J = 37.0, 8.5 Hz, 2H), 4.19-4.22 (t, J = 7.5 Hz, 1H), 7.09 (brs, 4H), 7.24-7.26 (m, 1H), 7.32-7.33 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (1C, Ar-**C**H_3), 30.6 (1C, O=C**C**H_3), 35.5 (1C, SCH_2), 44.0 (1C, CH), 50.1 (1C, **C**H_2C=O), 127.5 (1C, Ar-C), 128.1 (2C, Ar-C), 128.7 (2C, Ar-C), 128.9 (2C, Ar-C), 129.3 (2C, Ar-C), 134.8 (1C, Ar-C), 136.7 (1C, Ar-C), 141.7 (1C, Ar-C), 205.5 (1C, C=O). MS (ESI) *m/z*: 284.25 $[M+H]^+$. Anal. Calcd for $C_{18}H_{20}OS$: C, 76.01%; H, 7.09%. Found: C, 76.36%; H, 7.45%.



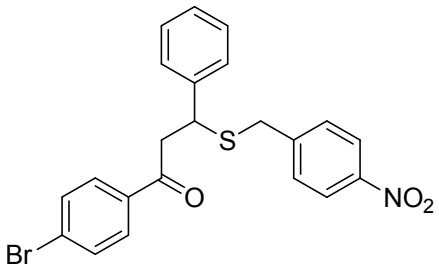
Chemical Formula: $C_{17}H_{17}NO_3S$
Mass: 315.09
Elemental Analysis: C, 64.74; H, 5.43; N, 4.44;
O, 15.22; S, 10.17

4-((4-Nitrobenzyl)thio)-4-phenylbutan-2-one **3j**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.02 (s, 3H), 2.93 (d, J = 7.0 Hz, 2H), 3.48-3.57 (dd, J = 34.0, 8.0 Hz, 2H), 4.17-4.19 (t, J = 7.5 Hz, 1H), 7.21-7.31 (m, 7H), 8.08 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.7 (1C, CH_3), 35.2 (1C, SCH_2), 44.2 (1C, CH), 49.9 (1C, **C**H_2C=O), 123.7 (2C, Ar-C), 127.8 (1C, Ar-C), 128.0 (2C, Ar-C), 129.8 (2C, Ar-C), 141.1 (1C, Ar-C), 146.0 (1C, Ar-C), 147.0 (1C, Ar-C), 205.0 (1C, C=O). MS (ESI) *m/z*: 314.98 $[M+H]^+$. Anal. Calcd for $C_{17}H_{17}NO_3S$: C, 64.74%; H, 5.43%; N, 4.44%. Found: C, 64.38%; H, 5.29%; N, 4.75%.



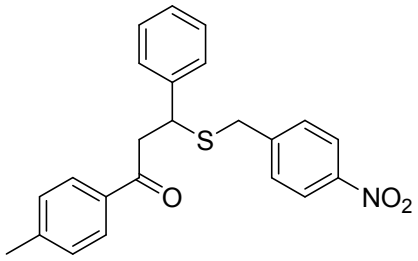
Chemical Formula: $C_{23}H_{21}NO_4S$
Mass: 407.12
Elemental Analysis: C, 67.79; H, 5.19; N, 3.44;
O, 15.71; S, 7.87

3-(4-Methoxyphenyl)-3-((4-nitrobenzyl)thio)-1-phenylpropan-1-one **3k**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.42 (d, J = 7.0 Hz, 2H), 3.51-3.60 (dd, J = 32, 14 Hz, 2H), 3.79 (s, 3H), 4.39-4.42 (t, J = 7.0 Hz, 1H), 6.84 (d, J = 8.5 Hz, 2H), 7.19-7.36 (m, 7H), 7.81 (d, J = 8.5 Hz, 2H), 8.04 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.4 (1C, SCH_2), 44.7 (1C, CH), 44.9 (1C, **C**H_2C=O), 55.6 (1C, OCH_3), 113.9 (2C, Ar-C), 123.7 (2C, Ar-C), 127.7 (1C, Ar-C), 128.1 (2C, Ar-C), 128.8 (2C, Ar-C), 129.7 (1C, Ar-C), 129.8 (2C, Ar-C), 130.5 (2C, Ar-C), 141.6 (1C, Ar-C), 146.1 (1C, Ar-C), 146.9 (1C, Ar-C), 163.8 (1C, Ar-C), 195.0 (1C, C=O). MS (ESI) *m/z*: 407.13 $[M+H]^+$. Anal. Calcd for $C_{23}H_{21}NO_4S$: C, 67.79%; H, 5.19%; N, 3.44%. Found: C, 67.81%; H, 5.32%; N, 3.74%.



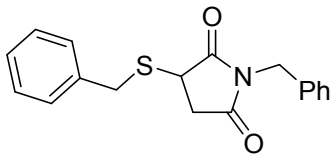
Chemical Formula: $C_{22}H_{18}BrNO_3S$
Mass: 455.02
Elemental Analysis: C, 57.90; H, 3.98; Br, 17.51;
N, 3.07; O, 10.52; S, 7.03

1-(4-Bromophenyl)-3-((4-nitrobenzyl)thio)-3-phenylpropan-1-one **3l**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.41-3.42 (dd, *J* = 7.0, 1.0 Hz, 2H), 3.50-3.59 (dd, *J* = 32.5, 13.5 Hz, 2H), 4.34-4.37 (t, *J* = 7.0 Hz, 1H), 7.19-7.32 (m, 7H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.4 (1C, SCH_2), 44.4 (1C, CH), 45.2 (1C, **C**H_2C=O), 123.7 (2C, Ar-C), 127.8 (1C, Ar-C), 128.1 (2C, Ar-C), 128.7 (1C, Ar-C), 128.8 (2C, Ar-C), 129.7 (2C, Ar-C), 129.8 (2C, Ar-C), 132.0 (2C, Ar-C), 135.4 (1C, Ar-C), 141.2 (1C, Ar-C), 145.9 (1C, Ar-C), 147.0 (1C, Ar-C), 195.5 (1C, C=O). MS (ESI) *m/z*: 455.18 $[M+H]^+$. Anal. Calcd for $C_{22}H_{18}BrNO_3S$: C, 57.90%; H, 3.98%; N, 3.07%. Found: C, 57.68%; H, 4.17%; N, 2.86%.



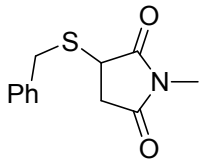
Chemical Formula: $C_{23}H_{21}NO_3S$
Mass: 391.12
Elemental Analysis: C, 70.56; H, 5.41;
N, 3.58; O, 12.26; S, 8.19

3-((4-Nitrobenzyl)thio)-3-phenyl-1-(*p*-tolyl)propan-1-one **3m**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.45-3.47 (dd, *J* = 7.0, 1.5 Hz, 2H), 3.53-3.62 (dd, *J* = 32, 14 Hz, 2H), 4.40-4.43 (t, *J* = 7.0 Hz, 1H), 7.19-7.25 (m, 3H), 7.29-7.36 (m, 6H), 7.75 (d, *J* = 8.5 Hz, 2H), 8.08 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7 (1C, Ar-**C**H_3), 35.4 (1C, CH_2S), 44.6 (1C, CH), 45.2 (1C, **C**H_2C=O), 123.7 (2C, Ar-C), 127.7 (1C, Ar-C), 128.1 (2C, Ar-C), 128.3 (2C, Ar-C) 128.8 (2C, Ar-C), 129.4 (2C, Ar-C), 129.8 (2C, Ar-C), 134.2 (1C, Ar-C), 141.5 (1C, Ar-C), 144.4, 146.1, 147.0, 196.0. MS (ESI) *m/z*: 391.20 $[M+H]^+$. Anal. Calcd for $C_{23}H_{21}NO_3S$: C, 70.56%; H, 5.41%; N, 3.58%. Found: C, 70.29%; H, 5.17%; N, 3.96%.



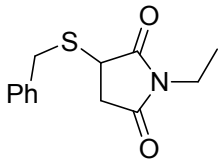
Mass: 311.10

1-Benzyl-3-(benzylthio)pyrrolidine-2,5-dione **3n**.[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38-2.43 (dd, *J* = 18.5, 6.0 Hz, 1H), 2.93-2.99 (dd, *J* = 19.0, 9.0 Hz, 1H), 3.49-3.51 (q, *J* = 4.0 Hz, 1H), 3.82 (d, *J* = 13.5 Hz, 1H), 4.19 (d, *J* = 13.5 Hz, 1H), 4.61-4.69 (dd, *J* = 25.0, 14.0 Hz, 2H), 7.25-7.34 (m, 10 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.6 (1C, **C**H_2C=O), 36.0 (1C, SCH_2), 37.5 (1C, CH), 42.7 (1C, CH_2N), 127.7 (1C, Ar-C), 128.2 (1C, Ar-C), 128.8 (6C, Ar-C), 129.3 (2C, Ar-C), 135.5 (1C, Ar-C), 136.9 (1C, Ar-C), 174.5 (1C, C=O), 176.6 (1C, C=O). MS (ESI) *m/z*: 311.25 $[M+H]^+$.



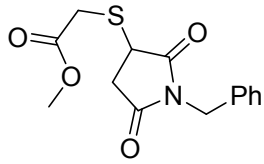
Mass: 235.07

3-(Benzylthio)-1-methylpyrrolidine-2,5-dione **3o**.[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42-2.46 (dd, *J* = 19.0, 4.0 Hz, 1H), 2.96-3.04 (m, 4H), 3.51-3.54 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.88 (d, *J* = 13.5 Hz, 1H), 4.24 (d, *J* = 13.5 Hz, 1H), 7.29-7.42 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.2 (1C, NCH_3), 35.6 (1C, CH_2C=O), 36.1 (1C, SCH_2), 37.5 (1C, CH), 127.7 (1C, Ar-C), 128.8 (2C, Ar-C), 129.3 (2C, Ar-C), 136.8 (1C, Ar-C), 174.9 (1C, C=O), 177.0 (1C, C=O). MS (ESI) *m/z*: 235.16 $[M+H]^+$.



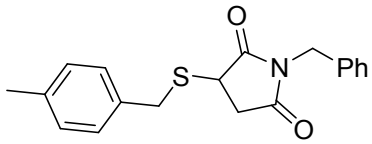
Chemical Formula: $C_{13}H_{15}NO_2S$
Mass: 249.08
Elemental Analysis: C, 62.62; H, 6.06;
N, 5.62; O, 12.83; S, 12.86

3-(Benzylthio)-1-ethylpyrrolidine-2,5-dione **3p**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18-1.21 (t, J = 7.0 Hz, 3H), 2.39-2.43 (dd, *J* = 18.5, 1.5 Hz, 1H), 2.94-2.99 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.49-3.51 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.55-3.59 (q, *J* = 7.5 Hz, 2H), 3.87 (d, *J* = 13.5 Hz, 1H), 4.24 (d, *J* = 13.5 Hz, 1H), 7.29-7.42 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0 (1C, CH_3), 34.1 (1C, CH_2N), 35.6 (1C, **C**H_2C=O), 36.0 (1C, SCH_2), 37.4 (1C, CH), 127.7 (1C, Ar-C), 128.8 (2C, Ar-C), 129.3 (2C, Ar-C), 136.9 (1C, Ar-C), 174.7 (1C, C=O), 176.8 (1C, C=O). MS (ESI) *m/z*: 249.18 $[M+H]^+$. Anal. Calcd for $C_{13}H_{15}NO_2S$: C, 62.62%; H, 6.06%; N, 5.62%. Found: C, 62.38%; H, 5.87%; N, 5.37%.



Chemical Formula: $C_{14}H_{15}NO_4S$
Mass: 293.07
Elemental Analysis: C, 57.32; H, 5.15; N, 4.77;
O, 21.82; S, 10.93

Methyl 2-((1-benzyl-2,5-dioxopyrrolidin-3-yl)thio)acetate **3q**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50-2.54 (dd, *J* = 19.0, 4.0 Hz, 1H), 3.11-3.17 (q, *J* = 9.5 Hz, 1H), 3.34-3.37 (d, *J* = 16.0 Hz, 1H), 3.74 (s, 3H), 3.90-3.93 (d, *J* = 16.0 Hz, 1H), 4.01-4.04 (dd, *J* = 9.5, 3.5 Hz, 1H), 4.62-4.70 (q, *J* = 9.0 Hz, 2H), 7.28-7.37 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 33.0 (1C, SCH_2), 35.5 (1C, CH**C**H_2C=O), 38.4 (1C, CH), 42.8 (1C, Ph-**C**H_2), 52.8 (1C, OCH_3), 128.2 (1C, Ar-C), 128.8 (4C, Ar-C), 135.2 (1C, Ar-C), 170.1 (1C, O-C=O), 174.1 (1C, N-C=O), 176.1 (1C, N-C=O). MS (ESI) *m/z*: 293.22 $[M+H]^+$. Anal. Calcd for $C_{14}H_{15}NO_4S$: C, 57.32%; H, 5.15%; N, 4.77%. Found: C, 57.65%; H, 5.41%; N, 4.59%.



Chemical Formula: $C_{19}H_{19}NO_2S$
Mass: 325.11
Elemental Analysis: C, 70.12; H, 5.88;
N, 4.30; O, 9.83; S, 9.85

1-Benzyl-3-((4-methylbenzyl)thio)pyrrolidine-2,5-dione **3s**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.40-2.45 (dd, *J* = 19.0, 1.5 Hz, 1H), 2.95-3.00 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.81 (d, *J* = 13.5 Hz, 1H), 4.17 (d, *J* = 13.5 Hz, 1H), 4.63-4.71 (q, *J* = 9.0 Hz, 2H), 7.13-7.14 (d, *J* = 8.0 Hz, 2H), 7.25-7.40 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (1C, CH_3), 35.6 (1C, **C**H_2C=O), 35.7 (1C, CH_2S), 37.6 (1C, CH), 42.7 (1C, NCH_2), 128.1 (1C, Ar-C), 128.8 (4C, Ar-C), 129.2 (2C, Ar-C), 129.5 (2C, Ar-C), 133.7 (1C, Ar-C), 135.5 (1C, Ar-C), 137.4 (1C, Ar-C), 174.5 (1C, C=O), 176.6 (1C, C=O). MS (ESI) *m/z*: 325.12 $[M+H]^+$. Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.12%; H, 5.88%; N, 4.30%. Found: C, 70.42%; H, 6.01%; N, 4.41%.

[1] Khatik, G. L.; Sharma, G.; Kumar, R.; Chakraborti, A. K., Scope and limitations of $HClO_4$–SiO_2 as an extremely efficient, inexpensive, and reusable catalyst for chemoselective carbon–sulfur bond formation. *Tetrahedron* **2007**, *63* (5), 1200-1210.

[2] Ricci, P.; Carlone, A.; Bartoli, G.; Bosco, M.; Sambri, L.; Melchiorre, P., Organocatalytic Asymmetric Sulfa-Michael Addition to α,β-Unsaturated Ketones. *Advanced Synthesis & Catalysis* **2008,** *350* (1), 49-53.

[3] Firouzabadi, H.; Iranpoor, N.; Abbasi, M., Pronounced Catalytic Effect of a Micellar Solution of Sodium Dodecyl Sulfate (SDS) on the Efficient C-S Bond Formation via an Odorless Thia-Michael Addition Reaction through the in situ Generation of S-Alkylisothiouronium Salts. *Advanced Synthesis & Catalysis* **2009,** *351* (5), 755-766.

[4] Commercial chemical, CAS number: 200627-99-2.

[5] Chu, C.-M.; Huang, W.-J.; Lu, C.; Wu, P.; Liu, J.-T.; Yao, C.-F., The iron(III) chloride-mediated 1,4-addition of mercaptans to α,β-unsaturated ketones and esters under solvent free conditions. *Tetrahedron Letters* **2006,** *47* (41), 7375-7380.

[6] Azizi, N.; Khajeh-Amiri, A.; Ghafuri, H.; Bolourtchian, M., A highly efficient, operationally simple and selective thia-Michael addition under solvent-free condition. *Green Chemistry Letters and Reviews* **2009,** *2* (1), 43-46.

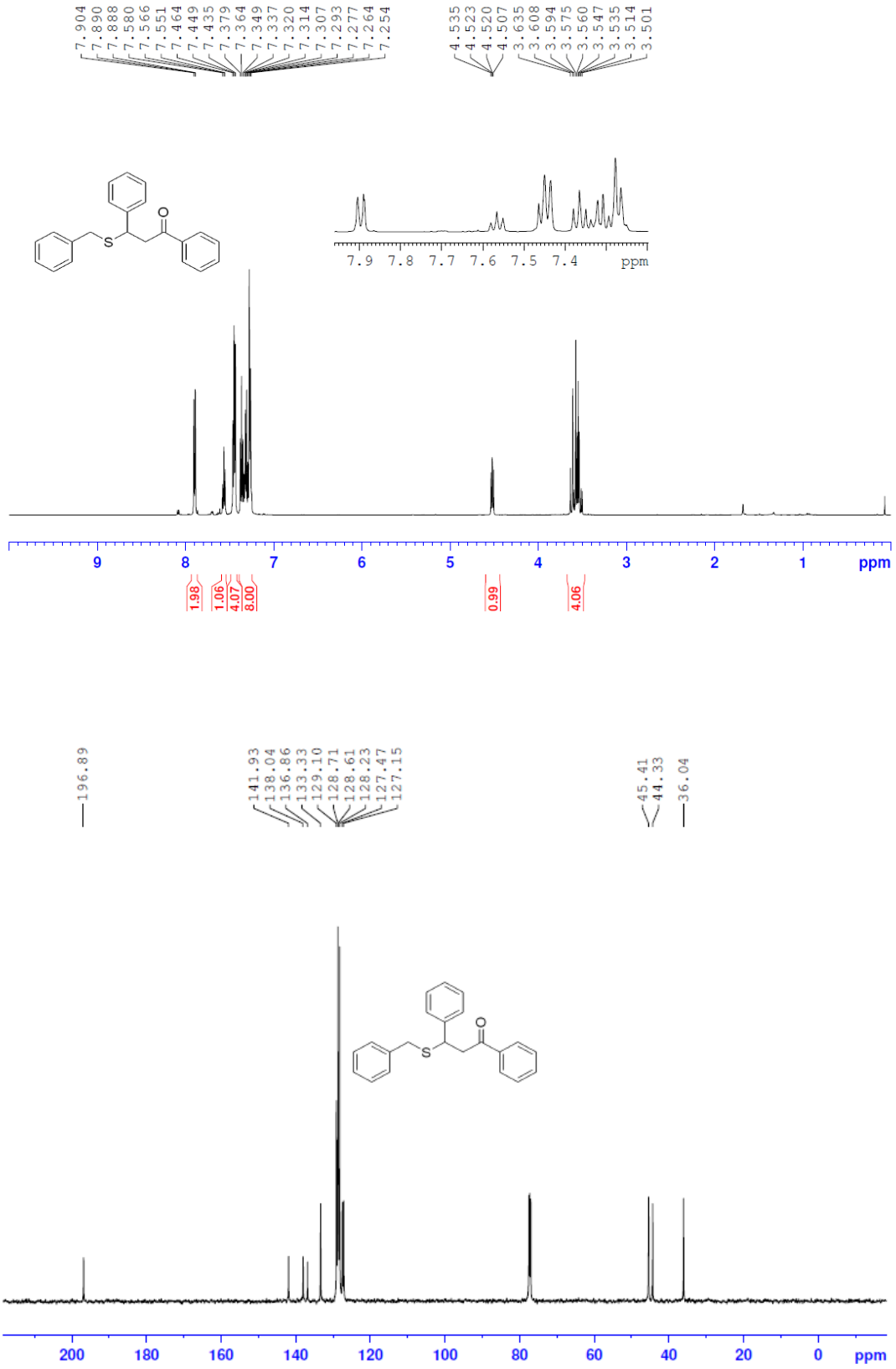
[7] Hui, Y.; Jiang, J.; Wang, W.; Chen, W.; Cai, Y.; Lin, L.; Liu, X.; Feng, X., Highly Enantioselective Conjugate Addition of Thioglycolate to Chalcones Catalyzed by Lanthanum: Low Catalyst Loading and Remarkable Chiral Amplification. *Angewandte Chemie International Edition* **2010,** *49* (25), 4290-4293.

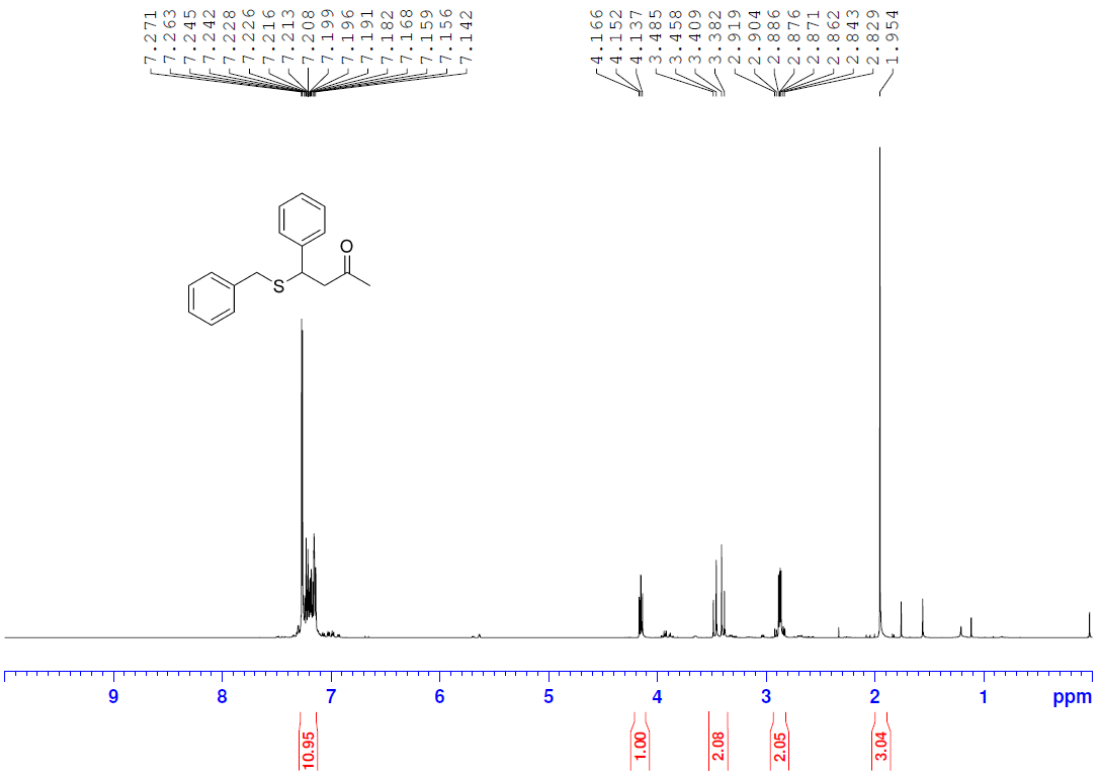
[8] Known compound, CAS number: 939741-08-9.

[9] Known compound, CAS number: 128535-18-2.

[10] Reeves, J. T.; Camara, K.; Han, Z. S.; Xu, Y.; Lee, H.; Busacca, C. A.; Senanayake, C. H., The Reaction of Grignard Reagents with Bunte Salts: A Thiol-Free Synthesis of Sulfides. *Organic Letters* **2014,** *16* (4), 1196-1199.

3 NMR Spectra of All Products

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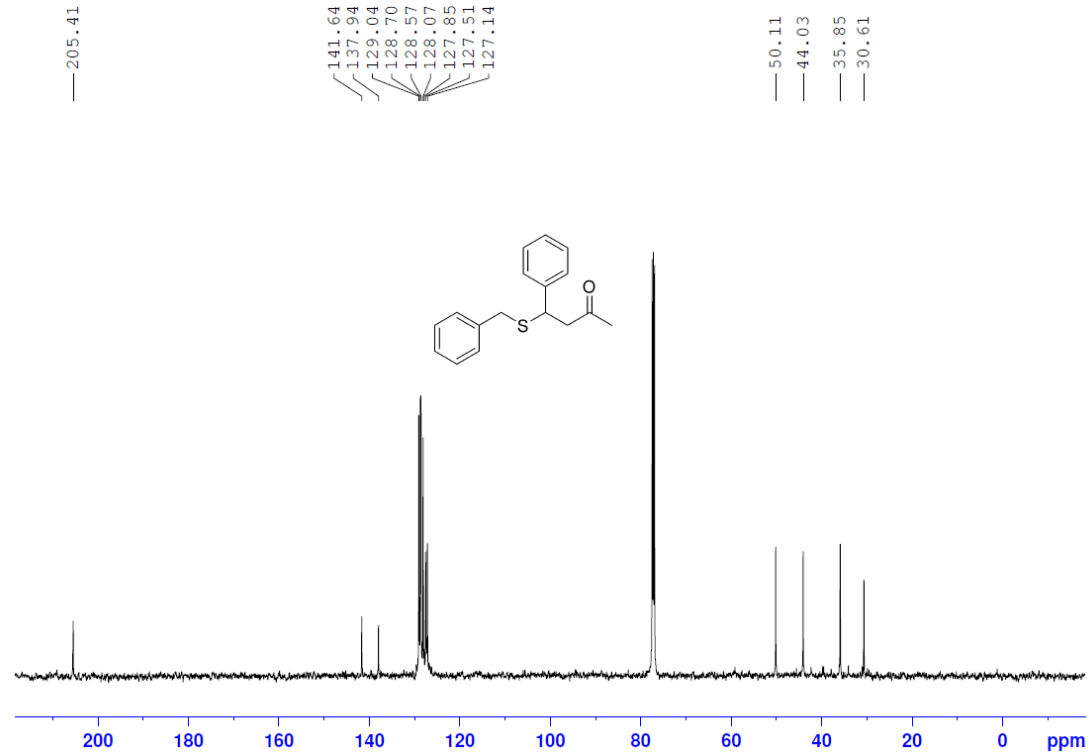
3.04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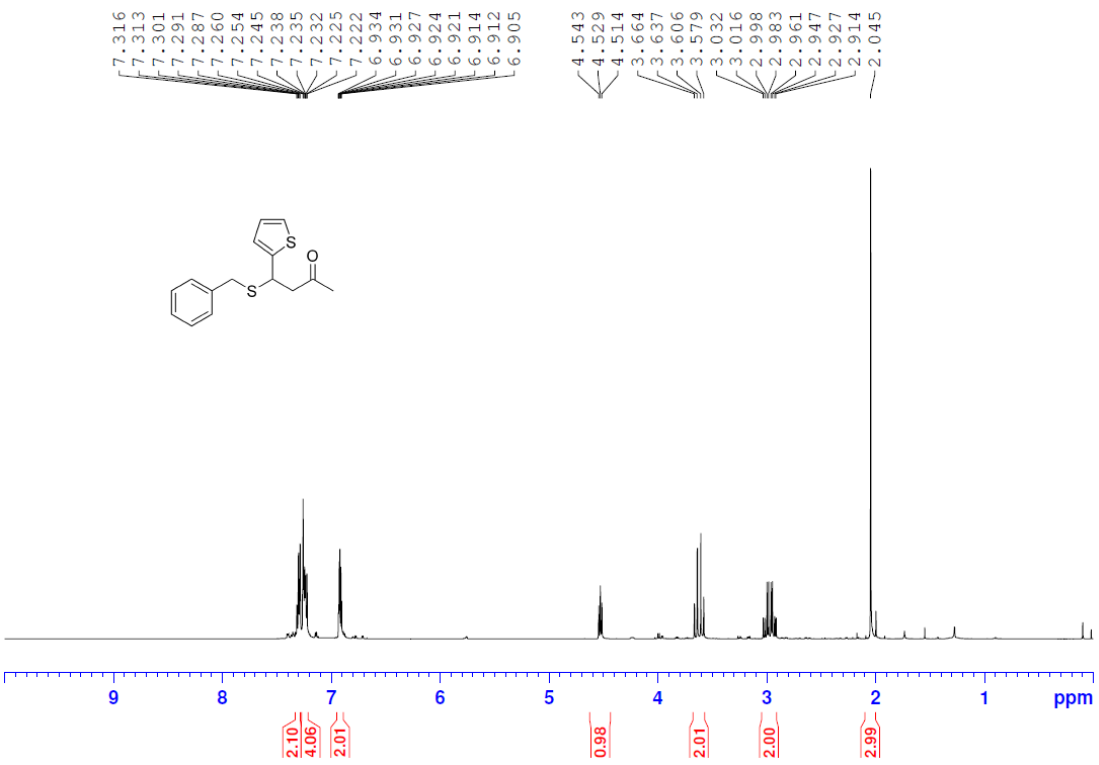
ppm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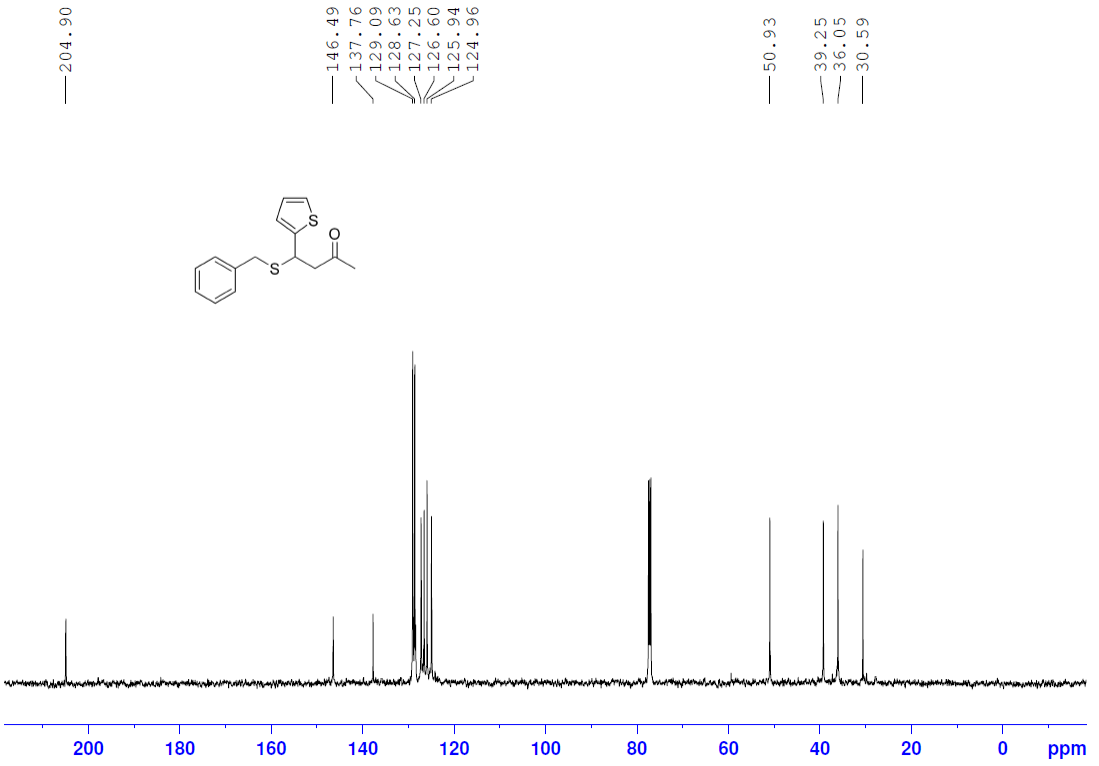
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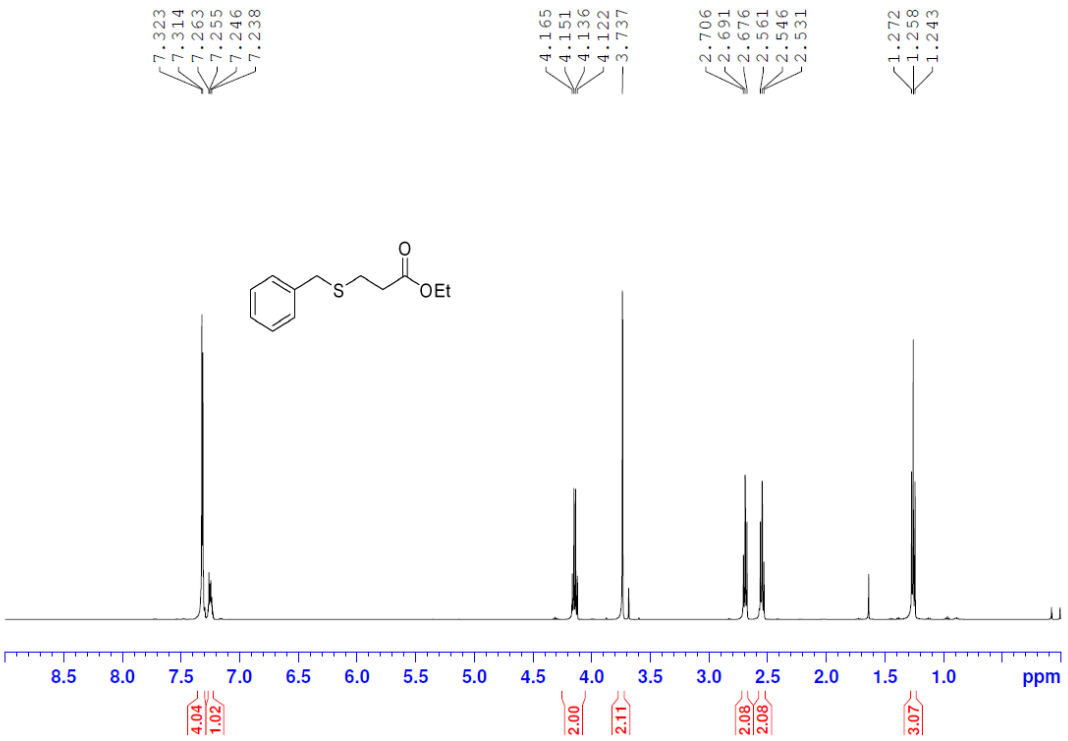
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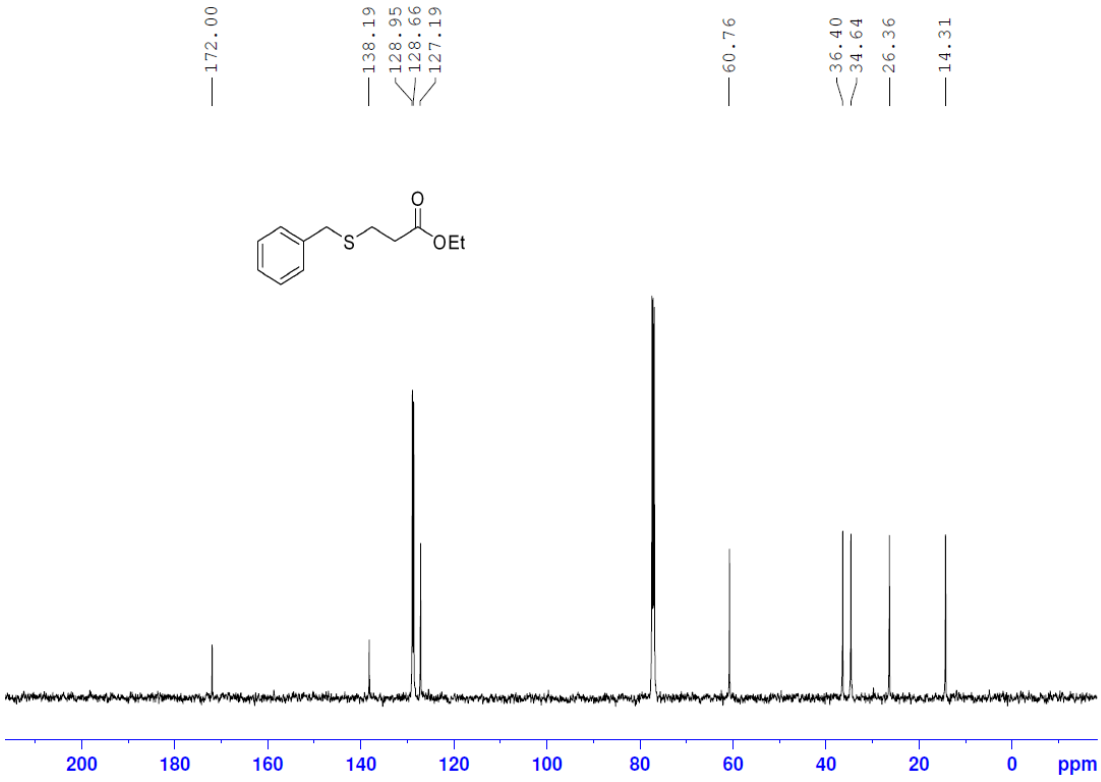
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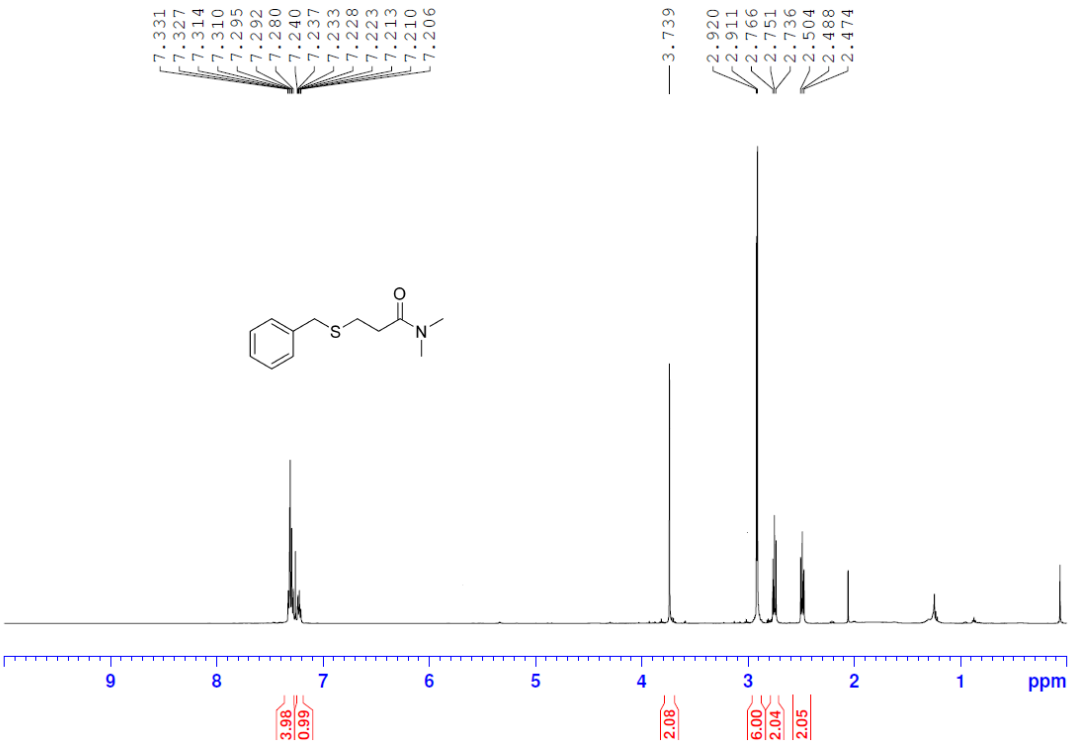
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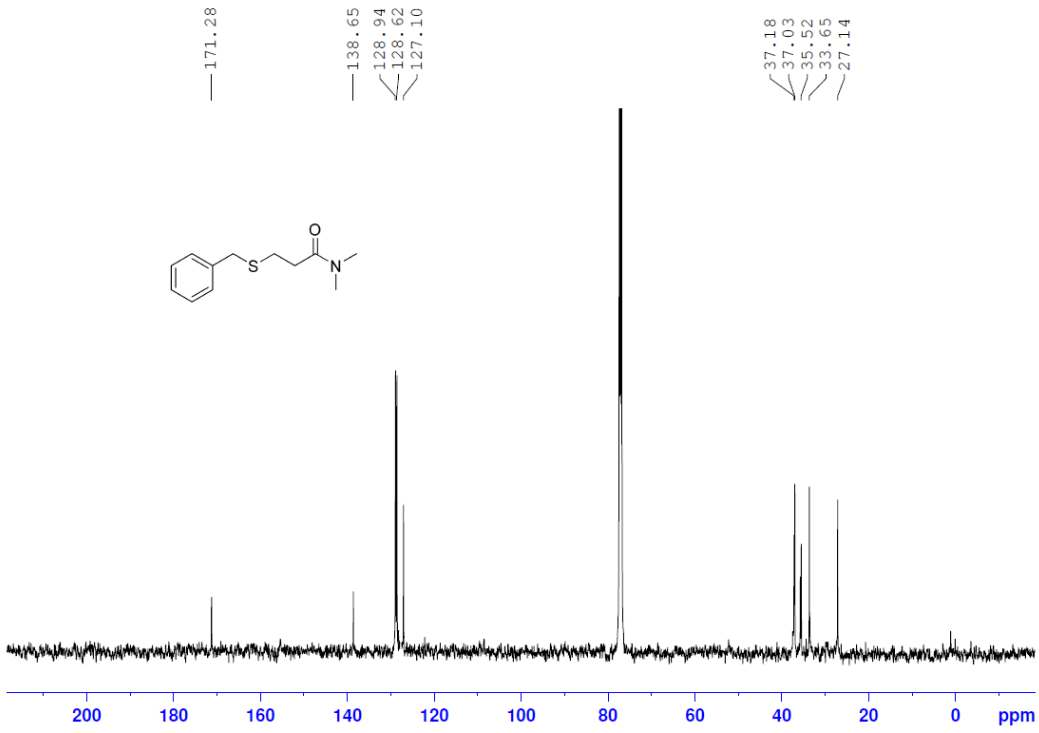
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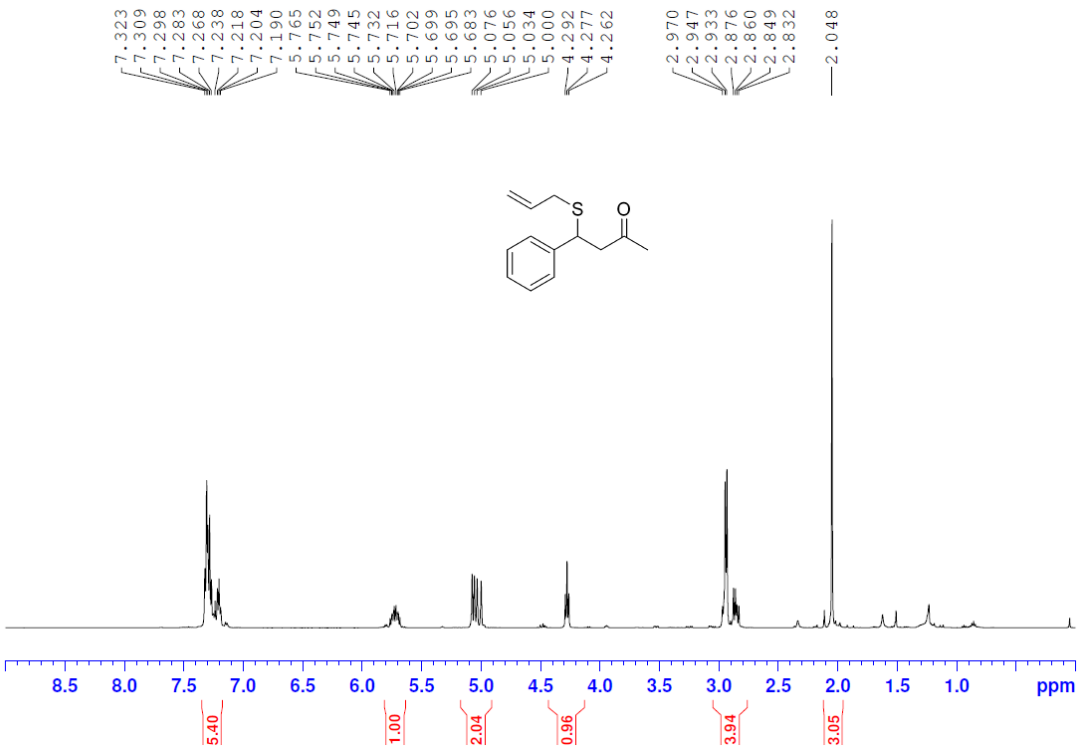
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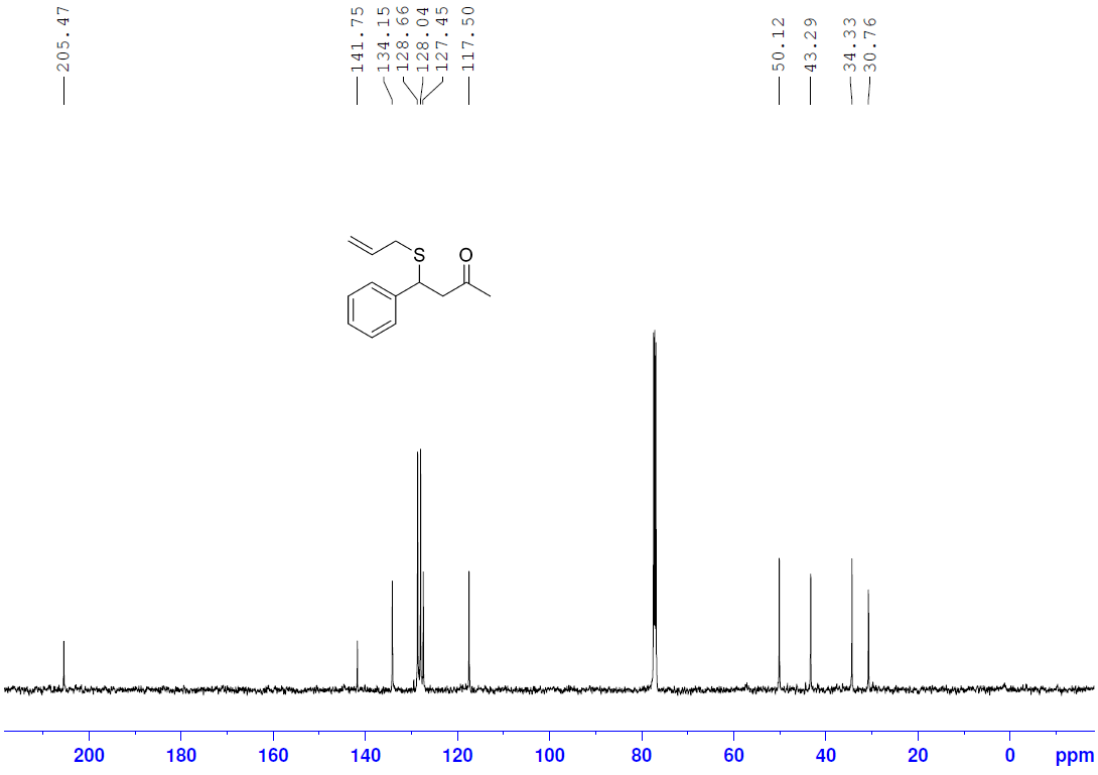
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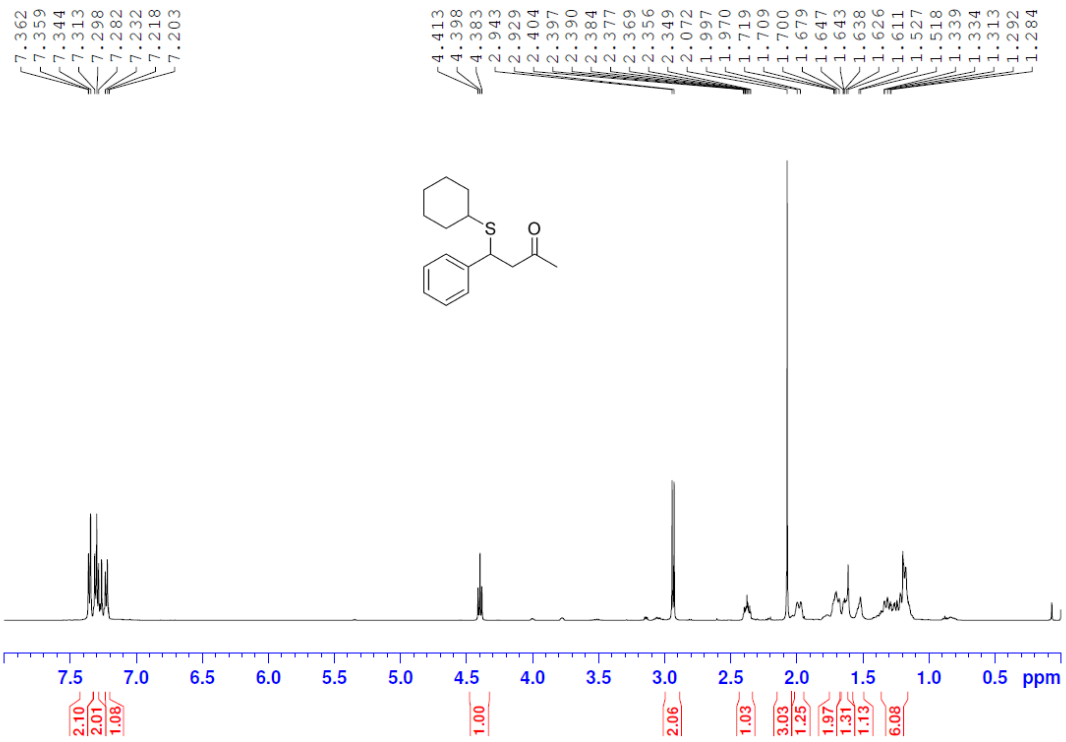
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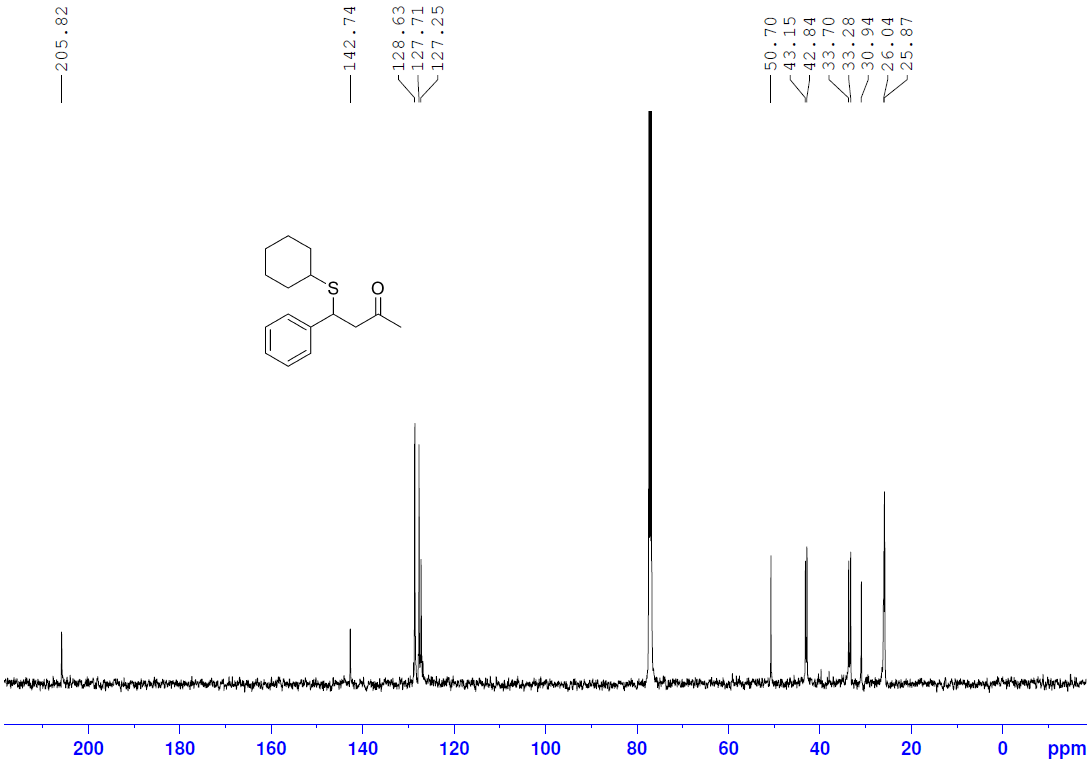
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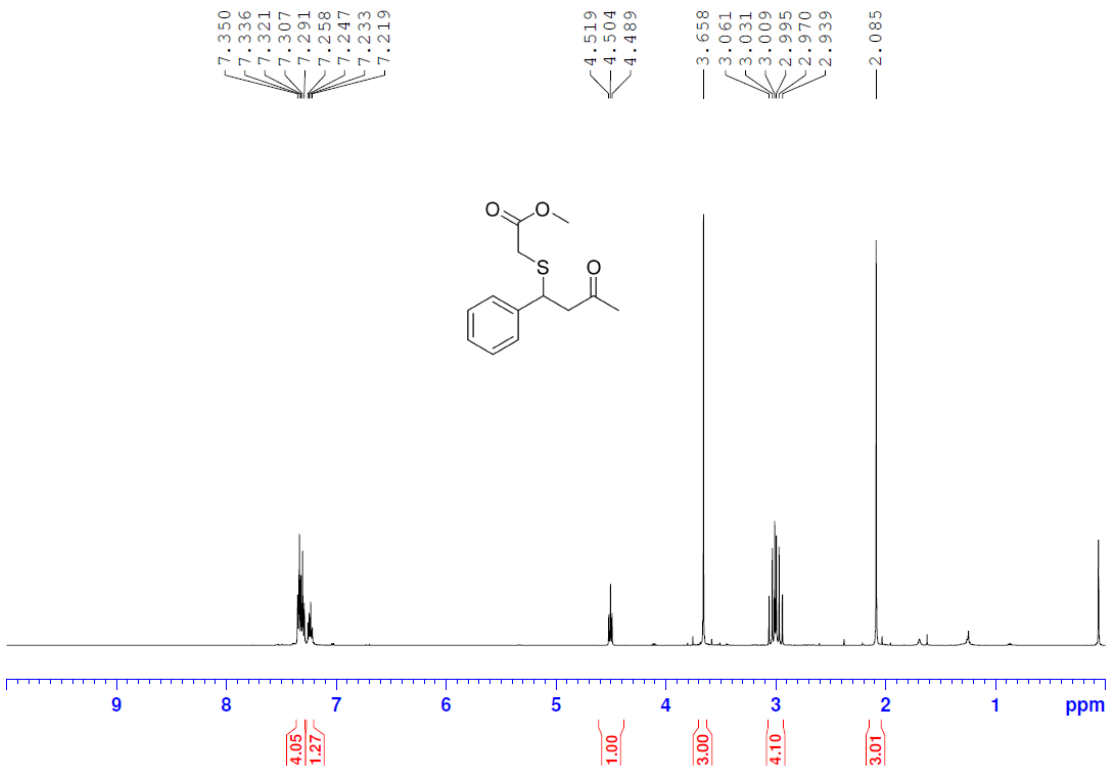
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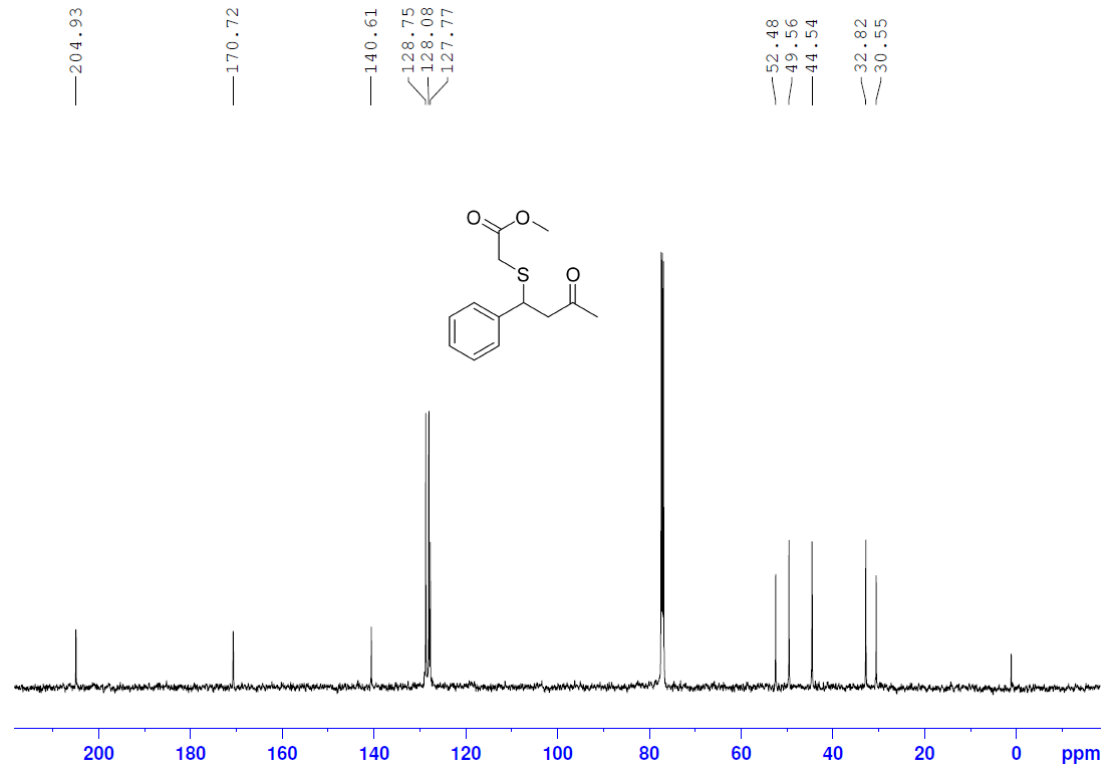
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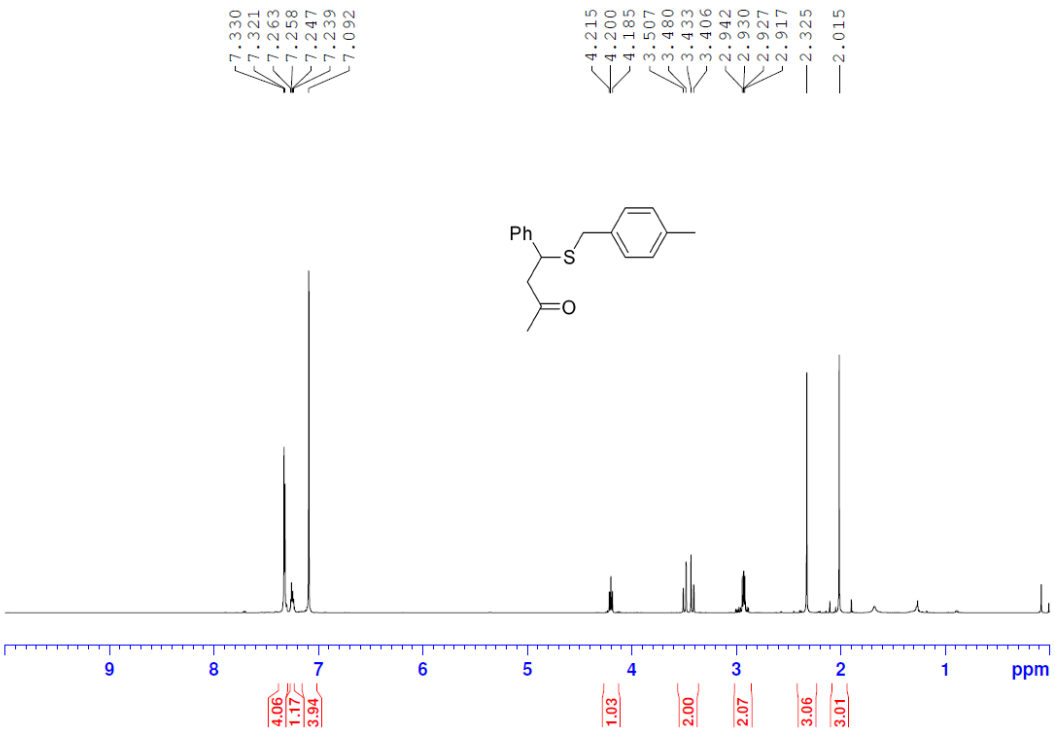
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ppm
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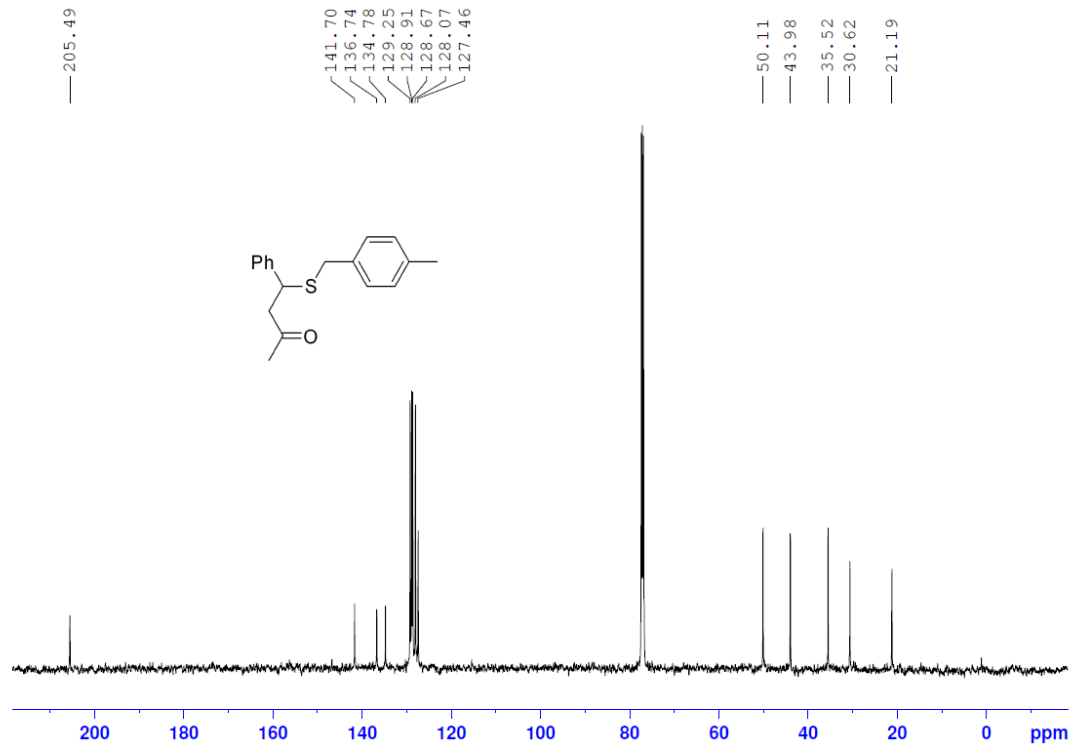
3.06
3.01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128.67
128.07
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43.98
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Ph
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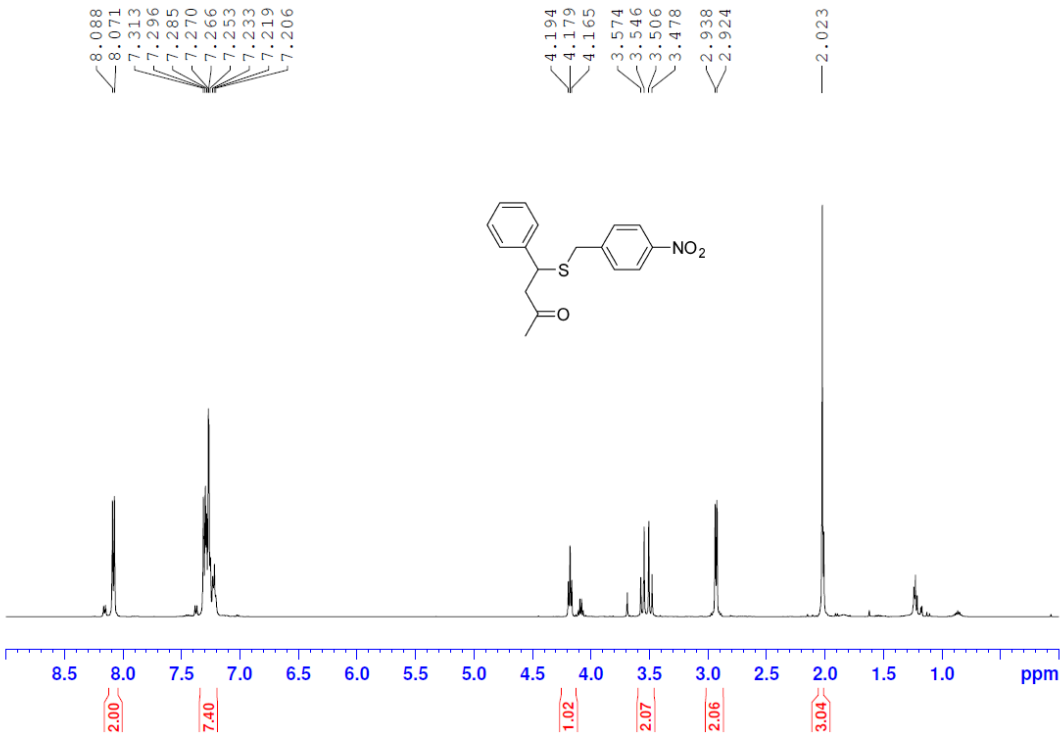
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7.270
7.266
7.253
7.233
7.219
7.206
4.194
4.179
4.165
3.574
3.546
3.506
3.478
2.938
2.924
2.023
NO2
S
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.0
1.5
1.0
ppm
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7.40
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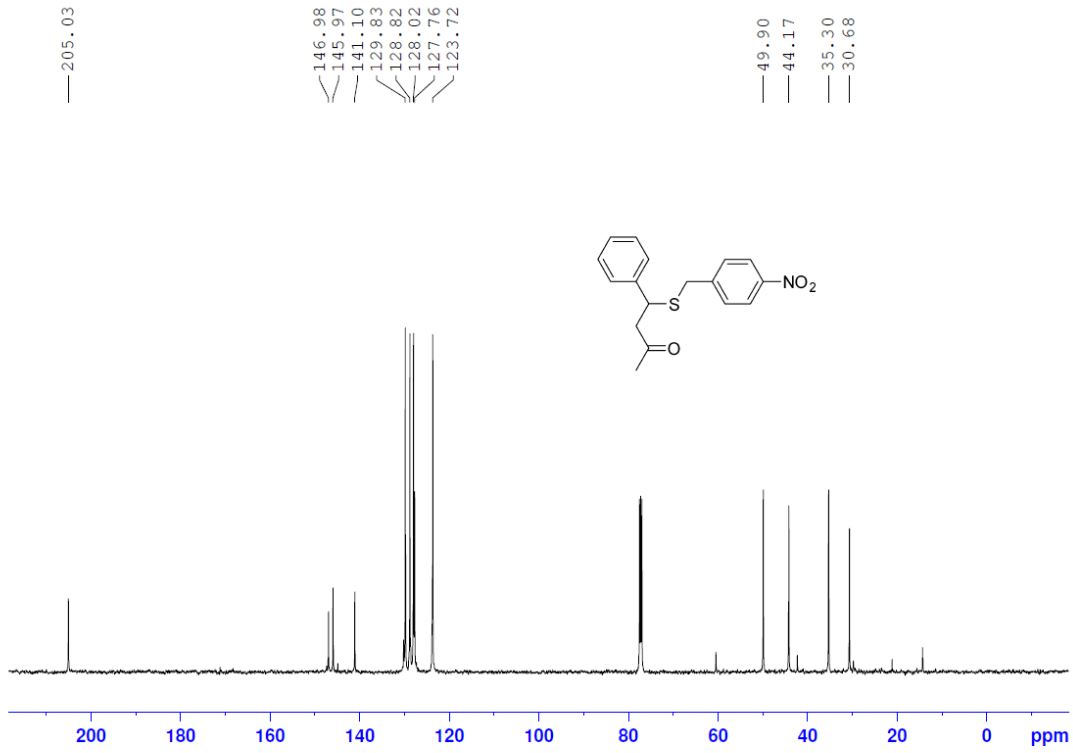
2.07
2.06
3.04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145.97
141.10
129.83
128.82
128.02
127.76
123.72
49.90
44.17
35.30
30.68
NO2
S
O
200
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120
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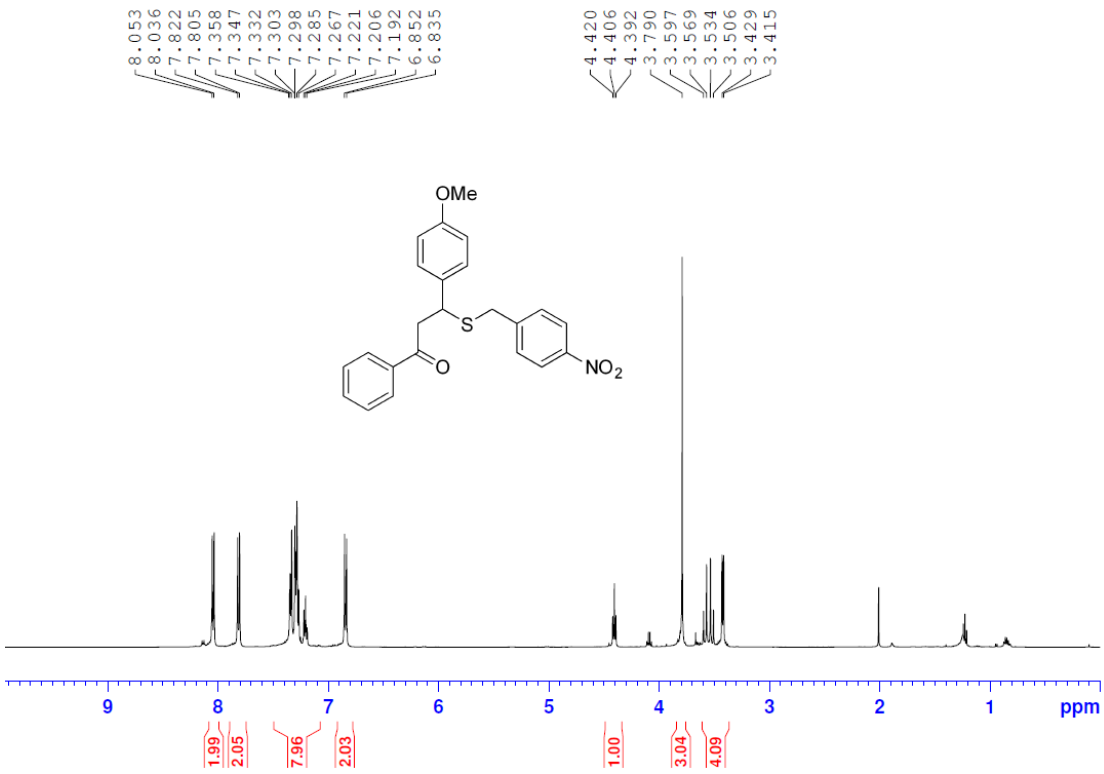
60
40
20
0
ppm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7.303
7.298
7.285
7.267
7.221
7.206
7.192
6.852
6.835
4.420
4.406
4.392
3.790
3.597
3.569
3.534
3.506
3.429
3.415
OMe
S
O
NO2
9
8
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4
3
2
1
ppm
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7.96
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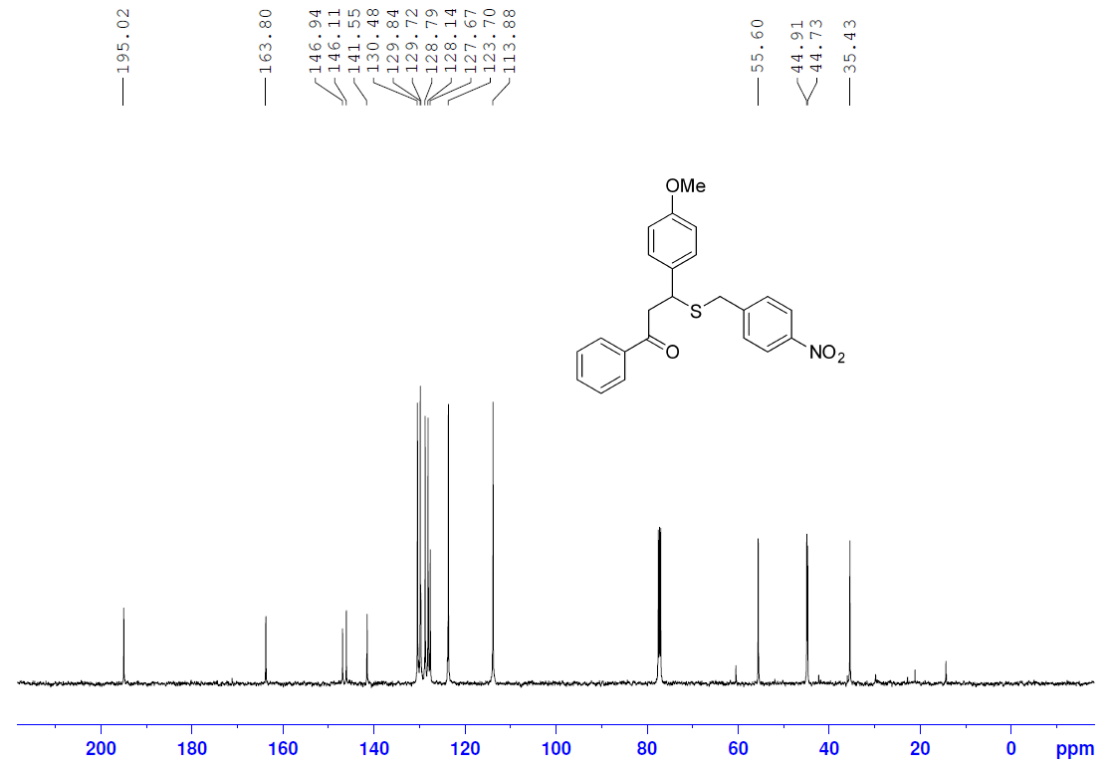
1.00
3.04
4.09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163.80
146.94
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141.55
130.48
129.84
129.72
128.79
128.14
127.67
123.70
113.88
55.60
44.91
44.73
35.43
OMe
S
O
NO2
200
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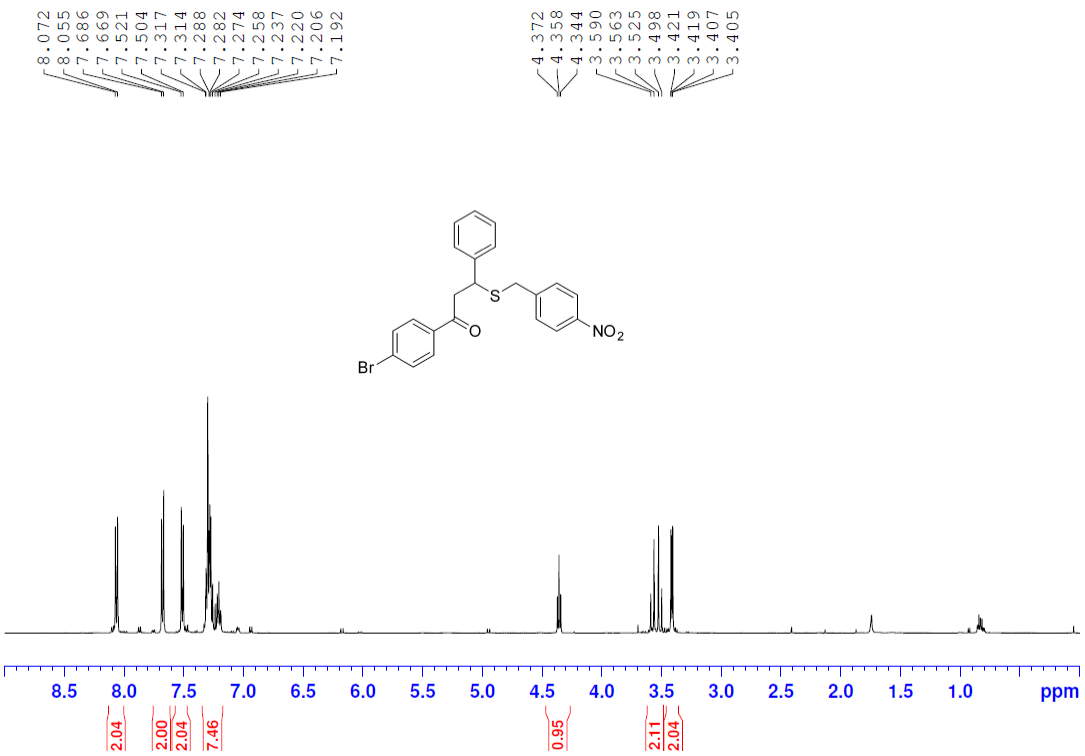
160
140
120
100
80
60
40
20
0
ppm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7.314
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7.274
7.258
7.237
7.220
7.206
7.192
4.372
4.358
4.344
3.590
3.563
3.525
3.498
3.421
3.419
3.407
3.405
S
O
NO2
Br
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.04
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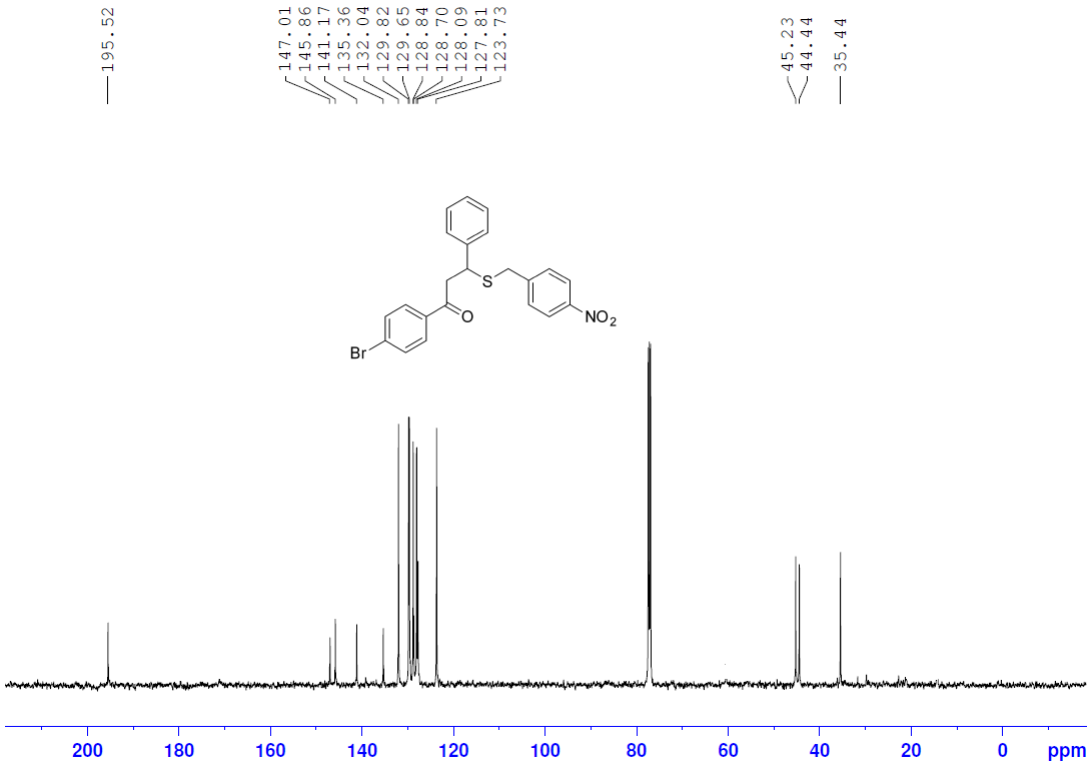
2.04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132.04
129.82
129.65
128.84
128.70
128.09
127.81
123.73
45.23
44.44
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O
NO2
Br
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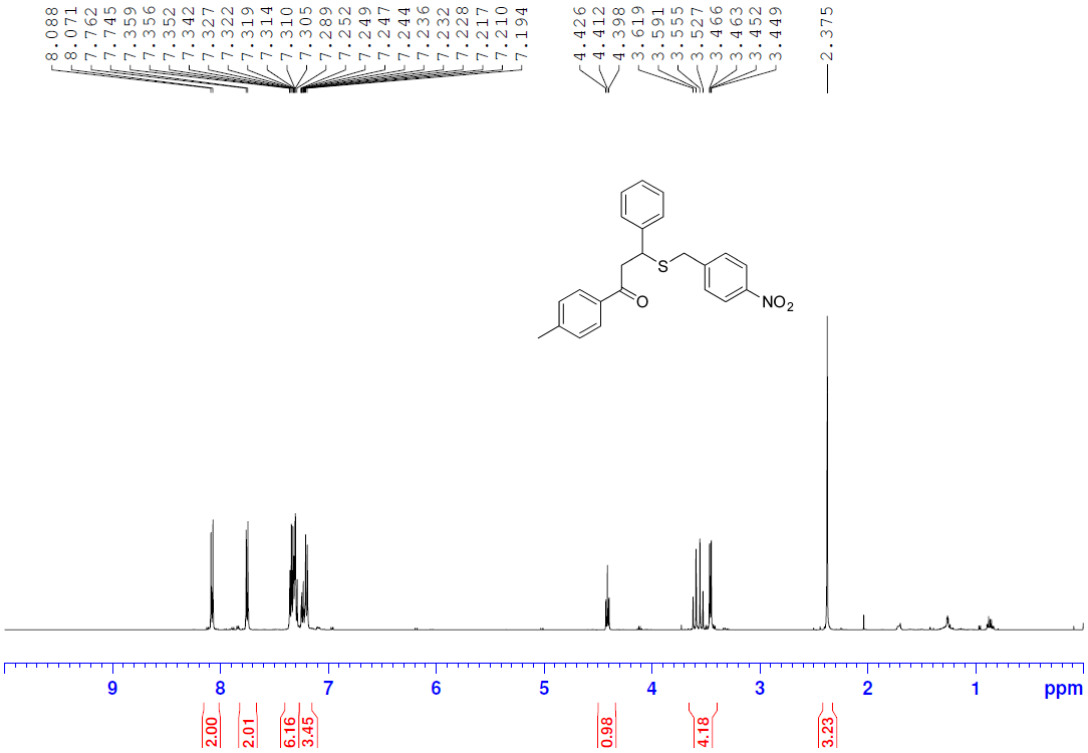
120
100
80
60
40
20
0
ppm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7.342
7.327
7.322
7.319
7.314
7.310
7.305
7.289
7.252
7.249
7.247
7.244
7.236
7.232
7.228
7.217
7.210
7.194
4.426
4.412
4.398
3.619
3.591
3.555
3.527
3.466
3.463
3.452
3.449
2.375
S
O
NO2
9
8
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4
3
2
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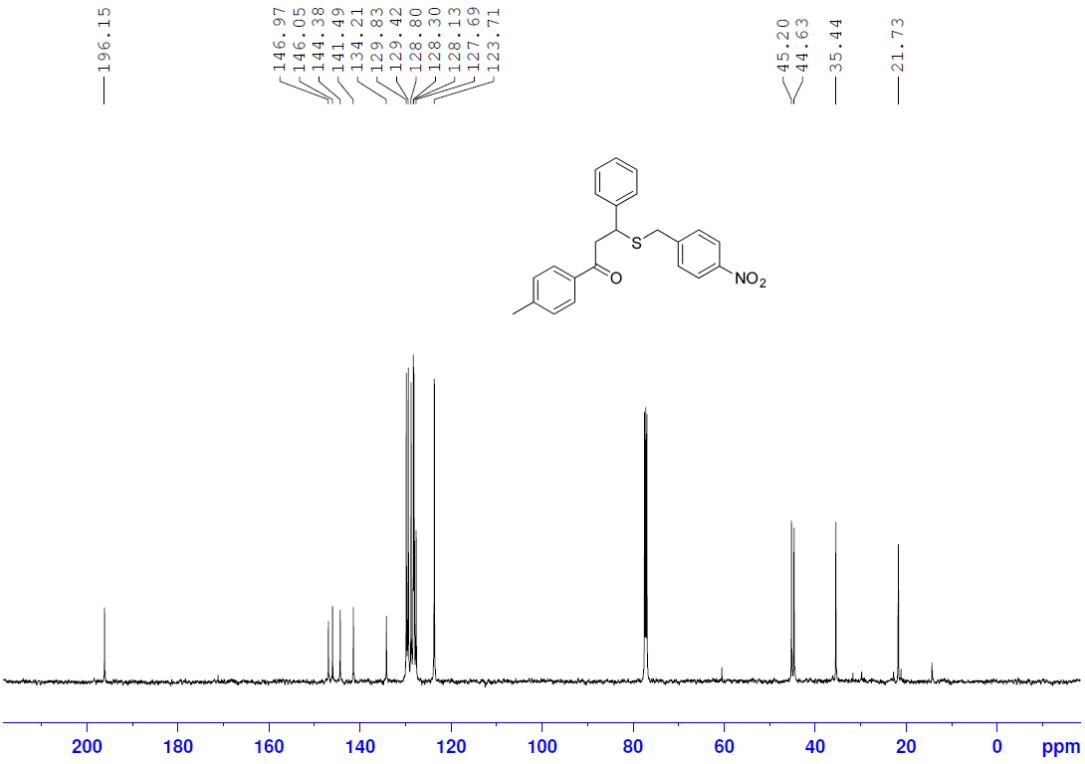
3.23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144.38
141.49
134.21
129.83
129.42
128.80
128.30
128.13
127.69
123.71
45.20
44.63
35.44
21.73
S
O
NO2
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140
120
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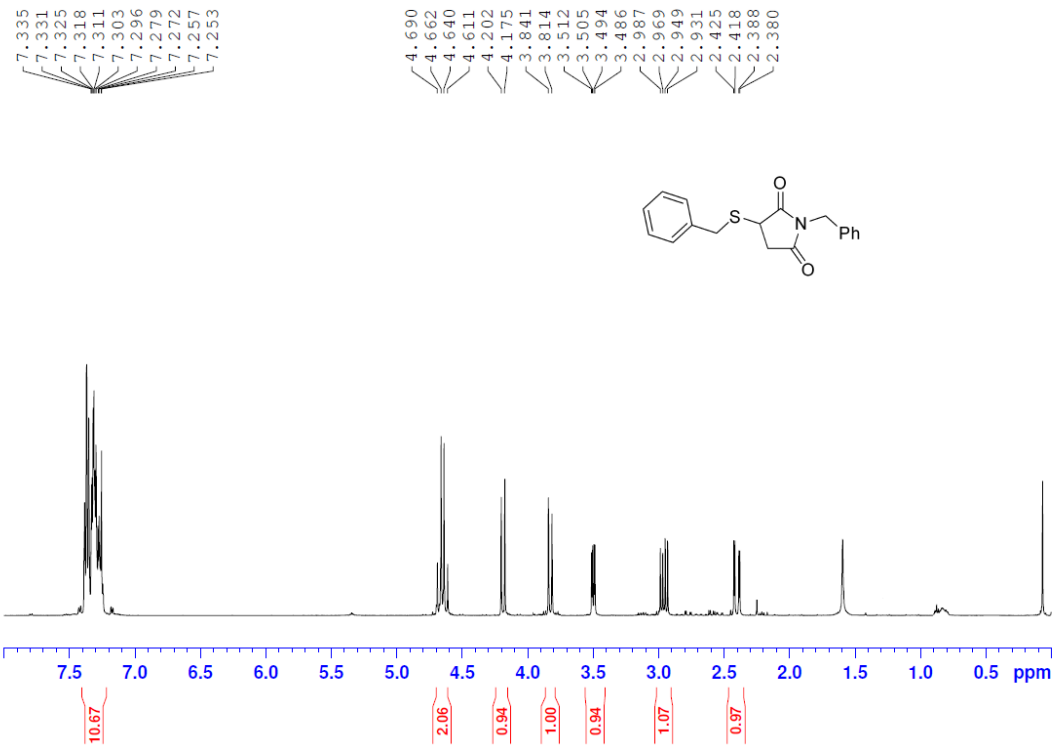
80
60
40
20
0
ppm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7.303
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7.279
7.272
7.257
7.253
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4.662
4.640
4.611
4.202
4.175
3.841
3.814
3.512
3.505
3.494
3.486
2.987
2.969
2.949
2.931
2.425
2.418
2.388
2.380
S
N
O
O
Ph
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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0.5
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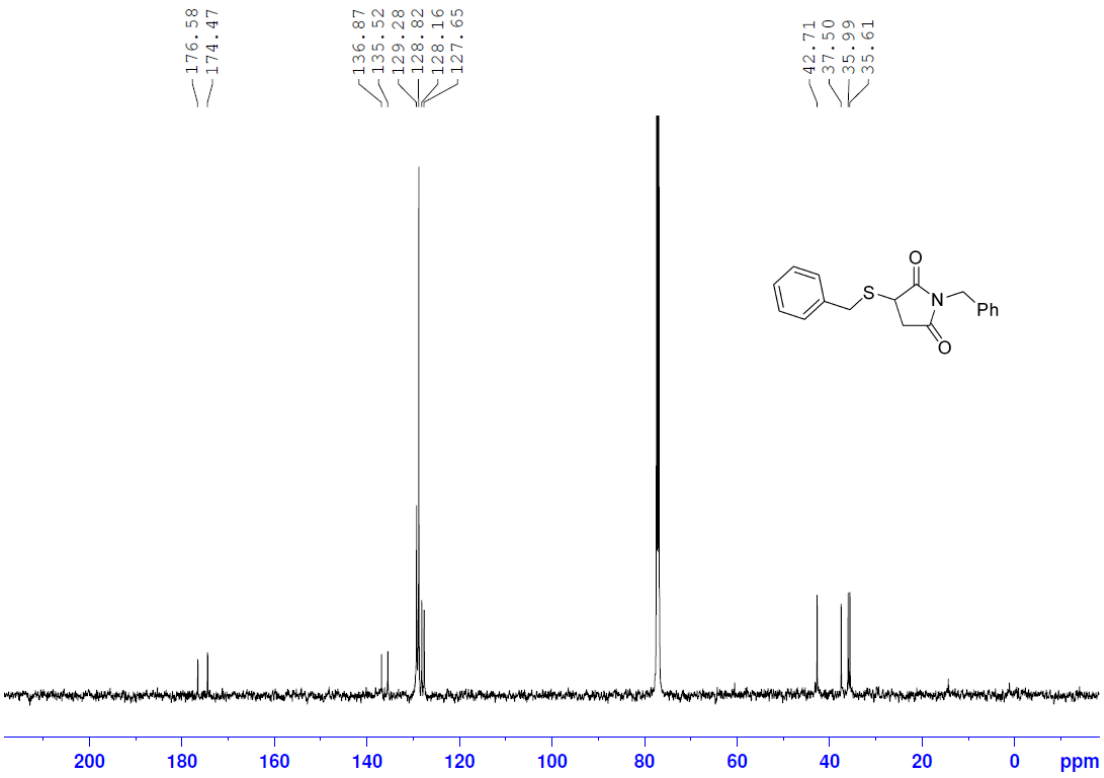
0.94
1.07
0.97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128.82
128.16
127.65
42.71
37.50
35.99
35.61
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N
O
O
Ph
200
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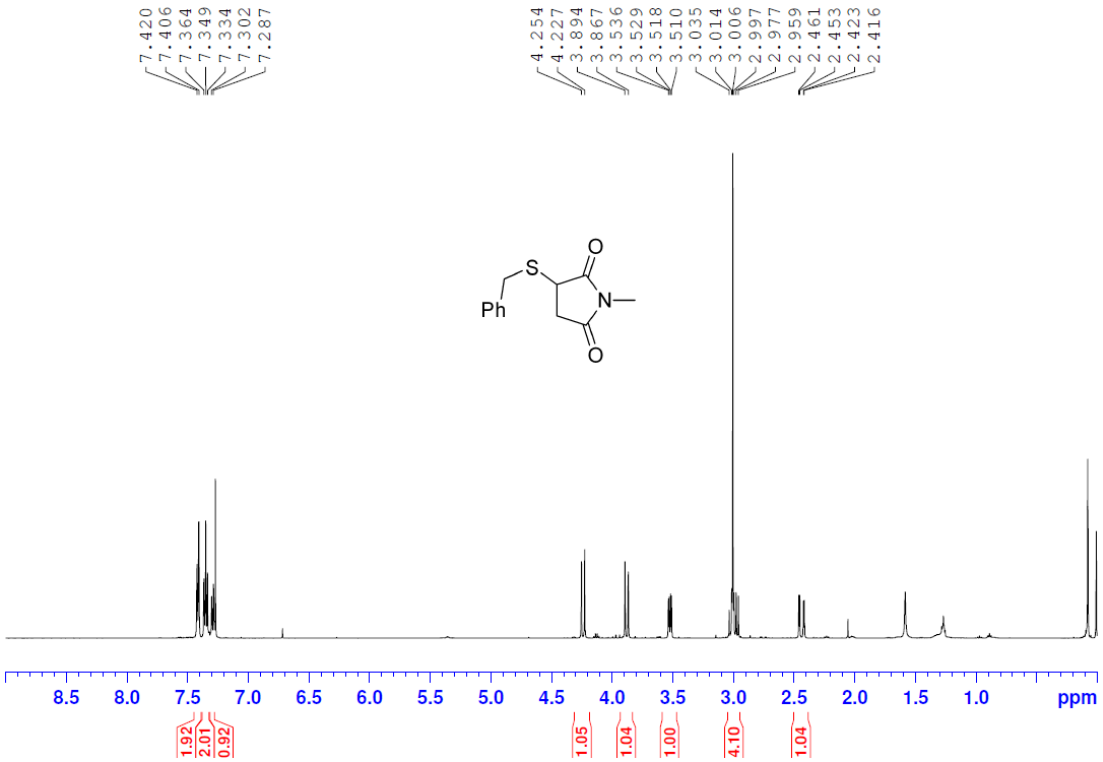
140
120
100
80
60
40
20
0
ppm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7.287
4.254
4.227
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3.867
3.536
3.529
3.518
3.510
3.035
3.014
3.006
2.997
2.977
2.959
2.461
2.453
2.423
2.416
S
Ph
O
N
O
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
ppm
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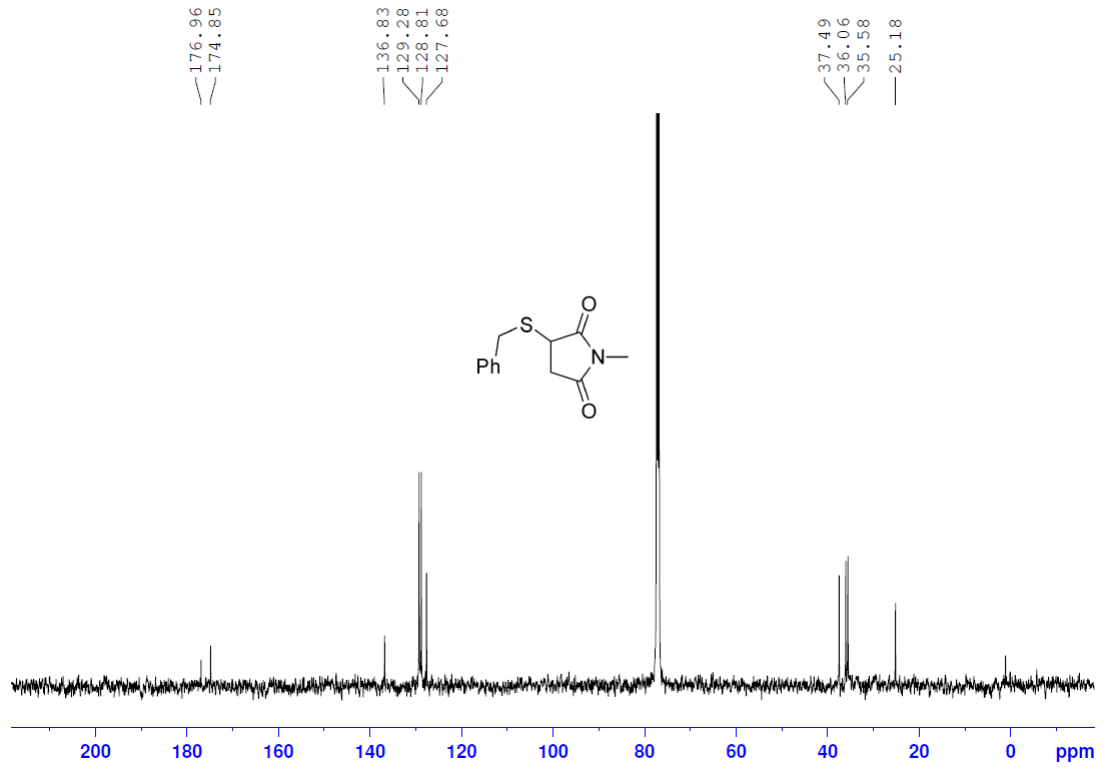
1.04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127.68
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36.06
35.58
25.18
S
Ph
O
N
O
200
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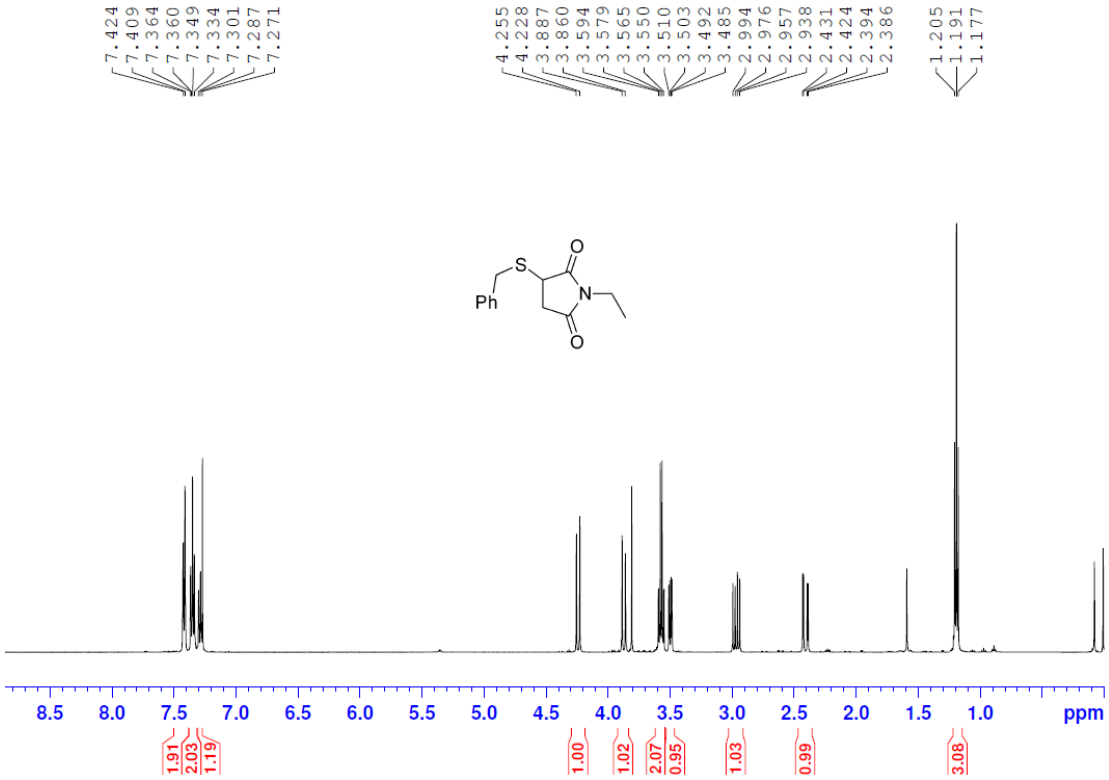
140
120
100
80
60
40
20
0
ppm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3.860
3.594
3.579
3.565
3.550
3.510
3.503
3.492
3.485
2.994
2.976
2.957
2.938
2.431
2.424
2.394
2.386
1.205
1.191
1.177
Ph
S
O
N
O
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5.5
5.0
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4.0
3.5
3.0
2.5
2.0
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2.07
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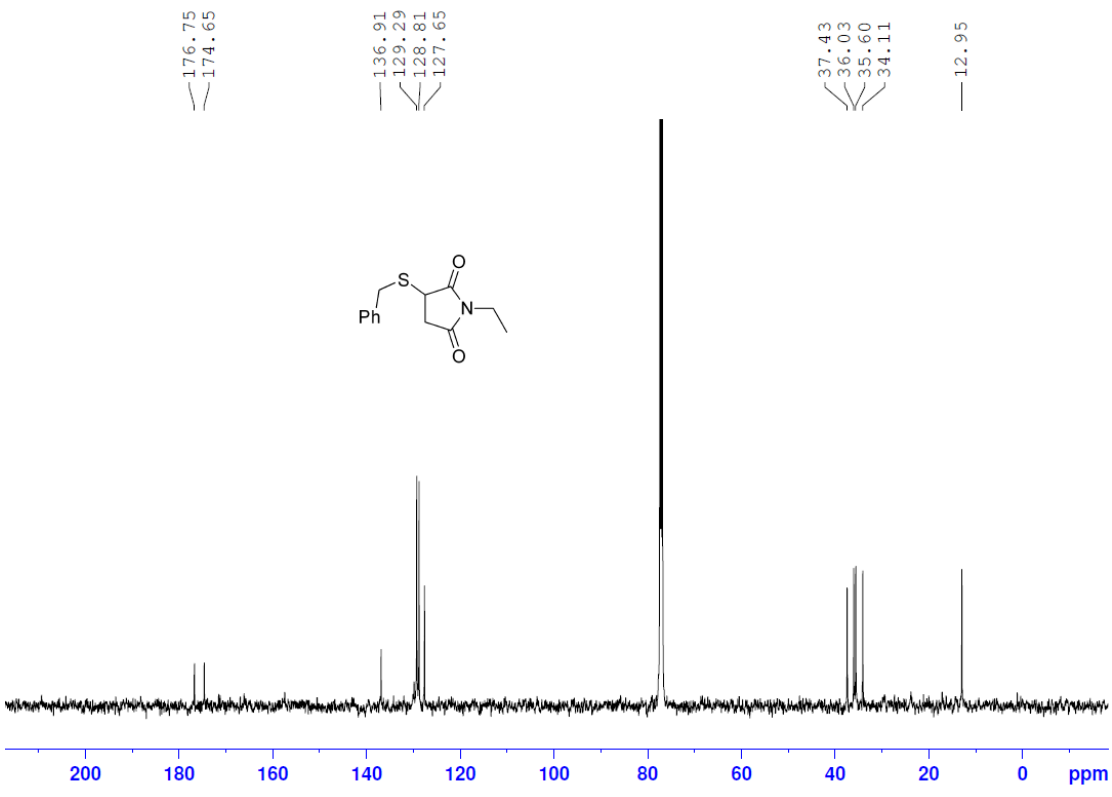
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36.03
35.60
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200
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120
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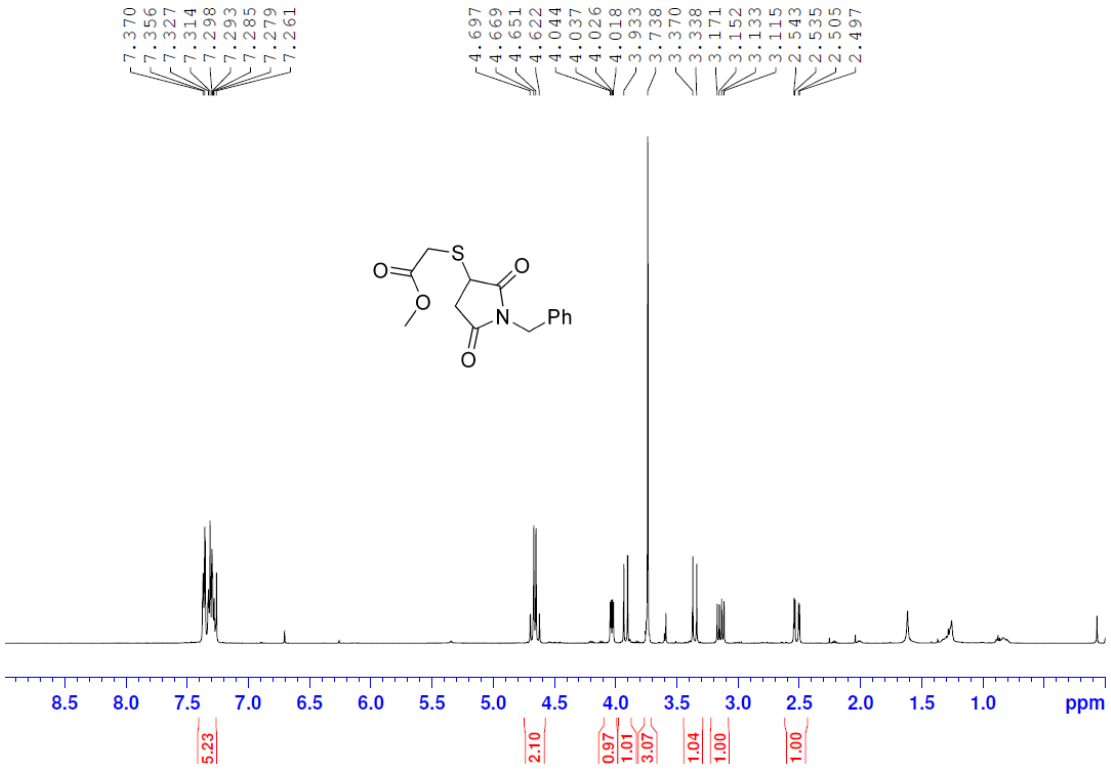
0
ppm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4.044
4.037
4.026
4.018
3.933
3.738
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3.338
3.171
3.152
3.133
3.115
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2.535
2.505
2.497
S
O
O
O
N
Ph
O
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
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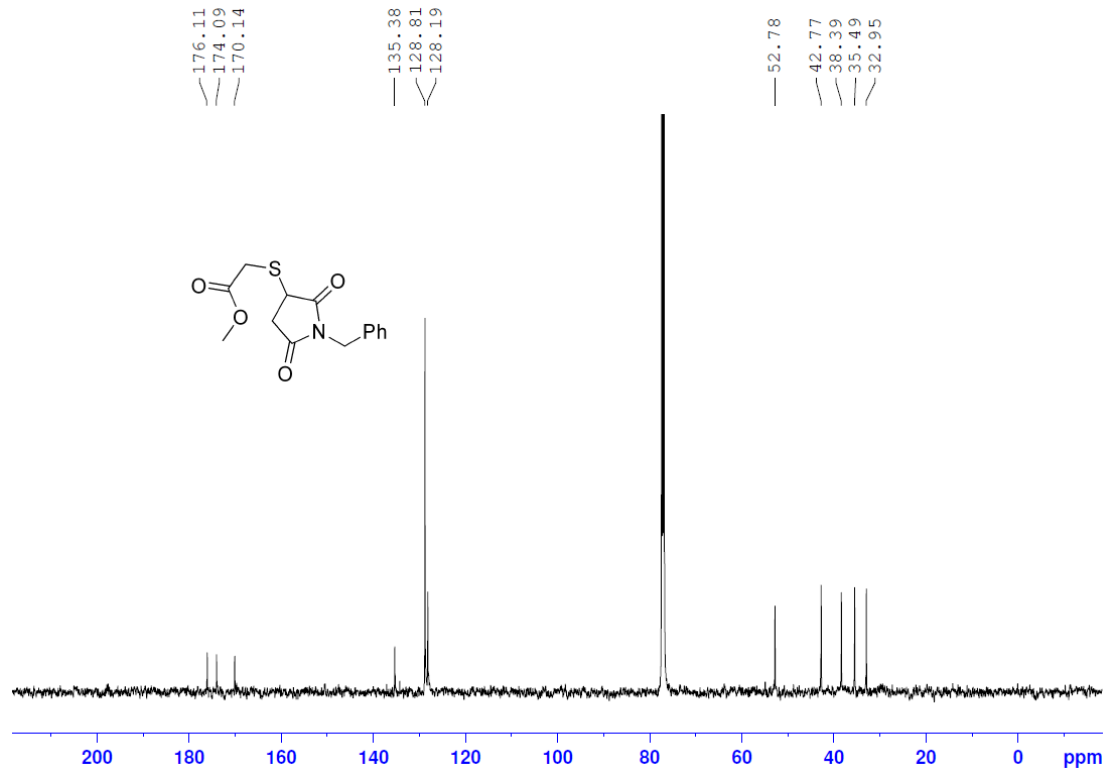
1.00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N
Ph
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200
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120
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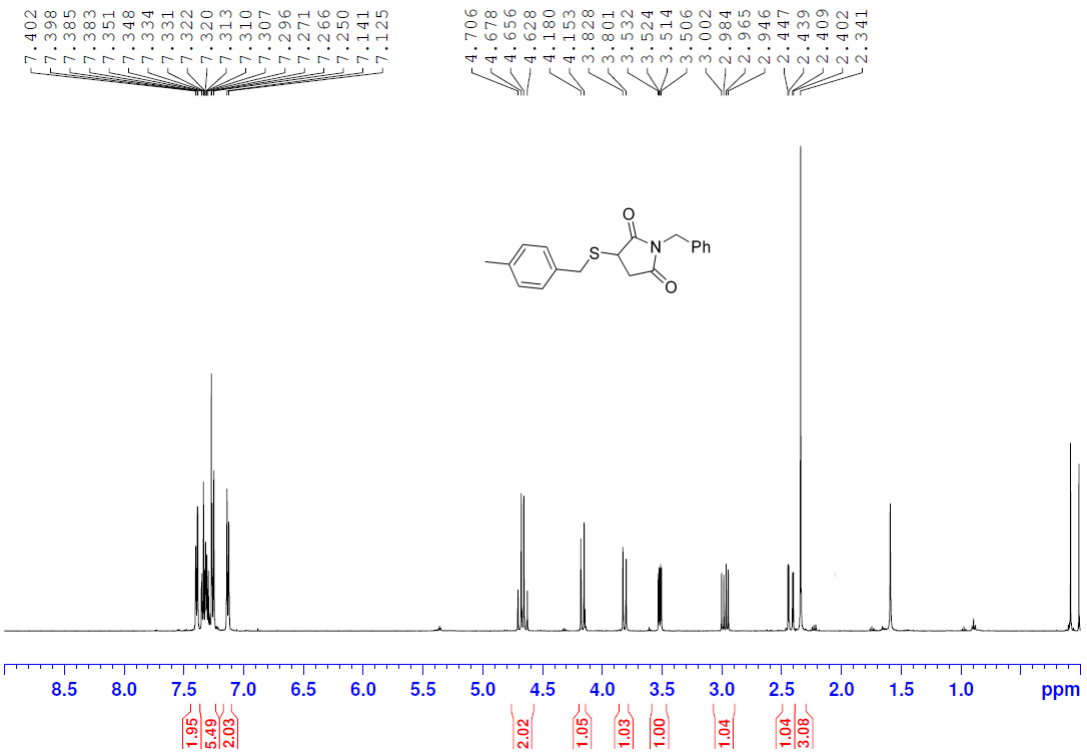
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7.307
7.296
7.271
7.266
7.250
7.141
7.125
4.706
4.678
4.656
4.628
4.180
4.153
3.828
3.801
3.532
3.524
3.514
3.506
3.002
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2.965
2.946
2.447
2.439
2.409
2.402
2.341
O
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Ph
S
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7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.02
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1.03
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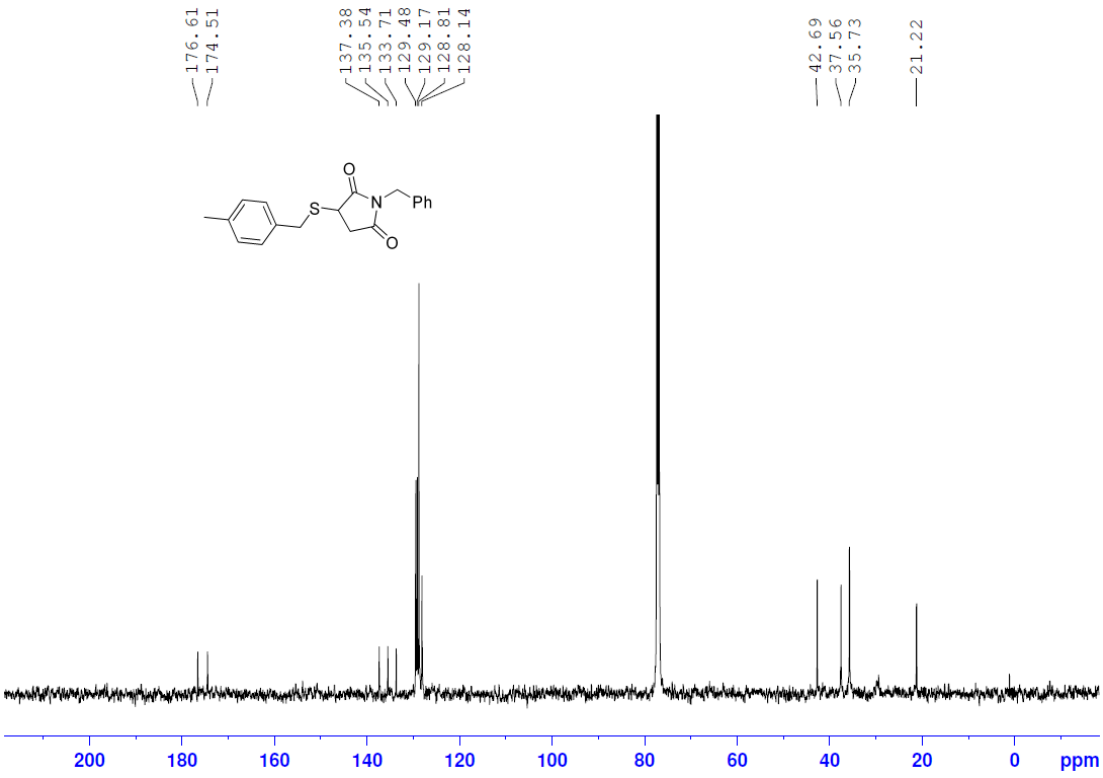
1.04
3.08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37.56
35.73
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O
N
Ph
S
O
200
180
160
140
120
100
80
60
40
20
0
ppm