

Supporting information

**Elemental Sulfur Mediated Decarboxylative Redox Cyclization Reaction of
o-Chloronitroarenes and Arylacetic acids**

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General information

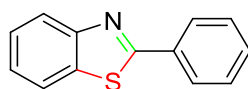
All the reagents were purchased from Sigma-Aldrich Corporation, USA; Alfa Aesar, UK and E. Merck, Germany and were used as received. The reactions were monitored by thin layer chromatography (TLC) using Merck Kieselgel 60 GF 254 plates (thickness 0.25 mm). Visualization of TLC was performed using UV light; products purification was done using Merck silica gel (100-200 mesh) column chromatography. NMR spectra were recorded with a 300 or 400 MHz spectrometer for ^1H NMR, and 75 or 100 MHz for ^{13}C NMR spectroscopy using CDCl_3 or DMSO-d_6 solution. HRMS was recorded by using Q-TOF mass spectrometer. Chemical shifts are given in δ ppm and are measured relative to tetramethylsilane (TMS) as internal standard.

General procedure for the synthesis of 2-arylbenzothiazoles:

A mixture of *o*-chlonitroarene (1.0 mmol), arylacetic acid (1.0 mmol), elemental sulfur (3.0 mmol) and *N*-methylmorpholine (3.0 mmol) was placed in a vial (10 mL) containing a magnetic stirring bar and then capped and stirred at 110 °C for 15 h. After the reaction was completed (TLC), the mixture was cooled to room temperature and the crude reaction mixture was purified by silica gel column chromatography using *n*-hexane and ethyl acetate as eluent. For product **3w**, the reaction mixture was made acidic with HCl (10%) after cooling and then extracted with ethylacetate. The organic phase was dried over anhyd Na_2SO_4 , filtered, evaporated under reduced pressure and purified by column chromatography using *n*-hexane and ethyl acetate as eluent.

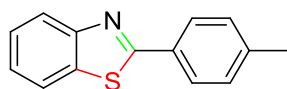
Characterization Data of the Products:

2-Phenylbenzo[d]thiazole (3a)¹



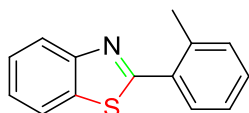
Light yellow solid (75%, 158 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.09 (m, 3H), 7.90 (d, J = 8.4 Hz, 1H), 7.50-7.40 (m, 4H), 7.35 (t, J = 9.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 168.7, 154.7, 135.6, 134.2, 131.5, 129.6, 128.1, 126.9, 125.7, 123.8, 122.2.

2-(*p*-Tolyl)benzo[d]thiazole (3b)¹



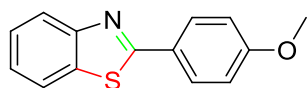
Light yellow solid (73%, 164 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.05 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 7.8 Hz, 2H), 7.82 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.32 (d, J = 5.7 Hz, 1H), 7.23 (d, J = 7.8 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 168.8, 154.7, 141.9, 135.5, 130.2, 128.3, 128.0, 126.7, 125.5, 123.5, 122.1, 21.9.

2-(*o*-Tolyl)benzo[d]thiazole (3c)³



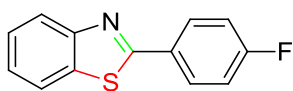
Light yellow solid (57%, 128 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.11 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.40-7.28 (m, 4H), 2.68 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 168.6, 154.4, 137.8, 136.2, 133.7, 132.1, 131.1, 130.6, 126.7, 125.7, 124.0, 122.0, 21.8.

2-(4-Methoxyphenyl)benzo[d]thiazole (3d)²



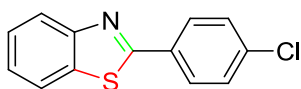
Light yellow solid (72%, 173 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.02 (m, 3H), 7.84 (d, $J = 9$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.0 (d, $J = 8.4$ Hz, 2H) 3.83 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.6, 161.7, 154.0, 134.6, 128.8, 126.2, 126.0, 124.5, 122.5, 121.2, 114.1, 55.09.

2-(4-Fluorophenyl)benzo[d]thiazole (3e)¹



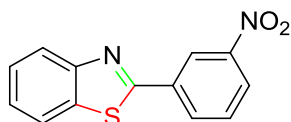
Light yellow solid (69%, 158 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.10-8.01 (m, 3H), 7.84 (d, $J = 7.2$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.20-7.10 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 166.5, 165.9, 162.5, 153.8, 134.8, 129.7, 129.6, 129.3, 129.2, 126.1, 124.9, 122.9, 121.3, 116.0, 115.7.

2-(4-Chlorophenyl)benzo[d]thiazole (3f)²



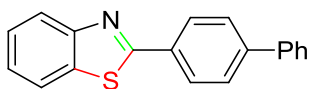
Light yellow solid (70%, 171 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.0 (d, $J = 7.5$ Hz, 1H), 7.92 (d, $J = 8.4$ Hz, 2H), 7.79 (d, $J = 9.6$ Hz, 1H), 7.41 (t, $J = 3.9$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.28 (t, $J = 8.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 166.8, 154.3, 137.2, 135.2, 132.3, 129.4, 128.9, 126.7, 125.6, 123.5, 121.8.

2-(3-Nitrophenyl)benzo[d]thiazole (3g)⁴



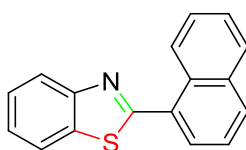
Yellow solid (68%, 174 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.91 (s, 1H), 8.41 (d, $J = 7.2$ Hz, 1H), 8.33 (d, $J = 6$ Hz, 1H), 8.12 (d, $J = 7.8$ Hz, 1H), 7.95 (d, $J = 8.7$ Hz, 1H), 7.68 (t, $J = 4.2$ Hz, 1H), 7.54 (t, $J = 3.6$ Hz, 1H), 7.45 (t, $J = 3.9$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 164.7, 153.7, 148.5, 135.1, 135.0, 132.8, 129.9, 126.6, 125.8, 124.9, 123.5, 122.1, 121.6.

2-([1,1'-Biphenyl]-4-yl)benzo[d]thiazole (3h)⁵



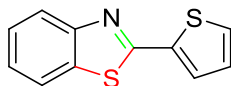
Light yellow solid (70%, 200 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.17 (d, $J = 8.1$ Hz, 2H), 8.10 (d, $J = 8.1$ Hz, 1H), 7.91 (d, $J = 7.8$ Hz, 1H), 7.73 (d, $J = 8.1$ Hz, 2H), 7.66 (d, $J = 7.2$ Hz, 2H), 7.52-7.44 (m, 3H), 7.38 (t, $J = 7.5$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.6, 154.0, 143.5, 139.8, 134.8, 132.3, 128.7, 127.8, 127.7, 127.4, 126.9, 126.2, 125.0, 123.0, 121.4.

2-(Naphthalen-1-yl)benzo[d]thiazole (3i)²



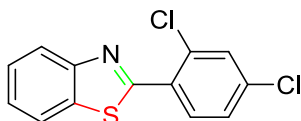
Light yellow solid (63%, 164 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.95 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.1 Hz, 1H), 7.96-7.89 (m, 4H), 7.60-7.52 (m, 4H), 7.41 (t, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.4, 154.0, 142.8, 135.2, 133.8, 130.8, 129.2, 128.2, 127.4, 126.3, 126.0, 125.7, 125.1, 124.7, 123.3, 121.1.

2-(Thiophen-2-yl)benzo[d]thiazole (3j)⁴



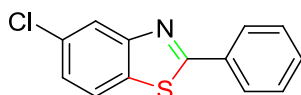
Light yellow solid (69%, 149 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.02 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 2.1 Hz, 1H), 7.46-7.40 (m, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.05 (t, J = 3.6 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 161.2, 153.5, 137.1, 134.5, 129.1, 128.4, 127.8, 126.2, 125.0, 122.7, 121.3.

2-(2,4-Dichlorophenyl)benzo[d]thiazole (3k)⁶



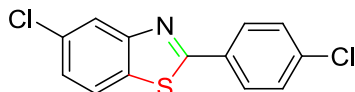
Light yellow solid (55%, 154 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.22 (d, J = 9.6 Hz, 1H), 8.12 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 3 Hz, 1H), 7.48-7.35 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 162.7, 152.1, 136.4, 135.8, 133.1, 132.3, 130.5, 130.3, 127.3, 126.7, 125.4, 123.2, 121.1.

5-Chloro-2-phenylbenzo[d]thiazole (3l)²



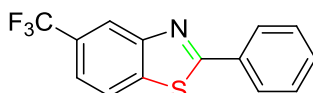
Light yellow solid (71%, 173 mg); ^1H NMR (300 MHz, CDCl_3): δ 7.96-7.91 (m, 3H), 7.64 (d, J = 8.4 Hz, 1H), 7.39-7.36 (m, 3H), 7.22 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.1, 155.2, 133.5, 132.5, 131.5, 129.2, 127.8, 127.7, 125.7, 123.2, 122.4.

5-Chloro-2-(4-chlorophenyl)benzo[d]thiazole (3m)²



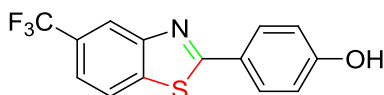
Light yellow solid (65%, 182 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.0 (d, J = 3 Hz, 1H), 7.96-7.93 (m, 2H), 7.76 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.35 (dd, J = 2.4 Hz, 6.6 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 169.1, 155.5, 138.1, 133.9, 133.1, 132.3, 129.9, 129.3, 126.4, 123.6, 122.9.

2-Phenyl-5-(trifluoromethyl)benzo[d]thiazole (3n)¹



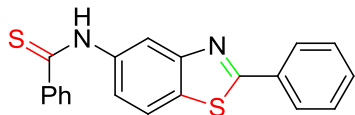
Light yellow solid (68%, 189 mg); ^1H NMR (300 MHz, CDCl_3): δ 8.30 (s, 1H), 8.10-8.03 (m, 2H), 7.94 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.50-7.46 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.7, 154.3, 139.1, 133.6, 132.2, 129.9, 129.7, 128.3, 122.8, 122.1, 121.0, 120.9.

4-(5-(Trifluoromethyl)benzo[d]thiazol-2-yl)phenol (3o)⁷



Light yellow solid (61%, 179 mg); **¹H NMR (300 MHz, DMSO):** δ 9.40 (bs, 1H), 7.39 (d, J = 9.6 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 6.78 (d, J = 8.4 Hz, 1H), 6.04 (d, J = 7.8 Hz, 2H); **¹³C NMR (75 MHz, DMSO):** δ 170.0, 160.9, 153.3, 138.2, 129.2, 127.5, 123.4, 123.3, 120.7, 118.8, 116.1, 116.03.

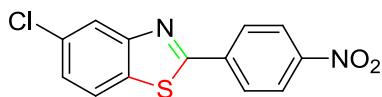
N-(2-Phenylbenzo[d]thiazol-5-yl)benzothioamide (3p)



Yellow solid (60%, 207 mg); **¹H NMR (300 MHz, CDCl₃):** δ 9.35 (bs, 1H), 8.44 (s, 1H), 8.07 (d, J = 3 Hz, 2H), 7.90-7.88 (m, 2H), 7.78 (d, J = 1.8 Hz, 1H), 7.51-7.49 (m, 7H); **¹³C NMR (75 MHz, CDCl₃):** δ 198.8, 174.4, 154.6, 142.8, 137.5, 135.4, 133.0, 131.2, 131.0, 128.9, 128.4, 127.4, 127.9, 126.6, 124.4, 121.6.

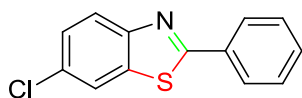
HRMS (ESI +): (M+H)⁺ calcd. For C₂₀H₁₄N₂S₂: 347.0671; Found: 347.0671.

5-Chloro-2-(4-nitrophenyl)benzo[d]thiazole (3q)⁸



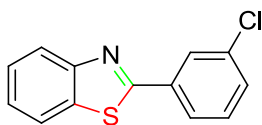
Yellow solid (59%, 171 mg); **¹H NMR (400 MHz, CDCl₃):** δ 8.37 (d, J = 10 Hz, 2H), 8.25 (d, J = 10.4 Hz, 2H), 8.11 (d, J = 2 Hz, 1H), 7.87 (d, J = 10 Hz, 1H), 7.44-7.42 (m, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 166.7, 154.9, 149.3, 138.8, 133.8, 133.1, 128.4, 126.8, 124.4, 123.7, 122.6.

6-Chloro-2-phenylbenzo[d]thiazole (3r)⁴



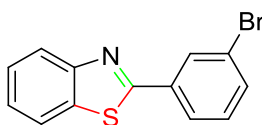
Light yellow solid (46%, 112 mg); **¹H NMR (400 MHz, CDCl₃):** δ 8.07–8.05 (m, 2H), 8.0 (d, J = 8.8 Hz, 1H), 7.87 (s, 1H), 7.51–7.49 (m, 3H), 7.46 (dd, J = 2 Hz, 6.4 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃):** δ 168.6, 152.8, 136.4, 133.4, 131.4, 131.2, 129.2, 127.7, 127.2, 124.1, 121.4.

2-(3-Chlorophenyl)benzo[d]thiazole (3s)²



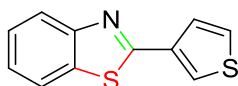
Light yellow solid (68%, 166 mg); **¹H NMR (400 MHz, CDCl₃):** δ 8.22 (s, 1H), 8.10 (d, J = 2 Hz, 1H), 8.07 (d, J = 4 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 2.8 Hz, 1H), 7.50-7.48 (m, 3H); **¹³C NMR (100 MHz, CDCl₃):** δ 169.8, 155.4, 133.9, 133.3, 131.4, 129.2, 128.4, 127.7, 126.2, 124.4, 124.3, 122.7, 120.0.

2-(3-Bromophenyl)benzo[d]thiazole (3t)²



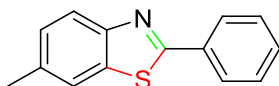
Light yellow solid (65%, 188 mg); **¹H NMR (400 MHz, CDCl₃):** δ 8.28 (s, 1H), 8.10 (d, J = 8 Hz, 1H), 8.0 (d, J = 7.2 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.53–7.49 (m, 1H), 7.43-7.34 (m, 2H); **¹³C NMR (100 MHz, CDCl₃):** δ 166.1, 154.0, 135.5, 135.2, 133.8, 130.5, 130.3, 126.6, 126.2, 125.6, 123.5, 123.2, 121.7.

2-(Thiophen-3-yl)benzo[d]thiazole (3u)³



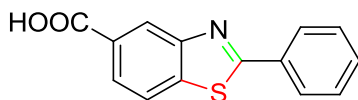
Light yellow solid (70%, 151 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, *J* = 12 Hz, 1H), 8.02 (m, 1H), 7.88 (d, *J* = 8 Hz, 1H), 7.72 (d, *J* = 6 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.44-7.42 (m, 1H), 7.40 (t, *J* = 8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 162.7, 154.0, 136.1, 134.8, 127.0, 126.7, 126.4, 126.5, 125.2, 123.1, 121.6.

6-Methyl-2-phenylbenzo[d]thiazole (3v)²



Light yellow solid (65%, 146 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.09-8.06 (m, 2H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.50-7.47 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 152.4, 135.5, 135.4, 133.9, 130.8, 129.1, 128.0, 127.5, 122.8, 121.5, 21.7.

2-Phenylbenzo[d]thiazole-5-carboxylic acid (3w)⁹

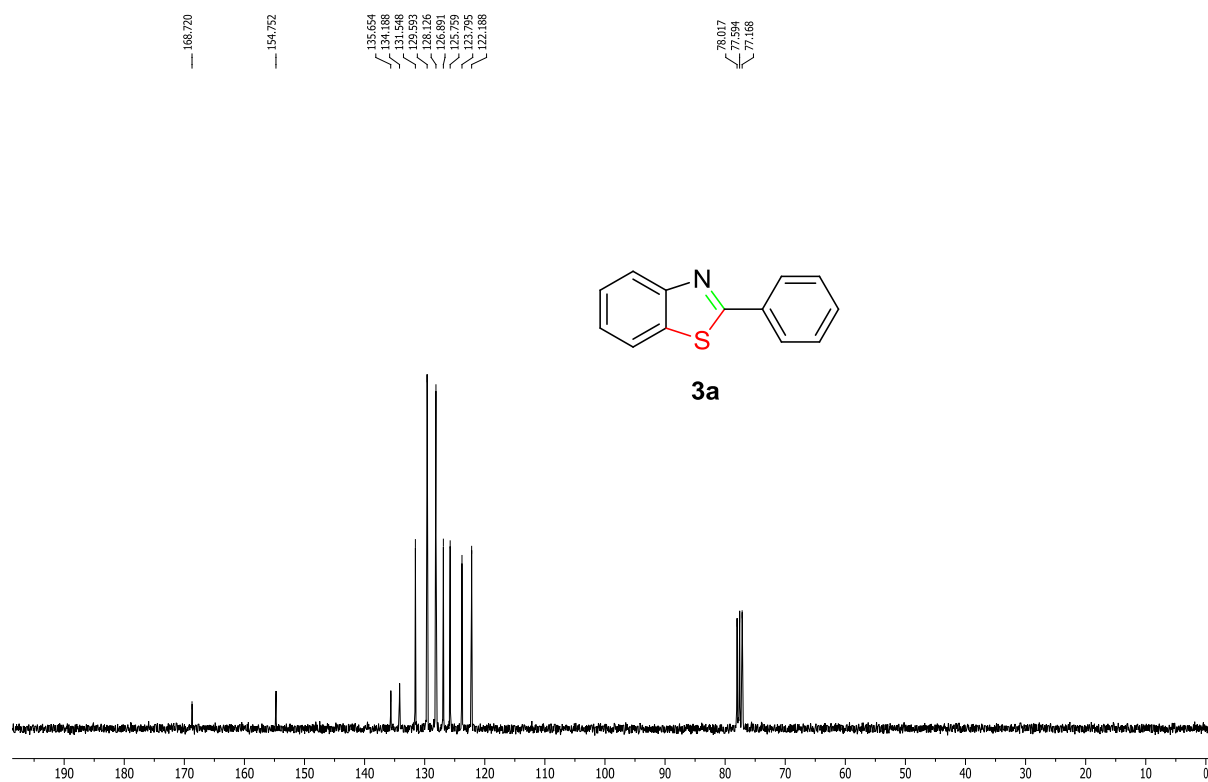
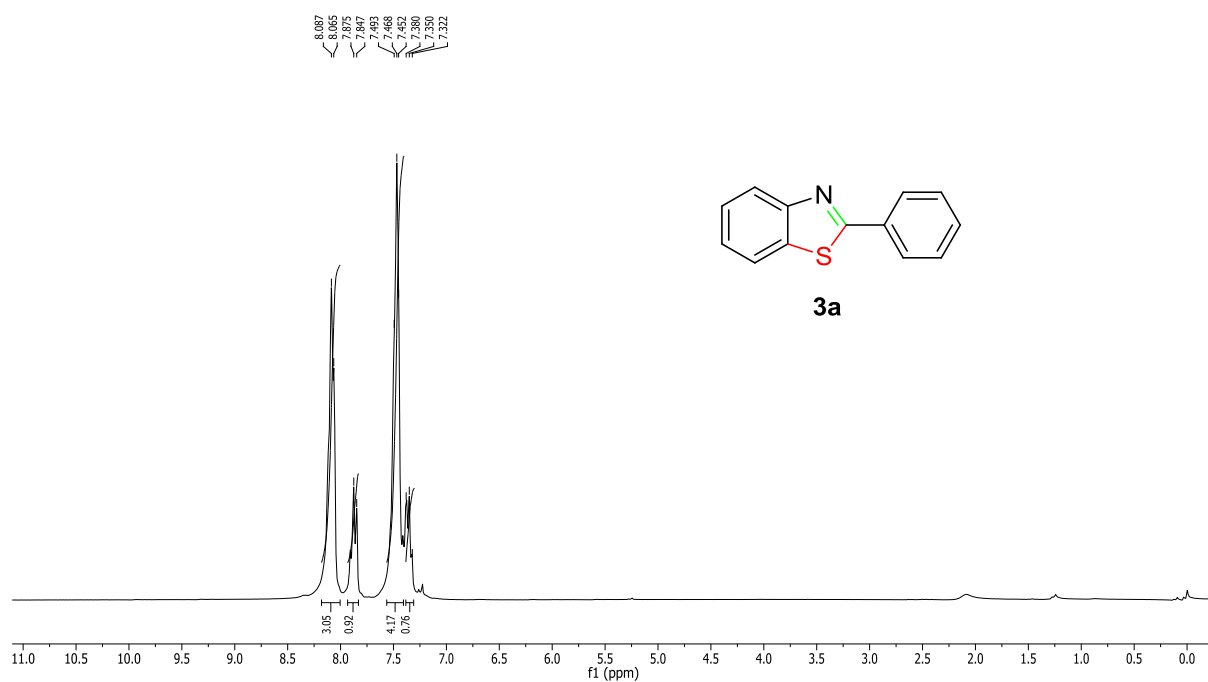


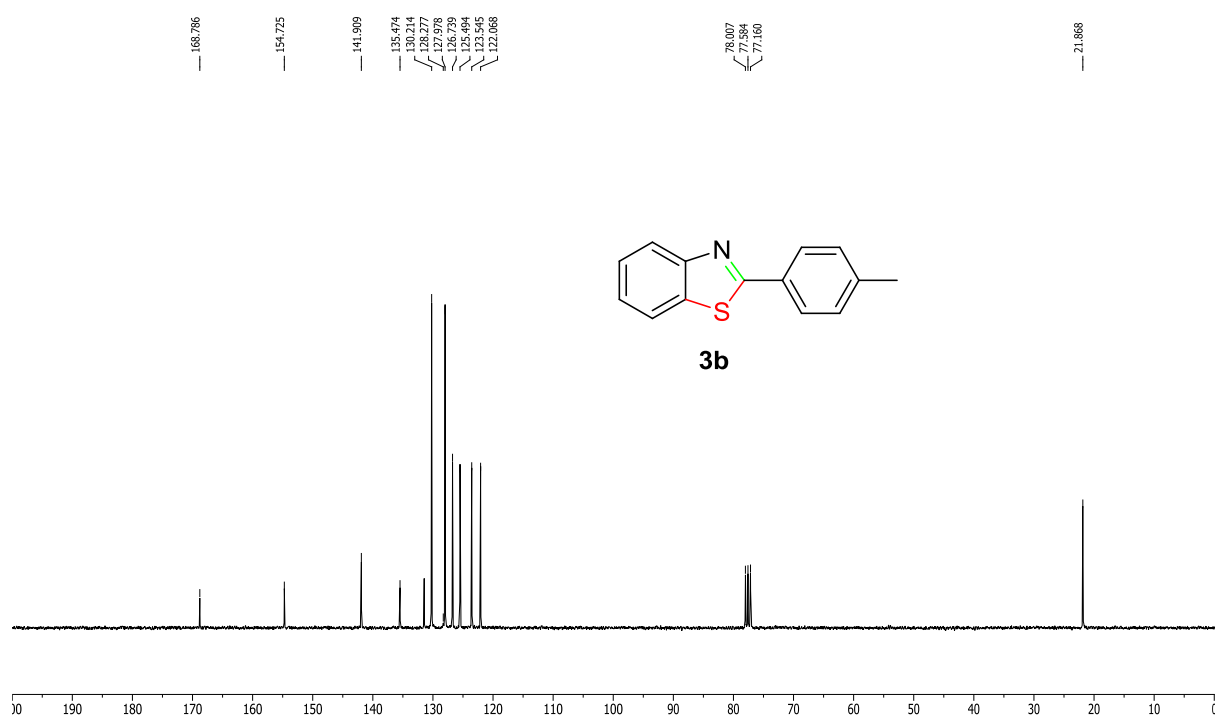
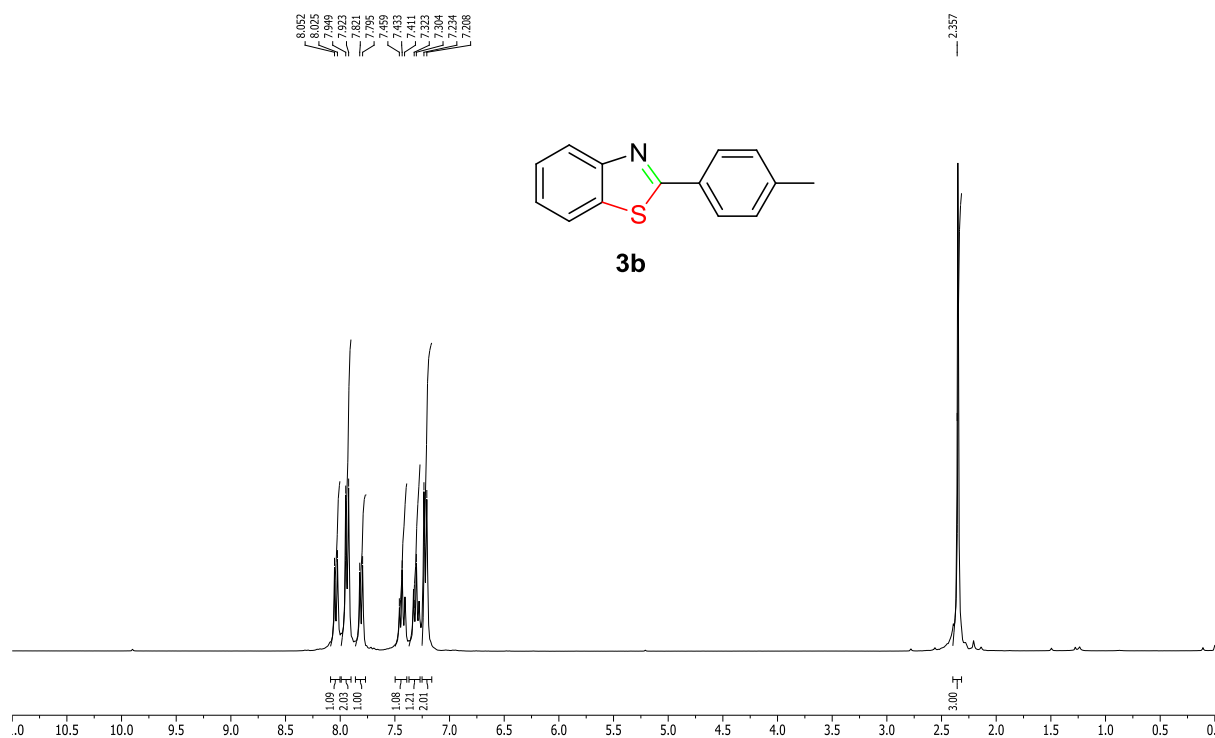
Light yellow solid (67%, 170 mg); ¹H NMR (400 MHz, DMSO): δ 8.54 (s, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 8.12 (m, 2H), 8.02 (m, 1H), 7.60 (m, 3H); ¹³C NMR (100 MHz, DMSO): δ 169.0, 167.1, 153.4, 139.1, 132.5, 131.8, 129.5, 129.4, 127.4, 125.8, 123.6, 122.6.

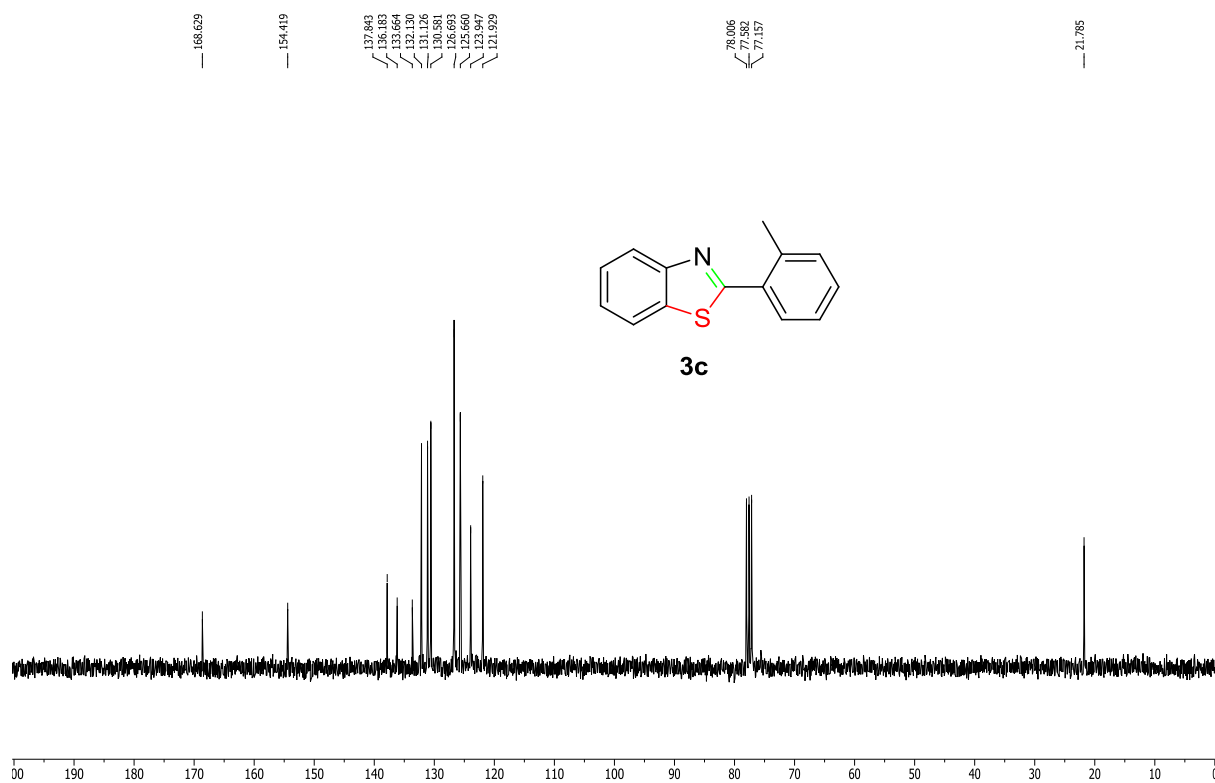
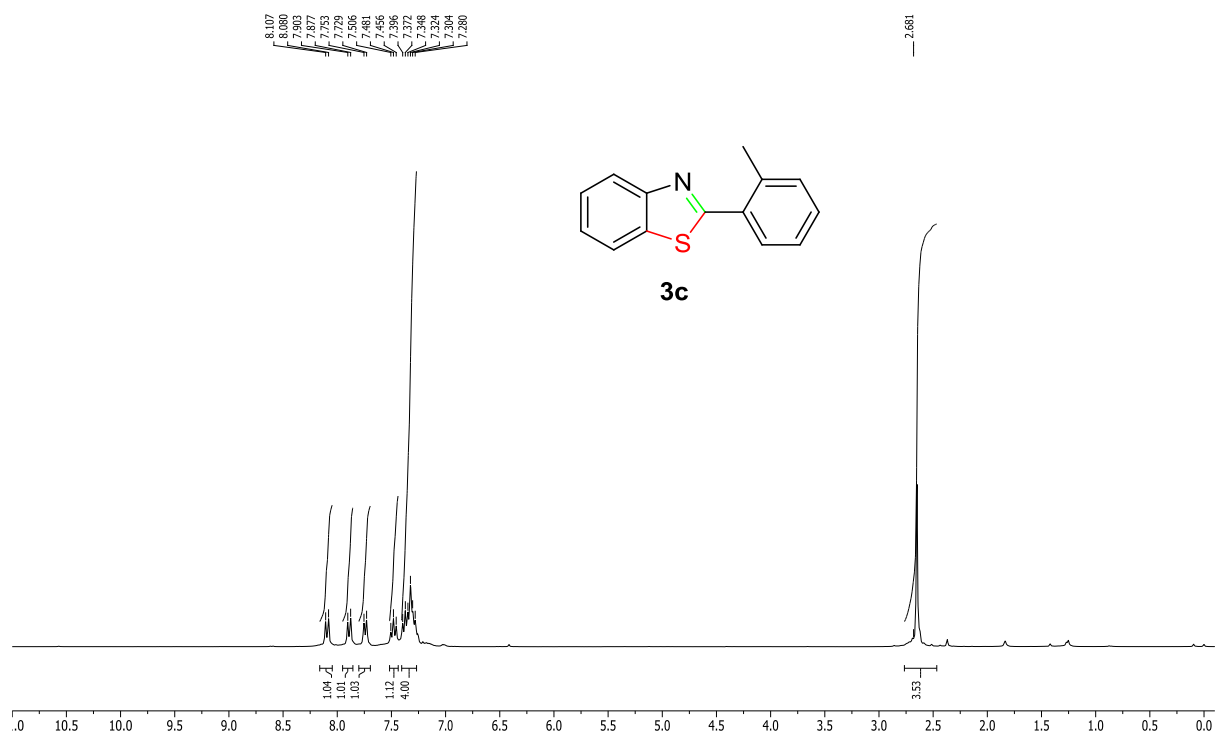
References:

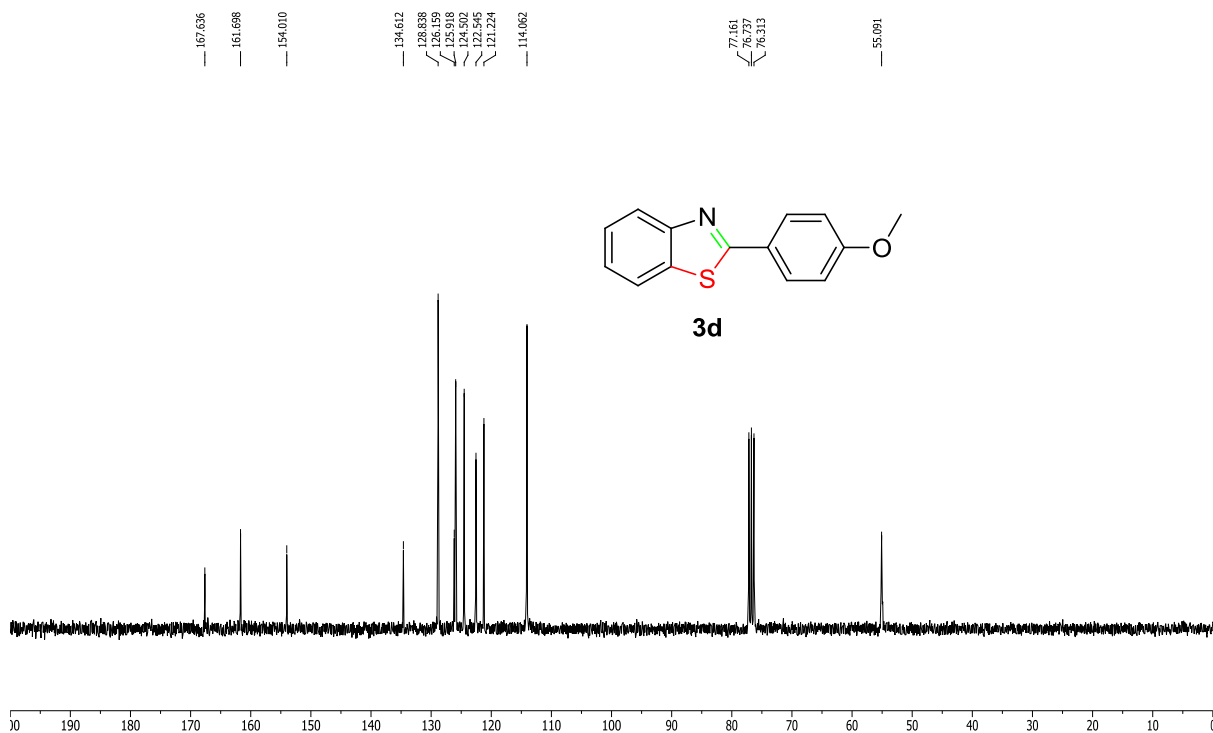
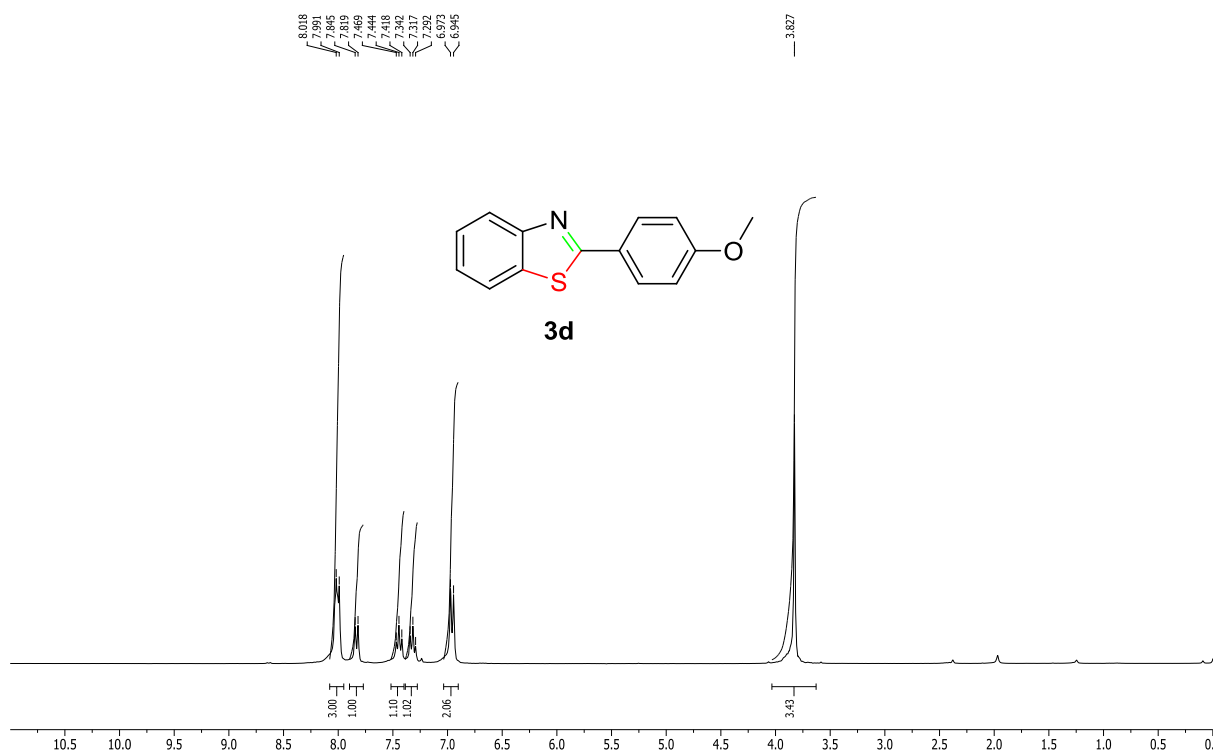
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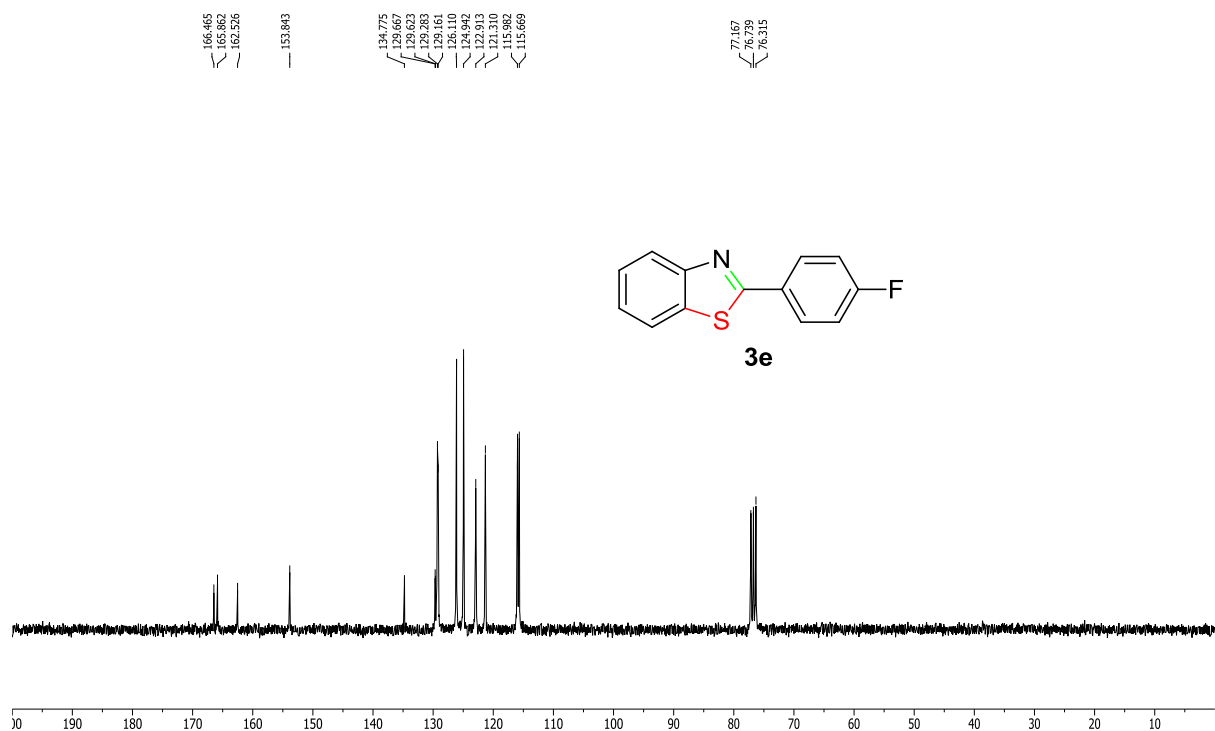
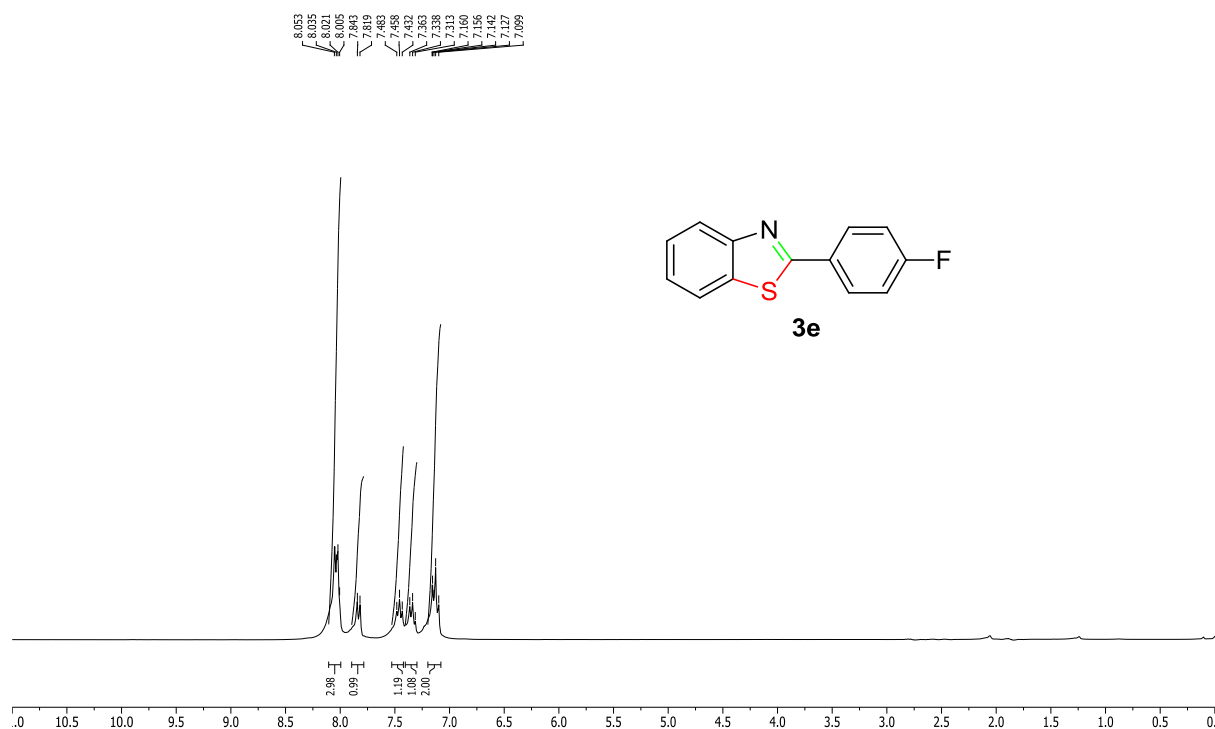
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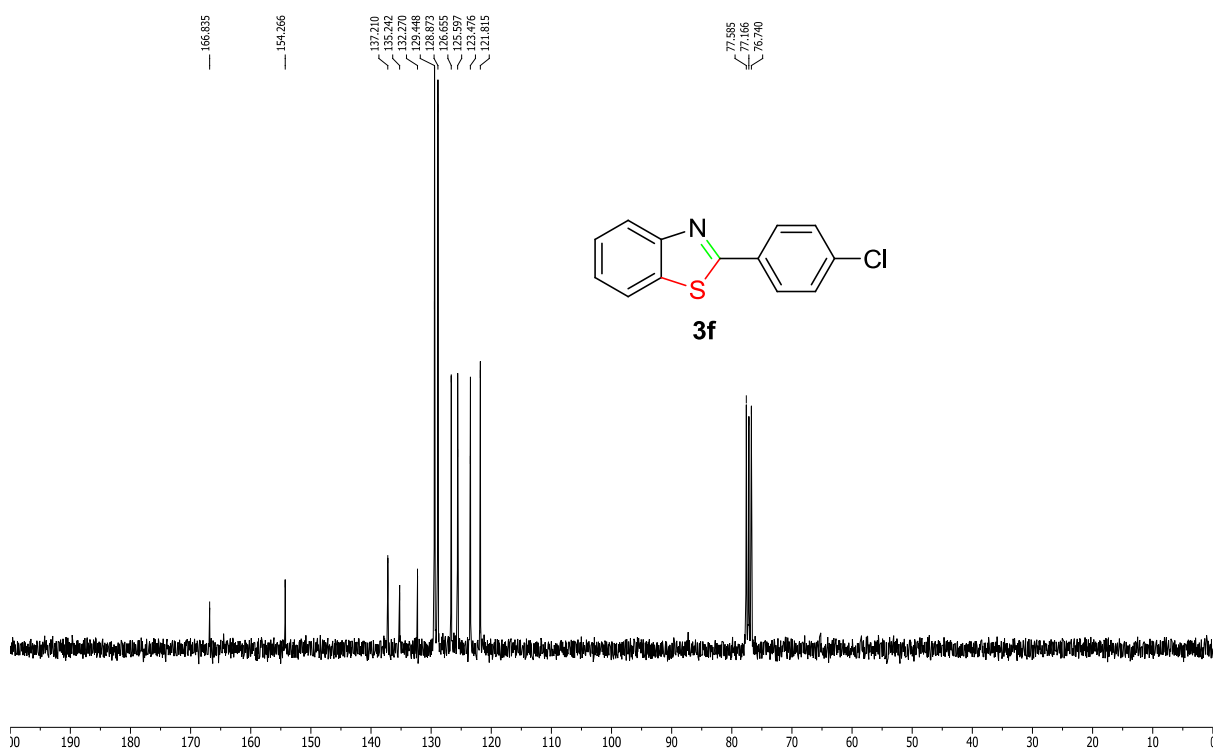
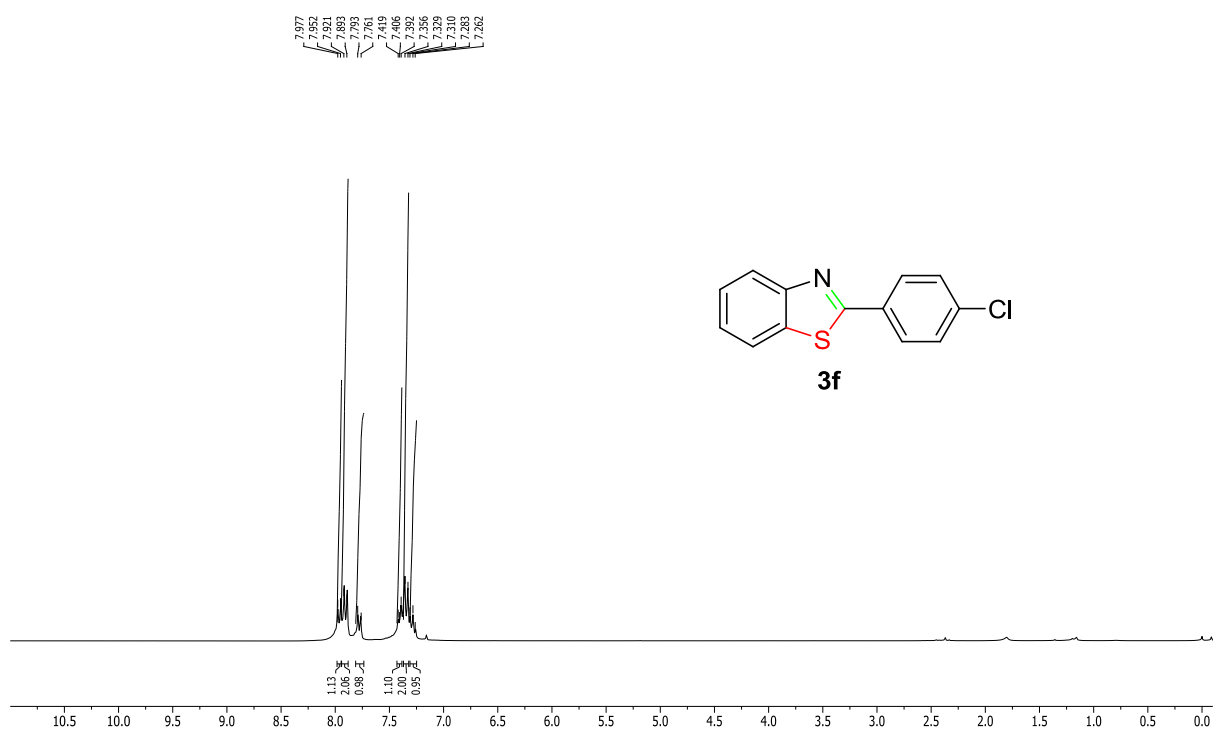


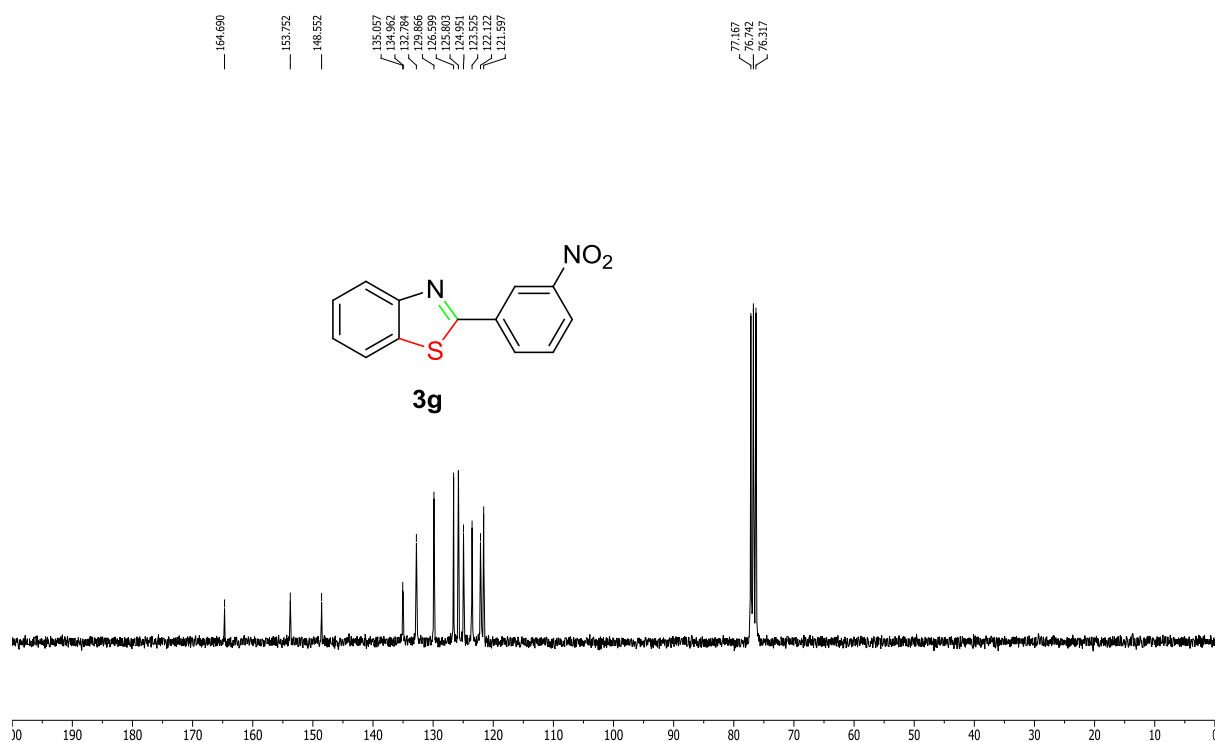
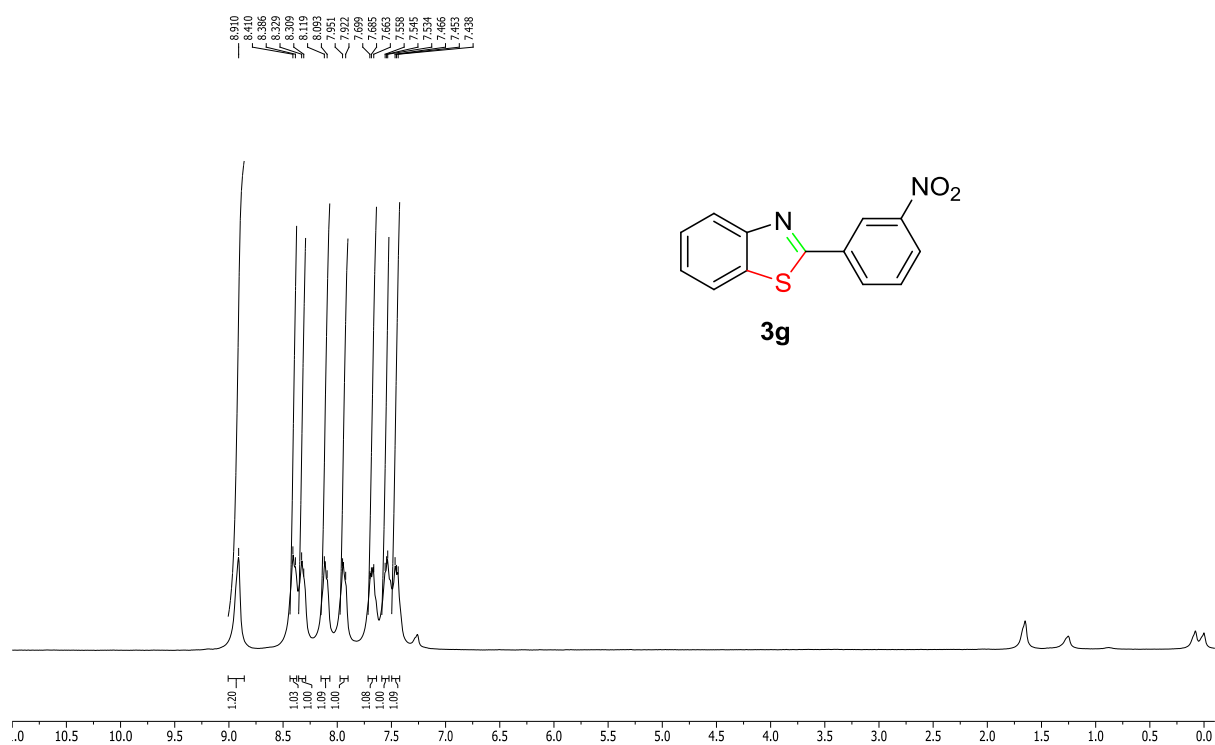


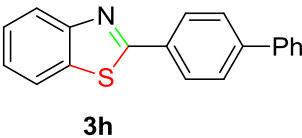
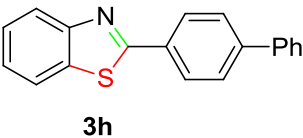


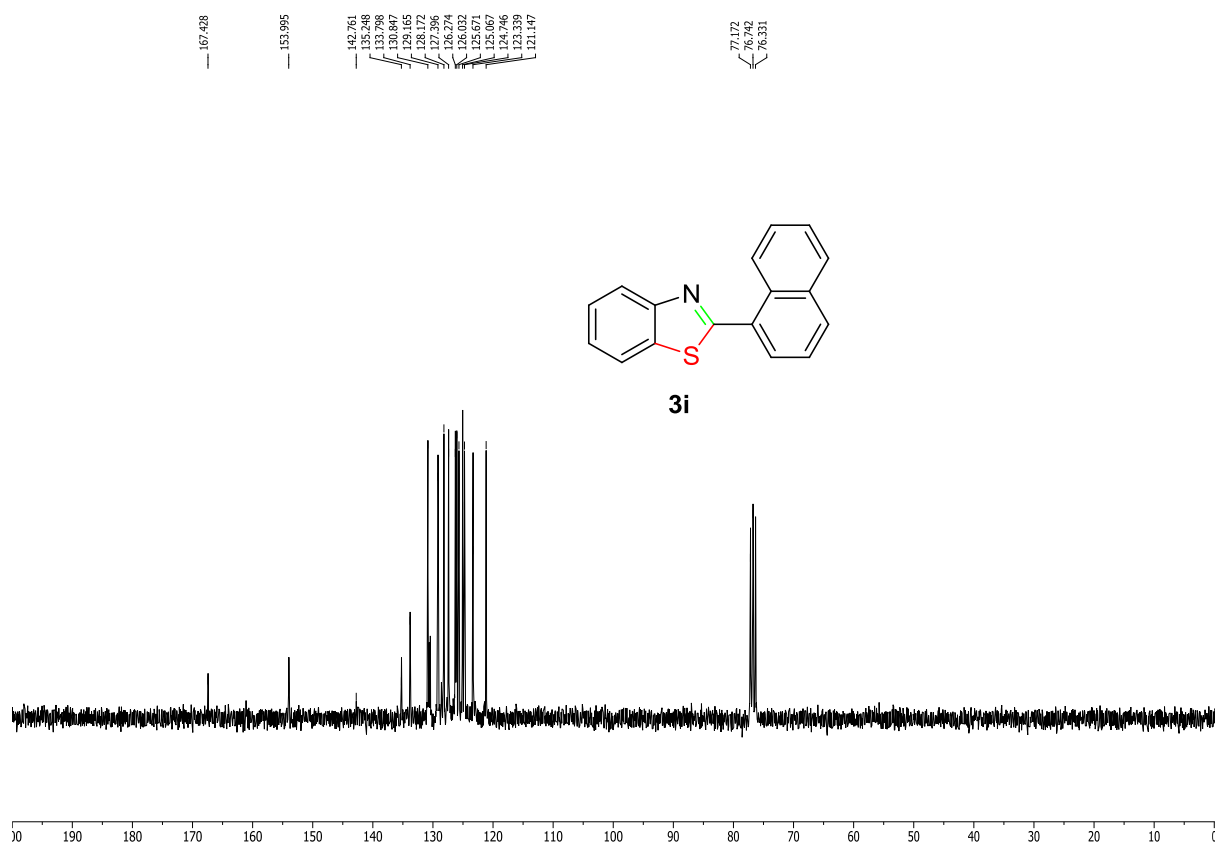
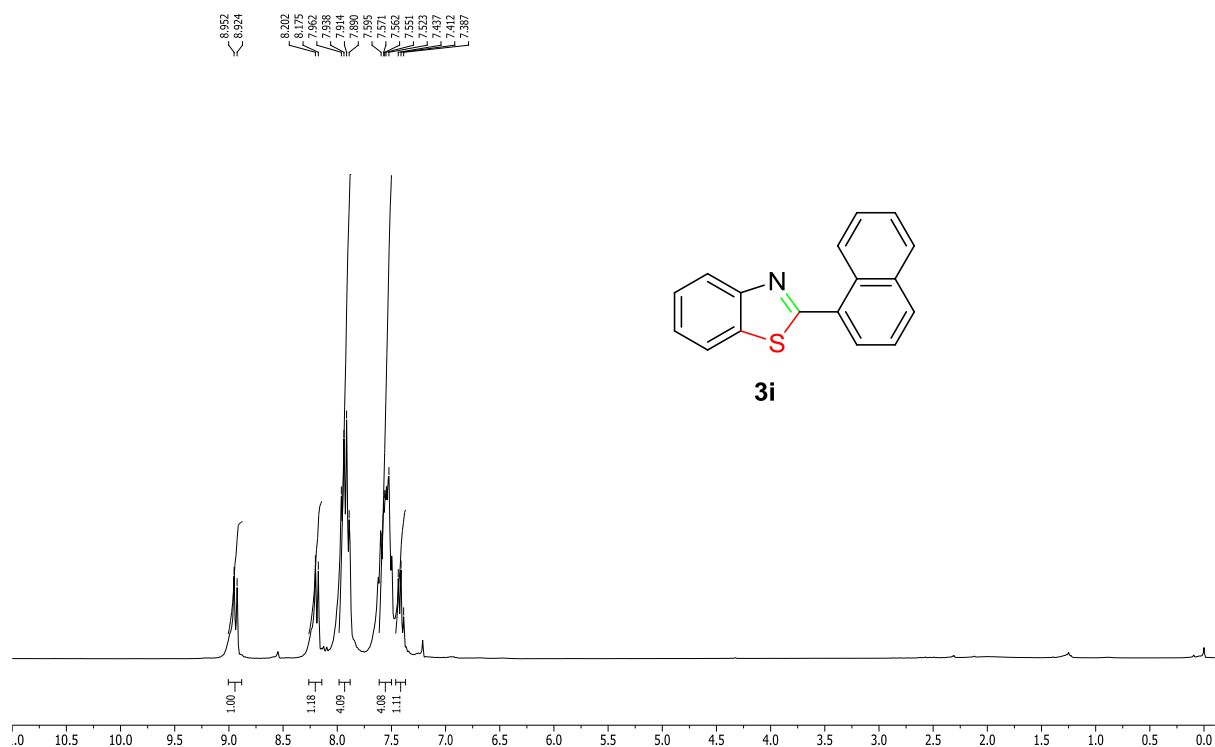


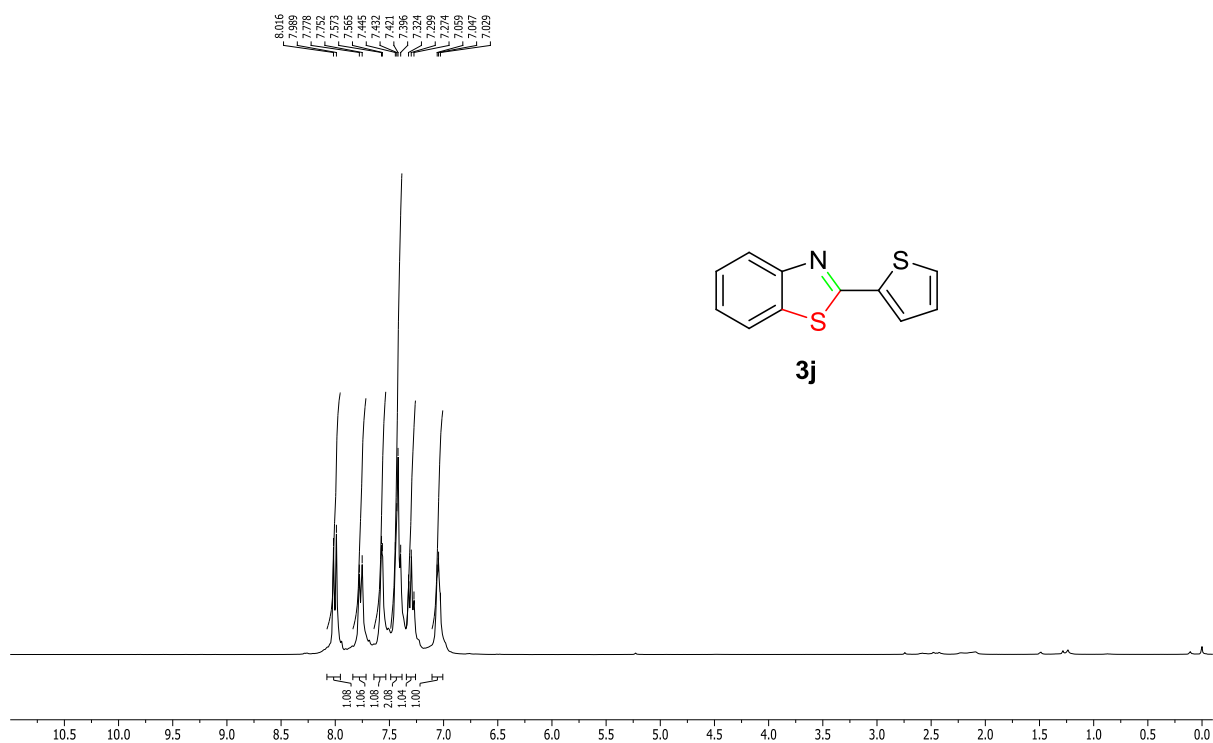




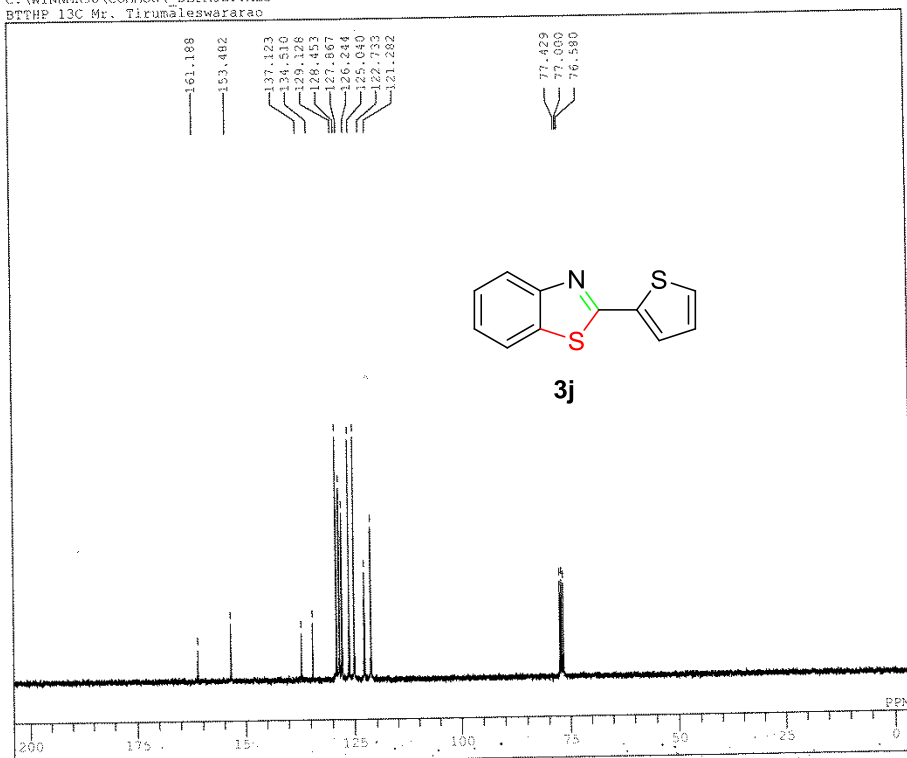








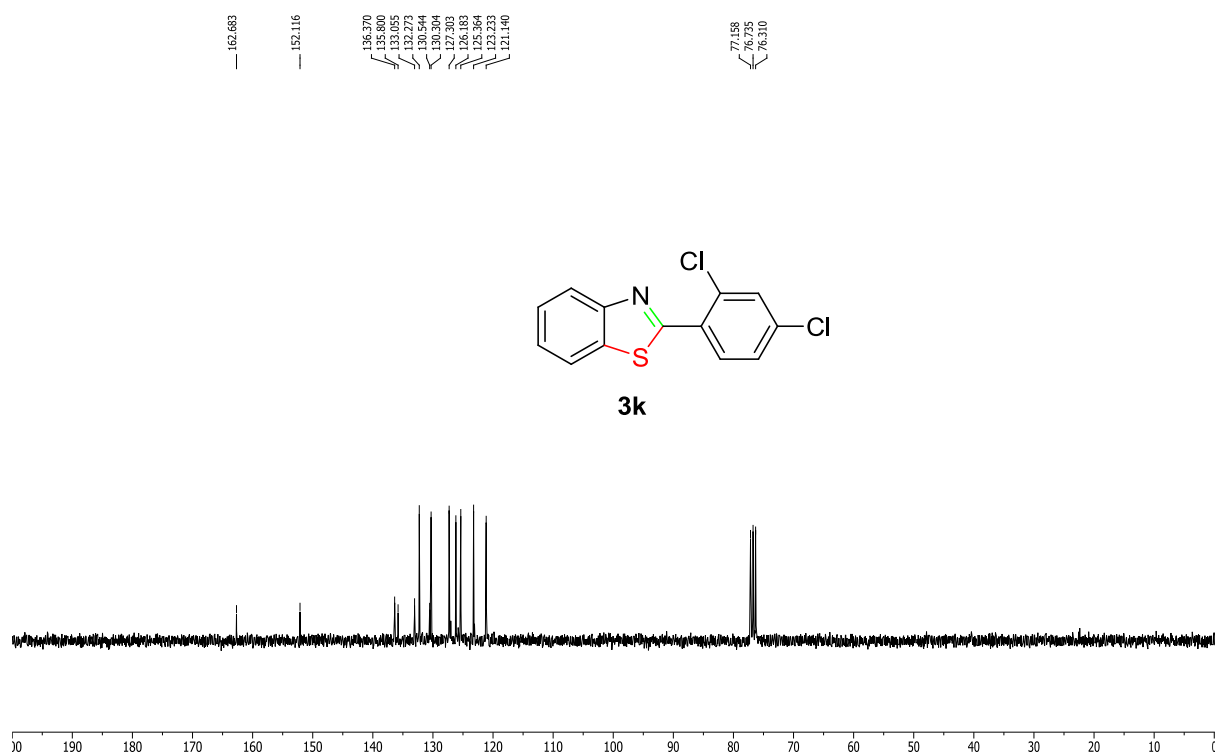
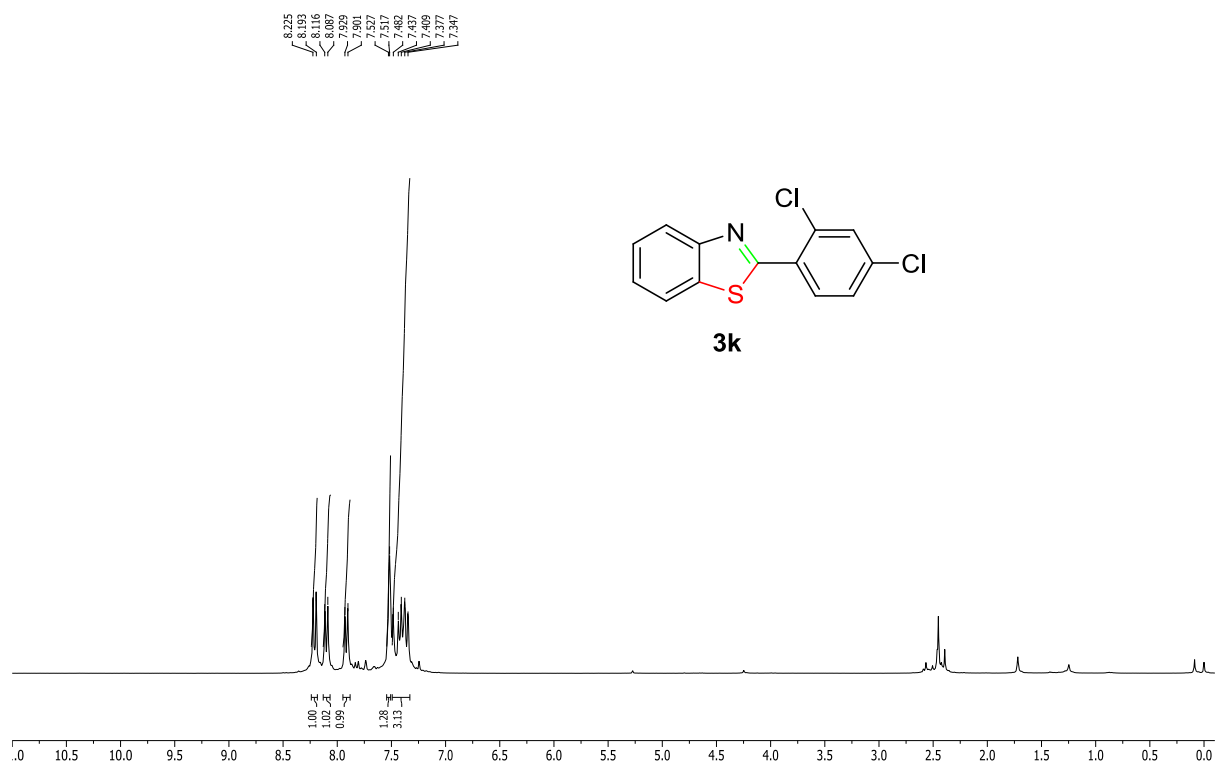
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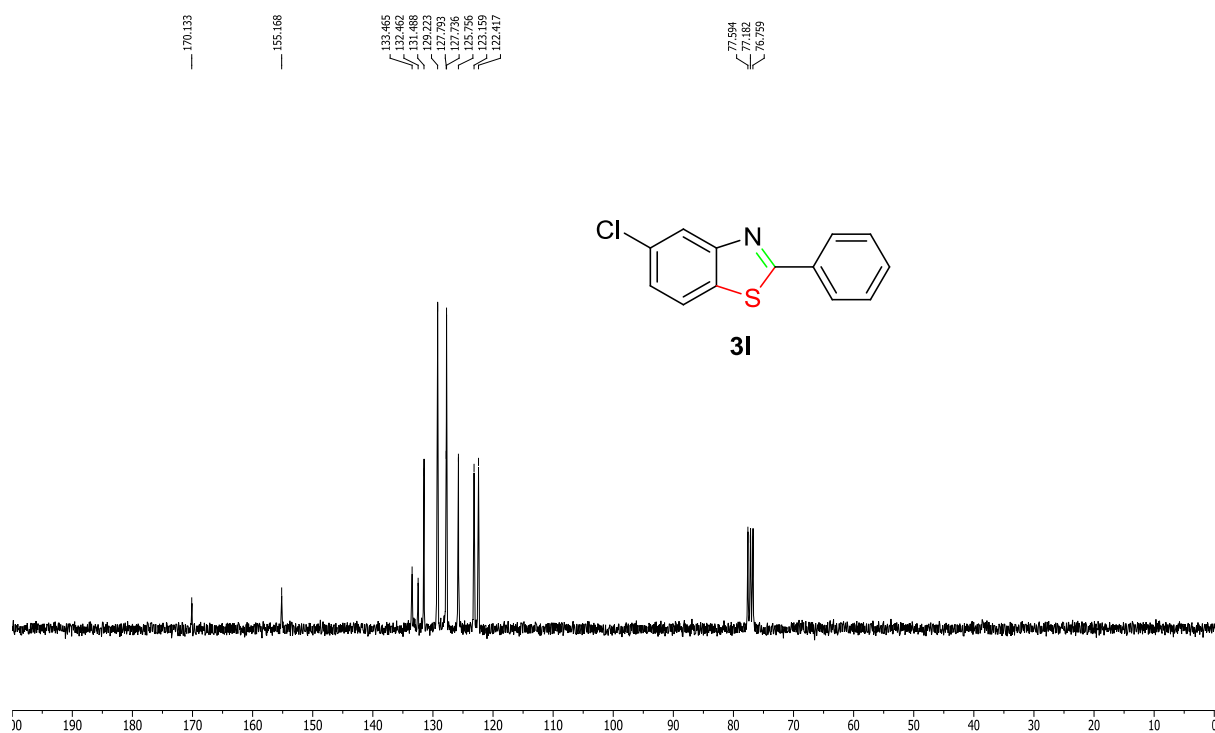
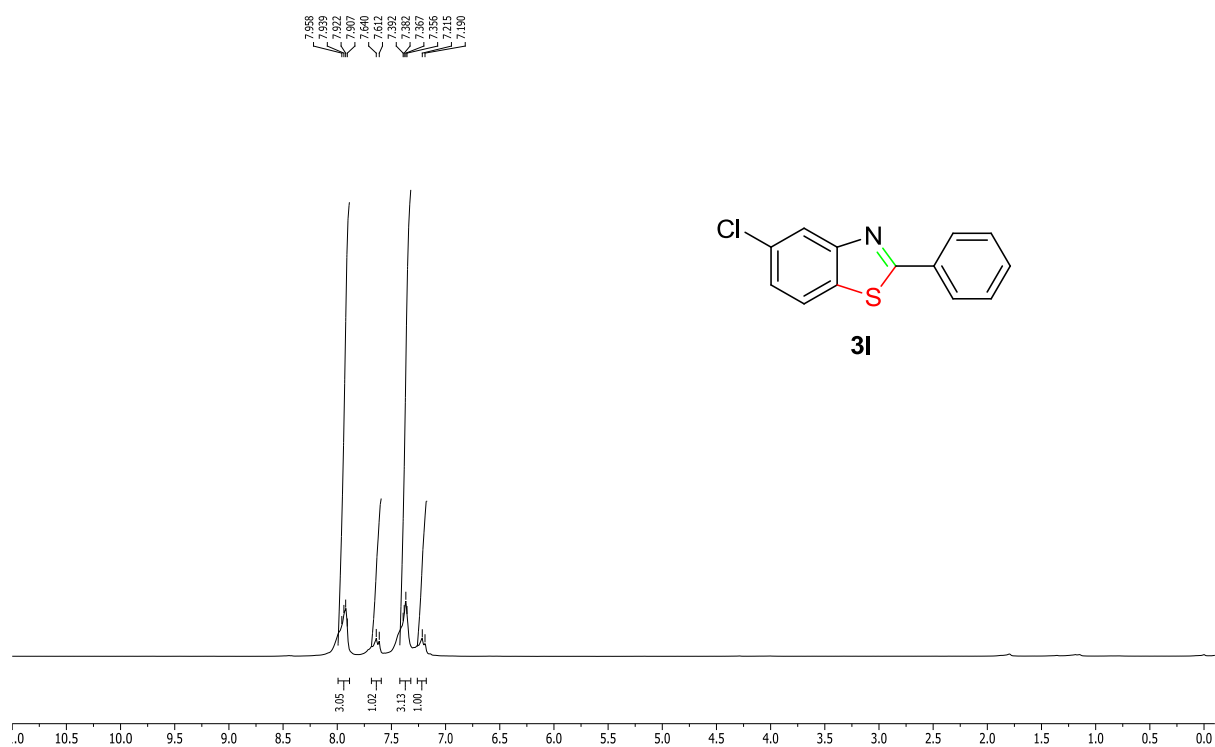


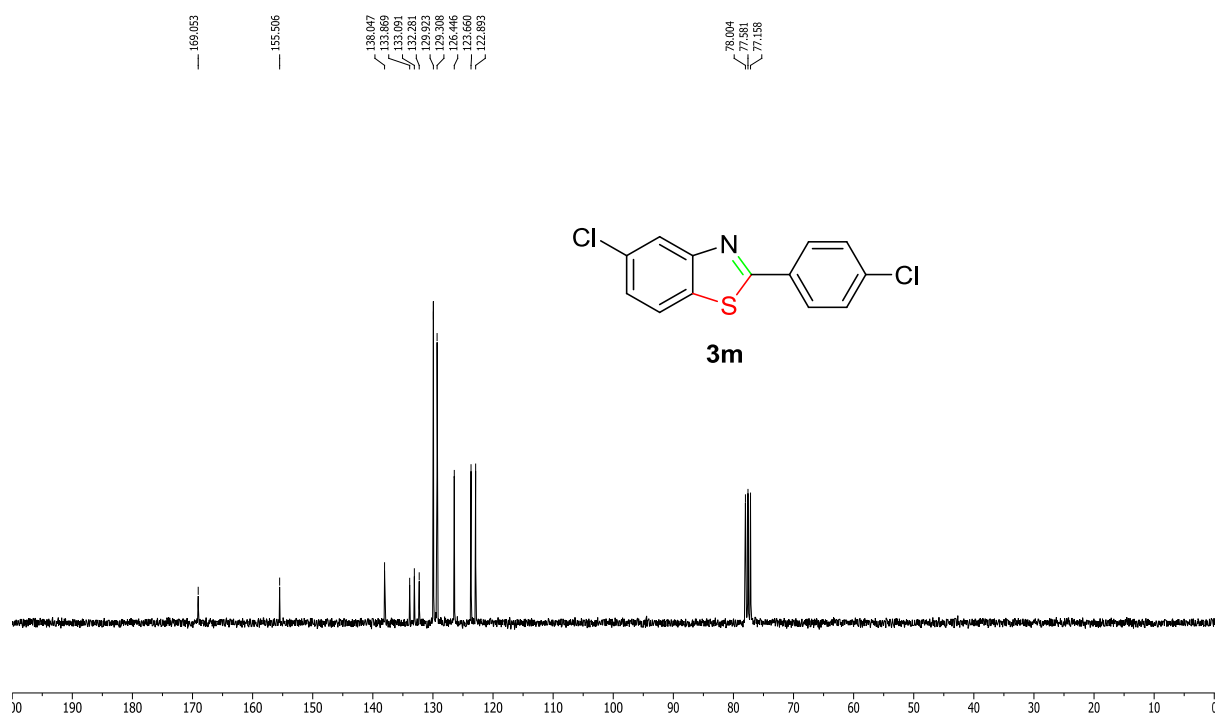
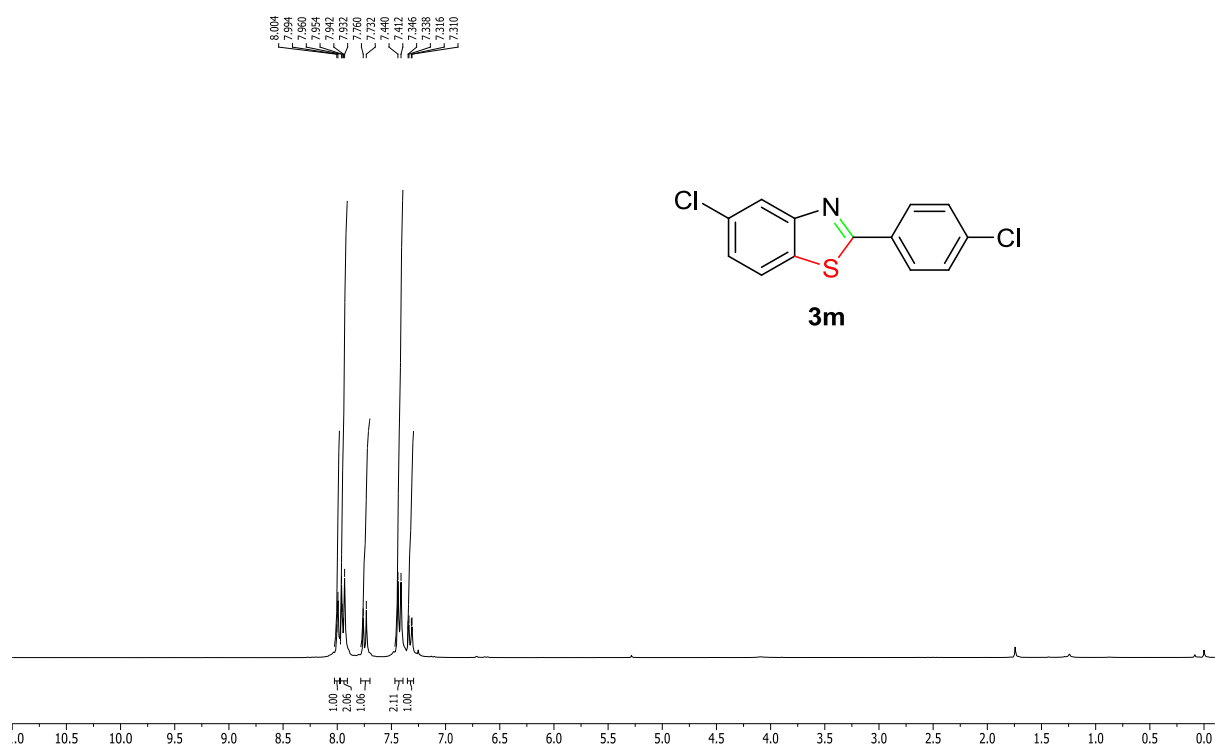
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Banaras Hindu University,
VARANASI-221005

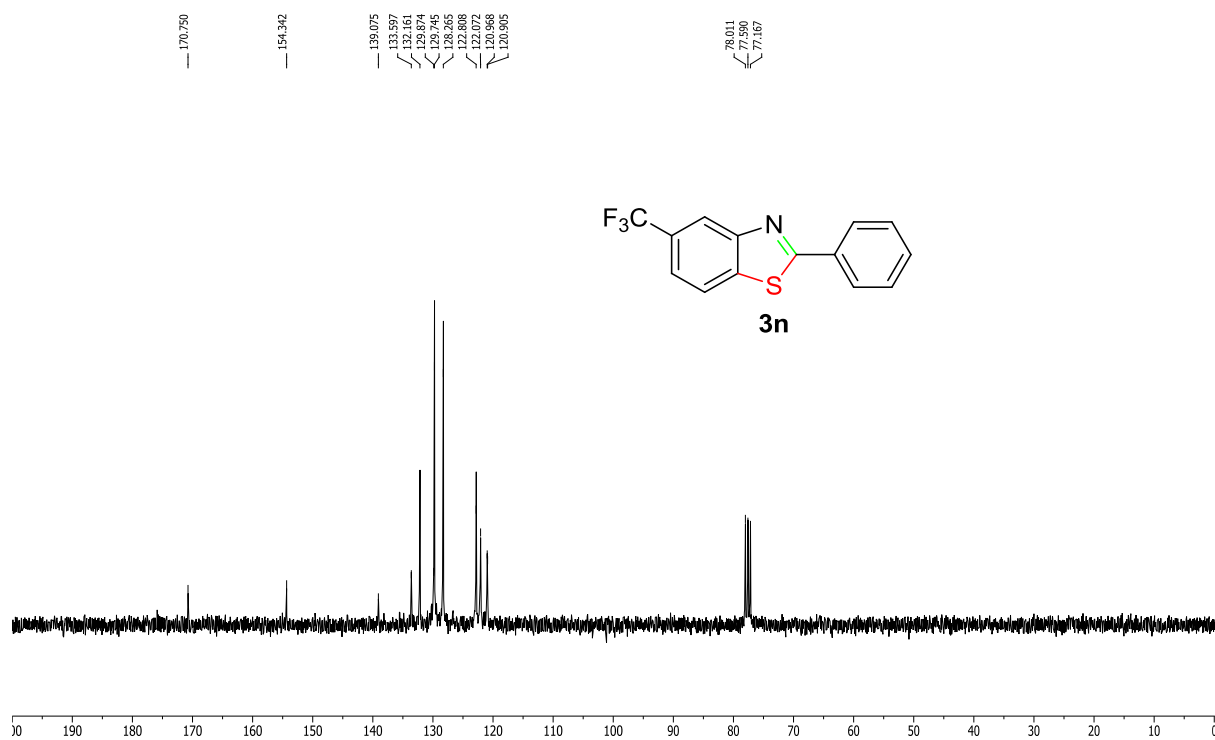
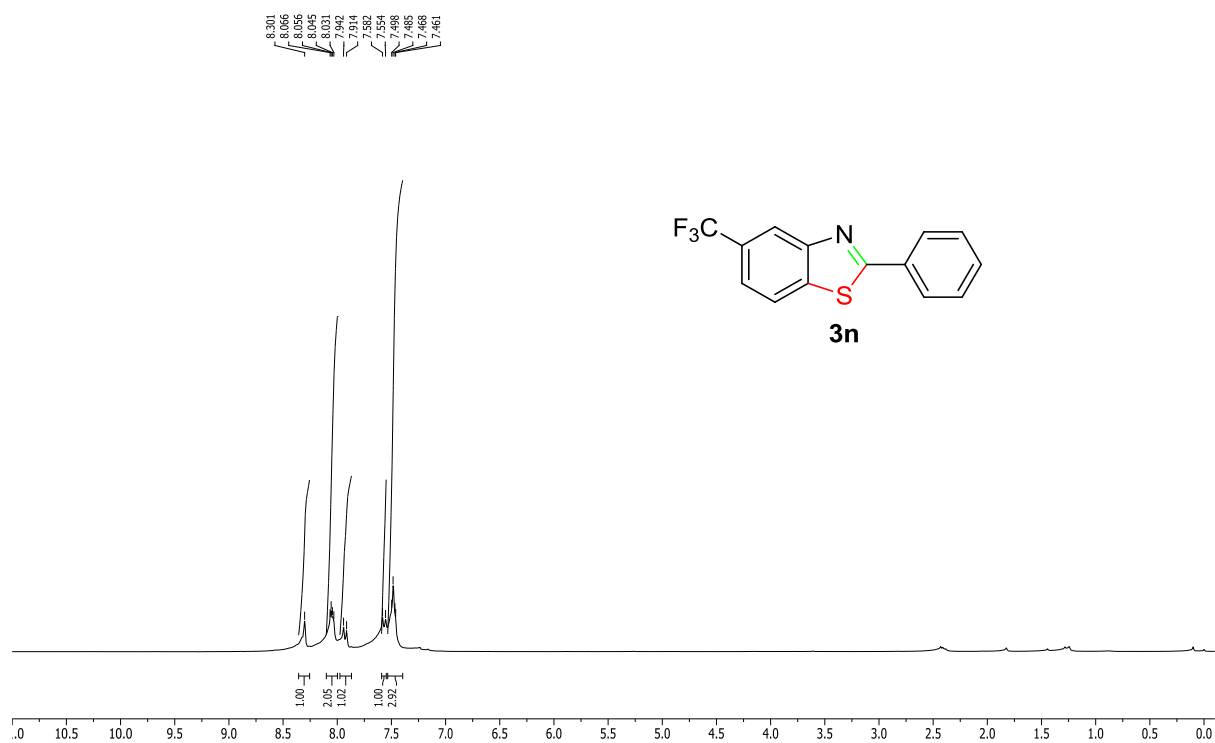
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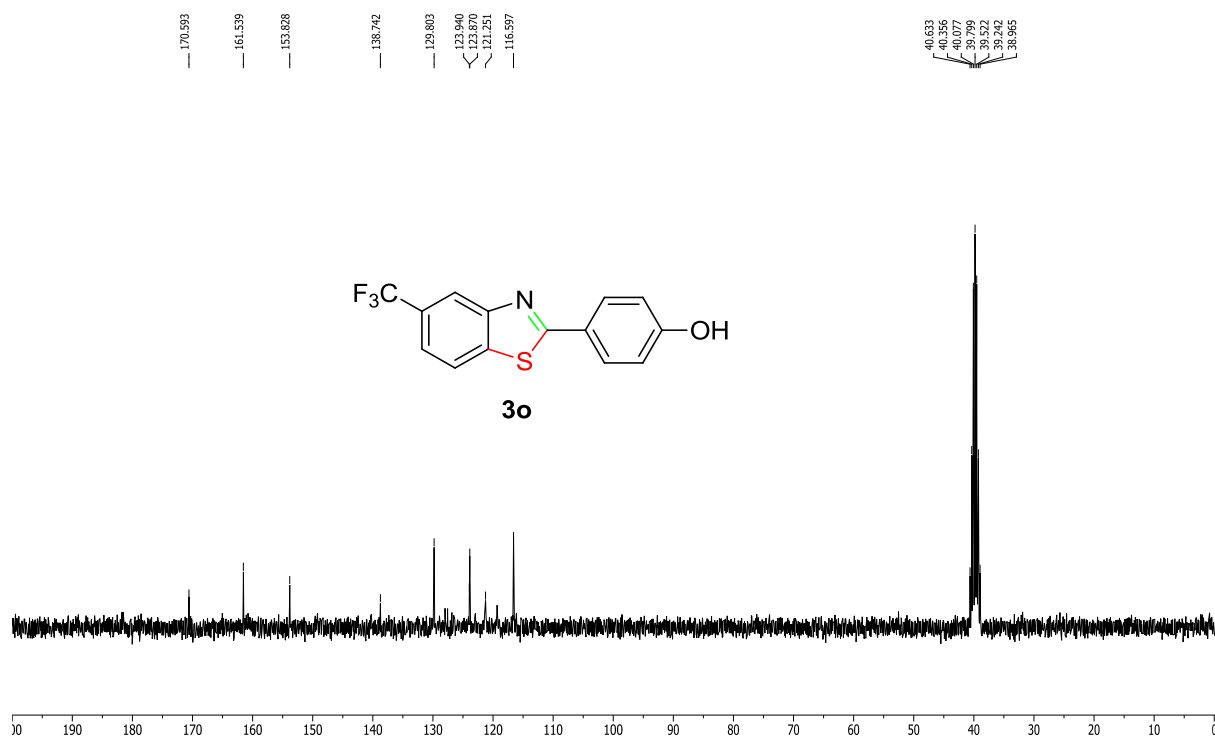
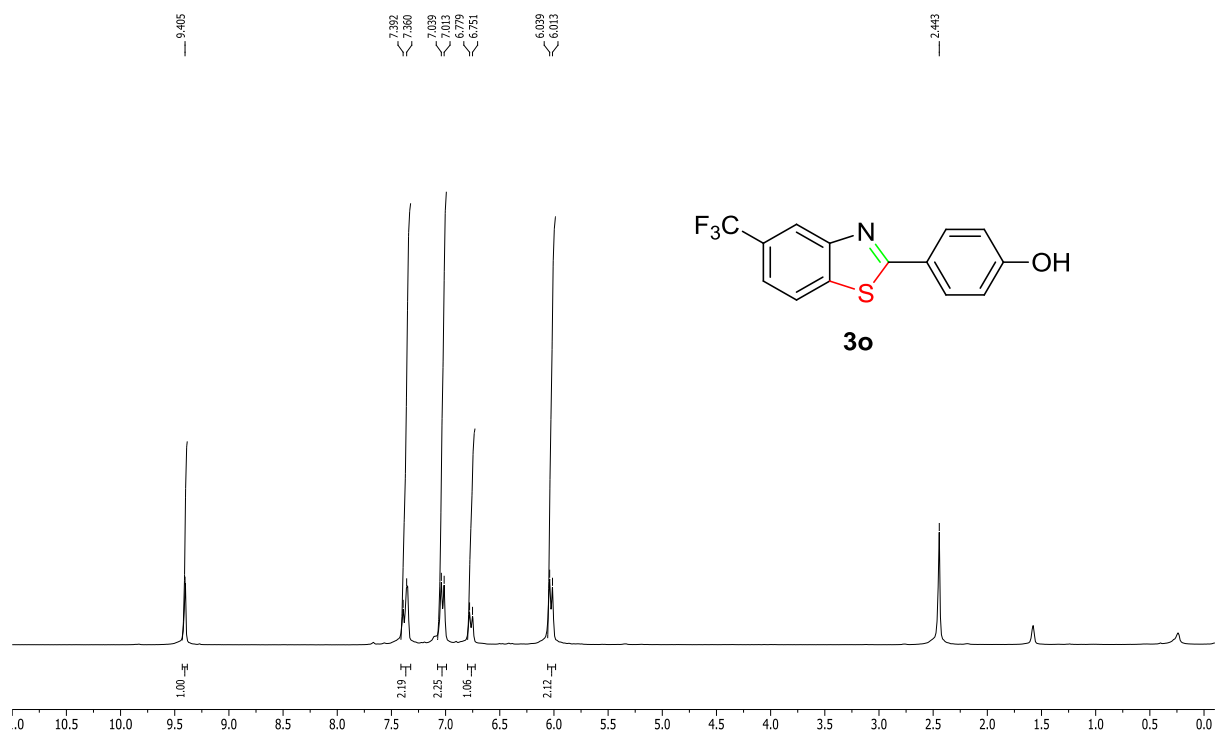
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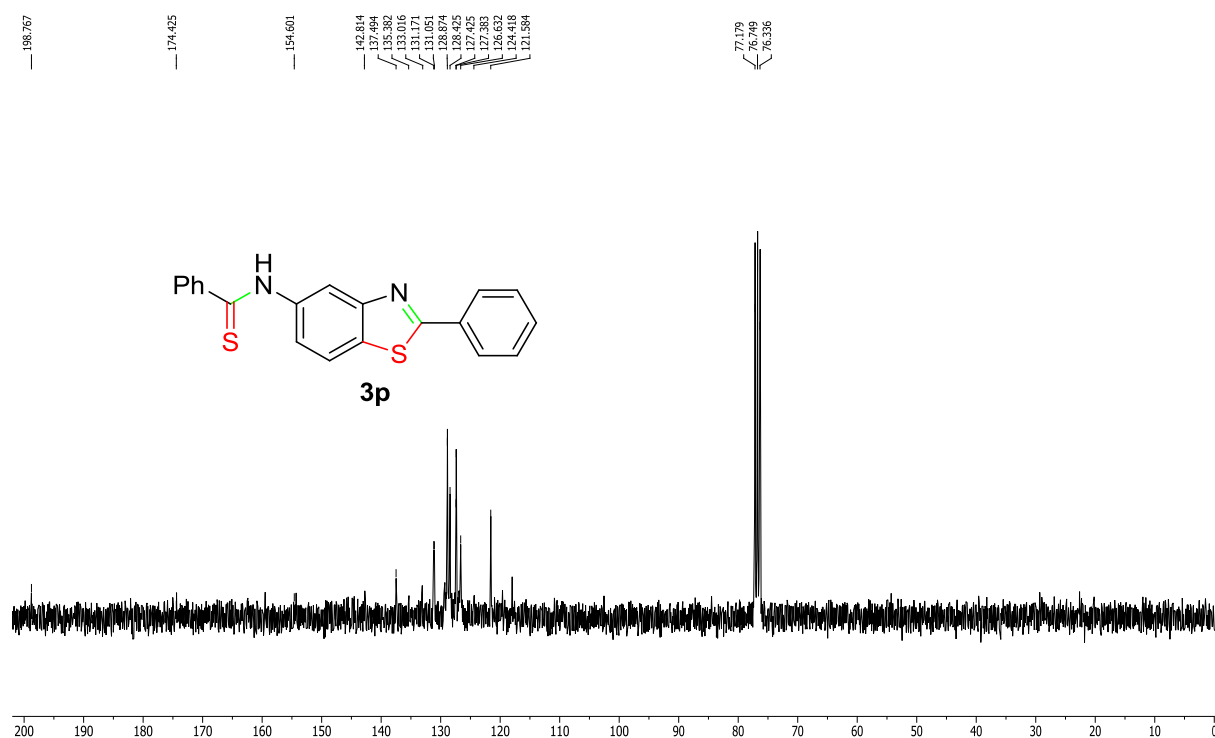
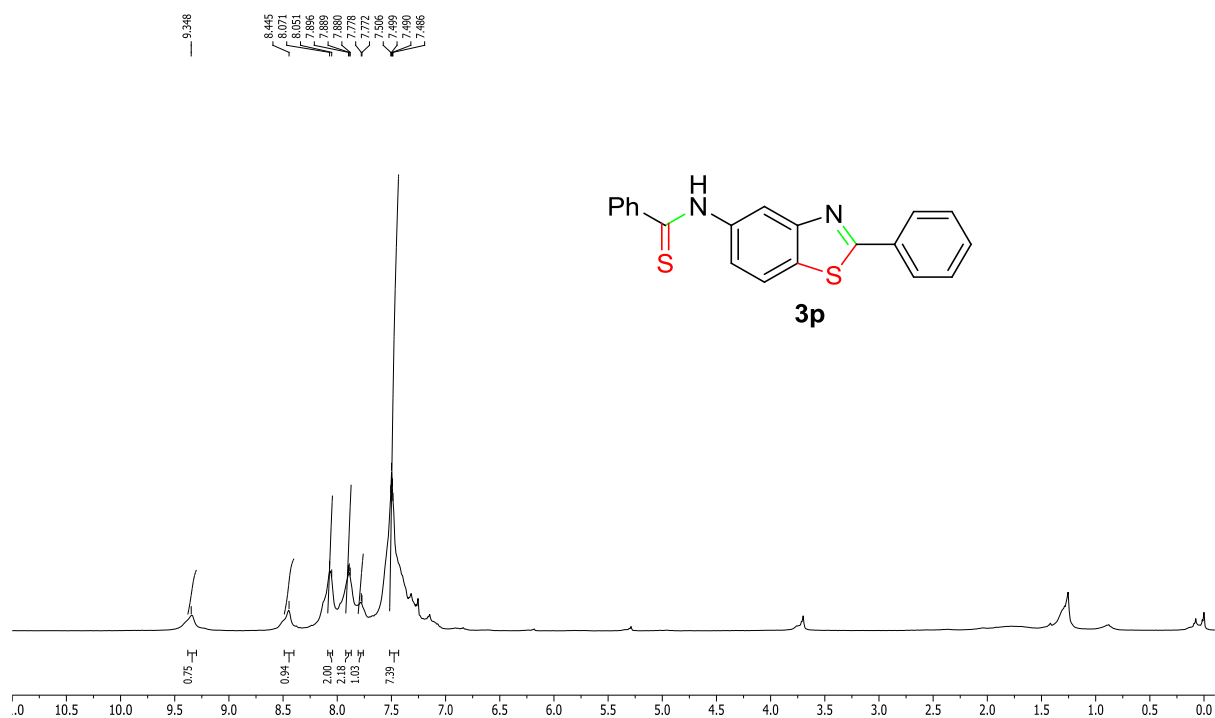




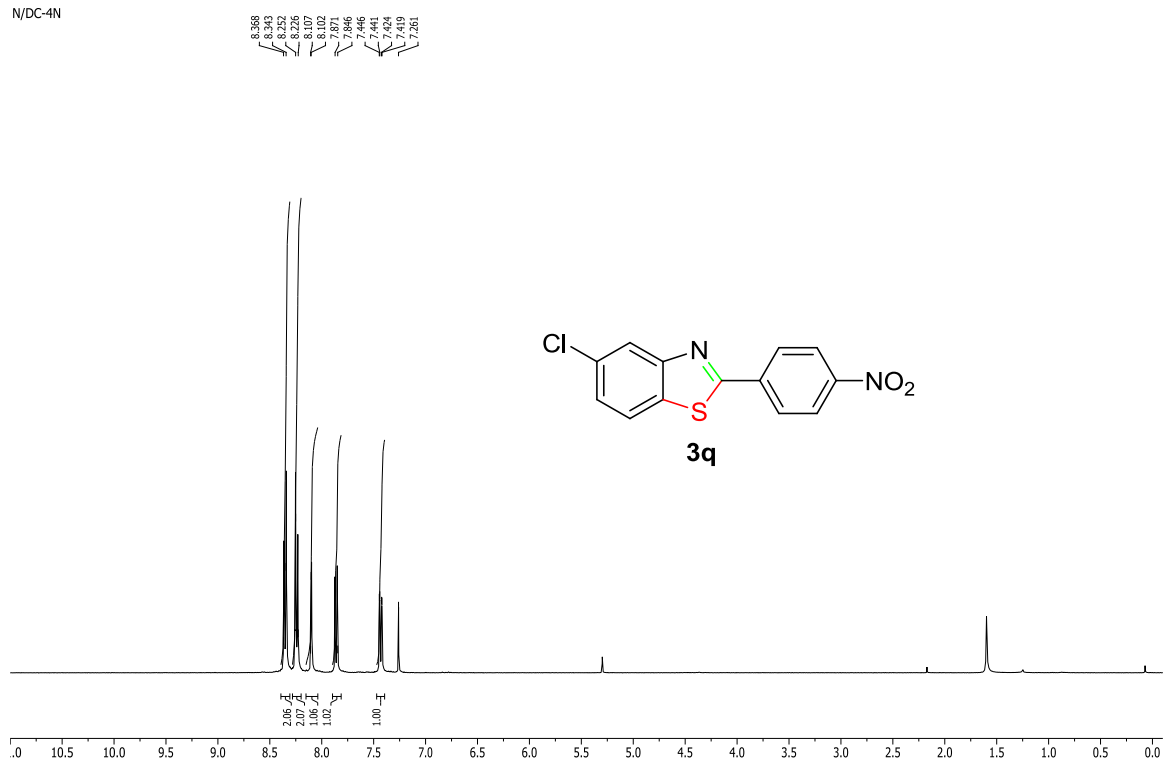




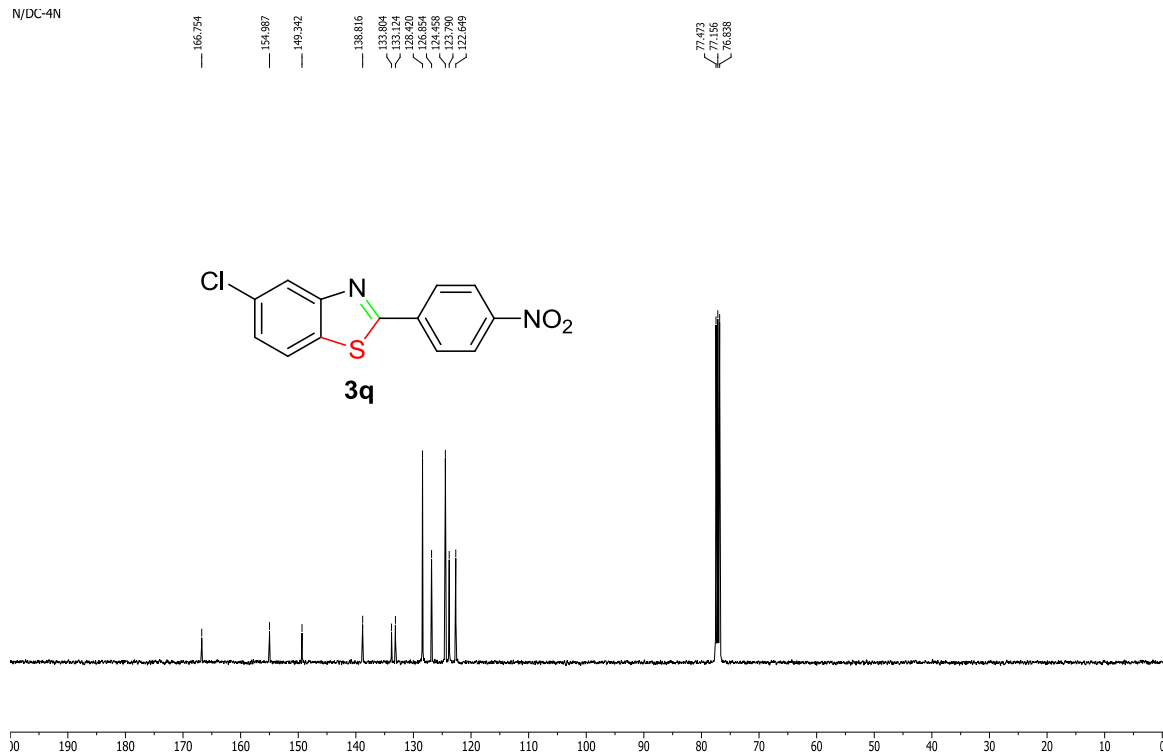




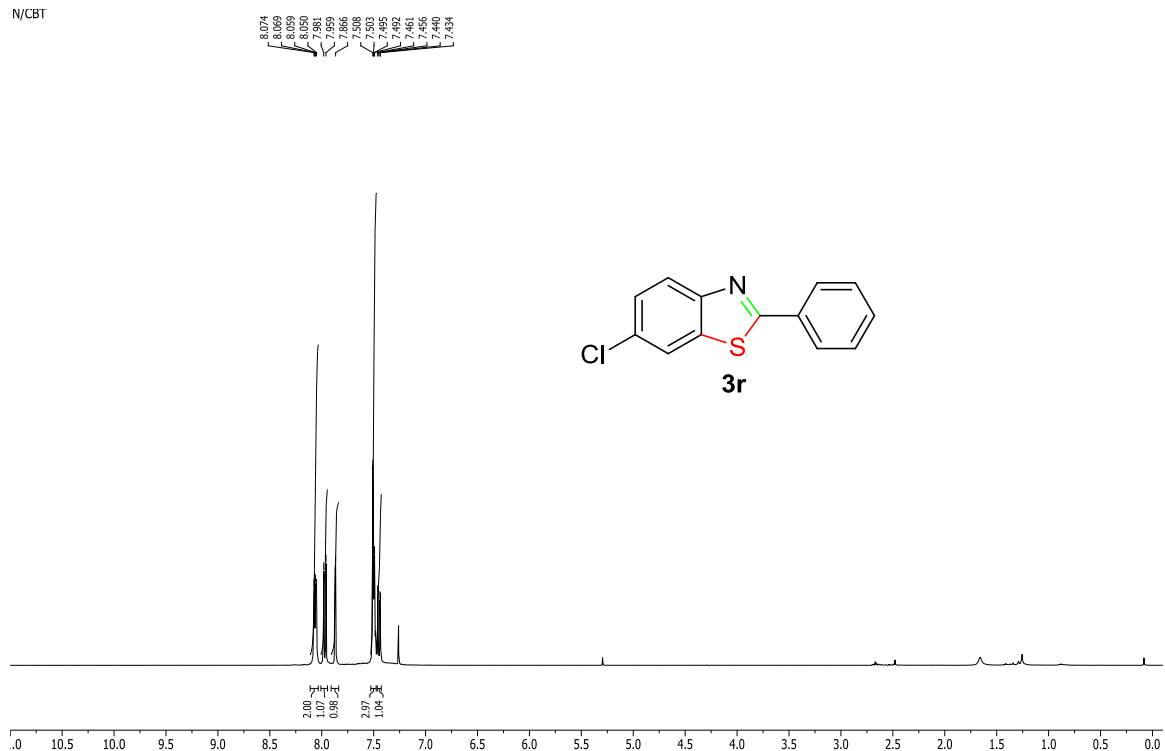
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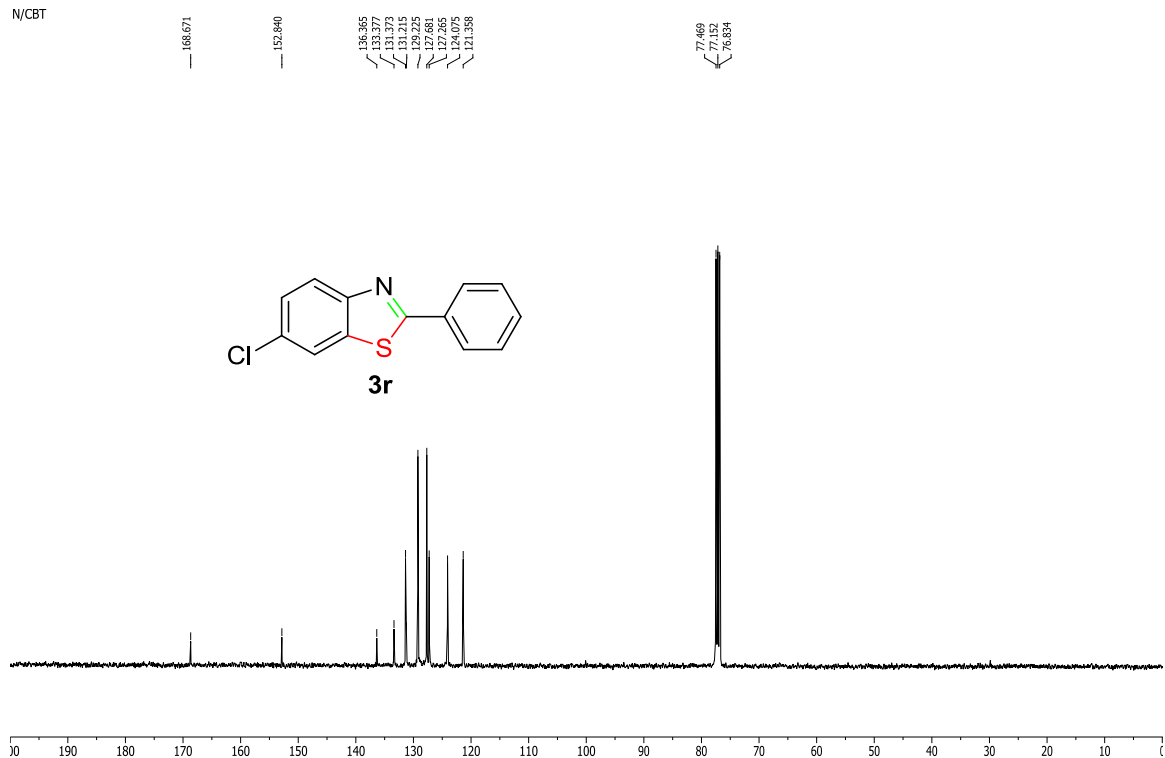
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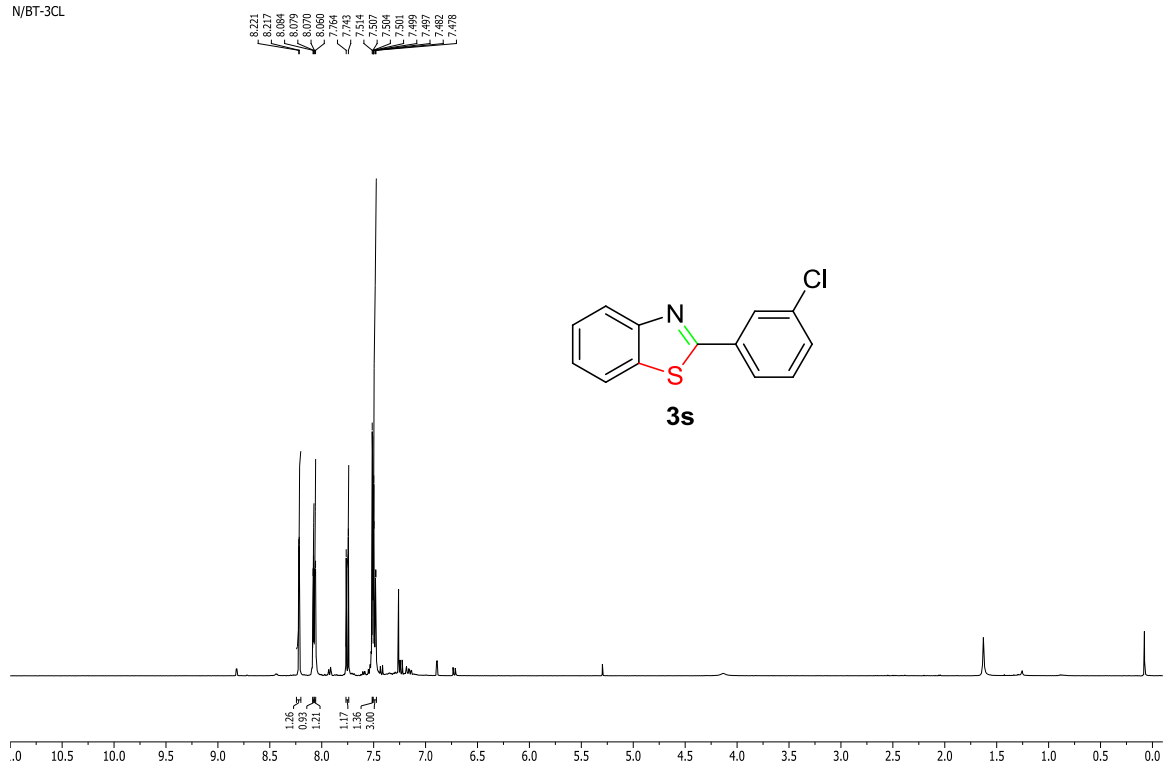
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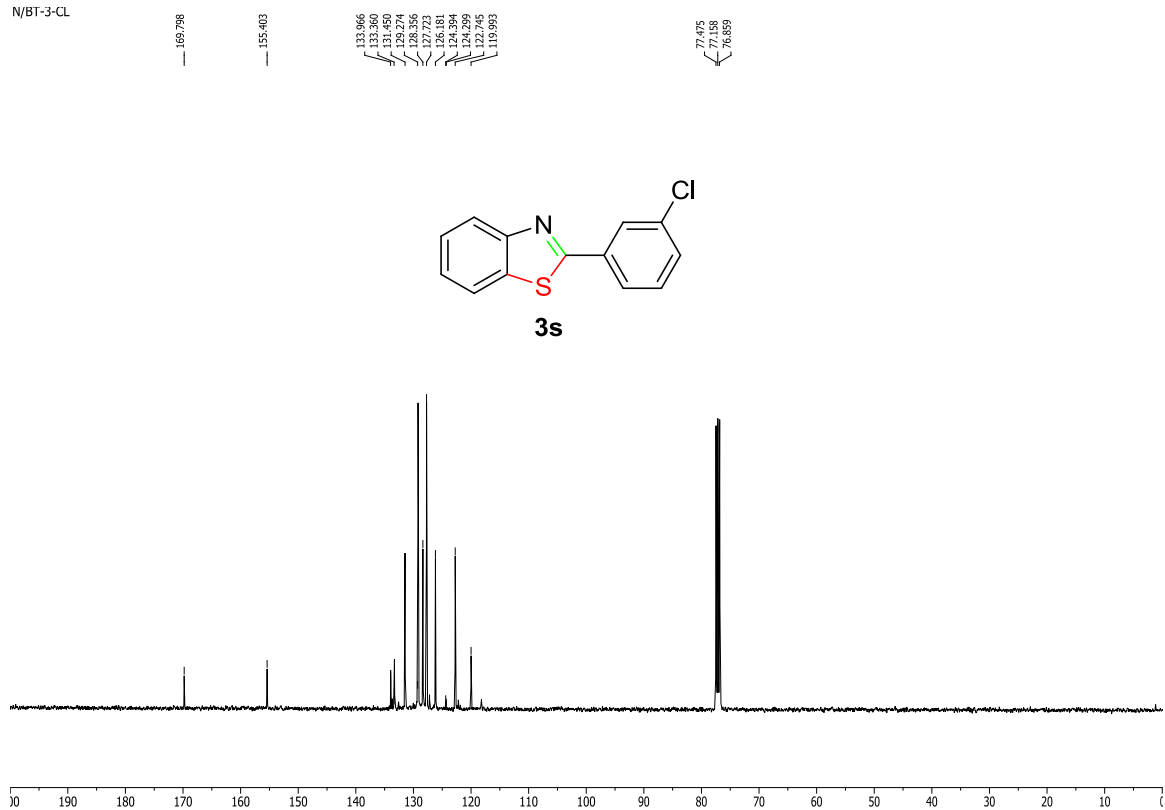
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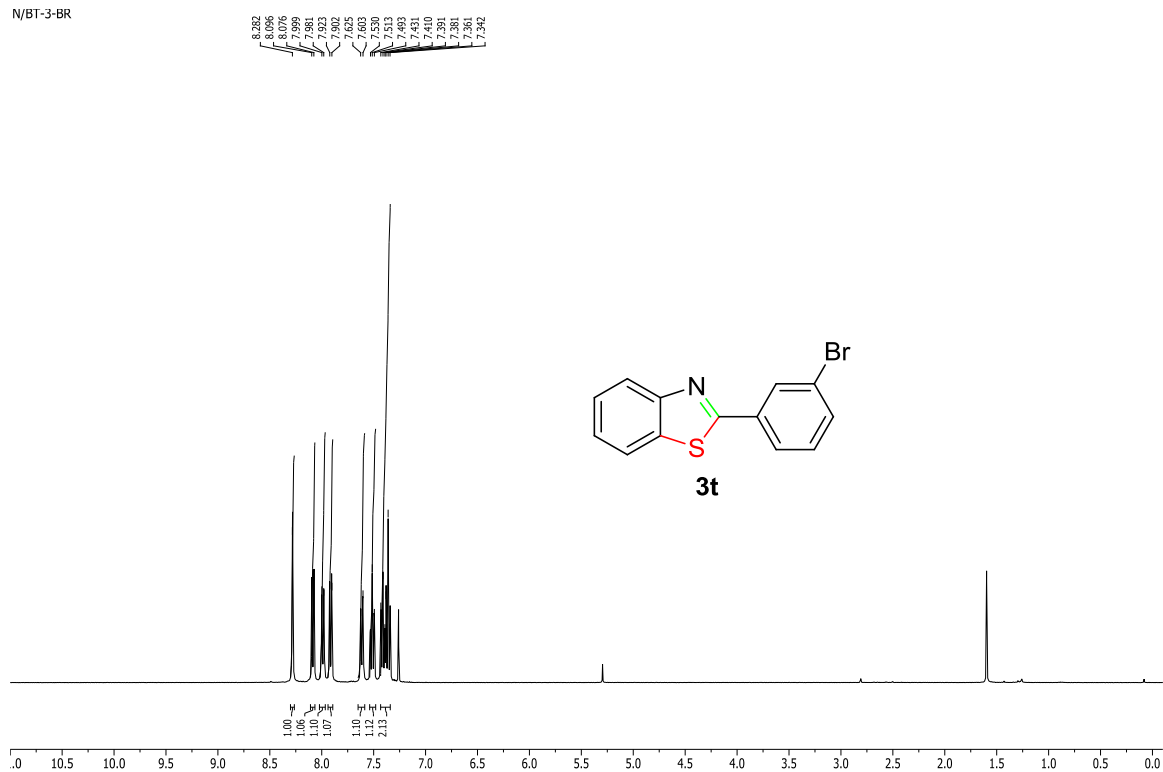
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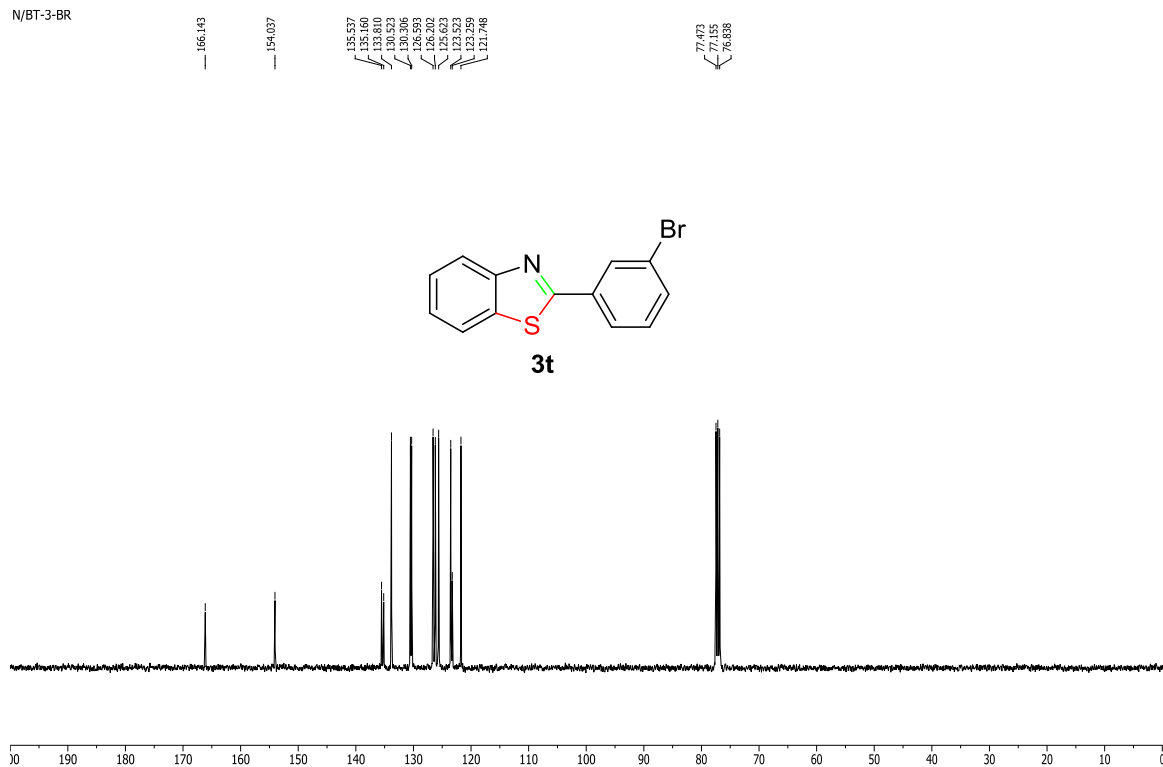
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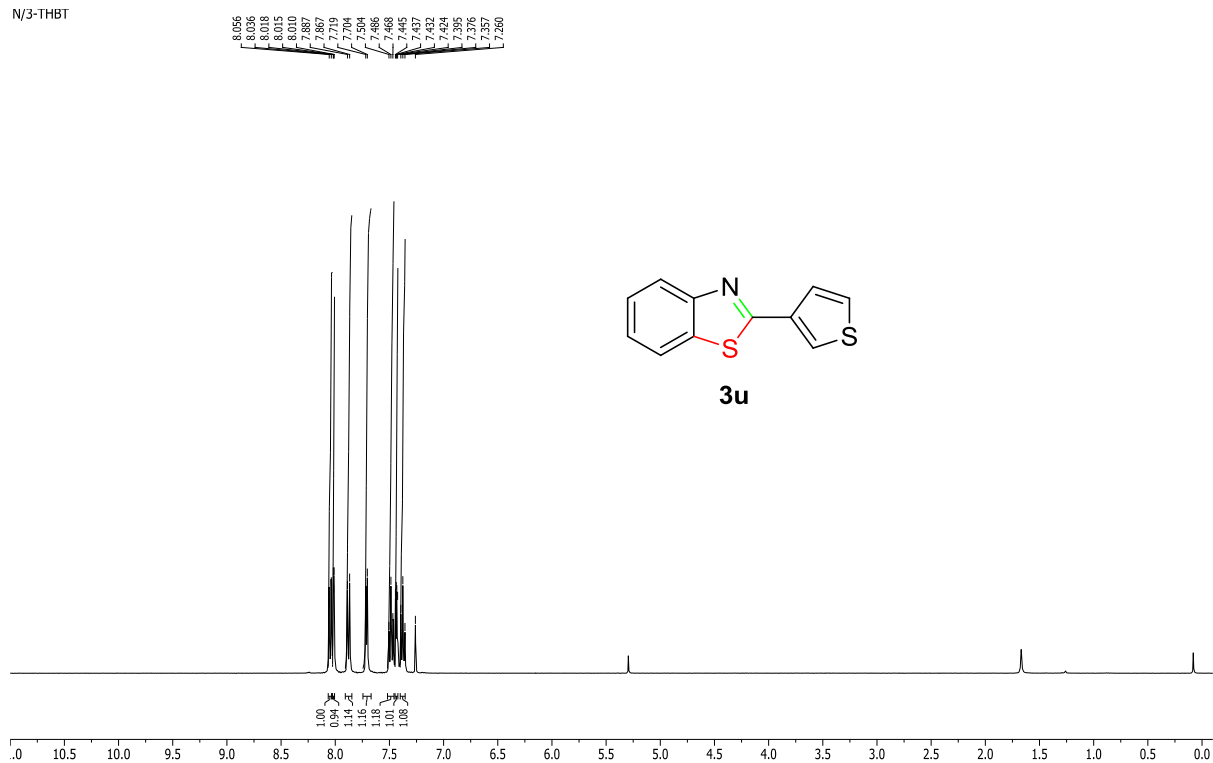
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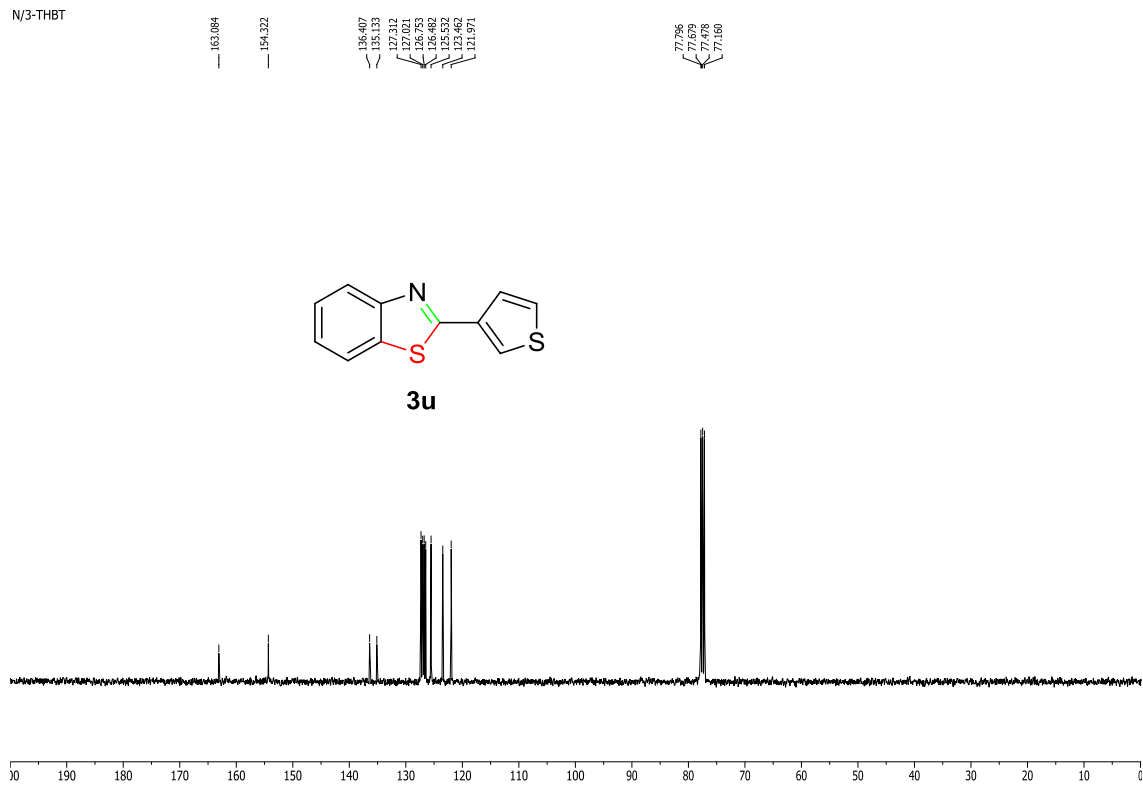
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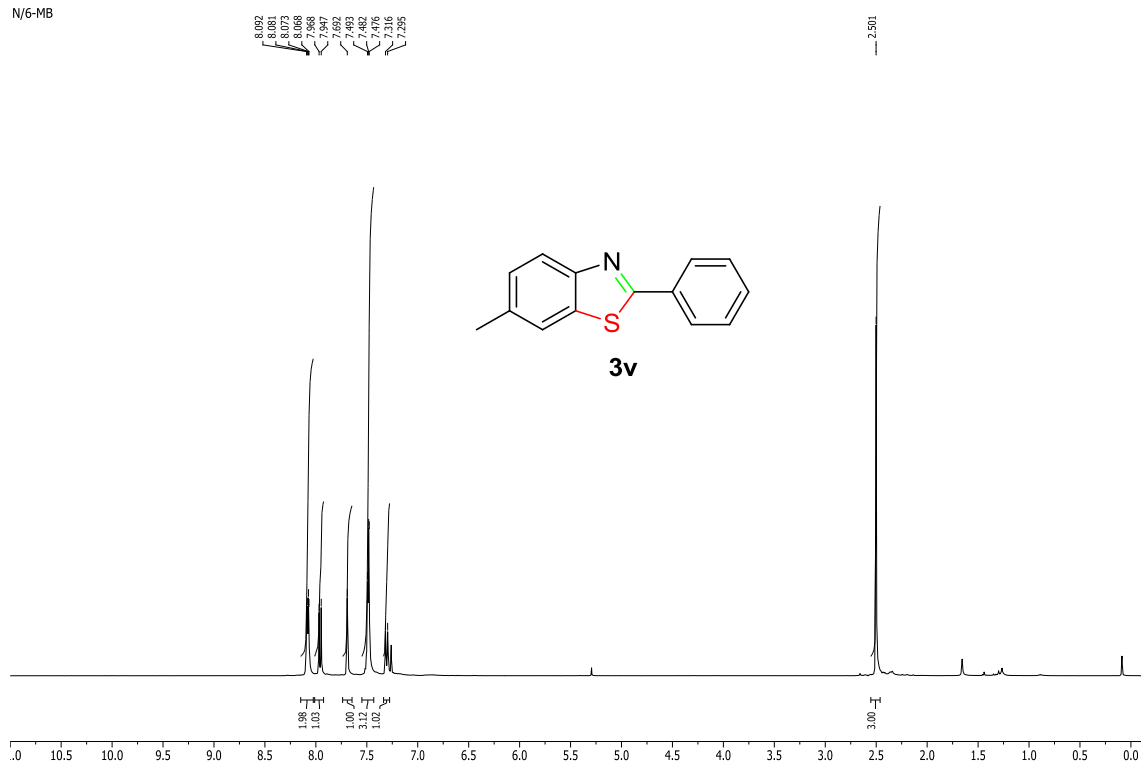
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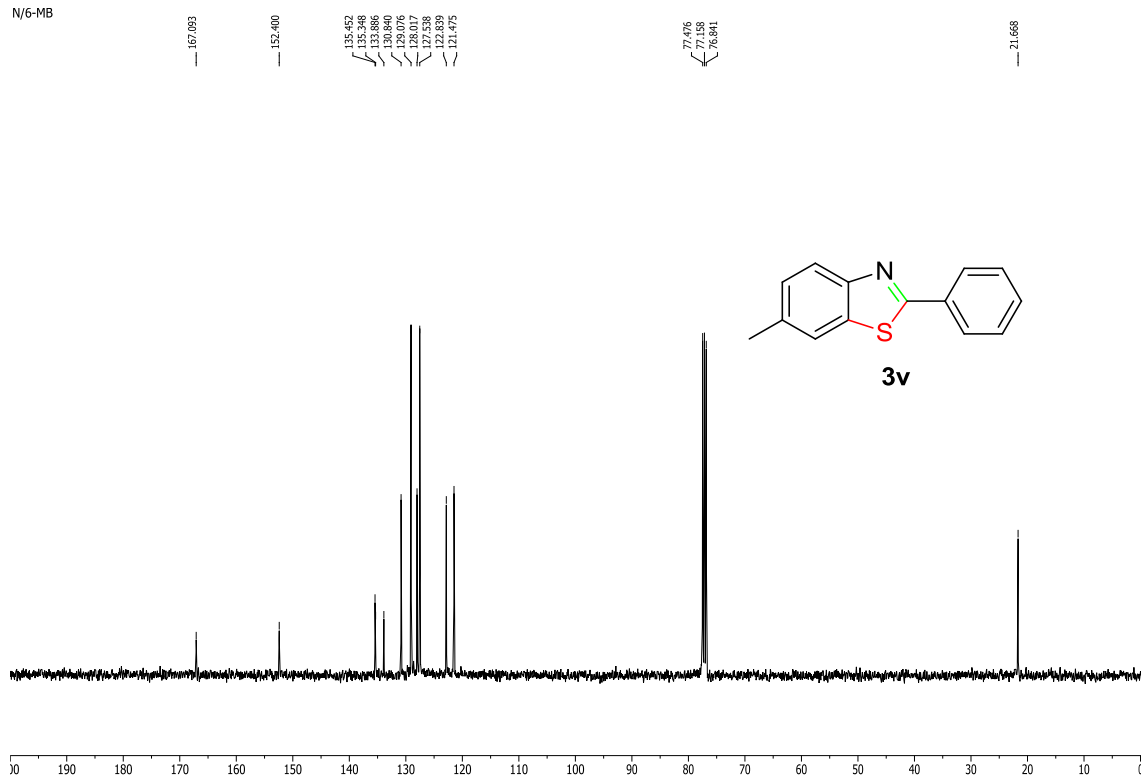
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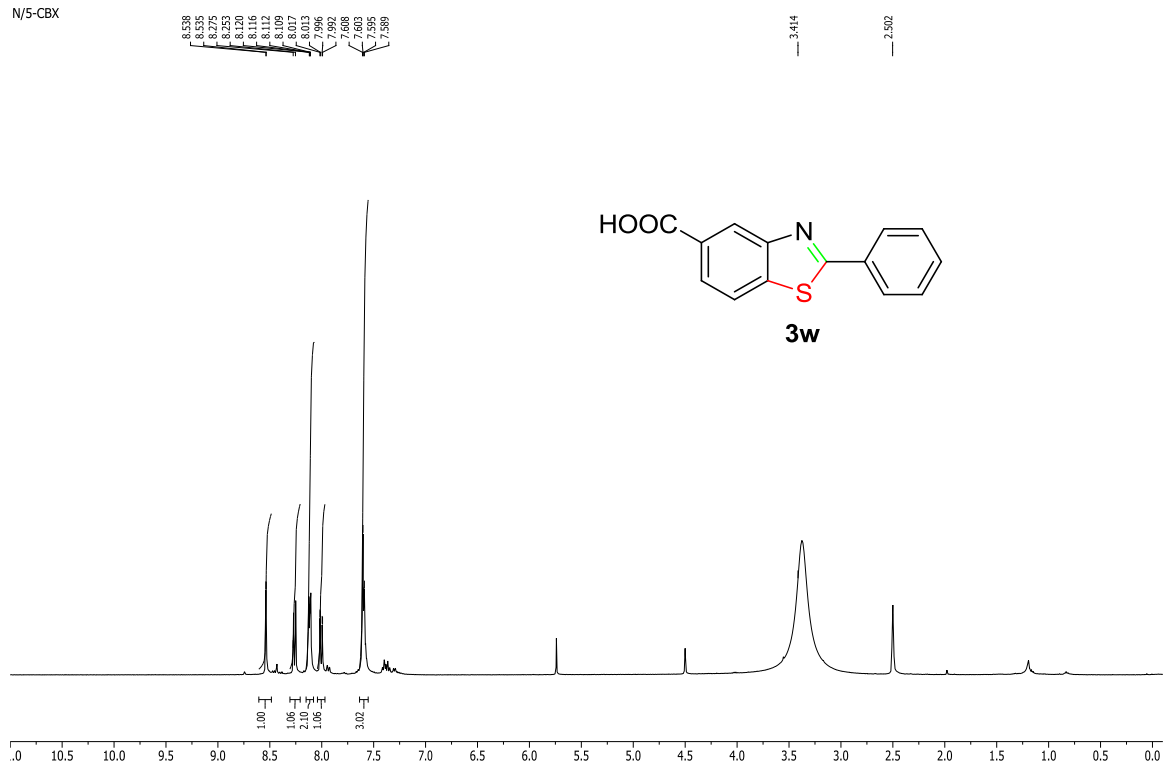
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N/6-MB



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N/5-CBX

