Electronic Supplementary Material (ESI) for RSC Advances.

Supporting materials

Formation of C(sp^2)–S bond through decarboxylation of α-Oxocarboxylic Acids with Disulfides or Thiophenols

Guangwei Rong[a], Jincheng Mao,[a,b] Defu Liu[a], Hong Yan[a], Yang Zheng[a], and Jie Chen[a]*

[a] Key Laboratory of Organic Synthesis of Jiangsu Province College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China

[b] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, P. R. China

jcmao@suda.edu.cn

Contents:

Experimental Section

General information

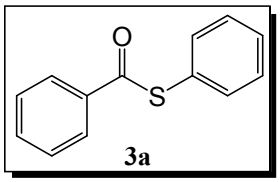
All manipulations were carried out under air atmosphere. *α*-Ooxocarboxylic acids, disulfides and thiophenols were purchased from Acros Organics and used without further purification. Copper catalysts and oxidants were purchased from Adamas corporation. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) data were recorded on Varian 400 M spectrometers using $CDCl_3$ as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. MS were performed by the State-authorized Analytical Center in Soochow University.

General procedure for copper-catalyzed decarboxylative coupling between *α*-oxocarboxylic acids with disulfides or thiophenols:

A mixture of *α*-oxocarboxylic acid (0.3 mmol), disulfide (0.3 mmol) or thiophenol (0.6 mmol), $(NH_4)_2S_2O_8$ (0.6 mmol), CuO (20 mol%), and DMSO/water (5/1) (2 mL) in a sealed tube was stirred in air at 80 ^{o}C for 12 h. At the end of the reaction, the reaction mixture was cooled to room temperature and was diluted with ethyl acetate (15 mL, three times) and water (20 mL) was added. The combined organic phase (45 mL) was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and petroleum ether mixtures to afford the corresponding product.

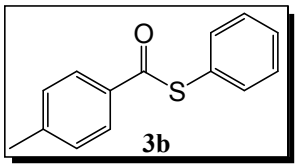
Characterization of the corresponding products:

_S_-Phenyl benzothioate [1,2]



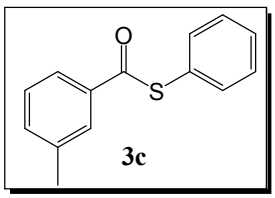
White solid, mp: 51 – 53°C; IR (neat, cm^{-1}) 1667 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.95 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.47 – 7.37 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 190.2, 136.7, 135.1, 133.7, 129.6, 129.3, 128.8, 127.5, 127.4; MS (m/z) calcd for $C_{13}H_{10}OS$ 215.1, found 215.1 $(M+H)^+$.

_S_-Phenyl 4-methylbenzothioate [3]



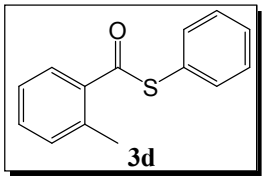
White solid, mp: 78 – 80°C; IR (neat, cm^{-1}) 1668 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.92 (d, *J* = 8.0 Hz, 2H), 7.53-7.48 (m, 2H), 7.46 – 7.41 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 189.7, 144.6, 135.2, 134.1, 129.4, 129.2, 127.6, 21.7; MS (m/z) calcd for $C_{14}H_{12}OS$ 229.1, found 229.1 $(M+H)^+$.

_S_-Phenyl 3-methylbenzothioate [4]



White solid, mp: 95 – 97°C; IR (neat, cm^{-1}) 1665 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.85 – 7.80 (m, 2H), 7.53 – 7.48 (m, 2H), 7.47 – 7.42 (m, 3H), 7.42 – 7.33 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 190.3, 138.7, 136.7, 135.1, 134.5, 129.5, 129.3, 128.7, 128.0, 127.5, 124.7, 21.4; MS (m/z) calcd for $C_{14}H_{12}OS$ 229.1, found 229.1 $(M+H)^+$.

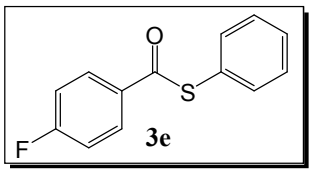
***S*-Phenyl 2-methylbenzothioate** [5]



3d

White solid, mp: 46 – 48°C; IR (neat, cm^{-1}) 1691 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.94 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.48 – 7.38 (m, 4H), 7.31 – 7.23 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 191.7, 137.0, 136.3, 134.4, 131.6, 131.3, 129.0, 128.8, 128.2, 127.8, 125.4, 20.3; MS (m/z) calcd for $C_{14}H_{12}OS$ 229.1, found 229.1 $(M+H)^+$.

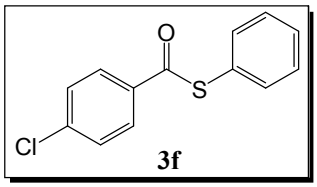
***S*-Phenyl 4-fluorobenzothioate** [2]



3e

White solid, mp: 60 – 62°C; IR (neat, cm^{-1}) 1676 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.08-8.02 (m, 2H), 7.53 – 7.48 (m, 2H), 7.47 – 7.43 (m, 3H), 7.15 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 188.7, 166.1 (d, *J* = 253.8 Hz), 135.1, 133.0 (d, *J* = 3.1 Hz), 130.1 (d, *J* = 9.3 Hz), 129.7, 129.3, 127.1, 115.9 (d, *J* = 22.0 Hz); MS (m/z) calcd for $C_{13}H_9FOS$ 233.0, found 233.0 $(M+H)^+$.

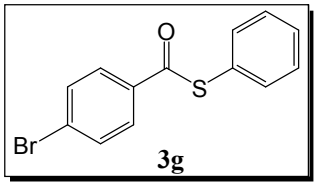
***S*-Phenyl 4-chlorobenzothioate** [3]



3f

White solid, mp: 56 – 58°C; IR (neat, cm^{-1}) 1675 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.97 (d, *J* = 8.8 Hz, 2H), 7.57 – 7.42 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 189.0, 140.1, 135.1, 135.0, 129.7, 129.3, 129.1, 128.8, 126.9; MS (m/z) calcd for $C_{13}H_9ClOS$ 249.0, found 249.0 $(M+H)^+$.

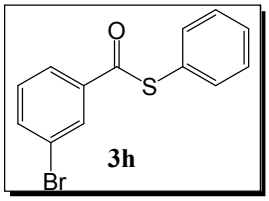
***S*-Phenyl 4-bromobenzothioate** [3]



3g

White solid, mp: 94 – 96°C; IR (neat, cm^{-1}) 1673 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.88 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 188.8, 134.9, 134.6, 131.6, 129.2, 128.9, 128.4, 128.3, 126.4; MS (m/z) calcd for $C_{13}H_9BrOS$ 293.0, found 293.0 $(M+H)^+$.

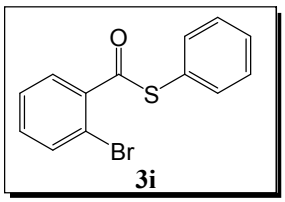
***S*-Phenyl 3-bromobenzothioate** [2]



3h

White solid, 42 – 44°C; IR (neat, cm^{-1}) 1674 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.14 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.45 (m, 5H), 7.37 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 188.5, 137.9, 136.0, 134.5, 130.0, 139.8, 129.3, 128.9, 126.3, 125.6, 122.5; MS (m/z) calcd for $C_{13}H_9BrOS$ 293.0, found 293.0 $(M+H)^+$.

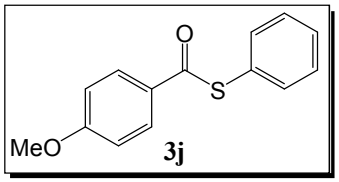
***S*-Phenyl 2-bromobenzothioate** [3]



3i

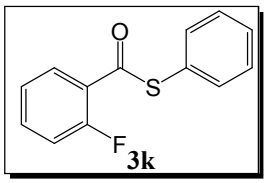
White solid, 56 – 58°C; IR (neat, cm^{-1}) 1702 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.71 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.49 – 7.43 (m, 3H), 7.42 – 7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 191.1, 139.2, 134.6, 134.1, 132.4, 129.8, 129.4, 129.0, 127.4, 127.3, 119.1; MS (m/z) calcd for $C_{13}H_9BrOS$ 293.0, found 293.0 $(M+H)^+$.

***S*-Phenyl 4-methoxybenzothioate** [2]



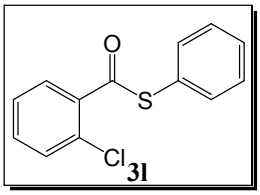
White solid, 92 – 94°C; IR (neat, cm^{-1}) 1666 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.00 (d, *J* = 9.2 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.46 – 7.41 (m, 3H), 6.95 (d, *J* = 9.2 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 188.6, 164.0, 135.2, 129.7, 129.4, 129.3, 129.2, 127.7, 113.9, 55.6; MS (m/z) calcd for $C_{14}H_{12}O_2S$ 267.0, found 267.0 $(M+Na)^+$.

***S*-Phenyl 2-fluorobenzothioate** [6]



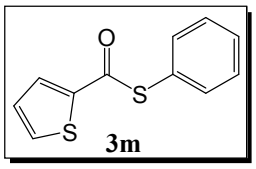
White solid, mp: 44 – 46°C; IR (neat, cm^{-1}) 1715; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.92 (t, *J* = 7.6 Hz, 1H), 7.58 – 7.50 (m, 3H), 7.49 – 7.43 (m, 3H), 7.29 – 7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 187.2 (d, *J* = 5.2 Hz), 160.5 (d, *J* = 256.5 Hz), 135.0, 134.6 (d, *J* = 8.8 Hz), 129.9 (d, *J* = 1.6 Hz), 129.7, 129.3, 127.2 (d, *J* = 4.2 Hz), 125.2 (d, *J* = 11.5 Hz), 124.3 (d, *J* = 3.7 Hz), 117.0 (d, *J* = 22.1 Hz); MS (m/z) calcd for $C_{13}H_9FOS$ 233.0, found 233.0 $(M+H)^+$.

***S*-Phenyl 2-chlorobenzothioate** [2]



White solid, mp: 53 – 55°C; IR (neat, cm^{-1}) 1705 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.76 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.49 – 7.39 (m, 5H), 7.35 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 190.2, 137.1, 134.7, 132.4, 131.1, 131.0, 129.8, 129.4, 129.2, 127.4, 126.7; MS (m/z) calcd for $C_{13}H_9ClOS$ 249.0, found 249.0 $(M+H)^+$.

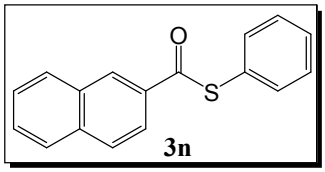
***S*-Phenyl thiophene-2-carbothioate** [2]



3m

Colorless oil; IR (neat, cm^{-1}) 1655 (C=O); ^1H NMR (400 MHz, $CDCl_3$); (δ, ppm): 7.90 (dd, J = 3.6 Hz, 1.2 Hz, 1H), 7.65 (dd, J = 5.2 Hz, 1.2 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.45 – 7.41 (m, 3H), 7.16 – 7.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 182.0, 141.4, 135.1, 133.3, 131.6, 129.7, 129.3, 128.0, 126.9; MS (m/z) calcd for $C_{11}H_8OS_2$ 221.0, found 221.0 $(M+H)^+$.

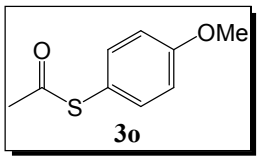
***S*-Phenyl naphthalene-2-carbothioate** [2]



3n

White solid, mp: 118 – 120°C; IR (neat, cm^{-1}) 1670 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.62 (s, 1H), 8.04 – 8.98 (m, 2H), 7.91 (t, J = 8.8 Hz, 2H), 7.64 – 7.55 (m, 4H), 7.50 – 7.46 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 90.1, 135.9, 135.2, 134.0, 132.5, 129.6, 129.5, 129.3, 129.0, 128.7, 128.7, 127.9, 127.5, 127.0, 123.3; MS (m/z) calcd for $C_{17}H_{12}OS$ 265.1, found 265.1 $(M+H)^+$.

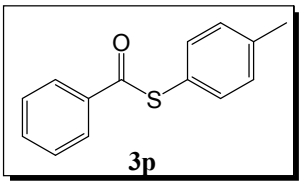
***S*-4-Methoxyphenyl ethanethioate** [4]



3o

Colorless oil; IR (neat, cm^{-1}) 1764 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.34 – 7.29 (m, 2H), 6.96 – 6.91 (m, 2H), 3.82 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 195.2, 160.7, 136.1, 118.7, 114.9, 55.3, 29.9; MS (m/z) calcd for $C_9H_{10}O_2S$ 205.0, found 205.0 $(M+Na)^+$.

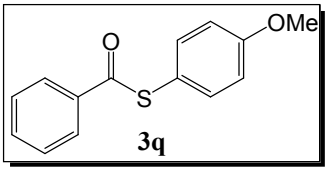
***S*-*p*-Tolyl benzothioate** [7]



3p

White solid, mp: 75 – 77°C; IR (neat, cm^{-1}) 1667 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.93 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 190.6, 139.8, 136.7, 135.1, 133.6, 130.1, 128.7, 127.5, 123.8, 21.4; MS (m/z) calcd for $C_{14}H_{12}OS$ 229.1, found 229.1 $(M+H)^+$.

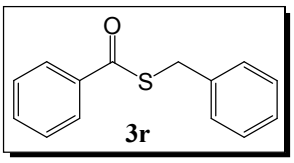
***S*-4-Methoxyphenyl benzothioate** [8]



3q

White solid, mp: 92 – 94°C; IR (neat, cm^{-1}) 1668 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.01 (dd, *J* = 8.0 Hz, 1.2 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.43 – 7.39 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 191.1, 160.8, 136.7, 133.6, 128.7, 127.5, 117.9, 115.0, 55.4; MS (m/z) calcd for $C_{14}H_{12}O_2S$ 245.1, found 245.1 $(M+H)^+$.

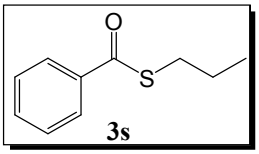
***S*-Benzyl benzothioate** [9]



3r

White solid, mp: 36 – 38°C; IR (neat, cm^{-1}) 1661 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.99 – 7.93 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 4.32 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 191.3, 137.5, 136.8, 133.5, 129.0, 128.7, 128.6, 127.4, 127.3, 33.4; MS (m/z) calcd for $C_{14}H_{12}OS$ 229.1, found 229.1 $(M+H)^+$.

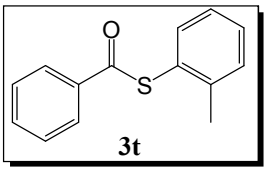
***S*-Propyl benzothioate** [10]



3s

Colorless oil; IR (neat, cm^{-1}) 1663 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.90 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 2.99 (t, J = 7.2 Hz, 2H), 1.69 – 1.59 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 192.1, 137.3, 133.2, 128.6, 127.2, 30.9, 23.0, 13.5; MS (m/z) calcd for $C_{10}H_{12}OS$ 181.1, found 181.1 $(M+H)^+$.

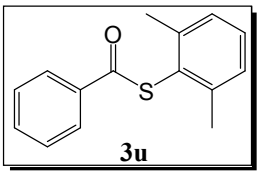
***S*-*o*-Tolyl benzothioate** [11]



3t

White solid, mp: 62 – 64°C; IR (neat, cm^{-1}) 1665 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.07 – 8.03 (m, 2H), 7.62 – 7.57 (m, 1H), 7.51 – 7.45 (m, 3H), 7.39 – 7.34 (m, 2H), 7.28 – 7.24 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 189.7, 142.7, 136.8, 136.4, 133.6, 130.8, 130.2, 128.7, 127.6, 126.8, 126.7, 20.8; MS (m/z) calcd for $C_{14}H_{12}OS$ 229.1, found 229.1 $(M+H)^+$.

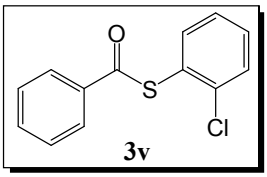
***S*-2,6-Dimethylphenyl benzothioate** [12]



3u

White solid, 56 – 58°C; IR (neat, cm^{-1}) 1669 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.08 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.19 (d, J = 7.2 Hz, 2H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 189.1, 143.3, 137.0, 133.5, 130.0, 128.7, 128.4, 127.6, 126.7, 21.8; MS (m/z) calcd for $C_{15}H_{14}OS$ 243.1, found 243.1 $(M+H)^+$.

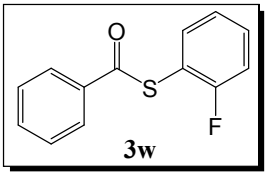
***S*-2-Chlorophenyl benzothioate** [3]



3v

White solid, mp: 72 – 74°C; IR (neat, cm^{-1}) 1676 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.07 – 8.01 (m, 2H), 7 64 – 7.58 (m, 2H), 7.58 – 7.54 (m, 1H), 7.52 – 7.46 (m, 2H), 7.43 – 7.38 (m, 1H), 7.36 – 7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 188.3, 139.2, 137.6, 136.4, 133.9, 131.3, 130.4, 128.9, 127.7, 127.4, 127.0; MS (m/z) calcd for $C_{13}H_9ClOS$ 249.0, found 249.0 $(M+H)^+$.

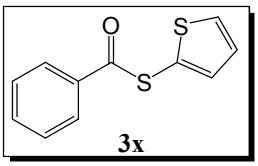
***S*-2-Fluorophenyl benzothioate**



3w

White solid, mp: 62 – 64°C; IR (neat, cm^{-1}) 1678 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.06 – 8.01 (m, 2H), 7.64 – 7.58 (m, 1H), 7.53 – 7.44 (m, 4H), 7.25 – 7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 188.2, 162.6 (d, J = 248.2 Hz), 137.2, 136.2, 133.9, 132.3 (d, J = 8.2 Hz), 128.8, 127.7, 124.7 (d, J = 3.8 Hz), 116.3 (d, J = 22.5 Hz), 114.8 (d, J = 18.5 Hz); MS (m/z) calcd for $C_{13}H_9FOS$ 233.0, found 233.0 $(M+H)^+$.

***S*-Thiophen-2-yl benzothioate**



3x

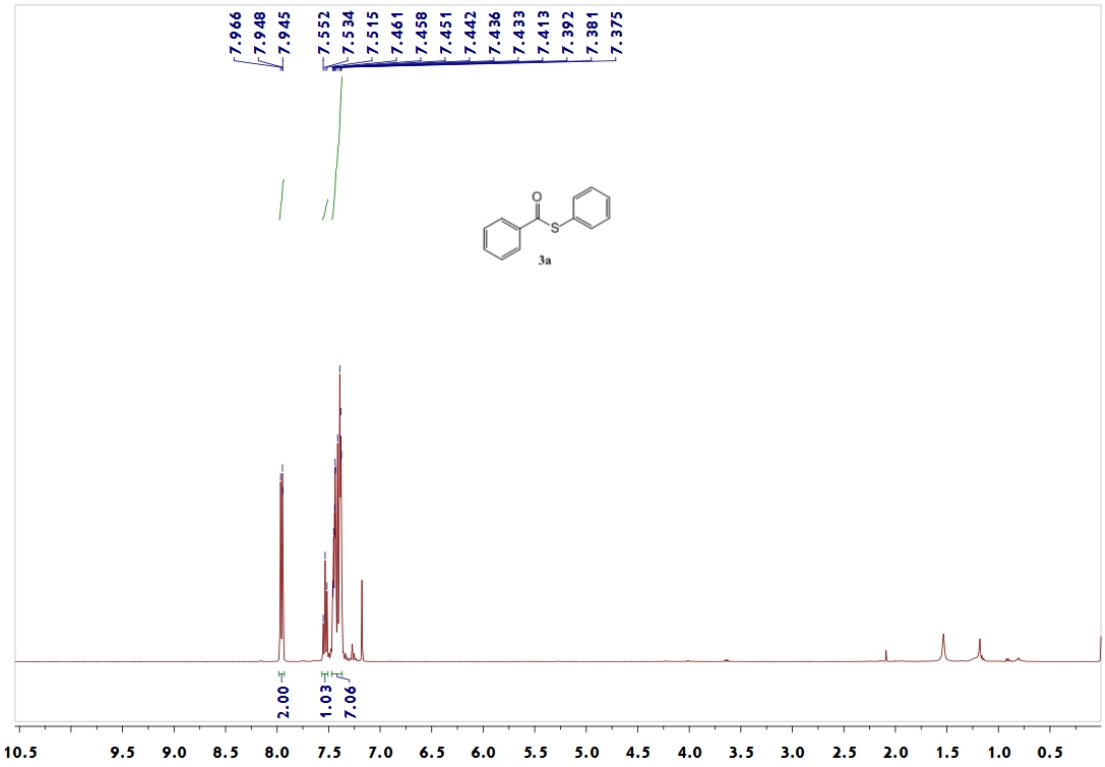
Colorless oil; IR (neat, cm^{-1}) 1662 (C=O); ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.07 – 8.01 (m, 2H), 7.68 – 7.62 (m, 2H), 7.52 (t, J = 8.0 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.21 – 7.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 189.8, 136.3, 136.0, 134.0, 132.2, 128.9, 127.9, 127.6, 124.2; MS (m/z) calcd for $C_{11}H_8OS_2$ 221.0, found 221.0 $(M+H)^+$.

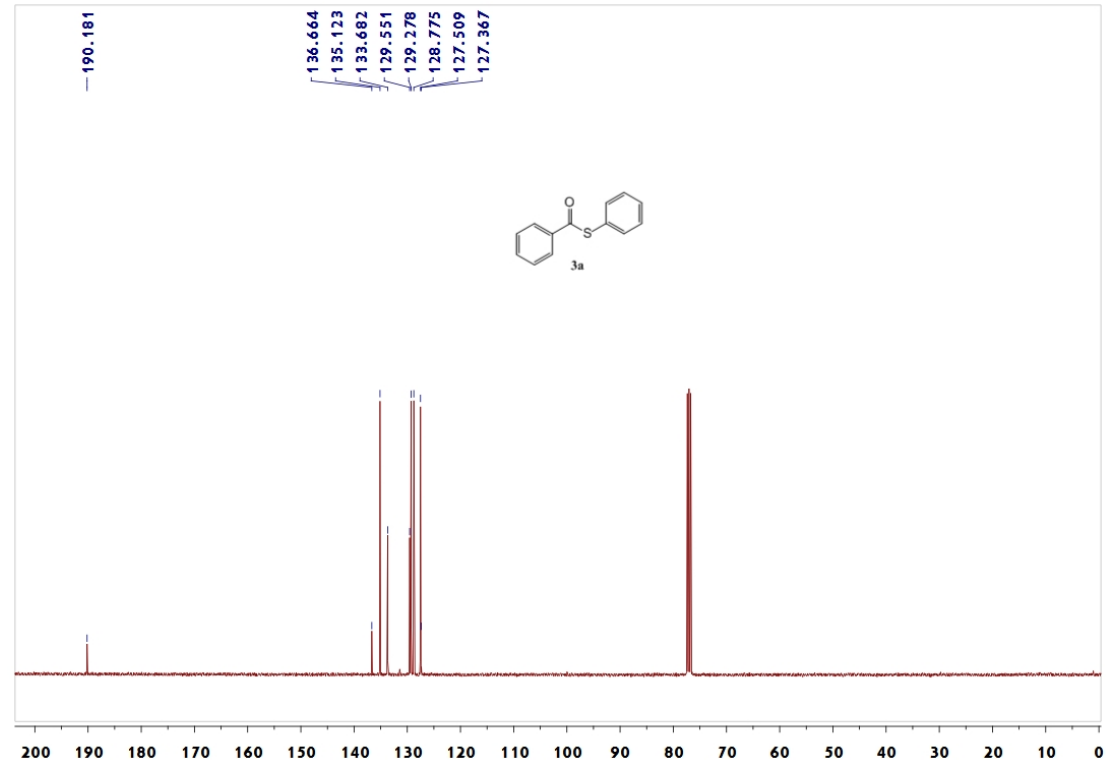
Reference:

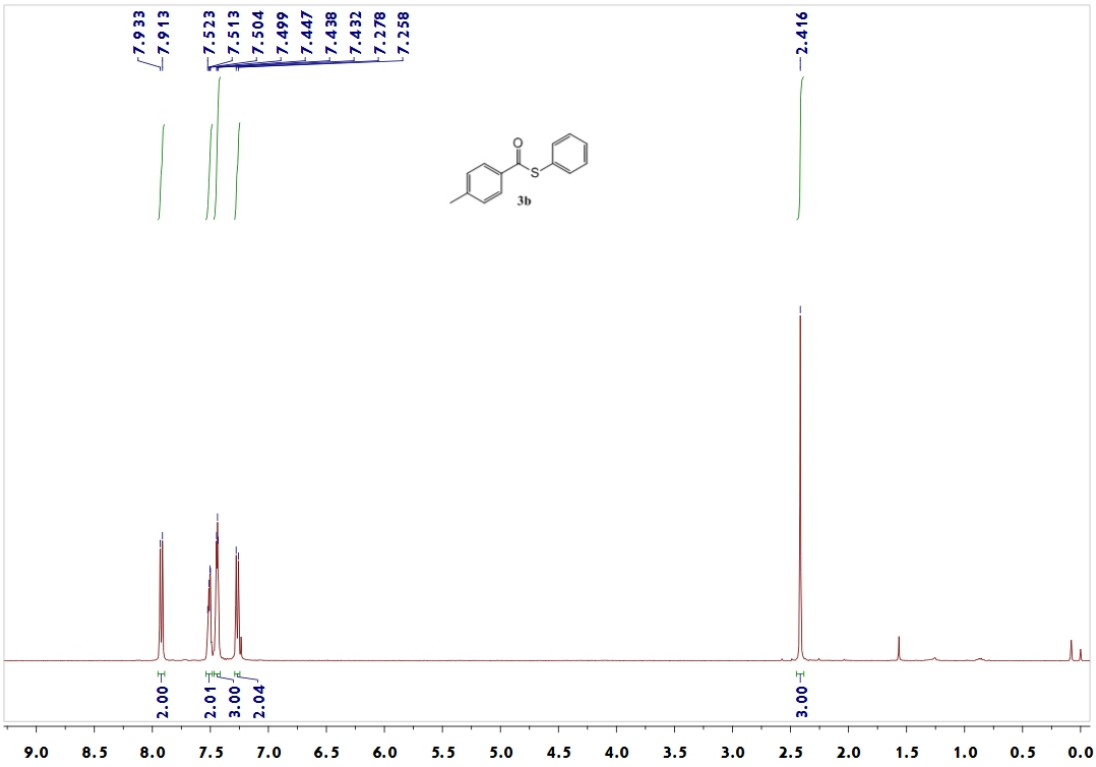
1. T. Uno, T. Inokuma, Y. Takemoto, *Chem. Commun.,* 2012, **48**, 1901.

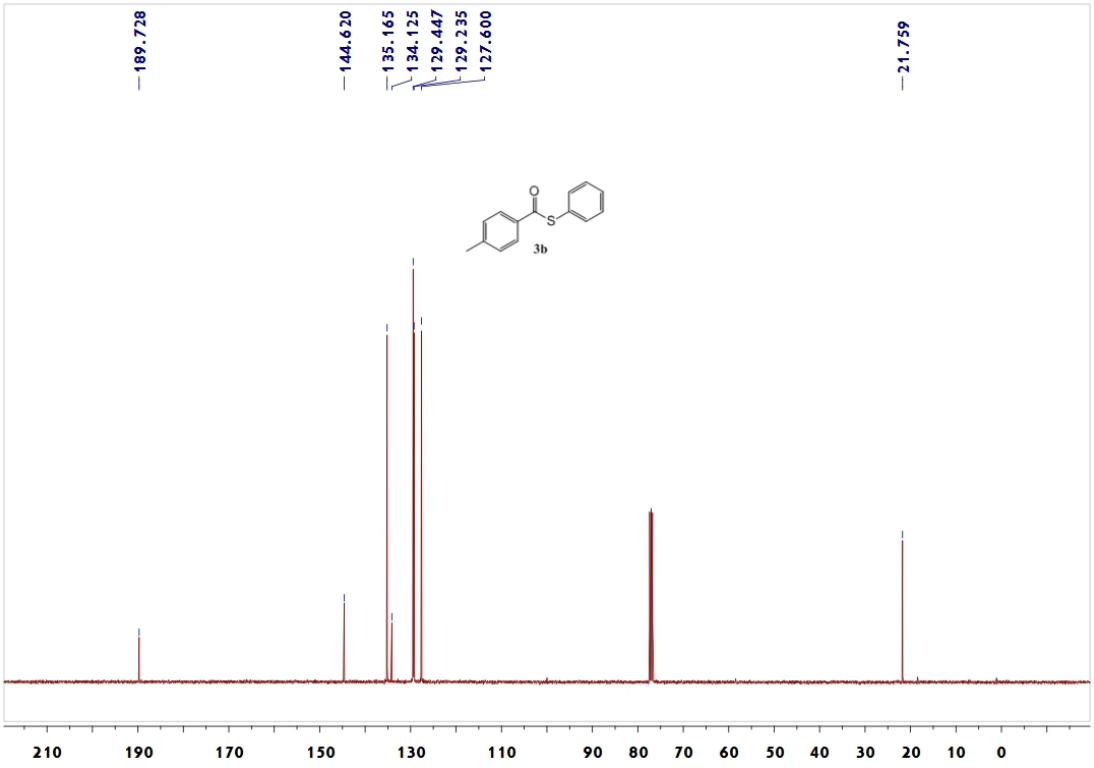
2. X. Zhu, Y. Shi, H. Mao, Y. Cheng, C. Zhu, *Adv. Synth. Catal.,* 2013, **355**, 3558.
3. C. He, X. Qian, P. Sun, *Org. Biomol. Chem.,* 2014, **12**, 6072.
4. W. Dan, H. Deng, J. Chen, M. Liu, J. Ding, H. Wu, *Tetrahedron.* 2010, **66**, 7384.
5. S. S. Friedrich, L. J. Andrews, R. M. Keefer, *J. Org. Chem.,* 1972, **37**, 3007.
6. L. Prangova, T. Strelow, J. Voss, *J. Chem. Res., miniprint,* 1985, **4**, 1401.
7. M. Arisawa, M. Kuwajima, F. Toriyama, G. Li, M. Yamaguchi, *Org. Lett.,* 2012, **14**, 3804.
8. T. Uno, T. Inokuma, Y. Takemoto, *Chem. Commun.,* 2012, **48**, 1901.
9. H. Nambu, K. Hata, M. Matsugi, Y. Kita, *Chem. Eur. J.,* 2005, **11**, 719.
10. N. Iranpoor, H. Firouzabadi, D. Khalili, S. Motevalli, *J. Org. Chem.,* 2008, **73**, 4882.
11. H. Cao, L. McNamee, H. Alper, *J. Org. Chem.,* 2008, **73**, 3530.
12. M. Barbero, I. Degani, S. Dughera, R. Fochi, *Syhthesis,* 2003, **8**, 1225

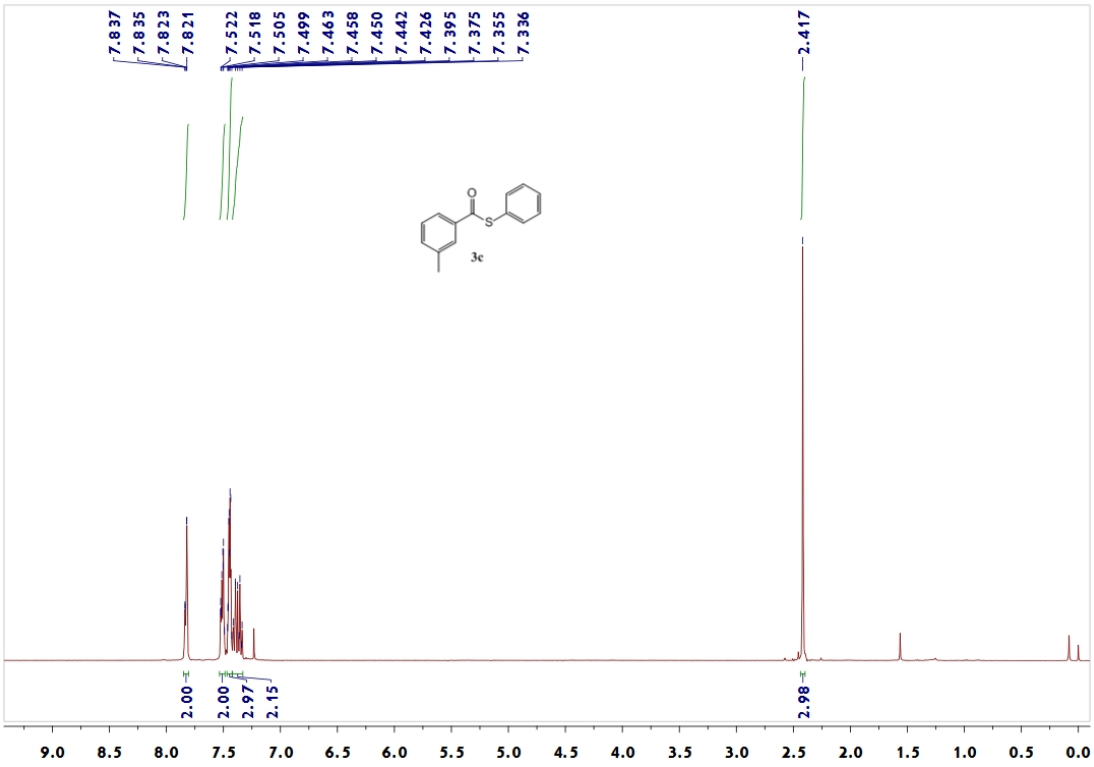
Copy of HRMS and NMR Spectra for desired products:

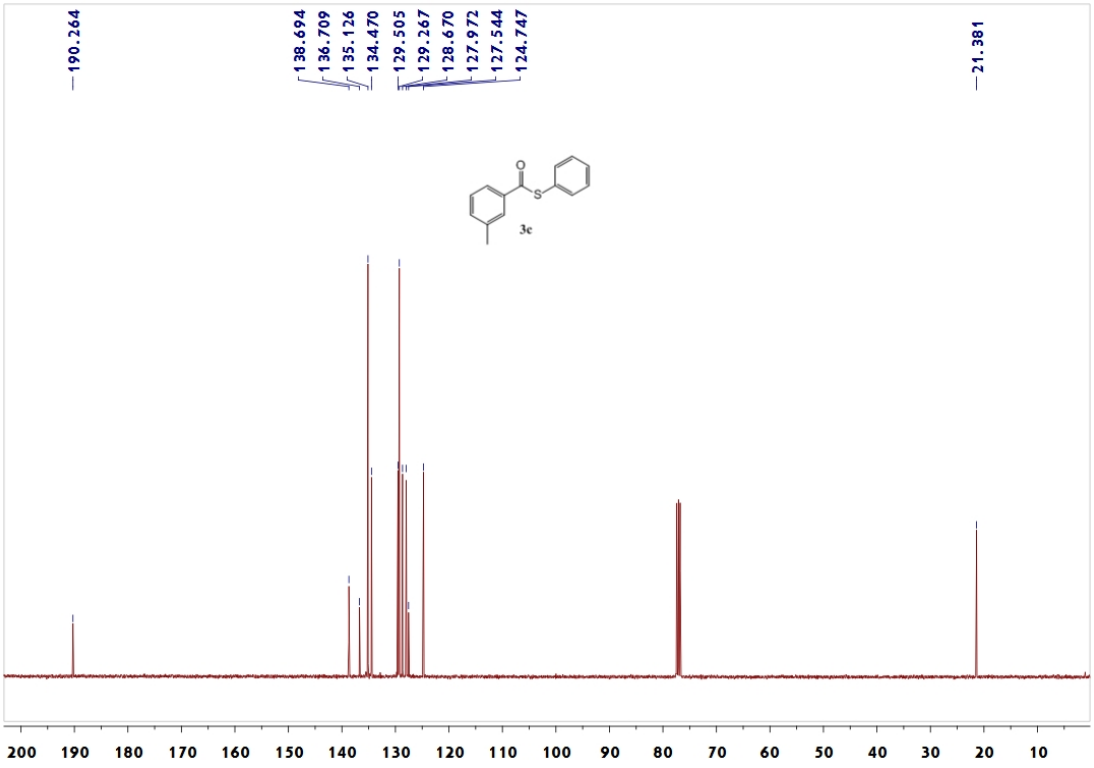


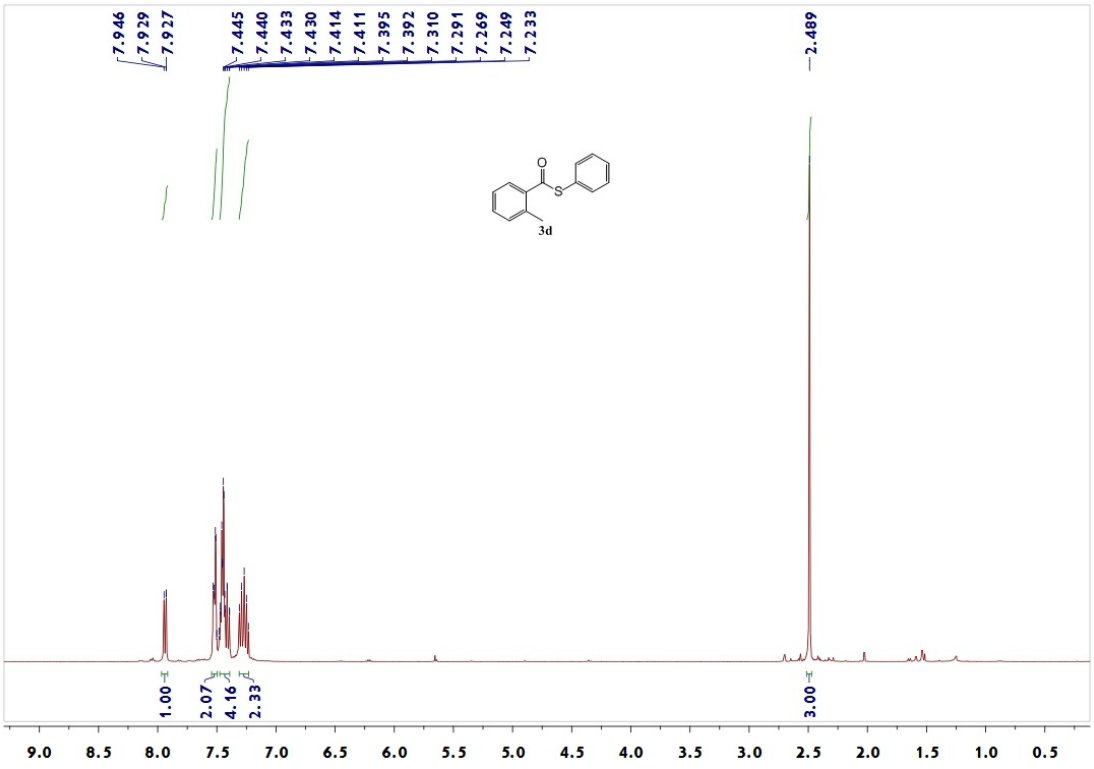


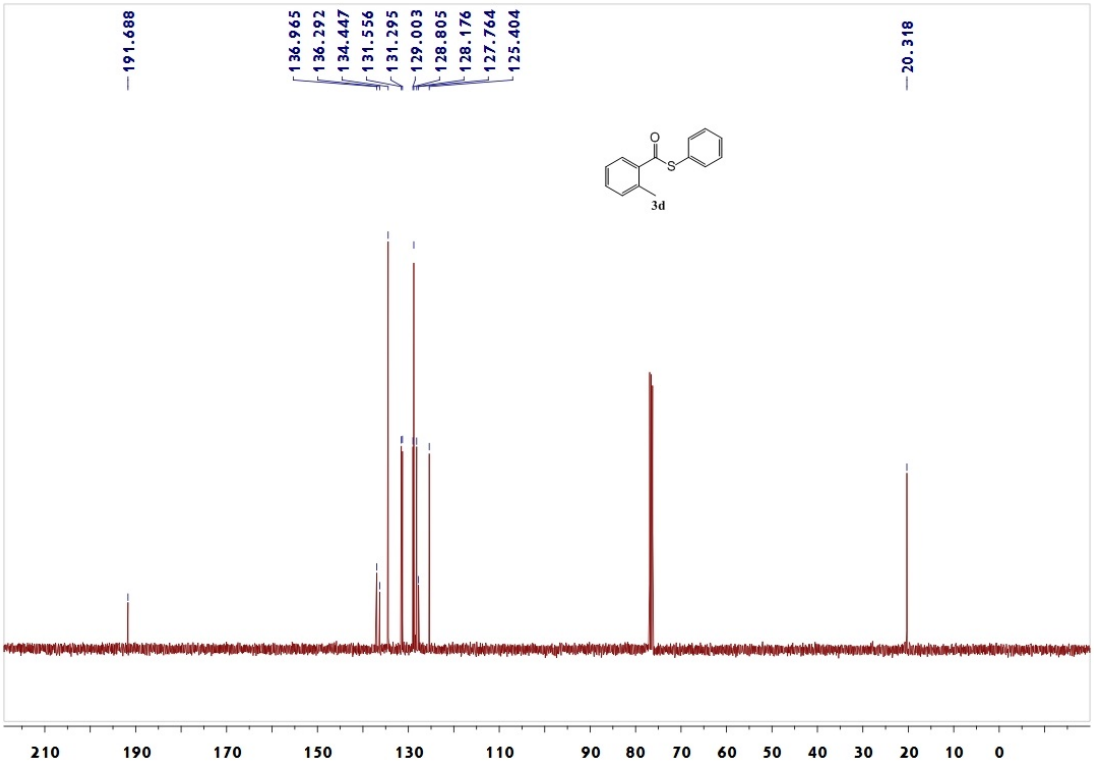

7.933
7.913
7.523
7.513
7.504
7.499
7.447
7.438
7.432
7.278
7.258
2.416
3b
2.00
2.01
3.00
2.04
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

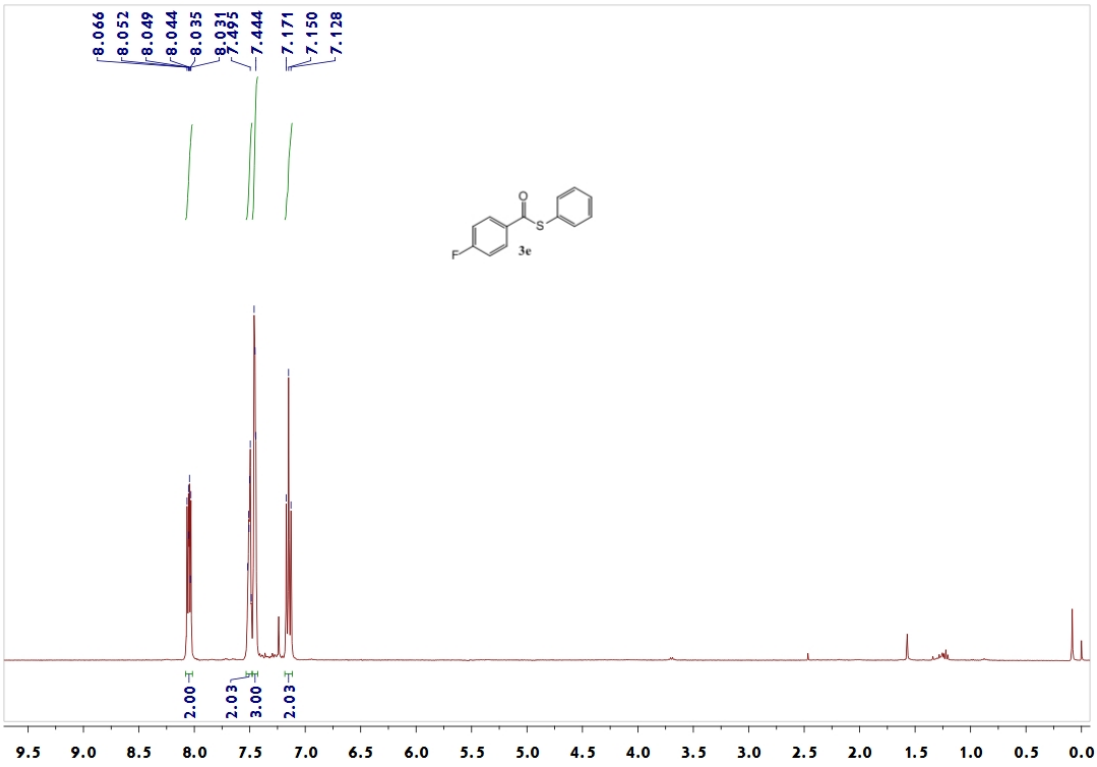

189.728
144.620
135.165
134.125
129.447
129.235
127.600
21.759
3b
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

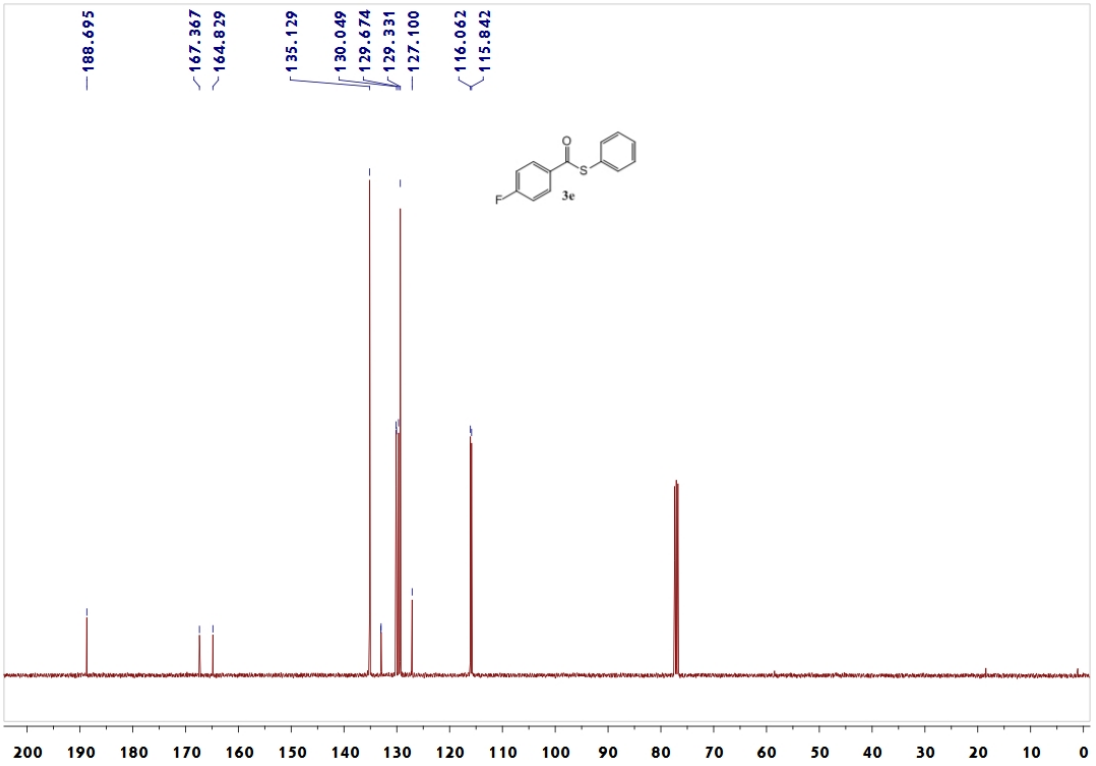

7.837
7.835
7.823
7.821
7.522
7.518
7.505
7.499
7.463
7.458
7.450
7.442
7.426
7.395
7.375
7.355
7.336
2.417
3e
2.00
2.00
2.97
2.15
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

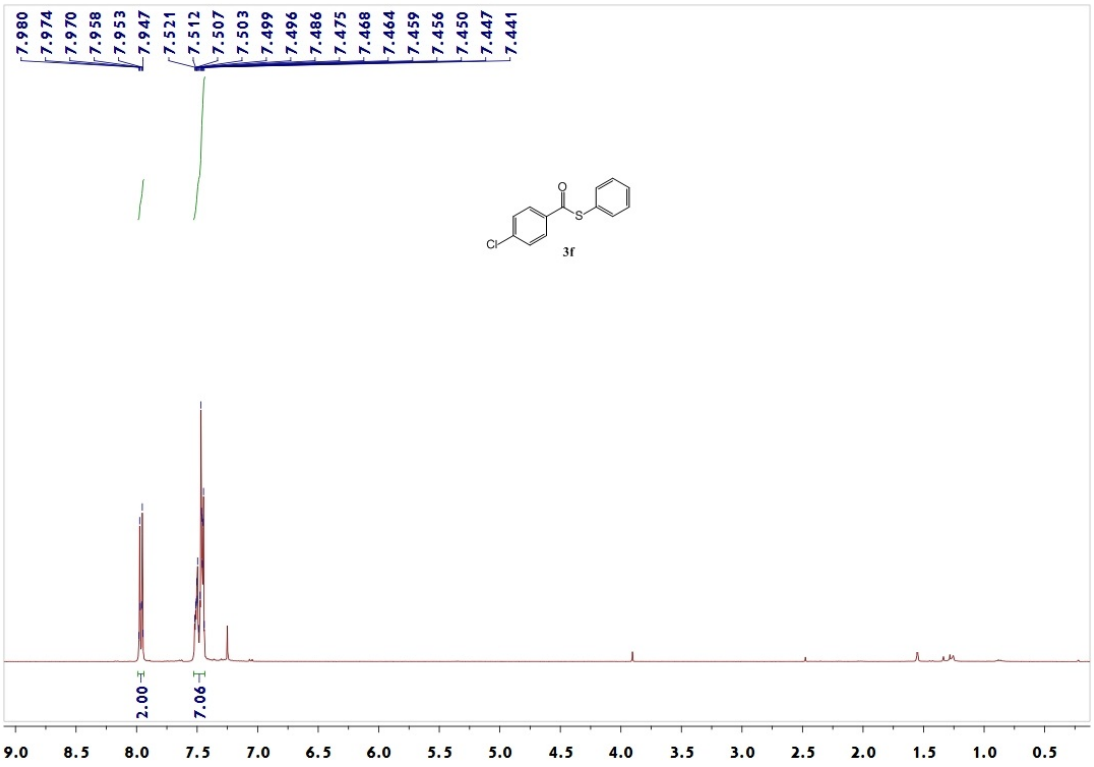

190.264
138.694
136.709
135.126
134.470
129.505
129.267
128.670
127.972
127.544
124.747
21.381
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

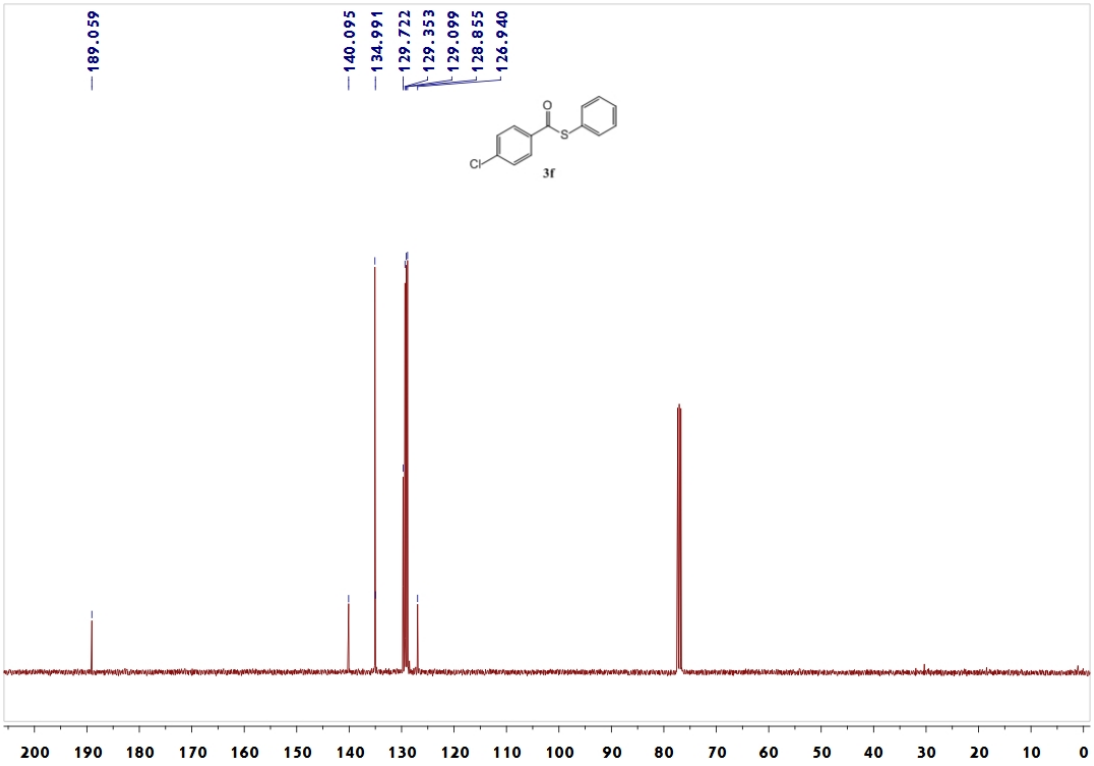

7.946
7.929
7.927
7.445
7.440
7.433
7.430
7.414
7.411
7.395
7.392
7.310
7.291
7.269
7.249
7.233
2.489
3d
1.00
2.07
4.16
2.33
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

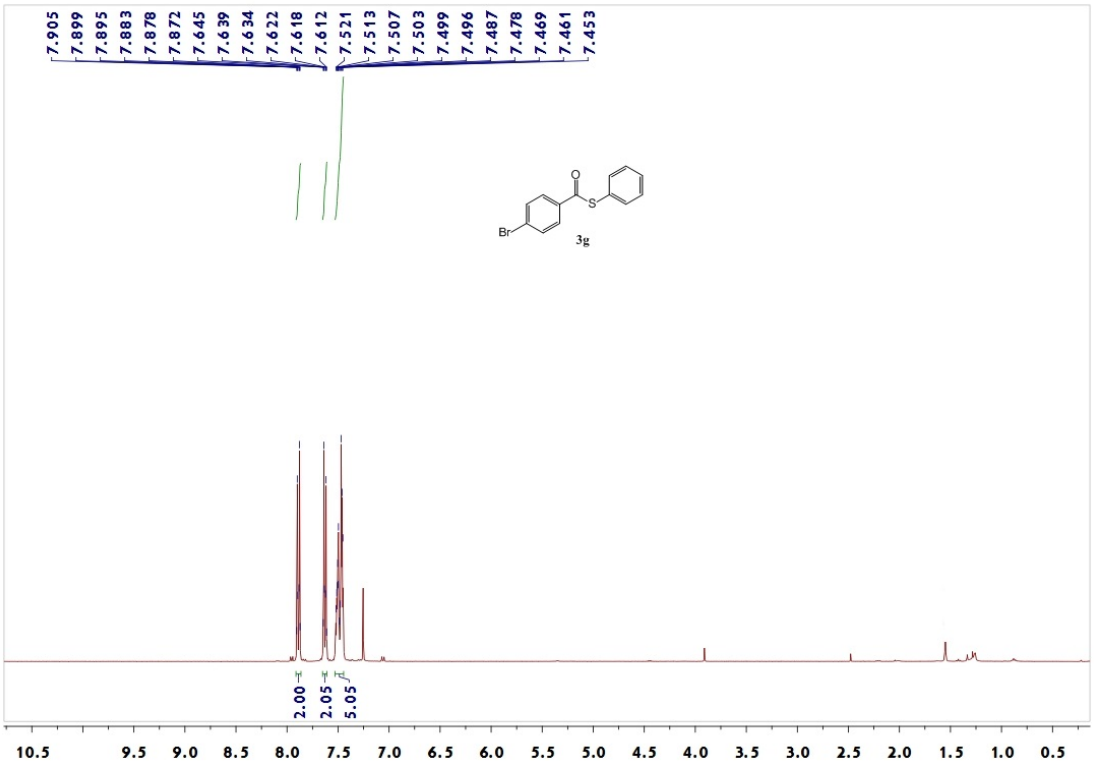

191.688
136.965
136.292
134.447
131.556
131.295
129.003
128.805
128.176
127.764
125.404
20.318
3d
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

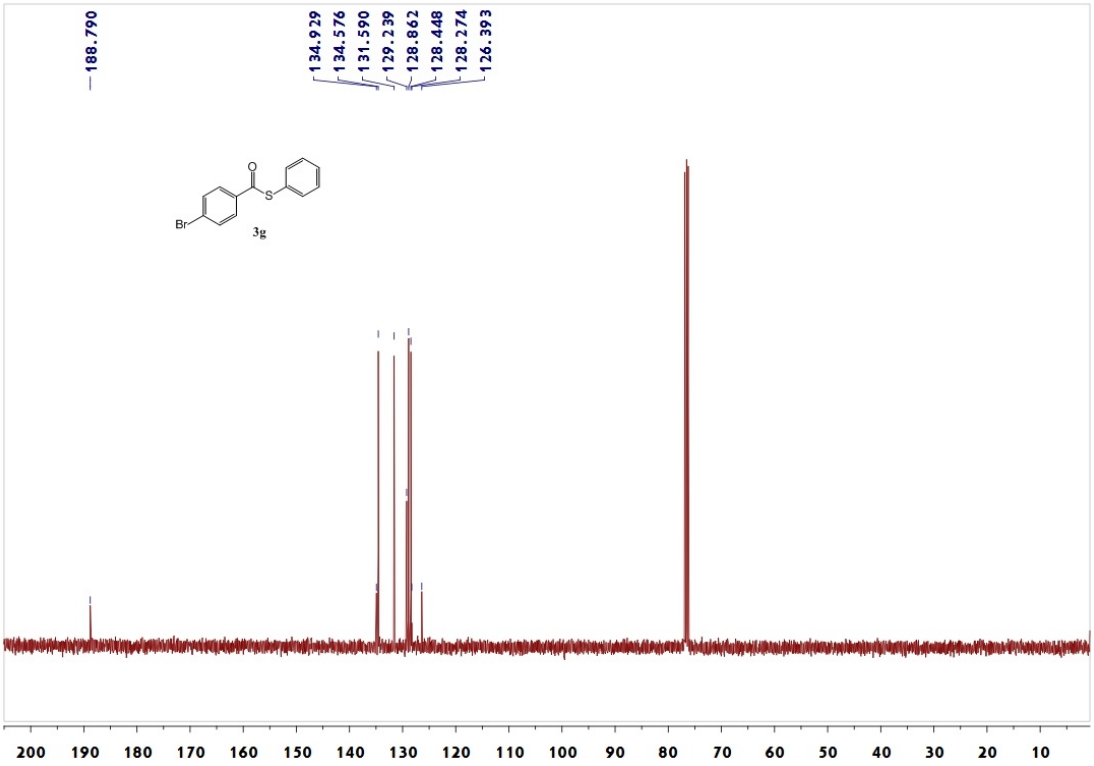

8.066
8.052
8.049
8.044
8.035
8.031
7.495
7.444
7.171
7.150
7.128
3e
2.00
2.03
3.00
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

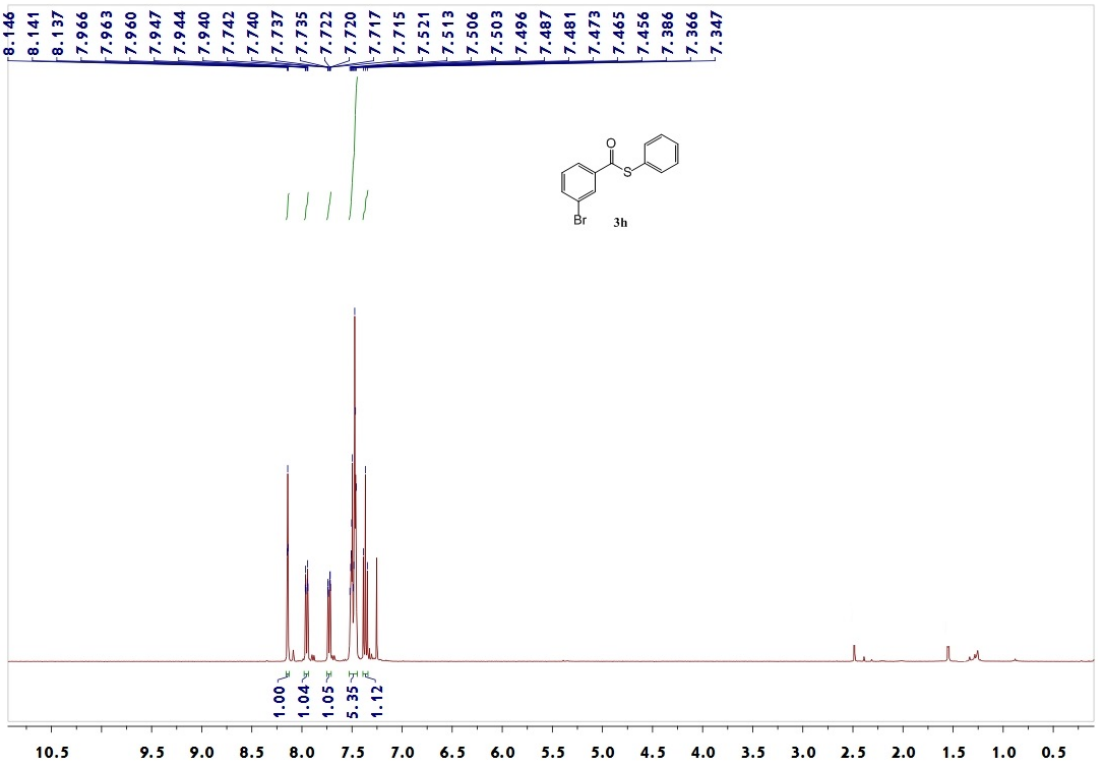

188.695
167.367
164.829
135.129
130.049
129.674
129.331
127.100
116.062
115.842
3e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

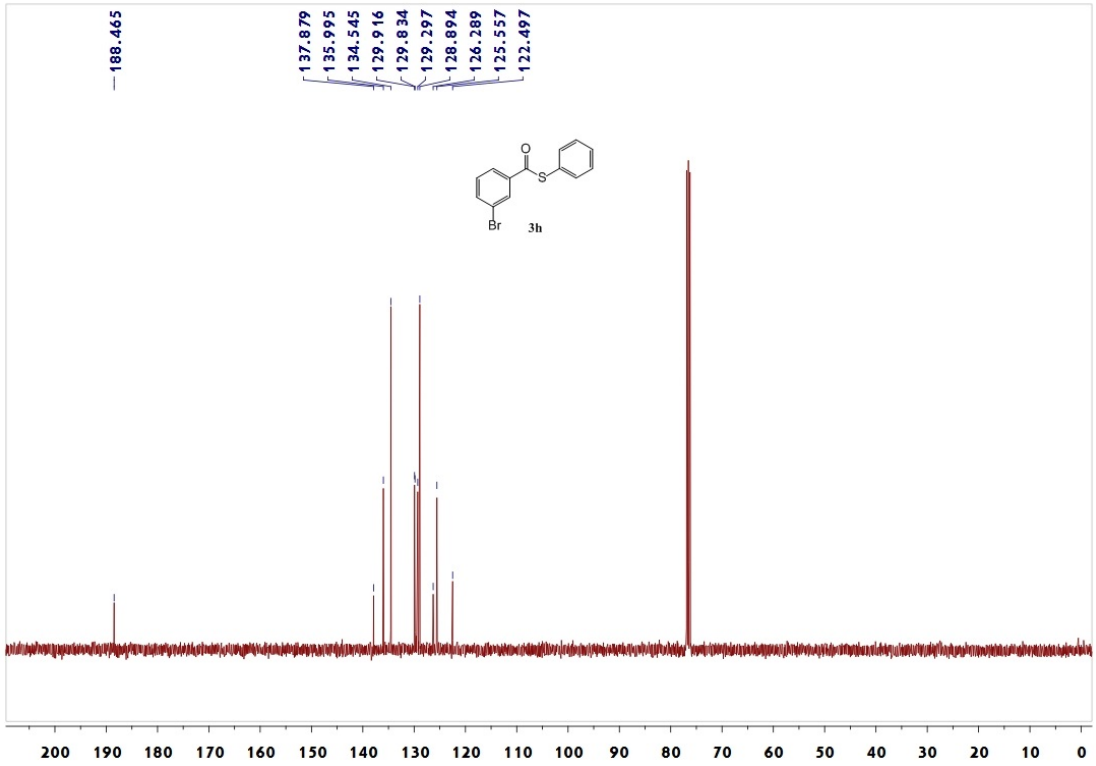

7.980
7.974
7.970
7.958
7.953
7.947
7.521
7.512
7.507
7.503
7.499
7.496
7.486
7.475
7.468
7.464
7.459
7.456
7.450
7.447
7.441
O
S
Cl
3f
2.00
7.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

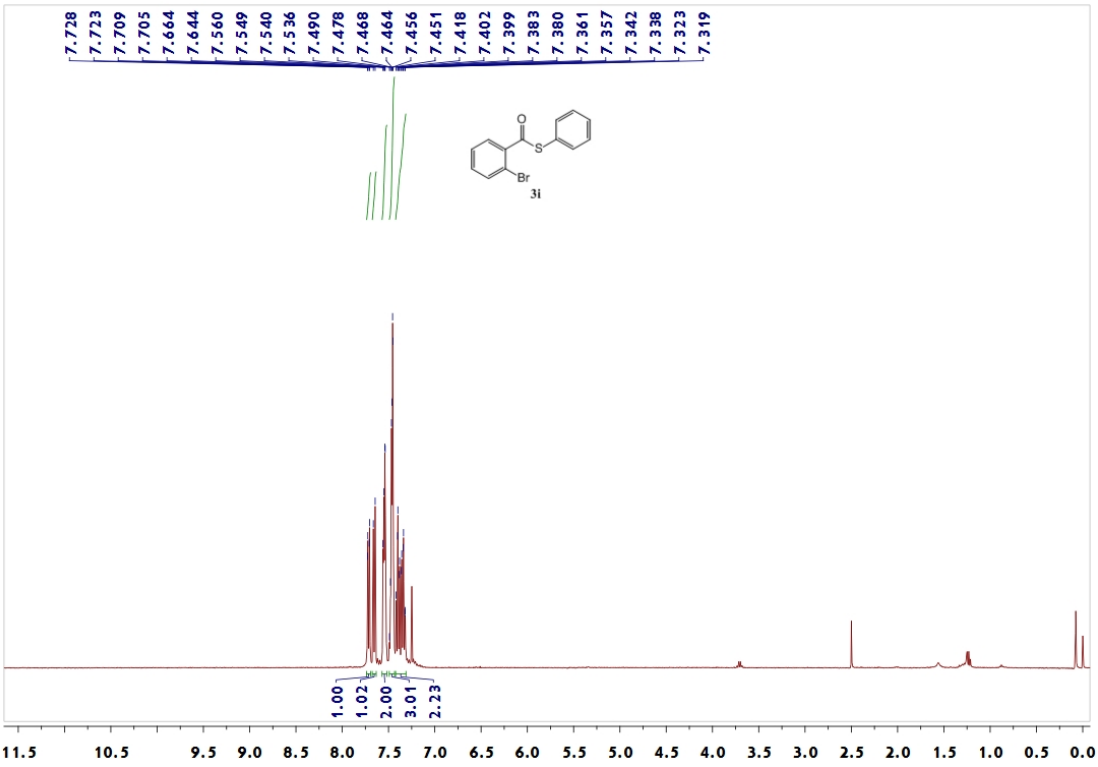

189.059
140.095
134.991
129.722
129.353
129.099
128.855
126.940
O
S
Cl
3f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

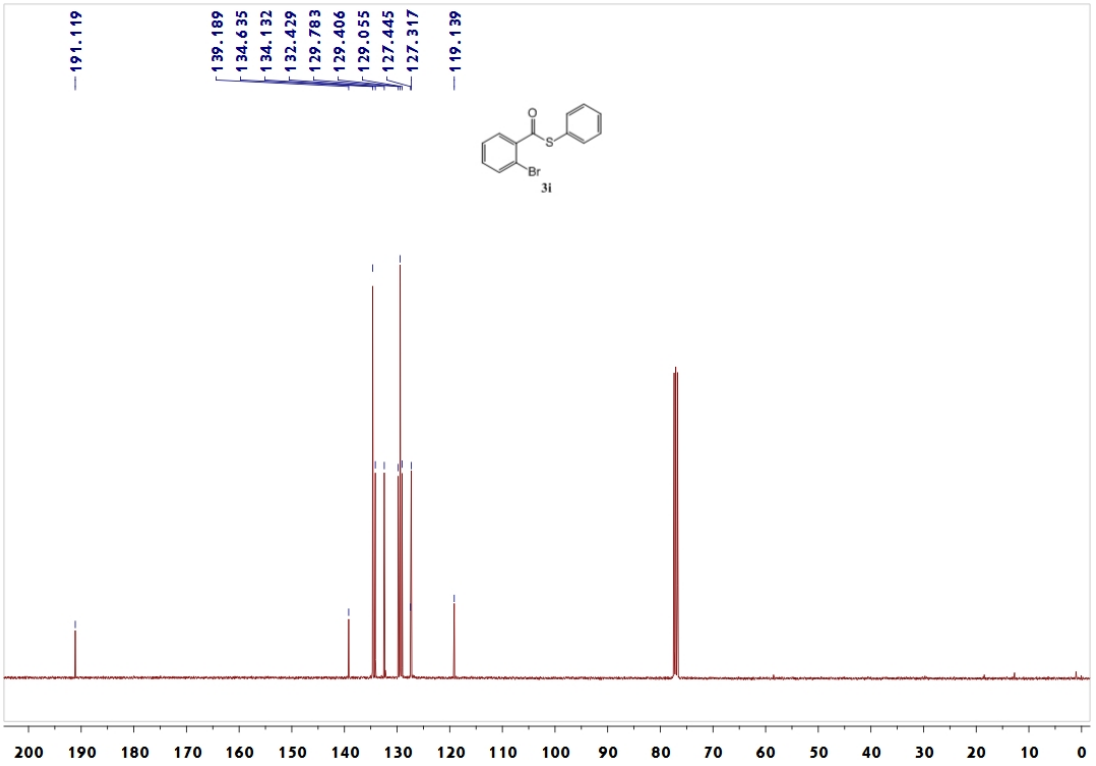

7.905
7.899
7.895
7.883
7.878
7.872
7.645
7.639
7.634
7.622
7.618
7.612
7.521
7.513
7.507
7.503
7.499
7.496
7.487
7.478
7.469
7.461
7.453
Br
3g
2.00
2.05
5.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

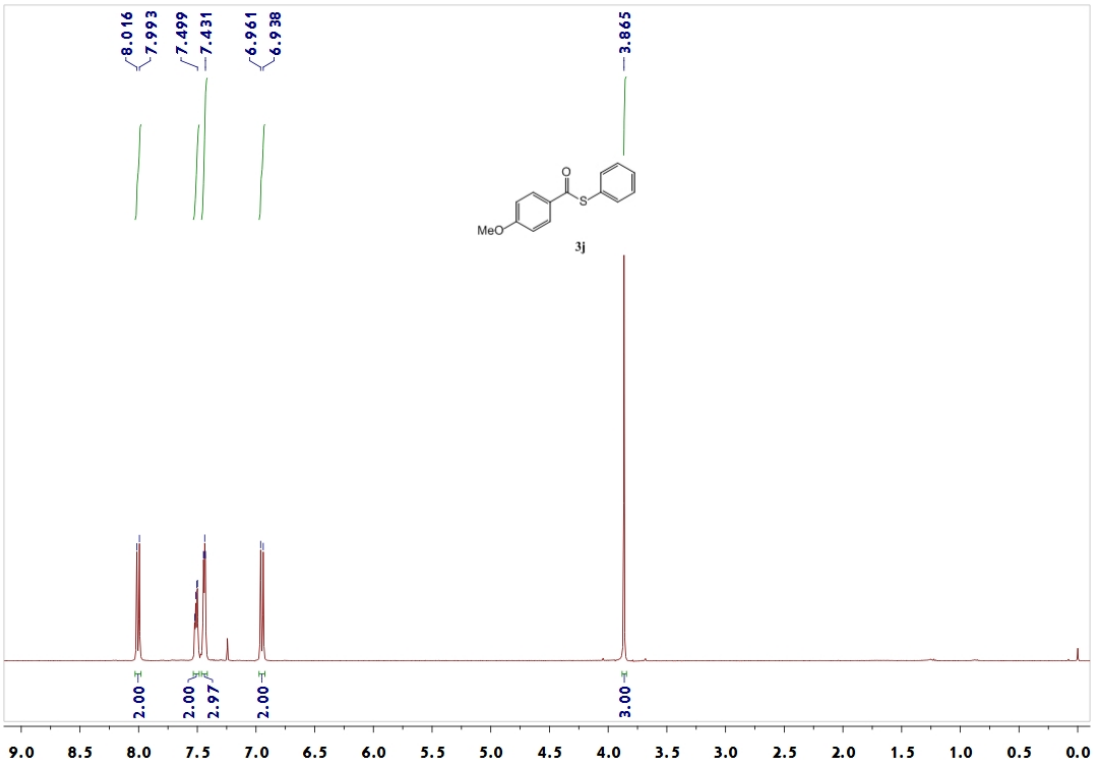

188.790
134.929
134.576
131.590
129.239
128.862
128.448
128.274
126.393
Br
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

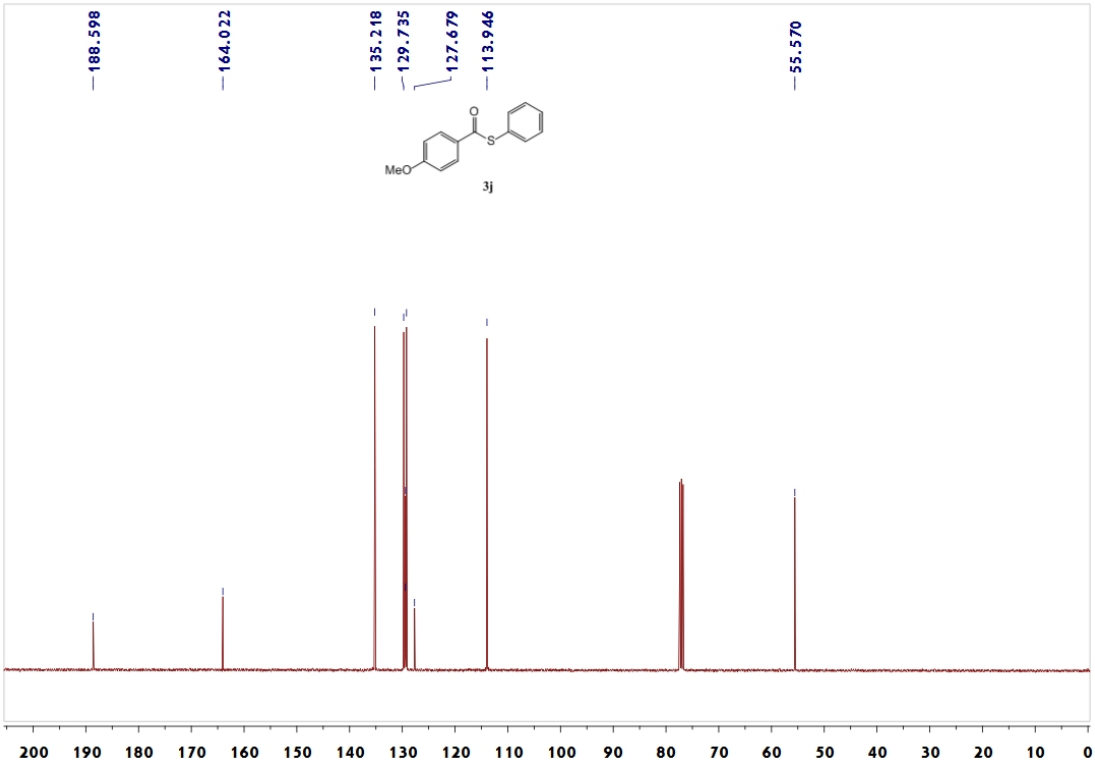

8.146
8.141
8.137
7.966
7.963
7.960
7.947
7.944
7.940
7.742
7.740
7.737
7.735
7.722
7.720
7.717
7.715
7.521
7.513
7.506
7.503
7.496
7.487
7.481
7.473
7.465
7.456
7.386
7.366
7.347
O
S
Br
3h
1.00
1.04
1.05
5.35
1.12
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

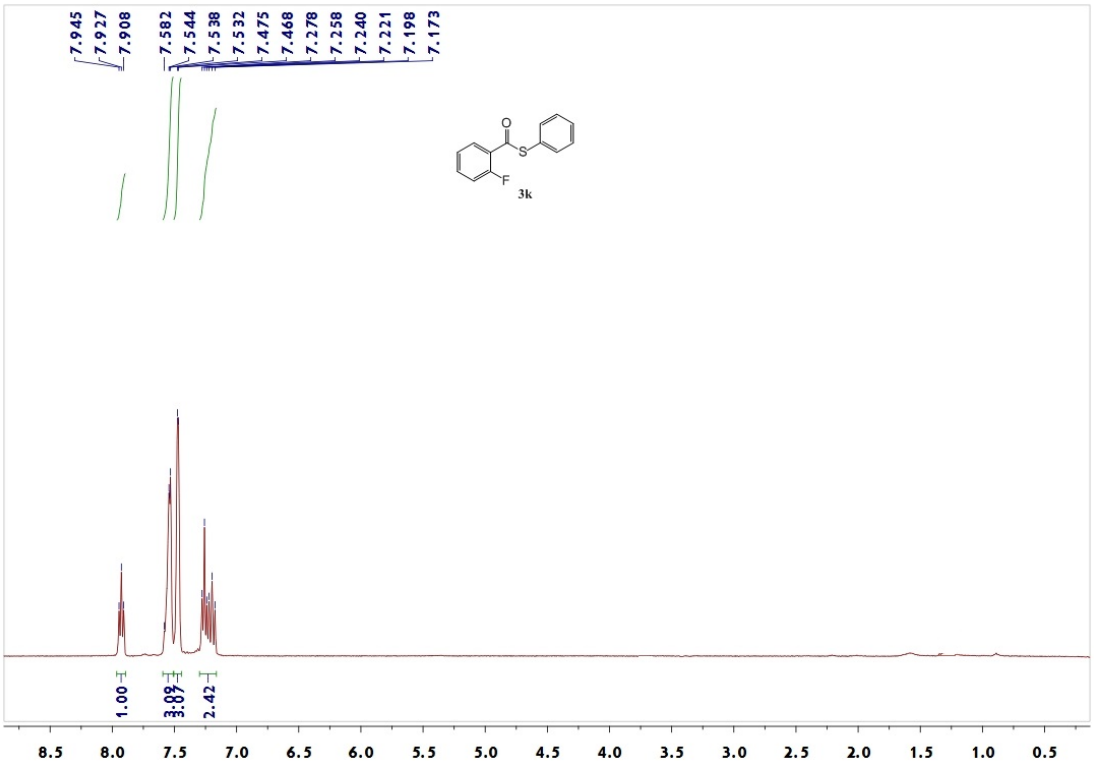

188.465
137.879
135.995
134.545
129.916
129.834
129.297
128.894
126.289
125.557
122.497
O
S
Br
3h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

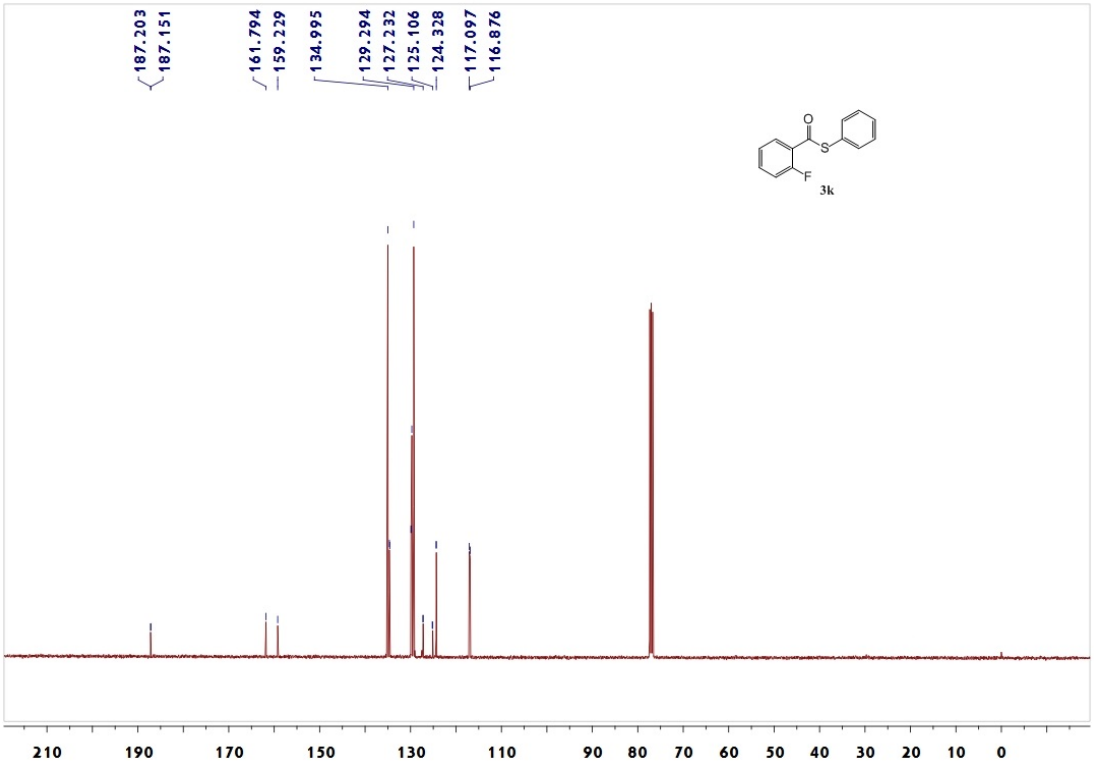

7.728
7.723
7.709
7.705
7.664
7.644
7.560
7.549
7.540
7.536
7.490
7.478
7.468
7.464
7.456
7.451
7.418
7.402
7.399
7.383
7.380
7.361
7.357
7.342
7.338
7.323
7.319
Br
3i
1.00
1.02
2.00
3.01
2.23
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

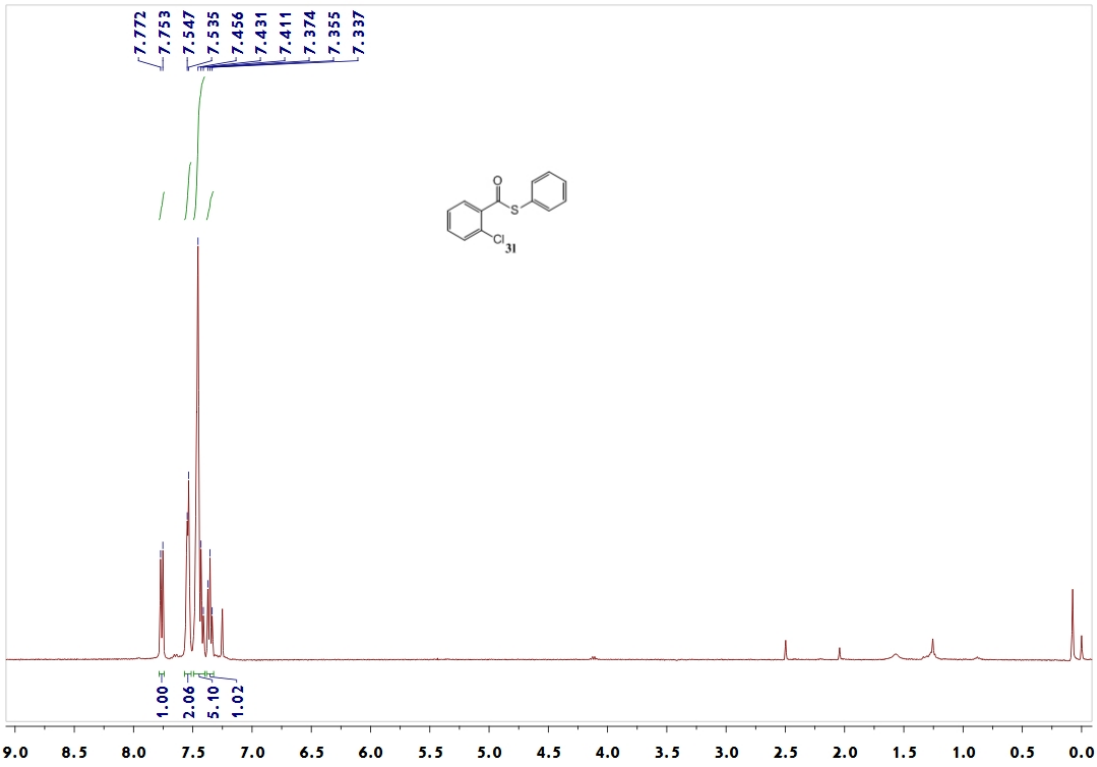

191.119
139.189
134.635
134.132
132.429
129.783
129.406
129.055
127.445
127.317
119.139
Br
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

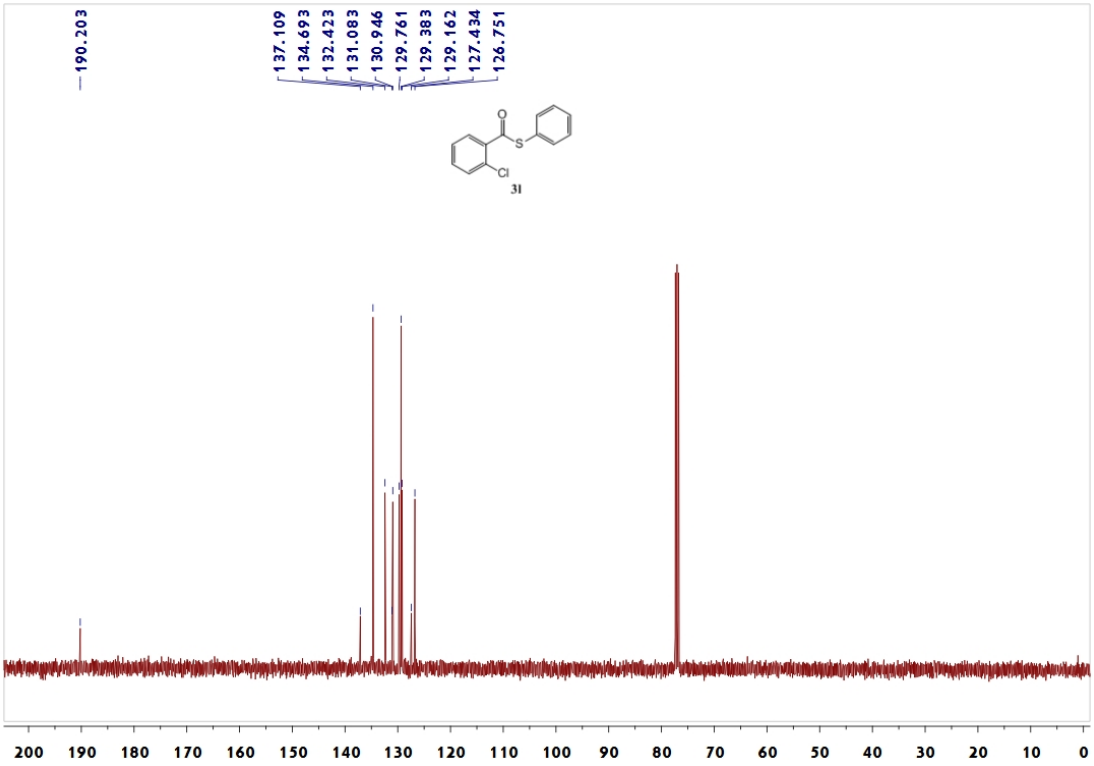

8.016
7.993
7.499
7.431
6.961
6.938
3.865
MeO
3j
2.00
2.00
2.97
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

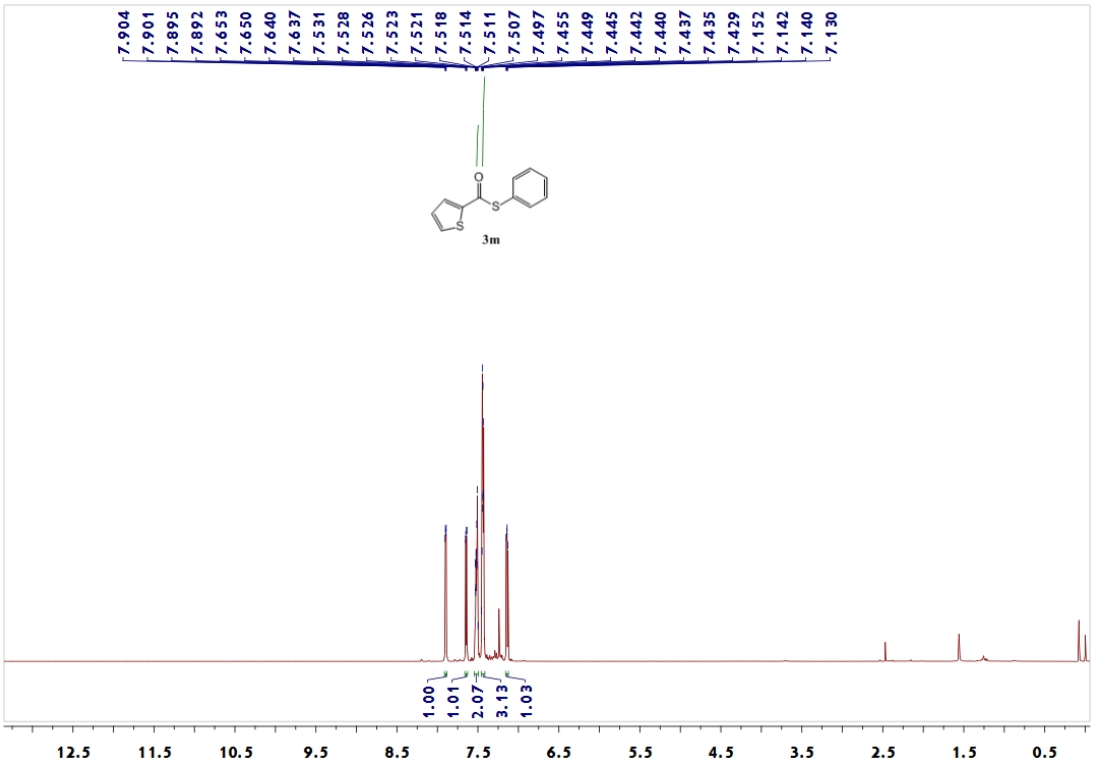

188.598
164.022
135.218
129.735
127.679
113.946
55.570
MeO
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

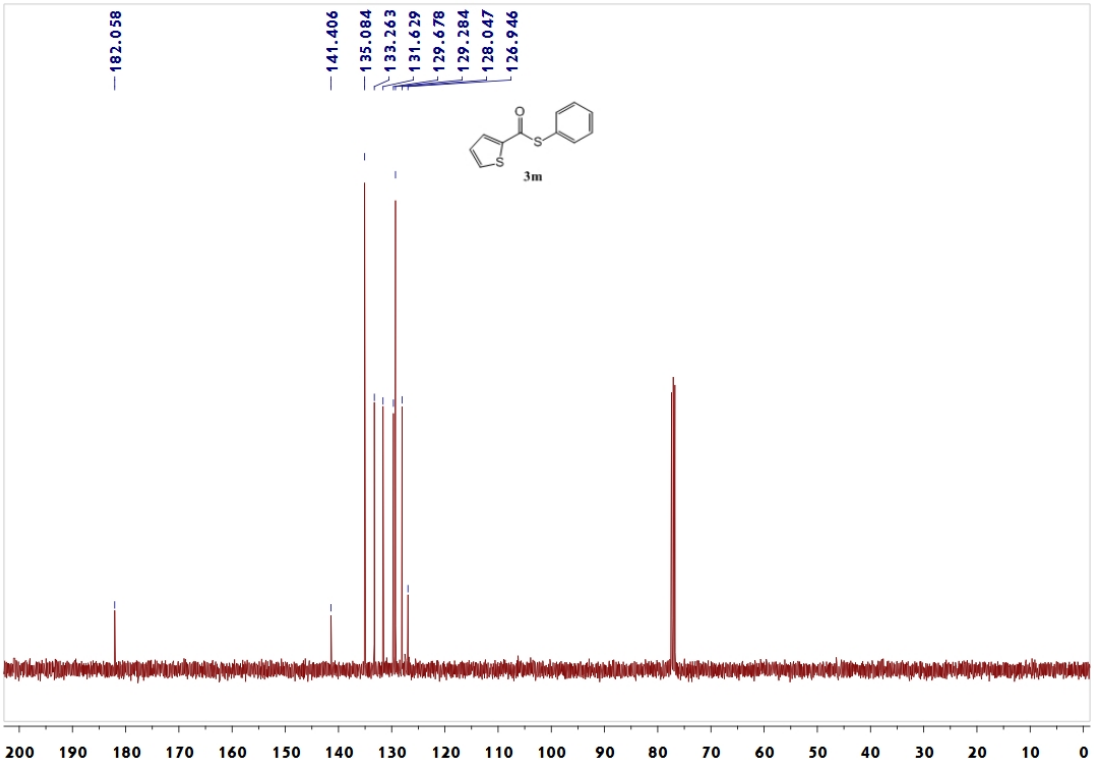

7.945
7.927
7.908
7.582
7.544
7.538
7.532
7.475
7.468
7.278
7.258
7.240
7.221
7.198
7.173
3k
1.00
3.07
2.42
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

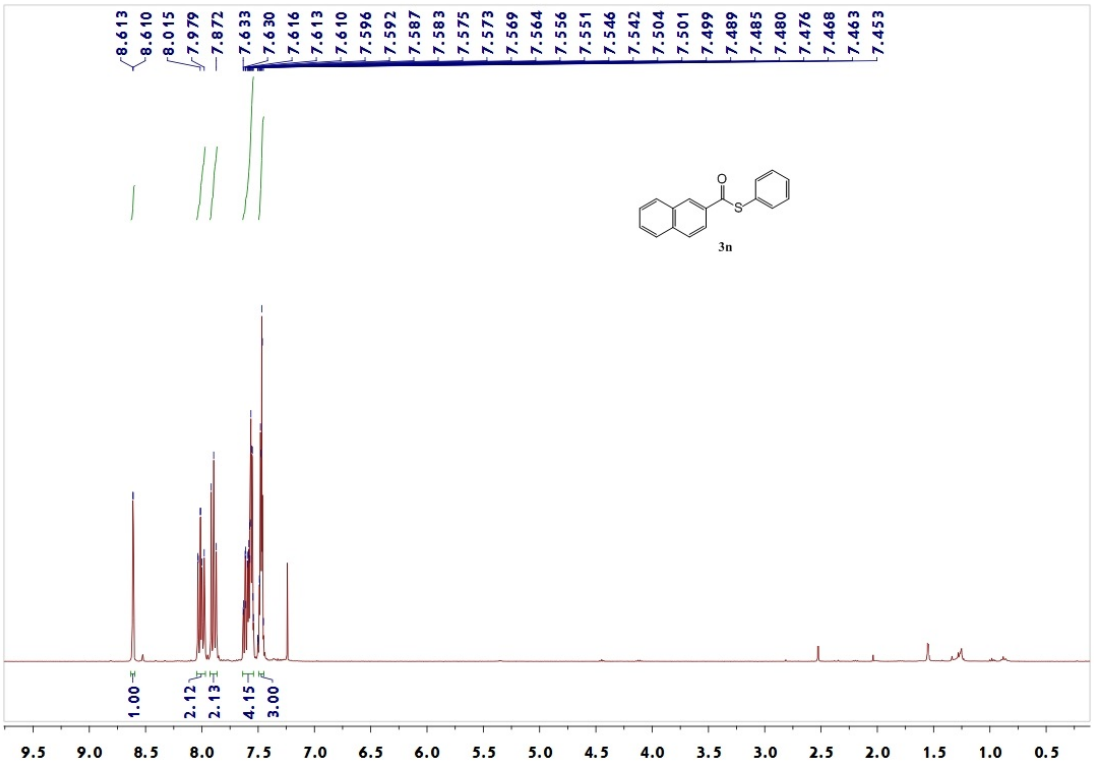

187.203
187.151
161.794
159.229
134.995
129.294
127.232
125.106
124.328
117.097
116.876
3k
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

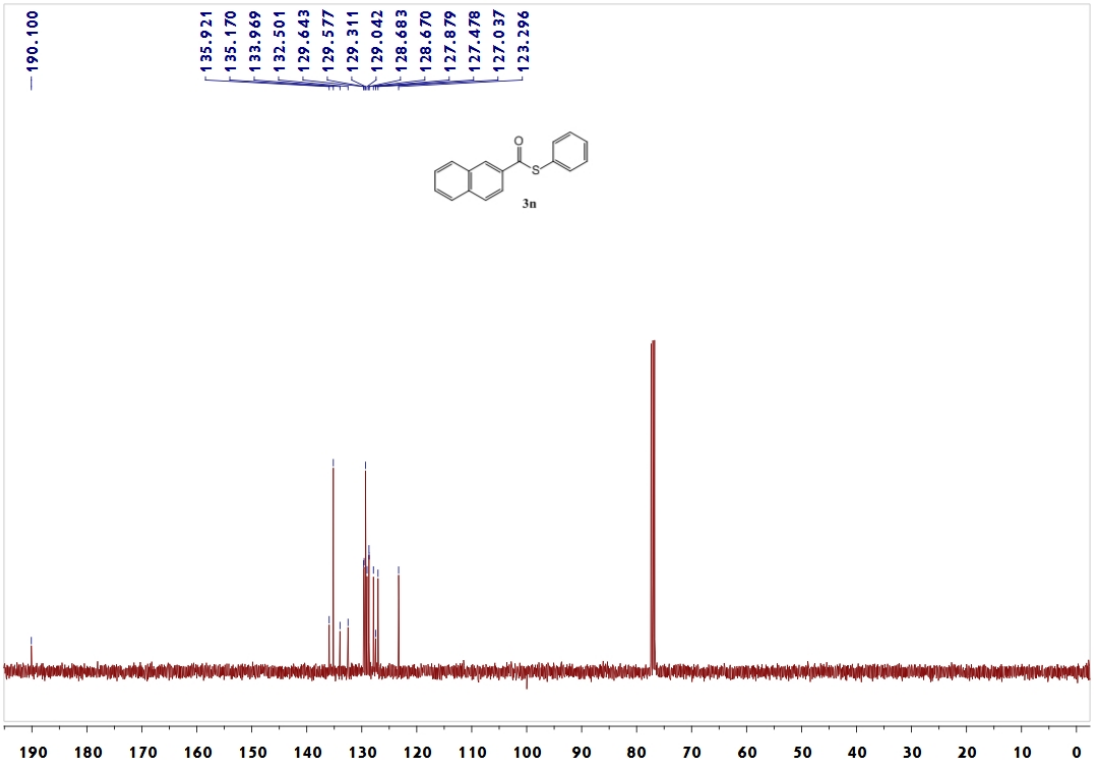

7.772
7.753
7.547
7.535
7.456
7.431
7.411
7.374
7.355
7.337
1.00
2.06
5.10
1.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

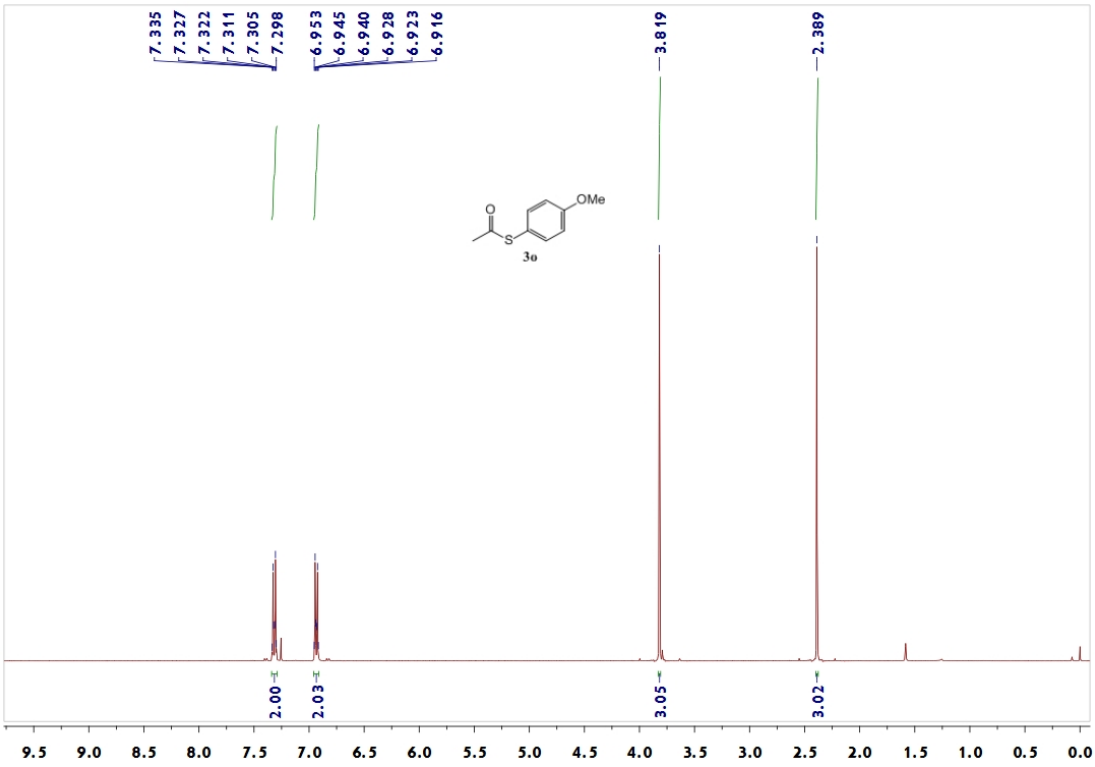

190.203
137.109
134.693
132.423
131.083
130.946
129.761
129.383
129.162
127.434
126.751
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

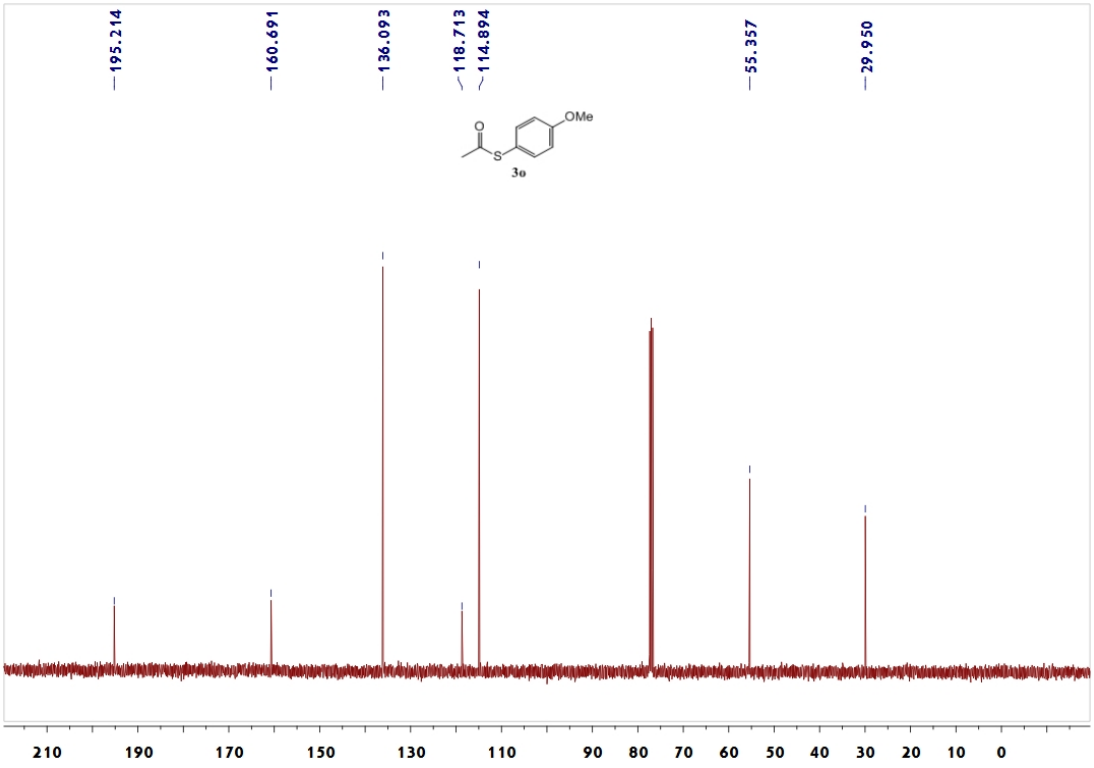

7.904
7.901
7.895
7.892
7.653
7.650
7.640
7.637
7.531
7.528
7.526
7.523
7.521
7.518
7.514
7.511
7.507
7.497
7.455
7.449
7.445
7.442
7.440
7.437
7.435
7.429
7.152
7.142
7.140
7.130
3m
1.00
1.01
2.07
3.13
1.03
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5

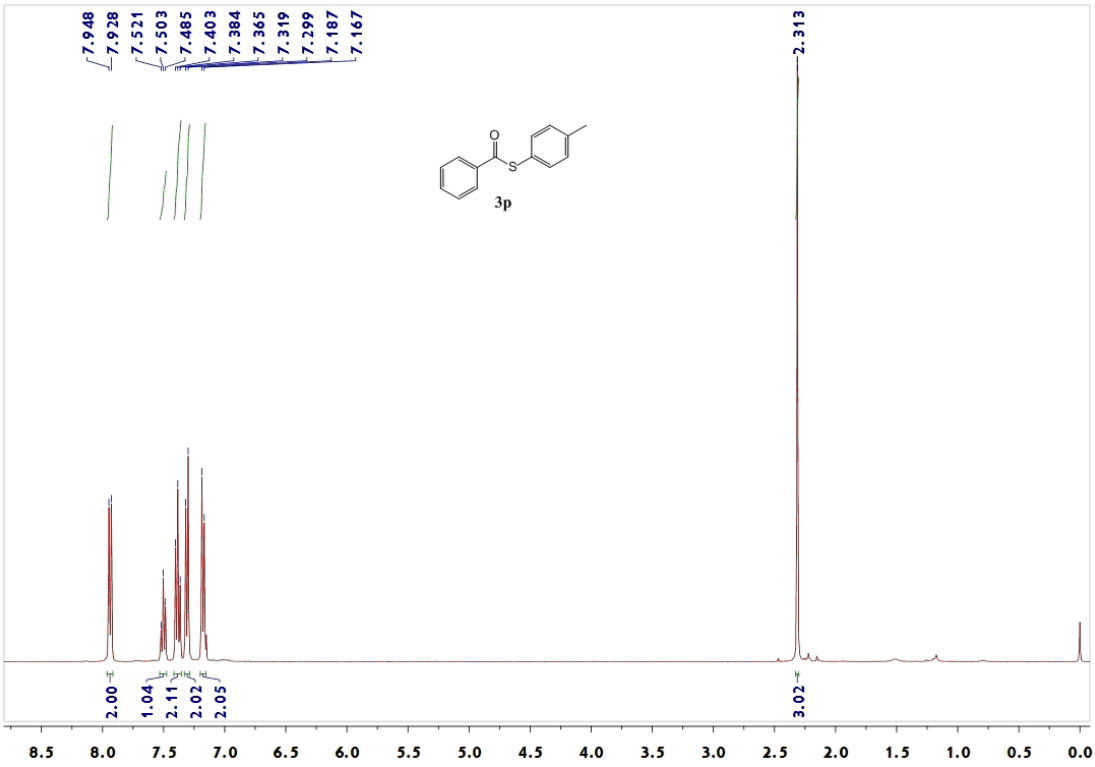

182.058
141.406
135.084
133.263
131.629
129.678
129.284
128.047
126.946
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

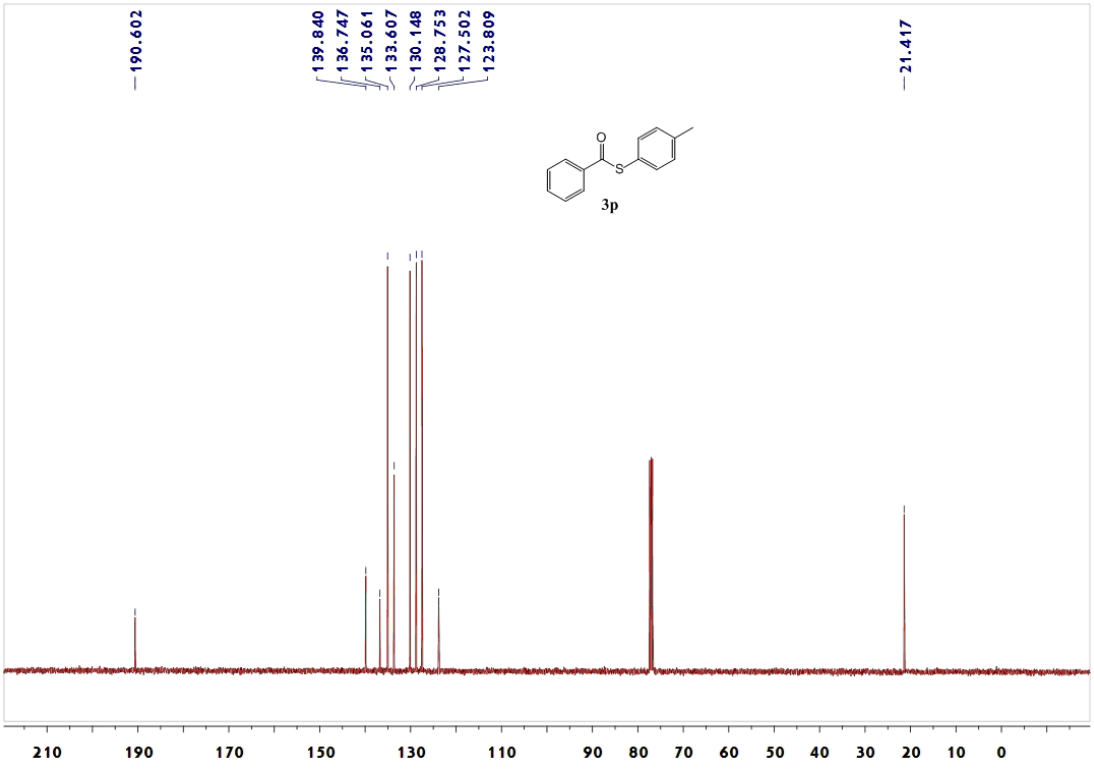

8.613
8.610
8.015
7.979
7.872
7.633
7.630
7.616
7.613
7.610
7.596
7.592
7.587
7.583
7.575
7.573
7.569
7.564
7.556
7.551
7.546
7.542
7.504
7.501
7.499
7.489
7.485
7.480
7.476
7.468
7.463
7.453
3n
1.00
2.12
2.13
4.15
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

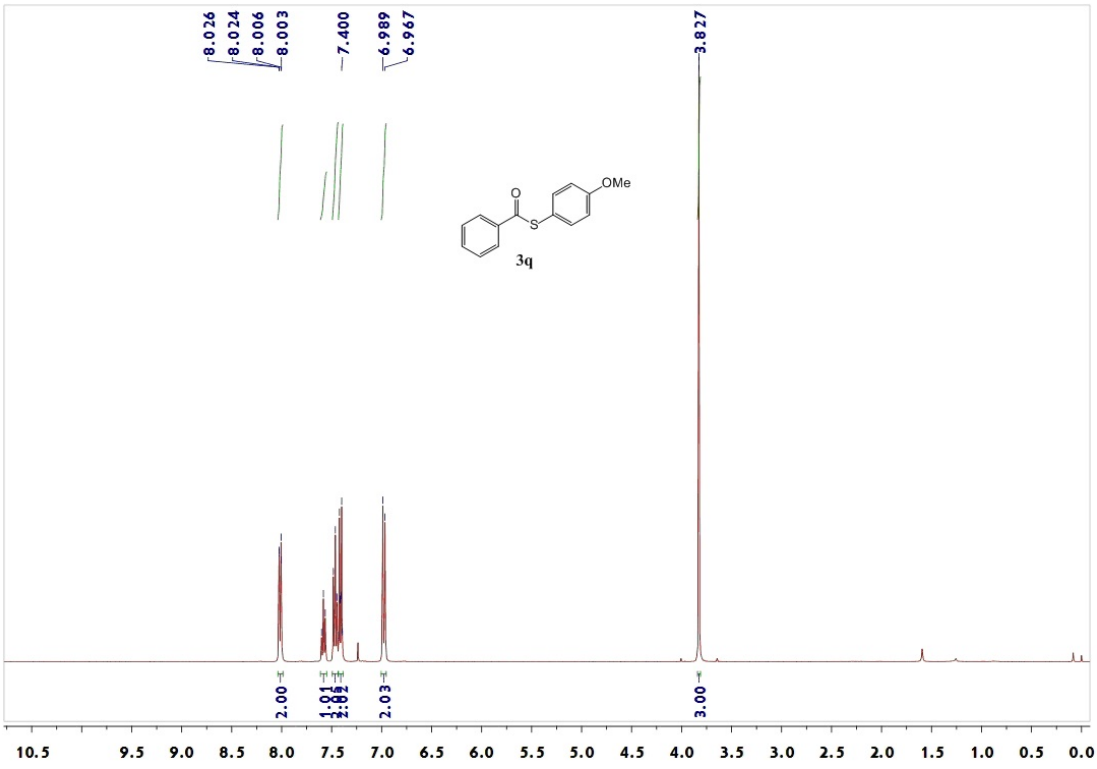

190.100
135.921
135.170
133.969
132.501
129.643
129.577
129.311
129.042
128.683
128.670
127.879
127.478
127.037
123.296
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

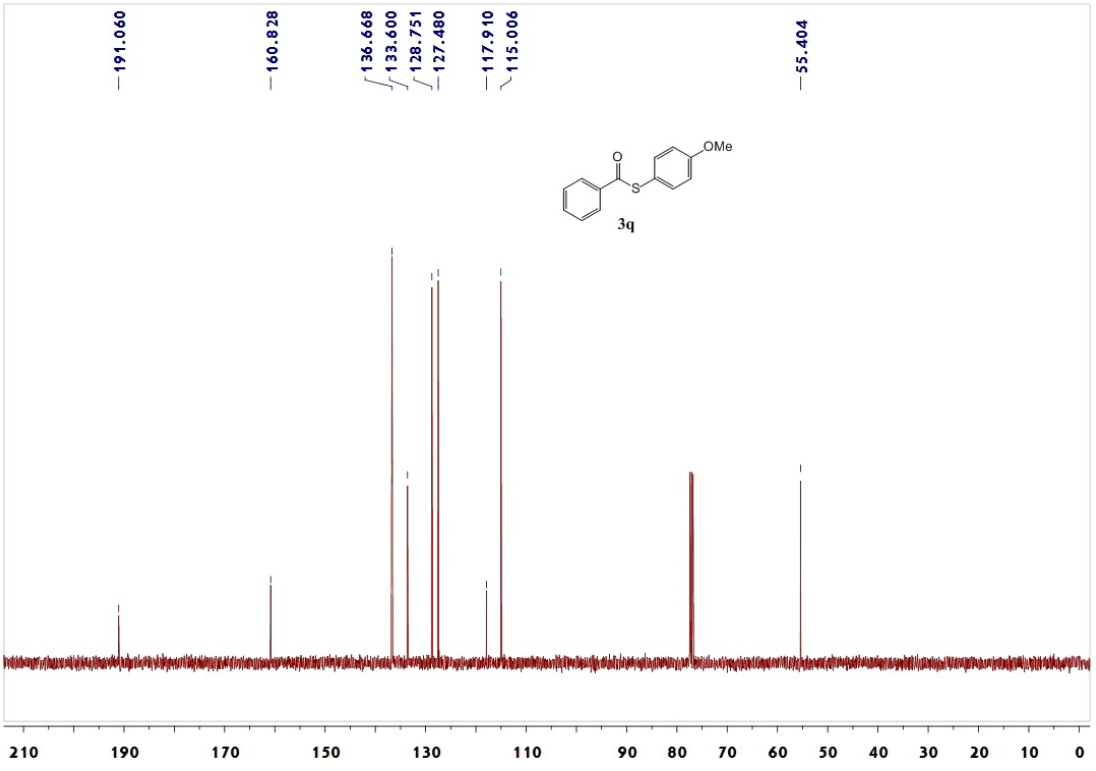

7.335
7.327
7.322
7.311
7.305
7.298
6.953
6.945
6.940
6.928
6.923
6.916
3.819
2.389
OMe
3e
2.00
2.03
3.05
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

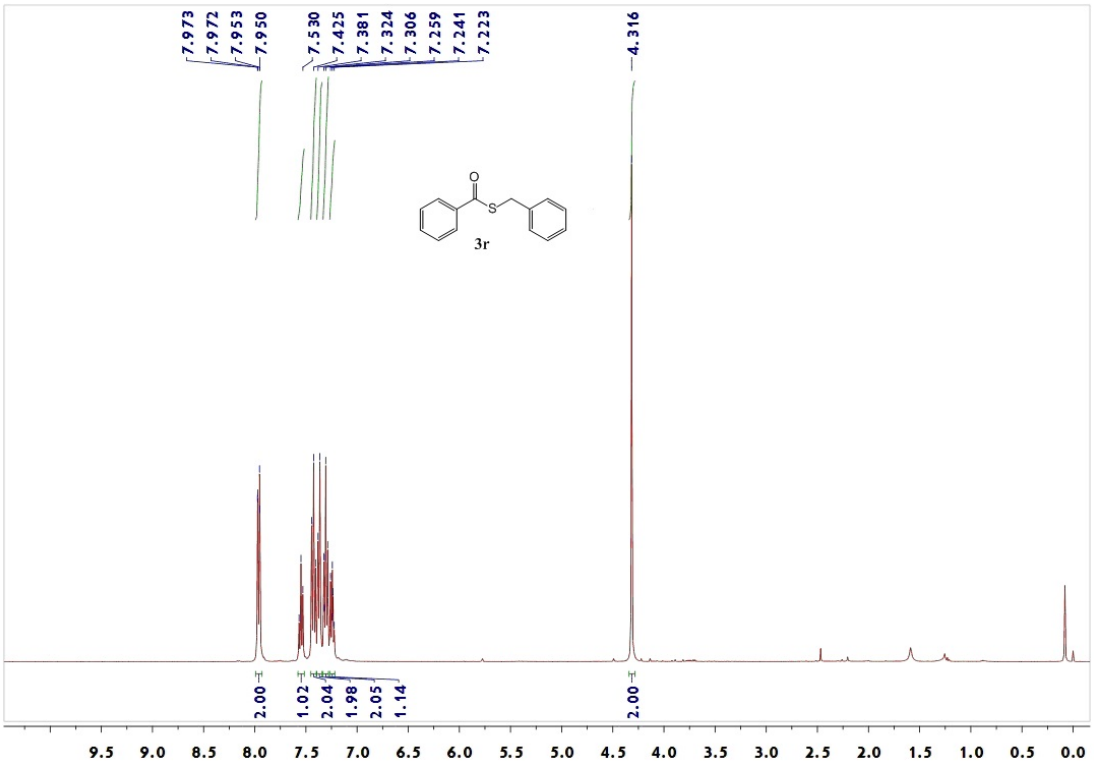

195.214
160.691
136.093
118.713
114.894
55.357
29.950
OMe
3e
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

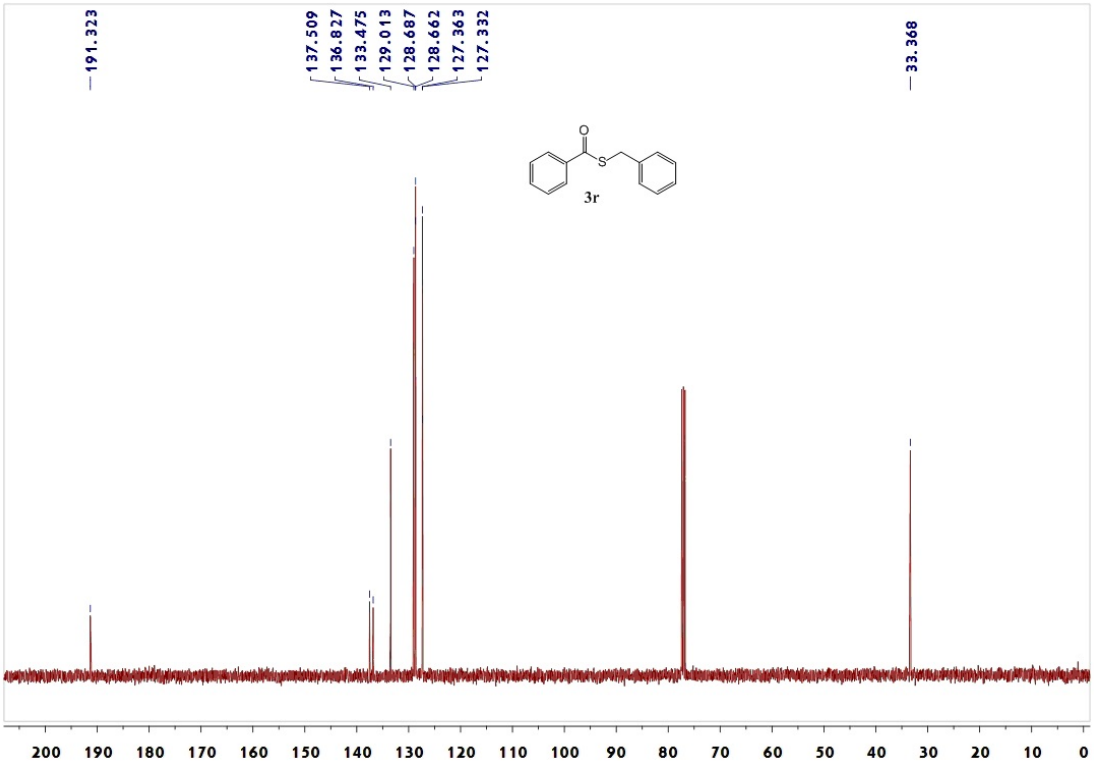

7.948
7.928
7.521
7.503
7.485
7.403
7.384
7.365
7.319
7.299
7.187
7.167
2.313
3p
2.00
1.04
2.11
2.02
2.05
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

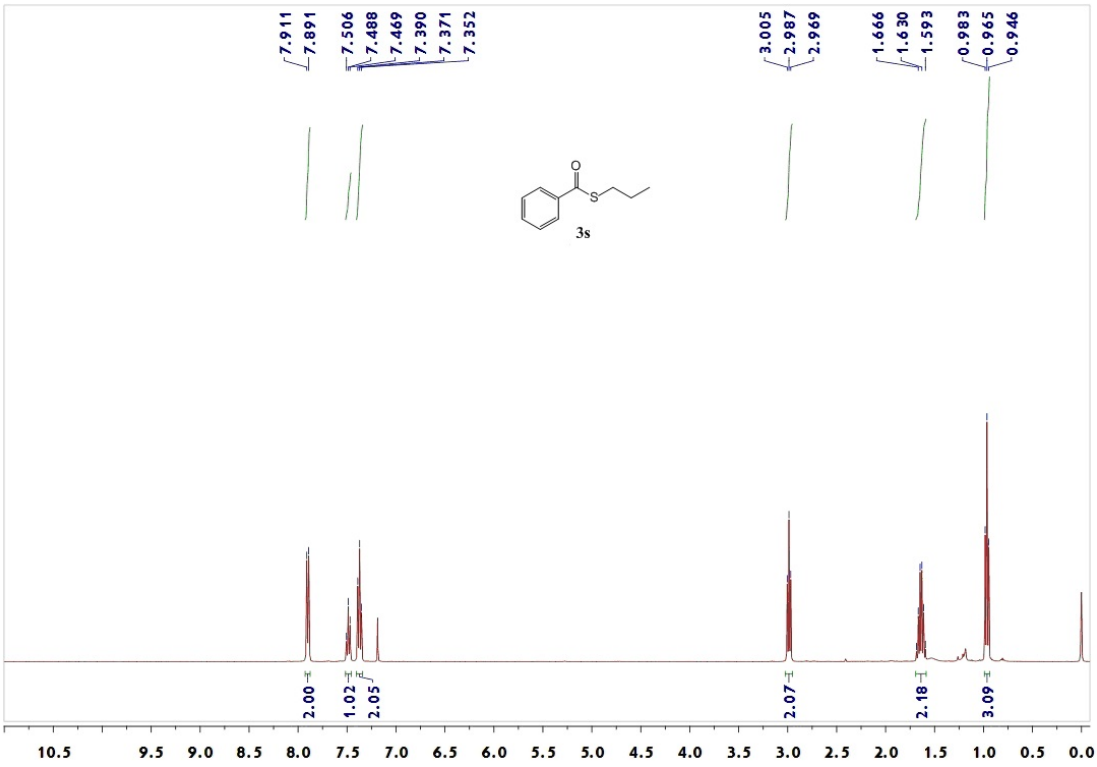

190.602
139.840
136.747
135.061
133.607
130.148
128.753
127.502
123.809
21.417
3p
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

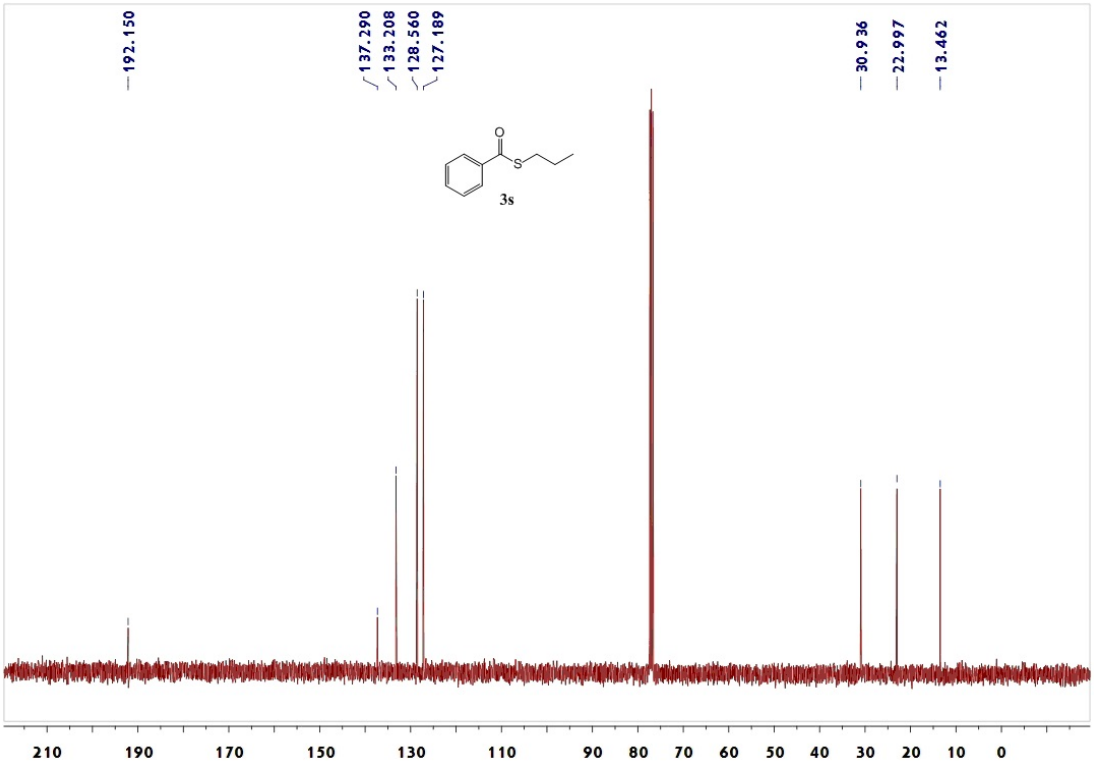

8.026
8.024
8.006
8.003
7.400
6.989
6.967
3.827
OMe
O
S
3q
2.00
1.01
1.01
2.02
2.03
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

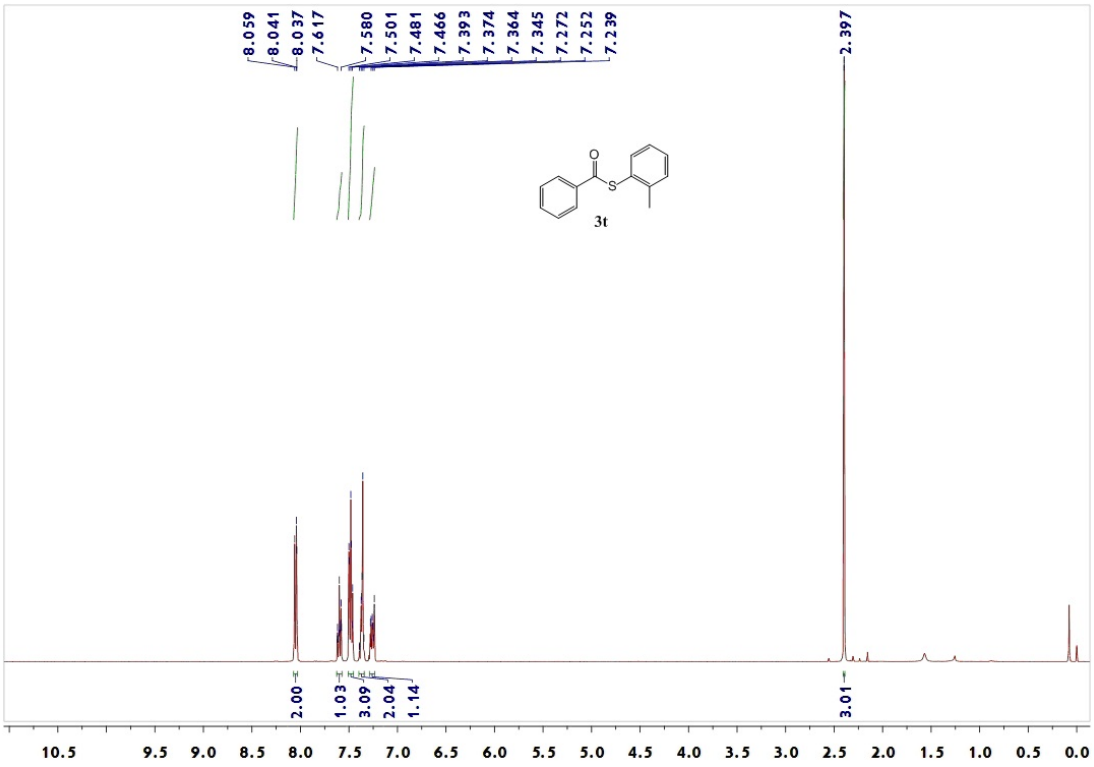

191.060
160.828
136.668
133.600
128.751
127.480
117.910
115.006
55.404
OMe
O
S
3q
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

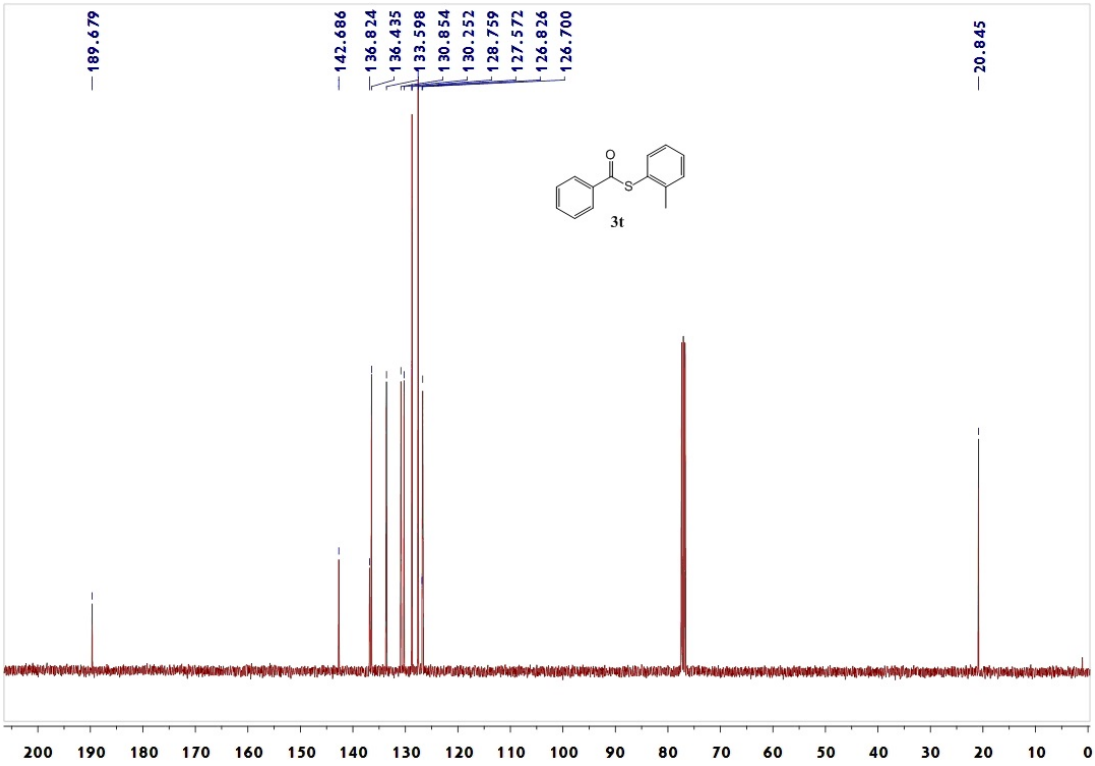

7.973
7.972
7.953
7.950
7.530
7.425
7.381
7.324
7.306
7.259
7.241
7.223
4.316
3r
2.00
1.02
2.04
1.98
2.05
1.14
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

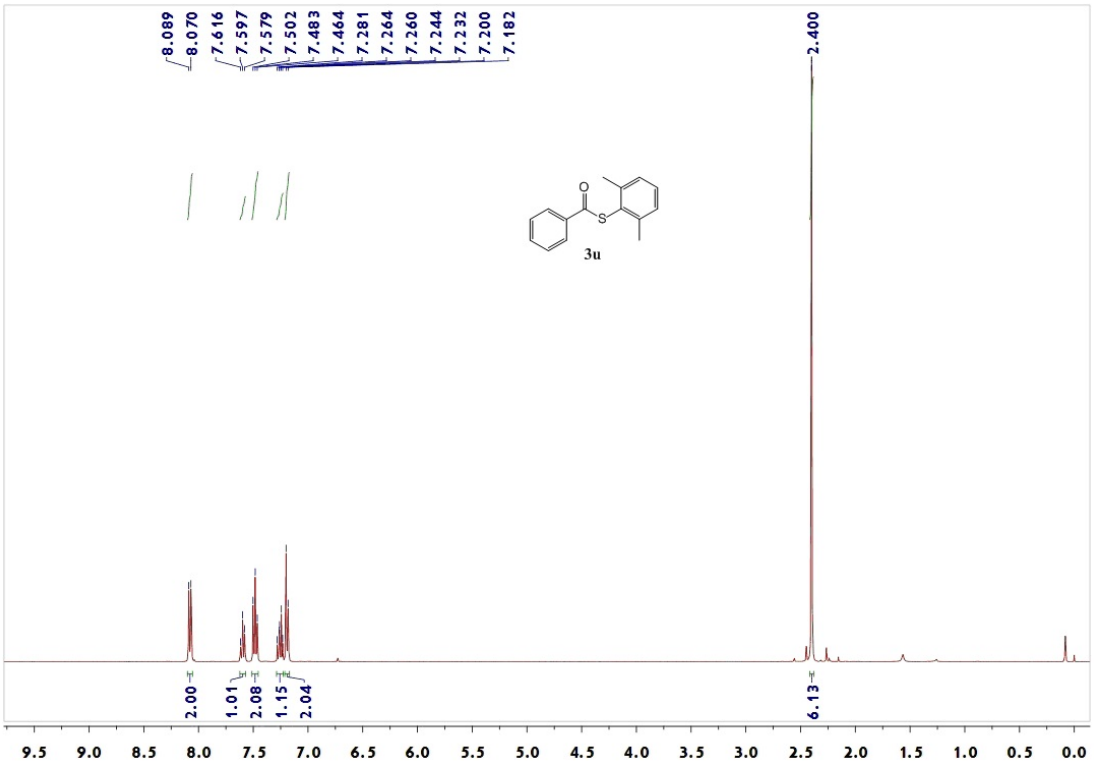

191.323
137.509
136.827
133.475
129.013
128.687
128.662
127.363
127.332
33.368
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

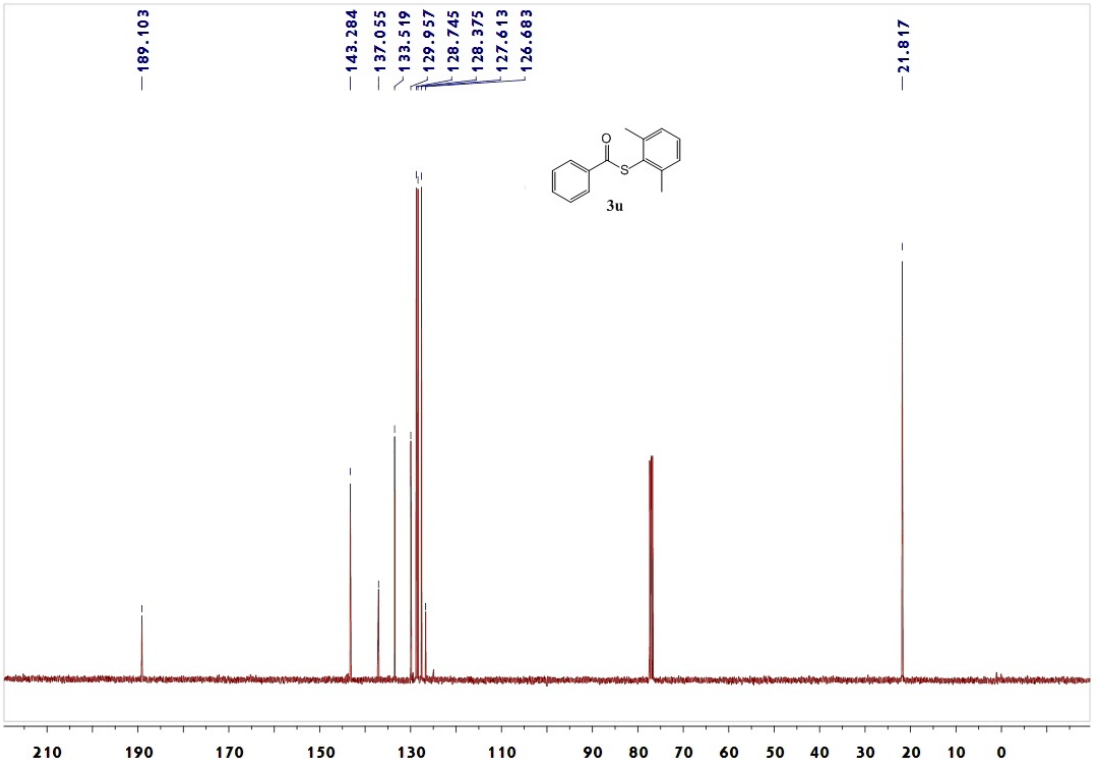

7.911
7.891
7.506
7.488
7.469
7.390
7.371
7.352
3.005
2.987
2.969
1.666
1.630
1.593
0.983
0.965
0.946
3s
2.00
1.02
2.05
2.07
2.18
3.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

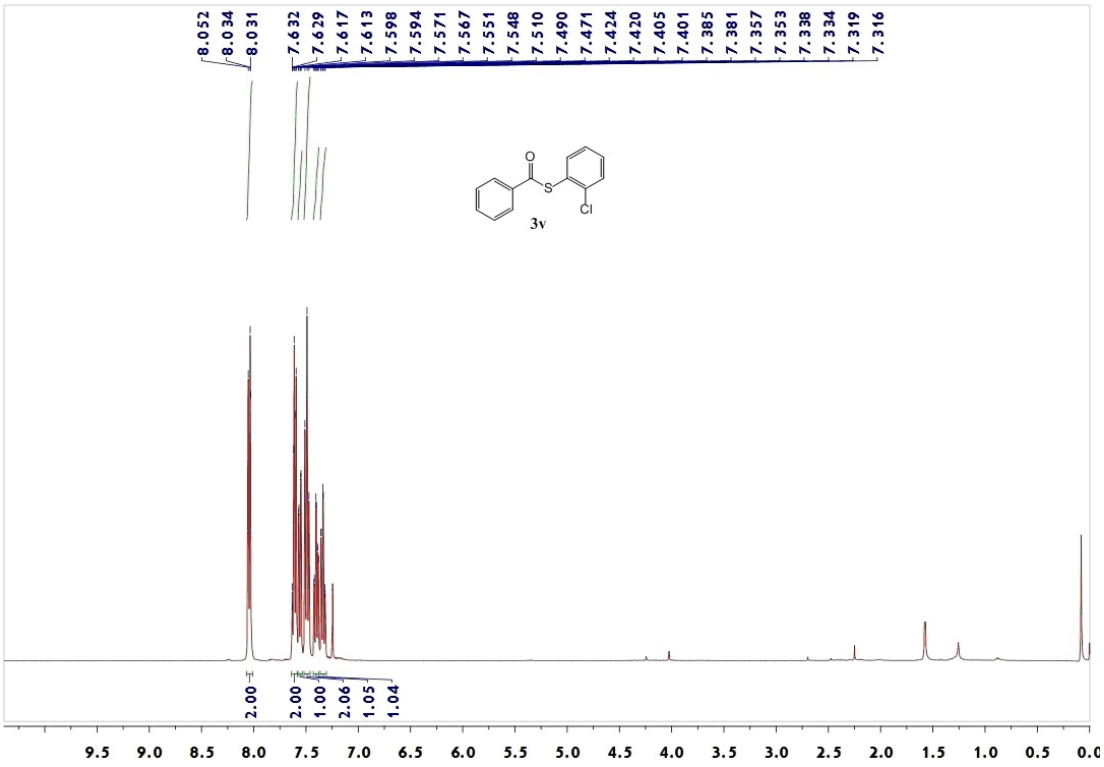

192.150
137.290
133.208
128.560
127.189
30.936
22.997
13.462
3s
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

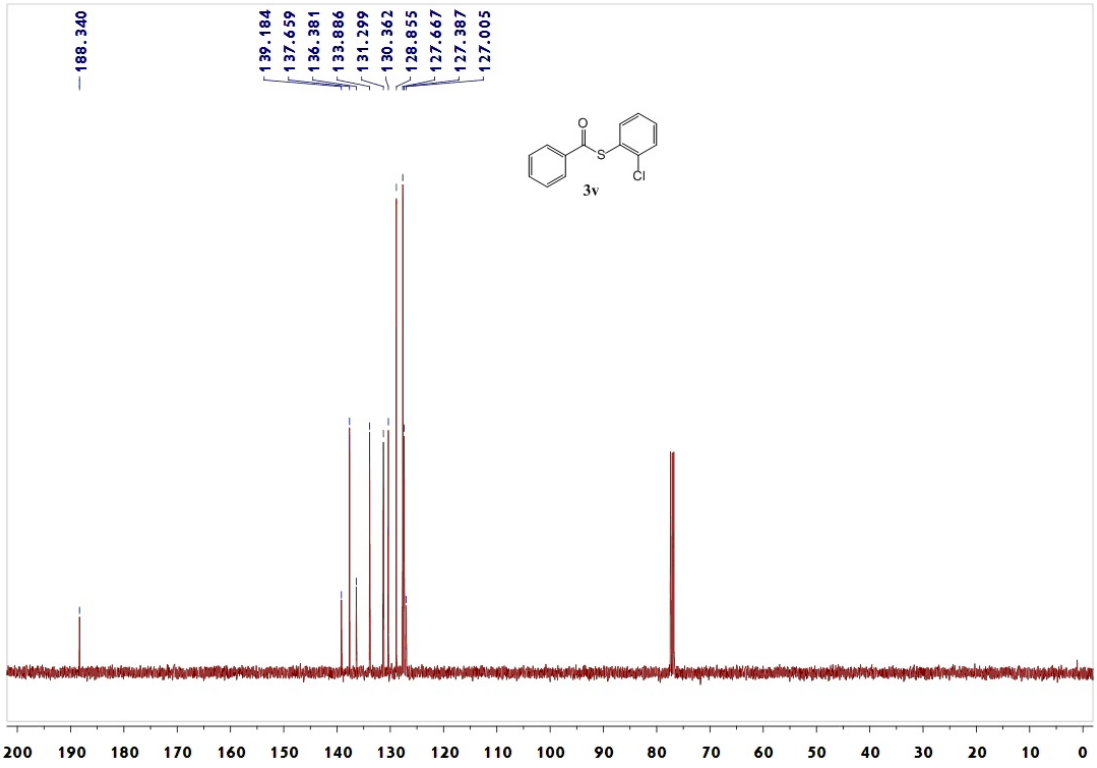

8.059
8.041
8.037
7.617
7.580
7.501
7.481
7.466
7.393
7.374
7.364
7.345
7.272
7.252
7.239
2.397
3t
2.00
1.03
3.09
2.04
1.14
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

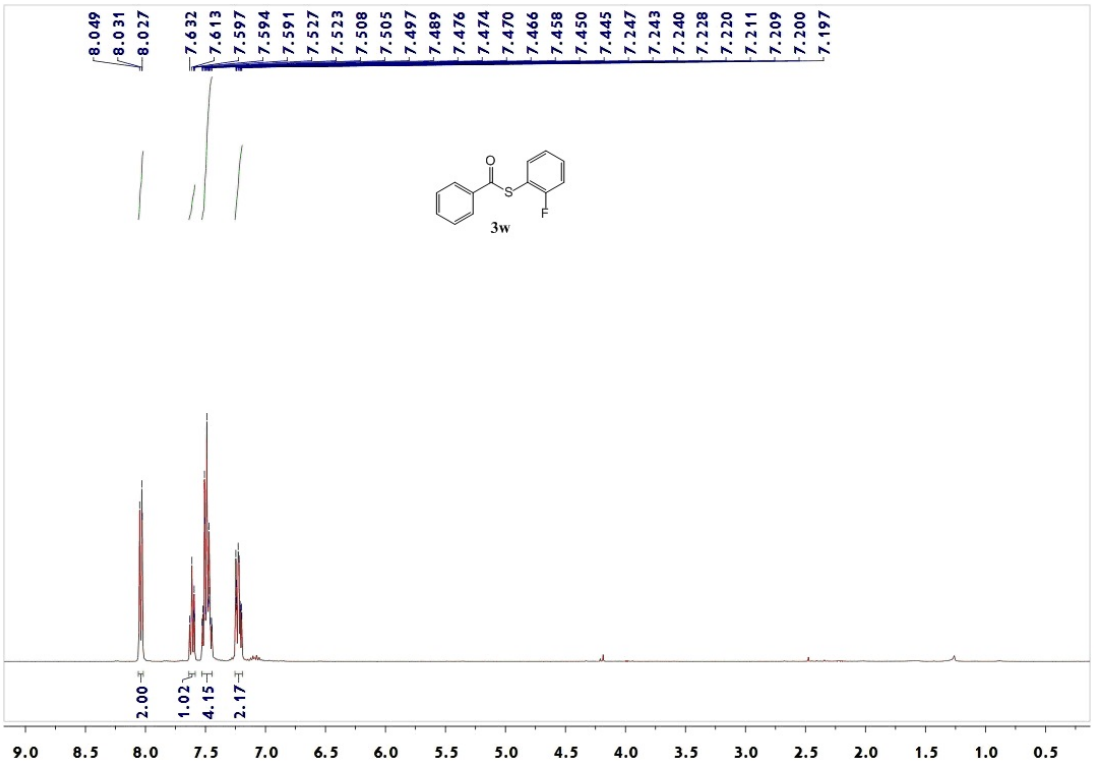

189.679
142.686
136.824
136.435
133.598
130.854
130.252
128.759
127.572
126.826
126.700
20.845
3t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

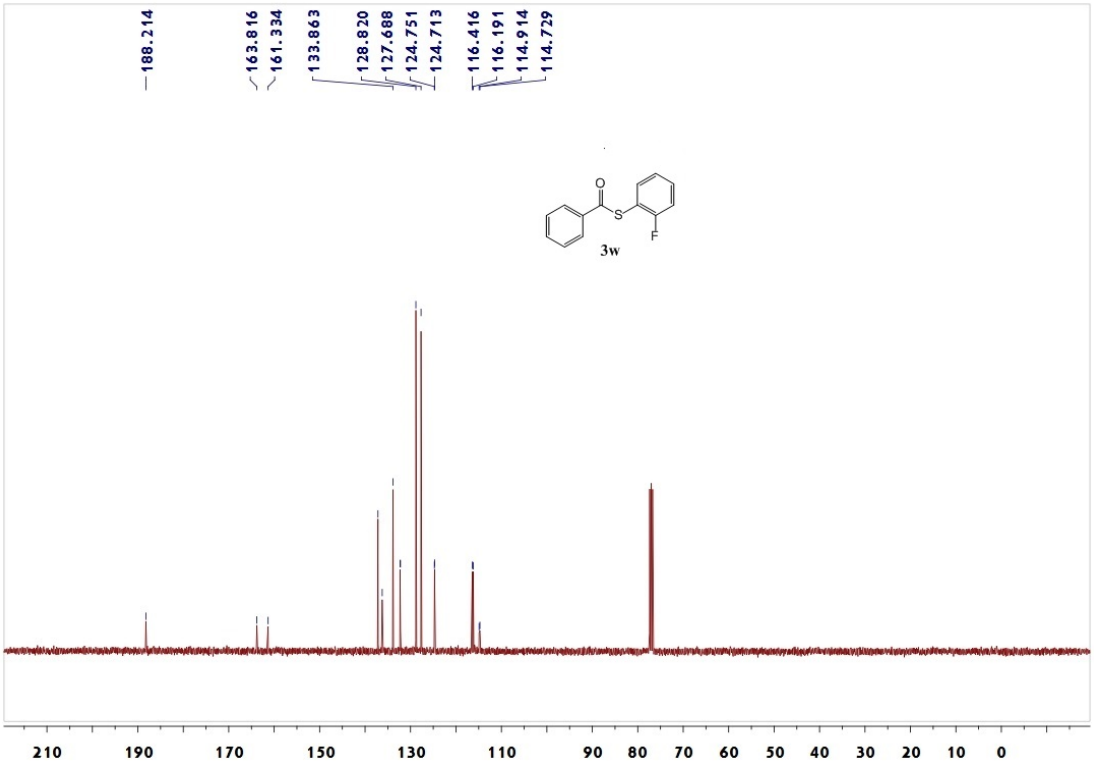

8.089
8.070
7.616
7.597
7.579
7.502
7.483
7.464
7.281
7.264
7.260
7.244
7.232
7.200
7.182
2.400
3u
2.00
1.01
2.08
1.15
2.04
6.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

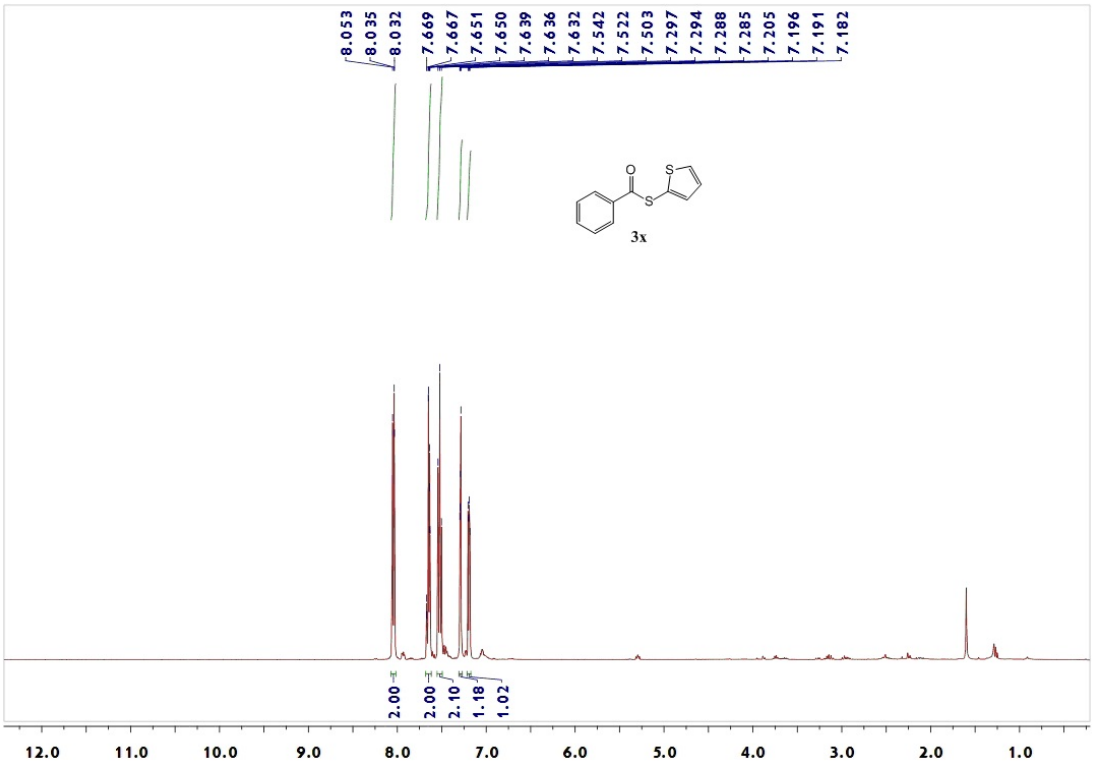

189.103
143.284
137.055
133.519
129.957
128.745
128.375
127.613
126.683
21.817
3u
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

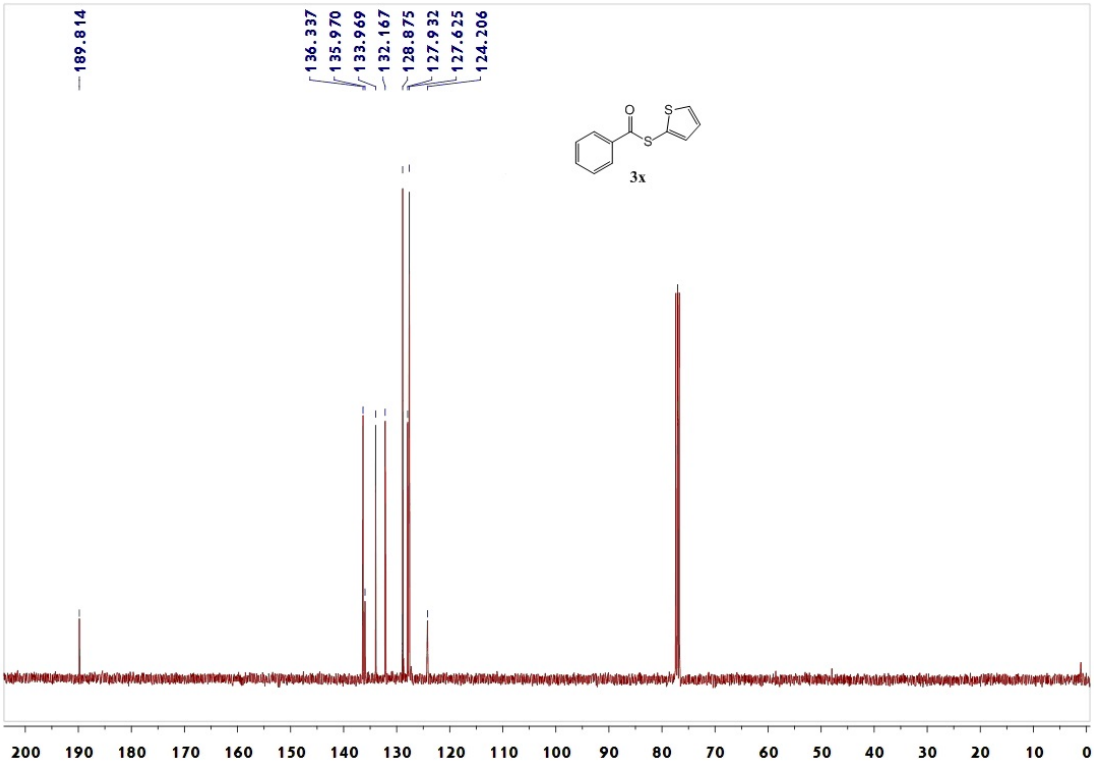

8.052
8.034
8.031
7.632
7.629
7.617
7.613
7.598
7.594
7.571
7.567
7.551
7.548
7.510
7.490
7.471
7.424
7.420
7.405
7.401
7.385
7.381
7.357
7.353
7.338
7.334
7.319
7.316
O
S
Cl
3v
2.00
2.00
1.00
2.06
1.05
1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


188.340
139.184
137.659
136.381
133.886
131.299
130.362
128.855
127.667
127.387
127.005
O
S
Cl
3v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.049
8.031
8.027
7.632
7.613
7.597
7.594
7.591
7.527
7.523
7.508
7.505
7.497
7.489
7.476
7.474
7.470
7.466
7.458
7.450
7.445
7.247
7.243
7.240
7.228
7.220
7.211
7.209
7.200
7.197
O
S
F
3w
2.00
1.02
4.15
2.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


188.214
163.816
161.334
133.863
128.820
127.688
124.751
124.713
116.416
116.191
114.914
114.729
O
S
F
3w
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


8.053
8.035
8.032
7.669
7.667
7.651
7.650
7.639
7.636
7.632
7.542
7.522
7.503
7.297
7.294
7.288
7.285
7.205
7.196
7.191
7.182
3x
2.00
2.00
2.10
1.18
1.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


189.814
136.337
135.970
133.969
132.167
128.875
127.932
127.625
124.206
3x
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0