Supporting Information

Tuning chemoselectivity in *O*-/*N*-arylation of 3-aryl-1,2,4-oxadiazolones with *ortho*-(trimethylsilyl)phenyl triflates via aryne insertion

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1. General considerations

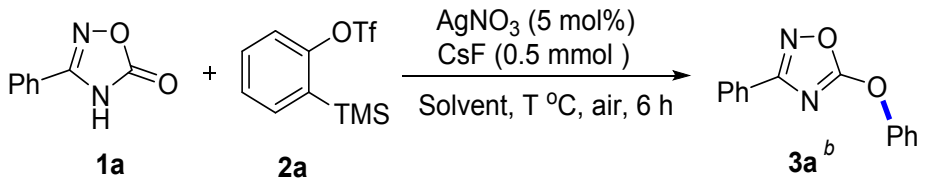
All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet. dd, doublet doublet; m, multiplet; td, triplet doublet; The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument. High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumber (cm^{-1}). Melting points were determined in open capillary tube using WRS-1B digital melting point apparatus.

3-Aryl-1,2,4-oxadiazolones were prepared according to reported method (X.-G. Yu, K.-H. Chen, F. Yang, S.-K. Zha and J. Zhu, *Org. Lett.,* 2016, **18**, 5412), and *o*-trimethylsilyphenyl triflates were prepared according to reported method (D. Peña, A. Cobas, D. Pérez and E. Guitián, *Synthesis,* **2002**, 1454). The chemicals were purchased from commercial suppliers Aldrich in USA, Energy Chemical Company in China, or TCI in Japan. All the solvents were dried and freshly distilled in N_2 prior to use. Products were purified by flash chromatography on 200–300 mesh silica gels (SiO_2) with petroleum ether/ethyl acetate as eluant.

2. Typical procedure for the *O*-arylation of 3-phenyl-1,2,4-oxadiazolone

A 10 mL Schlenk tube was charged with 3-phenyl-1,2,4-oxadiazolone (**1a**, 0.20 mmol), *o*-trimethylsilyphenyl triflate (**2a**, 0.40 mmol), $AgNO_3$ (0.01 mmol), CsF (0.50 mmol). Then anhydrous acetonitrile (2.0 mL) was injected into the Schlenk tube under air. The reaction tube was sealed with a Teflon plug valve and placed in an oil bath. After the reaction was carried out at 80 ^{o}C for 6 h, it was cooled to room temperature and detected by TLC, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1 to 50:1), affording the desired product **3a** as a white solid (42.4 mg, 89% yield).

Table S1. Effect of solvent and temperature on the *O*-arylation of 1a with 2a[a]



1a 2a 3a[b]

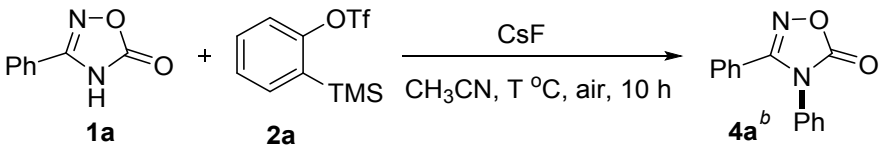
Entry	Solvent	T (°C)	Yield (%)[b]
1	CH_3CN	r.t.	0
2	CH_3CN	40	16
3	CH_3CN	60	73
4	CH_3CN	80	89
5	CH_3CN	90	88
6	THF	80	0
7	1,4-Dioxane	80	0
8	Toluene	80	0
9	DMF	80	0

[a] Reaction conditions: 3-phenyl-1,2,4-oxadiazolone (**1a**, 0.20 mmol), *ortho*-(trimethylsilyl)phenyl triflate (**2a**, 0.40 mmol), $AgNO_3$ (5 mol%), CsF (0.50 mmol), anhydrous acetonitrile (2.0 mL). [b] isolated yield. r.t. = room temperature.

3. Typical procedure for the *N*-arylation of 3-phenyl-1,2,4-oxadiazolone

A 10 mL Schlenk tube was charged with 3-phenyl-1,2,4-oxadiazolone (**1a**, 0.20 mmol), *ortho*-(trimethylsilyl)phenyl triflate (**2a**, 0.40 mmol), CsF (0.50 mmol), Then anhydrous acetonitrile (2.0 mL) was injected into the Schlenk tube and sealed with a Teflon plug valve under air. The reaction tube was placed in an oil bath. After the reaction was carried out at 80 °C for 10 h, it was cooled to room temperature and detected by TLC, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1 to 10:1), affording the desired product **4a** as a white solid (43.8 mg, 92% yield).

Table S2. Optimization of reaction conditions on the *N*-arylation of 1a with 2a[a]

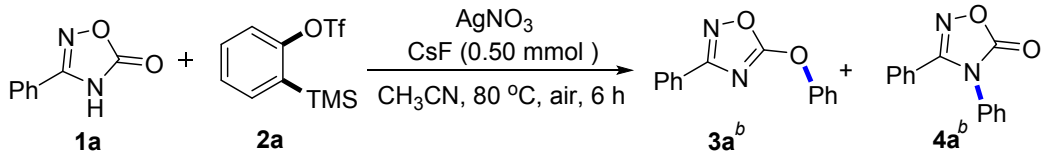


Entry	CsF (mmol)	T (°C)	Yield (%)[b]
1	0.5	r.t.	0
2	0.5	60	21
3	0.5	70	53
4	0.5	80	92
5	0.5	90	94
6	0.4	80	75
7	0.6	80	92

[a] Reaction conditions: 3-phenyl-1,2,4-oxadiazolone (**1a**, 0.20 mmol), *ortho*-(trimethylsilyl)phenyl triflate (**2a**, 0.40 mmol), CsF (mmol), anhydrous acetonitrile (2.0 mL), air, 10 h. [b] isolated yields. r.t. = room temperature.

4. Insight into the role of $AgNO_3$ in the arylation of 1a with 2a

Table S3. Effect of silver nitrate on the *N*- and *O*-arylation[a]



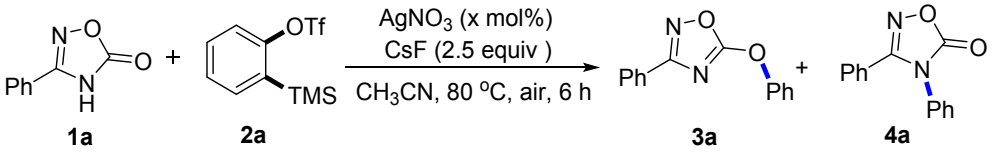
Entry	$AgNO_3$ (%)	**3a,** yield (%)[b]	**4a**, yield (%)[b]
1	0	0	67
2	0.1	12	41
3	0.5	37	trace
4	1	51	0
5	3	68	0
6	5	89	0

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), CsF (0.50 mmol) and $AgNO_3$ at 80 °C under ambient air for 6 h. [b]Isolated yield.

5. Typical procedure for the gram-scale synthesis of 3a

A 100 mL Schlenk tube was charged with 3-phenyl-1,2,4-oxadiazolone (**1a**, 5.0 mmol), *ortho*-(trimethylsilyl)phenyl triflate (**2a**, 10.0 mmol), $AgNO_3$ (1.0 mmol), CsF (12.5 mmol). Then anhydrous acetonitrile (40 mL) was injected into the Schlenk tube and sealed with a Teflon plug valve under air. The reaction tube was placed in an oil bath. After the reaction was carried out at 80 °C for 6 h, it was cooled to room temperature and detected by TLC, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1 to 50:1), affording the desired product **3a** as a white solid (0.93 g, 78% yield).

6. Typical procedure for investigation into the effect of $AgNO_3$

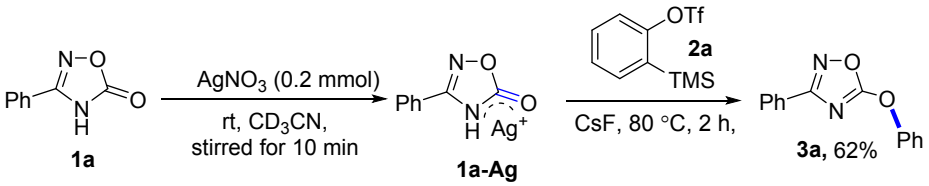


1a **2a** **3a** **4a**

A solution of $AgNO_3$ in CH_3CN (0.04 M) was prepared prior to use. The use of 1 mol% $AgNO_3$ in *O*-arylation was illustrated as following.

A 10 mL Schlenk tube was charged with 3-phenyl-1,2,4-oxadiazolone (**1a**, 0.20 mmol), *ortho*-(trimethylsilyl)phenyl triflate (**2a**, 0.40 mmol), $AgNO_3$ solution (50 μL, 0.04 M in CH_3CN), CsF (0.50 mmol). Then anhydrous acetonitrile (2.0 mL) was injected into the Schlenk tube under air. The reaction tube was sealed with a Teflon plug valve and placed in an oil bath. After the reaction was carried out at 80 °C for 6 h, it was cooled to room temperature and detected by TLC, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1 to 50:1), affording the desired product **3a** as a white solid (24.3 mg, 51% yield).

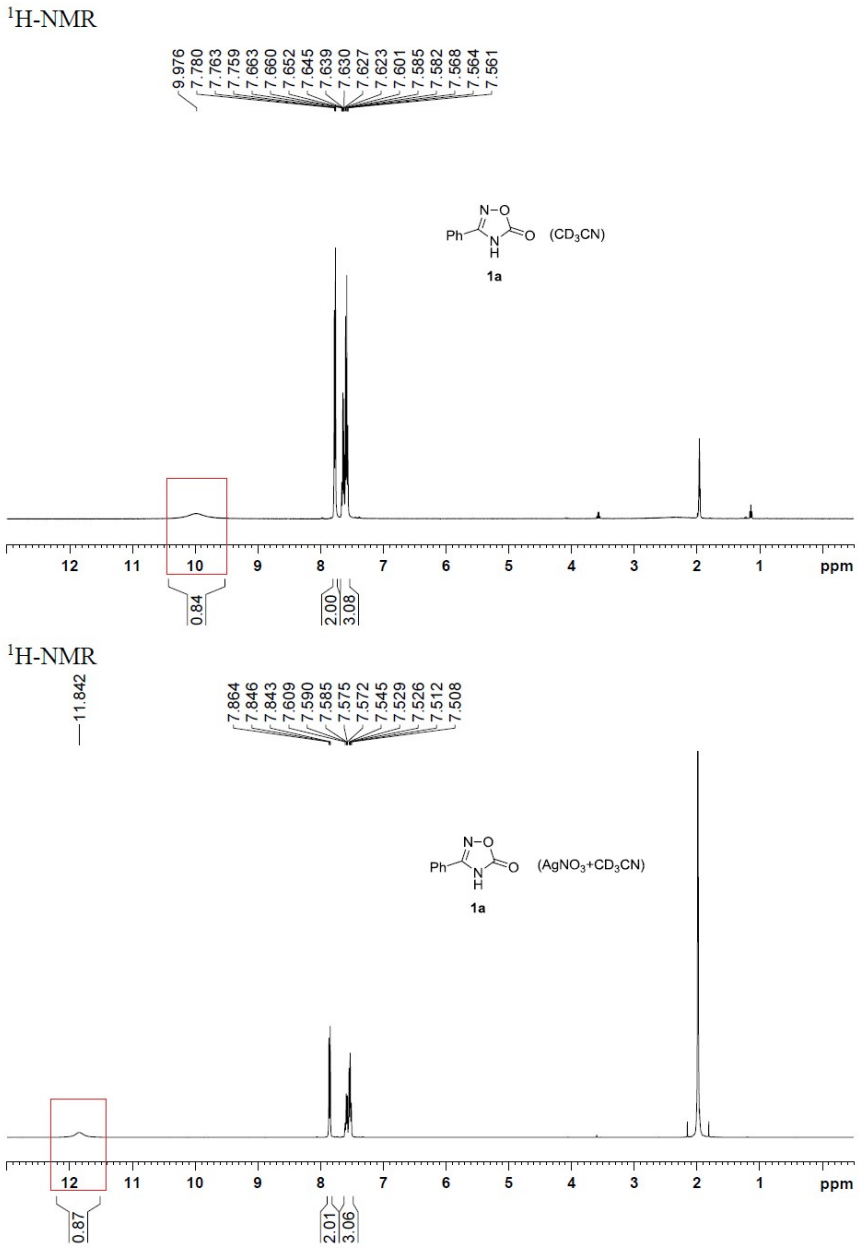
7. Typical procedure for $AgNO_3$-assisted *O*-arylation of 1a in CD_3CN



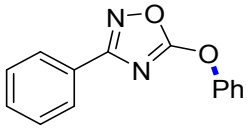
1a **1a-Ag** not isolated, characterized by ^1H NMR **3a**, 62%

A 10 mL dried glass tube with a magnetic stirring bar was charged with 3-

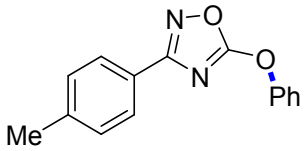
phenyl-1,2,4-oxadiazolone (**1a**, 32.4 mg, 0.20 mmol), CD_3CN (1.0 mL) and $AgNO_3$ (34.0 mg, 0.20 mmol). The resulted mixture was stirred at room temperature for 10 min, which was then directly used for ^{1}H-NMR analysis (Figure S1). In addition, all the **1a-**Ag generated in situ was transferred into a Schlenk tube (10 mL) and diluted by CD_3CN (total volume: 2 mL), followed by addition of **2a** (64.8 mg, 0.40 mmol) and CsF (76.0 mg, 0.50 mmol). After the reaction was carried out at 80 ^{o}C for 2 h, it was cooled to room temperature and detected by TLC, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1 to 50:1), affording the desired product **3a** as a white solid (29.5 mg, 62% yield).



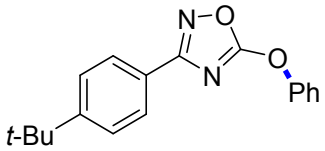
8. Characterization data for the products



5-Phenoxy-3-phenyl-1,2,4-oxadiazole (3a)[1]: White solid; mp 114–116 °C, 42.4 mg, 89% yield; IR (KBr): 2334, 1896, 1604, 1380, 1118, 907, 845, 738, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.99 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.48–7.41(m, 7H), 7.35–7.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.09, 169.25, 152.94, 131.33, 129.92, 128.71, 127.18, 126.88, 126.70, 119.70. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{14}H_{11}N_2O_2$ 239.0815, Found: 239.0818.

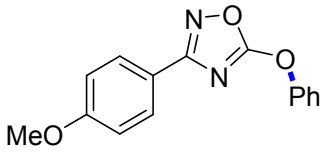


5-Phenoxy-3-(*p*-tolyl)-1,2,4-oxadiazole (3b):White solid; mp 94–96 °C, 42.9 mg, 85% yield; IR (KBr): 3039, 2359, 2064, 1515, 1457, 1311, 938, 904, 850, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 8.2 Hz, 2H), 7.48–7.41 (m, 4H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.96, 169.27, 152.93, 141.71, 129.92, 129.42, 127.11, 126.67, 124.04, 119.72, 21.56. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{13}N_2O_2$: 253.0972, Found: 253.0970.

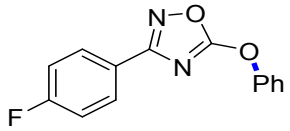


3-(4-(*tert*-Butyl)phenyl)-5-phenoxy-1,2,4-oxadiazole (3c): White solid; mp 79–81 °C, 51.2 mg, 87% yield; IR (KBr): 2963, 2289, 1606, 1564, 1486, 1378, 1185, 1020, 909, 795, 763, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 8.4 Hz, 2H), 7.49–7.42 (m. 6H), 7.33 (t, *J* = 6.9 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.94, 169.23, 154.82, 152.93, 129.91, 126.98, 126.66, 125.69, 124.00, 119.70, 34.97, 31.15. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{18}H_{19}N_2O_2$: 295.1441, Found:

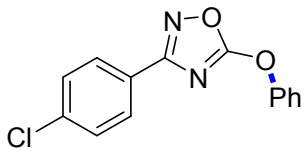
295.1444.



3-(4-Methoxyphenyl)-5-phenoxy-1,2,4-oxadiazole (3d): White solid; mp 96–98 °C, 49.3 mg, 92 % yield; IR (KBr): 3063, 2984, 2559, 2044, 1894, 1825, 1611, 1377, 1020, 896, 840, 781, 729, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 8.9 Hz, 2H), 7.48–7.41 (m, 4H), 7.32 (d, *J* = 7.0 Hz, 1H), 6.93 (dd, *J* = 7.0, 1.9 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.80, 168.89, 161.99, 152.86, 129.84, 128.75, 126.59, 119.66, 119.23, 114.05, 55.27. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{13}N_2O_3$: 269.0921, Found: 269.0925.

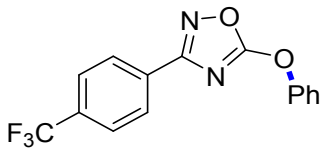


3-(4-Fluorophenyl)-5-phenoxy-1,2,4-oxadiazole (3e): White solid; mp 77–79 °C, 35.3 mg, 69% yield; IR (KBr): 2363, 1618, 1576, 1492, 1382, 1154, 844, 621 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.99 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.49–7.41 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.16, 168.41, 164.67 (d, *J* = 250.4 Hz), 152.88, 129.95, 129.38 (d, *J* = 8.7 Hz), 126.80, 123.08 (d, *J* = 3.2 Hz), 119.72, 115.92 (d, *J* = 21.9 Hz). HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{14}H_{10}FN_2O_2$:257.0721, Found: 257.0724.

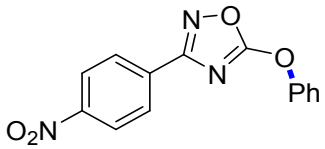


3-(4-Chlorophenyl)-5-phenoxy-1,2,4-oxadiazole (3f): White solid; mp 89–91 °C, 41.3 mg, 76% yield; IR (KBr): 2923, 1606, 1564, 1482, 1410, 1313, 1182, 1090, 846, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 8.6 Hz, 2H), 7.47 (t, *J* = 8.6 Hz, 2H), 7.43–7.40 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.22, 168.42, 152.86, 137.53, 129.97, 129.05, 128.49, 126.82, 125.33, 119.71.

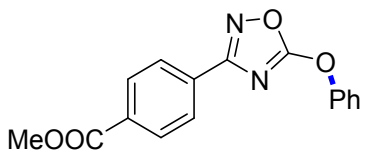
HRMS (ESI) ([M+H]$^+$) Calcd. For: $C_{14}H_{10}{}^{35}ClN_2O_2$ 273.0425, Found: 273.0426.



5-Phenoxy-3-(4-(trifluoromethyl)phenyl)-1,2,4-oxadiazole (3g): White solid; mp 75–77 ^{o}C, 41.6 mg, 68% yield; IR (KBr): 3077, 2924, 1615,1572, 1493, 1381, 1128, 853, 765, 686 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.49 (t, J = 8.4 Hz, 2H), 7.43 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.43, 168.18, 152.82, 133.06 (q, J = 32.5 Hz), 130.22, 130.01, 127.54, 126.93, 125.72 (q, J = 3.8 Hz), 123.72 (q, J = 270.9 Hz), 119.71. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{10}F_3N_2O_2$: 307.0689, Found: 307.0691.

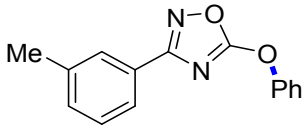


3-(4-Nitrophenyl)-5-phenoxy-1,2,4-oxadiazole (3h)[2]: White solid; mp 112–114 ^{o}C, 35.7 mg, 63% yield; IR (KBr): 2921, 1610, 1531, 1485, 1416, 1380, 1341, 1309, 1185, 1127, 1105, 916, 854, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (dd, J = 7.0, 1.9 Hz, 2H), 8.18 (dd, J = 7.1, 2.0 Hz, 2H), 7.50 (t, J = 8.4 Hz, 2H), 7.43 (dd, J = 9.8, 2.2 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.65, 167.60, 152.77, 149.56, 132.65, 130.07, 128.16, 127.06, 123.97, 119.70. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{14}H_{10}N_3O_4$: 284.0666, Found: 284.0664.

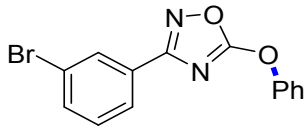


Methyl 4-(5-phenoxy-1,2,4-oxadiazol-3-yl)benzoate (3i): White solid; mp 103–105 ^{o}C, 39.1 mg, 66% yield; IR (KBr): 3064, 2963, 2639, 1951, 1716, 1532, 1414, 1382, 1280, 1130, 1105, 1018, 957, 864, 744, 707, 681 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ:

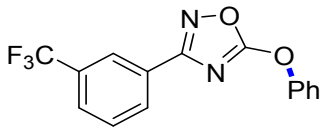
8.12–8.05 (m, 4H), 7.51–7.42 (m, 4H), 7.35 (t, J = 7.2 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.35, 168.50, 166.33, 152.84, 132.58, 130.85, 130.00, 129.92, 127.14, 126.88, 119.71, 52.34. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{16}H_{13}N_2O_4$: 279.0870, Found: 279.0871.



5-Phenoxy-3-(*m*-tolyl)-1,2,4-oxadiazole (3j): White solid; mp 94–96 °C, 41.8 mg, 83% yield; IR (KBr): 3065, 2960, 2925, 1736, 1610, 1572, 1487, 1457, 1368, 1315, 1193, 1098, 849, 746, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J = 7.8 Hz, 1H), 7.47–7.43 (m, 4H), 7.37–7.31 (m, 2H), 7.30–7.23 (m, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.41, 170.03, 152.94, 138.09, 131.29, 130.68, 130.01, 129.87, 126.62, 126.05, 125.84, 119.64, 22.00. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{13}N_2O_2$: 253.0972, Found: 253.0976.

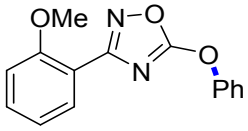


3-(3-Bromophenyl)-5-phenoxy-1,2,4-oxadiazole (3k): Yellow solid; mp 88–90 °C, 49.3 mg, 78% yield; IR (KBr): 2924, 2854, 1608, 1576, 1483, 1381, 1362, 1193, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (t, J = 1.5 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 8.5 Hz, 2H), 7.42 (d, J = 7.6 Hz, 2H), 7.37–7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.27, 168.07, 152.82, 134.33, 130.30, 130.16, 130.02, 128.76, 126.89, 125.64, 122.82, 119.73. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{14}H_{10}{}^{79}BrN_2O_2$: 316.9920, Found: 316.9919.

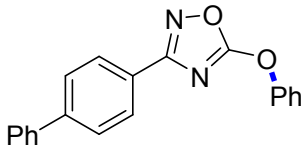


5-Phenoxy-3-(3-(trifluoromethyl)phenyl)-1,2,4-oxadiazole (3l): White solid; mp

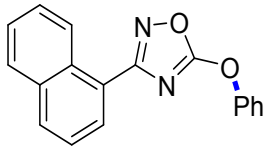
85–87 °C, 39.8 mg, 65% yield; IR (KBr): 2925, 2361, 1610, 1576, 1532, 1488, 1394, 1373, 1323, 1170, 1129, 1073, 913, 806, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.25 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.43, 168.17, 152.82, 131.36 (q, *J* = 32.7 Hz), 130.28, 130.04, 128.13 (q, *J* = 240.0 Hz), 127.83 (q, *J* = 16.3 Hz), 127.75, 125.05, 124.14 (q, *J* = 3.8 Hz), 122.35, 119.71. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{10}F_3N_2O_2$: 307.0689, Found: 307.0694.



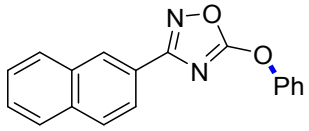
3-(2-Methoxyphenyl)-5-phenoxy-1,2,4-oxadiazole (3m): White solid; mp 68–70 °C, 39.1 mg, 73% yield; IR (KBr): 2930, 2841, 2332, 2046, 1950, 1877, 1774, 1606, 1489, 1317, 1193, 1025, 886, 752, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.90 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.48–7.42 (m, 5H), 7.32 (t, *J* = 6.7 Hz, 1H), 7.04 (d, *J* = 1.4 Hz, 1H), 7.01 (d, *J* = 2.8 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.29, 168.04, 158.16, 152.98, 132.47, 131.42, 129.89, 126.60, 120.57, 119.70, 111.61, 55.97. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{13}N_2O_3$: 269.0921, Found: 269.0919.



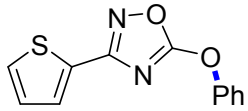
3-([1,1'-Biphenyl]-4-yl)-5-phenoxy-1,2,4-oxadiazole (3n): White solid; mp 116–118 °C, 44.0 mg, 70% yield; IR (KBr): 2922, 1943, 1604, 2559, 1480, 1375, 1185, 1124, 1021, 901, 848, 750, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.50–7.43 (m, 6H), 7.39–7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.10, 169.06, 152.94, 144.13, 140.15, 129.95, 128.90, 127.95, 127.64, 127.39, 127.15, 126.74, 125.69, 119.74. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{20}H_{15}N_2O_2$: 315.1128, Found: 315.1125.



3-(Naphthalen-1-yl)-5-phenoxy-1,2,4-oxadiazole (3o): White solid; mp 120–122 °C, 38.6 mg, 67% yield; IR (KBr): 3058, 2357, 1860, 1732, 1683, 1607, 1575, 1338, 1189, 903, 810, 778, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.90 (d, *J* = 8.6 Hz, 1H), 8.15 (dd, *J* = 7.2, 0.9 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.61 (td, *J* = 6.9, 1.3 Hz, 1H), 7.55–7.49 (m, 2H), 7.46 (t, *J* = 3.2 Hz, 4H), 7.35–7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.57, 169.94, 153.00, 133.85, 132.07, 130.46, 130.01, 129.59, 128.68, 127.66, 126.78, 126.36, 126.28, 125.00, 123.77, 119.77. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{18}H_{13}N_2O_2$: 289.0972, Found: 289.0977.

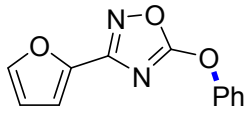


3-(Naphthalen-2-yl)-5-phenoxy-1,2,4-oxadiazole (3p): White solid; mp 115–117 °C, 41.5 mg, 72% yield; IR (KBr): 2920, 2362, 1605, 1570, 1512, 1388, 1310, 1183, 910, 863, 765 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.49 (s, 1H), 8.05 (dd, *J* = 8.1, 0.5 Hz, 1H), 7.90–7.83 (m, 3H), 7.55–7.45 (m, 6H), 7.35 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.16, 169.34, 152.96, 134.73, 132.93, 130.00, 128.85, 128.60, 127.98, 127.87, 127.56, 126.78, 126.72, 124.17, 123.31, 119.79. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{18}H_{13}N_2O_2$: 289.0972, Found: 289.0973.

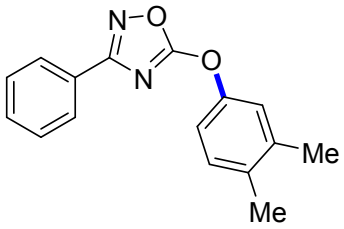


5-Phenoxy-3-(thiophen-2-yl)-1,2,4-oxadiazole (3q): White solid; mp 99–101 °C, 39.5 mg, 81% yield; IR (KBr): 3095, 2362, 1755, 1606, 1569, 1434, 1378, 1313, 1185, 904, 842, 751, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.71 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.49–7.45 (m, 3H), 7.41(d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.11 (dd, *J*

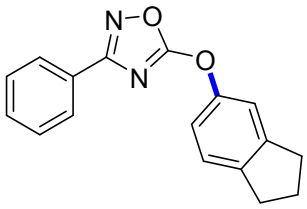
= 4.5, 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.86, 165.41, 152.82, 129.96, 129.88, 129.39, 128.33, 127.80, 126.80, 119.68. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{12}H_9N_2O_2S$: 245.0379, Found: 245.0380.



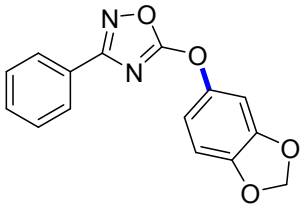
3-(Furan-2-yl)-5-phenoxy-1,2,4-oxadiazole (3r): White solid; mp 86–88 °C, 36.5 mg, 80% yield; IR (KBr): 2921, 1601, 1571, 1515, 1449, 1356, 1316, 1182, 890, 790, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, J = 1.0 Hz, 1H), 7.47 (t, J = 8.5 Hz, 2H), 7.39 (d, J = 7.7 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.06 (d, J = 3.4 Hz, 1H), 6.52 (dd, J = 3.4, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.05, 162.08, 152.79, 145.22, 142.03, 130.01, 126.88, 119.70, 114.12, 111.72. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{12}H_9N_2O_3$: 229.0608, Found: 229.0602.



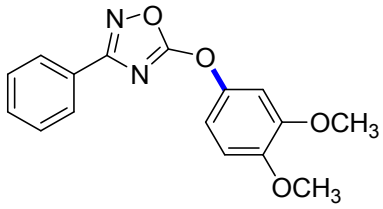
5-(3,4-Dimethylphenoxy)-3-phenyl-1,2,4-oxadiazole (3s): White solid; mp 73–75 °C, 43.6 mg, 82% yield; IR (KBr): 3063, 2921, 2415, 1602, 1575, 1489, 1380, 1321, 1189, 1024, 1068, 898, 744, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, J = 6.8 Hz, 2H), 7.46–7.41 (m, 3H), 7.20–7.15 (m, 3H), 2.29 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.44, 169.27, 150.97, 138.59, 135.24, 131.29, 130.71, 128.69, 127.21, 126.95, 120.65, 116.84, 19.99, 19.25. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{16}H_{15}N_2O_2$: 267.1128, Found: 267.1133.



5-((2,3-Dihydro-1*H*-inden-5-yl)oxy)-3-phenyl-1,2,4-oxadiazole (3t): White solid; mp 80–82 °C, 46.7 mg, 84% yield; IR (KBr): 3072, 2964, 2334, 1899, 1780, 1572, 1444, 1379, 1315, 1217, 1117, 1021, 934, 896, 827, 750, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 6.8 Hz, 2H), 7.45–7.37 (m, 3H), 7.24–7.21 (m, 2H), 7.12 (dd, *J* = 8.2, 2.2 Hz, 1H), 2.94–2.87 (m, 4H), 2.14–2.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.40, 169.12, 151.55, 146.20, 142.60, 131.12, 128.53, 127.05, 126.83, 125.03, 117.30, 115.68, 32.92, 32.17, 25.65. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{17}H_{15}N_2O_2$: 279.1128, Found: 279.1130.

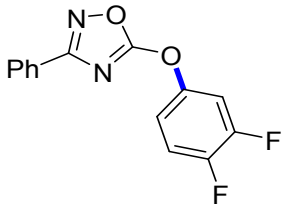


5-(Benzo[*d*][1,3]dioxol-5-yloxy)-3-phenyl-1,2,4-oxadiazole (3u): White solid; mp 91–93 °C, 49.1 mg, 87% yield; IR (KBr): 2907, 2359, 1483, 1424, 1211, 1141, 1039, 940, 866, 808, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 6.8 Hz, 2H), 7.50–7.41 (m, 3H), 6.94 (d, *J* = 2.3 Hz, 1H), 6.88–6.81 (m, 2H), 6.03 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.38, 169.24, 148.31, 147.31, 146.08, 131.35, 128.71, 127.18, 126.82, 112.50, 108.11, 102.22, 102.11. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{11}N_2O_4$: 283.0713, Found: 283.0717.

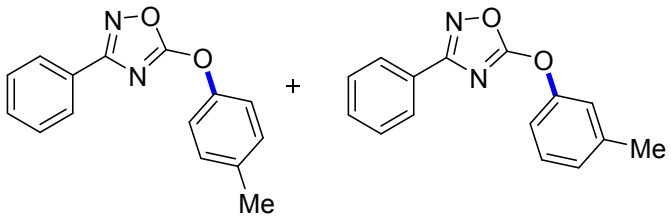


5-(3,4-Dimethoxyphenoxy)-3-phenyl-1,2,4-oxadiazole (3v): White solid; mp 101–103 °C, 48.3 mg, 81% yield; IR (KBr): 3089, 2917, 2837, 2608, 2361, 2052, 1988, 1836, 1576, 1266, 1154, 1025, 899, 852, 766, 740, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 6.8 Hz, 2H), 7.47–7.39 (m, 3H), 6.99–6.95 (m, 2H), 6.87 (d, *J* = 8.7 Hz, 1H), 3.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.23, 169.01, 149.50,

147.38, 146.48, 131.11, 128.50, 126.93, 126.69, 111.08, 110.98, 104.03, 56.02, 55.94. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{16}H_{15}N_2O_4$: 299.1026, Found: 299.1030.



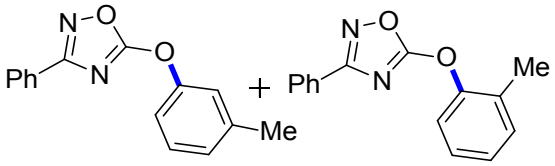
5-(3,4-Difluorophenoxy)-3-phenyl-1,2,4-oxadiazole (3w): White solid; mp 80–82 ^oC, 41.1 mg, 75% yield; IR (KBr): 3092, 2922, 2617, 2069, 1956, 1728, 1579, 1515, 1386, 1250, 1114, 896, 861, 735, 685 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (dd, *J* = 8.1, 1.3 Hz, 2H) 7.52–7.38 (m, 4H), 7.30–7.21 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.43, 169.18, 151.44 (d, *J* = 14.1 Hz), 149.99 (d, *J* = 12.3 Hz), 148.07 (d, *J* = 3.9 Hz), 147.52, (d, *J* = 12.4 Hz), 131.53, 127.96 (d, *J* = 164.2 Hz), 126.51, 117.80 (d, *J* = 19.8 Hz), 115.87 (d, *J* = 3.4 Hz), 110.13 (d, *J* = 21.0 Hz). HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{14}H_9F_2N_2O_2$: 275.0627, Found: 275.0631.



(3x:3x'= 1:1)

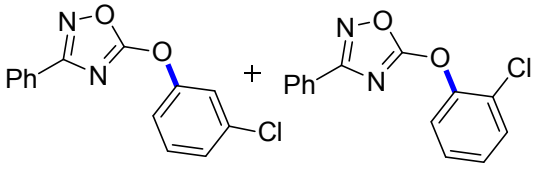
3-Phenyl-5-*(p*-tolyloxy)-1,2,4-oxadiazole(3x) and 3-phenyl-5-(*m*-tolyloxy)-1,2,4-oxadiazole (3x') (**3x**:**3x′** = 1:1)**:** Colorless oil; 39.3 mg, 78% yield; IR (KBr): 3040, 2922, 2737, 2361, 1895, 1718, 1602, 1574, 1485, 1380, 1321, 1122, 1022, 900, 783, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00–7.97 (m, 3.5H), 7.49–7.40 (m, 6H), 7.35–7.28 (m, 3H), 7.22 (d, *J* = 8.6 Hz, 4H), 7.13 (d, *J* = 7.5 Hz, 2H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.33, 172.21, 169.27, 169.25, 152.90, 150.88, 140.36, 136.55, 131.33, 130.37, 129.62, 128.71, 127.53, 127.19, 126.91, 120.27, 119.48, 116.70, 21.39, 20.89. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{13}N_2O_2$:

253.0972, Found: 253.0974.



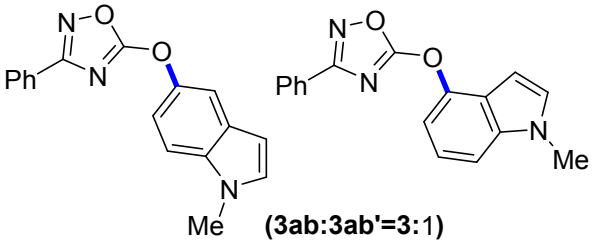
(3y:3y' = 1:1)

3-Phenyl-5-(*m*-tolyloxy)-1,2,4-oxadiazole (3y) and 3-phenyl-5-(*o*-tolyloxy)-1,2,4-oxadiazole (3y') (**3y**:**3y′** = 1:1)**:** Colorless oil; 36.1 mg, 73% yield; IR (KBr): 3062, 2360, 1690, 1570, 1530, 1486, 1377, 1322, 1232, 1172, 1107, 899, 743, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.99–7.94 (m, 4H), 7.44–7.36 (m, 7H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.28–7.26 (m, 2.5H), 7.24–7.18 (m, 4H), 7.10 (d, *J* = 7.6 Hz, 1.4H), 2.37 (m, 3H), 2.28 (m, 3.1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.25, 169.43, 169.29, 152.94, 151.64, 140.38, 131.79, 131.36, 129.65, 129.39, 128.74, 127.55, 127.48, 127.22, 127.02, 126.95, 126.93, 120.31, 120.26, 116.73, 21.39, 15.92. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{13}N_2O_2$: 253.0972, Found: 253.0968.

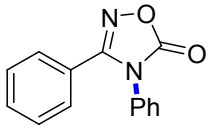


(3z:3z' = 1:1)

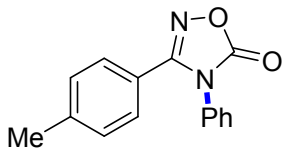
5-(3-Chlorophenoxy)-3-phenyl-1,2,4-oxadiazole (3z) and 5-(2-chlorophenoxy)-3-phenyl-1,2,4-oxadiazole (3z') (**3z**:**3z′**= 1:1)**:** Colorless oil; 37.6 mg, 69% yield; IR (KBr): 3070, 2959, 2361, 1609, 1571, 1474, 1440, 1380, 1323, 1200, 1070, 886, 740, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.00–7.99 (m, 2H), 7.98–7.98 (m, 2H), 7.50–7.42 (m, 9.8H)，7.40–7.31 (m, 6.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.57, 169.23, 153.01, 135.25, 131.50, 130.69, 128.78, 127.19, 127.08, 126.63, 120.43, 118.05. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{14}H_{10}{}^{35}ClN_2O_2$: 273.0425, Found: 273.0431



5-((1-Methyl-1*H*-indol-5-yl)oxy)-3-phenyl-1,2,4-oxadiazole (3ab) and 5-((1-Methyl-1*H*-indol-4-yl)oxy)-3-phenyl-1,2,4-oxadiazole (3ab') (3ab: 3ab' = 3:1): Colorless oil; 47.2 mg, 81% yield; IR (KBr): 2946, 2361, 1601, 1570, 1530, 1484, 1380, 1218, 1115, 947, 745, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.98–7.96 (m, 2.6H), 7.63–7.62 (m, 1H), 7.47–7.38 (m, 4.3H), 7.34–7.27 (m, 1.5H), 7.25–7.19 (m, 1.6H), 6.52–6.51 (m, 1H), 6.48–6.47 (m, 0.3H), 3.79 (m, 3.5H);^{13}C NMR (100 MHz, $CDCl_3$) δ:173.20, 172.48, 169.43, 169.32, 147.01, 145.77, 138.99, 134.93, 131.21, 130.75, 129.64, 128.65, 128.55, 127.21, 127.08, 121.73, 120.27, 113.87, 111.45, 110.00, 109.67, 108.24, 101.54, 97.53, 33.20, 33.12. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{17}H_{14}N_3O_2$: 292.1081, Found: 292.1090.

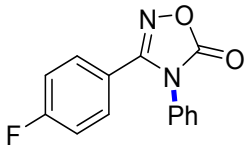


3,4-Diphenyl-1,2,4-oxadiazol-5(4*H*)-one (4a)[3]: White solid; 43.8 mg, mp 169–171 ^oC, 92% yield; IR (KBr): 3025, 2937, 2361, 2336, 1740, 1597, 1551, 1416, 1222, 995, 805, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ:7.50–7.46 (m, 1H), 7.44–7.43 (m, 3H), 7.36–7.35 (m, 4H), 7.23–7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.23, 157.44, 131.90, 131.83, 129.73, 129.46, 128.87, 128.11, 126.77, 122.95. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{14}H_{11}N_2O_2$: 239.0815, Found: 239.0818.

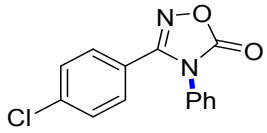


4-Phenyl-3-(*p*-tolyl)-1,2,4-oxadiazol-5(4*H*)-one (4b)[4]: White solid; mp 155–157 ^oC, 47.9 mg, 95% yield; IR (KBr): 3045, 2359, 1772, 1499, 1448, 1421, 1283, 826, 751

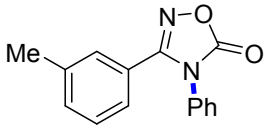
cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.43 (m, 3H), 7.24–7.21 (m, 4H), 7.15 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.39, 157.55, 142.52, 132.12, 129.78, 129.64, 129.47, 128.07, 126.91, 120.10, 21.49. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{15}H_{13}N_2O_2$: 253.0972, Found: 253.0977.



3-(4-Fluorophenyl)-4-phenyl-1,2,4-oxadiazol-5(4*H*)-one (4c)[3]: White solid; mp 136–138 °C, 44.6 mg, 87% yield; IR (KBr): 2924, 2058, 1899, 1776, 1607, 1563, 1431, 1321, 1158, 890, 842, 788, 842, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47–7.45 (m, 3H), 7.38–7.35 (m, 2H), 7.23 (dd, *J* = 6.3, 3.1 Hz, 2H), 7.06 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.67 (d, *J* = 252.8 Hz), 158.18, 156.69, 131.82, 130.52 (d, *J* = 8.9 Hz), 129.95, 129.73, 126.90, 119.20, 116.40 (d, *J* = 88.7 Hz). HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{14}H_{10}FN_2O_2$: 257.0721, Found: 257.0726.

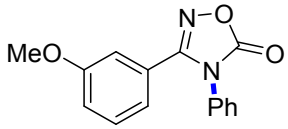


3-(4-Chlorophenyl)-4-phenyl-1,2,4-oxadiazol-5(4*H*)-one (4d)[3]: White solid; mp 130–132 °C, 49.5 mg, 91% yield; IR (KBr): 2921, 2563, 2068, 1910, 1777, 1598, 1545, 1499, 1426, 1319, 1141, 1092, 1010, 893, 831, 758, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48–7.46 (m, 3H), 7.36–7.34 (m, 2H), 7.30–7.28 (m, 2H), 7.24–7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.12, 156.61, 138.42, 131.73, 129.96, 129.76, 129.41, 129.37, 126.83, 121.44. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{14}H_{10}{}^{35}ClN_2O_2$: 273.0425, Found: 273.0426.

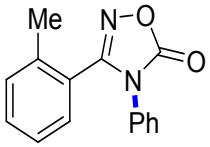


4-Phenyl-3-(*m*-tolyl)-1,2,4-oxadiazol-5(4*H*)-one (4e)[5]: White solid; mp 124–126 °C,

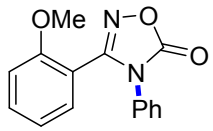
41.8 mg, 83% yield; IR (KBr): 3063, 2985, 1780, 1603, 1501, 1411, 1157, 1110, 970, 883, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33–7.30 (m, 3H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.13–7.10 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.10, 157.87, 137.78, 131.73, 130.98, 130.12, 129.49, 128.95, 126.25, 125.62, 122.84, 19.66. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{13}N_2O_2$: 253.0972, Found: 253.0972.



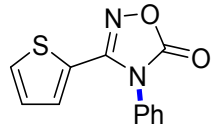
3-(3-Methoxyphenyl)-4-phenyl-1,2,4-oxadiazol-5(4*H*)-one (4f): White solid; mp 130–132 °C, 46.1 mg, 86% yield; IR (KBr): 3074, 2937, 2360, 1788, 1598, 1560, 1468, 1328, 1250, 1141, 1035, 885, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.46–7.45 (m, 3H), 7.27–7.23 (m, 3H), 7.03–7.00 (m, 1H), 6.90–6.85 (m, 2H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.69, 158.30, 157.36, 132.05, 130.08, 129.83, 129.57, 126.90, 124.06, 120.47, 118.24, 113.04, 55.29. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{13}N_2O_3$: 269.0921, Found: 269.0927.



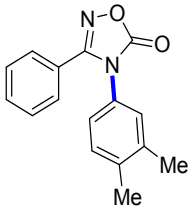
4-Phenyl-3-(*o*-tolyl)-1,2,4-oxadiazol-5(4*H*)-one (4g)[3]: White solid; mp 138–140 °C, 35.8 mg, 71% yield; IR (KBr): 3065, 2917, 2056, 1775, 1595, 1498, 1329, 1138, 886, 800, 752, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.43 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.25–7.19 (m, 4H), 7.04 (d, *J* = 7.7 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.36, 157.65, 139.02, 132.68, 132.04, 129.75, 129.49, 128.76, 128.74, 126.85, 125.27, 122.89, 21.24. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{13}N_2O_2$: 253.0972, Found: 253.0977.



3-(2-Methoxyphenyl)-4-phenyl-1,2,4-oxadiazol-5(4*H*)-one (4h): White solid; mp 145–147 °C, 35.9 mg, 67% yield; IR (KBr): 3007, 2938, 2359, 1778, 1593, 1498, 1466, 1439, 1415, 1256, 1158, 1024, 870, 777, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 8.3 Hz, 1H), 7.33–7.31 (m, 3H), 7.14–7.12 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.08, 157.40, 156.97, 133.88, 132.78, 131.05, 129.04, 128.60, 125.02, 121.13, 112.53, 111.38, 54.95. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{13}N_2O_3$: 269.0921, Found: 269.0919.

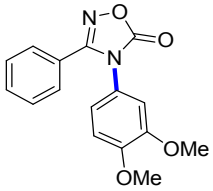


4-Phenyl-3-(thiophen-2-yl)-1,2,4-oxadiazol-5(4*H*)-one (4i): White solid; mp 127–129 °C, 42.5 mg, 87% yield; IR (KBr): 3116, 2361, 1774, 1576, 1510, 1454, 1309, 1125, 939, 850, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.57–7.52 (m, 3H), 7.49 (dd, *J* = 4.8, 1.3 Hz, 1H), 7.38–7.35 (m, 2H), 7.00–6.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.18, 153.36, 131.53, 130.67, 130.63, 130.53, 130.10, 128.02, 127.78, 123.25. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{12}H_9N_2O_2S$: 245.0379, Found: 245.0382.

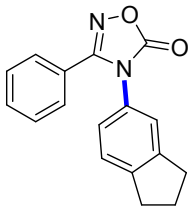


4-(3,4-Dimethylphenyl)-3-phenyl-1,2,4-oxadiazol-5(4*H*)-one (4j): White solid; mp 134–136 °C, 46.9 mg, 88% yield; IR (KBr): 3054, 2951, 2312, 1905, 1780, 1504, 1334, 1153, 1188, 1073, 832, 776, 750, 715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.50–7.46 (m, 1H), 7.39–7.34 (m, 4H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.06–7.05 (m, 1H),

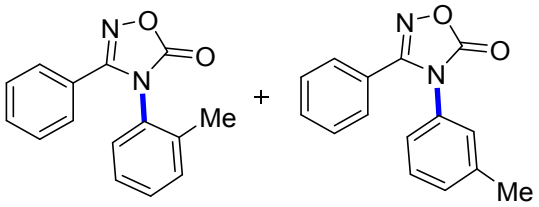
6.89 (dd, J = 8.0, 2.0 Hz, 1H), 2.28 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.66, 157.56, 138.67, 138.61, 131.81, 130.79, 129.50, 128.88, 128.13, 127.71, 124.25, 123.19, 19.81, 19.56. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{16}H_{15}N_2O_2$: 267.1128, Found: 267.1125.



4-(3,4-Dimethoxyphenyl)-3-phenyl-1,2,4-oxadiazol-5(4*H*)-one (4k): White solid; mp 142–144 °C, 48.9 mg, 82% yield; IR (KBr): 2936, 2840, 2358, 2031, 1779, 1616, 1558, 1515, 1409, 1349, 1255, 1136, 1022, 912, 864, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.48 (m, 1H), 7.41–7.35 (m, 4H), 6.88 (d, J = 8.5 Hz, 1H), 7.29 (dd, J = 8.5, 2.4 Hz, 1H), 6.73–72 (m, 1H), 3.91 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.61, 157.53, 149.92, 149.74, 131.86, 128.93, 128.09, 124.55, 123.13, 119.65, 111.35, 110.18, 56.14, 56.10. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{16}H_{15}N_2O_4$: 299.1026, Found: 299.1024.

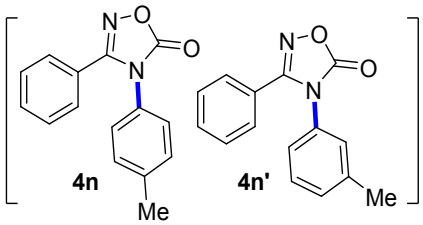


4-(2,3-Dihydro-1*H*-inden-5-yl)-3-phenyl-1,2,4-oxadiazol-5(4*H*)-one (4l): White solid; mp 135–137 °C, 50.1 mg, 90% yield; IR (KBr): 3064, 2962, 2844, 2306, 1751, 1586, 1456, 1182, 1020, 888, 823, 776, 754, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50–7.46 (m, 1H), 7.40–7.34 (m, 4H), 7.24 (d, J = 7.9 Hz, 1H), 7.12 (s, 1H), 6.91 (dd, J = 7.9, 1.74 Hz, 1H), 2.95–2.89 (m, 4H), 2.15–2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.75, 157.62, 146.39, 146.24, 131.81, 129.89, 128.89, 128.16, 125.37, 124.85, 123.21, 122.89, 32.80, 32.61, 25.46. HRMS (ESI) ($[M+H]^+$) Calcd. $C_{17}H_{15}N_2O_2$ For: 279.1128, Found: 279.1127.



(4m:4m'= 1:1)

3-Phenyl-4-(*o*-tolyl)-1,2,4-oxadiazol-5(4*H*)-one (4m) and 3-phenyl-4-(*m*-tolyl)-1,2,4-oxadiazol-5(4*H*)-one (4 m') (4m: 4m' = 1:1): Colorless oil; 40.9 mg, 81% yield; IR (KBr): 3062, 2361, 1798, 1587, 1499, 1324, 1213, 1145. 887, 758, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.51–7.44 (m, 2.1H), 7.42–7.38 (m,1.2H), 7.37–7.34 (m, 4.4H), 7.33–7.32 (m, 4.6H), 7.30–7.24 (m, 3.4H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.10 (s, 1.0H), 6.96 (d, *J* = 7.7 Hz, 1H), 2.35 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.46, 158.22, 157.67, 157.53, 140.21, 136.25, 131.97, 131.89, 131.86, 131.82, 130.93, 130.54, 130.43, 129.54, 129.00, 128.92, 128.48, 128.16, 127.61, 127.50, 127.37, 123.98, 123.20, 123.09, 21.27, 17.59. HRMS (ESI) ($[M+H]^+$) Calcd. $C_{15}H_{13}N_2O_2$ For: 253.0972, Found: 253.0980.

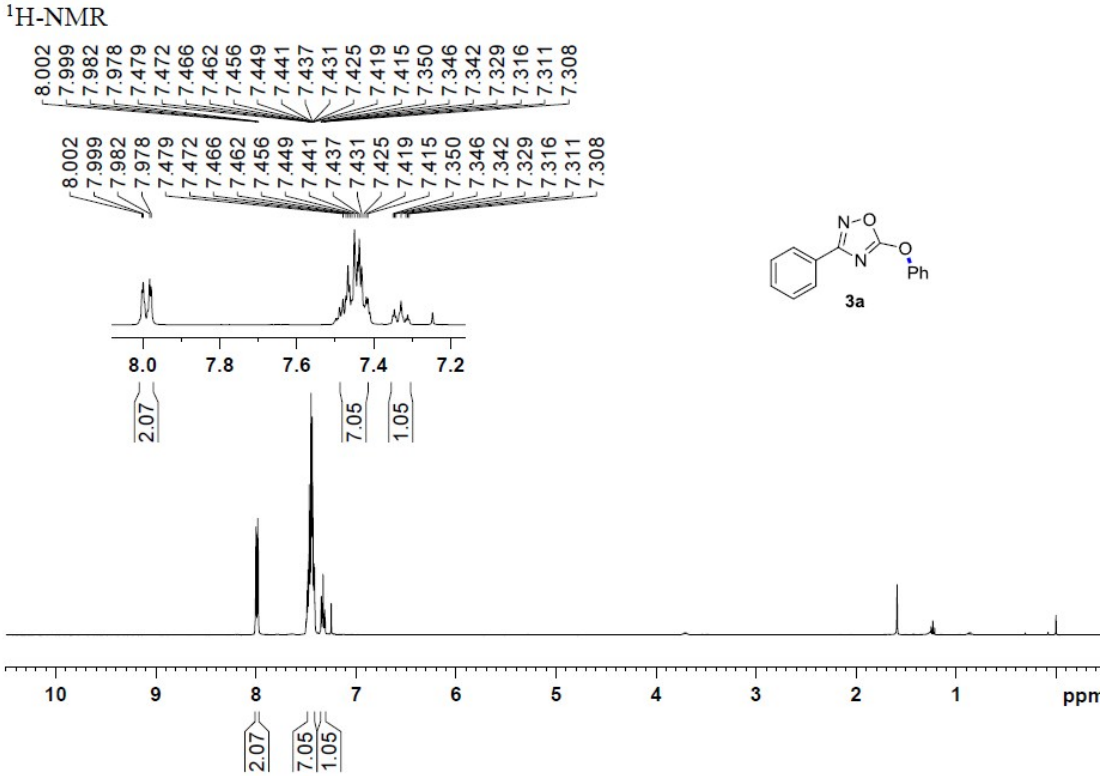


(4n:4n'= 3:2)

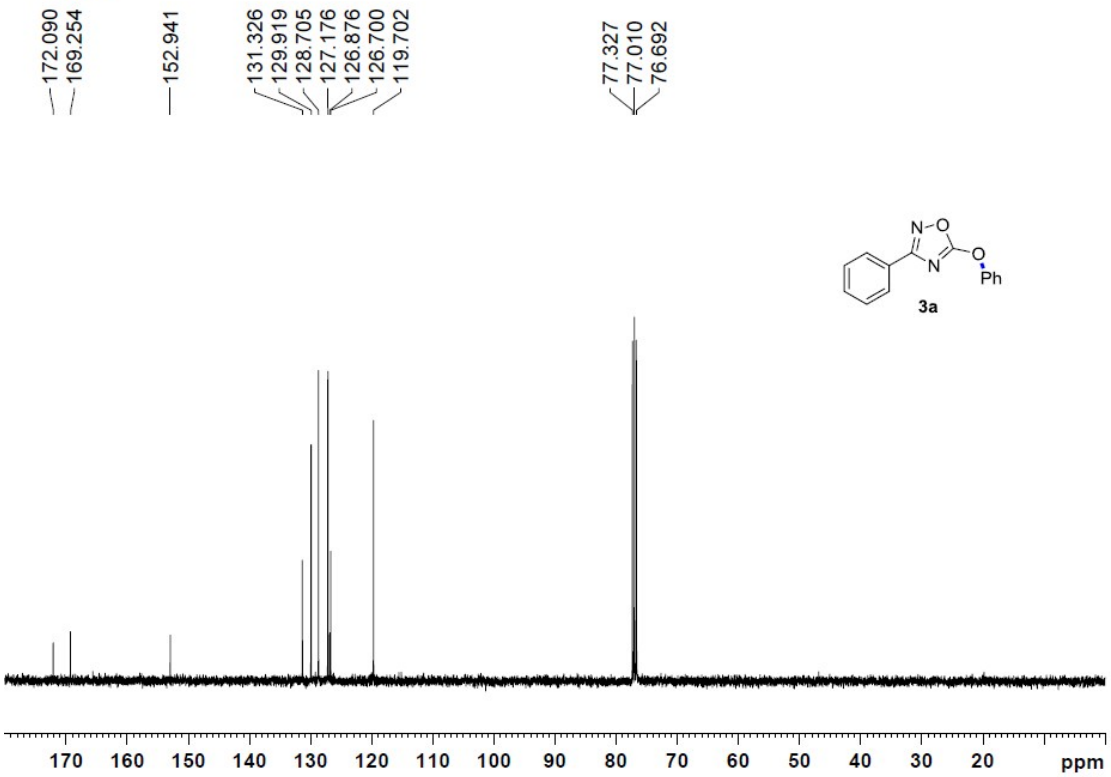
3-Phenyl-4-(*p*-tolyl)-1,2,4-oxadiazol-5(4*H*)-one (4n) and 3-phenyl-4-(*m*-tolyl)-1,2,4-oxadiazol-5(4*H*)-one (4n') (4n:4n' = 3:2): Colorless oil; 42.3 mg, 84% yield; IR (KBr): 3025, 2937, 2361, 2336, 1740, 1597, 1551, 1416, 1222, 995, 805, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.51–7.47 (m, 1.8H), 7.37–7.36 (m, 6.7H), 7.30 (t, *J* = 7.7 Hz, 1.0H), 7.25–7.23 (m, 2.4H), 7.11–7.09 (m, 2.6H), 6.96 (d, *J* = 7.6 Hz, 0.6H), 2.39 (s, 3.0H), 2.36 (s, 2.0H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.52, 158.45, 157.55, 140.21, 139.86, 131.85, 130.46, 129.54, 129.33, 128.92, 128.18, 128.16, 127.37,126.66, 123.97, 123.13, 21.27, 21.22. HRMS (ESI) ($[M+H]^+$) Calcd. $C_{15}H_{13}N_2O_2$ For: 253.0972, Found: 253.0968.

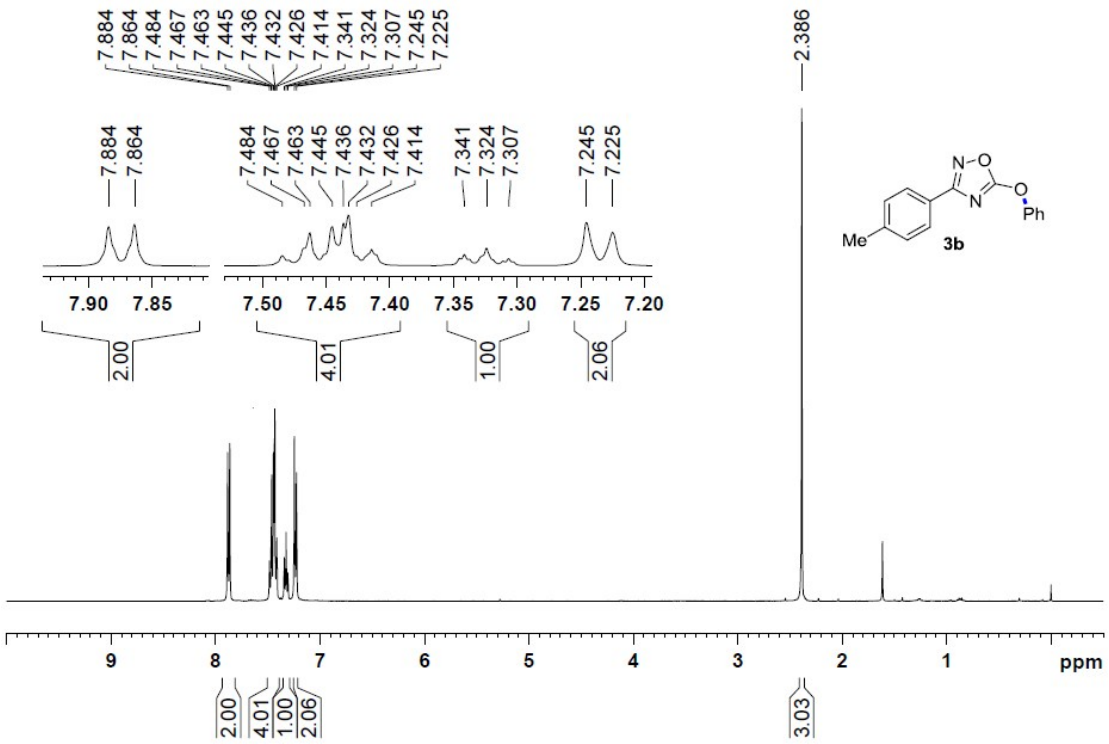
9. ^{1}H and ^{13}C NMR spectra of the products

^{1}H-NMR



^{13}C-NMR

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7.432
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7.414
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7.324
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7.245
7.225
2.386
7.90
7.85
7.50
7.45
7.40
7.35
7.30
7.25
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4.01
1.00
2.06
3.03
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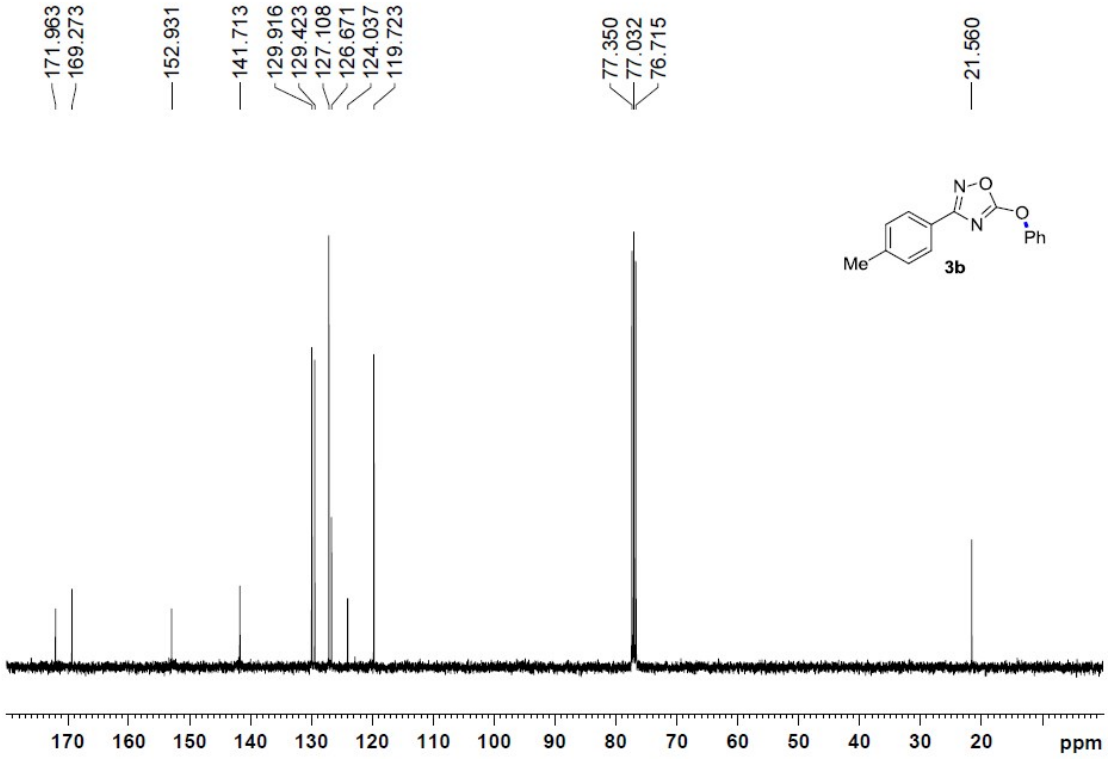
8
7
6
5
4
3
2
1
ppm
N
O
N
O
Ph
Me
3b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141.713
129.916
129.423
127.108
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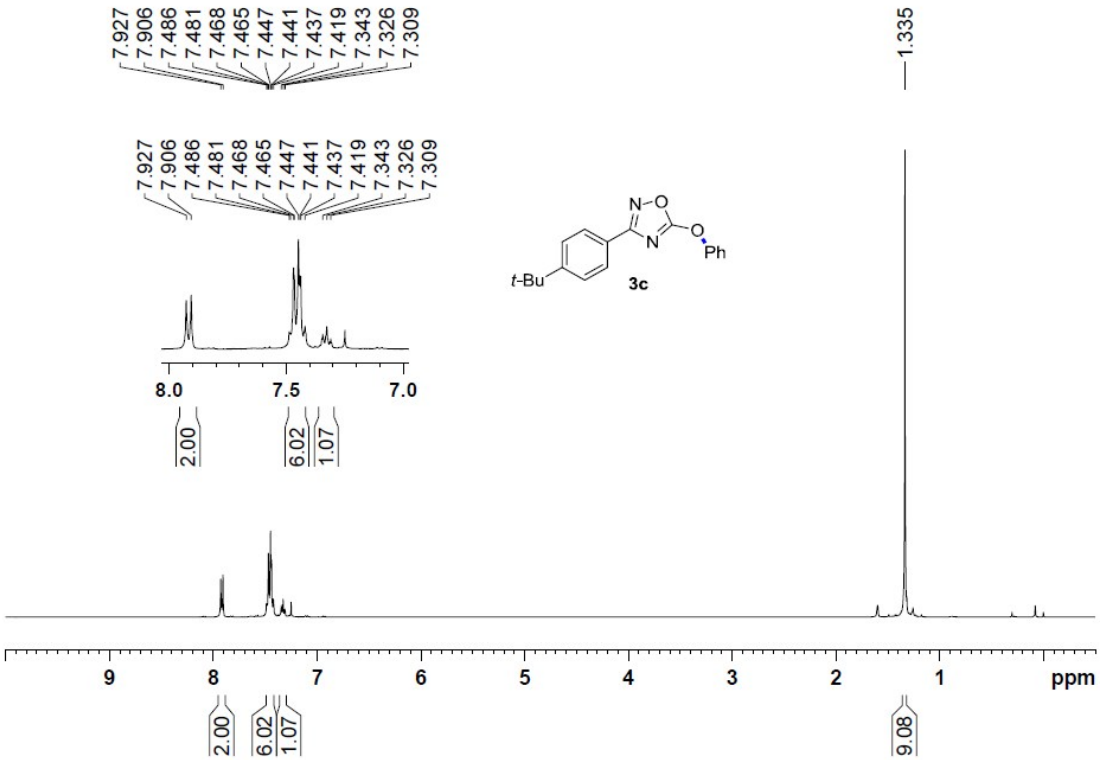
^{1}H-NMR



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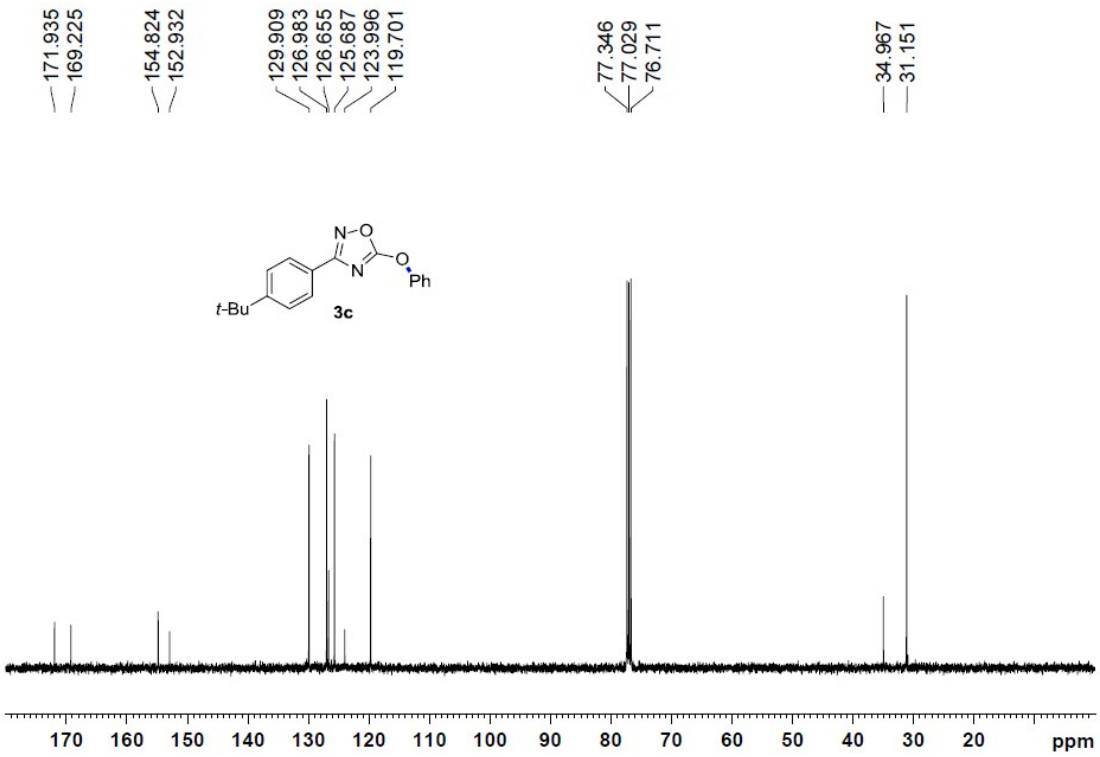

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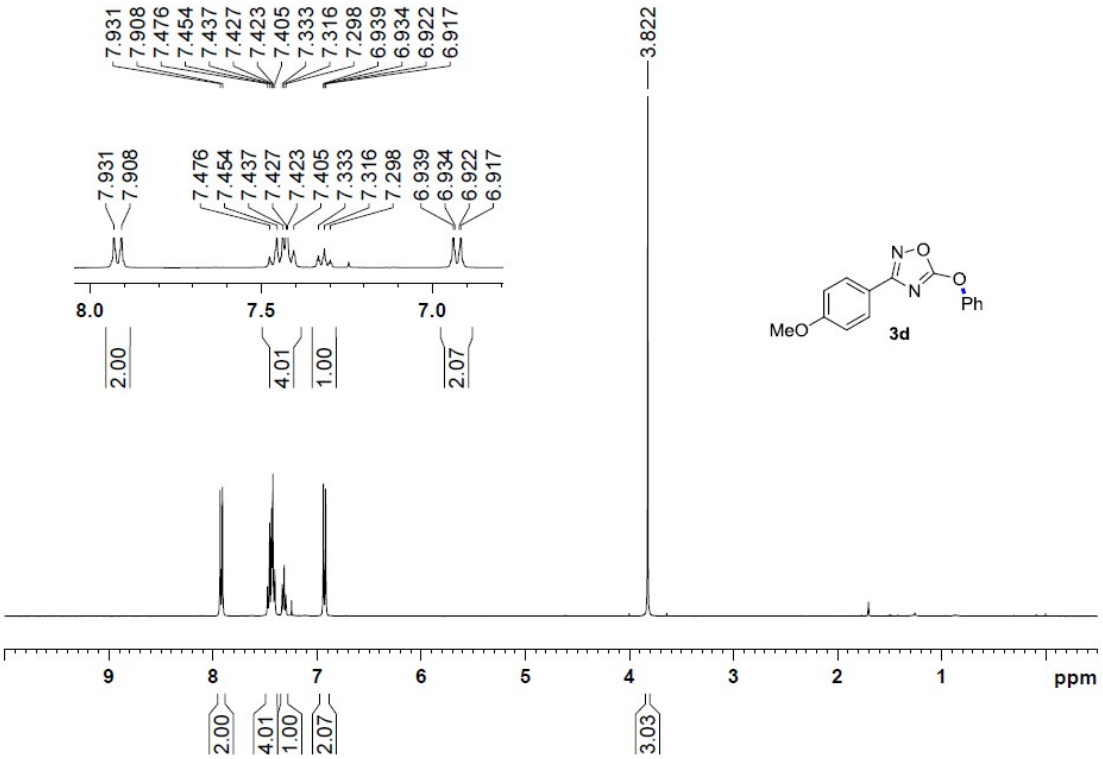

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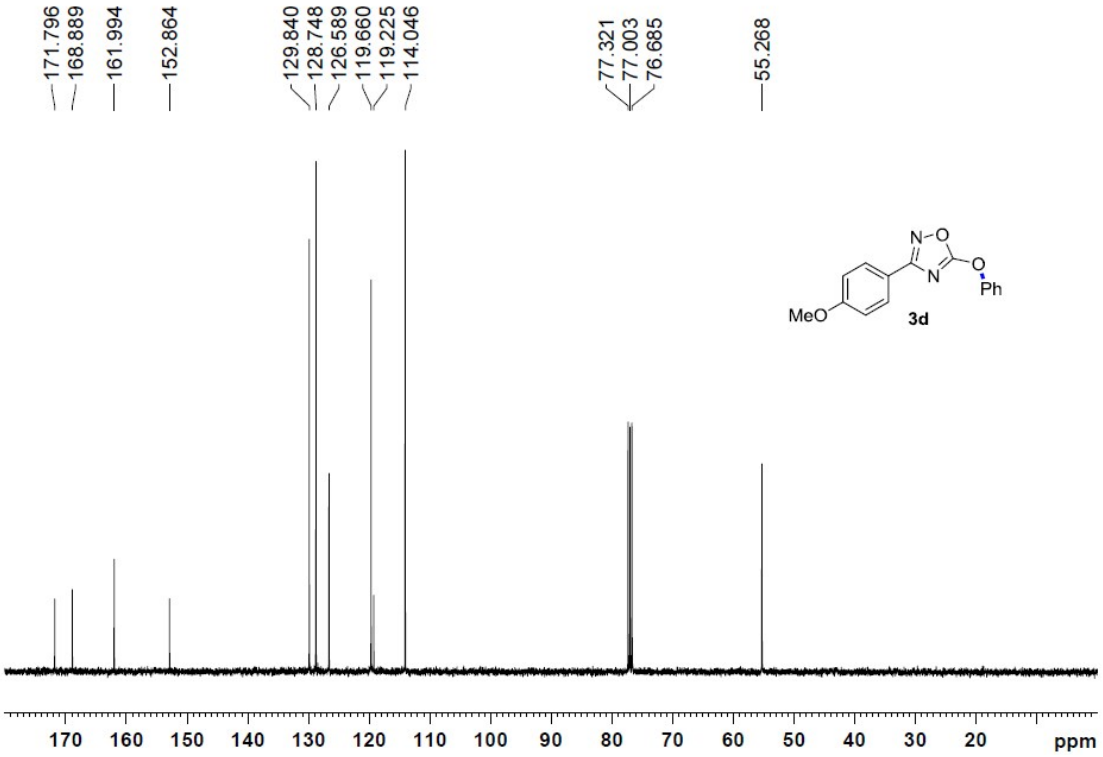

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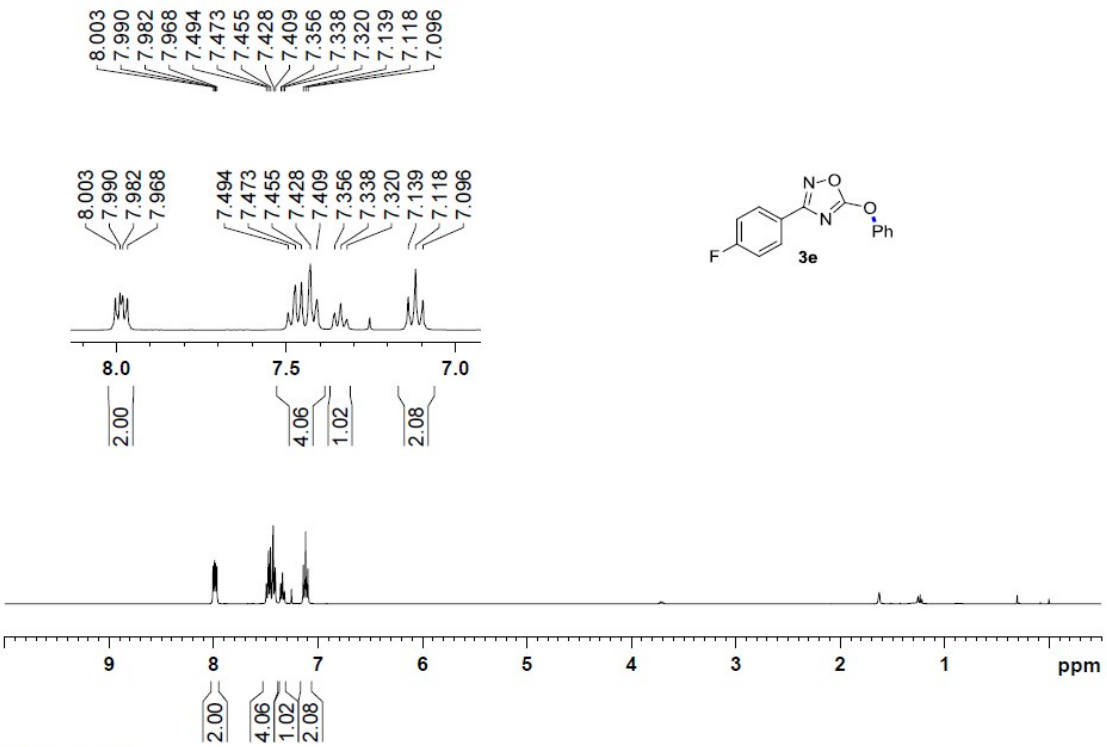

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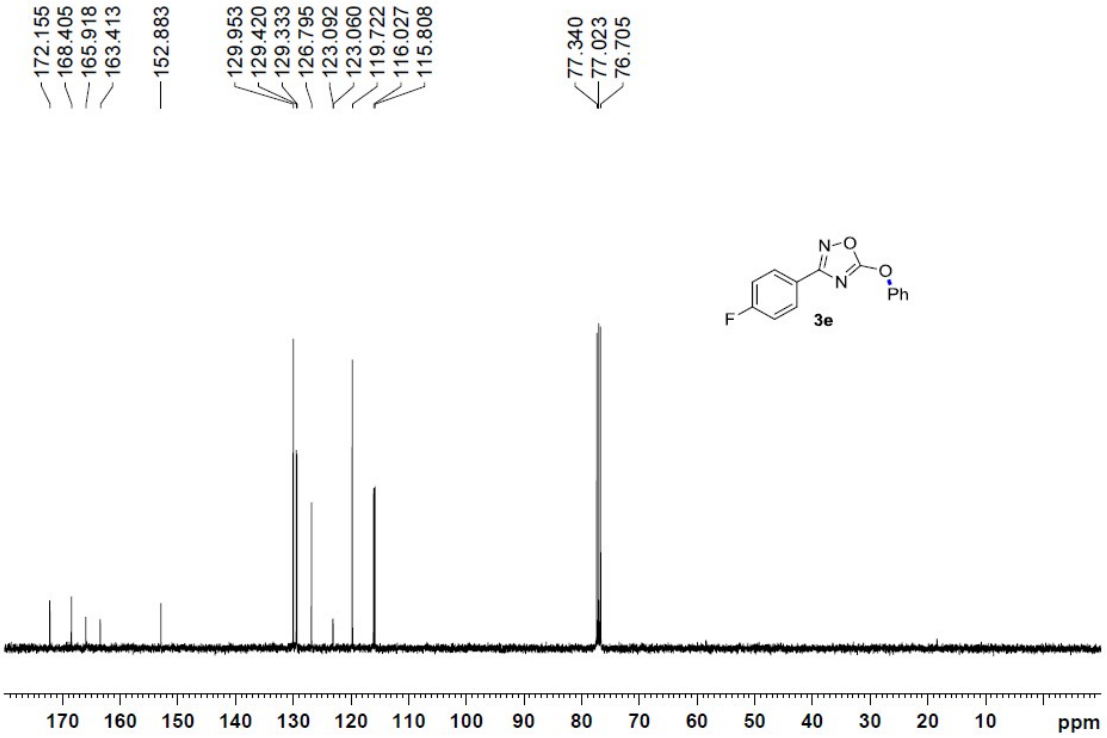

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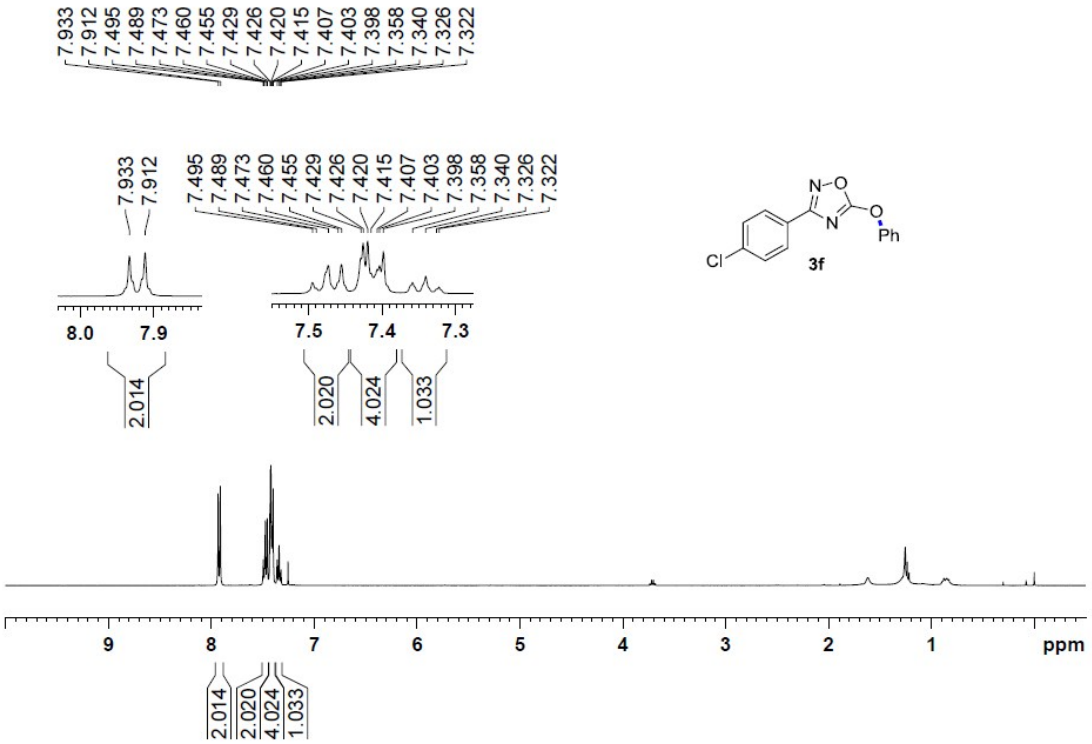

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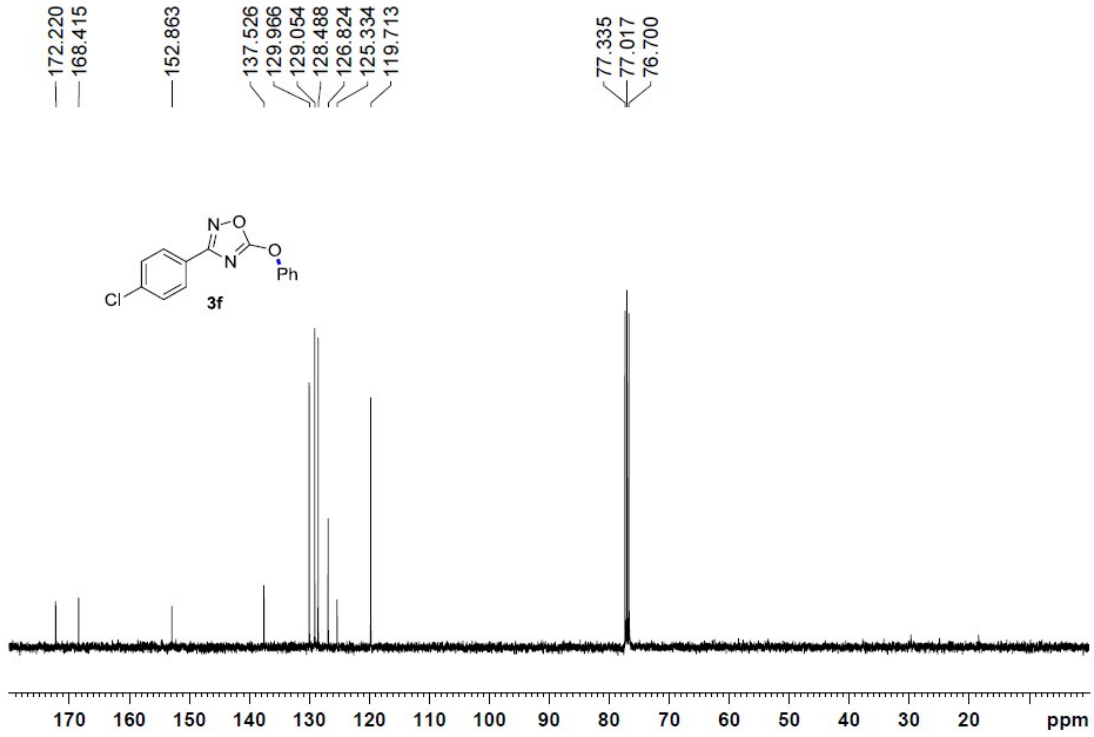

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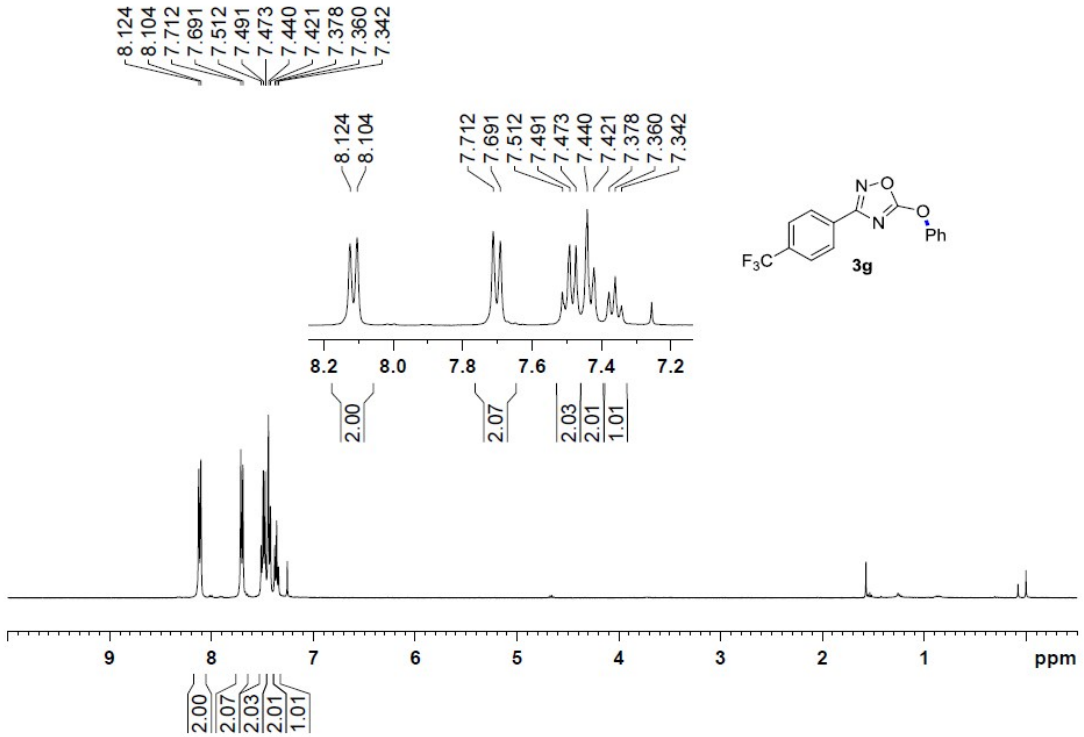

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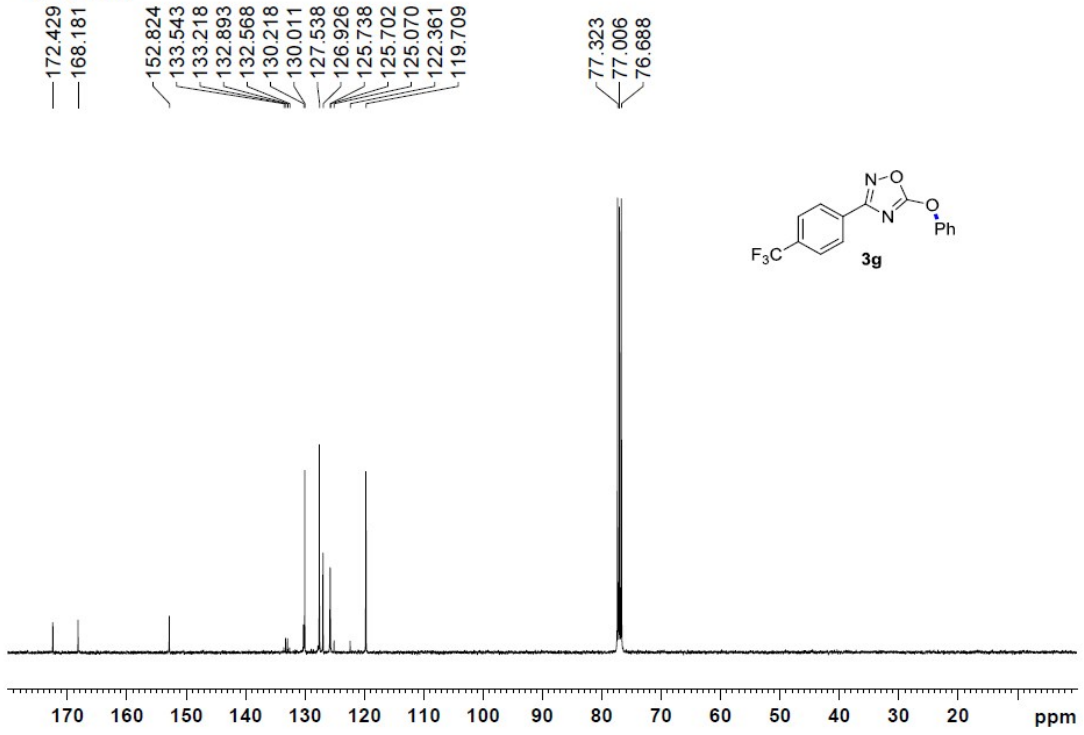

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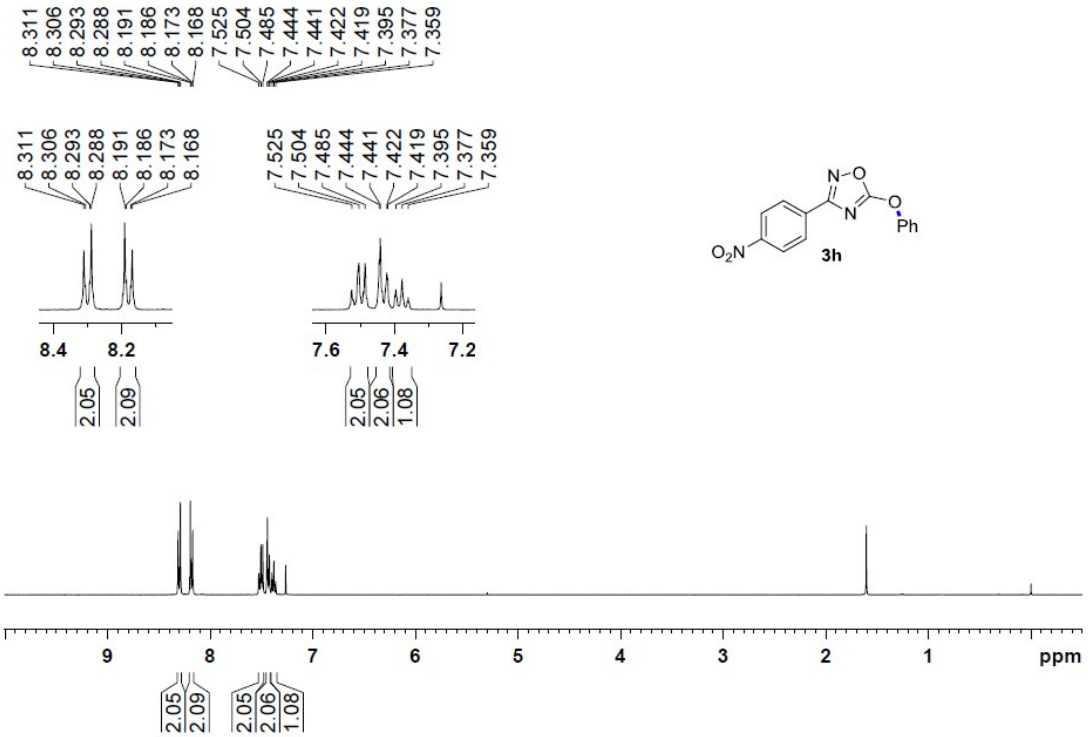

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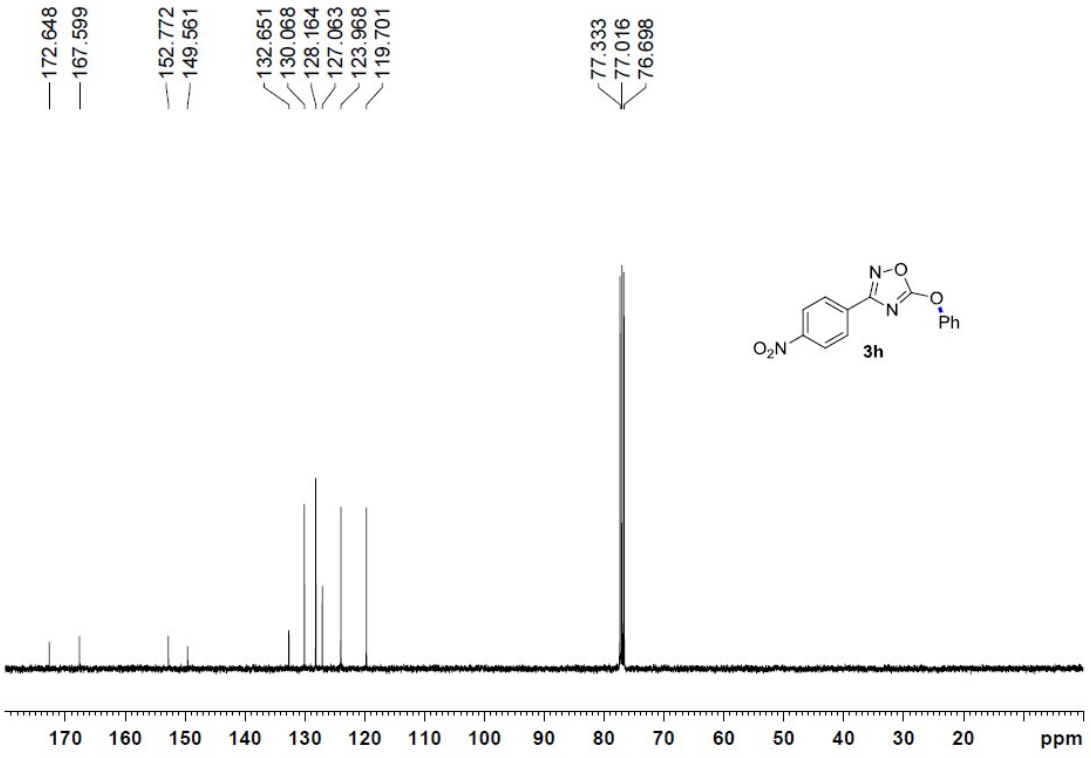

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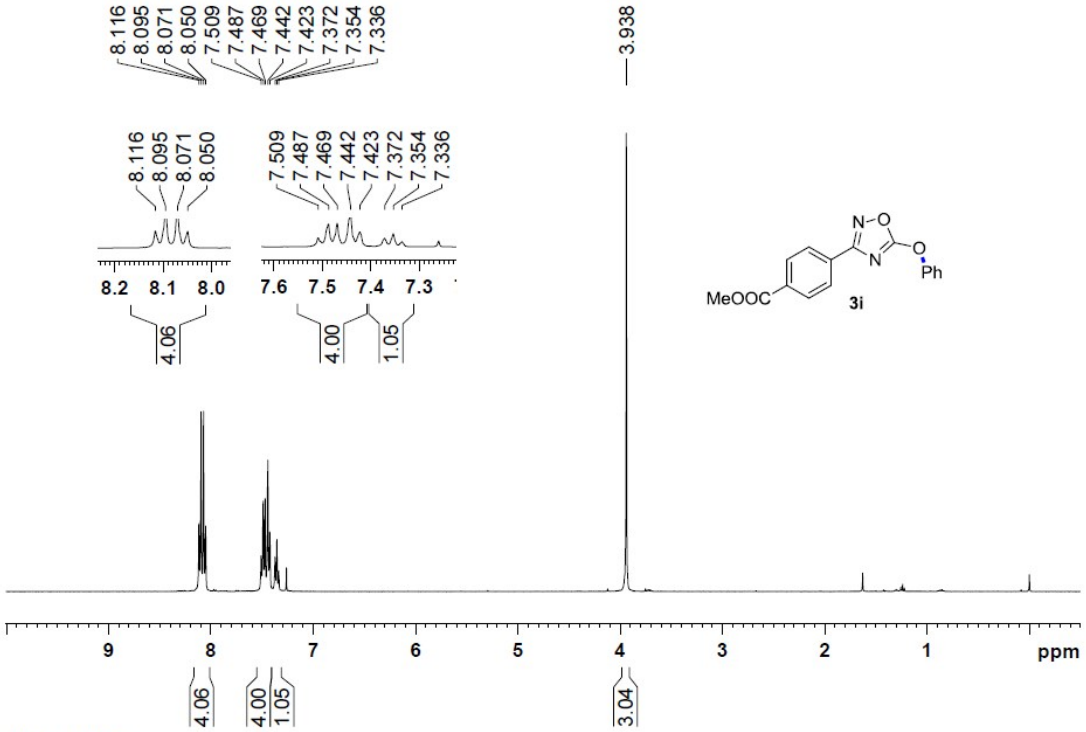

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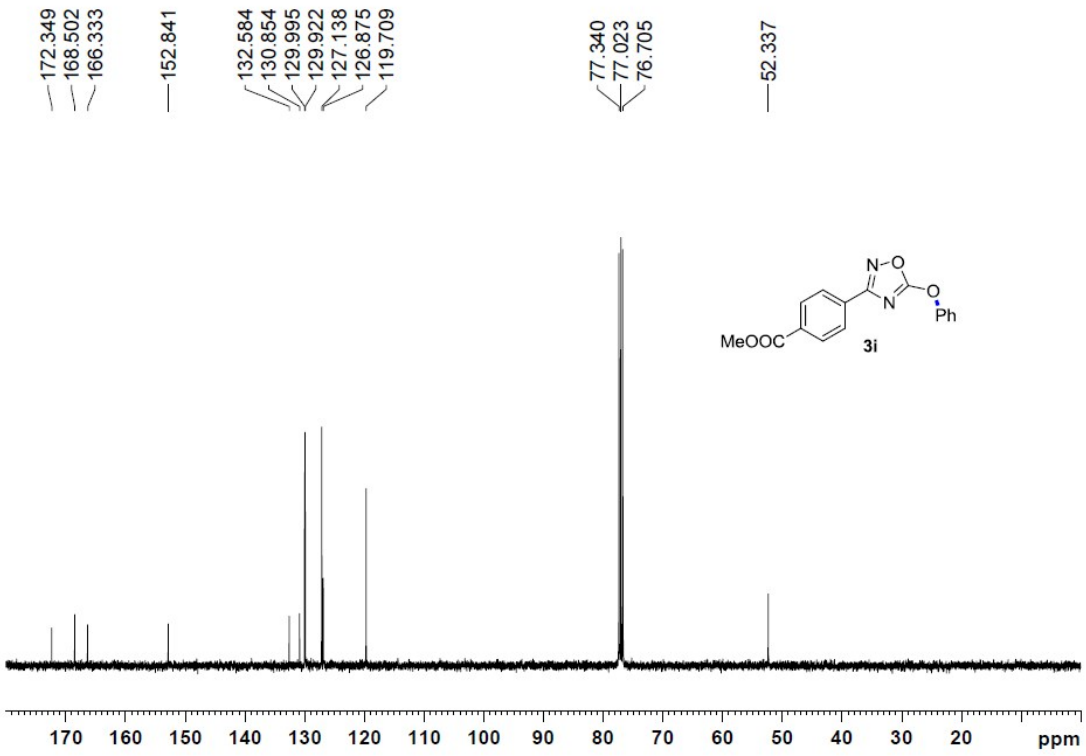

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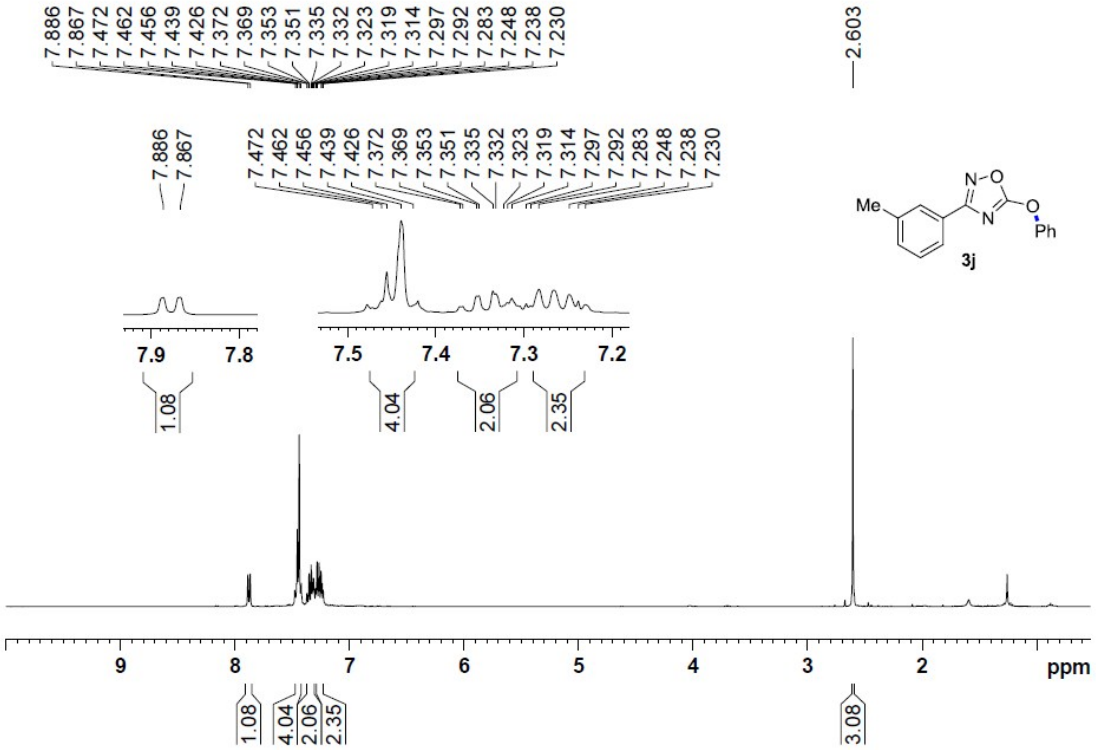

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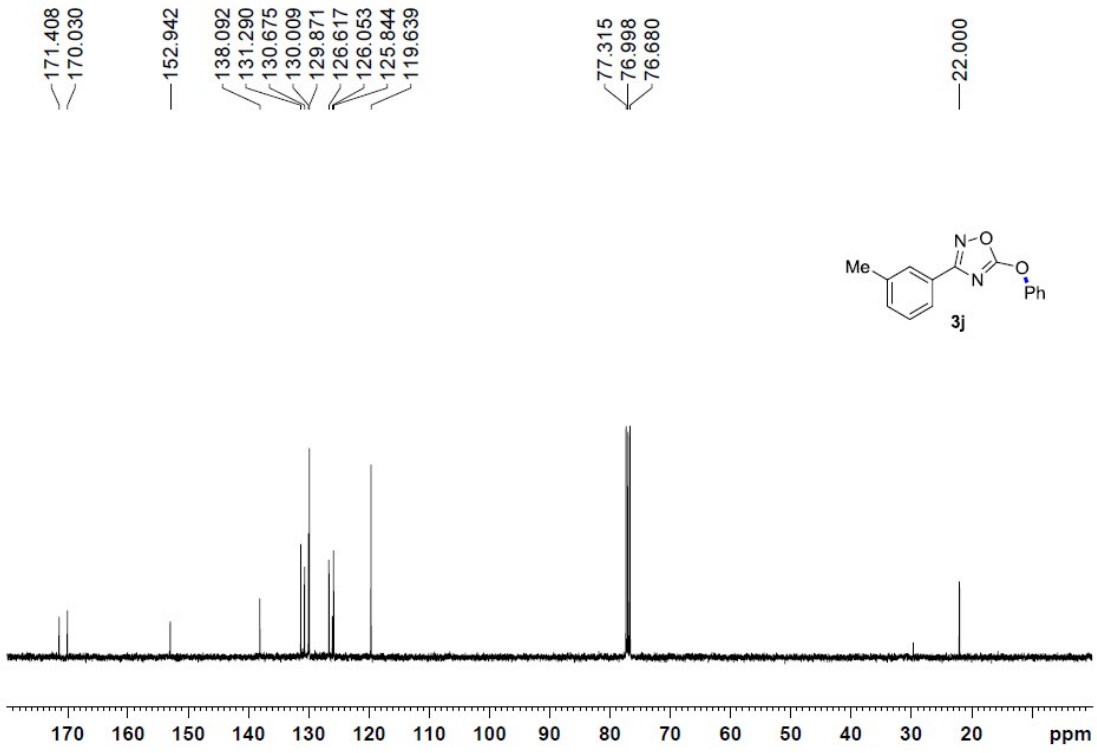

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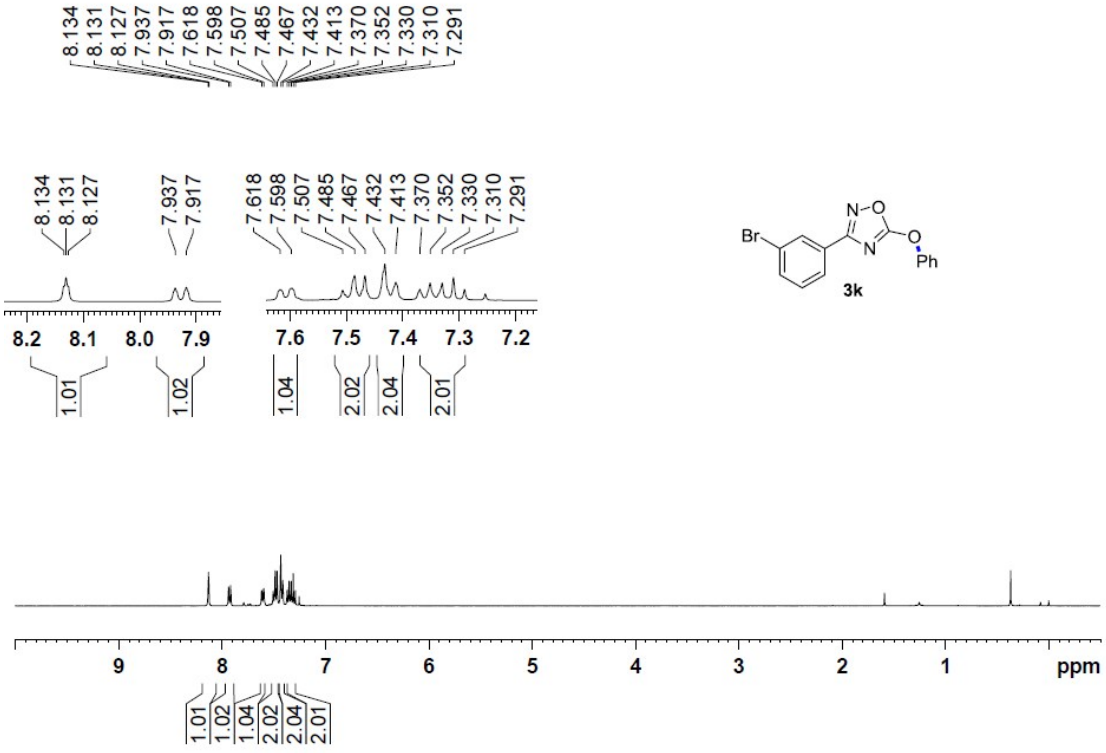

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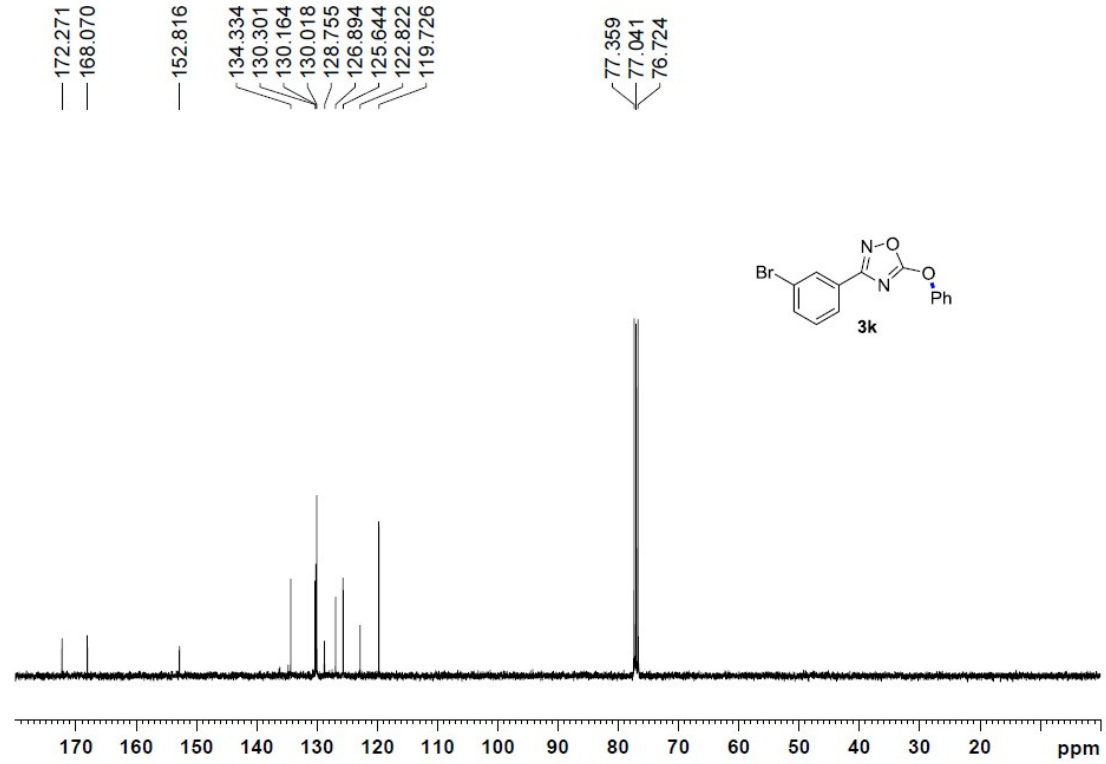

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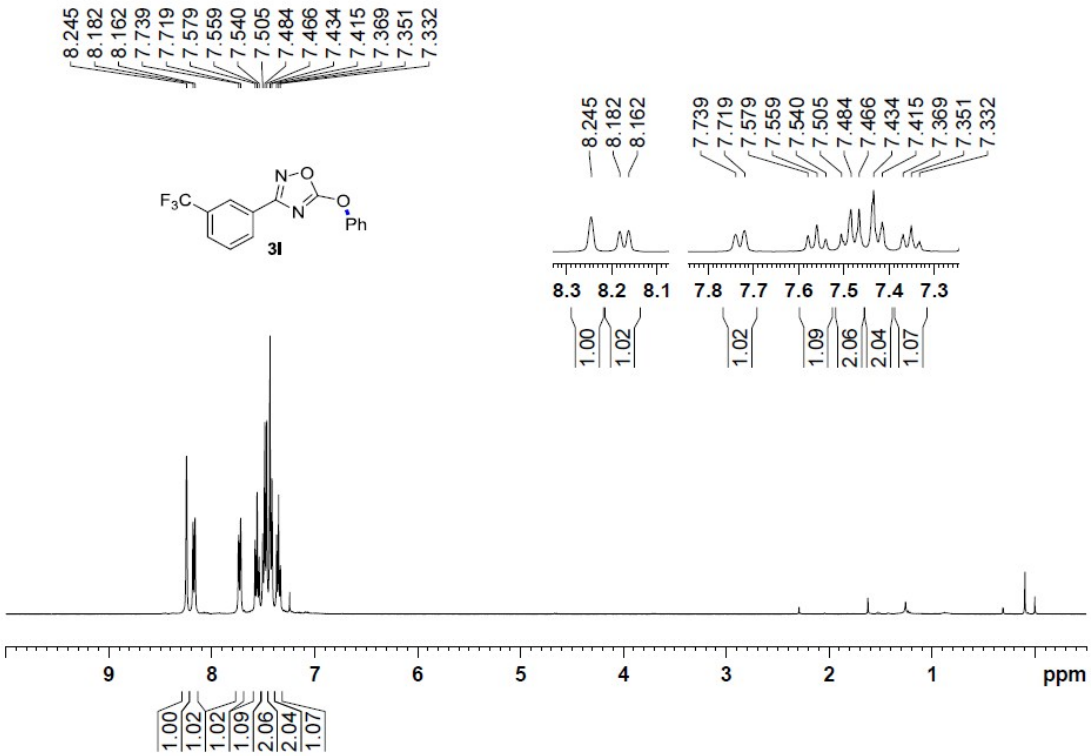

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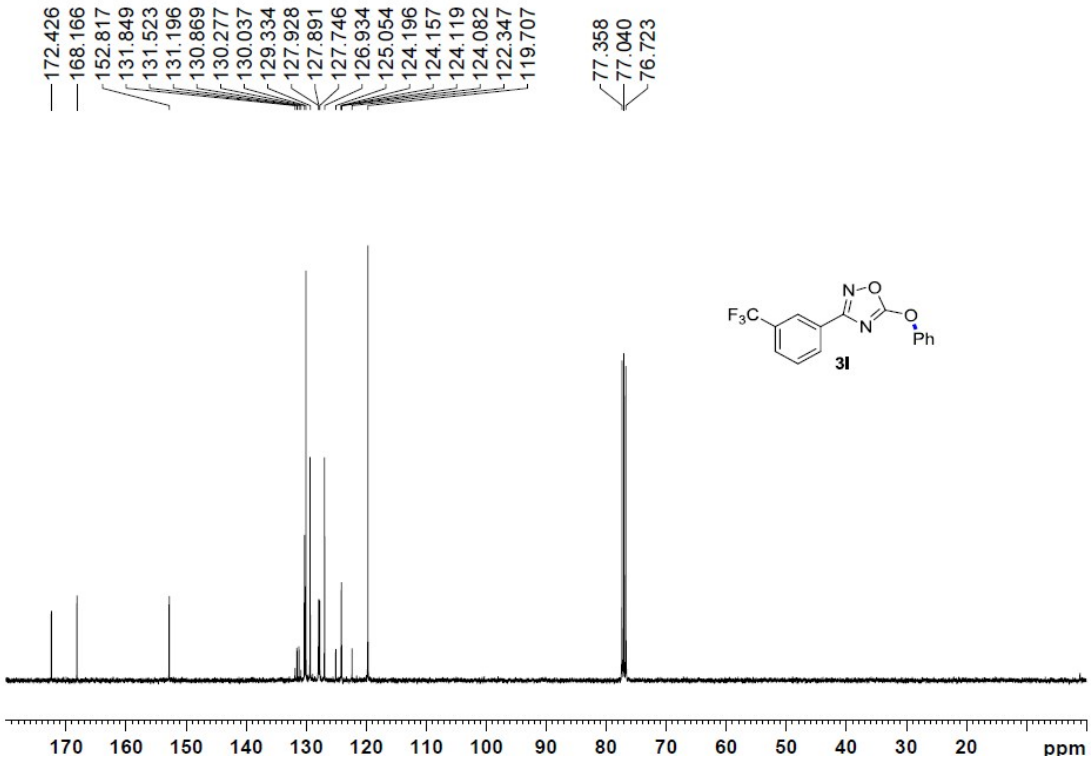

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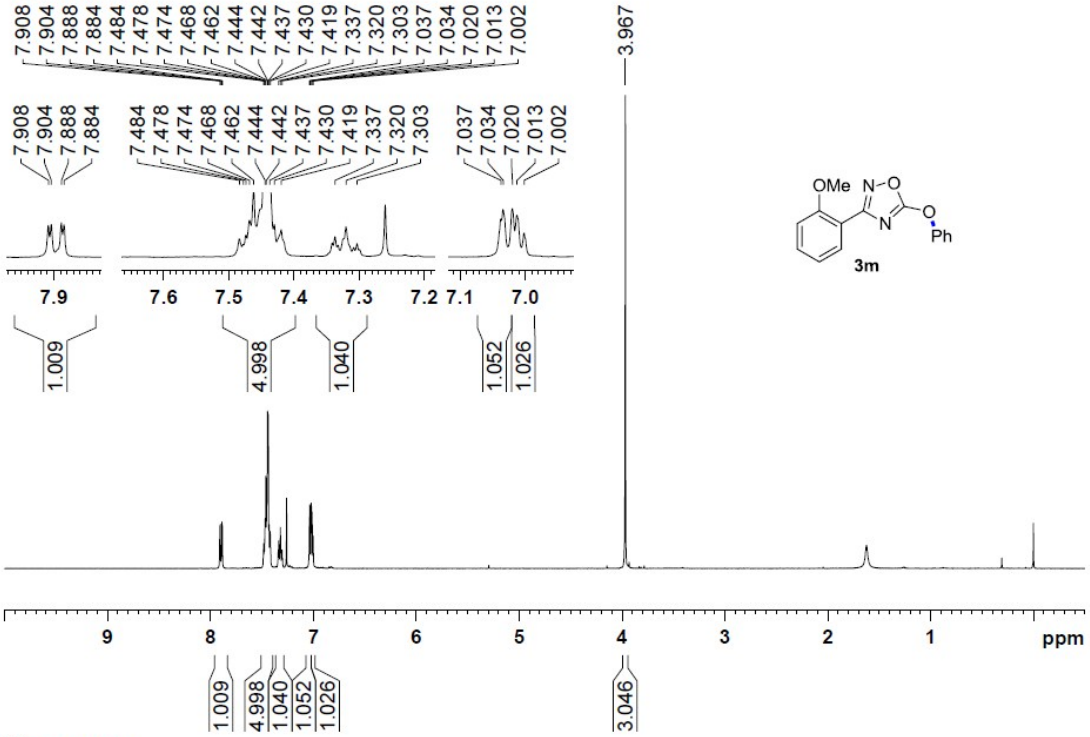

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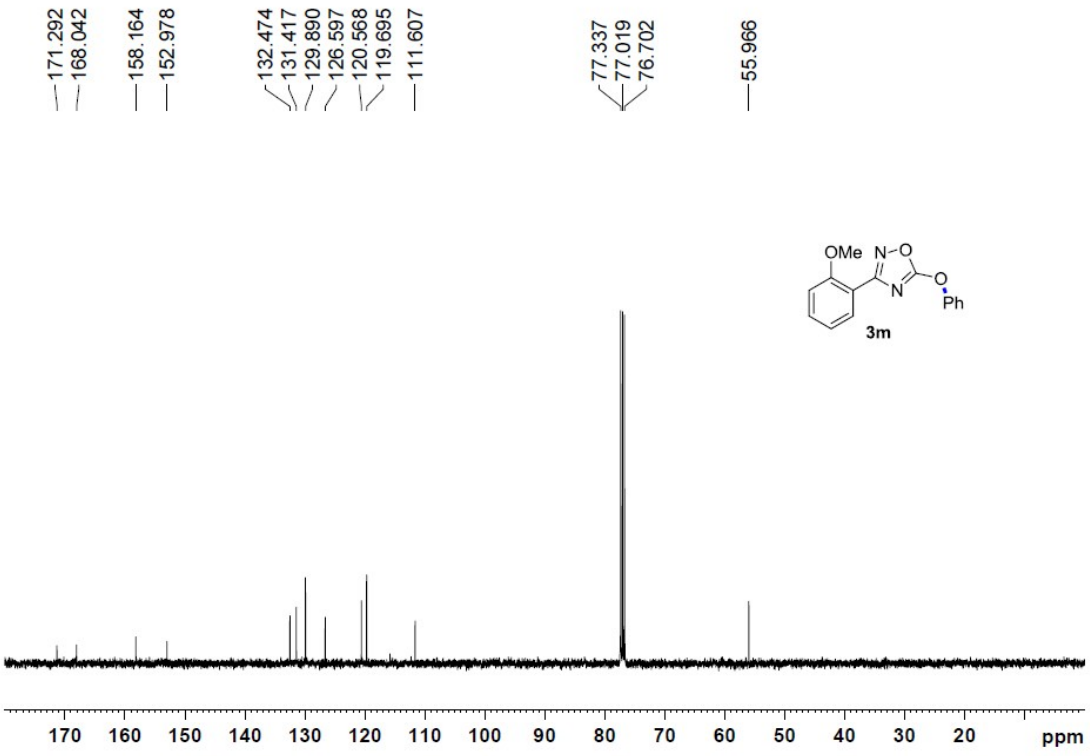

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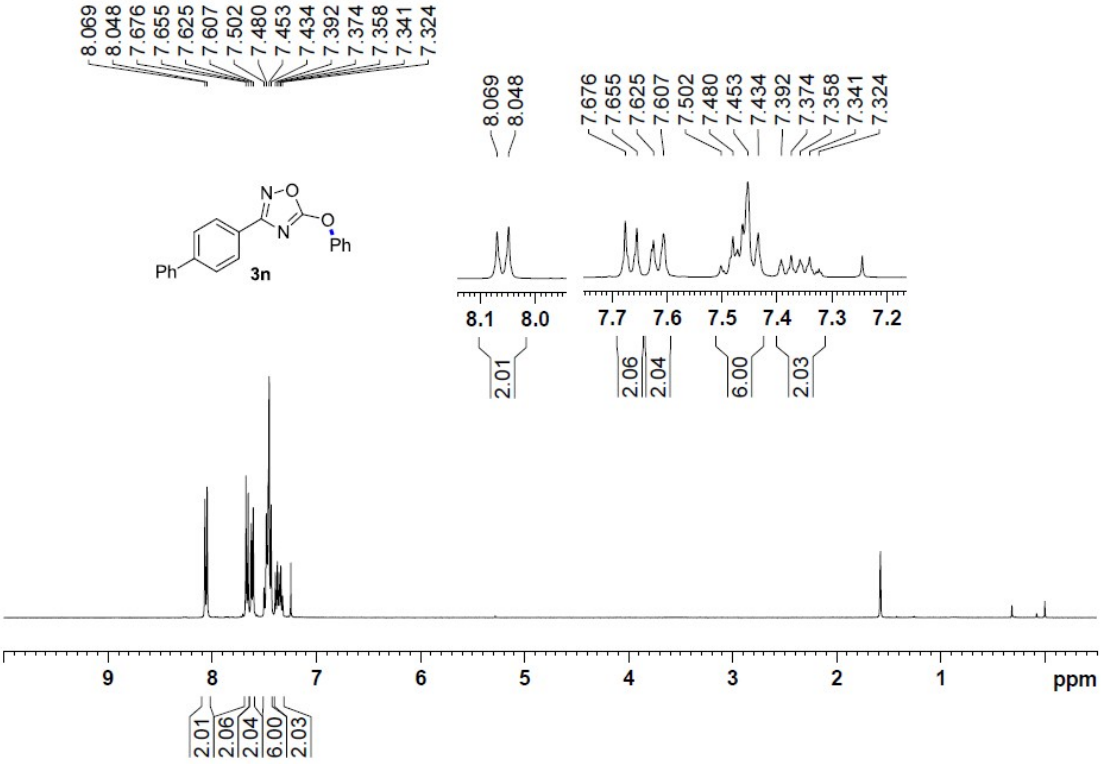

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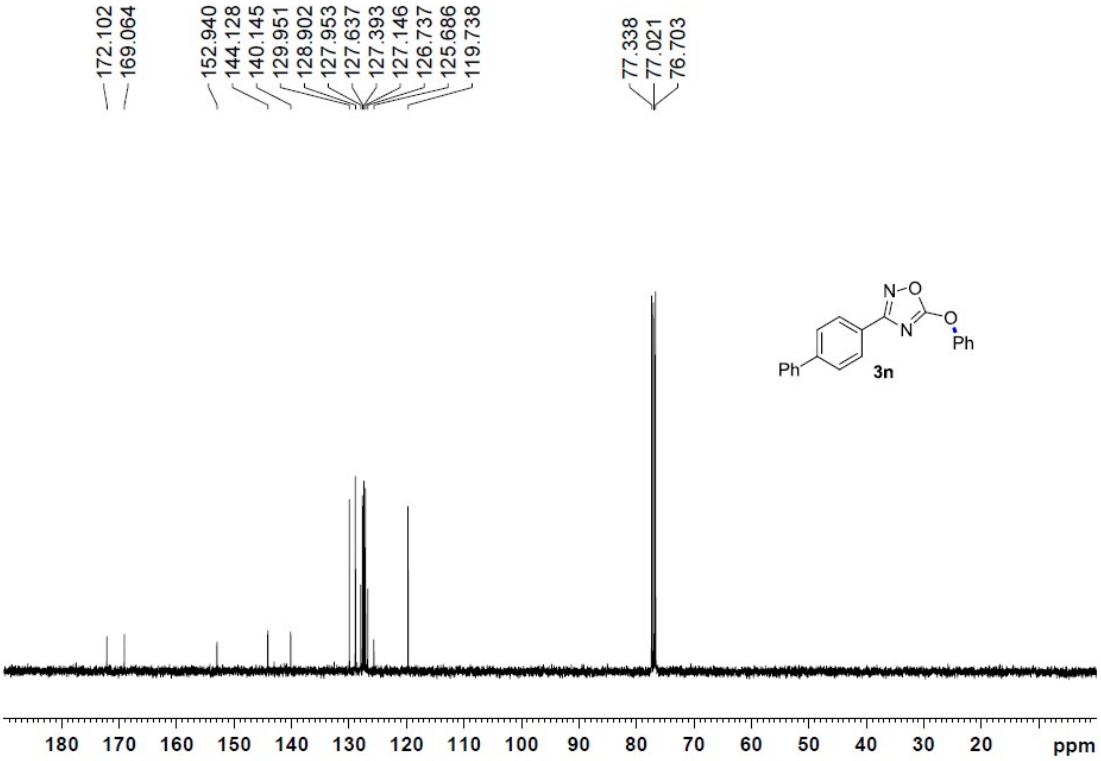

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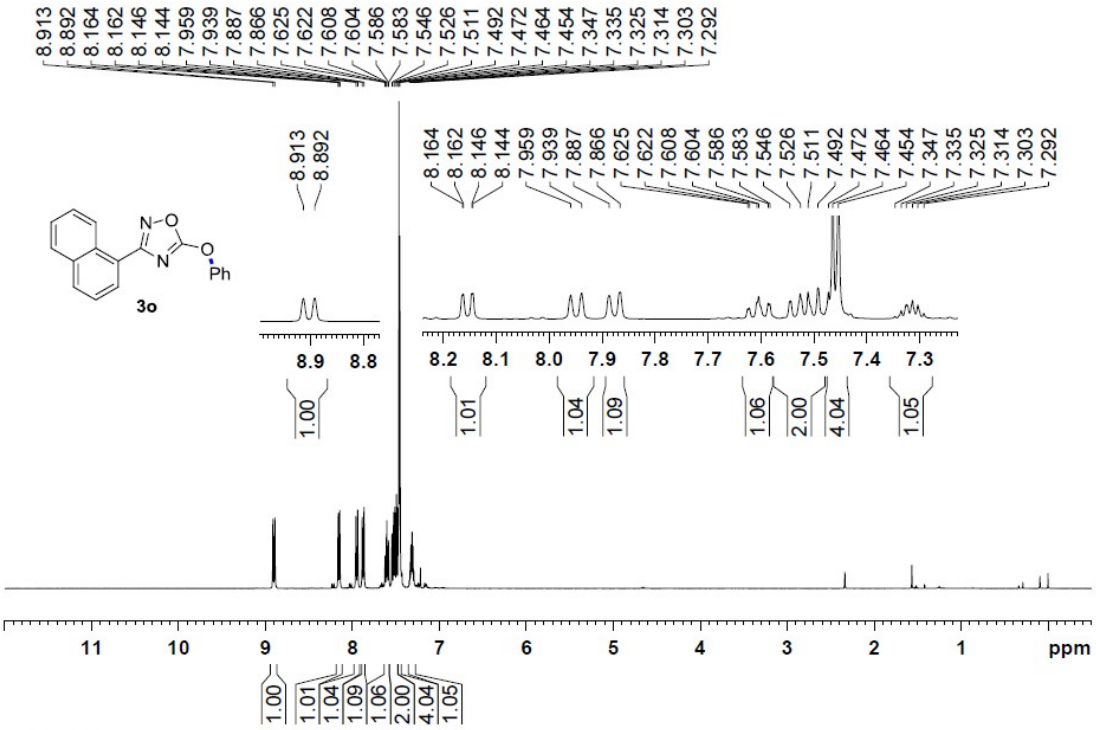

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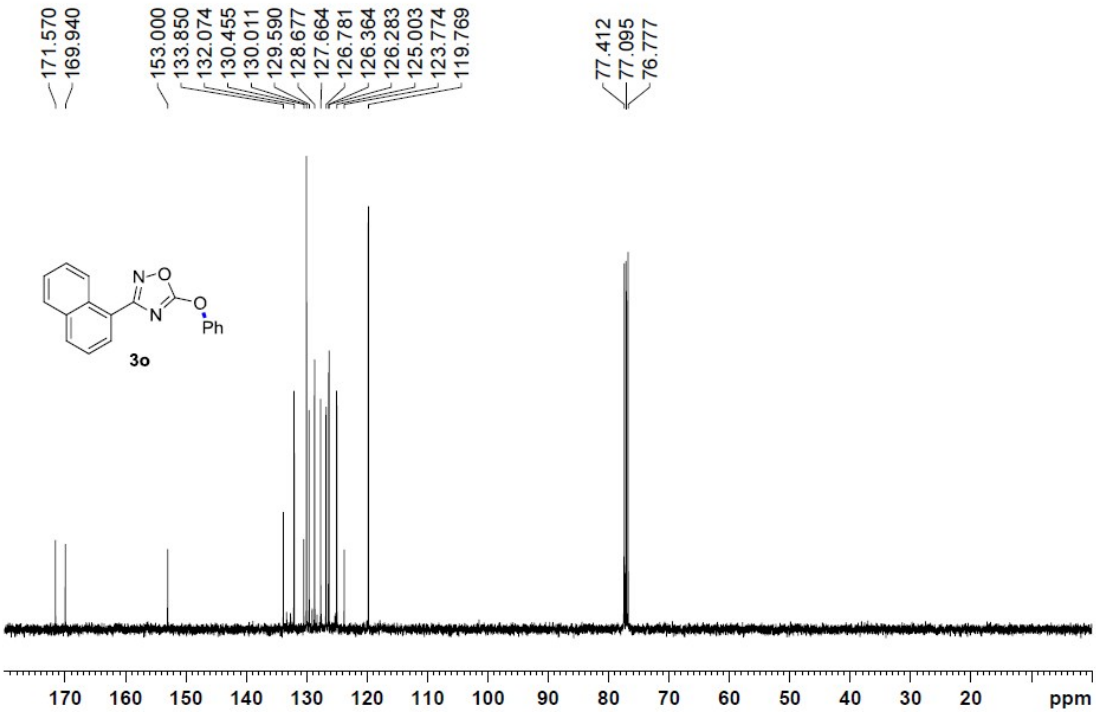

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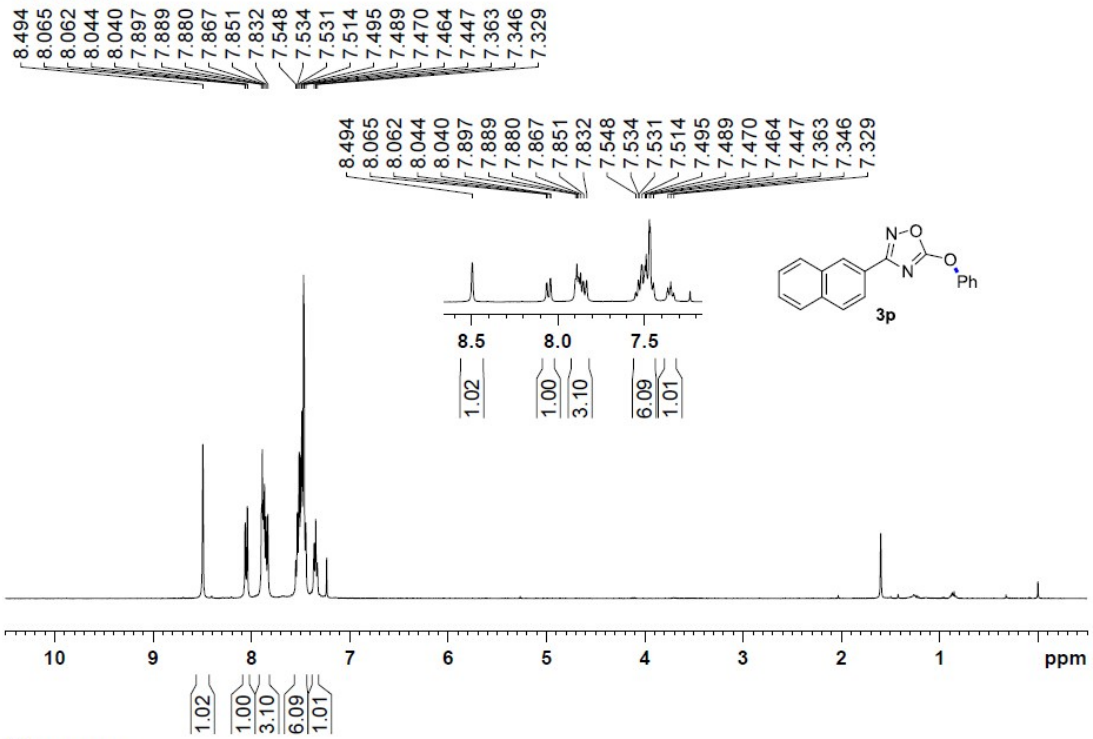

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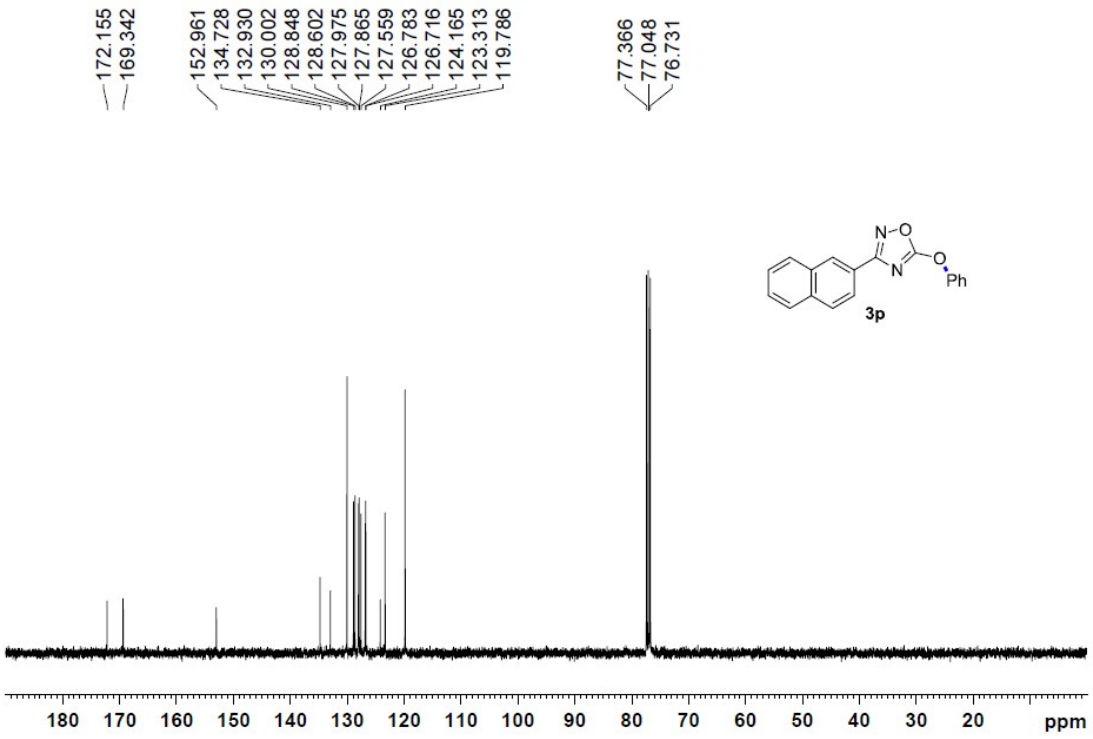

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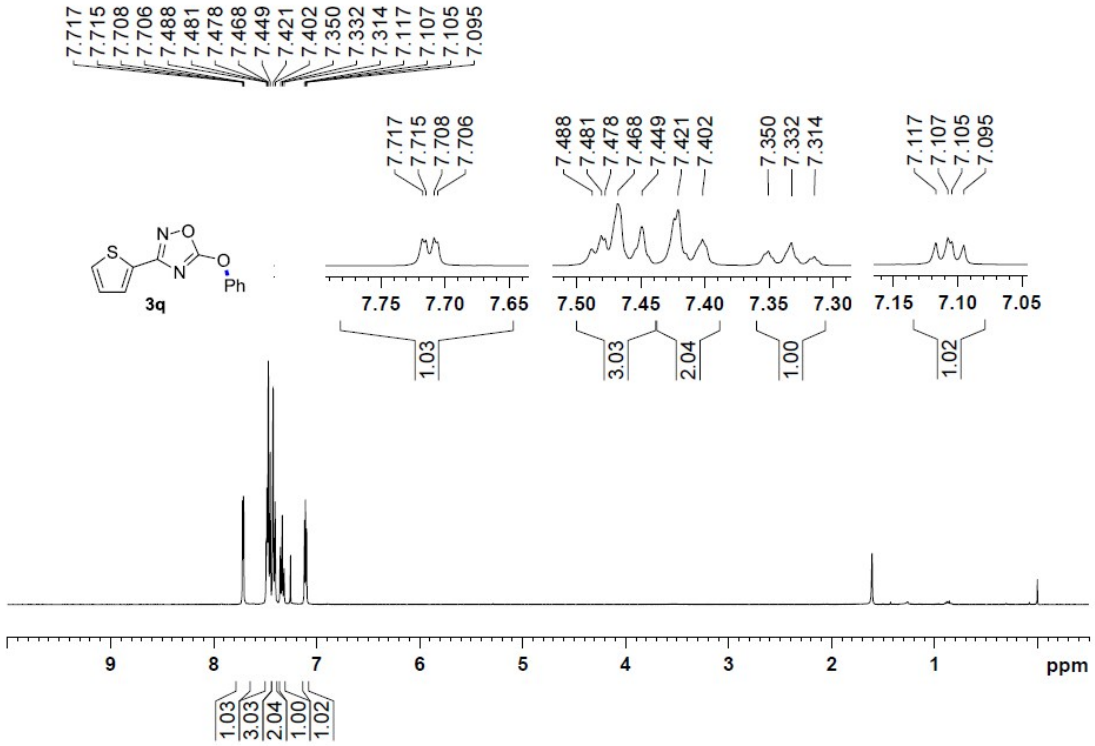

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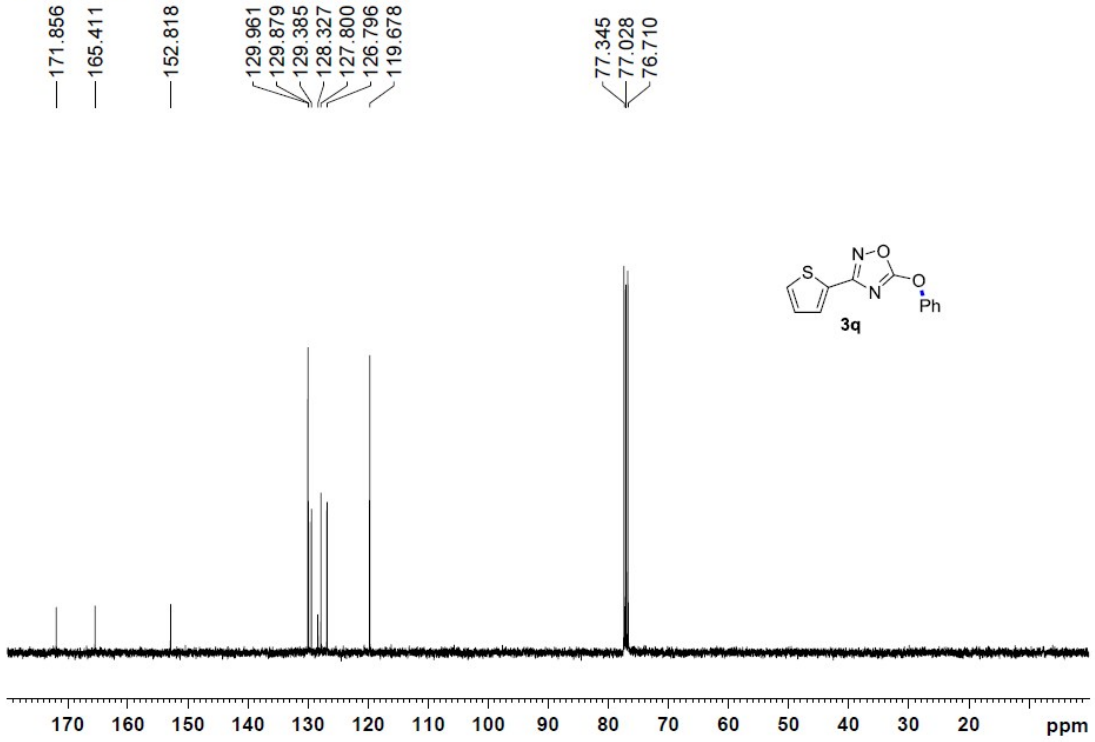

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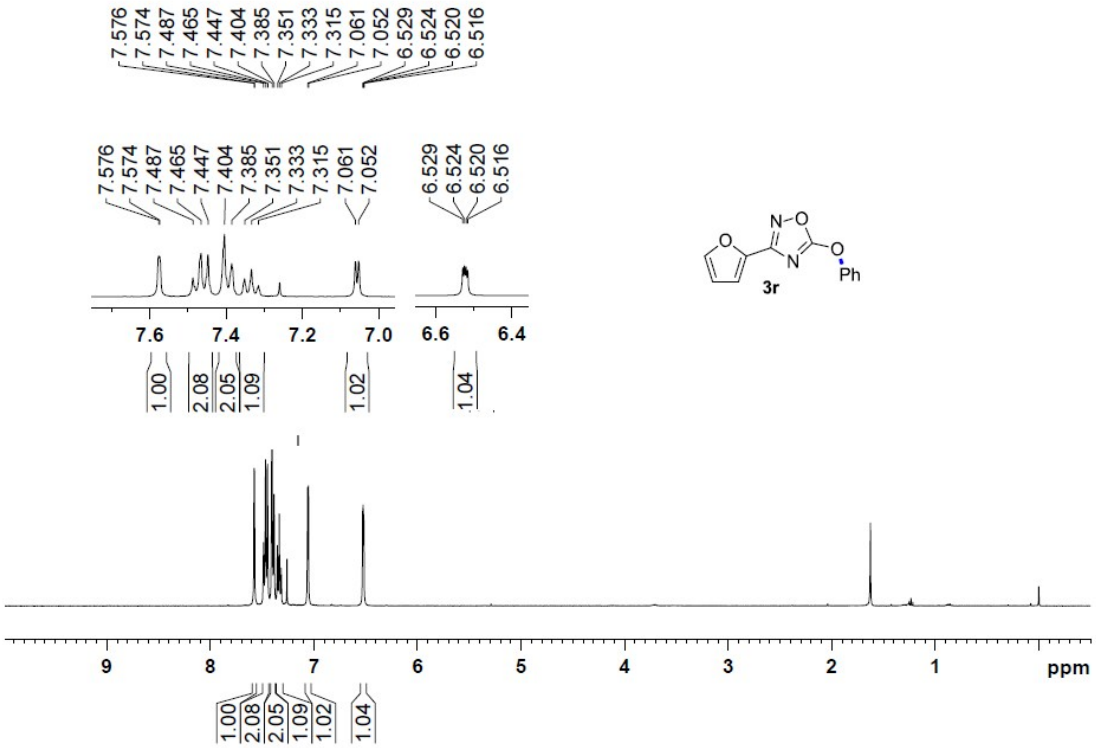

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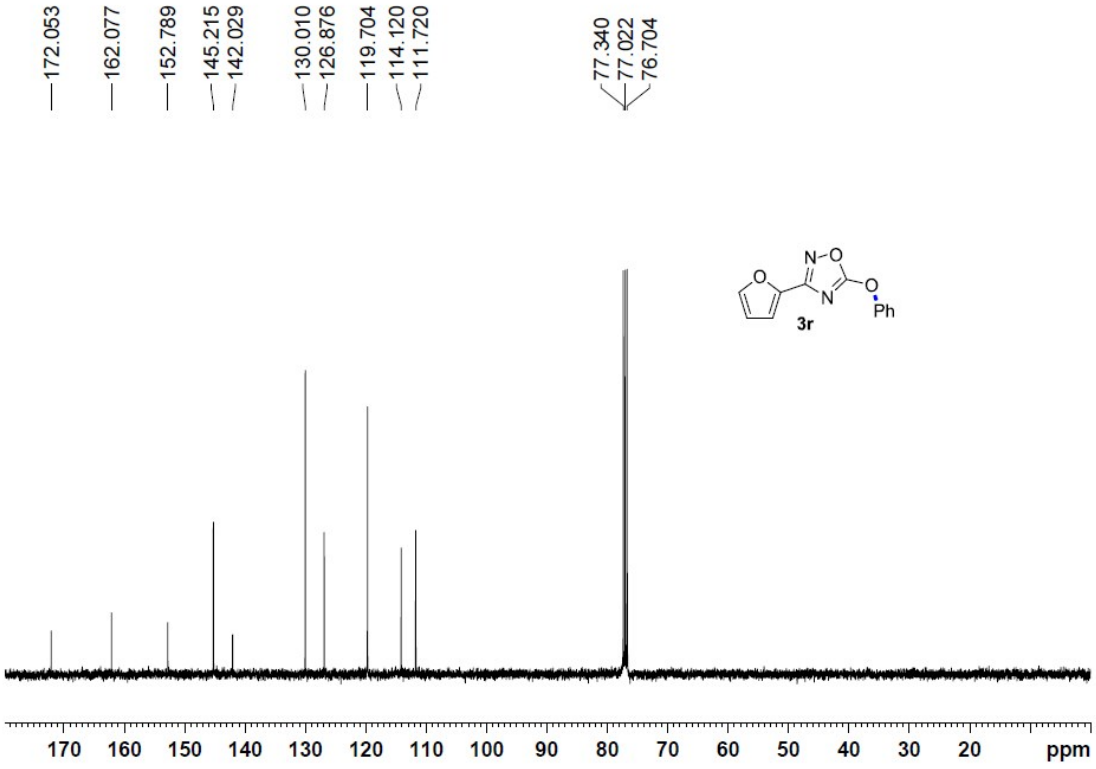

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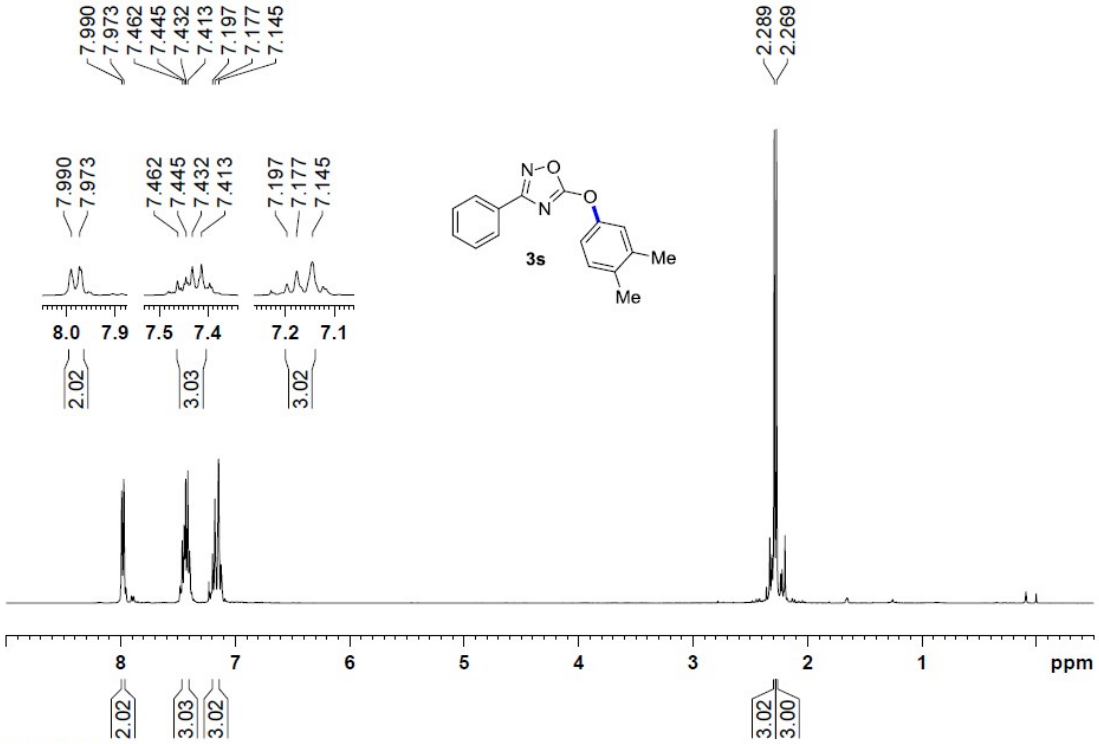

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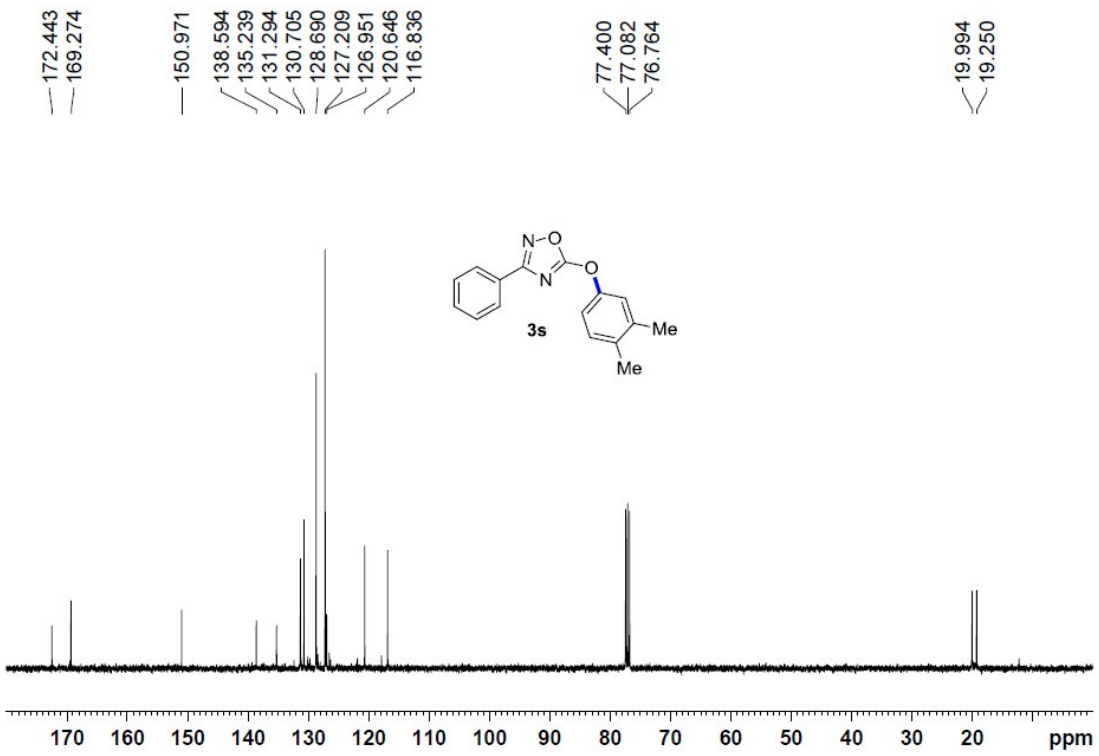

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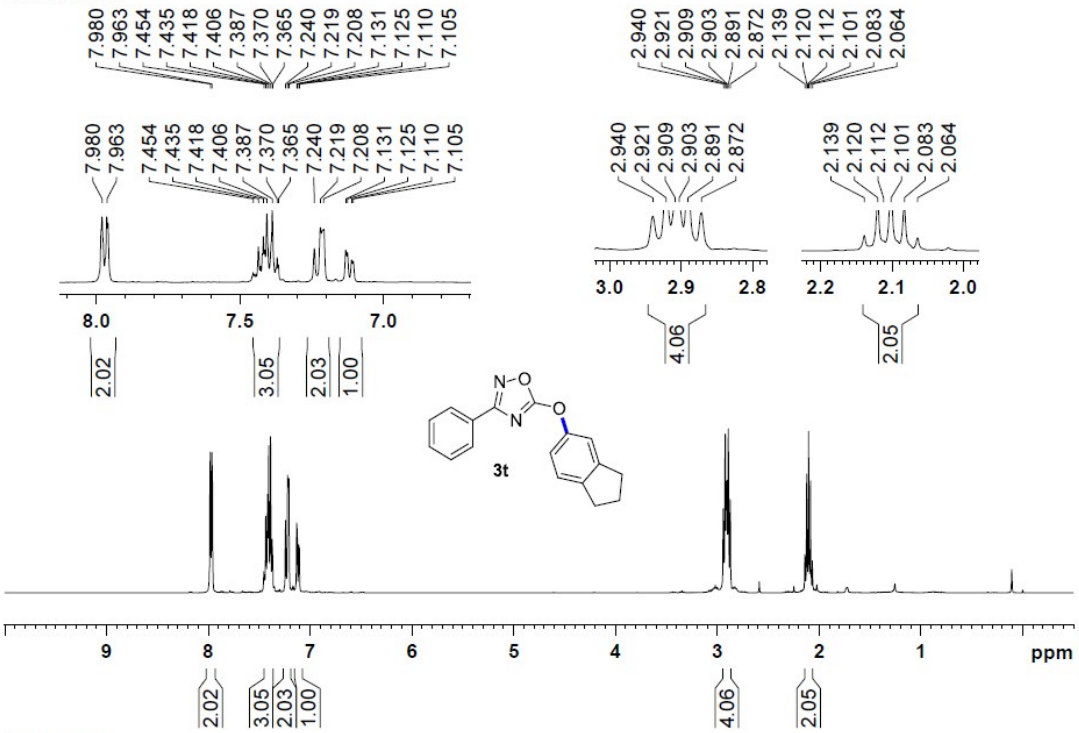
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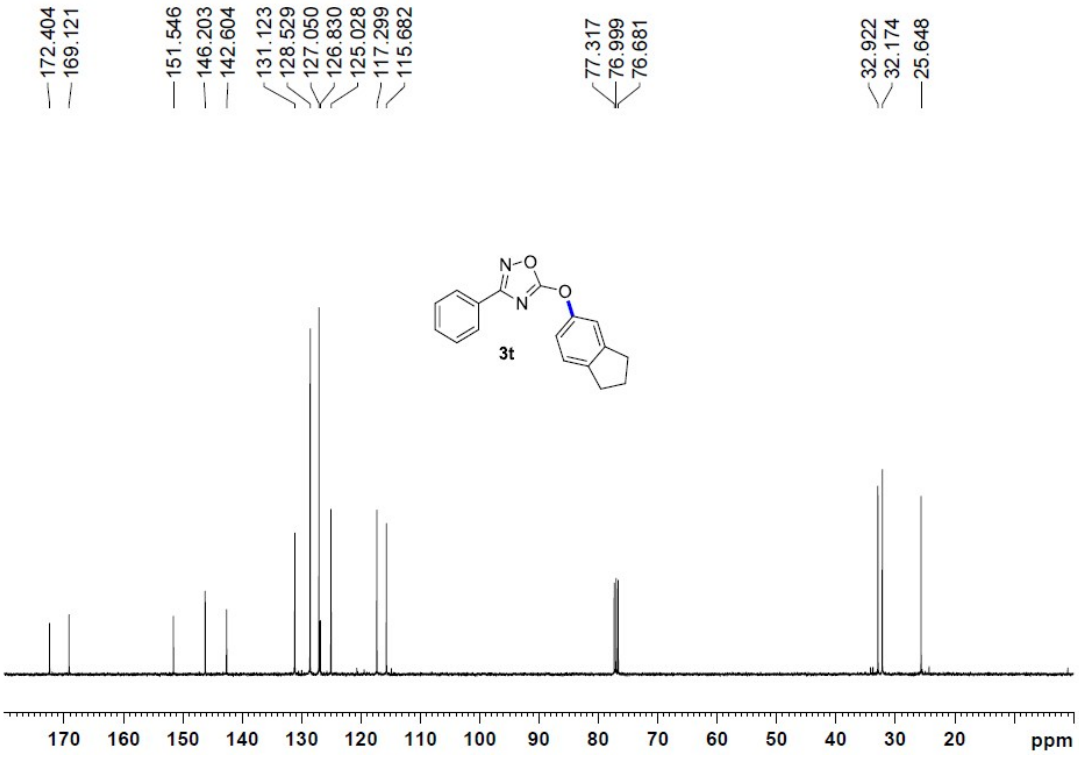
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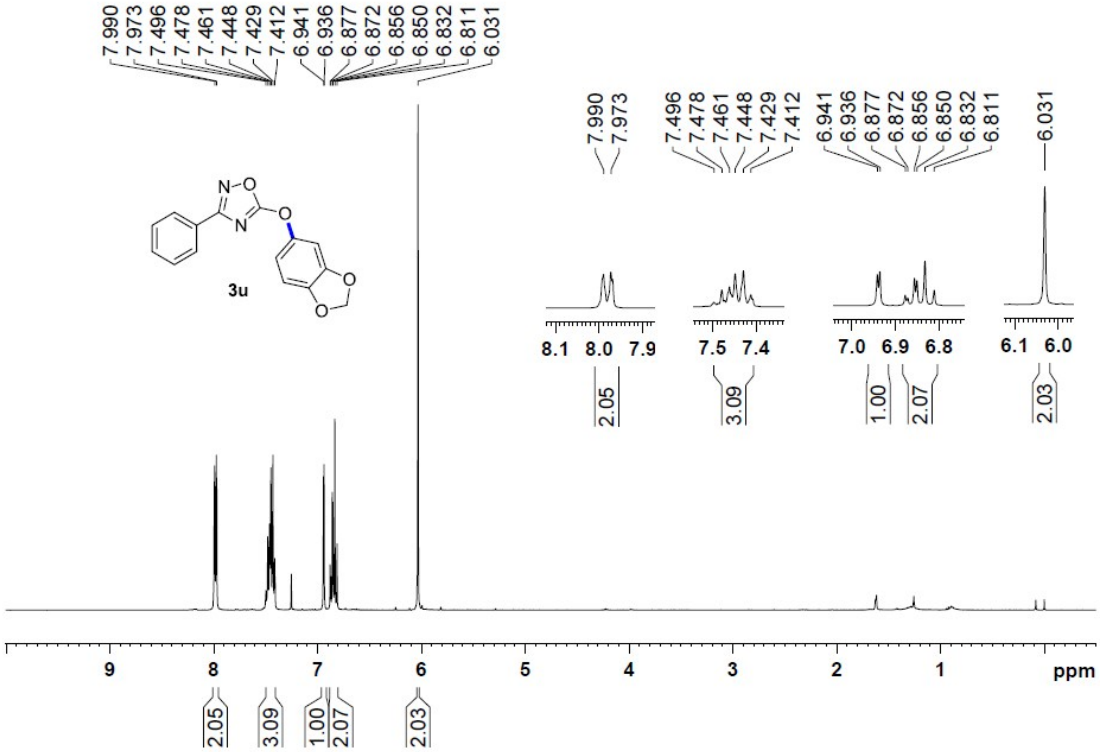

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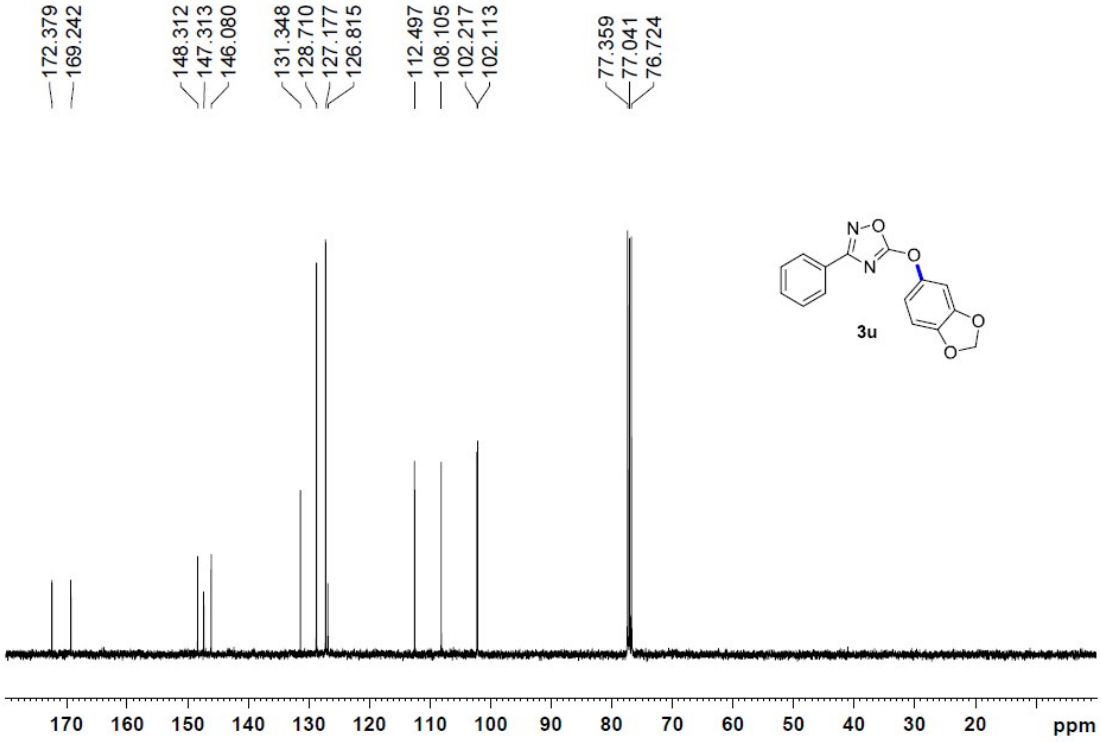

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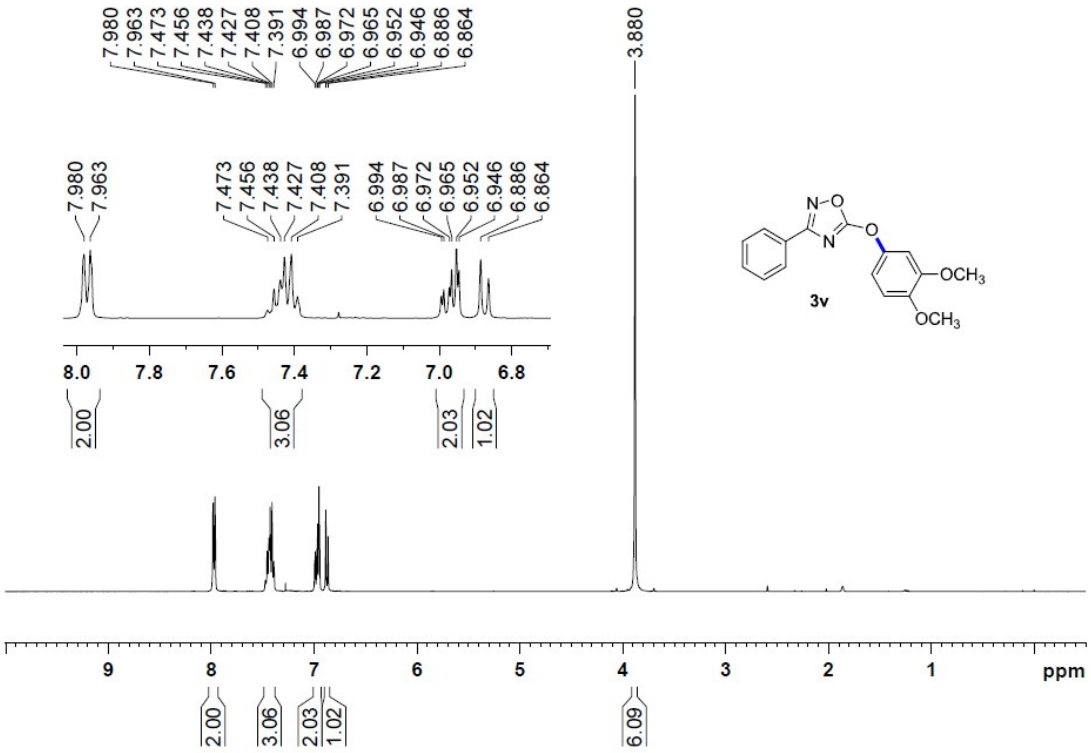

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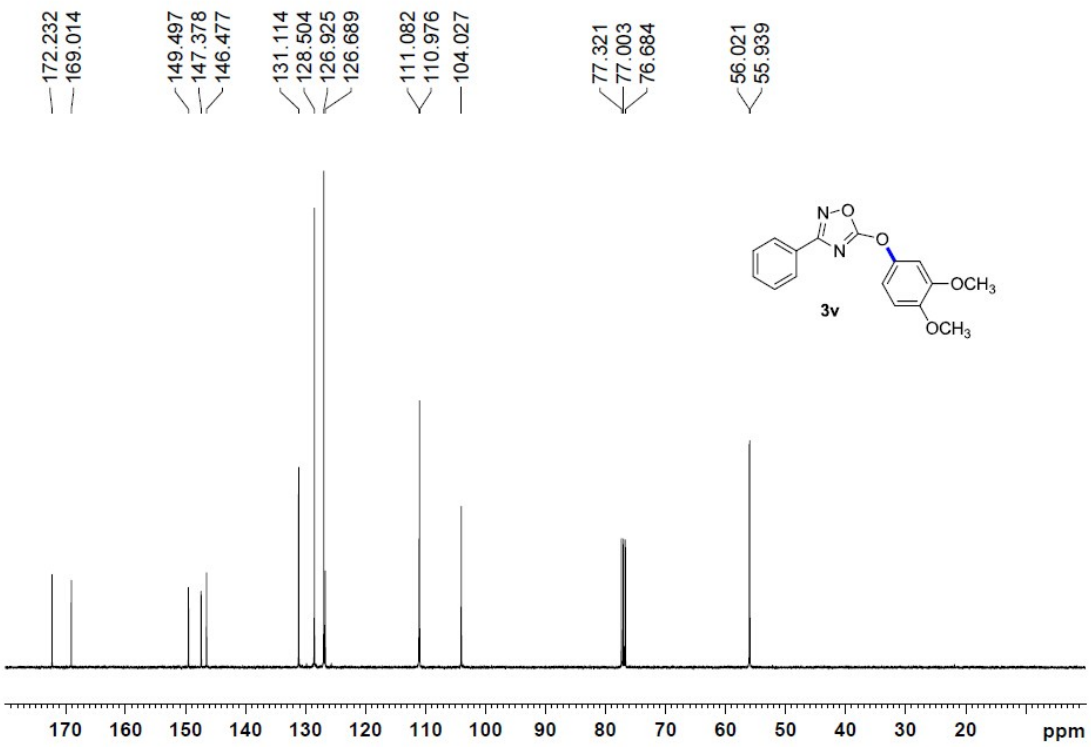

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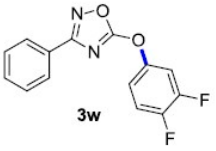

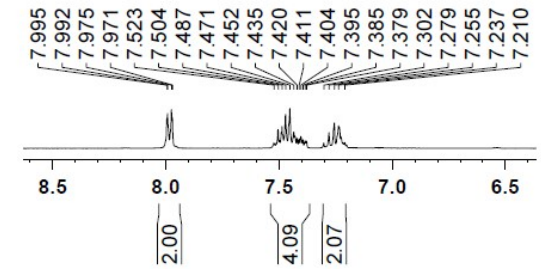

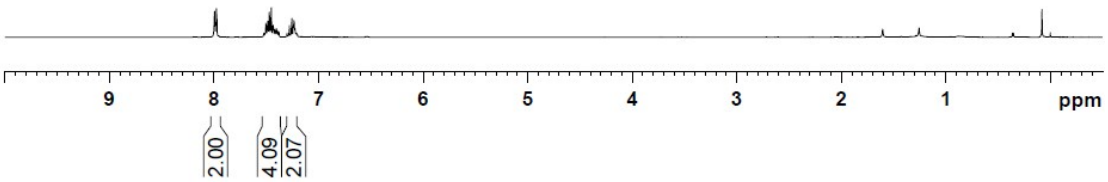

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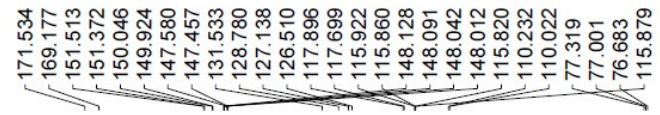

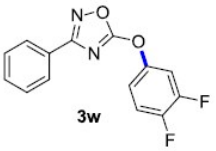

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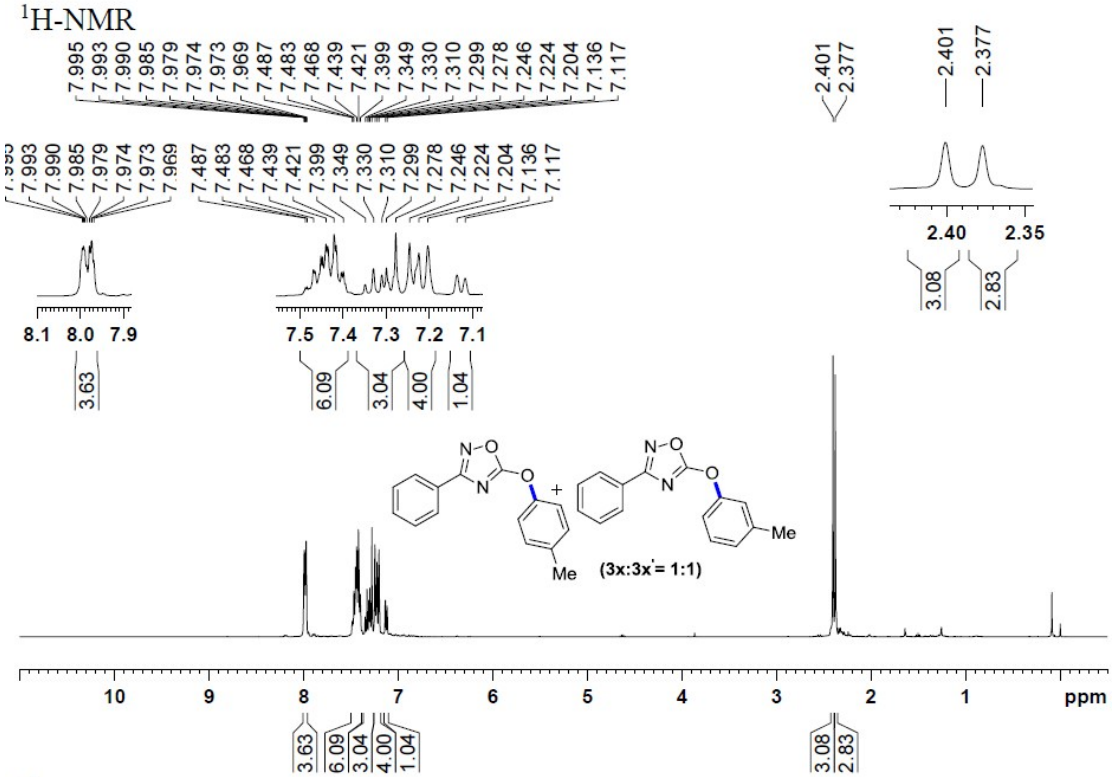

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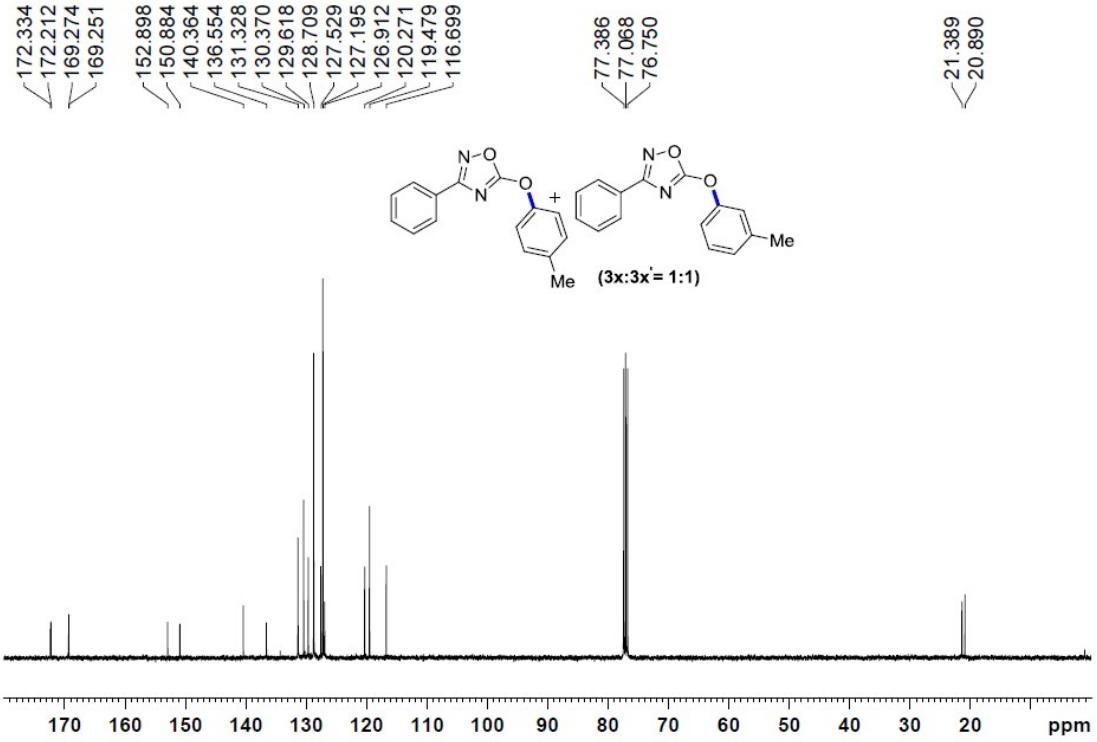

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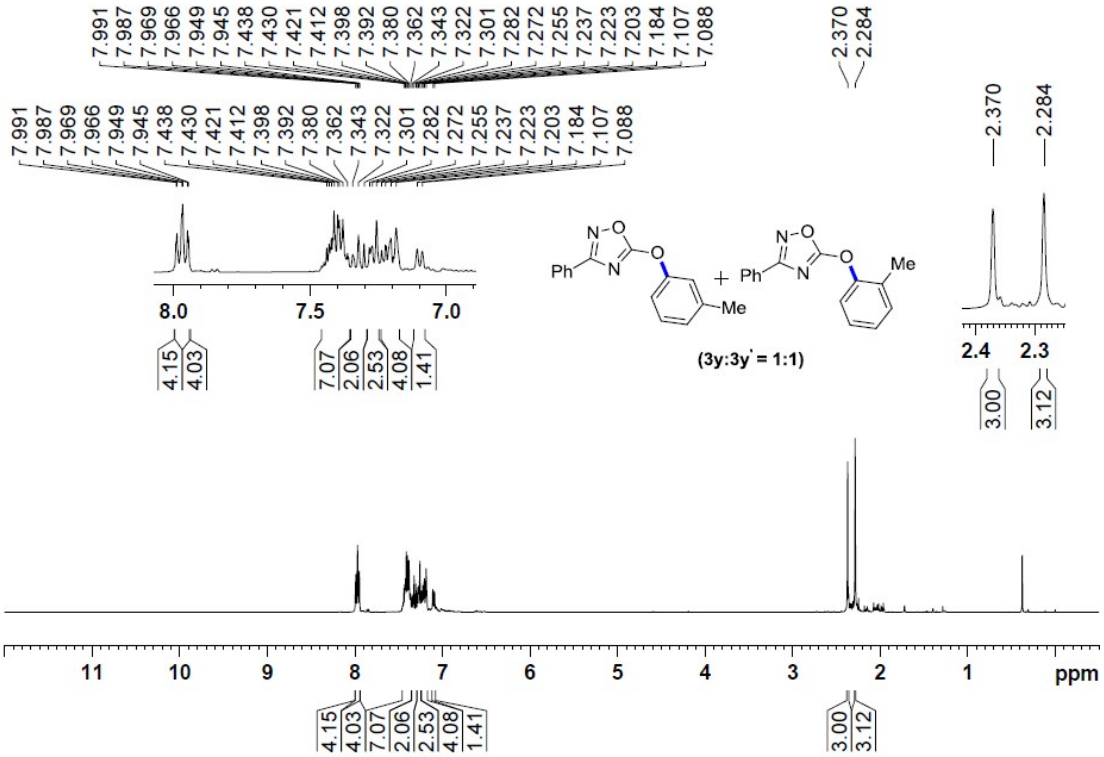

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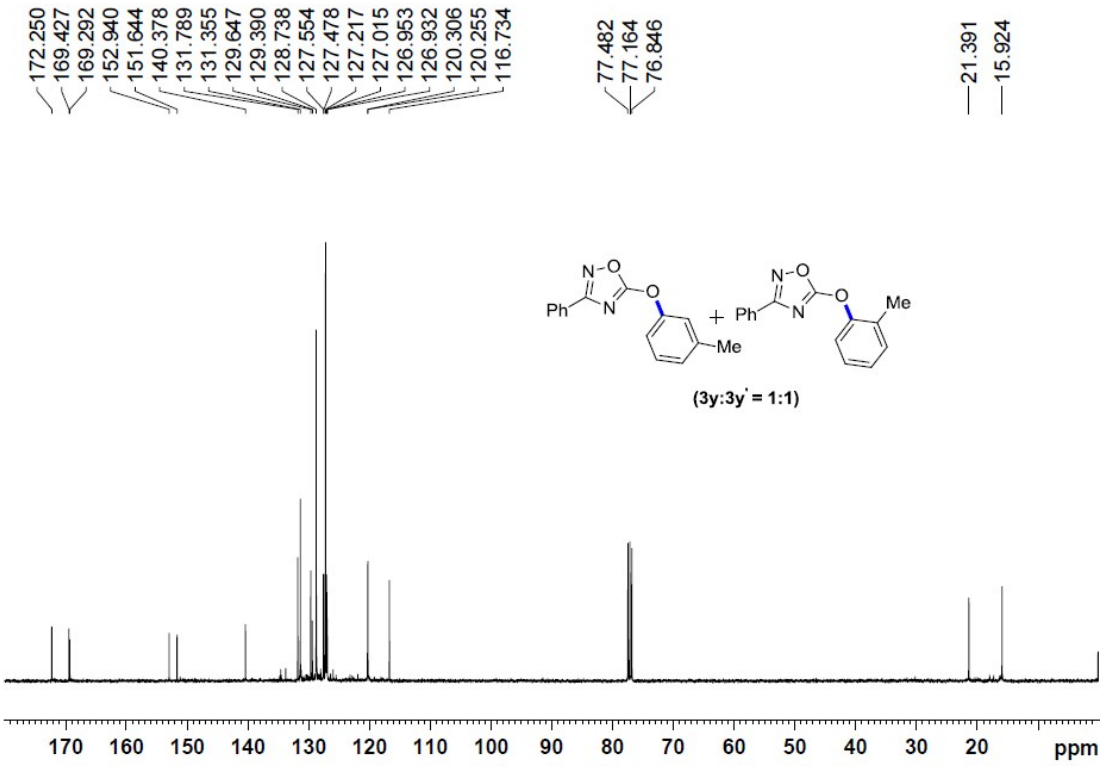

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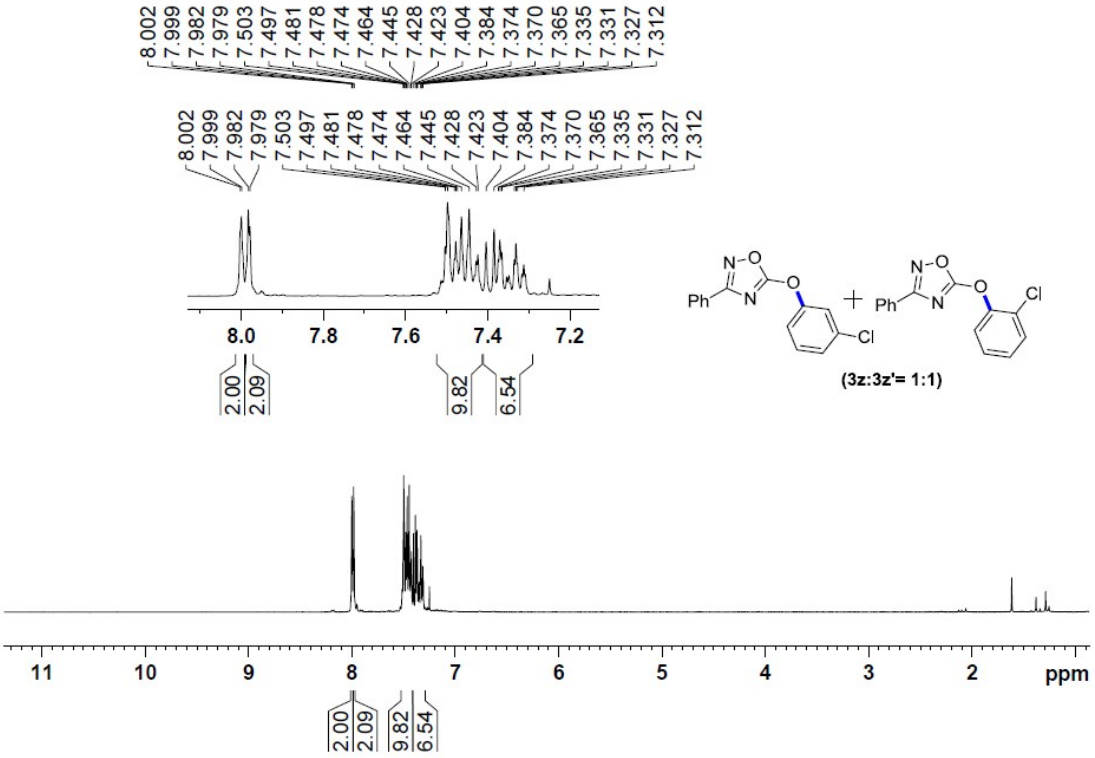

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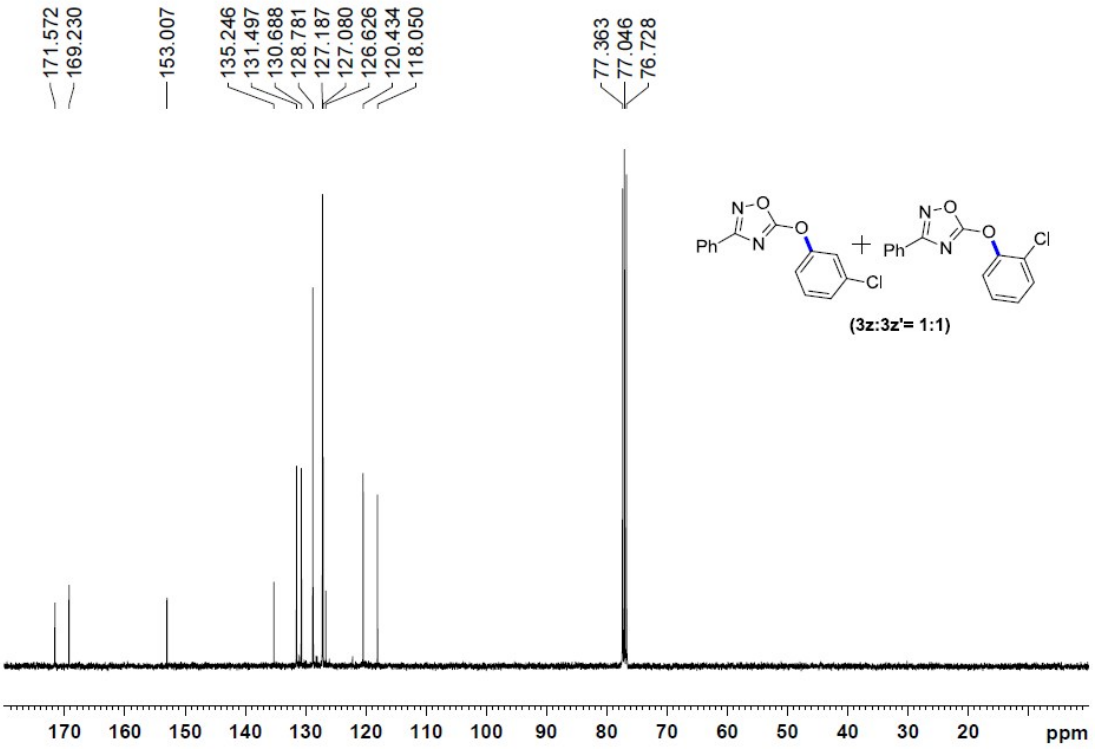

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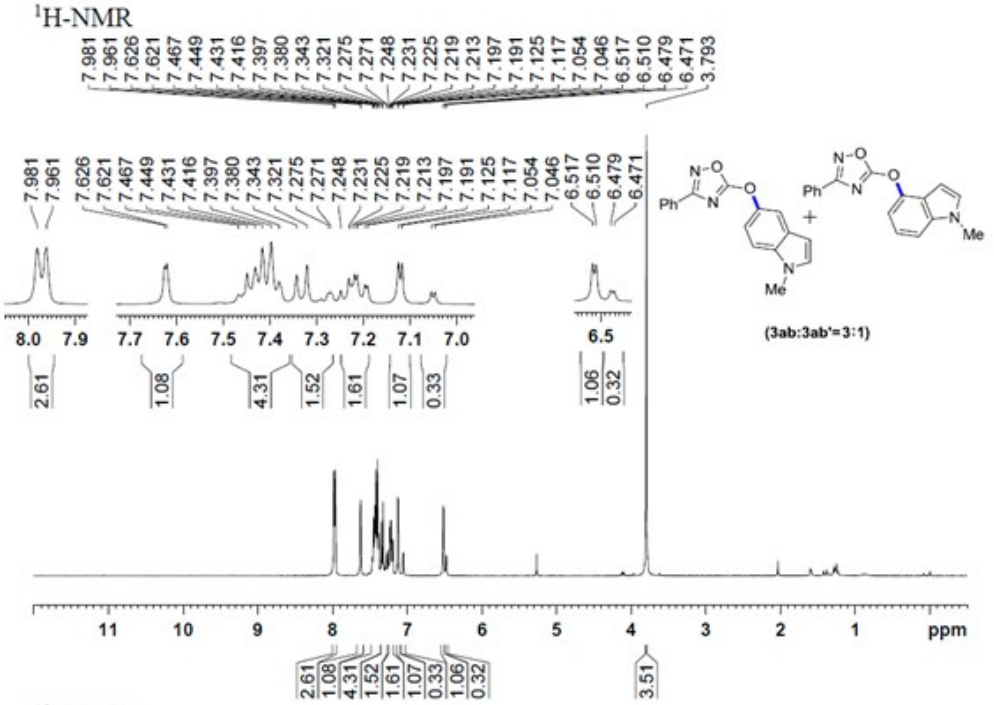

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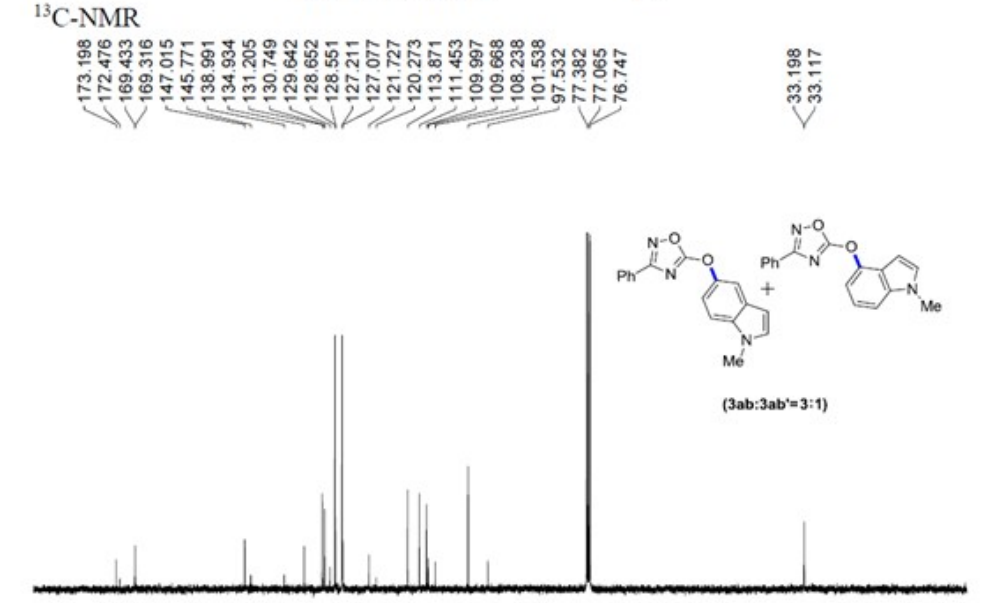

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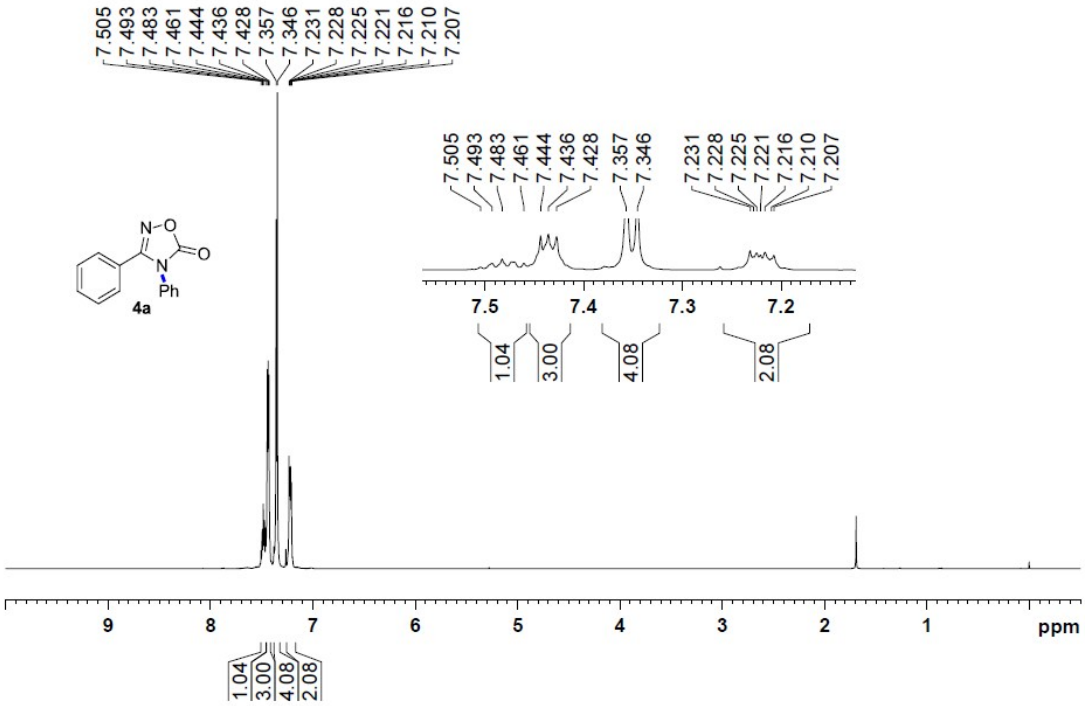

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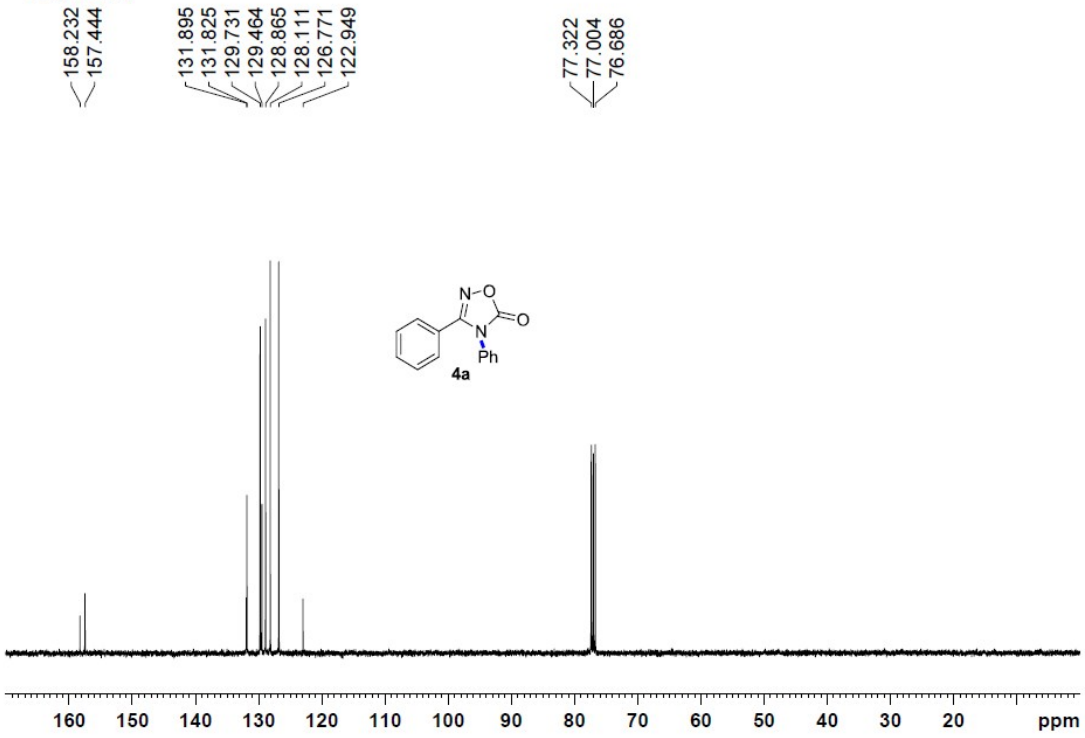

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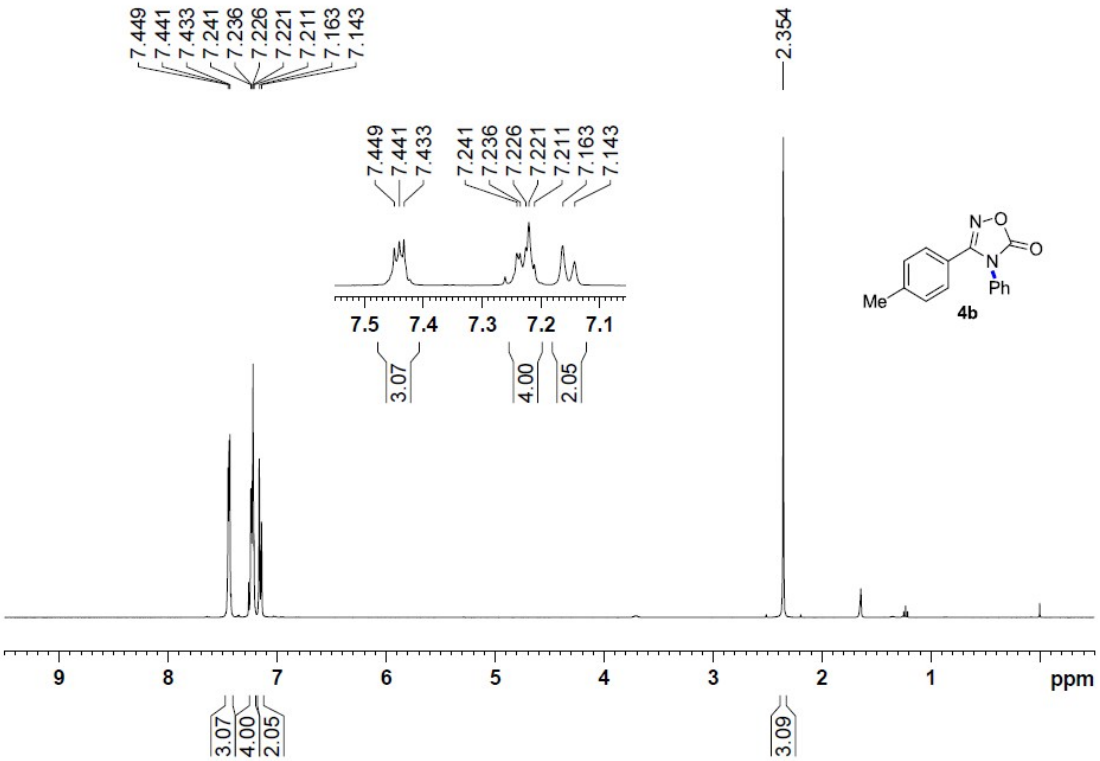

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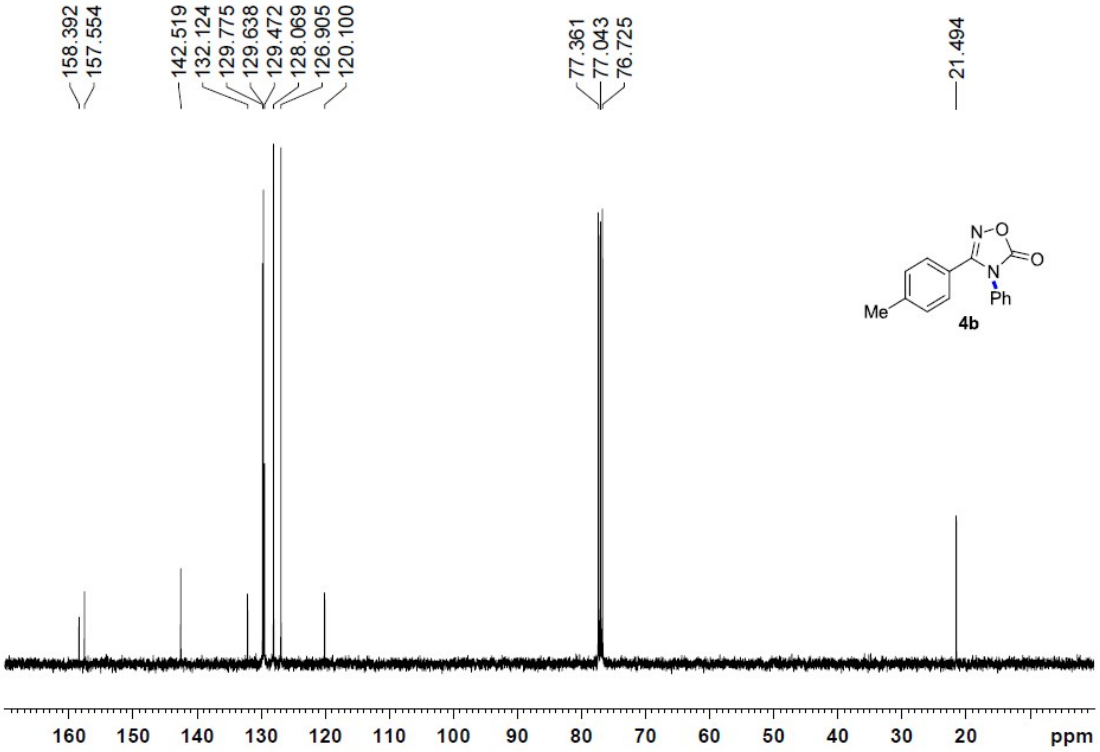

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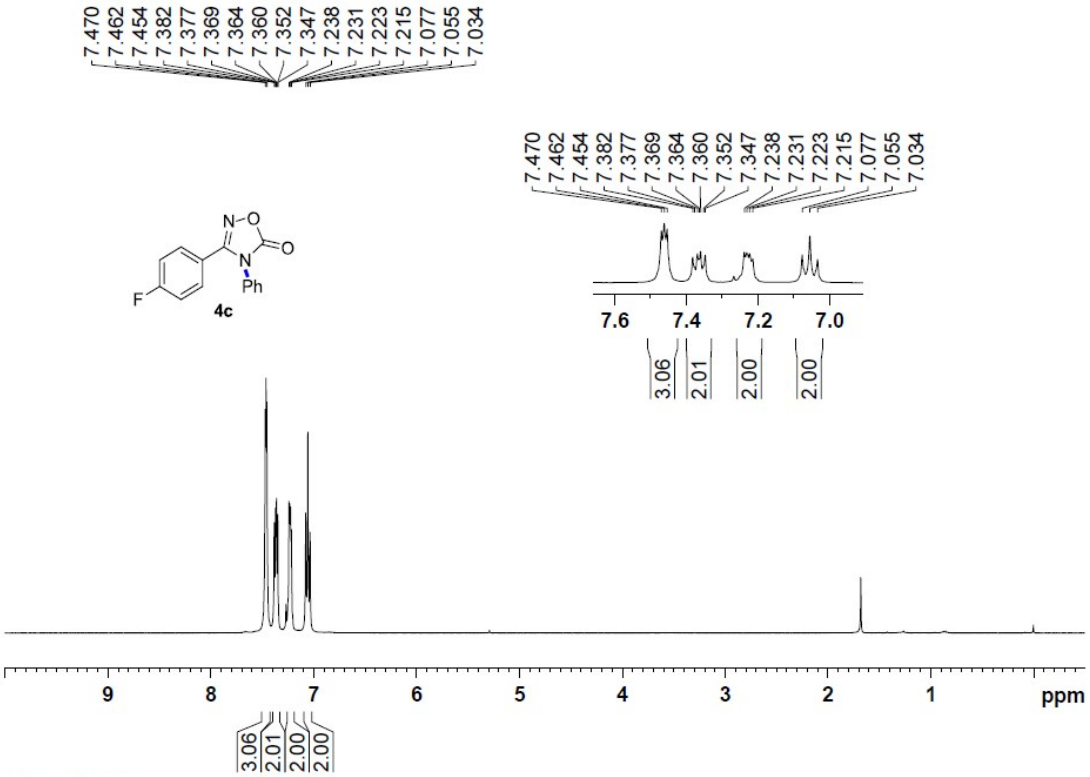

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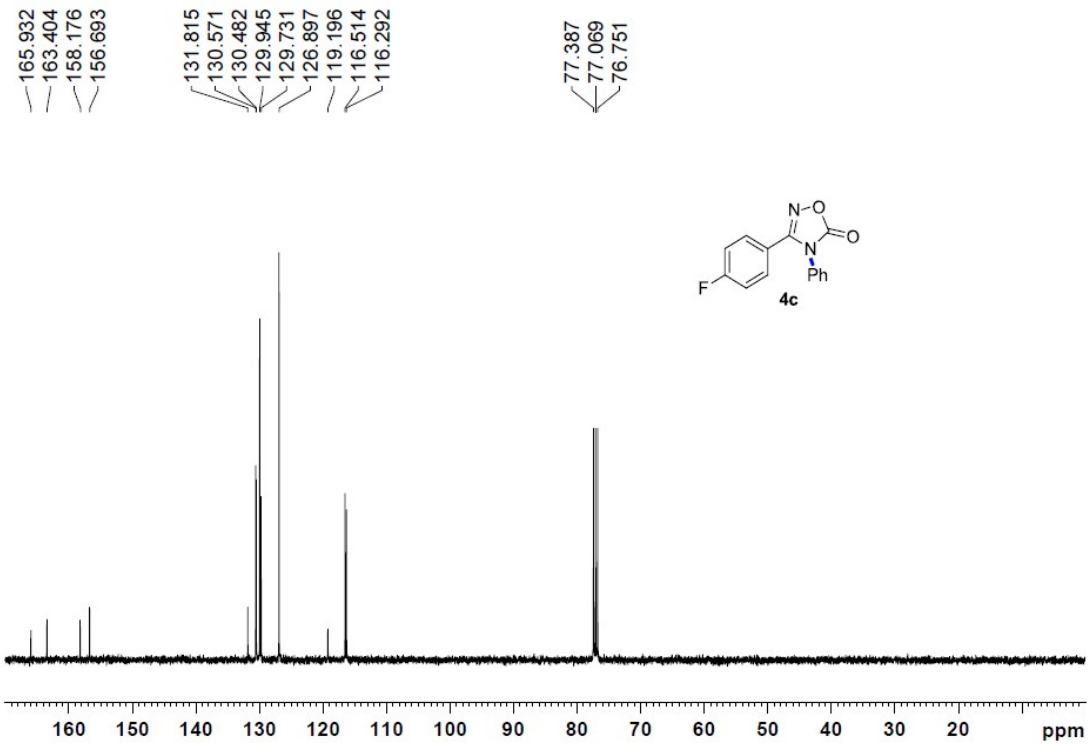

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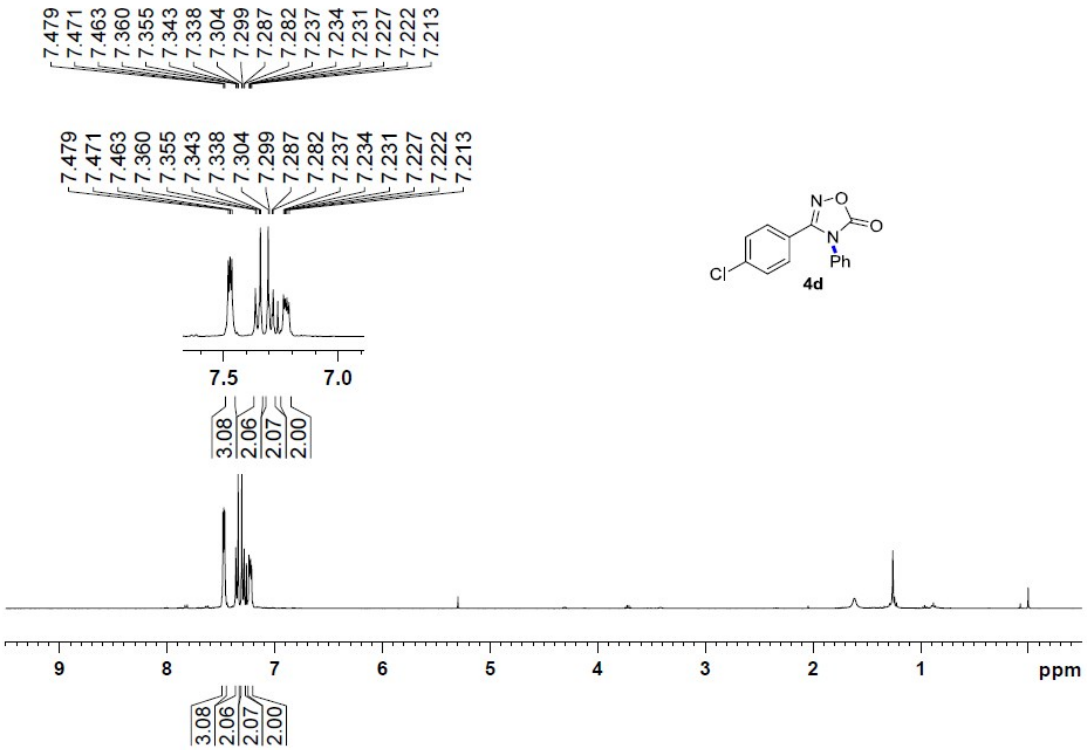

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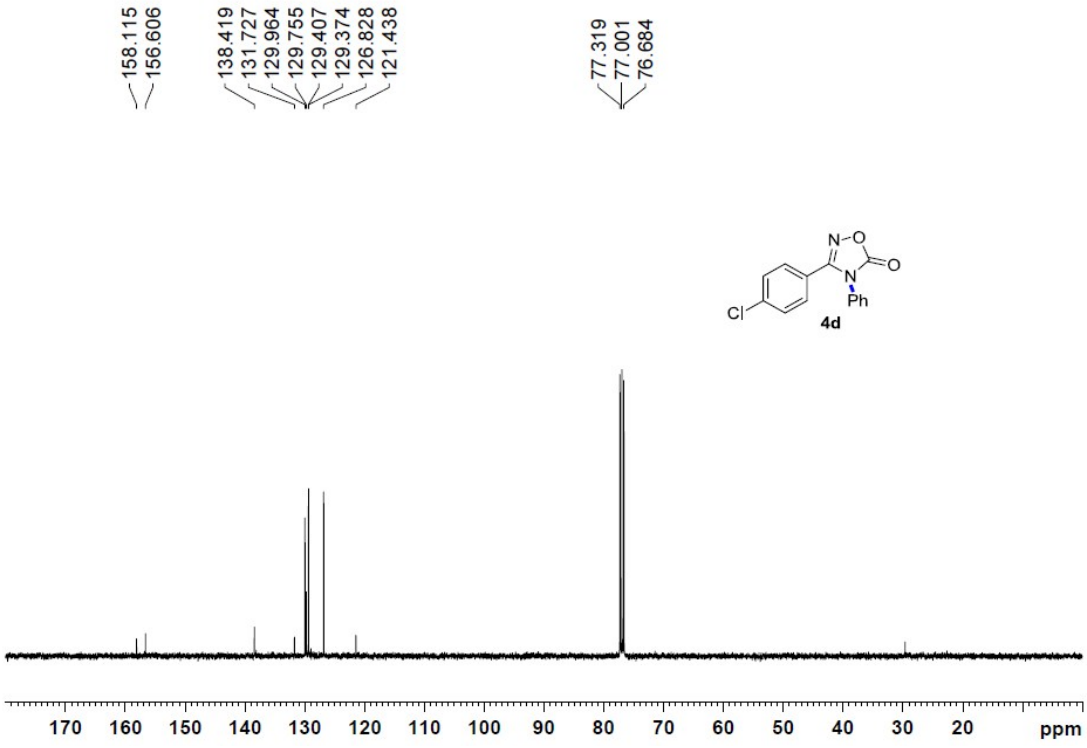

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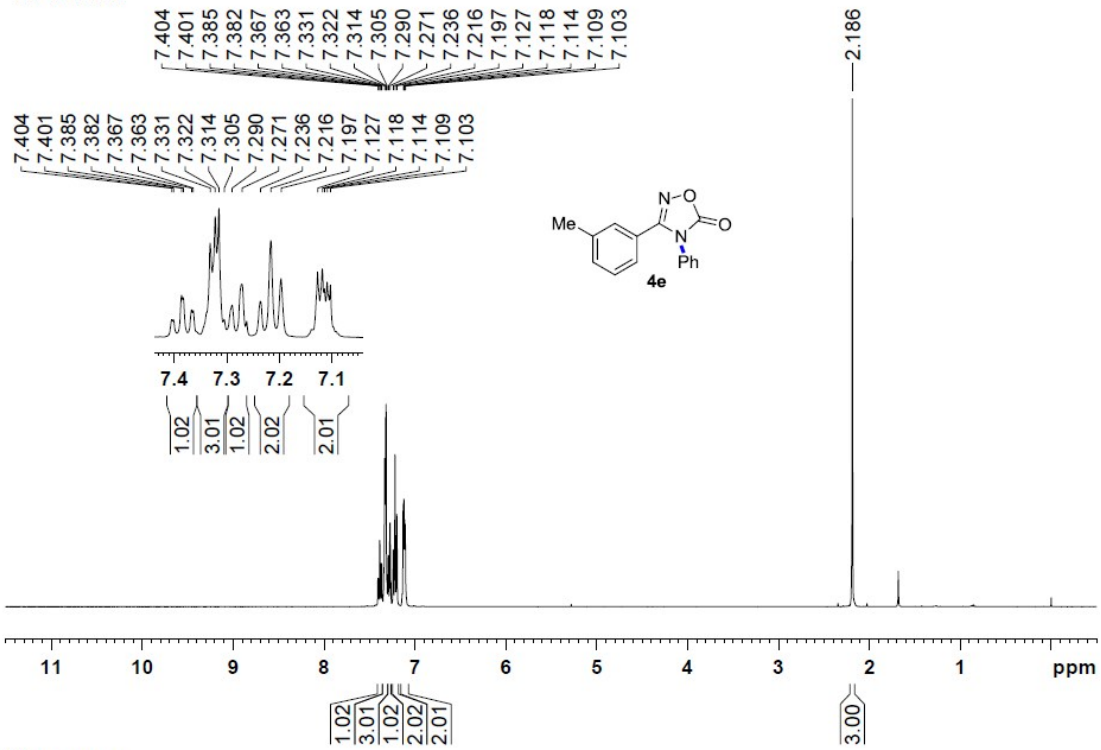

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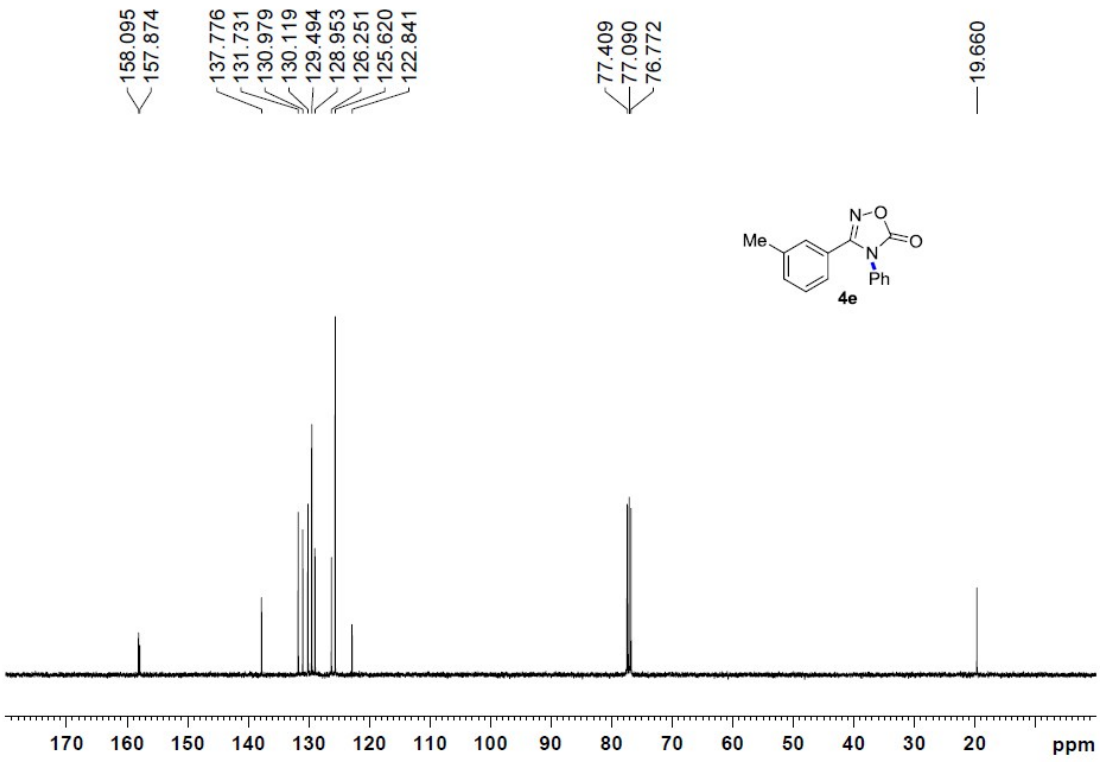

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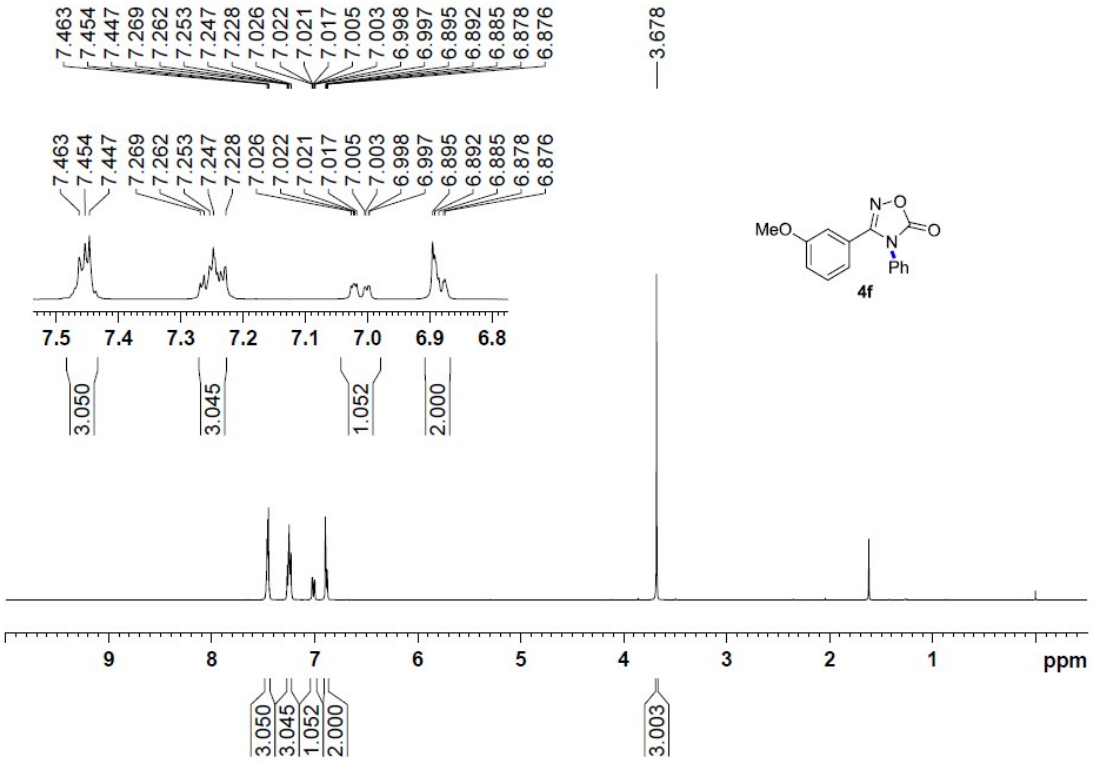

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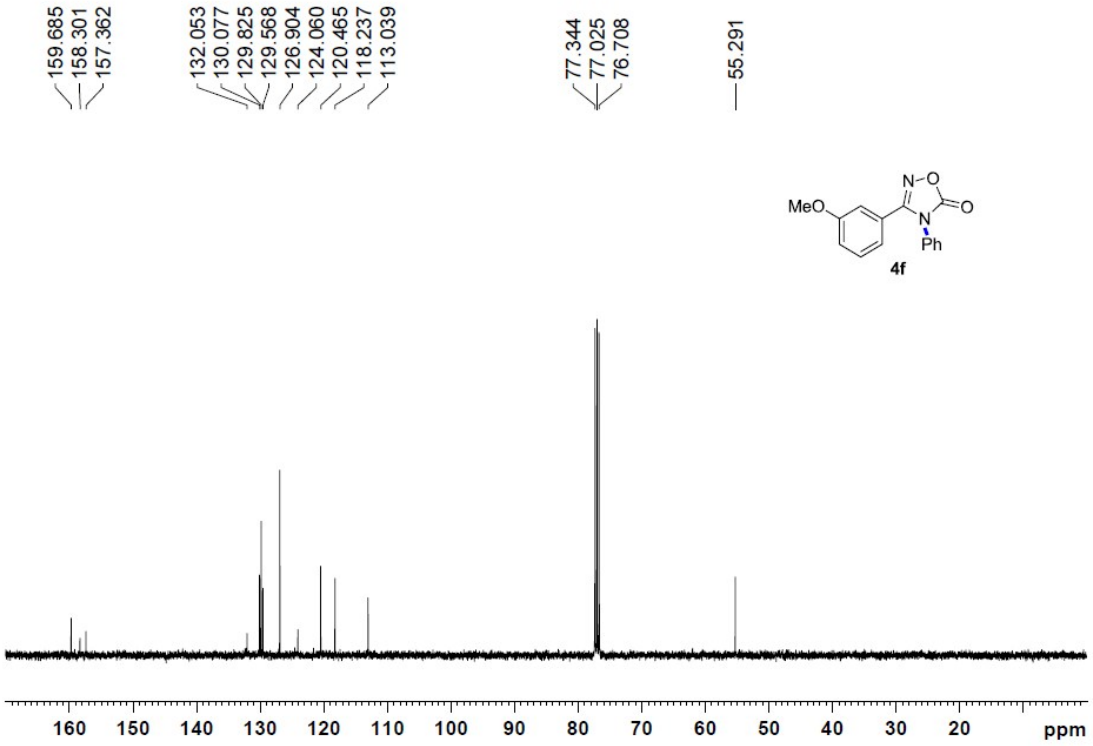

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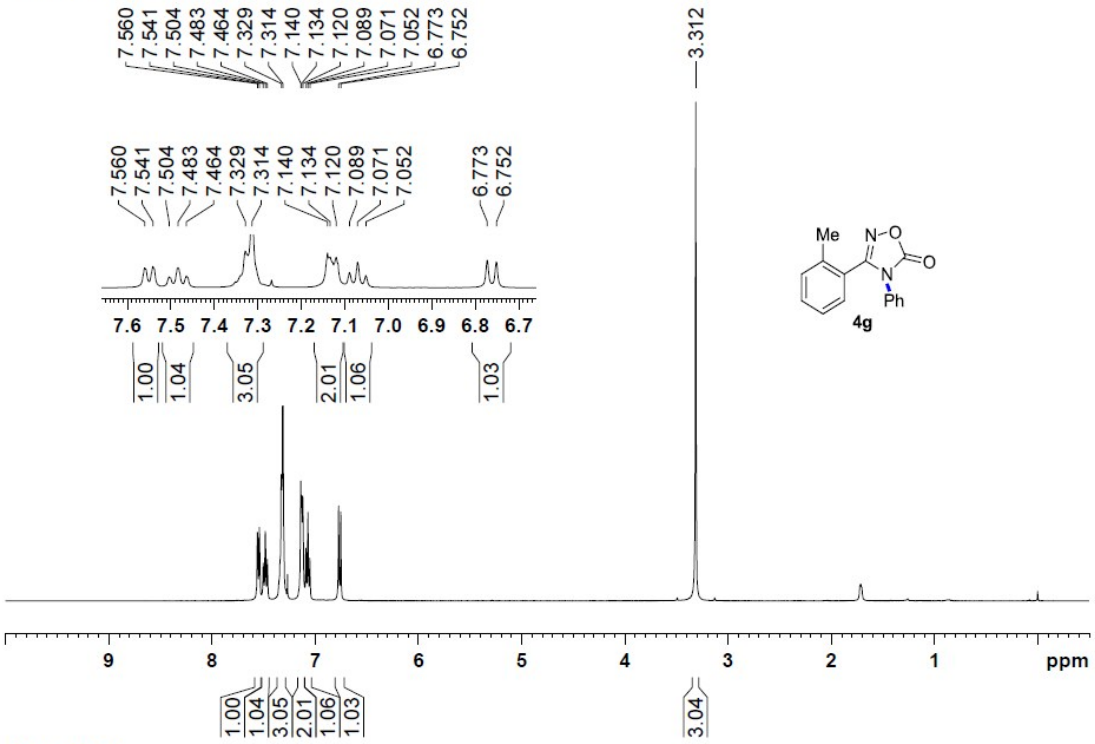

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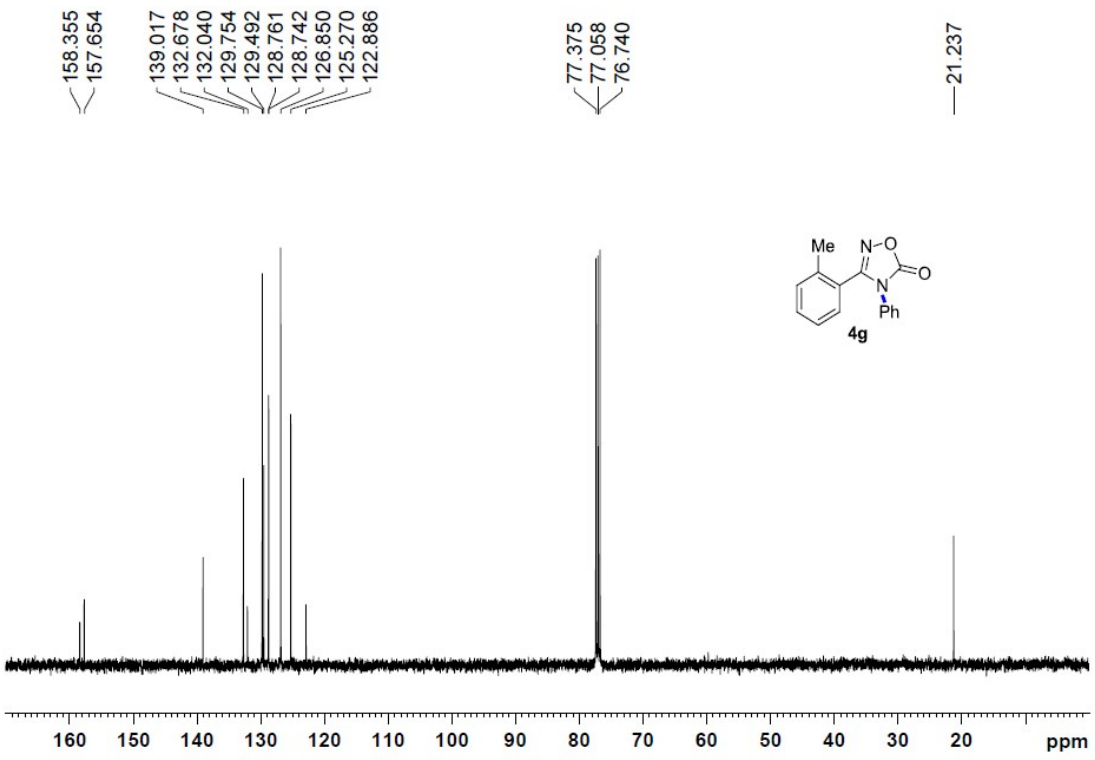

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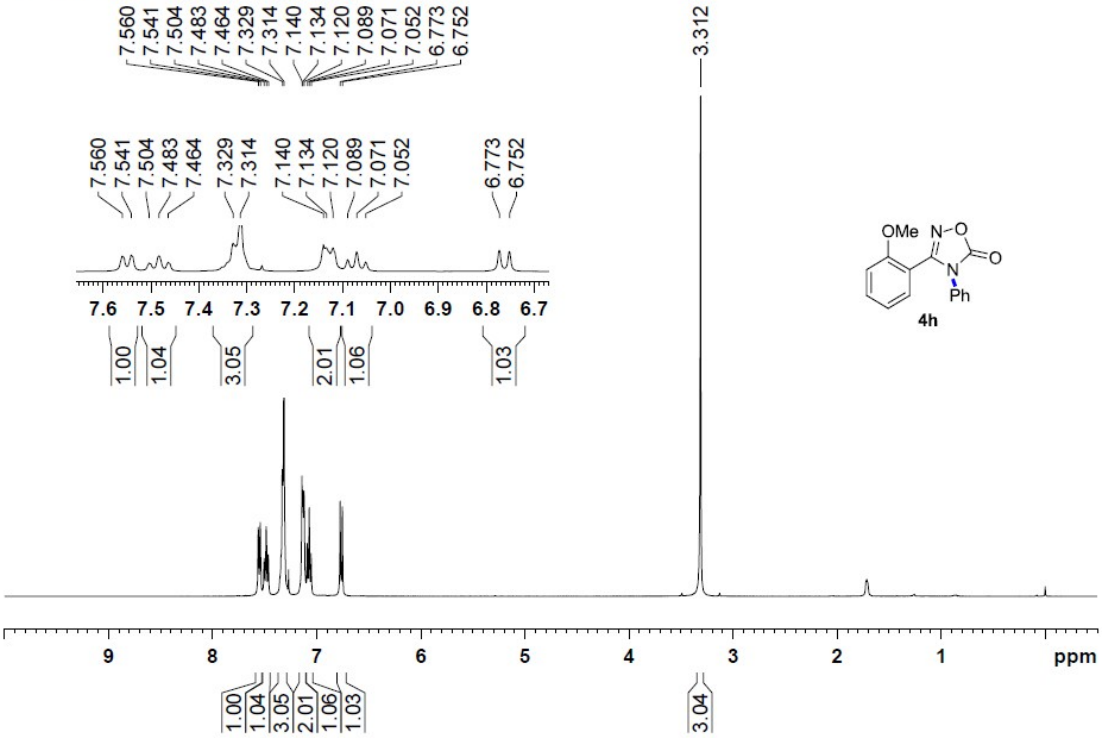

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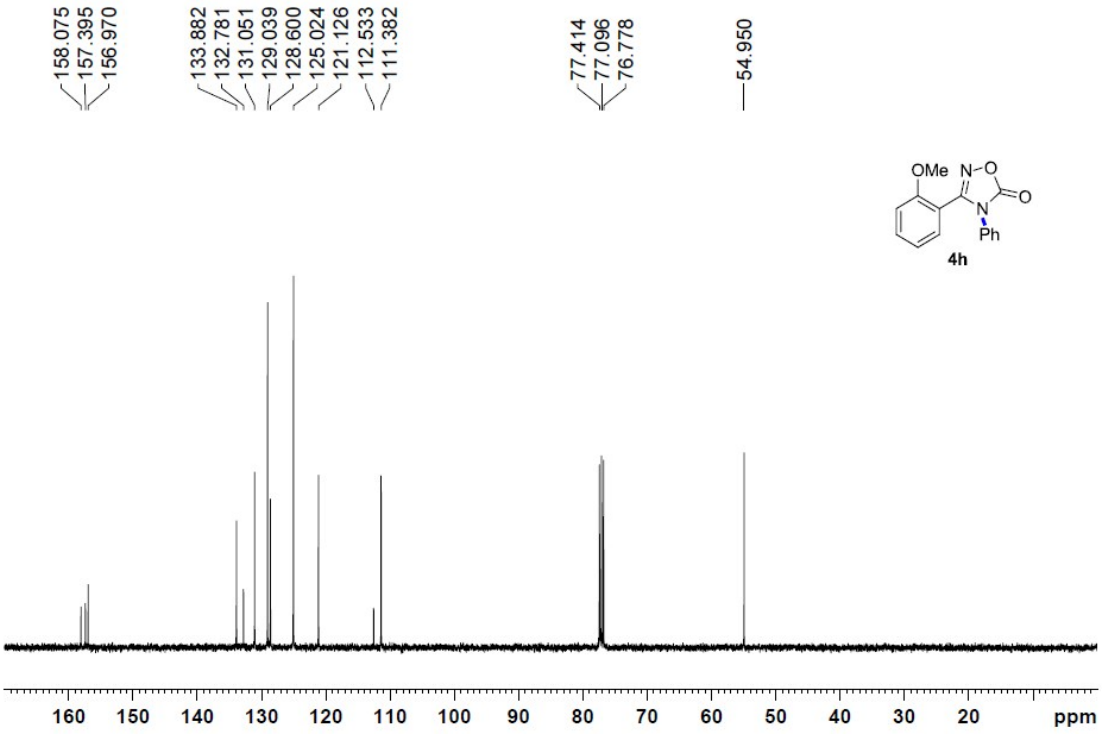

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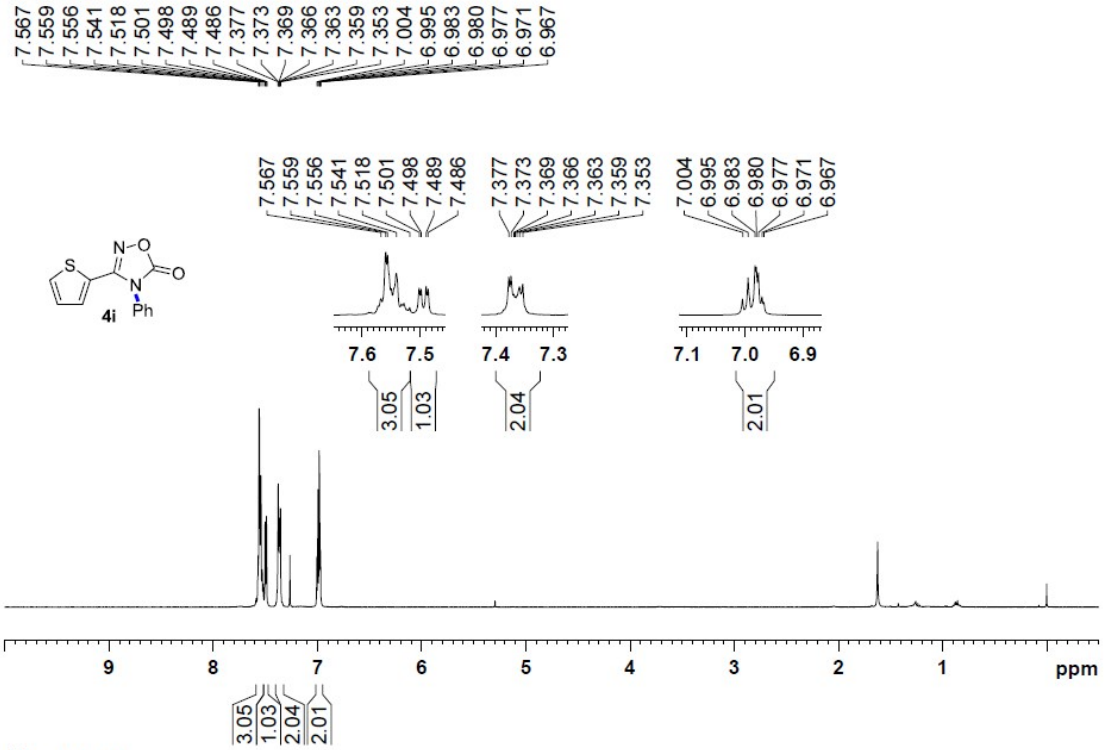

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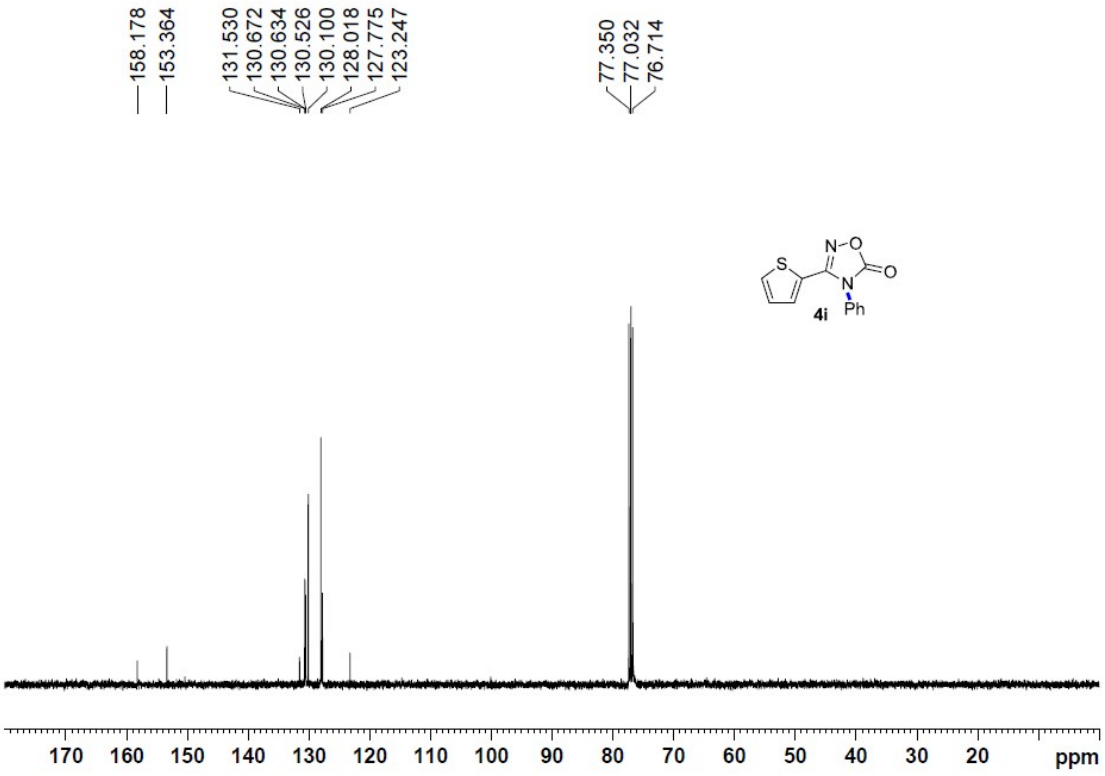

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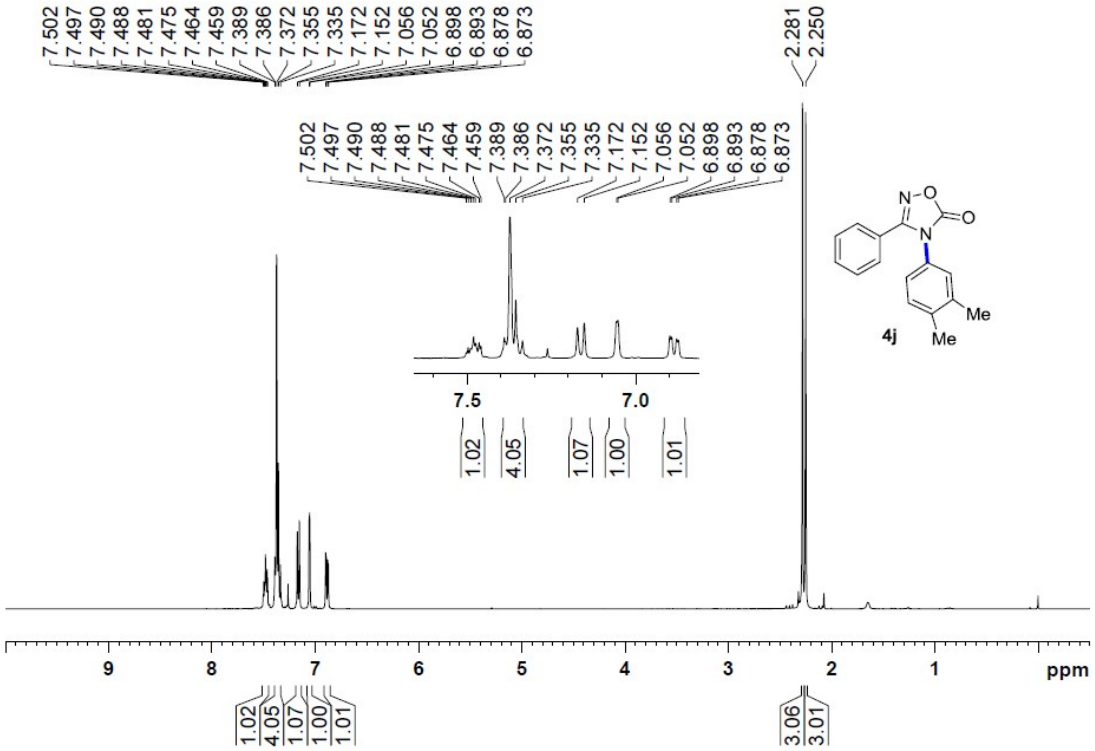

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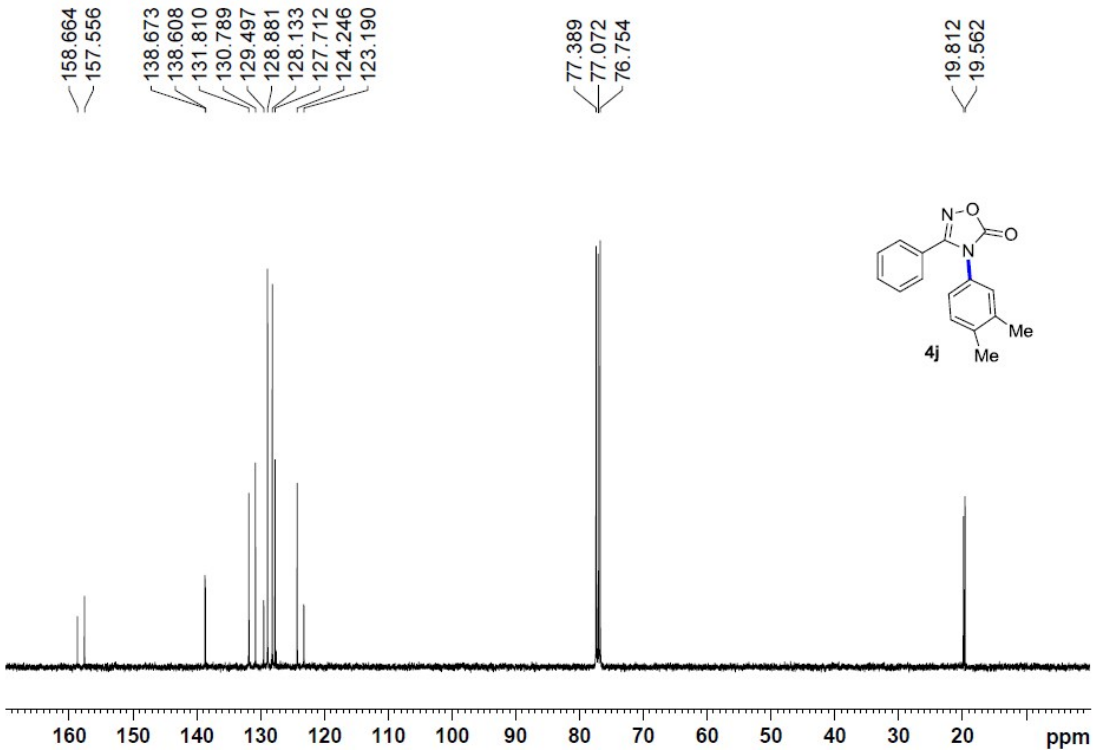

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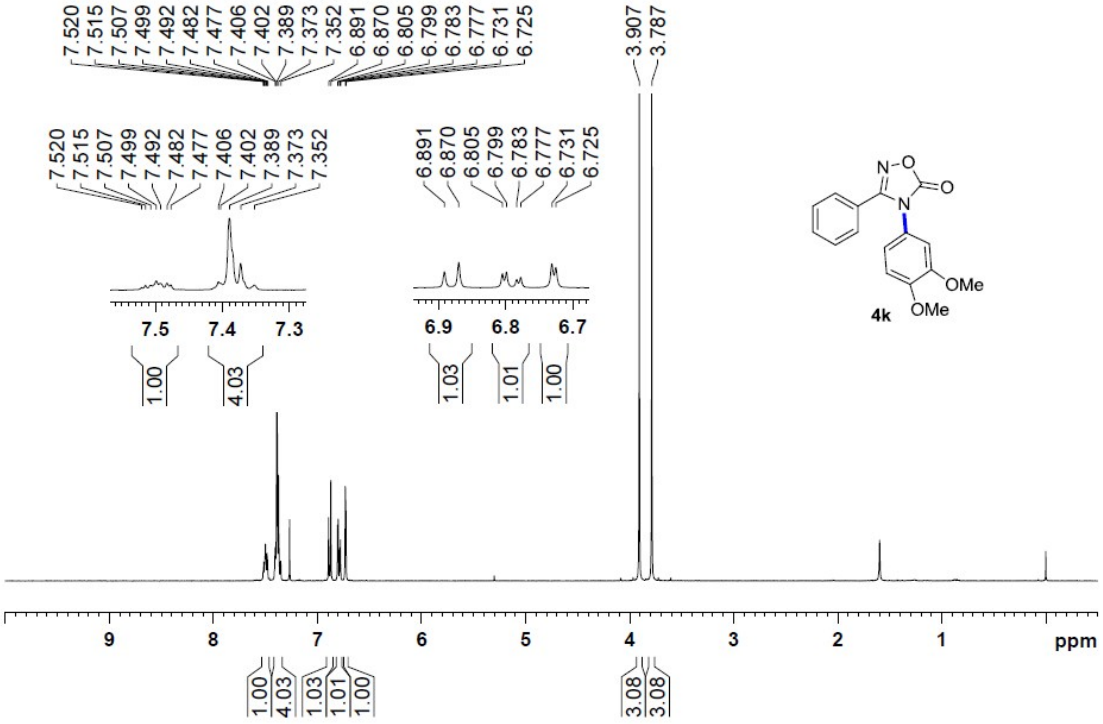

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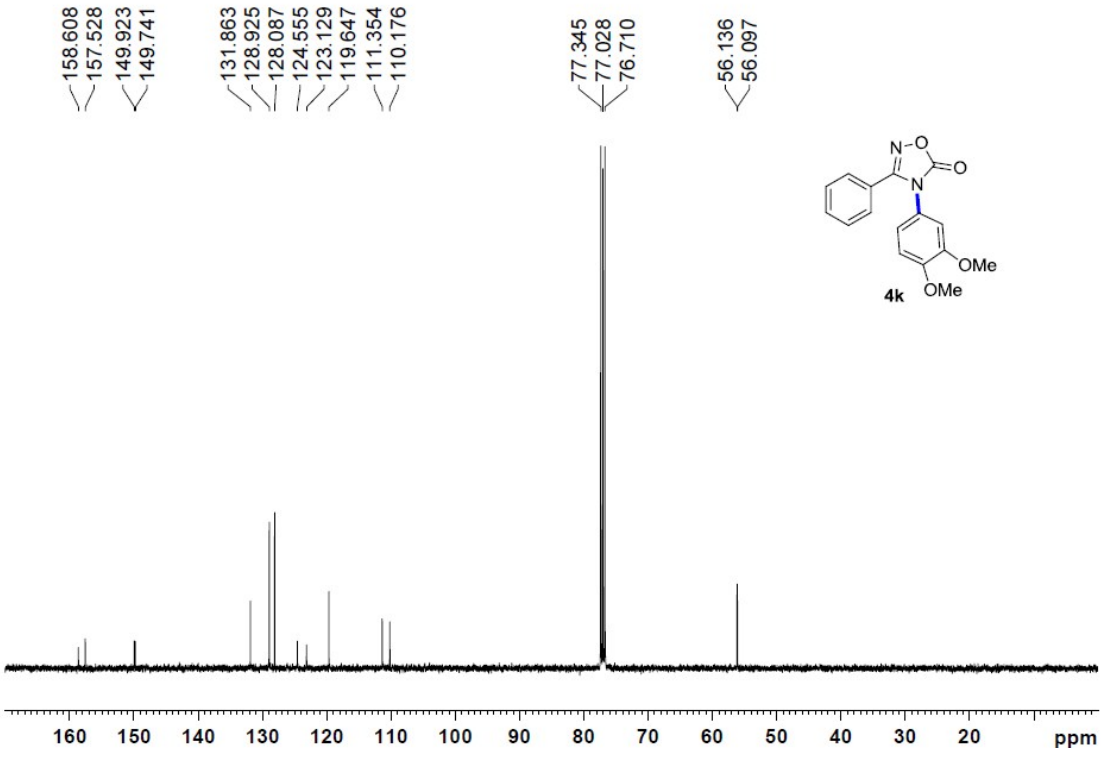

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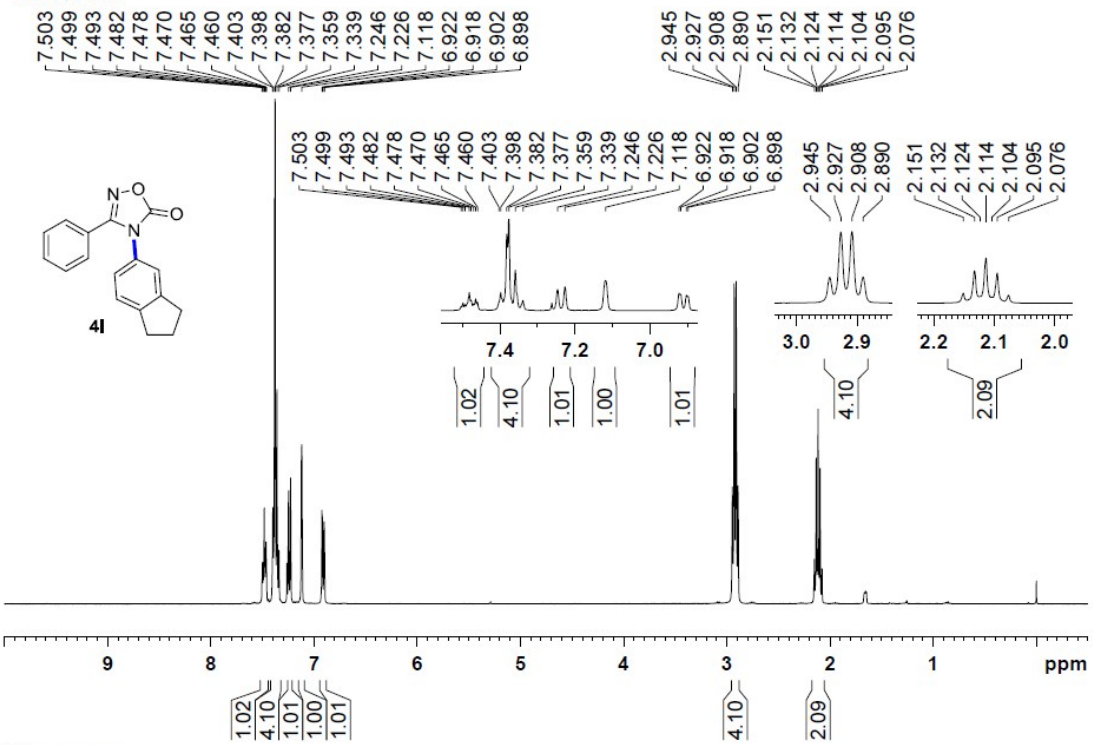

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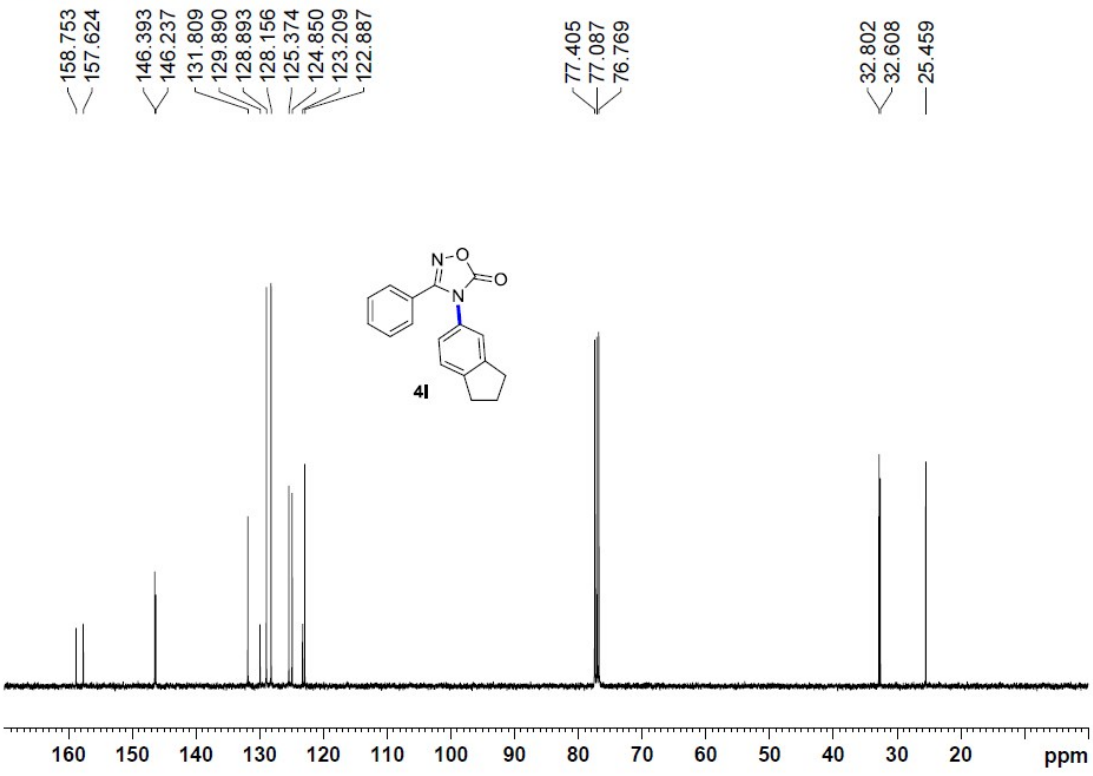

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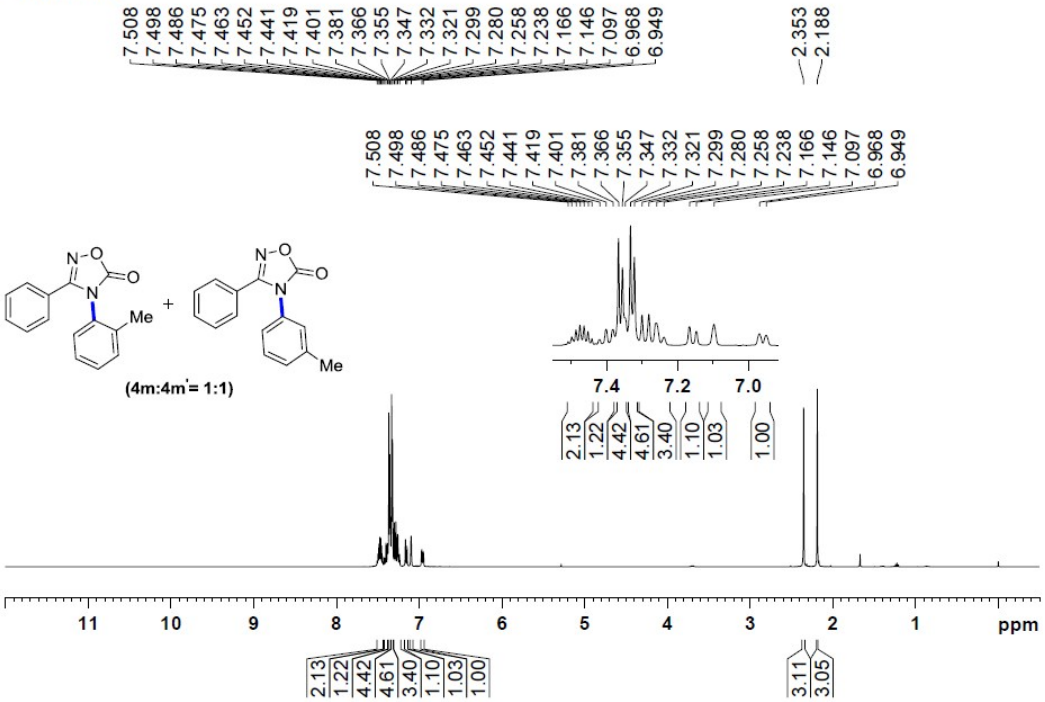

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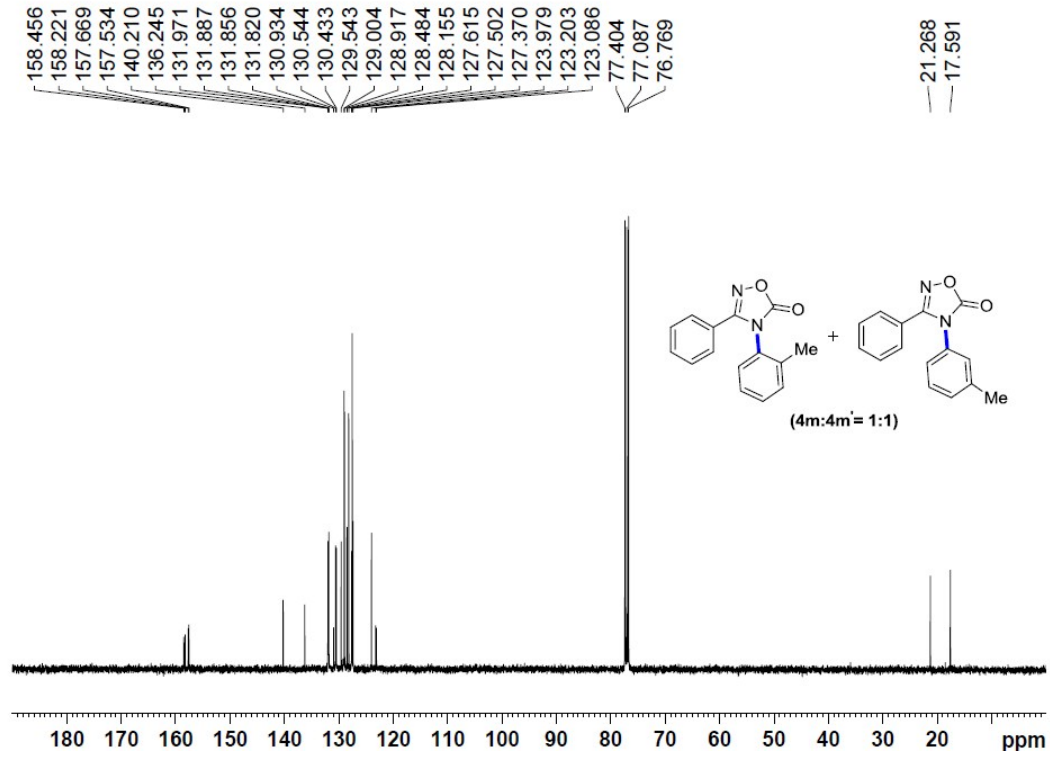

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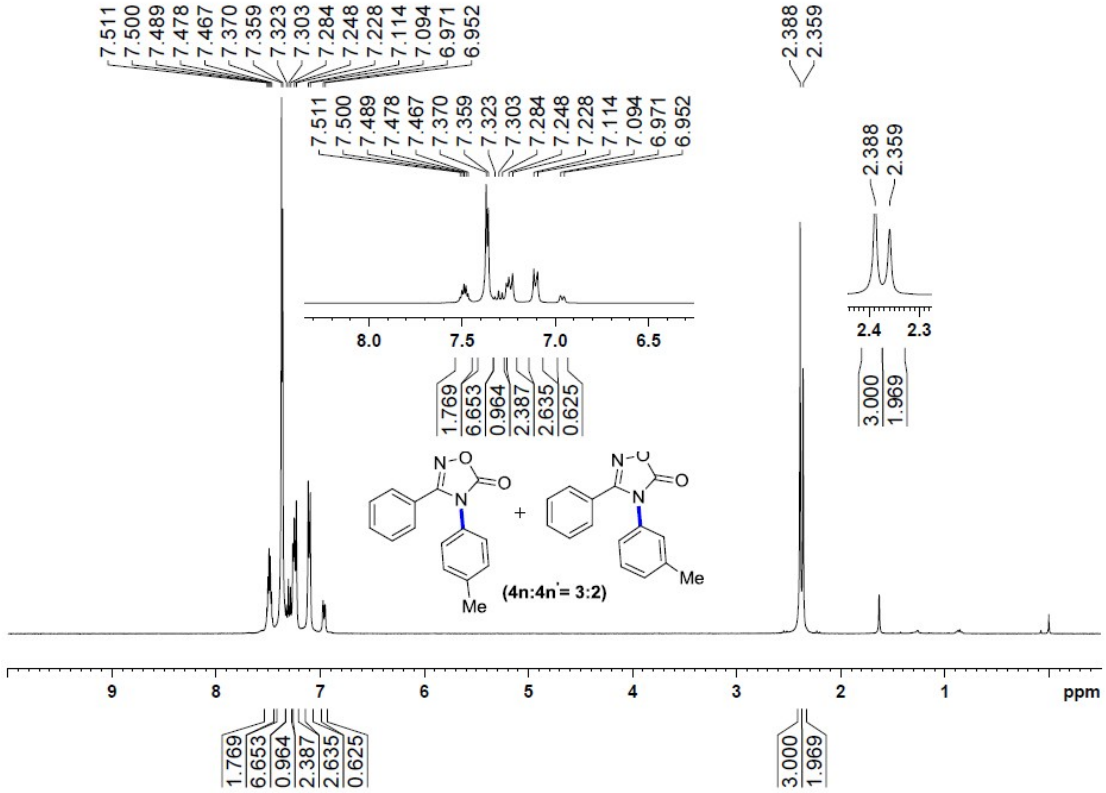

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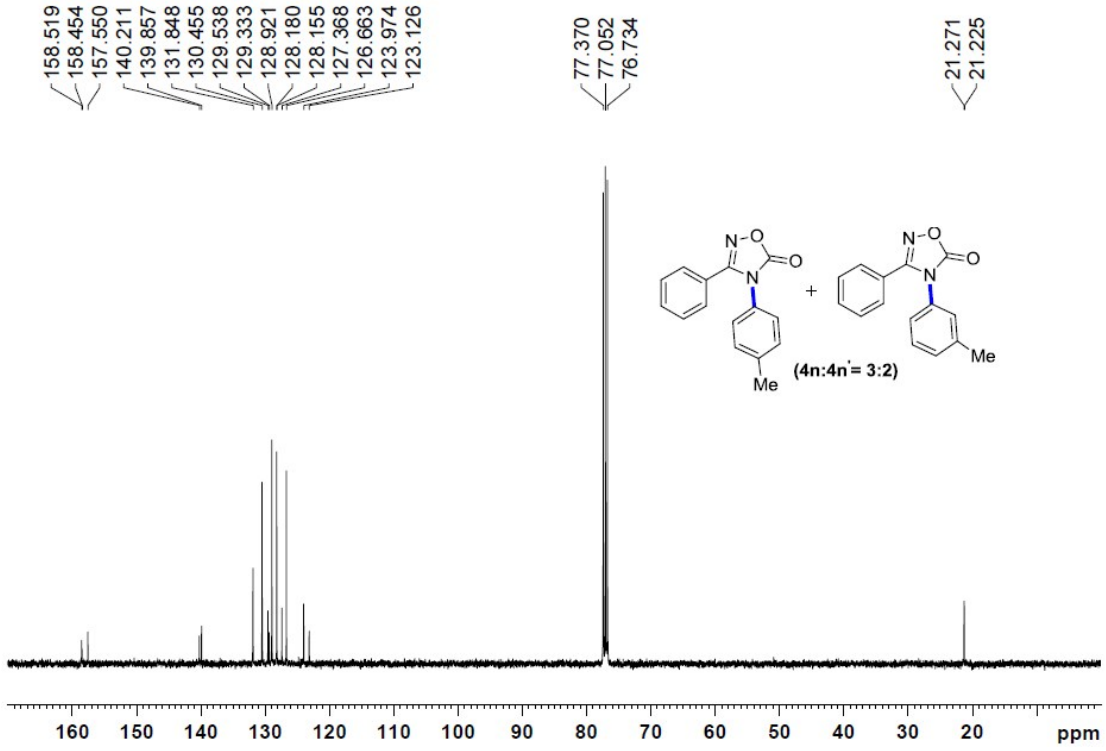
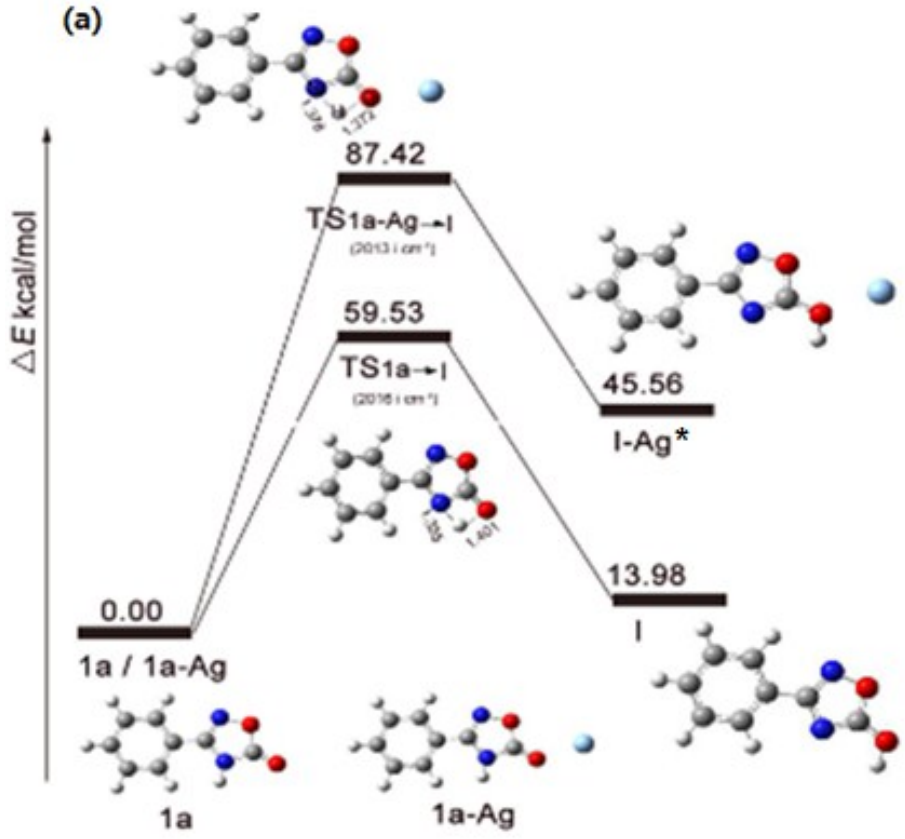


10. The computational study for the *O*-arylation

(1) Computational details

All the calculations were performed with the Gaussian 09 suite of program.[6] Geometry optimizations of the reactants, transition states, intermediates and products were carried out using the B3LYP[7] functional with the basis set combination of LanL2DZ[8] for Ag and 6-311G (d)[9] for all nonmetal atoms), and the PCM using the Integral Equation Formalism model (IEFPCM)[10] was adopted to simulate the solvation effect. Vibrational frequency computations were carried out at the same level to ensure that the optimized structures are energy minima without imaginary frequencies and the transition states have only one imaginary frequency. Intrinsic reaction coordinate (IRC)[11] computations were also performed at this level to verify that the transition state structures lead to the expected reactants and products.



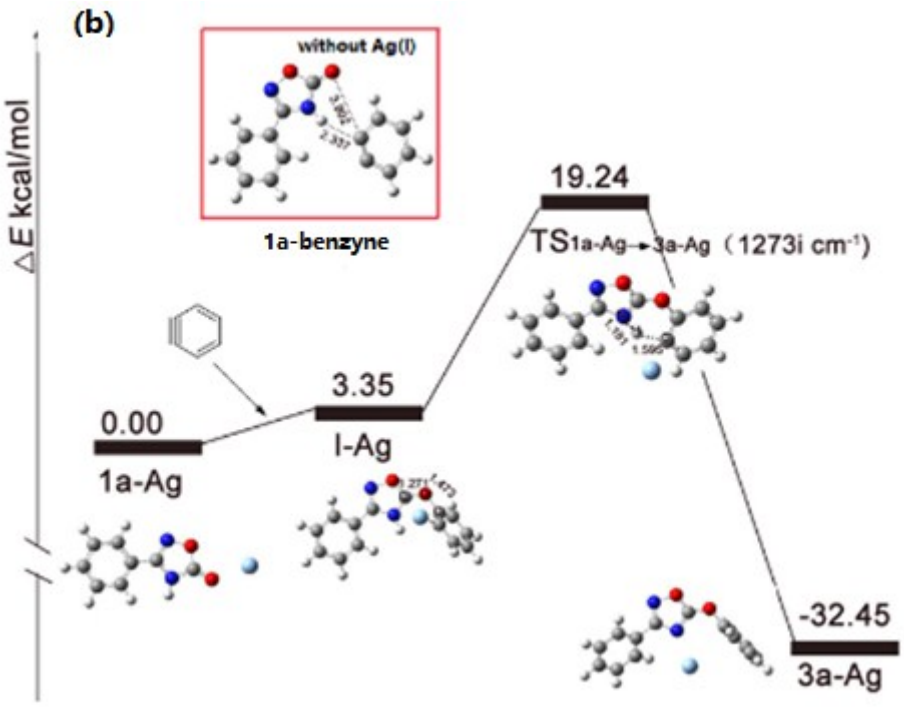


Figure S1. (a) Free energy profile of **1a** isomerization with and without the assistance of Ag(I); (b) Free energy profile of *O*-arylation pathway with the assistance of Ag(I).

(2) Molecular cartesian coordinates

1a E_{B3LYP} = -568.540060 a.u. $E_{ZPE\ (Zero\text{-}point\ vibrational\ energy)}$ = 82.90 kcal/mol

C	-2.808129	-1.340545	-0.000263
C	-1.420893	-1.219618	-0.000296
C	-0.825405	0.047883	-0.000013
C	-1.639033	1.191735	0.000306
C	-3.021580	1.064191	0.000329
C	-3.610638	-0.202000	0.000047
H	-3.258815	-2.326633	-0.000487
H	-0.820175	-2.122056	-0.000572
H	-1.180976	2.173441	0.000548
H	-3.642311	1.953314	0.000582
H	-4.690858	-0.298916	0.000073
C	2.814462	-0.289110	0.000112
C	0.632729	0.206478	-0.000077

N	1.230343	1.361107	-0.000491
N	1.544289	-0.820971	0.000282
O	2.621225	1.066407	-0.000362
O	3.888739	-0.829267	0.000328
H	1.361922	-1.811304	0.000716

1a-Ag E_{B3LYP} = -714.182146 a.u. E_{ZPE} = 83.49 kcal/mol

C	-4.970052	-1.351820	-0.000415
C	-3.584533	-1.219250	-0.000685
C	-3.000869	0.054261	-0.000081
C	-3.822755	1.192189	0.000798
C	-5.204039	1.051920	0.001034
C	-5.781524	-0.219525	0.000437
H	-5.412257	-2.341582	-0.000879
H	-2.977285	-2.117145	-0.001402
H	-3.374087	2.178197	0.001320
H	-5.832937	1.935072	0.001723
H	-6.860777	-0.325753	0.000652
C	0.623510	-0.266000	-0.000273
C	-1.545632	0.222393	-0.000370
N	-0.944895	1.376159	-0.000976
N	-0.628349	-0.805009	0.000071
O	0.448907	1.073121	-0.000898
O	1.700485	-0.833515	0.000002
H	-0.804968	-1.797309	0.000829
Ag	3.889260	-0.004923	0.000183

$TS_{1a\text{-}Ag\rightarrow I}$ E_{B3LYP} = -568.439226 a.u. E_{ZPE} = 79.15573kcal/mol Freq = 2016icm^{-1}

C	2.743729	-1.379366	0.000037

C	1.362469	-1.208012	0.000034
C	0.816784	0.081666	0.000001
C	1.666359	1.197650	-0.000028
C	3.044061	1.018969	-0.000025
C	3.585646	-0.268376	0.000005
H	3.161301	-2.380081	0.000066
H	0.706859	-2.071181	0.000058
H	1.244495	2.195735	-0.000046
H	3.697980	1.884021	-0.000050
H	4.661897	-0.403273	-0.000001
C	-2.728410	-0.182777	-0.000035
C	-0.637565	0.249471	-0.000007
N	-1.225083	1.427874	0.000070
N	-1.547554	-0.778265	-0.000133
O	-2.650601	1.129293	0.000028
O	-3.685591	-1.014199	0.000036
H	-2.492971	-1.748586	0.000019

$TS_{1a\text{-}Ag\rightarrow I}$ E_{B3LYP} = -714.077391 a.u. E_{ZPE} =79.56372 kcal/mol Freq = -2013 icm^{-1}

C	4.803725	-1.510892	0.000036
C	3.437736	-1.244837	0.000179
C	2.984019	0.080116	0.000018
C	3.908357	1.135501	-0.000302
C	5.269981	0.861466	-0.000447
C	5.720233	-0.460570	-0.000277
H	5.151351	-2.537894	0.000169
H	2.724636	-2.061075	0.000427
H	3.557248	2.160624	-0.000446
H	5.982434	1.678848	-0.000700

H	6.784485	-0.669719	-0.000392
C	-0.558407	0.070433	0.000359
C	1.546891	0.350152	0.000196
N	1.042408	1.566606	0.000392
N	0.562322	-0.613242	0.000210
O	-0.402320	1.365724	0.000517
O	-1.575712	-0.713592	0.000320
H	-0.469822	-1.526174	0.000134
Ag	-3.868391	-0.098371	-0.000185

I E_{B3LYP} = -568.517644 a.u. E_{ZPE} = 82.81 kcal/mol

C	-3.515325	-2.206382	-0.000953
C	-2.387244	-1.390161	-0.000783
C	-2.527323	0.003022	0.000021
C	-3.810880	0.568700	0.000653
C	-4.933287	-0.251000	0.000480
C	-4.789132	-1.640120	-0.000323
H	-3.398550	-3.284714	-0.001577
H	-1.394782	-1.824185	-0.001269
H	-3.923263	1.646676	0.001276
H	-5.922956	0.192869	0.000971
H	-5.667433	-2.276841	-0.000456
C	0.667963	1.424461	0.000010
C	-1.330206	0.854079	0.000193
N	-1.393198	2.164839	0.000933
N	-0.048115	0.342964	-0.000409
O	-0.028386	2.558524	0.000811
O	1.975686	1.562605	-0.000240
H	2.394827	0.689827	-0.000827

I-Ag* E_{B3LYP} = -714.149893 a.u. E_{ZPE} = 83.19 kcal/mol

C	4.848808	-1.380463	-0.334633
C	3.486296	-1.217399	-0.099485
C	2.946748	0.067436	0.038607
C	3.787624	1.186215	-0.055771
C	5.147244	1.016561	-0.288206
C	5.681009	-0.266149	-0.429636
H	5.259770	-2.378137	-0.444534
H	2.835063	-2.079808	-0.025372
H	3.373894	2.181663	0.056299
H	5.793117	1.885015	-0.357947
H	6.742546	-0.394747	-0.612278
C	-0.479855	-0.243321	0.627081
C	1.506723	0.228777	0.270891
N	0.916175	1.400920	0.284881
N	0.655692	-0.841483	0.480861
O	-0.446814	1.078908	0.533440
O	-1.675590	-0.771121	0.856547
H	-1.602193	-1.733180	0.950241
Ag	-3.786673	-0.004449	-0.306800

I-Ag E_{B3LYP} = -945.191738 a.u. E_{ZPE} =133.55 kcal/mol

C	-4.297526	0.999422	-1.936524
C	-3.164749	1.035183	-1.130818
C	-3.140595	0.307509	0.066888
C	-4.256381	-0.451880	0.451717
C	-5.382608	-0.479541	-0.360010
C	-5.404581	0.243341	-1.553991
H	-4.315303	1.565602	-2.860447
H	-2.321789	1.647261	-1.430623

H	-4.229772	-1.022981	1.371858
H	-6.241634	-1.071266	-0.065490
H	-6.284733	0.215863	-2.186668
C	3.188989	0.581022	-1.500106
C	3.692906	1.881905	-1.542679
C	3.417893	2.783843	-0.513768
C	2.627782	2.377394	0.557807
C	2.154812	1.073272	0.534754
C	2.391176	0.117363	-0.433144
H	3.431991	-0.092609	-2.315345
H	4.307863	2.193078	-2.381285
H	3.811038	3.793759	-0.541275
H	2.389260	3.044123	1.378387
C	0.109009	0.527311	1.586144
C	-1.967550	0.334439	0.934238
N	-1.977341	0.051335	2.203487
N	-0.679322	0.652216	0.519551
H	-0.351757	0.833171	-0.421280
O	-0.610922	0.172006	2.619895
O	1.362270	0.703062	1.720675
Ag	1.757005	-1.936487	-0.325462

$TS_{1a\text{-}Ag \rightarrow 3a\text{-}Ag}$ E_{B3LYP} = -945.176253 a.u E_{ZPE} = 130.13 kcal/mol Freq = -1273 icm^{-1}

C	3.818571	-1.614940	1.350390
C	2.743415	-0.827493	0.950345
C	2.972276	0.353051	0.231325
C	4.285090	0.737481	-0.082186
C	5.351820	-0.054351	0.321422
C	5.121365	-1.230937	1.037521

H	3.637204	-2.527283	1.907064
H	1.734782	-1.134390	1.201348
H	4.462309	1.650284	-0.638339
H	6.364927	0.245207	0.078131
H	5.957373	-1.846456	1.351068
C	-2.653422	-0.867192	1.471100
C	-3.846145	-0.329244	1.955848
C	-4.239479	0.955561	1.581296
C	-3.427041	1.716099	0.741454
C	-2.257503	1.131699	0.288471
C	-1.806795	-0.154001	0.591784
H	-2.368208	-1.865862	1.786224
H	-4.469213	-0.910817	2.627101
H	-5.165411	1.377830	1.955245
H	-3.683939	2.731272	0.462215
C	-0.161552	1.870314	-0.491146
C	1.849140	1.183695	-0.195189
N	1.968590	2.296760	-0.868296
N	0.518587	0.883630	0.056331
H	-0.233030	0.051240	0.426605
O	0.623399	2.754318	-1.062253
O	-1.441099	2.028612	-0.513418
Ag	-1.353274	-1.606716	-1.093237

3a-Ag E_{B3LYP} = -945.248966 a.u. E_{ZPE} = 133.65 kcal/mol

C	3.886359	-1.620085	0.774802
C	2.749876	-0.816373	0.780758
C	2.753883	0.409243	0.102543
C	3.910459	0.826927	-0.569706
C	5.043052	0.019392	-0.571049

C	5.032224	-1.205516	0.096881
H	3.878431	-2.565557	1.305584
H	1.874984	-1.126575	1.341017
H	3.911677	1.772653	-1.098666
H	5.932622	0.343162	-1.099834
H	5.915615	-1.834705	0.090449
C	-4.020624	-0.532076	1.274460
C	-4.522532	-1.007087	0.062922
C	-4.074812	-0.467315	-1.142508
C	-3.119984	0.550110	-1.145718
C	-2.630782	0.995222	0.075580
C	-3.065075	0.483856	1.290796
H	-4.375273	-0.944610	2.212004
H	-5.269600	-1.792690	0.058362
H	-4.472389	-0.827222	-2.084491
H	-2.772903	0.998881	-2.068839
C	-0.443766	1.898508	0.096615
C	1.563759	1.269414	0.109639
N	1.647654	2.572751	0.112024
N	0.259711	0.796944	0.106772
H	-2.674847	0.878171	2.221494
O	0.292001	2.998551	0.095153
O	-1.736328	2.098036	0.079334
Ag	-0.470585	-1.363561	-0.238737

1a-benzyne

C	-2.440172	-2.591540	0.257877
C	-1.718905	-1.400547	0.259179
C	-2.368221	-0.186701	0.001128

C	-3.747525	-0.181013	-0.256777
C	-4.461038	-1.372664	-0.254134
C	-3.809741	-2.580913	0.002065
H	-1.929610	-3.526567	0.459523
H	-0.656586	-1.430530	0.473903
H	-4.248990	0.756891	-0.463227
H	-5.526208	-1.360813	-0.457015
H	-4.368962	-3.510220	0.000608
C	3.999480	-2.458324	-0.012610
C	5.047054	-1.510063	-0.030330
C	4.812004	-0.124563	-0.033245
C	3.516681	0.426044	-0.018187
C	2.529376	-0.563337	-0.001603
C	2.804797	-1.779702	0.000946
H	4.165571	-3.526955	-0.009443
H	6.069052	-1.876554	-0.041576
H	5.662787	0.549926	-0.047710
H	3.332199	1.493002	-0.020867
C	0.061956	2.537407	-0.004496
C	-1.632267	1.081267	0.006415
N	-2.205287	2.248012	0.025359
N	-0.263816	1.201578	-0.004907
H	0.430171	0.464609	-0.052609
O	-1.140321	3.190904	0.014348
O	1.136116	3.082155	-0.018055

11. References

[1] D. Martin, D.-C. H.-J. Herrmann, C. C. S. Rackow and K. Nadolski, *Angew. Chem.,* 1965, **77**, 96.

[2] D. Martin and A. Weise, *Chem. Ber.,* 1966, **99**, 317.

[3] S. V. Bhat, D. Robinson, J. E. Moses and P. Sharma, *Org. Lett.,* 2016, **18**, 1100.

[4] T. Gerfaud, H.-L. Wei, L. Neuville and J.-P. Zhu, *Org. Lett.,* 2011, **13***,* 6172.

[5] J. L. Romine, S. W. Martin, V. K. Gribkoff, C. G. Boissard, S. I. Dworetzky, J. Natale, Y. Li, Q. Gao, N. A. Meanwell and J. E. Starrett, *J. Med. Chem.,* 2002, **45**, 2942.

[6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

[7] (*a*) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

[8] (*a*) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650; (*b*) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

[9] W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.

[11] J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.

[12] (a) K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363; (b) C. Gonzalez and B. Schlegel, *J.*

Chem. Phys., 1989, **90**, 2154.

12. Single crystal X-ray structure for compound 3a

The crystallographic data for the structure of **3a** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC: 1813383).