

Electronic Supplementary Information

Bimetallic Cu/Pd-catalyzed three-component azide-alkyne cycloaddition/isocyanide insertion: synthesis of fully decorated tricyclic triazoles

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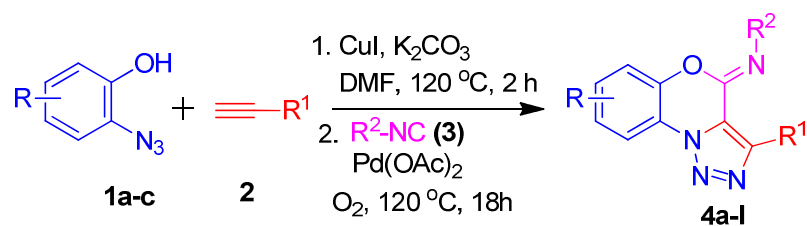
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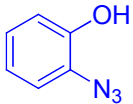
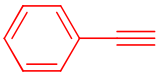

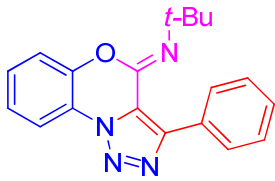
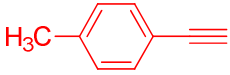
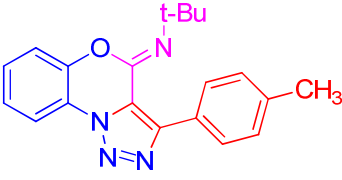
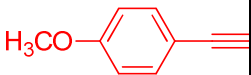
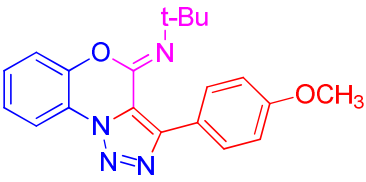
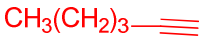
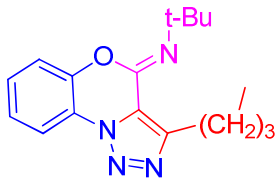
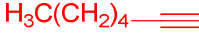
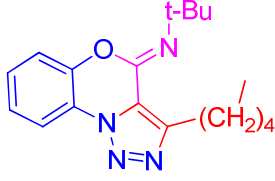
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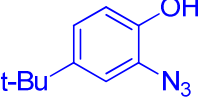
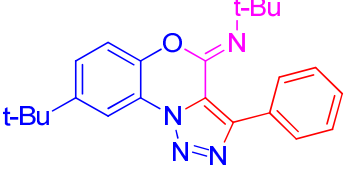
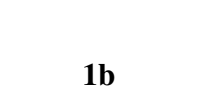
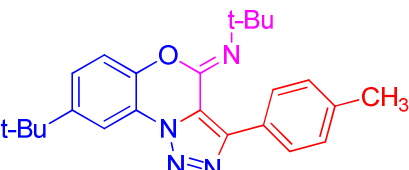
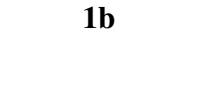
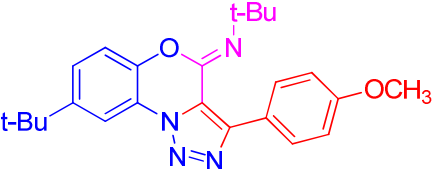
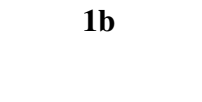
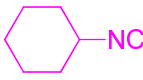
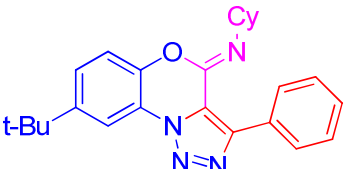
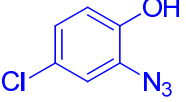
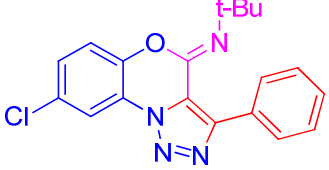
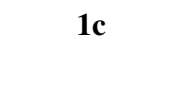
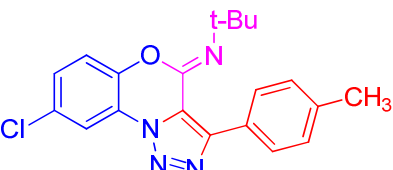
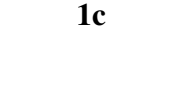
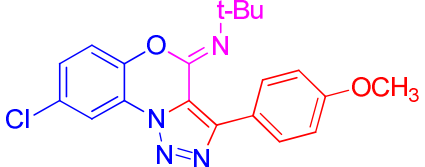
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1. Table S1: Reaction scope for 1,2,3-triazole fused oxazine (4a-l).^{a,b}



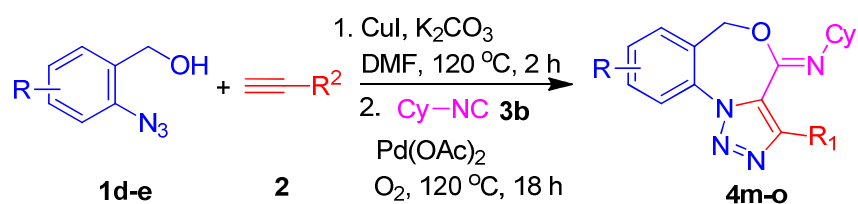
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1	 1a	 2a	 3a	 4a, 72%
2	1a	 2b	3a	 4b, 70%
3	1a	 2c	3a	 4c, 71%
4	1a	 2d	3a	 4d, 68%
5	1a	 2e	3a	 4e, 65%

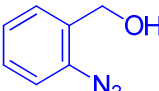
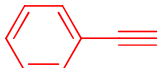
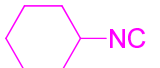
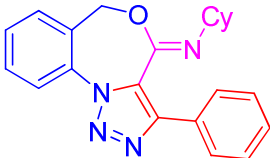
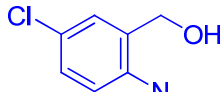
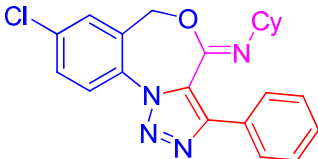
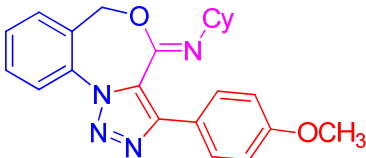
6	 <p>1b</p>	2a	3a	 <p>4f, 70%</p>
7	 <p>1b</p>	2b	3a	 <p>4g, 65%</p>
8	 <p>1b</p>	2c	3a	 <p>4h, 67%</p>
9	 <p>1b</p>	2a	 <p>3b</p>	 <p>4i, 68%</p>
10	 <p>1c</p>	2a	3a	 <p>4j, 72%</p>
11	 <p>1c</p>	2b	3a	 <p>4k, 72%</p>
12	 <p>1c</p>	2c	3a	

				4l, 70%
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^aConditions: **1a-c** (0.37 mmol), **2** (0.37 mmol), CuI (0.04 mol), K₂CO₃ (0.44 mmol), DMF (2 mL), 120 °C, 2 h, and then **3** (0.28 mmol), Pd(OAc)₂ (10 mol%), O₂ balloon; ^b Isolated yields; ^cReaction performed on 1 mmol scale.

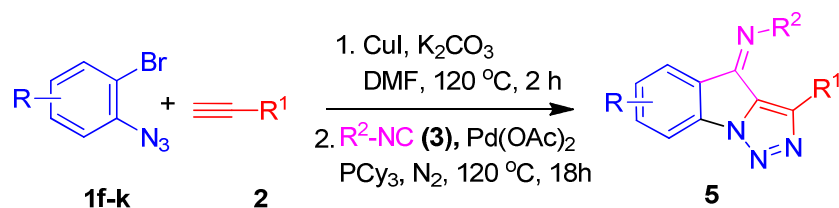
2. Table S2: Reaction scope for 1,2,3-triazole fused oxazepine (4m-o).^{a,b}

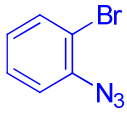
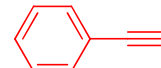
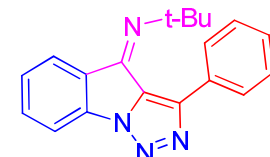
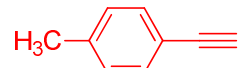
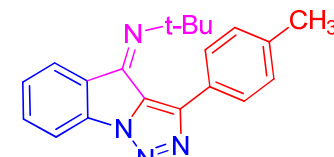
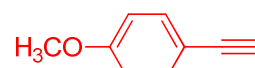
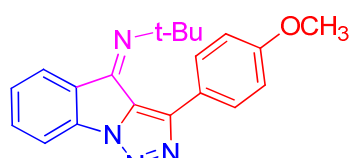
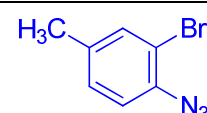
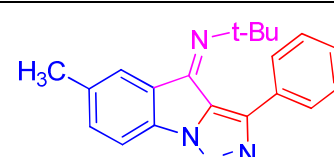
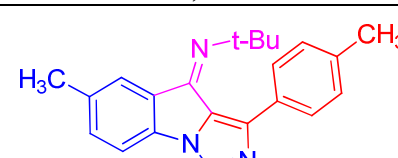


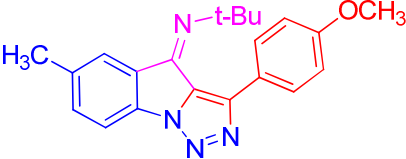
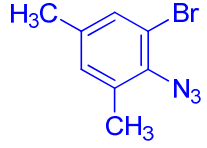
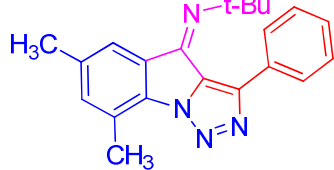
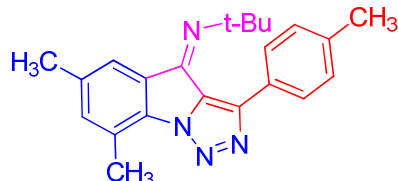
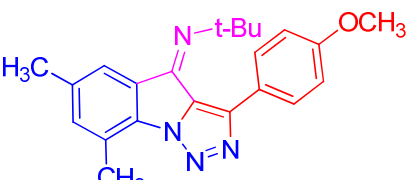
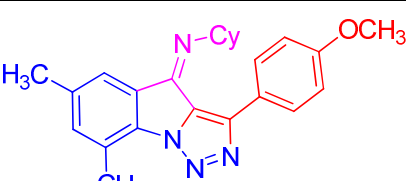
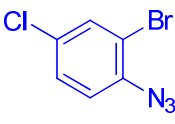
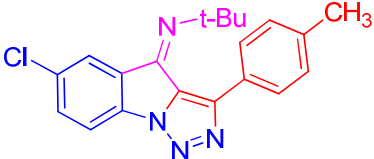
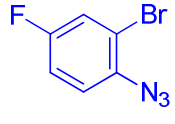
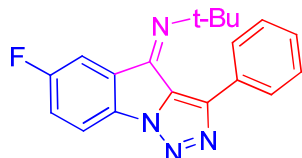
Entry	(2-Azidophenyl)methanol (2d-e)	Acetylene (2)	Isocyanide (3)	1,2,3-Triazole fused oxazepine (4m-o)
1	 1d	 2a	 3b	 4m, 65%
2	 1e	2a	3b	 4n, 68%
3	1d	2c	3b	 4o, 65%

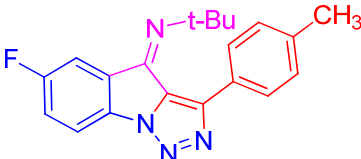
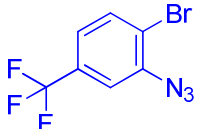
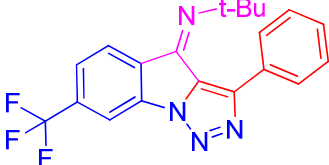
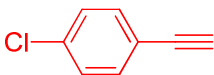
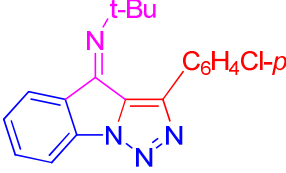
^aConditions: **1d-e** (0.37 mmol), **2** (0.37 mmol), CuI (0.04 mol), K₂CO₃ (0.44 mmol), DMF (2 mL), 120 °C, 2 h, and then **3** (0.28 mmol), Pd(OAc)₂ (10 mol%), O₂ balloon. ^b Isolated yields.

3. Table S3: Reaction scope for 1,2,3-triazole fused indol-ylidene (**5a-o**).^{a,b}



Entry	1-Azido-2-bromobenzene (1f-k)	Acetylene (2)	Isocyanide (3)	1,2,3-Triazole fused indol-ylidene (5)
1	 1f	 2a	t-Bu-NC 3a	 5a, 75%
2	1f	 2b	3a	 5b, 74%
3	1f	 2c	3a	 5c, 72%
4	 1g	2a	3a	 5d, 75%
5	1g	2b	3a	 5e, 73%

6	1g	2c	3a	 <p>5f, 70%</p>
7	 <p>1h</p>	2a	3a	 <p>5g, 68%</p>
8	1h	2b	3a	 <p>5h, 70%</p>
9	1h	2c	3a	 <p>5i, 72%</p>
10	1h	2c	3b	 <p>5j, 70%</p>
11	 <p>1i</p>	2b	3a	 <p>5k, 68%</p>
12	 <p>1j</p>	2a	3a	

				5l , 70%
13	1j	2b	3a	 5m , 72%
14	 1k	2a	3a	 5n , 70%
15	1f	 2f	3a	 5o , 70%

^aConditions: **1f-k** (0.25 mmol), **2** (0.25 mmol), CuI (0.03 mol), K₂CO₃ (0.30 mmol), DMF (2 mL), 120 °C, 2 h, and then **3** (0.19 mmol), Pd(OAc)₂ (10 mol%), PCy₃ (0.015 mmol), N₂, 120 °C, 18 h; ^bIsolated yields; ^cReaction performed on 1 mmol scale.

4. General methods. Unless stated otherwise, solvents and chemicals were obtained from commercial sources and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light or iodine spray. Flash chromatography was performed on silica gel (100-200 mesh) using hexane and ethyl acetate. IR spectra were recorded on a Thermo Scientific iD7 ATR FT IR spectrometer. Melting points were recorded on a DBK digital melting point apparatus and were uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Bruker Biospin Avance III FT-NMR spectrometer. ¹H and ¹³C NMR spectra were determined in CDCl₃ and DMSO-*d*₆ solutions by using 400 or 126 or 100 MHz spectrometers, respectively. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, δ = 0.00) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet). Coupling constants (*J*) are given in hertz. Melting points were determined using a melting point apparatus and are uncorrected. LC-MS spectra were recorded on a Agilent 1290

Infinity II. HPLC chromatogram were recorded on a Waters 2695. High-resolution mass spectra were recorded on a Bruker maxis-TOF mass spectrometer. Starting materials 2-azidophenols (1a),^[1a] 2-azido-4-(*tert*-butyl)phenol (1b),^{1a,1b} 2-azido-4-chlorophenol (1c),^{1a} (2-azidophenyl)methanol (1d),^{1a,1c} (2-azido-5chlorophenyl)methanol (1e),^{1a,1d} 1-azido-2-bromobenzene (1f),^{1a,2} 1-azido-2-bromo-4-methylbenzene (1g),^{1a,2} 2-azido-1-bromo-3,5-dimethylbenzene (1h),^{1a,2} 1-azido-2-bromo-4-chlorobenzene (1i),^{1a,1e} and 1-azido-2-bromo-4-fluorobenzene (1j)^{1a,2} were synthesized according to known procedures.

5. Procedure for the synthesis of 2-azido-1-bromo-4-(trifluoromethyl)benzene (1k)^{1a}

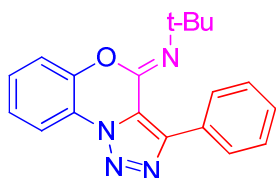
To a solution of 2-bromo-5-(trifluoromethyl)aniline (1.0 g, 4.16 mmol) in water (10.0 mL) was added concentrated aqueous HCl (2.0 mL) was added drop wise at 0 °C for 10 min. To this a solution of NaNO₂ (5.0 mmol) in water (2.0 mL) was added drop wise at 0-5 °C and stirred for 10 min. A solution of NaN₃ (6.2 mmol) in water (2.0 mL) was added drop wise at 0-5 °C and the reaction mixture was stirred at 0 °C for 1 h. After completion of the reaction, the mixture was diluted with water (20 ml), extracted with EtOAc (3×30 mL), and the combined EtOAc layer was washed with brine solution (30 ml). Then the organic layer was dried with anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc / hexane as eluent to give the corresponding pure products **1k**.

Yellow liquid; Yield: 886 mg, 80%; R_f = 0.8 (5% EtOAc/ *n*-hexane); IR (Neat): 2926, 2852, 1734, 1360, 1220; 731; ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 1.2 Hz, 1H), 7.27-7.24 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 139.8, 134.5, 131.4 (d, *J* = 26.6 Hz), 124.3 (d, *J* = 217.2 Hz), 122.4, 117.8, 116.2; HR-MS (ESI+) *m/z* calculated for [C₇H₄BrF₃N₃]⁺ = [M+Na-BrN₂]⁺ 181.0116, found 181.1181.

6. General procedure for the synthesis of 1,2,3-triazole fused oxazin/oxazepin (4). In an oven-dried 25 mL schlenck tube containing the corresponding 2-azidophenol/2-(2-azidophenyl)methanol (**1a-e**) (0.37 mmol), acetylene (**2**) (0.37 mmol), in DMF (2 mL) were added CuI (0.04 mmol) and K₂CO₃ (0.44 mmol). The resulting reaction mixture was stirred at 120 °C for 2 h under open air atmosphere. After completion of the reaction was monitored by TLC. Up on cooling to room temperature, to the same pot Pd(OAc)₂ (10 mol %), isocyanide (**3**)

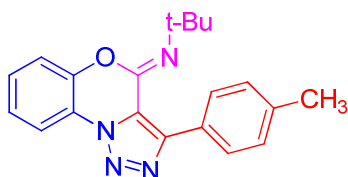
(0.28 mmol) were added. Subsequently, the vessel was back filled with O₂. The resulting reaction mixture was stirred at 120 °C for 18 h. After completion of the reaction, the reaction mixture was filtered through celite, and the residue was washed with diethyl ether (2×10 mL). The filtrate was washed with 30 mL of water, and the organic layer was collected. The aqueous phase was extracted with diethyl ether (2×10 mL). The combined organic phases was washed with brine solution (2×20 mL) and dried over anhydrous Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with EtOAc / hexane as eluent to give the corresponding pure products **4**.

(Z)-N-(tert-Butyl)-3-phenyl-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4a).



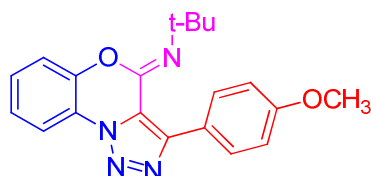
Following the general procedure, the desired product **4a** (84 mg, 72%) was obtained as white solid; mp: 148-152 °C; $R_f = 0.5$ (10% EtOAc/ *n*-hexane); IR (Neat): 3066, 2967, 1692, 1359, 1216, 1136, 1029, 756 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.74 (d, $J = 6.6$ Hz, 1H), 7.79 (dd, $J_1 = 1.2$ Hz, $J_2 = 7.6$ Hz, 1H), 7.51 (d, $J = 7.2$ Hz, 1H), 7.32 (t, $J = 6.0$ Hz, 1H), 7.27 (d, $J = 7.6$ Hz, 1H), 7.20 (t, $J = 5.8$ Hz, 1H), 7.00 (t, $J = 6.2$ Hz, 1H), 6.80-6.73 (m, 2H), 1.56 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 146.9, 143.3, 136.3, 129.6, 129.5, 129.1, 129.0, 127.7, 124.2, 121.4, 121.1, 116.5, 116.4, 55.5, 30.0; HPLC: 99.78% column: X-Bridge C-18 (150 × 4.6 mm 5μm, mobile phase A: 10 mM Ammonium acetate, mobile phase B: ACN; T/%B: 0/5, 1.5/5, 3/15, 7/55, 10/95, 14/95, 17/5, 20/5; flow rate: 1.0 mL/min, Diluent : ACN : Water (70 : 30) , retention time 20 min; Mass: m/z (CI) 319 (M + 1); HR-MS (ESI+) m/z calculated for [C₁₉H₁₉ON₄]⁺ = [M – N(CH₃)₃]⁺ 249.0902, found 249.1014.

(Z)-N-(tert-Butyl)-3-(*p*-tolyl)-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4b).



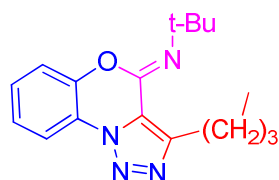
Following the general procedure, the desired product **4b** (232 mg, 70%) was obtained as brown solid; mp: 168-170 °C; $R_f = 0.6$ (10% EtOAc/ *n*-hexane); IR (Neat): 3066, 2961, 1689, 1498, 1284, 753 cm^{-1} ; ^1H NMR (400 Hz, CDCl_3): δ 8.39 (d, $J = 8.0$ Hz, 2H), 8.27 (d, $J = 8.2$ Hz, 1H), 7.39 (t, $J = 7.2$ Hz, 1H), 7.29-7.25 (m, 4H), 2.41 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.0, 143.2, 138.9, 136.4, 129.4, 128.9, 128.4, 126.8, 124.2, 121.5, 120.8, 116.5, 116.4, 55.5, 30.0, 21.4; HR-MS (ESI+) m/z calculated for $[\text{C}_{20}\text{H}_{21}\text{N}_4\text{O}]^+ = [\text{M} + \text{H}]^+$ 333.1710, found 333.1712.

(Z)-N-(tert-Butyl)-3-(4-methoxyphenyl)-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4c).



Following the general procedure, the desired product **4c** (91 mg, 71%) was obtained as orange solid; mp: 170-173 °C; $R_f = 0.5$ (20% EtOAc/ *n*-hexane); IR (Neat): 3071, 2959, 1693, 1546, 1302, 1261, 743 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.48 (d, $J = 8.8$ Hz, 2H), 8.26 (d, $J = 8.8$ Hz, 1H), 7.38 (t, $J = 7.2$ Hz, 1H), 7.29-7.26 (m, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 3.87 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.2, 146.8, 143.2, 136.6, 130.9, 128.9, 124.2, 122.2, 121.5, 120.4, 116.5, 116.4, 113.1, 55.4, 55.3, 30.0; HR-MS (ESI+) m/z calculated for $[\text{C}_{20}\text{H}_{21}\text{N}_4\text{O}_2]^+ = [\text{M} + \text{H}]^+$ 349.1664, found 349.1665.

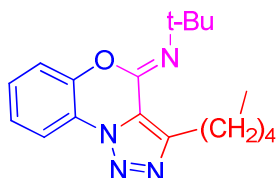
(Z)-N-(tert-Butyl)-3-butyl-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4d).



Following the general procedure, the desired product **4d** (75 mg, 68%) was obtained as white solid; mp: 102-105 °C; $R_f = 0.5$ (10% EtOAc/ *n*-hexane); IR (Neat): 2959, 2926, 1684, 1507, 1358, 1211, 1050, 750 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.19 (dd, $J_1 = 1.6$ Hz, $J_2 = 1.2$ Hz, 1H), 7.37-7.33 (m, 1H), 7.26-7.22 (m, 2H), 3.04 (t, $J = 7.8$ Hz, 2H), 1.78-1.70 (m, 2H), 1.45 (s,

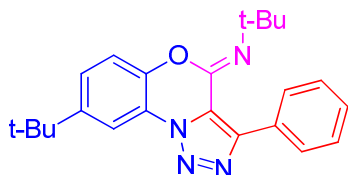
9H), 1.42-1.37 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 149.4, 143.5, 136.2, 128.7, 124.1, 121.6, 121.4, 116.7, 116.2, 54.9, 30.8, 30.1, 25.3, 22.3, 13.8; HR-MS (ESI+) m/z calculated for $[\text{C}_{17}\text{H}_{23}\text{N}_4\text{O}]^+ = [\text{M} + \text{H}]^+ 299.1872$, found 299.1874.

(Z)-N-(tert-Butyl)-3-pentyl-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4e).



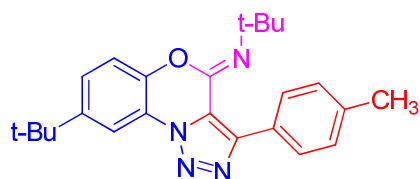
Following the general procedure, the desired product **4e** (75 mg, 65%) was obtained as brown solid; mp: 78-80 °C; $R_f = 0.4$ (10% EtOAc/ *n*-hexane); IR (Neat): 2957, 2927, 1685, 1384, 1259, 1049, 750 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.12 (d, $J = 7.6$ Hz, 1H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.18 (d, $J = 6.4$ Hz, 2H), 2.96 (t, $J = 7.6$ Hz, 2H), 1.70-1.66 (m, 2H), 1.38 (s, 9H), 1.30-1.29 (m, 4H), 0.82 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.4, 142.5, 135.2, 127.6, 123.0, 120.5, 120.4, 115.7, 115.1, 53.9, 30.4, 29.1, 27.4, 24.6, 21.3, 13.0; HR-MS (ESI+) m/z calculated for $[\text{C}_{18}\text{H}_{25}\text{N}_4\text{O}]^+ = [\text{M} + \text{H}]^+ 313.2028$, found 313.2028.

(Z)-N,8-Di-tert-butyl-3-phenyl-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4f).



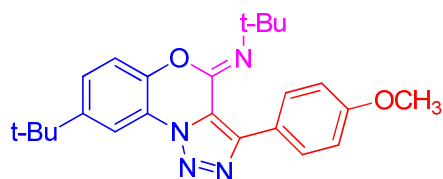
Following the general procedure, the desired product **4f** (69 mg, 70%) was obtained as off white solid; mp: 176-178 °C; $R_f = 0.7$ (10% EtOAc/ *n*-hexane); IR (Neat): 3054, 2964, 1685, 1508, 1481, 1215, 847, 735 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.47 (d, $J = 6.8$ Hz, 2H), 8.29 (d, $J = 2.4$ Hz, 1H), 7.47-7.40 (m, 4H), 7.21 (d, $J = 8.8$ Hz, 1H), 1.47 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.0, 147.0, 141.1, 136.7, 129.7, 129.6, 128.9, 127.7, 126.2, 121.2, 120.9, 116.0, 113.2, 55.4, 34.9, 31.3, 29.9; HR-MS (ESI+) m/z calculated for $[\text{C}_{23}\text{H}_{27}\text{N}_4\text{O}]^+ = [\text{M} + \text{H}]^+ 375.2185$, found 375.2179.

(Z)-N,8-Di-tert-butyl-3-(*p*-tolyl)-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4g).



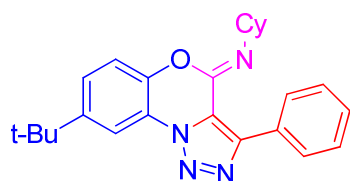
Following the general procedure, the desired product **4g** (66 mg, 65%) was obtained as yellow solid; mp: 184-186 °C; $R_f = 0.8$ (10% EtOAc/ *n*-hexane); IR: 3079, 2960, 1697, 1489, 1287, 853 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.39 (d, $J = 6.0$ Hz, 2H), 8.28 (s, 1H), 7.41 (d, $J = 5.6$ Hz, 1H), 7.26-7.19 (m, 3H), 2.41 (s, 3H), 1.47 (s, 9H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.9, 145.9, 140.1, 137.8, 135.8, 128.4, 127.4, 125.8, 125.0, 119.9, 114.9, 112.2, 54.3, 33.8, 30.3, 28.9, 20.4; HR-MS (ESI+) m/z calculated for $[\text{C}_{24}\text{H}_{29}\text{N}_4\text{O}]^+ = [\text{M} + \text{H}]^+$ 389.2341, found 389.2339.

(Z)-N,8-Di-tert-butyl-3-(4-methoxyphenyl)-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4h).



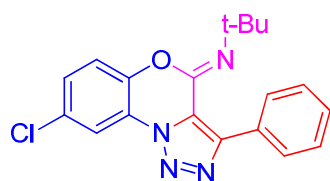
Following the general procedure, the desired product **4h** (70 mg, 67%) was obtained as pink solid; mp: 162-165 °C; $R_f = 0.4$ (10% EtOAc/ *n*-hexane); IR (Neat): 3076, 2957, 1686, 1555, 1486, 1301, 1291, 1034, 855 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.49 (d, $J = 8.8$ Hz, 2H), 8.27 (d, $J = 2.0$ Hz, 1H), 7.41 (dd, $J_1 = 2.4$ Hz, $J_2 = 2.4$ Hz, 1H), 7.20 (d, $J = 8.8$ Hz, 1H), 6.97 (d, $J = 8.8$ Hz, 2H), 3.87 (s, 3H), 1.48 (s, 9H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.2, 147.9, 146.8, 141.1, 137.1, 131.0, 126.1, 122.3, 120.9, 120.5, 115.9, 113.2, 113.1, 55.3, 34.9, 31.3, 30.0; HR-MS (ESI+) m/z calculated for $[\text{C}_{24}\text{H}_{29}\text{N}_4\text{O}_2]^+ = [\text{M} + \text{H}]^+$ 405.2290, found 405.2291.

(Z)-8-(tert-Butyl)-N-cyclohexyl-3-phenyl-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4i).



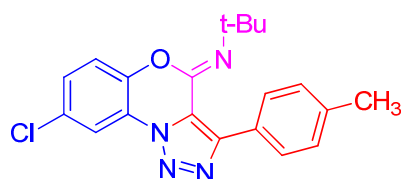
Following the general procedure, the desired product **4i** (71 mg, 68%) was obtained as white solid; mp: 150-152 °C; $R_f = 0.6$ (20% EtOAc/ *n*-hexane); IR (Neat): 3071, 2923, 1678, 1507, 1259, 1005, 825 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.51 (d, $J = 6.8$ Hz, 2H), 8.28 (d, $J = 2.4$ Hz, 1H), 7.48-7.40 (m, 4H), 7.21 (d, $J = 8.4$ Hz, 1H), 4.16-4.12 (m, 1H), 1.83-1.81 (m, 4H), 1.55-1.42 (m, 6H), 1.39 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3): δ 147.9, 146.9, 141.1, 138.2, 129.6, 129.4, 128.9, 127.8, 126.2, 120.9, 120.7, 115.9, 113.2, 54.3, 34.9, 33.3, 31.3, 25.9, 24.1; HR-MS (ESI+) m/z calculated for $[\text{C}_{25}\text{H}_{29}\text{N}_4\text{O}]^+ = [\text{M} + \text{H}]^+$ 401.2341, found 401.2341.

(Z)-N-(tert-Butyl)-8-chloro-3-phenyl-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4j).



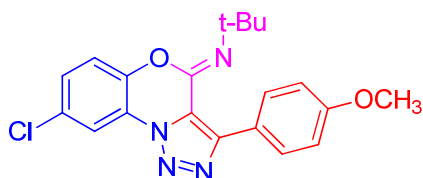
Following the general procedure, the desired product **4j** (75 mg, 72%) was obtained as off white solid; mp: 142-144 °C; $R_f = 0.7$ (10% EtOAc/ *n*-hexane); IR (Neat): 3052, 2965, 1693, 1473, 1274, 983, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.37 (d, $J = 6.4$ Hz, 2H), 8.20 (d, $J = 2.4$ Hz, 1H), 7.40-7.34 (m, 3H), 7.28 (dd, $J_1 = 2.4$ Hz, $J_2 = 2.4$ Hz, 1H), 7.16 (t, $J = 8.6$ Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.1, 140.7, 134.5, 128.5, 128.3, 128.1, 128.0, 126.7, 120.9, 119.9, 116.7, 115.5, 54.6, 28.9; HR-MS (ESI+) m/z calculated for $[\text{C}_{19}\text{H}_{18}\text{ClN}_4\text{O}]^+ = [\text{M} + \text{H}]^+$ 353.1169, found 353.1169.

(Z)-N-(tert-Butyl)-8-chloro-3-(*p*-tolyl)-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4k).



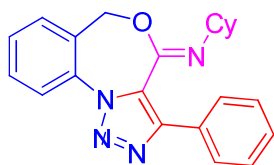
Following the general procedure, the desired product **4k** (78 mg, 72%) was obtained as violet solid; mp: 178-182 °C; $R_f = 0.8$ (10% EtOAc/ *n*-hexane); IR (Neat): 3069, 2965, 1683, 1488, 1302, 1053, 839 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.36 (d, $J = 8.4$ Hz, 2H), 8.26 (d, $J = 2.4$ Hz, 1H), 7.34 (dd, $J_1 = 2.4$ Hz, $J_2 = 2.4$ Hz, 1H), 7.26 (d, $J = 2.8$ Hz, 1H), 7.24 (s, 1H), 7.21 (d, $J = 8.8$ Hz, 1H), 2.41 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.2, 141.7, 139.2, 135.7, 129.5, 129.4, 128.9, 128.5, 126.5, 122.0, 120.6, 117.7, 116.5, 55.6, 30.0, 21.4; HR-MS (ESI+) m/z calculated for $[\text{C}_{20}\text{H}_{19}\text{ClN}_4\text{NaO}]^+ = [\text{M} + \text{Na}]^+$ 389.1145, found 389.1147.

(Z)-N-(tert-Butyl)-8-chloro-3-(4-methoxyphenyl)-4H-benzo[*b*][1,2,3]triazolo[1,5-*d*][1,4]oxazin-4-imine (4l).



Following the general procedure, the desired product **4l** (79 mg, 70%) was obtained as pink solid; mp: 164-166 °C; $R_f = 0.4$ (20% EtOAc/ *n*-hexane); IR (Neat): 3064, 2961, 1692, 1472, 1260, 981, 865 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.46 (d, $J = 8.8$ Hz, 2H), 8.26 (d, $J = 2.4$ Hz, 1H), 7.34 (dd, $J_1 = 2.4$ Hz, $J_2 = 2.4$ Hz, 1H), 7.22 (d, $J = 8.8$ Hz, 1H), 6.97 (d, $J = 9.2$ Hz, 2H), 3.87 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.3, 147.1, 141.7, 135.9, 131.0, 129.5, 128.9, 122.1, 121.9, 120.2, 117.7, 116.5, 113.2, 55.6, 55.3, 30.0; HR-MS (ESI+) m/z calculated for $[\text{C}_{20}\text{H}_{20}\text{ClN}_4\text{O}_2]^+ = [\text{M} + \text{H}]^+$ 383.1275, found 383.1275.

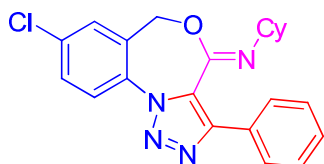
(Z)-N-Cyclohexyl-3-phenyl-4H,6H-benzo[*e*][1,2,3]triazolo[5,1-*c*][1,4]oxazepin-4-imine (4m).



Following the general procedure, the desired product **4m** (78 mg, 65%) was obtained as off white solid; mp: 178-180 °C; $R_f = 0.4$ (30% EtOAc/ *n*-hexane); IR (Neat): 3282, 2922, 1647, 1489, 1264, 1089, 747 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.10-8.04 (m, 3H), 7.67-7.63 (m, 1H), 7.52-7.51 (m, 2H), 7.45-7.38 (m, 3H), 5.00 (s, 2H), 3.79-3.74 (m, 1H), 1.68-1.62 (m, 4H), 1.31-1.13 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.3, 145.1, 136.8, 131.1, 129.8,

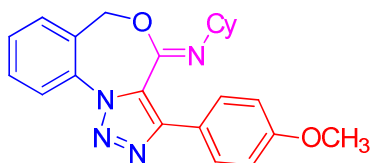
129.5, 129.3, 128.9, 128.7, 128.6, 128.0, 127.8, 122.9, 67.2, 55.5, 32.9, 25.7, 24.7; HR-MS (ESI+) m/z calculated for $[C_{22}H_{23}N_4O]^+ = [M + H]^+$ 359.1872, found 359.1873.

(Z)-8-Chloro-N-cyclohexyl-3-phenyl-4H,6H-benzo[e][1,2,3]triazolo[5,1-c][1,4]oxazepin-4-imine (4n).



Following the general procedure, the desired product **4n** (73 mg, 68%) was obtained as orange solid; mp: 219-221 °C; $R_f = 0.5$ (30% EtOAc/ *n*-hexane); IR (Neat): 3083, 2920, 1660, 1488, 1286, 1023, 797 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, $J = 8.0$ Hz, 2H), 8.00 (d, $J = 8.8$ Hz, 1H), 7.62 (dd, $J_1 = 2.4$ Hz, $J_2 = 2.0$ Hz, 1H), 7.52 (d, $J = 2.0$ Hz, 1H), 7.45-7.37 (m, 3H), 4.96 (s, 2H), 3.80-3.74 (m, 1H), 1.71-1.66 (m, 4H), 1.31-1.14 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 144.6, 135.3, 135.0, 131.1, 130.3, 129.6, 129.5, 128.9, 128.6, 128.1, 127.6, 124.2, 66.5, 55.6, 32.9, 25.6, 24.7; HR-MS (ESI+) m/z calculated for $[C_{22}H_{22}ClN_4O]^+ = [M + H]^+$ 393.1482, found 393.1483.

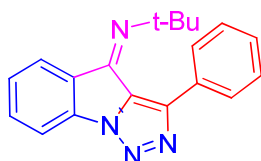
(Z)-N-Cyclohexyl-3-(4-methoxyphenyl)-4H,6H-benzo[e][1,2,3]triazolo[5,1-c][1,4]oxazepin-4-imine (4o).



Following the general procedure, the desired product **4o** (85 mg, 65%) was obtained as yellow solid; mp: 116-118 °C; $R_f = 0.4$ (30% EtOAc/ *n*-hexane); IR (Neat): 2926, 2853, 1668, 1504, 1250, 1018, 832 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 8.05 (t, $J = 9.2$ Hz, 3H), 7.66-7.62 (m, 1H), 7.50 (t, $J = 2.6$ Hz, 2H), 6.95 (d, $J = 8.8$ Hz, 2H), 4.99 (s, 2H), 3.87 (s, 3H), 3.80-3.76 (m, 1H), 1.70-1.69 (m, 4H), 1.35-1.14 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 148.1, 145.3, 136.9, 131.0, 129.9, 129.4, 129.2, 128.9, 127.0, 122.8, 122.5, 113.4, 67.1, 55.5, 55.3, 33.0, 25.7, 24.7; HR-MS (ESI+) m/z calculated for $[C_{23}H_{25}N_4O_2]^+ = [M + H]^+$ 389.1977, found 389.1998.

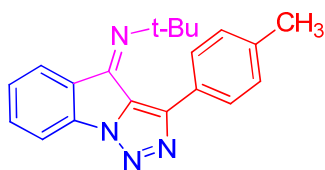
7. General procedure for the synthesis of 1,2,3- triazole fused indol-ylidene (5). In an oven-dried 25 mL sealed tube containing 1-azido-2-bromobenzene (**1f-k**) (0.25 mmol), acetylene (**2**) (0.25 mmol), in DMF (2 mL) were added CuI (0.03 mmol) and K₂CO₃ (0.30 mmol). The resulting reaction mixture was stirred at 120 °C for 2h under open air atmosphere. After completion of the reaction was monitored by TLC. Up on cooling to room temperature, to the same pot Pd(OAc)₂ (10 mol%), isocyanide (**3**) (0.19 mmol) and PCy₃ (0.015 mmol) were added. The tube was purged with nitrogen gas and stirred at 120 °C for 18 h. After completion of the reaction, the reaction mixture was filtered through celite, and the residue was washed with diethyl ether (2×10 mL). The filtrate was washed with 30 mL of water, and the organic layer was collected. The aqueous phase was extracted with diethyl ether (2×10 mL). The combined organic phases was washed with brine solution (2×20 mL) and dried over anhydrous Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with EtOAc / hexane as eluent to give the corresponding pure products **5**.

(Z)-N-(tert-Butyl)-3-phenyl-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5a).



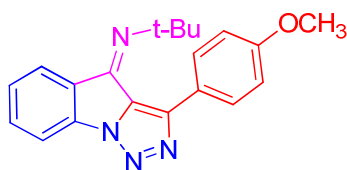
Following the general procedure, the desired product **5a** (57 mg, 75%) was obtained as light yellow solid; mp: 158-161 °C; R_f = 0.5 (10% EtOAc/ *n*-hexane); IR (Neat): 2923, 2852, 1622, 1461, 1218, 773 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.73 (d, *J* = 7.2 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49-7.38 (m, 4H), 1.68 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 146.5, 143.5, 139.7, 134.4, 131.9, 130.1, 130.0, 129.1, 128.2, 127.7, 127.1, 124.9, 113.0, 57.0, 29.8; HR-MS (ESI+) *m/z* calculated for [C₁₉H₁₉N₄]⁺ = [M + H]⁺ 303.1610, found 303.1617.

(Z)-N-(tert-Butyl)-3-(*p*-tolyl)-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5b).



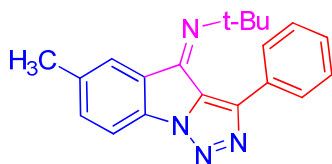
Following the general procedure, the desired product **5b** (236 mg, 74%) was obtained as light yellow solid; mp: 183-186 °C; $R_f = 0.6$ (10% EtOAc/ *n*-hexane); IR (Neat): 2921, 2852, 1623, 1462, 733 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.62 (d, $J = 8.4$ Hz, 2H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 2.41 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.5, 143.6, 139.7, 139.1, 134.0, 131.8, 130.0, 128.9, 127.6, 127.3, 127.0, 124.9, 112.9, 56.9, 29.8, 21.5; HR-MS (ESI+) m/z calculated for $[\text{C}_{20}\text{H}_{21}\text{N}_4]^+ = [\text{M} + \text{H}]^+$ 317.1766, found 317.1774.

(Z)-N-(tert-Butyl)-3-(4-methoxyphenyl)-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5c).



Following the general procedure, the desired product **5c** (61 mg, 72%) was obtained as yellow solid; mp: 166-168 °C; $R_f = 0.5$ (20% EtOAc/ *n*-hexane); IR (Neat): 2920, 2851, 1625, 1462, 1254 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.69 (d, $J = 8.8$ Hz, 2H), 8.00 (d, $J = 7.6$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.41 (t, $J = 7.4$ Hz, 1H), 6.99 (d, $J = 9.2$ Hz, 2H), 3.88 (s, 3H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.3, 146.5, 143.4, 139.6, 133.5, 131.8, 130.0, 129.2, 127.0, 125.0, 122.9, 113.5, 112.9, 56.9, 55.3, 29.8; HR-MS (ESI+) m/z calculated for $[\text{C}_{20}\text{H}_{21}\text{ON}_4]^+ = [\text{M} + \text{H}]^+$ 333.1710, found 333.1703.

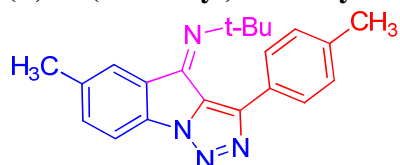
(Z)-N-(tert-Butyl)-6-methyl-3-phenyl-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5d).



Following the general procedure, the desired product **5d** (56 mg, 75%) was obtained as yellow solid; mp: 202-205 °C; $R_f = 0.5$ (10% EtOAc/ *n*-hexane); IR (Neat): 2921, 2852, 1623, 1471, 771

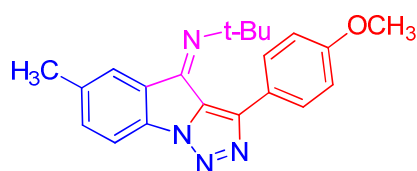
cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.72 (d, *J* = 6.8 Hz, 2H), 7.77 (s, 2H), 7.46-7.40 (m, 4H), 2.49 (s, 3H), 1.68 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 146.7, 143.3, 137.7, 137.1, 134.4, 132.3, 130.6, 130.2, 129.1, 128.2, 127.6, 125.1, 112.6, 56.9, 29.8, 21.8; HR-MS (ESI+) *m/z* calculated for [C₂₀H₂₁N₄]⁺ = [M + H]⁺ 317.1761, found 317.1756.

(Z)-N-(tert-Butyl)-6-methyl-3-(p-tolyl)-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5e).



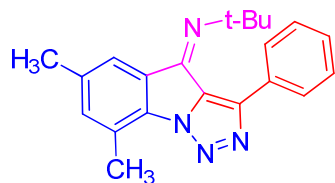
Following the general procedure, the desired product **5e** (57 mg, 73%) was obtained as light yellow solid; mp: 220-224 °C; *R_f* = 0.6 (10% EtOAc/ *n*-hexane); IR (Neat): 2920, 2852, 1623, 1476, 1219, 816 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.61 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 3H), 2.48 (s, 3H), 2.41 (s, 3H), 1.67 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 146.7, 143.5, 139.0, 137.7, 137.0, 134.1, 132.2, 130.6, 128.9, 127.6, 127.4, 125.1, 112.5, 56.8, 29.8, 21.8, 21.5; HR-MS (ESI+) *m/z* calculated for [C₂₁H₂₃N₄]⁺ = [M + H]⁺ 331.1917, found 331.1914.

(Z)-N-(tert-Butyl)-3-(4-methoxyphenyl)-6-methyl-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5f).



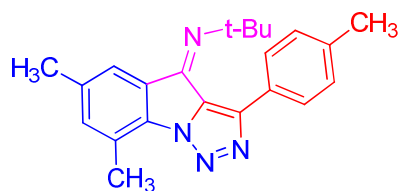
Following the general procedure, the desired product **5f** (57 mg, 70%) was obtained as yellow solid; mp: 219-222 °C; *R_f* = 0.4 (10% EtOAc/ *n*-hexane); IR (Neat): 2921, 2852, 1621, 1474, 1252, 770 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.69 (d, *J* = 8.4 Hz, 2H), 7.77 (s, 2H), 7.38 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 2.49 (s, 3H), 1.67 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 160.3, 146.7, 143.3, 137.7, 137.0, 133.5, 132.2, 130.6, 129.2, 125.1, 123.0, 113.5, 112.5, 56.8, 55.3, 29.9, 21.8; HR-MS (ESI+) *m/z* calculated for [C₂₁H₂₃ON₄]⁺ = [M + H]⁺ 347.1866, found 347.1863.

(Z)-N-(tert-Butyl)-6,8-dimethyl-3-phenyl-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5g).



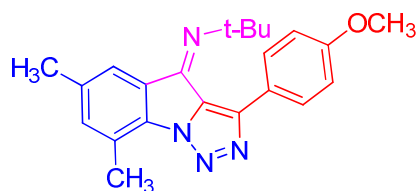
Following the general procedure, the desired product **5g** (50 mg, 68%) was obtained as yellow solid; mp: 208-212 °C; $R_f = 0.5$ (10% EtOAc/ *n*-hexane); IR (Neat): 2921, 2851, 1627, 1463, 1210, 762 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.75 (d, $J = 7.2$ Hz, 2H), 7.61 (s, 1H), 7.46 (t, $J = 7.4$ Hz, 2H), 7.39 (t, $J = 7.2$ Hz, 1H), 7.19 (s, 1H), 2.80 (s, 3H), 2.44 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.9, 142.5, 136.6, 136.5, 134.8, 134.7, 130.3, 128.9, 128.1, 127.7, 127.6, 125.3, 125.2, 56.8, 29.7, 21.6, 17.9; HR-MS (ESI+) m/z calculated for $[\text{C}_{21}\text{H}_{23}\text{N}_4]^+ = [\text{M} + \text{H}]^+$ 331.1917, found 331.1915.

(Z)-N-(tert-Butyl)-6,8-dimethyl-3-(p-tolyl)-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5h).



Following the general procedure, the desired product **5h** (53 mg, 70%) was obtained as yellow solid; mp: 205-210 °C; $R_f = 0.6$ (10% EtOAc/ *n*-hexane); IR (Neat): 2921, 2852, 1627, 1463, 1219, 765 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.63 (d, $J = 8.4$ Hz, 2H), 7.60 (s, 1H), 7.27 (d, $J = 9.2$ Hz, 2H), 7.18 (s, 1H), 2.80 (s, 3H), 2.44 (s, 3H), 2.41 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.9, 142.6, 138.9, 136.5, 136.4, 134.6, 134.5, 128.8, 128.1, 127.6, 127.5, 125.3, 56.7, 29.7, 21.6, 21.5, 17.9; HR-MS (ESI+) m/z calculated for $[\text{C}_{22}\text{H}_{25}\text{N}_4]^+ = [\text{M} + \text{H}]^+$ 345.2074, found 345.2072.

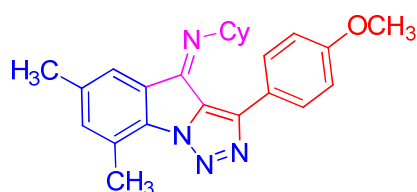
(Z)-N-(tert-Butyl)-3-(4-methoxyphenyl)-6,8-dimethyl-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5i).



Following the general procedure, the desired product **5i** (57 mg, 72%) was obtained as yellow

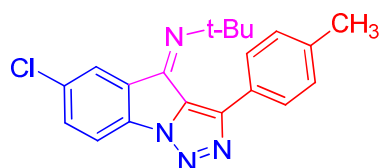
solid; mp: 182-185 °C; R_f = 0.3 (10% EtOAc/ *n*-hexane); IR (Neat): 2920, 2852, 1611, 1501, 1247, 1176, 834 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.71 (d, J = 8.8 Hz, 2H), 7.60 (s, 1H), 7.18 (s, 1H), 6.98 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.79 (s, 3H), 2.44 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.2, 146.9, 142.4, 136.5, 136.3, 134.6, 133.9, 129.2, 128.1, 125.3, 125.2, 123.1, 113.4, 56.6, 55.3, 29.8, 21.6, 17.9; HR-MS (ESI+) m/z calculated for $[\text{C}_{22}\text{H}_{25}\text{ON}_4]^+ = [\text{M} + \text{H}]^+$ 361.2023, found 361.2020.

(Z)-N-Cyclohexyl-3-(4-methoxyphenyl)-6,8-dimethyl-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5j).



Following the general procedure, the desired product **5j** (60 mg, 70%) was obtained as yellow solid; mp: 178-180 °C; R_f = 0.5 (5% EtOAc/ *n*-hexane); IR (Neat): 2924, 2854, 1624, 1505, 1462, 1247, 858 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.67 (d, J = 8.8 Hz, 2H), 7.46 (s, 1H), 7.16 (s, 1H), 6.99 (d, J = 8.8 Hz, 2H), 4.39-4.37 (m, 1H), 3.87 (s, 3H), 2.77 (s, 3H), 2.41 (s, 3H), 2.01-1.94 (m, 4H), 1.79-1.74 (m, 2H), 1.57-1.46 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.2, 147.7, 142.7, 137.1, 134.6, 131.3, 129.1, 126.5, 126.1, 125.2, 123.0, 113.7, 60.2, 55.3, 33.7, 25.8, 24.2, 21.6, 17.8; HR-MS (ESI+) m/z calculated for $[\text{C}_{24}\text{H}_{27}\text{ON}_4]^+ = [\text{M} + \text{H}]^+$ 387.2179, found 387.2176.

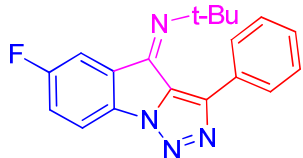
(Z)-N-(tert-Butyl)-6-chloro-3-(*p*-tolyl)-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5k).



Following the general procedure, the desired product **5k** (52 mg, 68%) was obtained as brown solid; mp: 210-213 °C; R_f = 0.4 (5% EtOAc/ *n*-hexane); IR (Neat): 2921, 2852, 1622, 1462, 1214, 821 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.58 (d, J = 7.6 Hz, 2H), 7.95 (s, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 9.6 Hz, 2H), 2.41 (s, 3H), 1.67 (s, 9H);

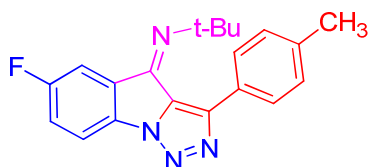
^{13}C NMR (100 MHz, CDCl_3): δ 145.1, 143.9, 139.4, 137.9, 133.9, 132.6, 131.6, 130.1, 128.9, 127.6, 127.0, 126.1, 113.8, 57.2, 29.9, 21.5; HR-MS (ESI+) m/z calculated for $[\text{C}_{20}\text{H}_{20}\text{ClN}_4]^+ = [\text{M} + \text{H}]^+$ 351.1371, found 351.1366.

(Z)-N-(tert-Butyl)-6-fluoro-3-phenyl-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5l).



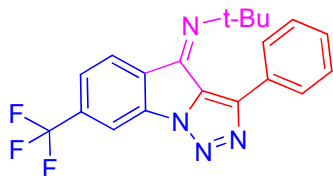
Following the general procedure, the desired product **5l** (52 mg, 70%) was obtained as light yellow solid; mp: 198-200 °C; $R_f = 0.4$ (10% EtOAc/ *n*-hexane); IR (Neat): 3059, 3005, 1625, 1472, 1209, 830 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.69 (d, $J = 7.2$ Hz, 2H), 7.90-7.87 (m, 1H), 7.71 (dd, $J_1 = 2.0$ Hz, $J_2 = 2.4$ Hz, 1H), 7.48-7.39 (m, 3H), 7.34-7.29 (m, 1H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.2 (d, $J = 245.5$ Hz), 145.3, 143.8, 136.0, 134.6, 129.9, 129.3, 128.2, 127.6, 126.2 (d, $J = 7.2$ Hz), 118.6 (d, $J = 24.3$ Hz), 117.8 (d, $J = 26.7$ Hz), 114.0 (d, $J = 8.7$ Hz), 57.2, 29.9; HR-MS (ESI+) m/z calculated for $[\text{C}_{19}\text{H}_{18}\text{FN}_4]^+ = [\text{M} + \text{H}]^+$ 321.1510, found 321.1506.

(Z)-N-(tert-Butyl)-6-fluoro-3-(*p*-tolyl)-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5m).



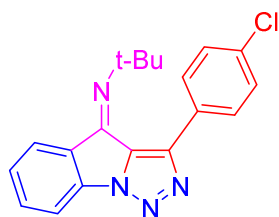
Following the general procedure, the desired product **5m** (56 mg, 72%) was obtained as light yellow solid; mp: 298-302 °C; $R_f = 0.3$ (10% EtOAc/ *n*-hexane); IR (Neat): 3036, 2967, 1627, 1504, 1473, 1262, 817 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.58 (d, $J = 8.4$ Hz, 2H), 7.89-7.86 (m, 1H), 7.70 (dd, $J_1 = 2.4$ Hz, $J_2 = 2.0$ Hz, 1H), 7.33-7.26 (m, 3H), 2.41 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.1 (d, $J = 245.2$ Hz), 145.3, 144.0, 139.4, 135.9, 134.3, 128.9, 127.6, 127.1, 126.3 (d, $J = 7.3$ Hz), 118.5 (d, $J = 24.3$ Hz), 117.7 (d, $J = 26.6$ Hz), 113.9 (d, $J = 8.6$ Hz), 57.1, 29.9, 21.5; HR-MS (ESI+) m/z calculated for $[\text{C}_{20}\text{H}_{20}\text{FN}_4]^+ = [\text{M} + \text{H}]^+$ 335.1672, found 335.1673.

(Z)-N-(tert-Butyl)-3-(*p*-tolyl)-7-(trifluoromethyl)-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5n).



Following the general procedure, the desired product **5n** (50 mg, 70%) was obtained as yellow solid; mp: 201-204 °C; $R_f = 0.6$ (10% EtOAc/ *n*-hexane); IR (Neat): 2968, 1638, 1505, 1458, 1315, 1143 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.59 (d, $J = 8.4$ Hz, 2H), 8.18 (s, 1H), 8.13 (d, $J = 8.0$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 2H), 2.42 (s, 3H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 145.1, 143.9, 139.6 (2C), 134.1, 133.9 (d, $J = 33.5$ Hz), 130.3, 128.9, 127.6, 126.9, 124.3 (d, $J = 3.7$ Hz), 123.9, 121.6, 110.2 (d, $J = 3.9$ Hz), 57.4, 29.9, 21.5; HR-MS (ESI+) m/z calculated for $[\text{C}_{21}\text{H}_{20}\text{F}_3\text{N}_4]^+ = [\text{M} + \text{H}]^+$ 385.1640, found 385.1640.

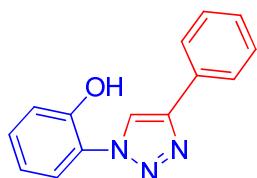
(Z)-N-(tert-Butyl)-3-(4-chlorophenyl)-4H-[1,2,3]triazolo[1,5-a]indol-4-imine (5o).



Following the general procedure, the desired product **5o** (35 mg, 70%) was obtained as white solid; mp: 185-190 °C; $R_f = 0.5$ (10% EtOAc/ *n*-hexane); IR (Neat): 2962, 1624, 1460, 1211, 1089, 840, 732; ^1H NMR (400 MHz, CDCl_3): δ 8.69 (d, $J = 8.8$ Hz, 2H), 8.00 (d, $J = 7.6$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.45-7.41 (m, 3H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.5, 142.4, 139.7, 134.8, 134.4, 132.0, 130.1, 128.9, 128.6, 128.4, 127.3, 124.8, 113.1, 57.1, 29.8; HR-MS (ESI+) m/z calculated for $[\text{C}_{19}\text{H}_{18}\text{ClN}_4]^+ = [\text{M} + \text{H}]^+$ 337.1220, found 337.1228.

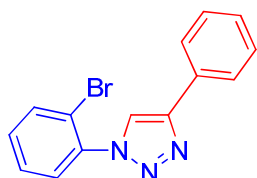
8. Procedure for the synthesis of 2-(4-Phenyl-1H-1,2,3-triazol-1-yl)phenol (1a). To a round bottom flask containing 2-azidophenol (**1a**) (100 mg, 0.74 mmol), phenyl acetylene (**2a**) (76 mg, 0.74 mmol) in DMF (2 mL) were added CuI (14 mg, 0.07 mmol), K_2CO_3 (123 mg, 0.88 mmol). The resulting mixture and stirred at 120 °C for 2h under open air. After completion of the

reaction was monitored by TLC. The reaction mixture was cooled to room temperature and diluted with water and extracted with EtOAc (20 mL × 2). The combined EtOAc layer was collected, dried over anhydrous Na₂SO₄ and concentrated under vacuum. The residue was purified using column chromatography over silica gel with EtOAc / hexane to give desired product of **Ia**.



Beige solid, 140 mg (80%); mp: 193-195 °C (lit³ 193.3-193.7 °C); $R_f = 0.4$ (20% EtOAc/ *n*-hexane); IR (Neat): 2965, 2717, 1415, 748 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.91 (s, 1H), 8.31 (s, 1H), 7.91 (d, $J = 7.6$ Hz, 2H), 7.49 (t, $J = 7.2$ Hz, 3H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.32 (d, $J = 6.8$ Hz, 1H), 7.22 (d, $J = 7.2$ Hz, 1H), 7.03 (t, $J = 7.0$ Hz, 1H); ¹³C NMR (75 MHz, CDCl₃+DMSO-*d*₆) δ 149.0, 146.9, 130.4, 129.6, 128.7, 128.0, 125.6, 124.4, 123.7, 121.2, 119.8, 117.5.

9. Procedure for the synthesis of 1-(2-bromophenyl)-4-phenyl-1H-1,2,3-triazole (IIa). To a round bottom flask containing 1-azido-2-bromobenzene (**1f**) (100 mg, 0.50 mmol), phenyl acetylene (**2a**) (52 mg, 0.50 mmol) in DMF (2 mL). then after CuI (10 mg, 0.05 mmol), K₂CO₃ (84 mg, 0.60 mmol) were added to reaction mixture and stirred at 120 °C for 2h under open air. After completion of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature and diluted with water and extracted with EtOAc (20 mL × 2). The combined EtOAc layer was collected, dried over anhydrous Na₂SO₄ and concentrated under vacuum. The residue was purified using column chromatography over silica gel with EtOAc / hexane to give desired product of **IIa**.



Yellow solid, 114 mg, 75%; mp: 102-104 °C (lit² 104-105 °C); $R_f = 0.4$ (10% EtOAc/ *n*-hexane); IR (Neat): 3130, 1496, 1093, 808, 761 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.16 (s, 1H), 7.93-7.91 (m, 2H), 7.77 (dd, $J_1 = 1.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.60 (dd, $J_1 = 1.6$ Hz, $J_2 = 1.6$

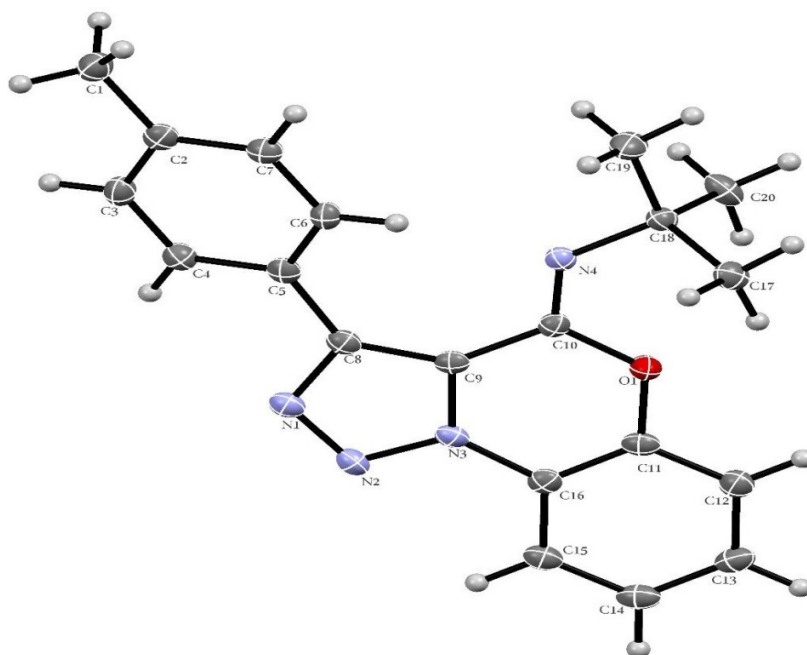
Hz, 1H), 7.52-7.34 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.6, 136.6, 134.0, 131.2, 130.2, 128.9, 128.6, 128.4, 128.2, 125.9, 121.7, 118.6.

10. Crystal Structure Determination:

X-ray intensity data measurements were carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with Mo micro-focus sealed tube diffraction source ($\text{Cu-K}\alpha = 0.72 \text{ \AA}$) at 100(2) K temperature. The X-ray generator was operated at 50 kV and 1.4 mA. A preliminary set of cell constants and an orientation matrix were calculated from two sets of 20 frames. Data were collected with ω scan width of 0.5° at different settings of ϕ and 2θ with a frame time of 40 seconds keeping the sample-to-detector distance fixed at 4.00 cm. The X-ray data collection was monitored by APEX3 program (Bruker, 2016). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2 . Molecular diagrams were generated using ORTEP-33 and Mercury programs. Geometrical calculations were performed using SHELXT and PLATON. All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. An ORTEP III view of both compounds were drawn with 50% probability displacement ellipsoids and H-atoms are shown as small spheres of arbitrary radii.

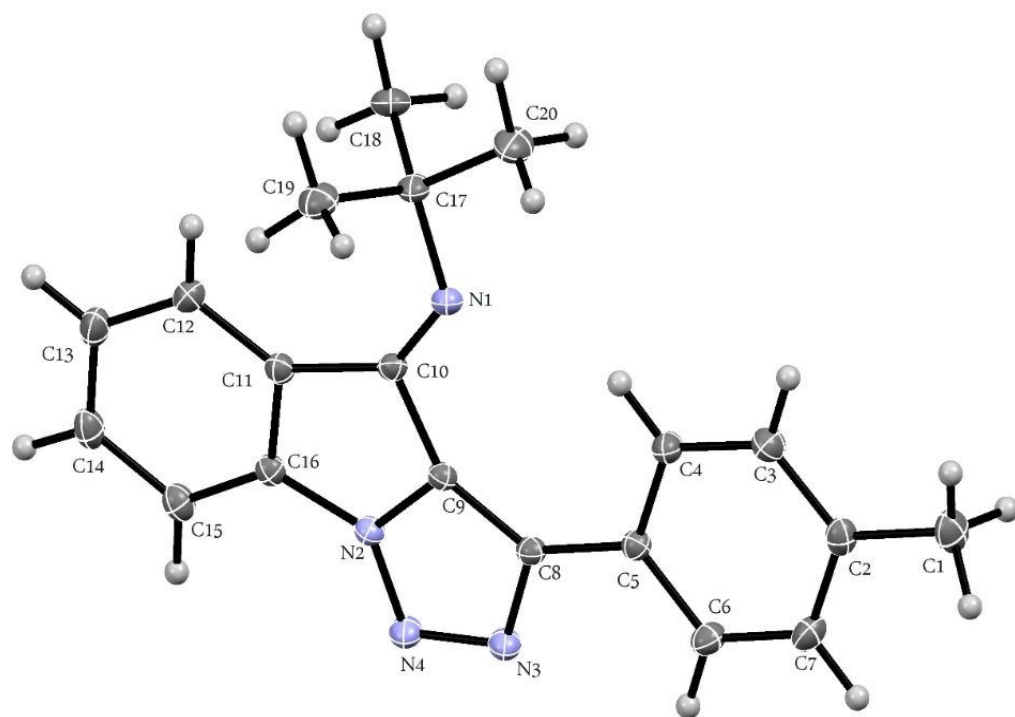
Crystallographic data for 4b:

Crystallographic data for 4b ($\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}$): $M = 332.40$, Crystal dimensions $0.410 \times 0.300 \times 0.180 \text{ mm}^3$, Triclinic, space group P-1, $a = 9.1911(11) \text{ \AA}$, $b = 10.2029(14) \text{ \AA}$, $c = 10.5844(14) \text{ \AA}$, $\alpha = 105.786(4)^\circ$ $\beta = 112.987(4)^\circ$ $\gamma = 97.227(4)^\circ$, $V = 848.58(19) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.301 \text{ Mg/m}^3$, $\mu (\text{Cu-K}\alpha) = 0.083 \text{ mm}^{-1}$, $F(000) = 352$, $2\theta_{\text{max}} = 28.8^\circ$, $T = 100(2) \text{ K}$, 28075 reflections collected, 4402 unique reflections ($R(\text{int}) = 0.0768$), 4402 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, $T_{\text{min}} = 0.967$, $T_{\text{max}} = 0.985$, 230 refined parameters, No. of restraints 0, $S = 1.148$, $R1 = 0.0670$, $wR2 = 0.1294$ (all data $R1 = 0.0942$, $wR2 = 0.1388$), maximum and minimum residual electron densities; $\Delta\rho_{\text{max}} = 0.355$, $\Delta\rho_{\text{min}} = -0.290 \text{ (e}\text{\AA}^{-3})$. Crystallographic data for compound intermediate deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 1587528.



Crystallographic data for **5b**:

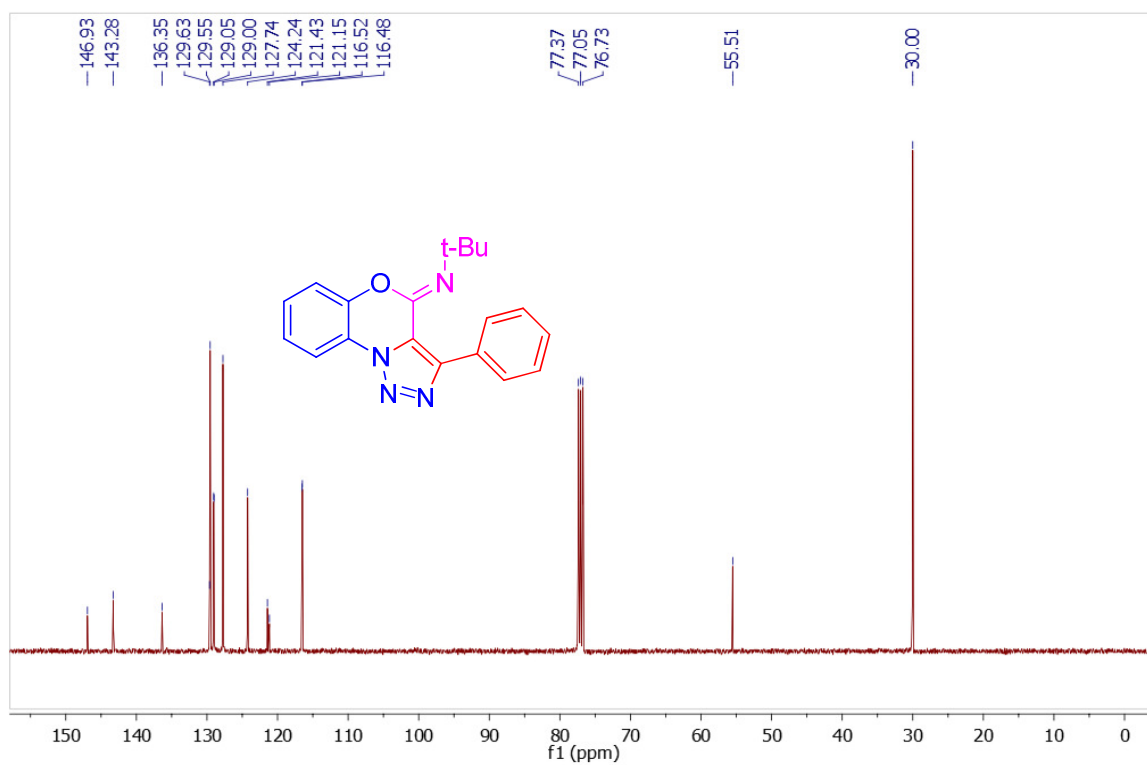
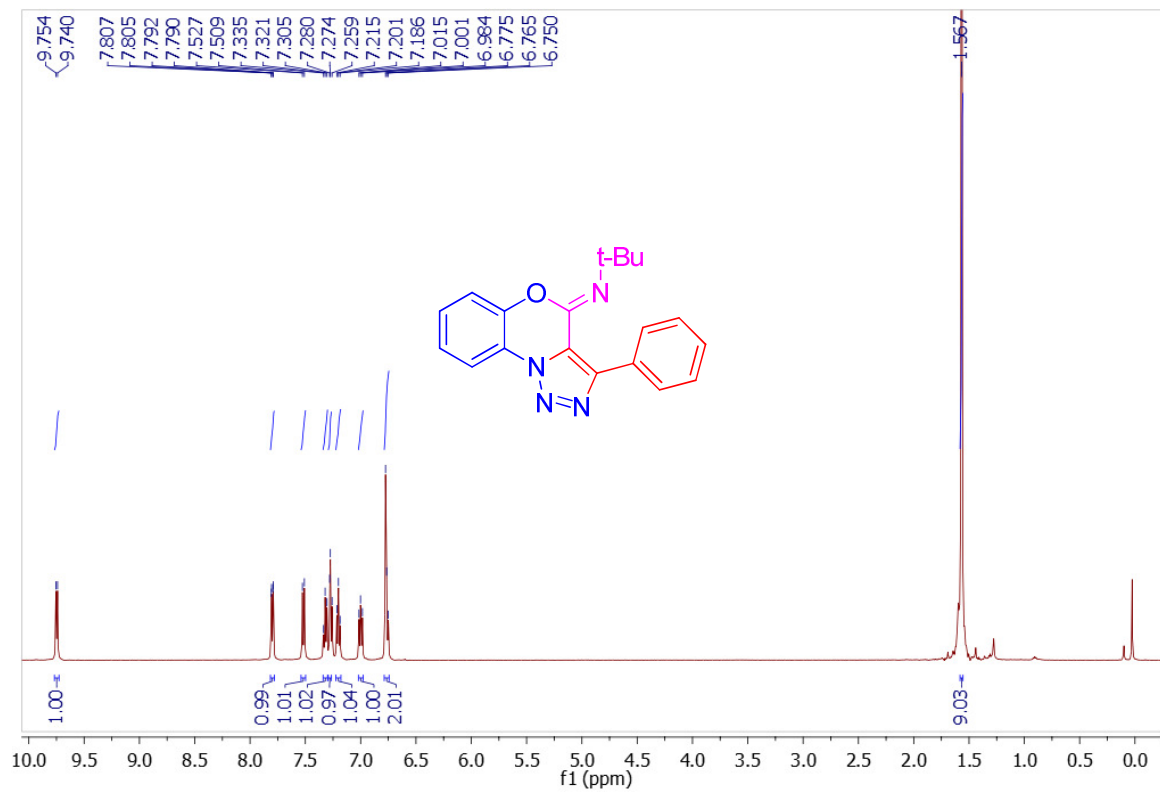
Crystallographic data for **5b** (C₂₀H₂₀N₄): M = 316.40, Crystal dimensions 0.420 x 0.340 x 0.190 mm³, monoclinic, space group *P2₁/n*, a = 9.0962(5) Å, b = 10.1454(6) Å, c = 18.0969(10) Å, α = 90° β = 102.269(2)° γ = 90°, V = 1668.64(16) Å³, Z = 4, ρ_{calcd} = 1.259 Mg/m³, μ (Cu-Kα) = 0.077 mm⁻¹, F(000) = 672, 2Θ_{max} = 30.58°, T = 100(2) K, 62594 reflections collected, 5099 unique reflections (R(int) = 0.0607), 5099 observed (I > 2σ(I)) reflections, multi-scan absorption correction, T_{min} = 0.968, T_{max} = 0.986, refined parameters, No. of restraints 0, S = 1.110, R1 = 0.0460, wR2 = 0.1212 (all data R1 = 0.0575, wR2 = 0.1325), maximum and minimum residual electron densities; Δρ_{max} = 0.474, Δρ_{min} = -0.515 (eÅ⁻³). Crystallographic data for compound intermediate deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 1864070.



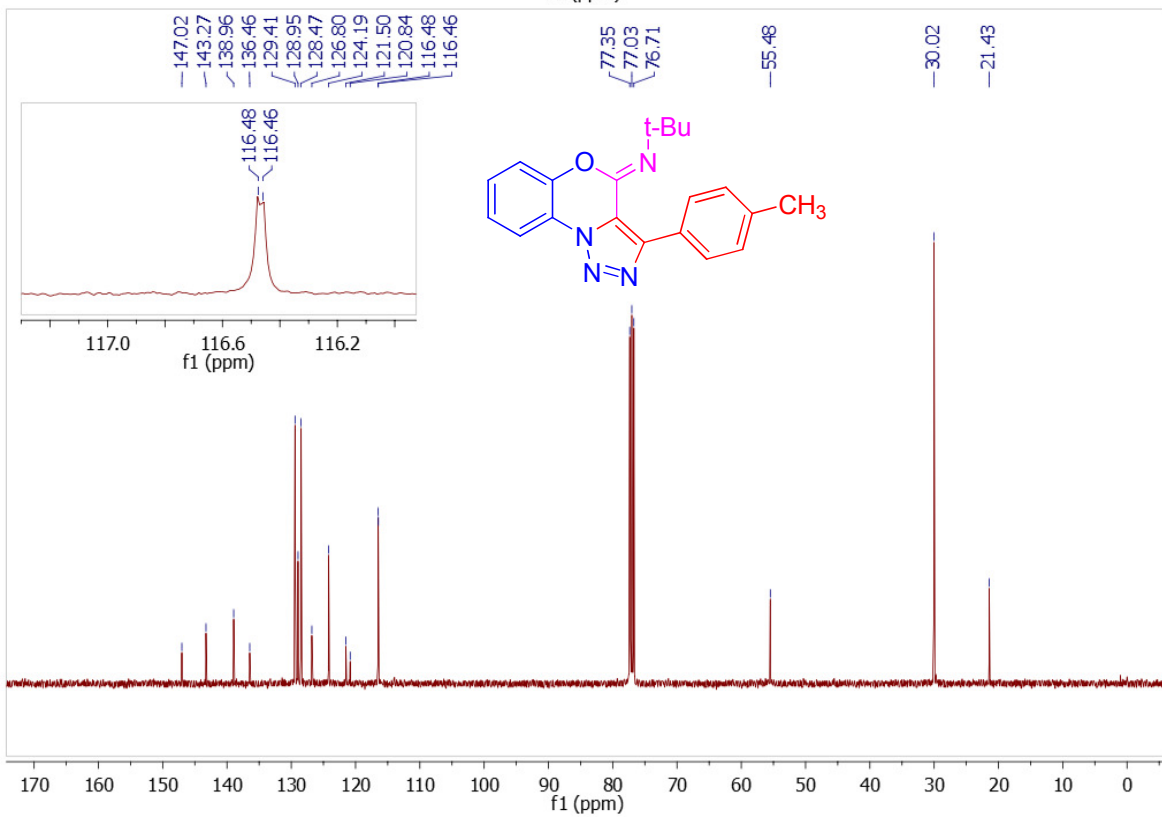
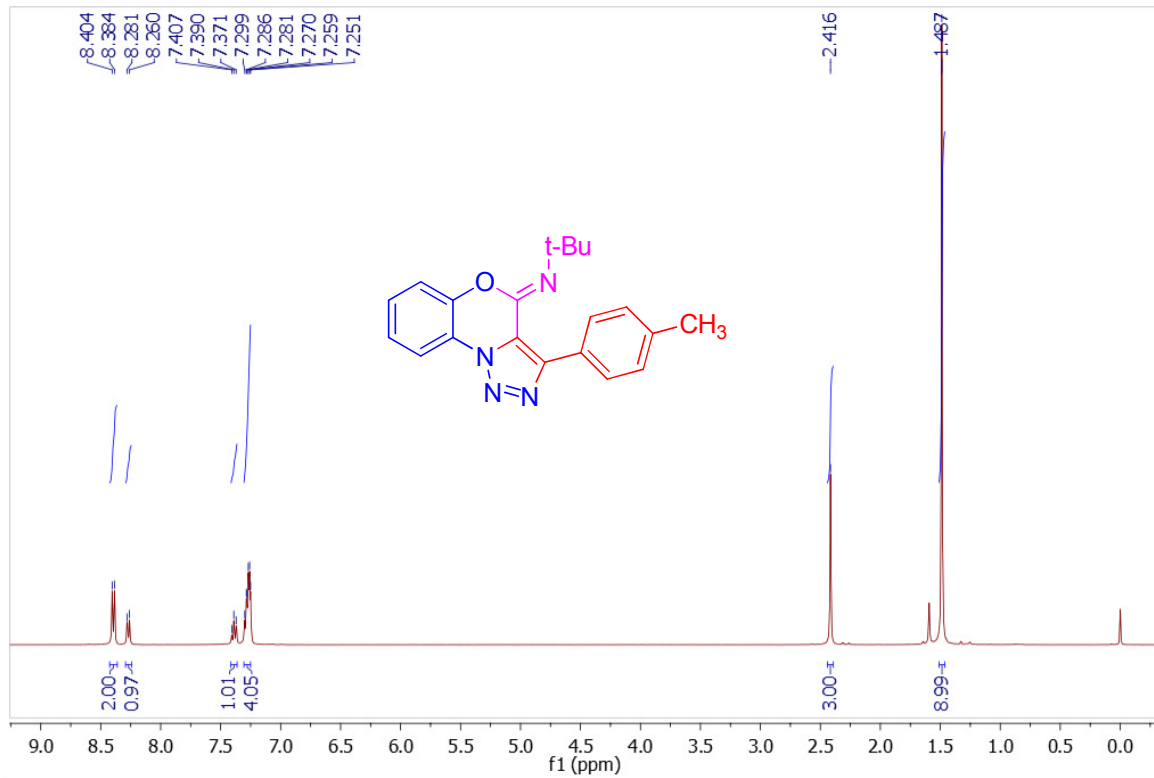
11. References:

1. a) Y. N. Kotovshchikov, G. V. Latyshev, M. A. Navasardyan, D. A. Erzunov, I. P. Beletskaya, N. V. Lukashov, *Org. Lett.* 2018, **20**, 4467; b) M. Novak, A. M. Brinster, J. M. Dickhoff, J. M. Erb, M. P. Jones, S. H. Leopold, A. T. Vollman, S. A. Glover, *J. Org. Chem.* **2007**, *72*, 9954; c) G. J. Smolinsky, *J. Org. Chem.* 1961, **26**, 4106; d) M. Alajarín, A. López-Lázaro, A. Vidal, J. Berná, *Chem. - Eur. J.* 1998, **4**, 2558; e) H. Jin, Z. D. Huang, C. X. Kuang, X. K. Wang, *Chin. Chem. Lett.* 2011, **22**, 310.
2. C. Veryser, G. Steurs, L. Van Meervelt, W. M. De Borggraeve, *Adv. Synth. Catal.* 2017, **359**, 1271.
3. D. Ghosh, S. Rhodes, K. Hawkins, D. Winder, A. Atkinson, W. Ming, C. Padgett, J. Orvis, K. Aiken, S. A. Landge, *New J. Chem.* 2015, **39**, 295.

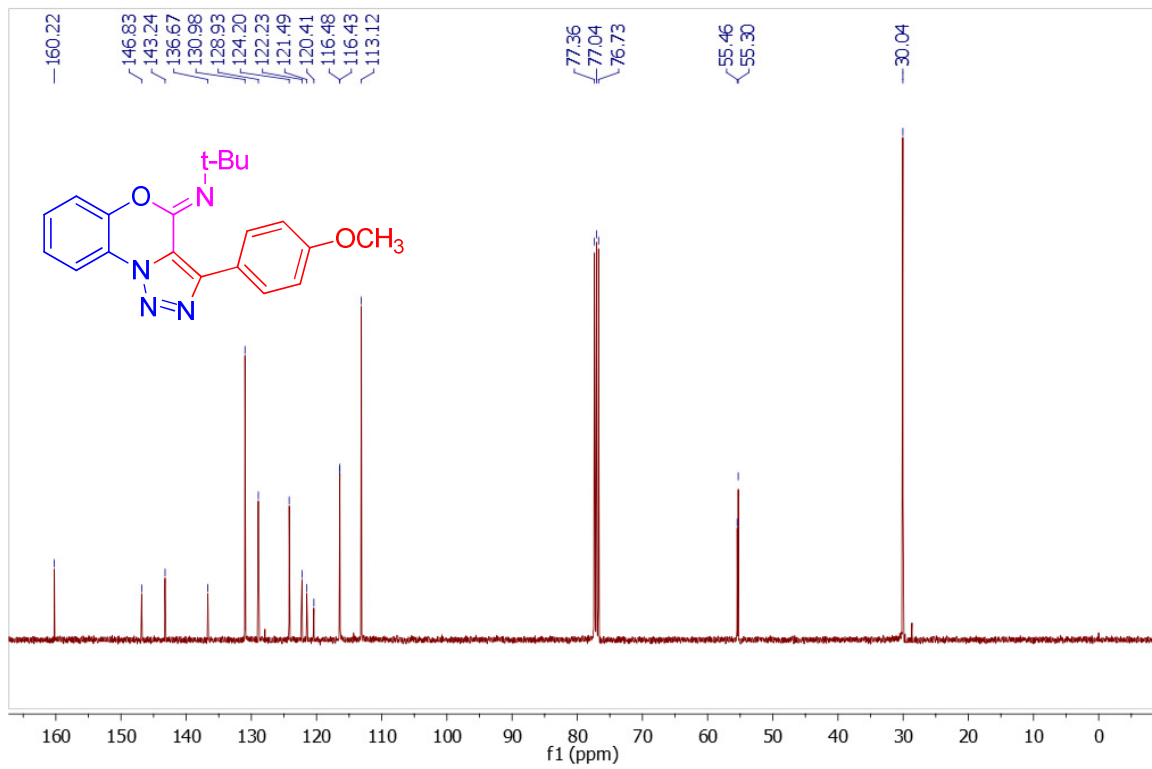
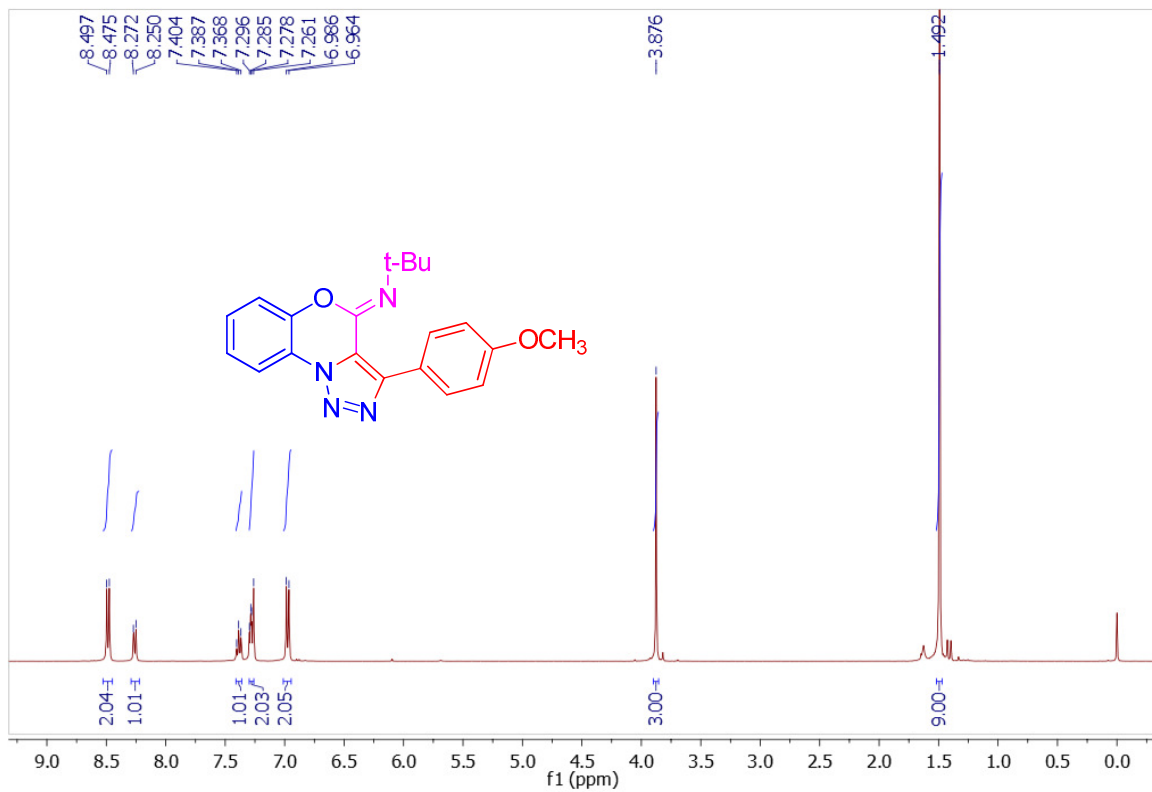
12. Copies of ^1H and ^{13}C NMR Spectra of Products Compound-4a



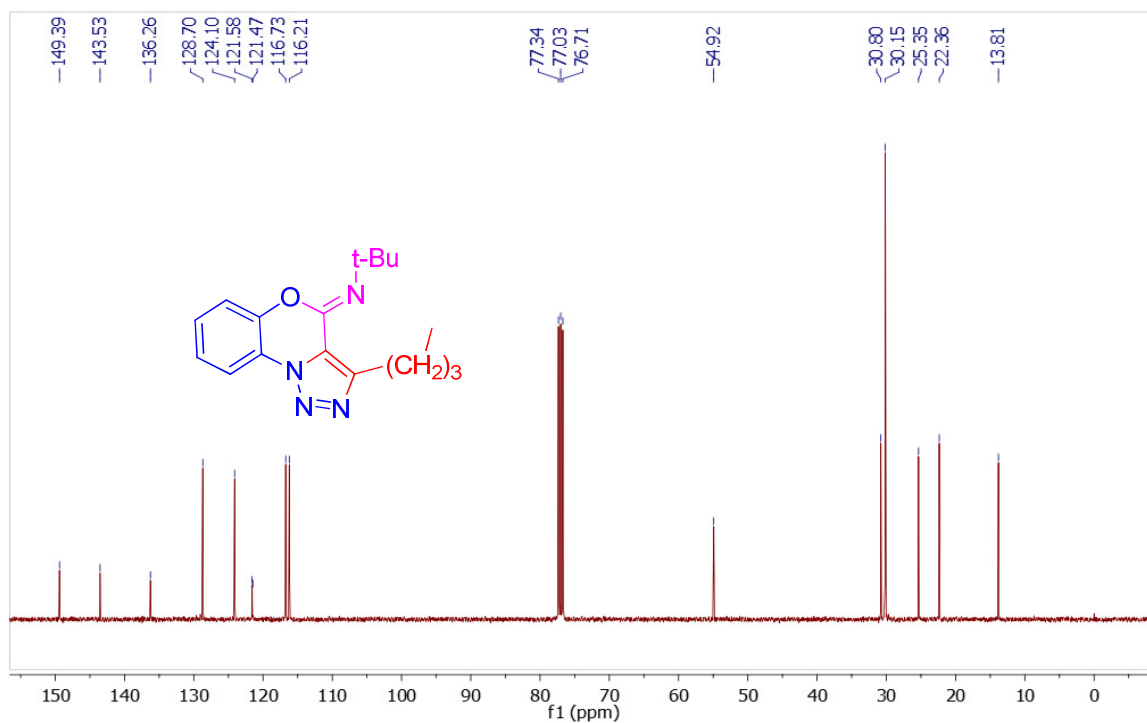
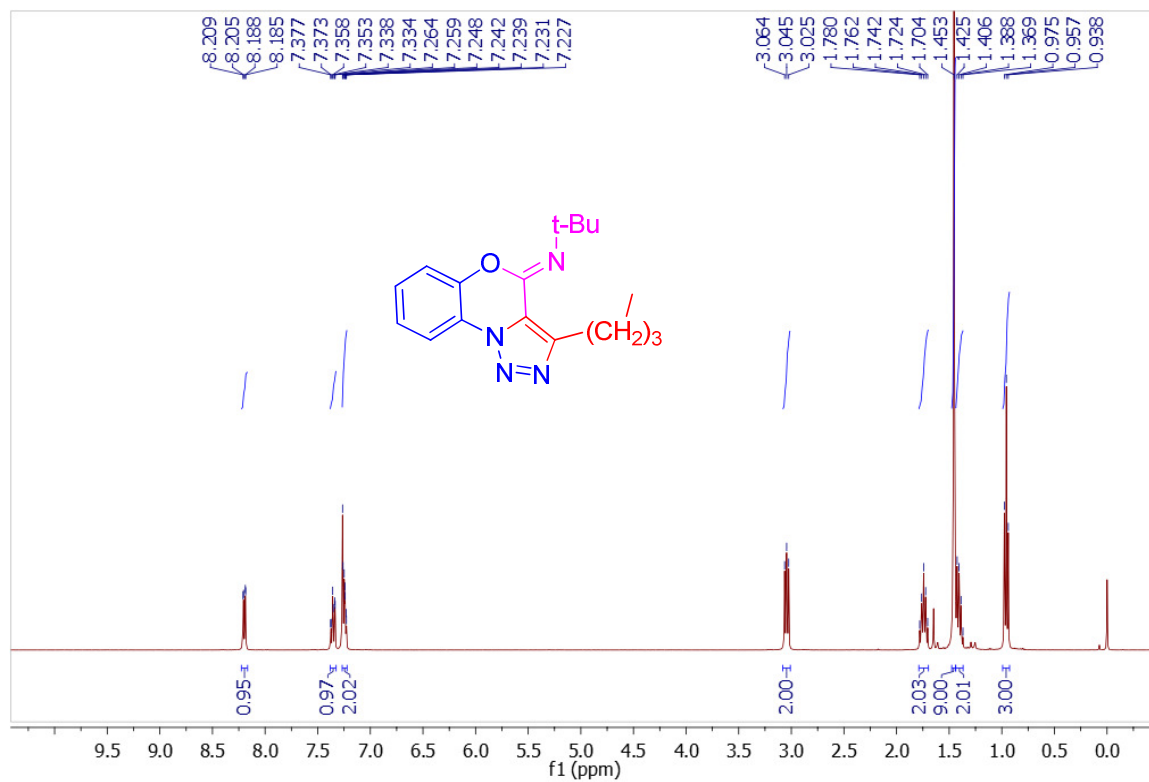
Compound-4b



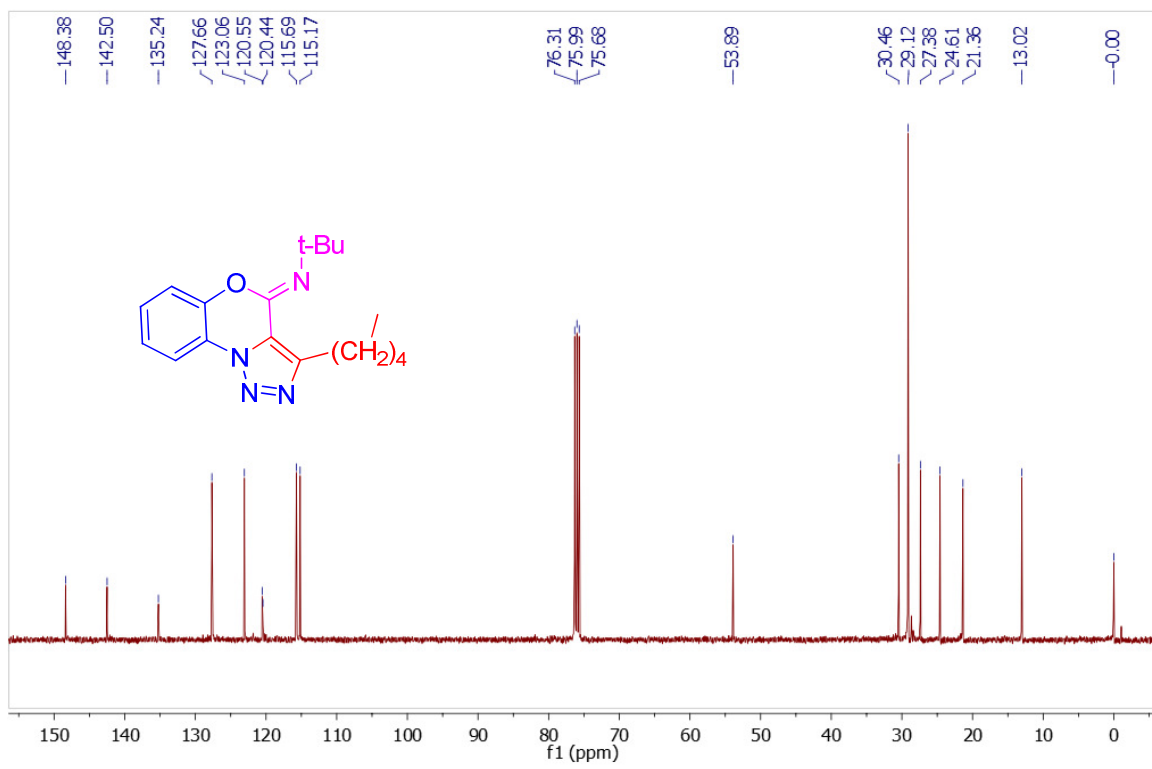
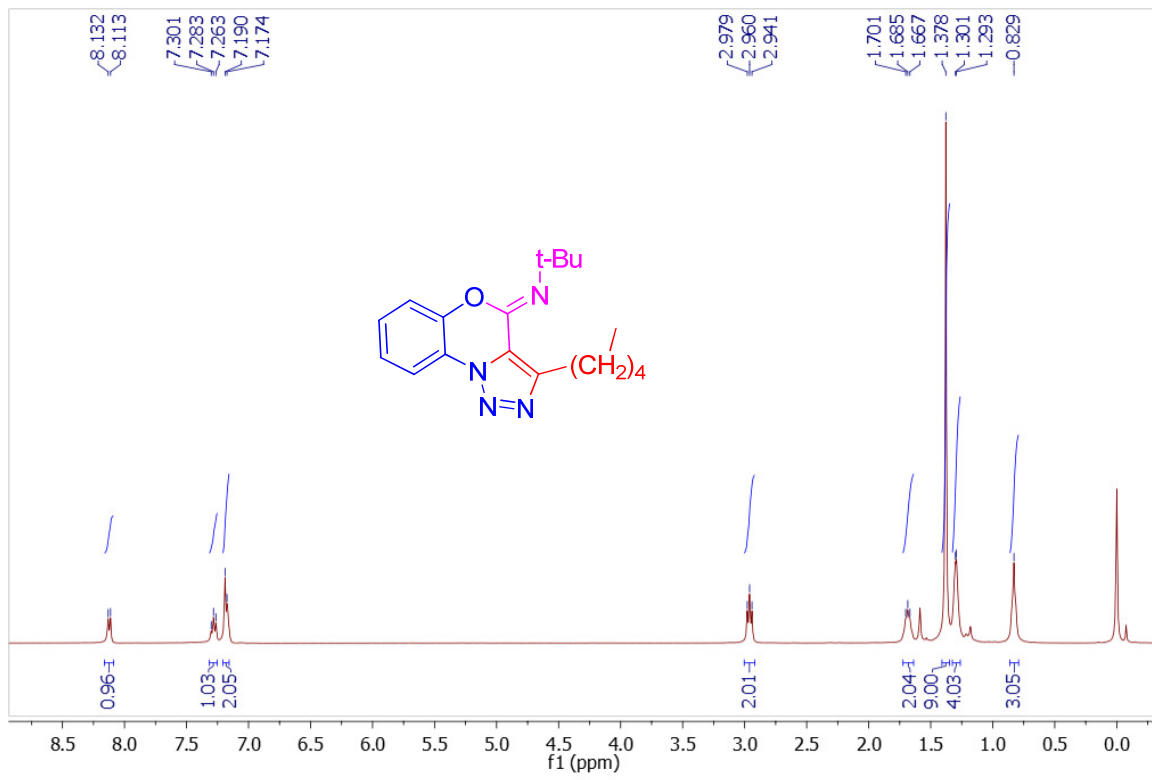
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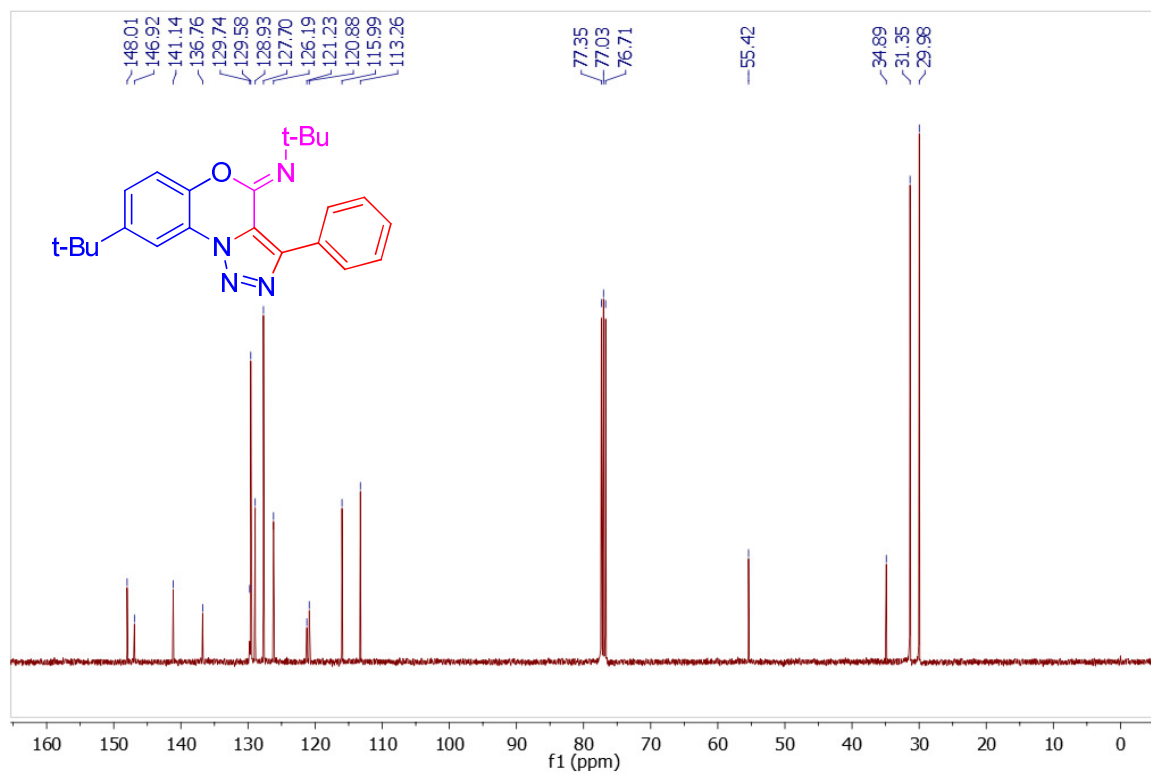
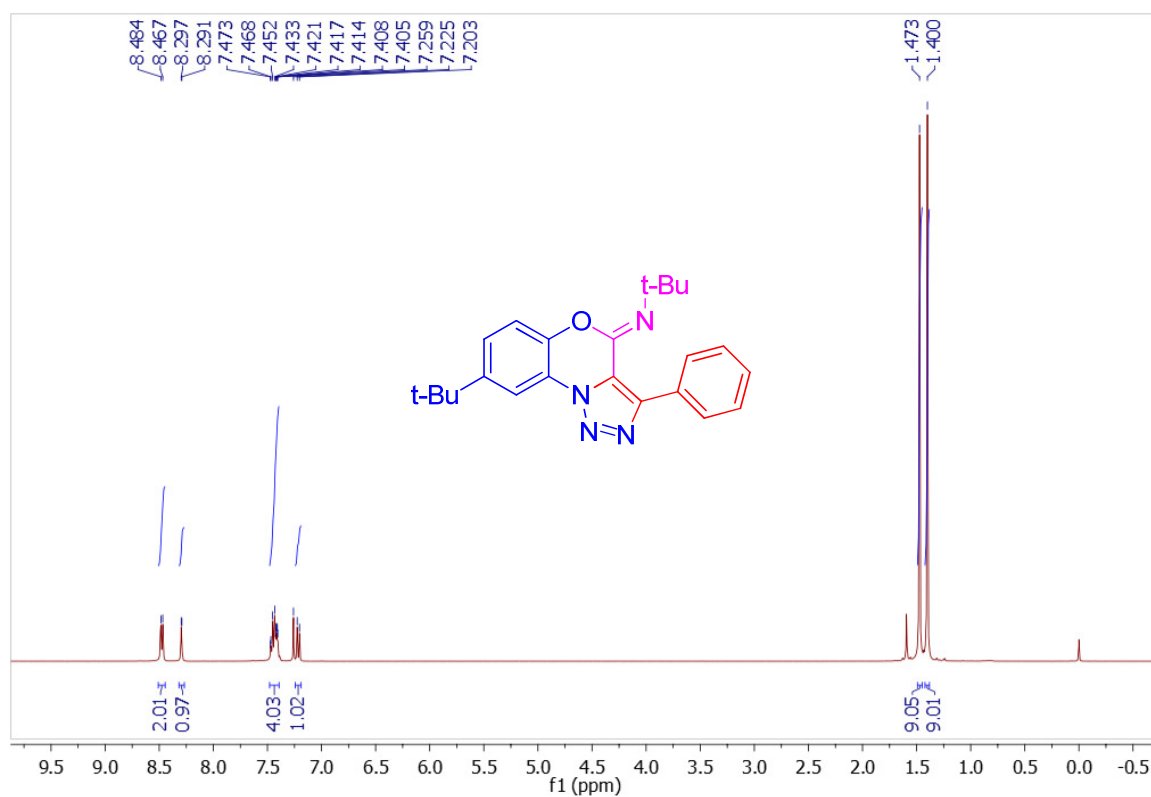
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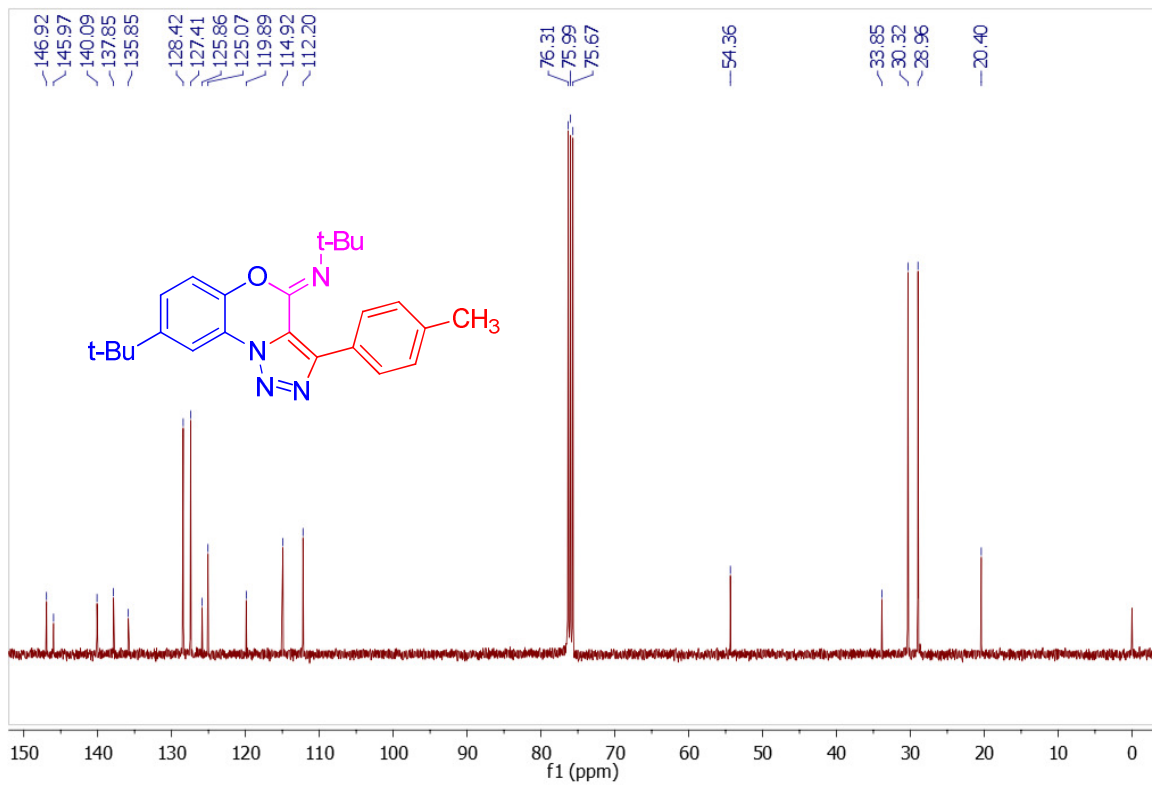
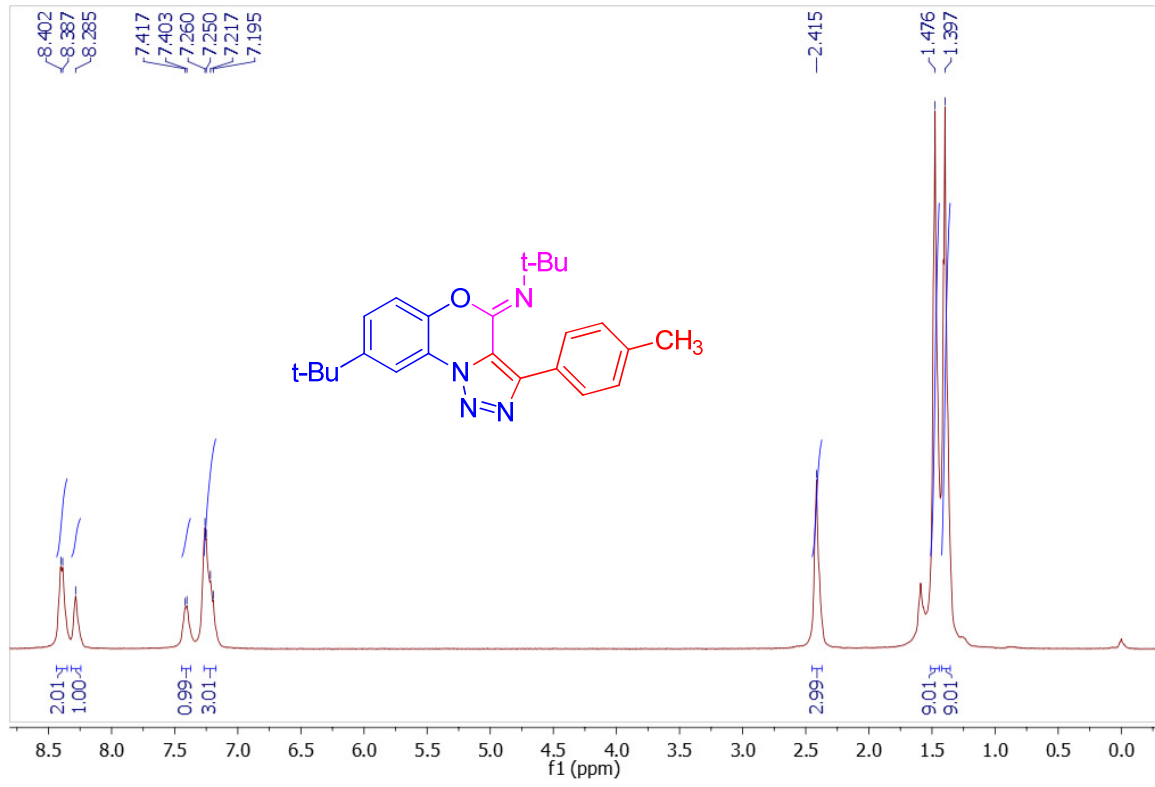
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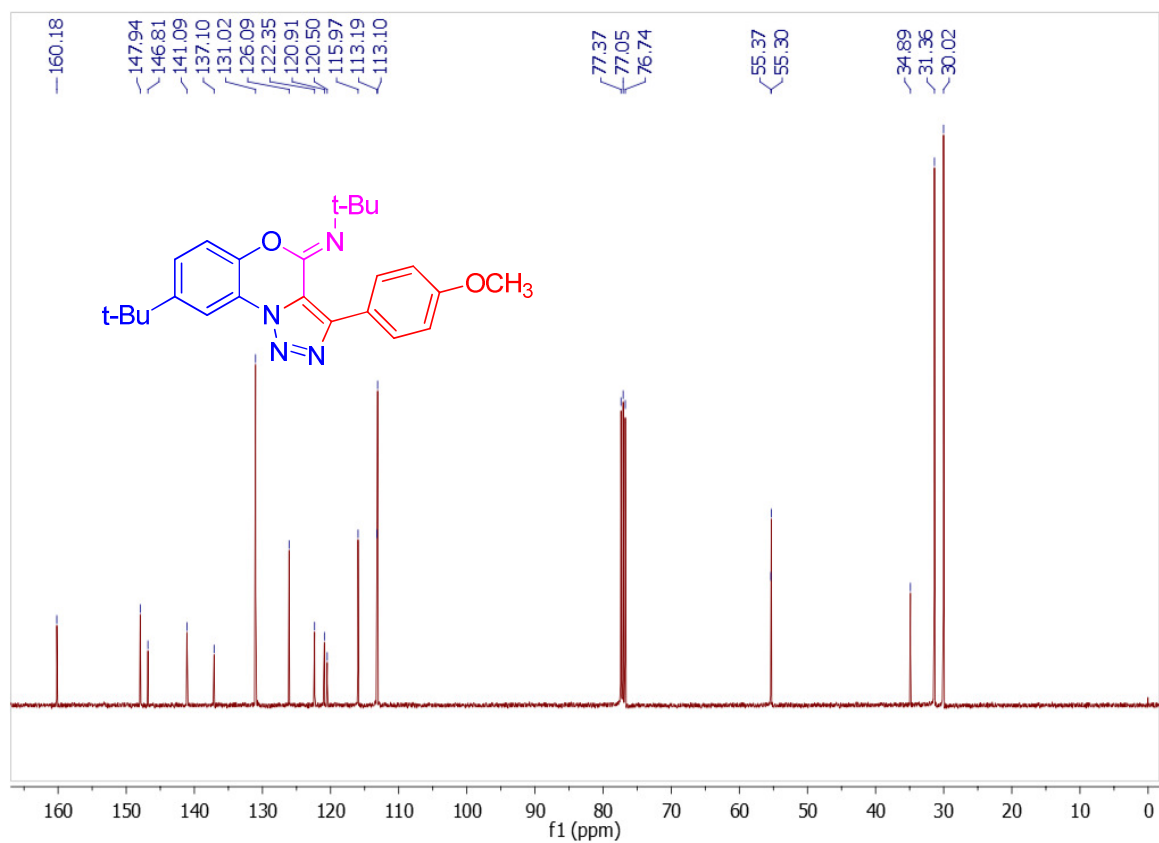
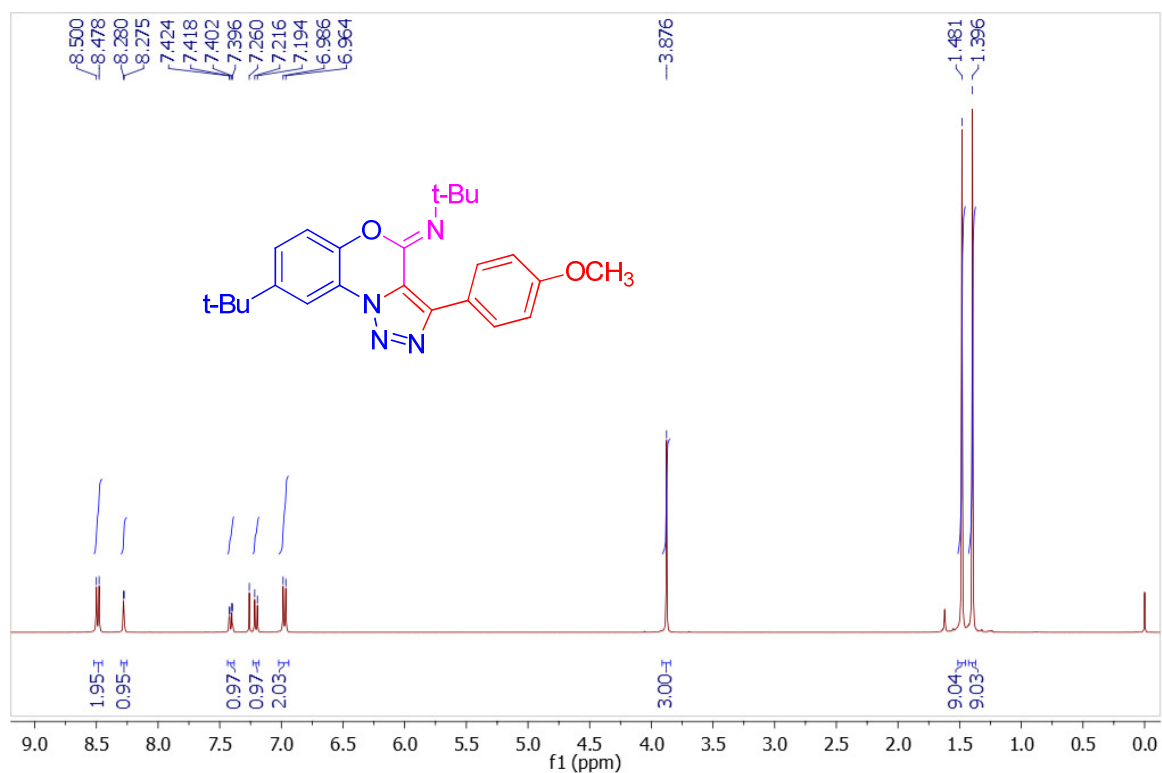
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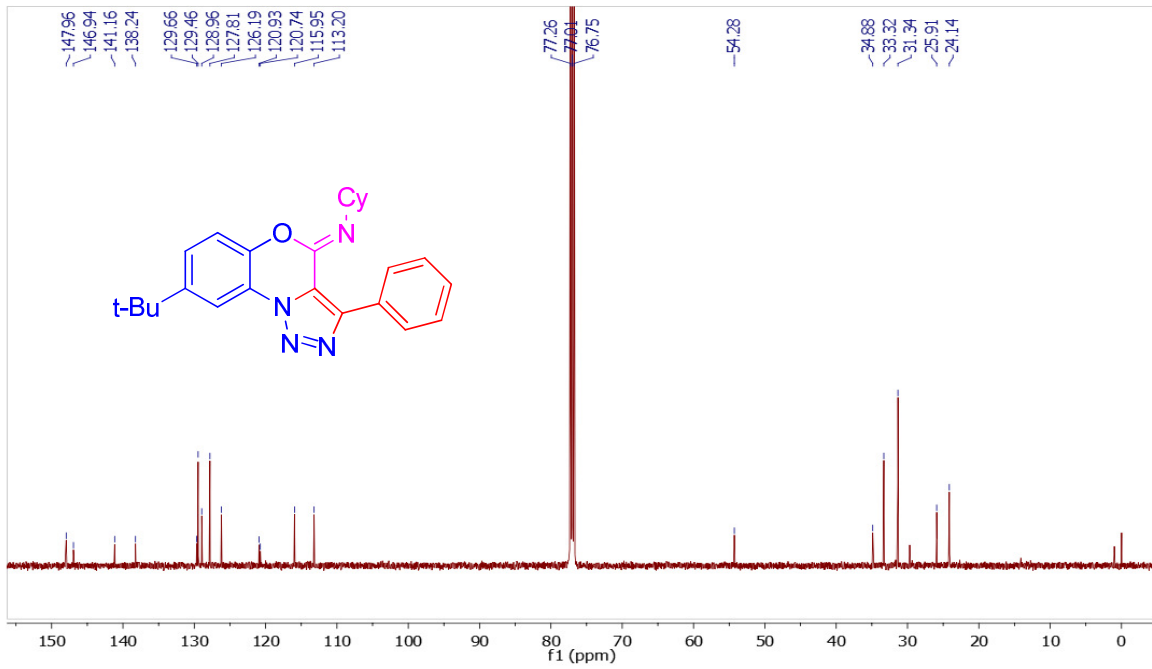
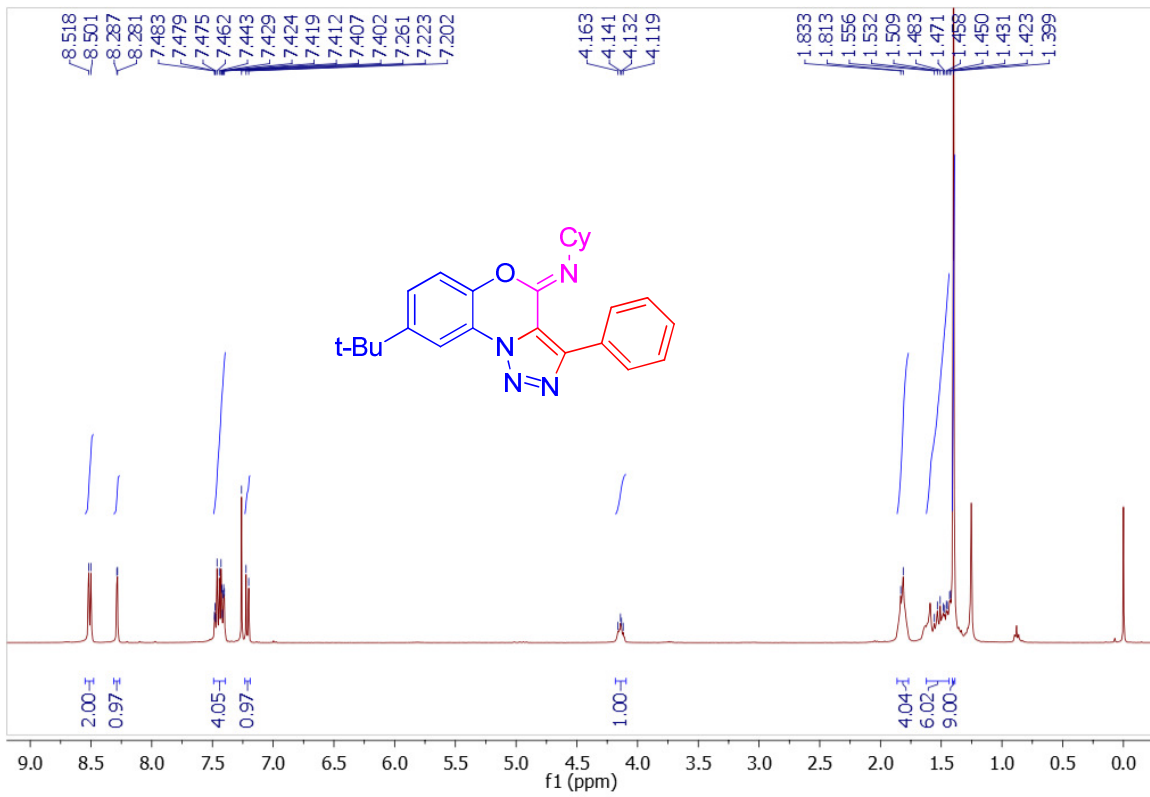
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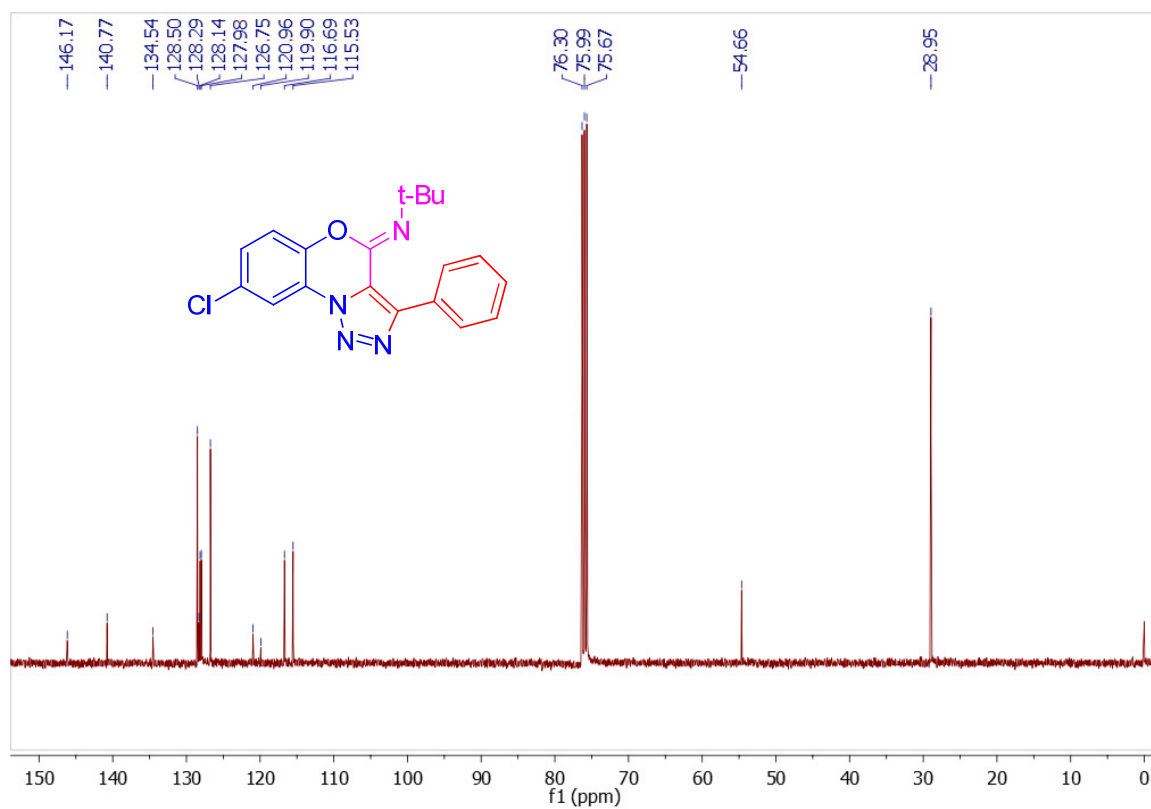
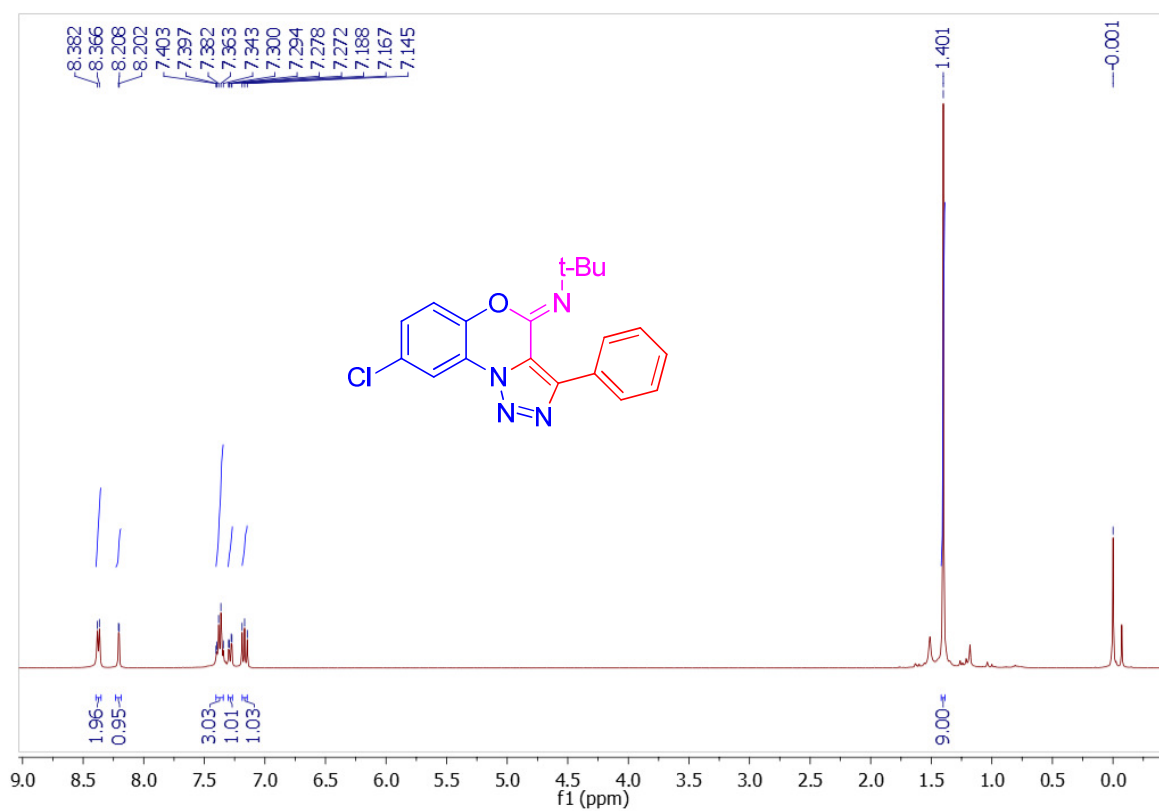
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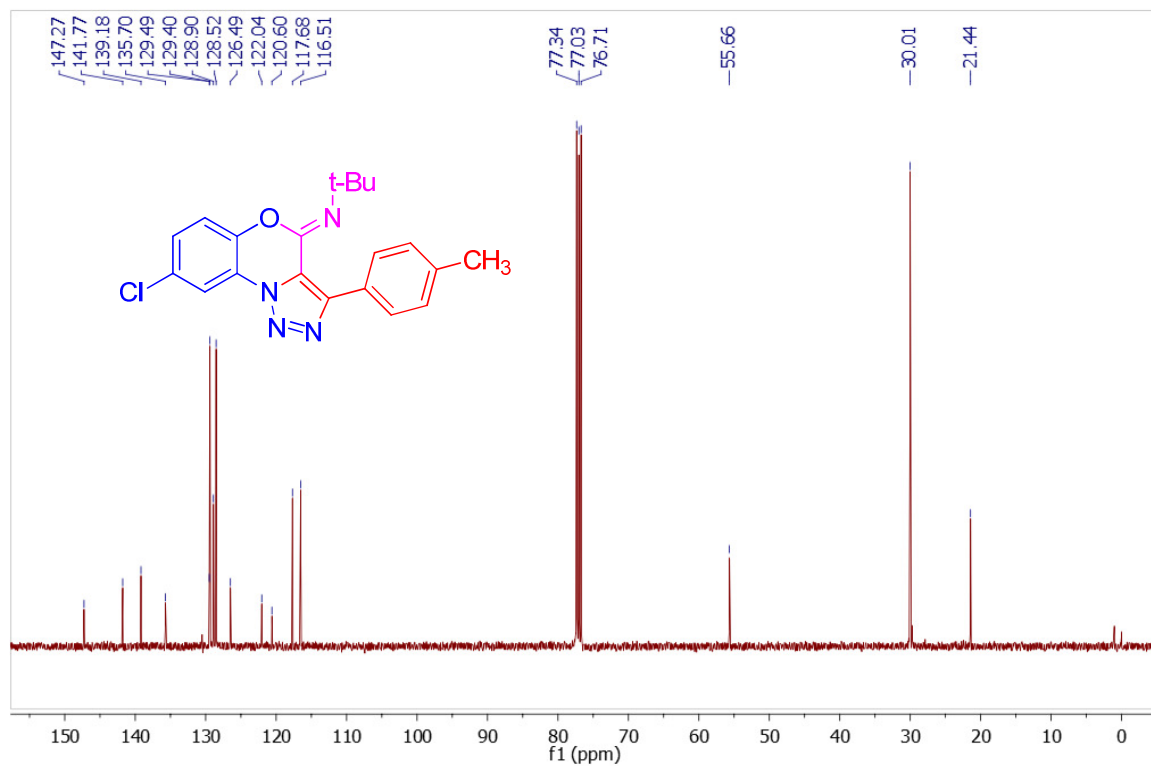
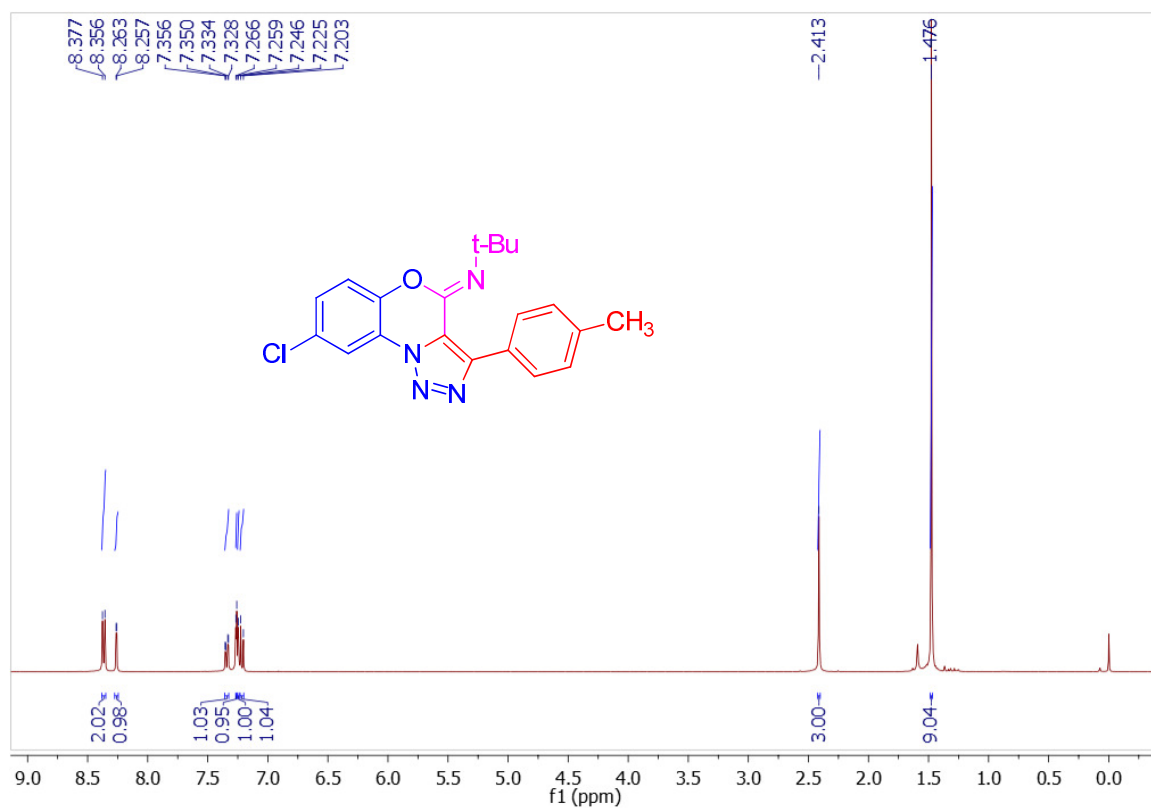
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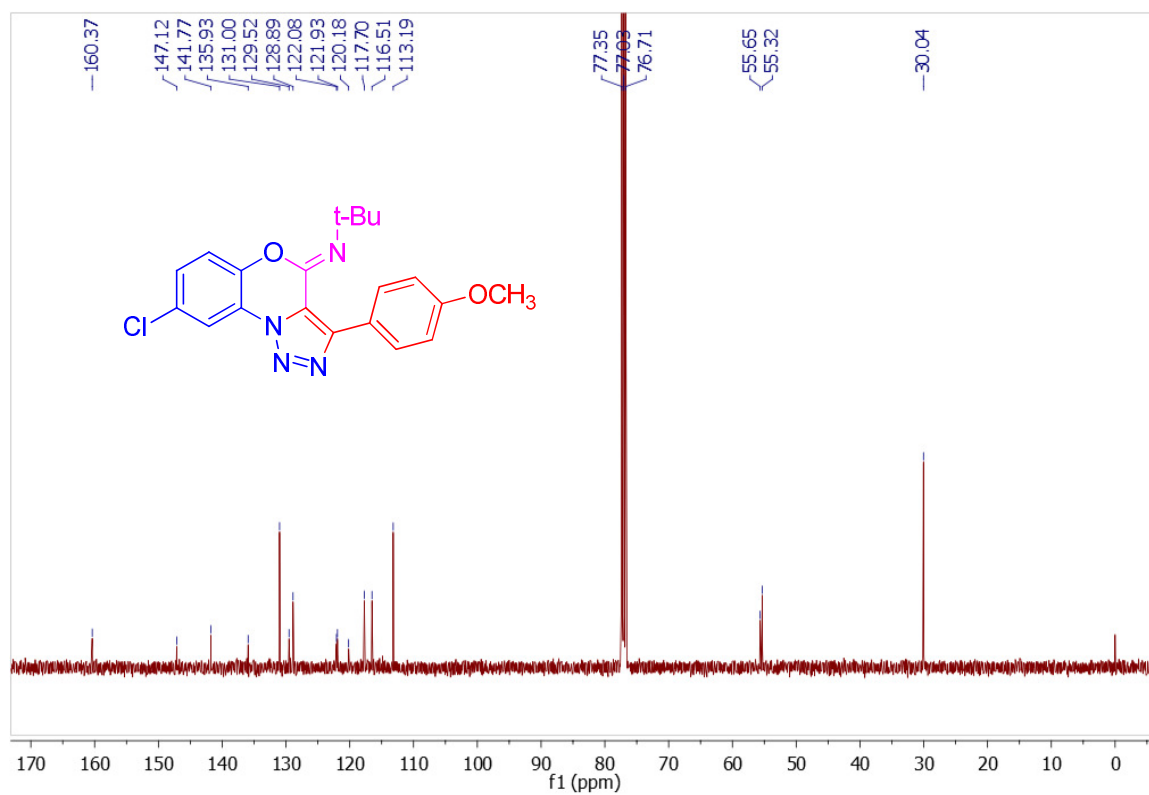
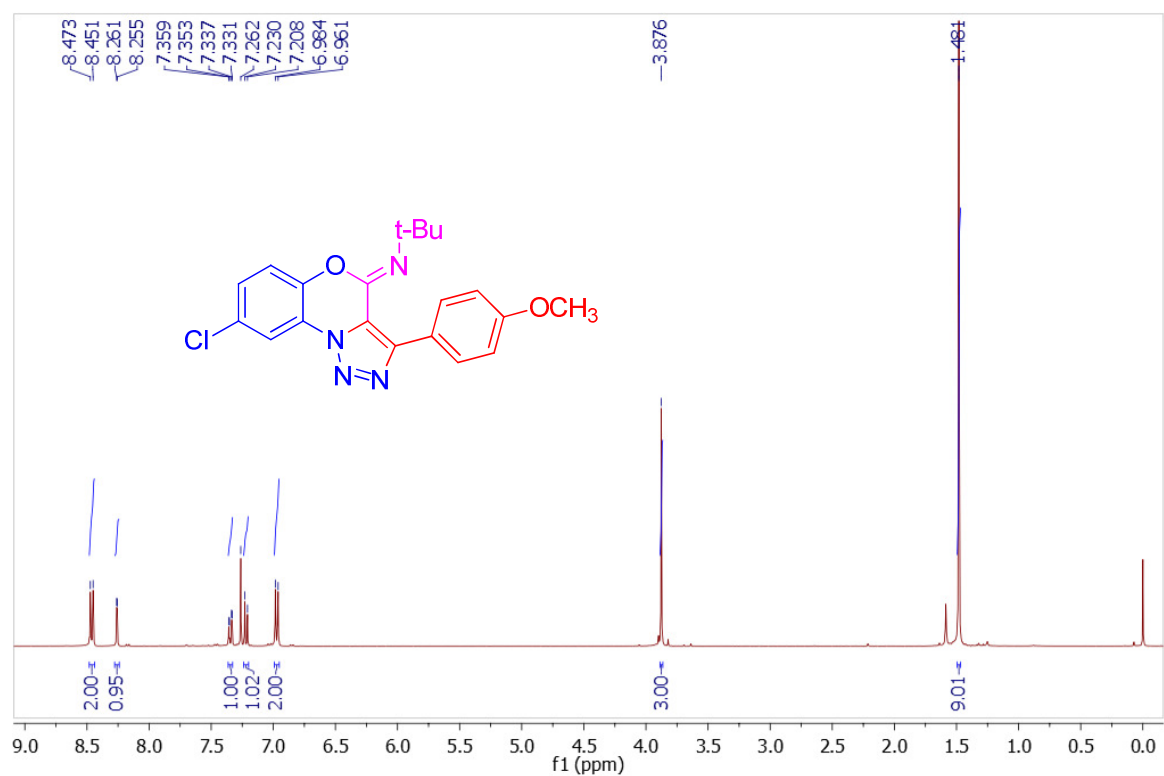
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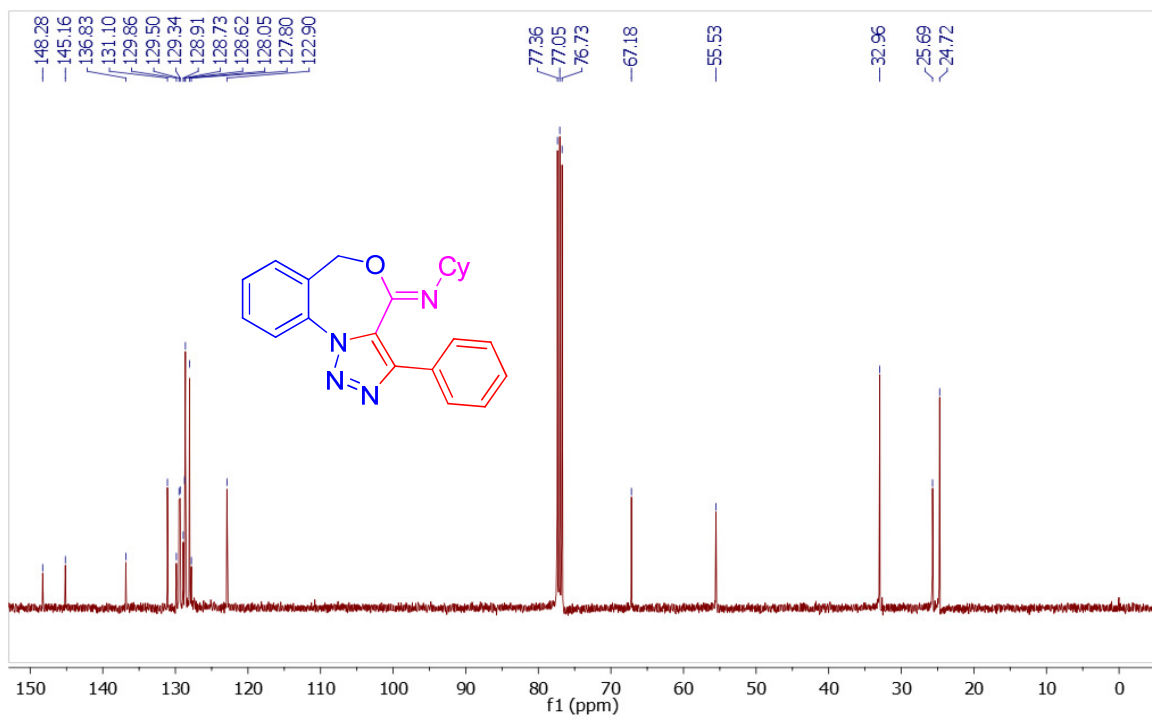
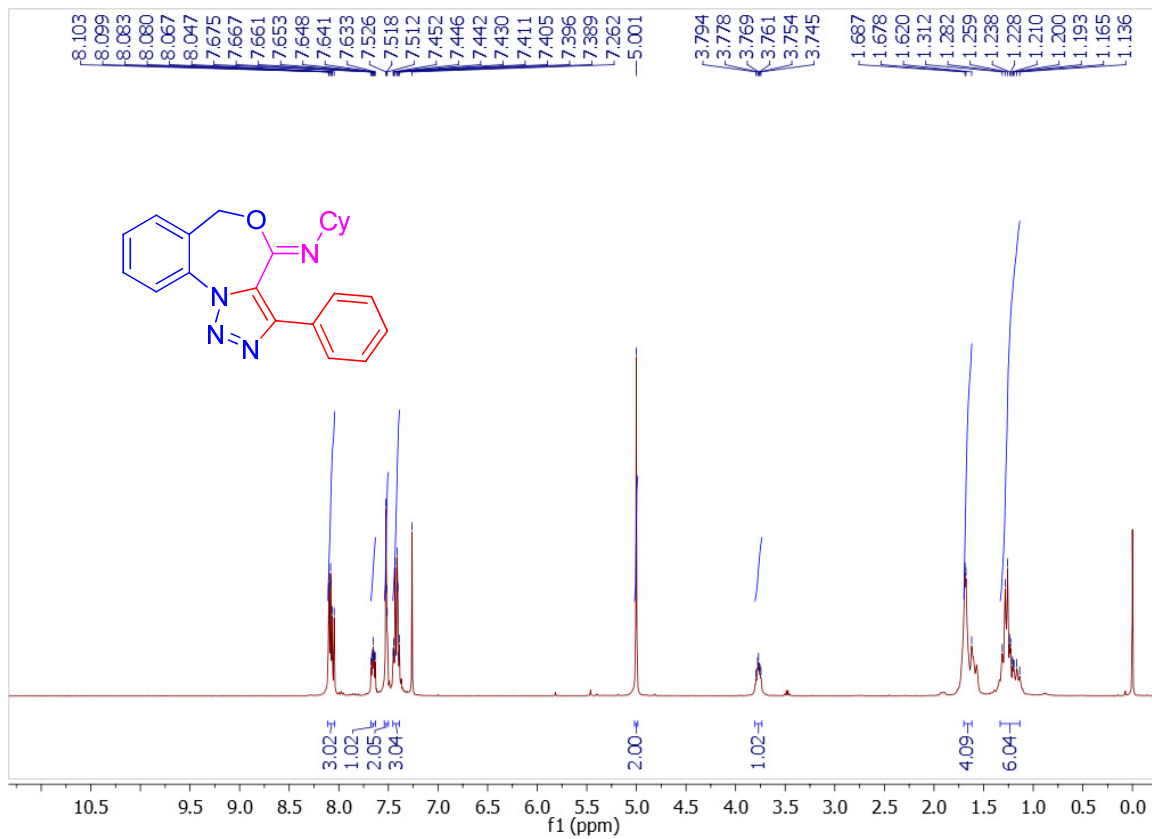
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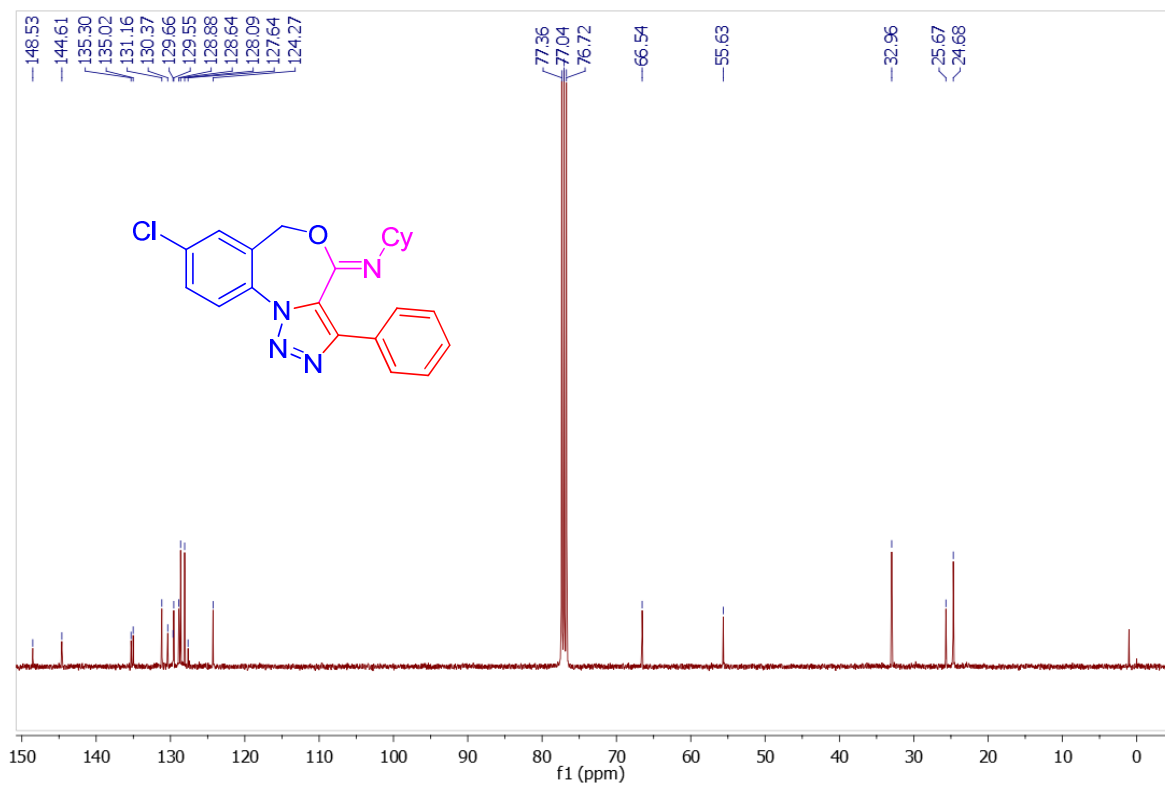
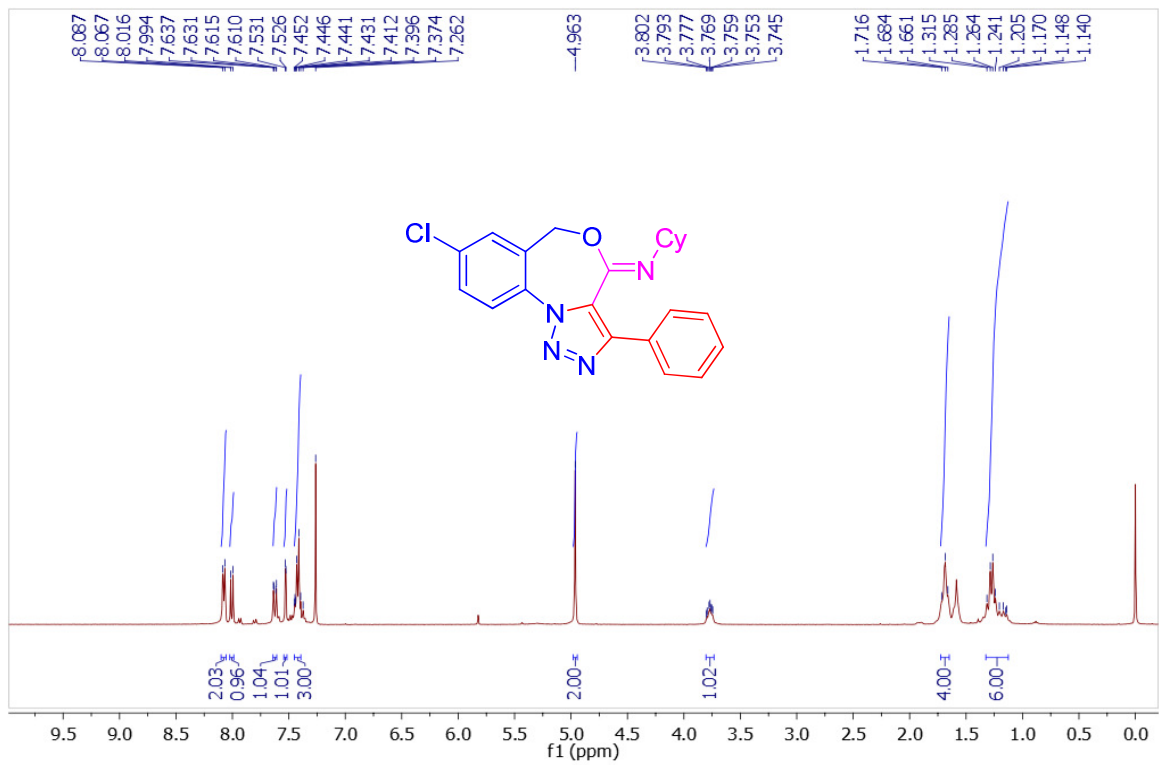
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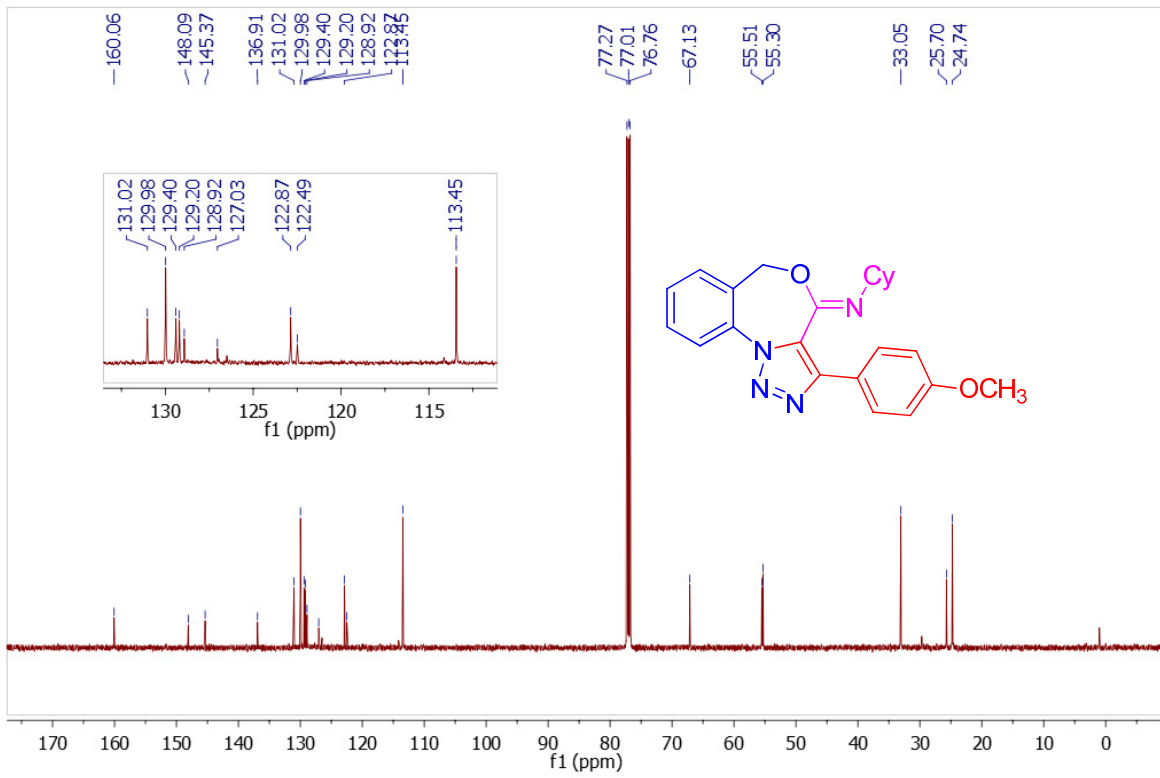
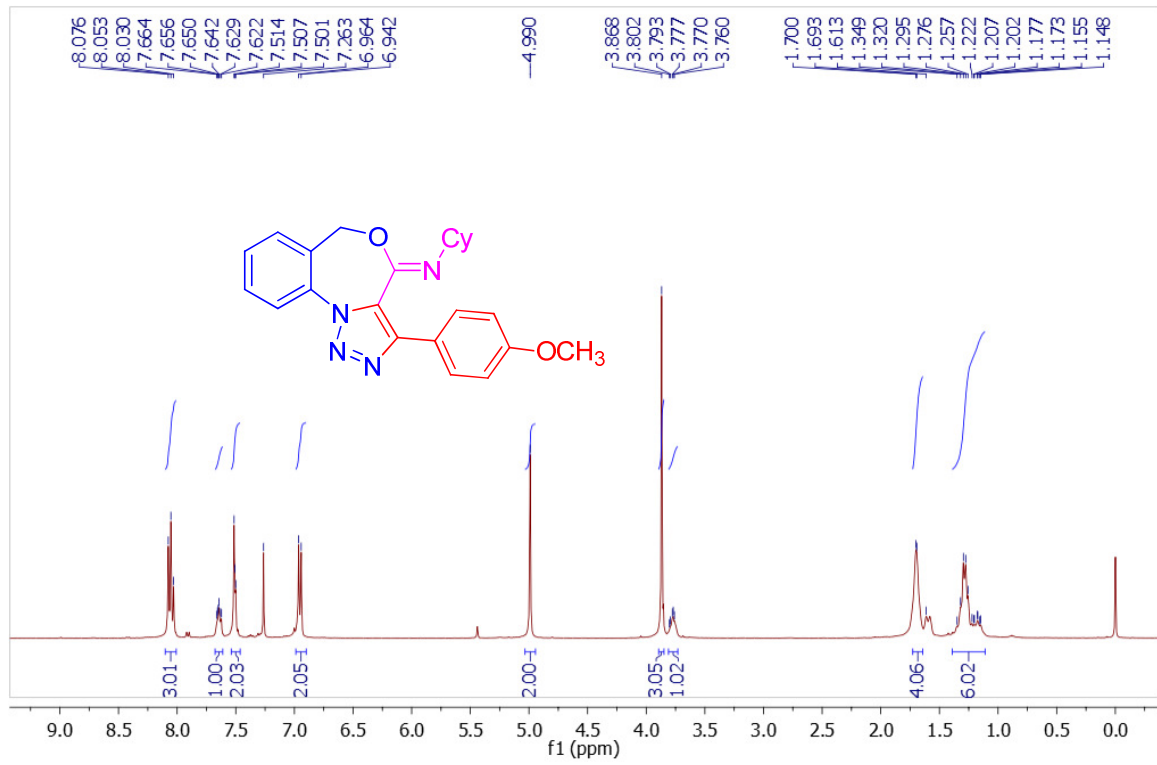
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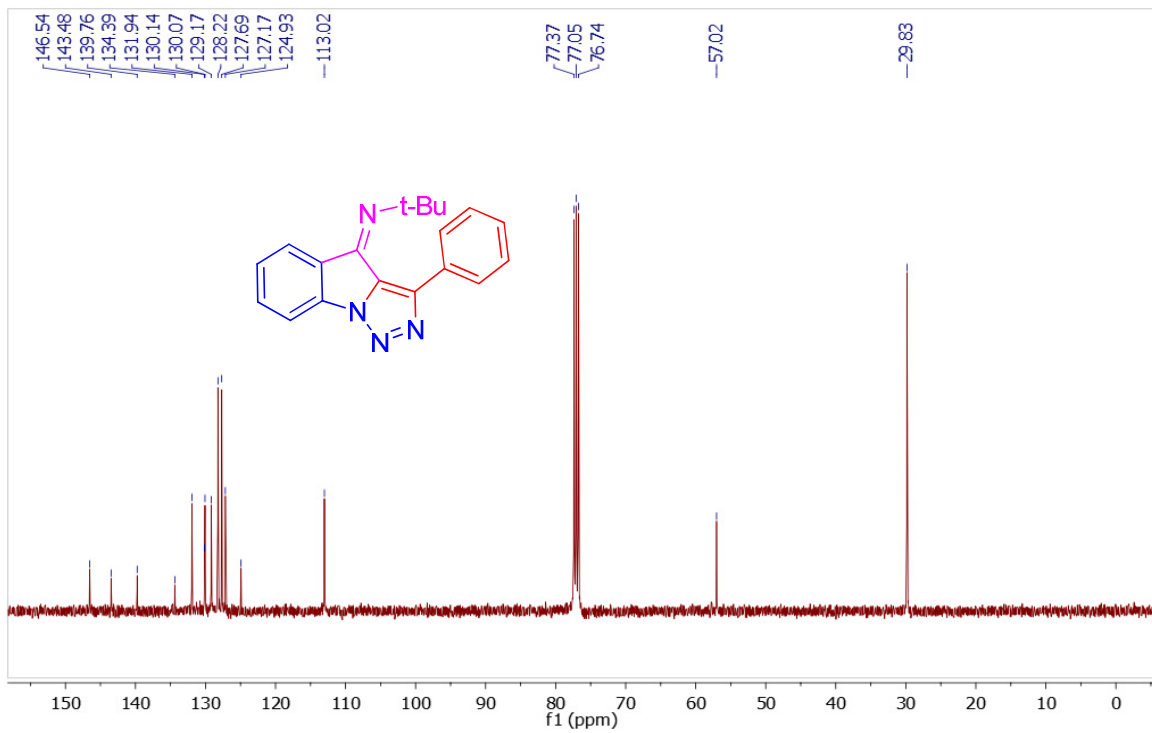
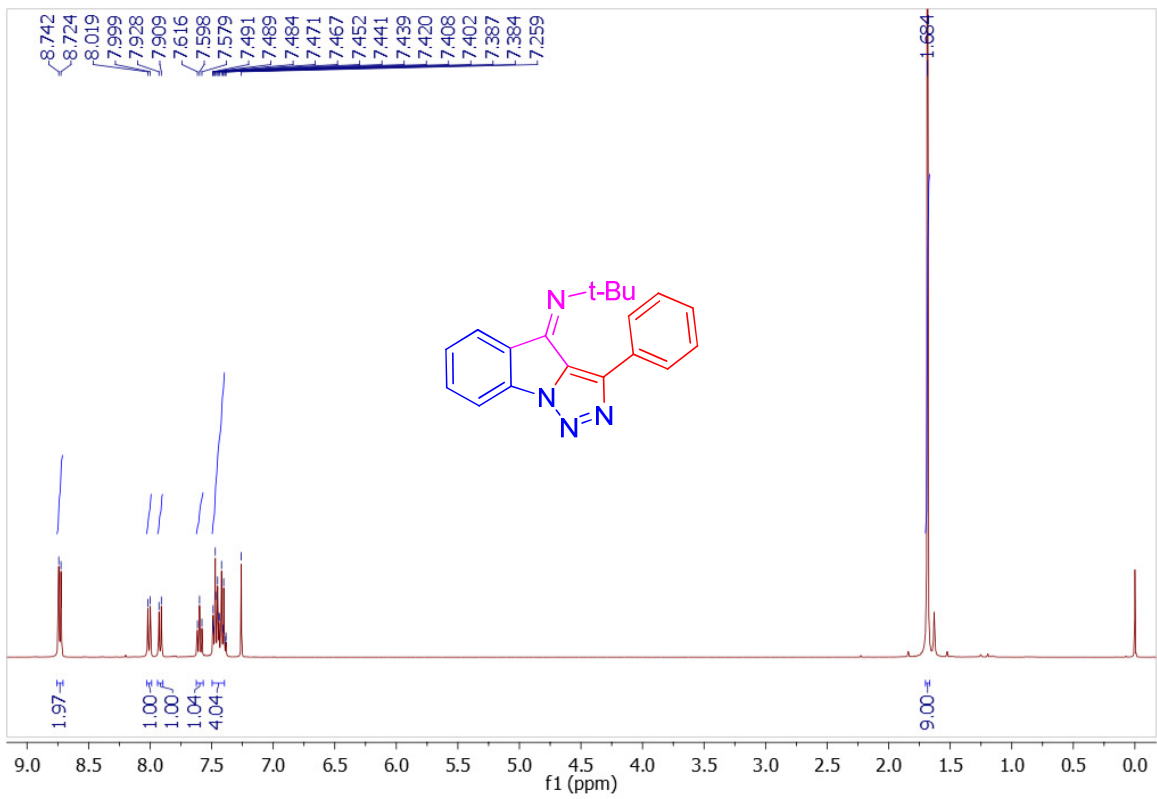
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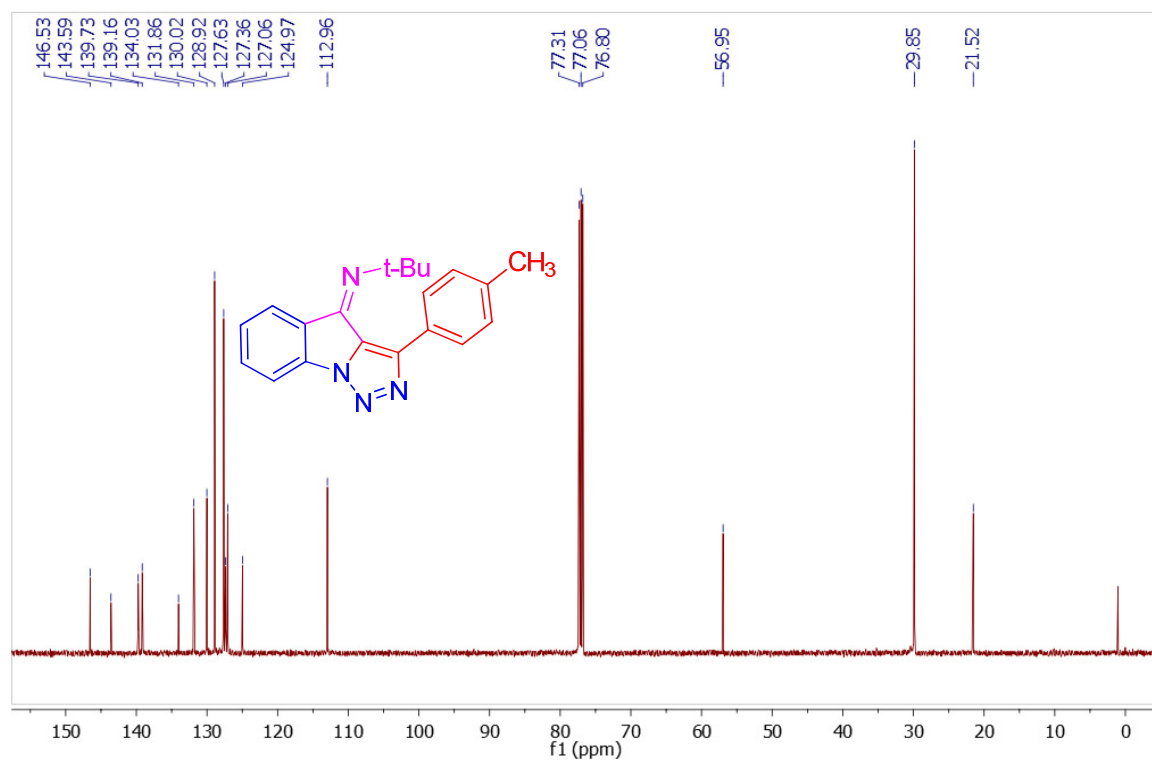
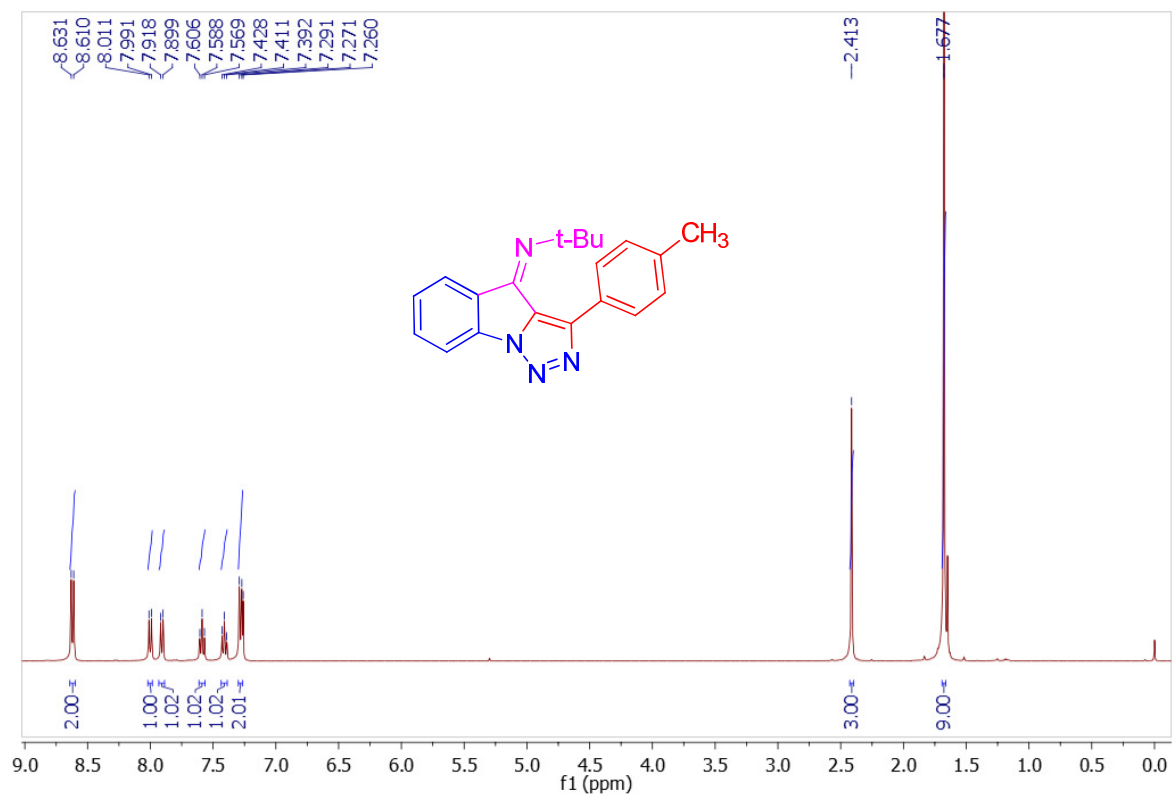
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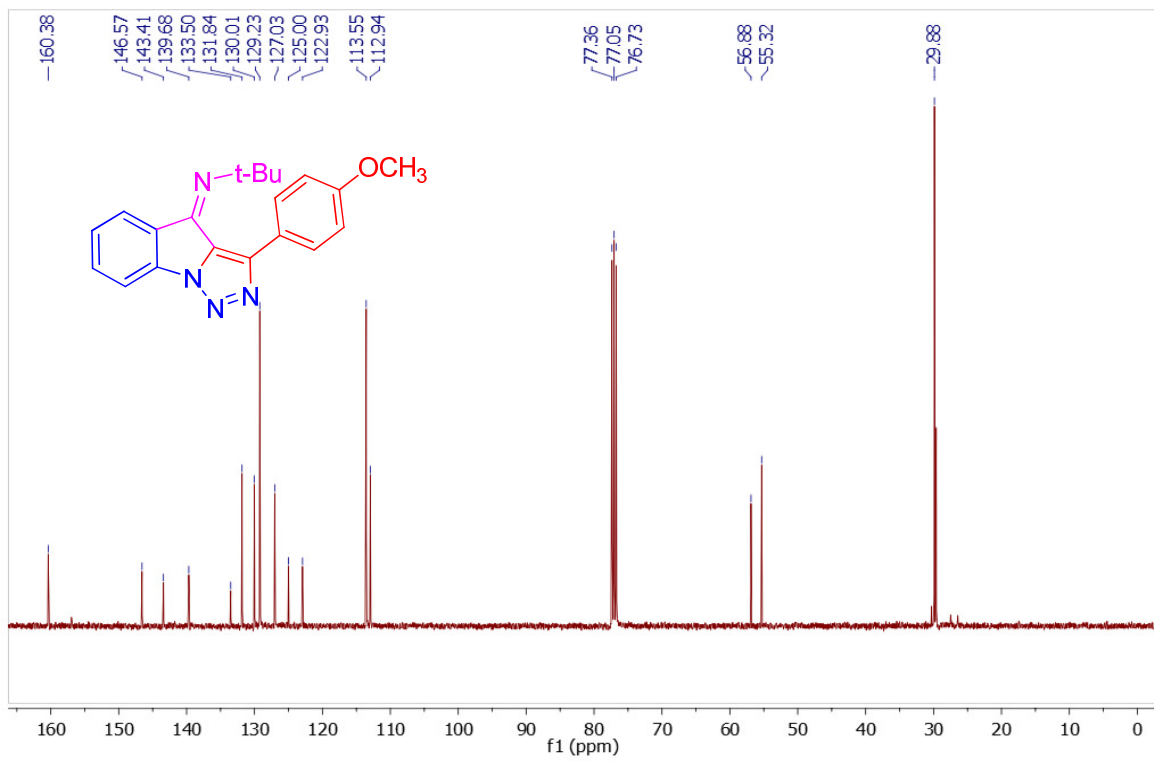
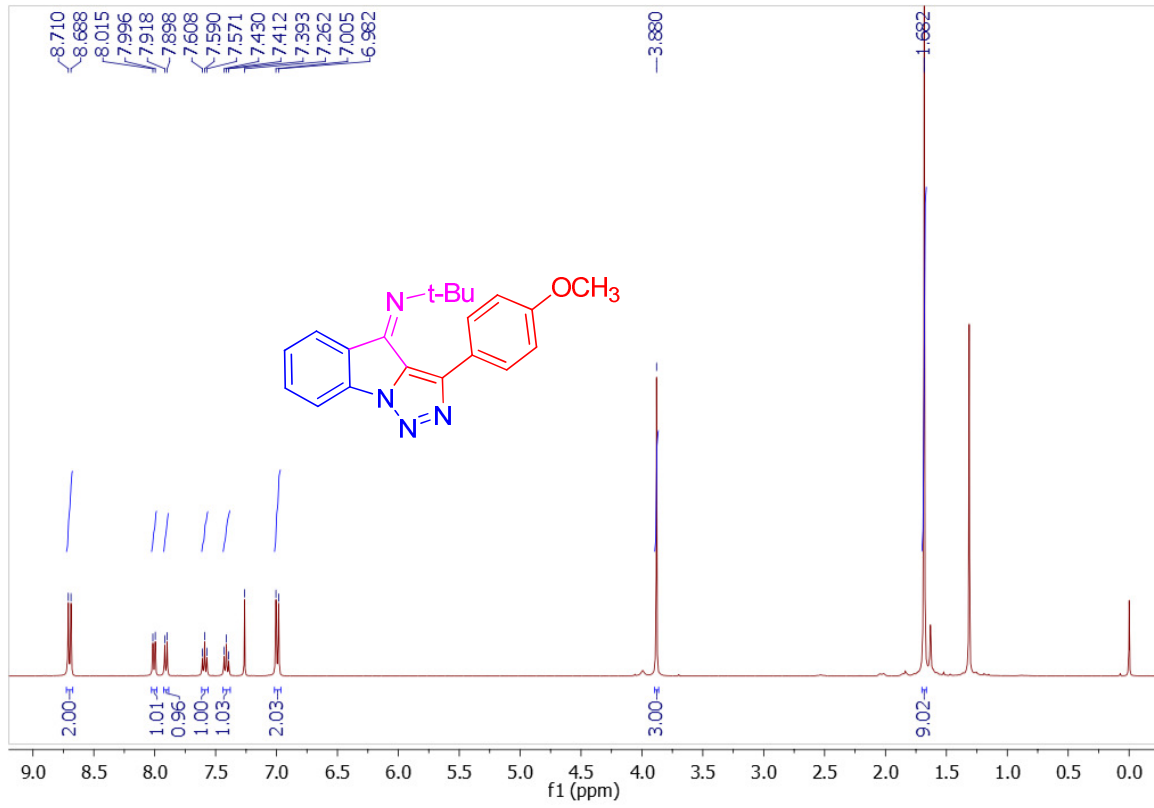
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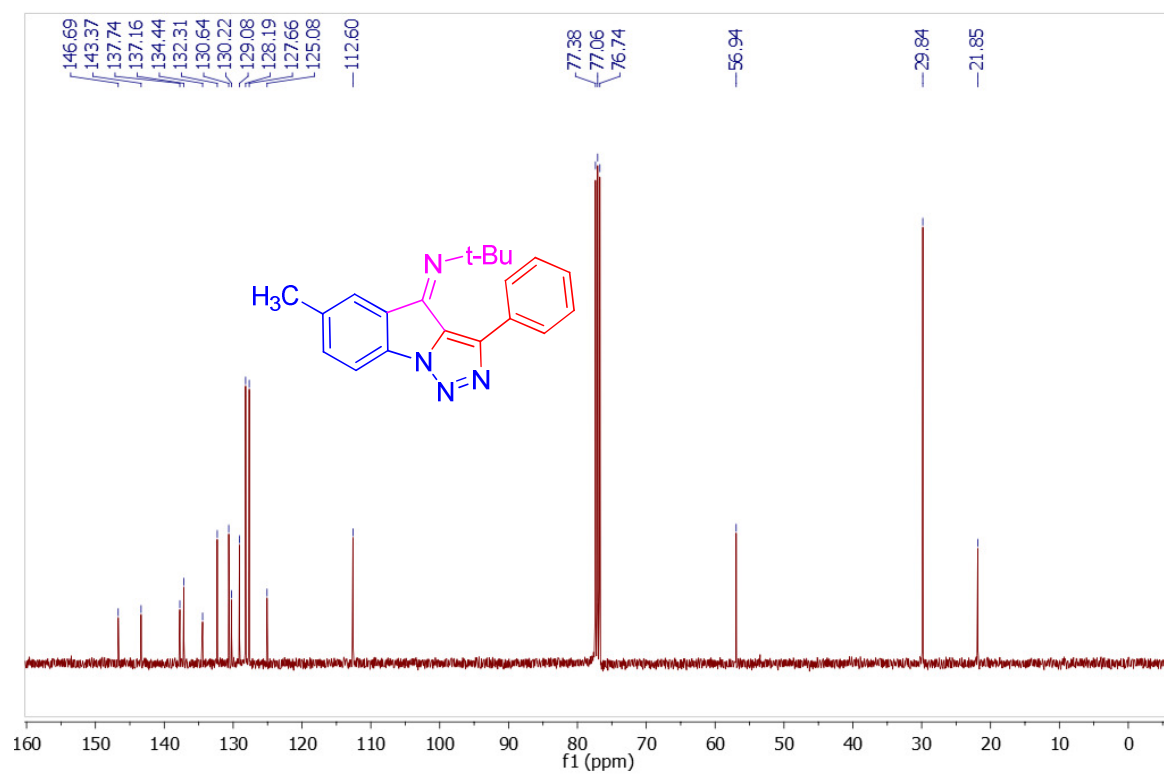
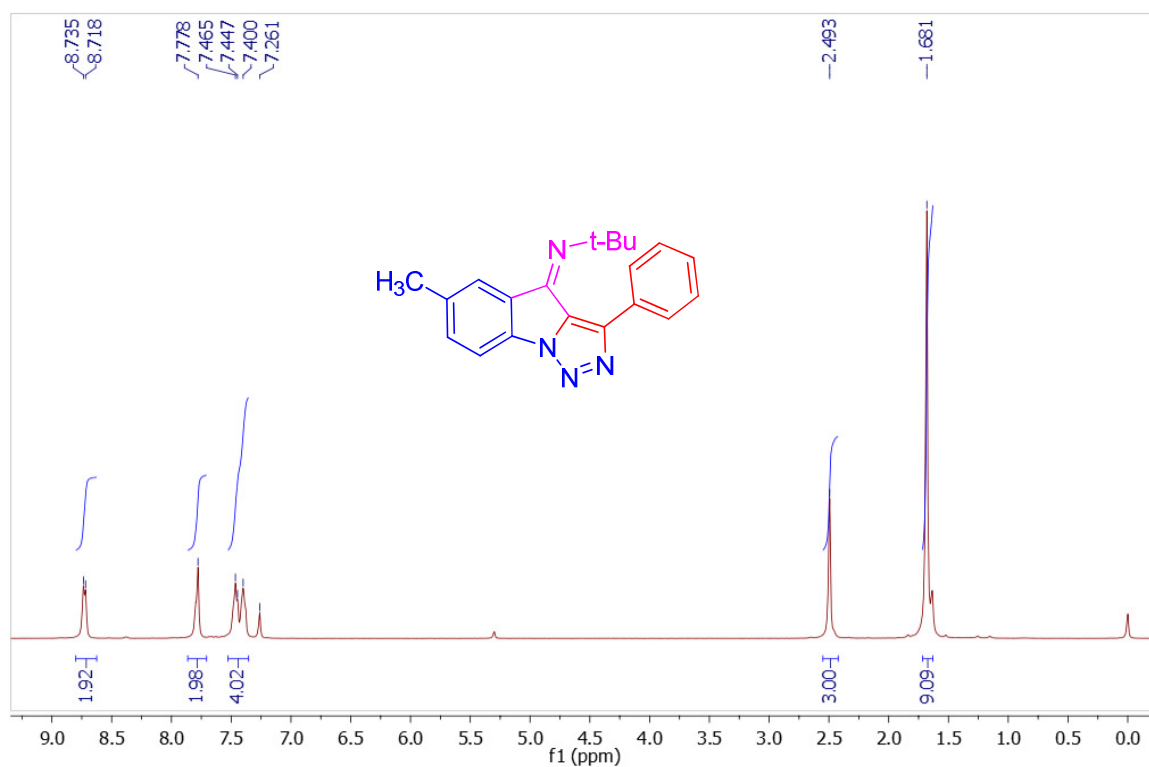
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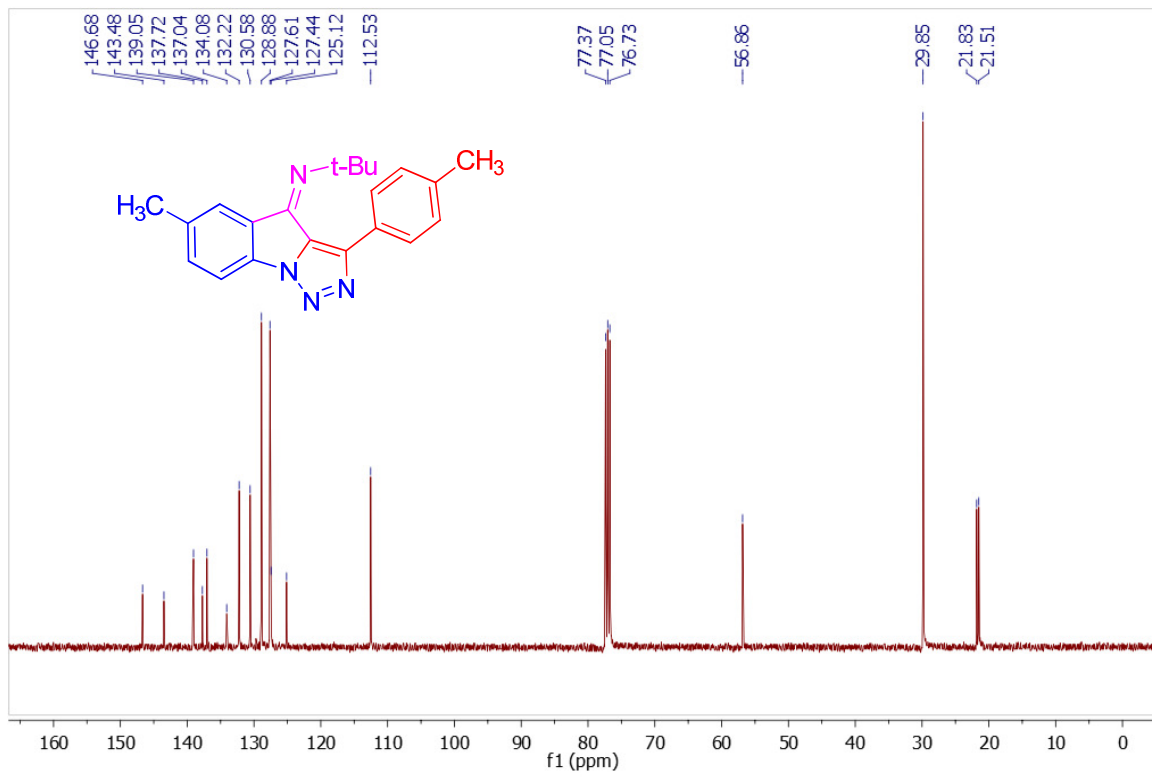
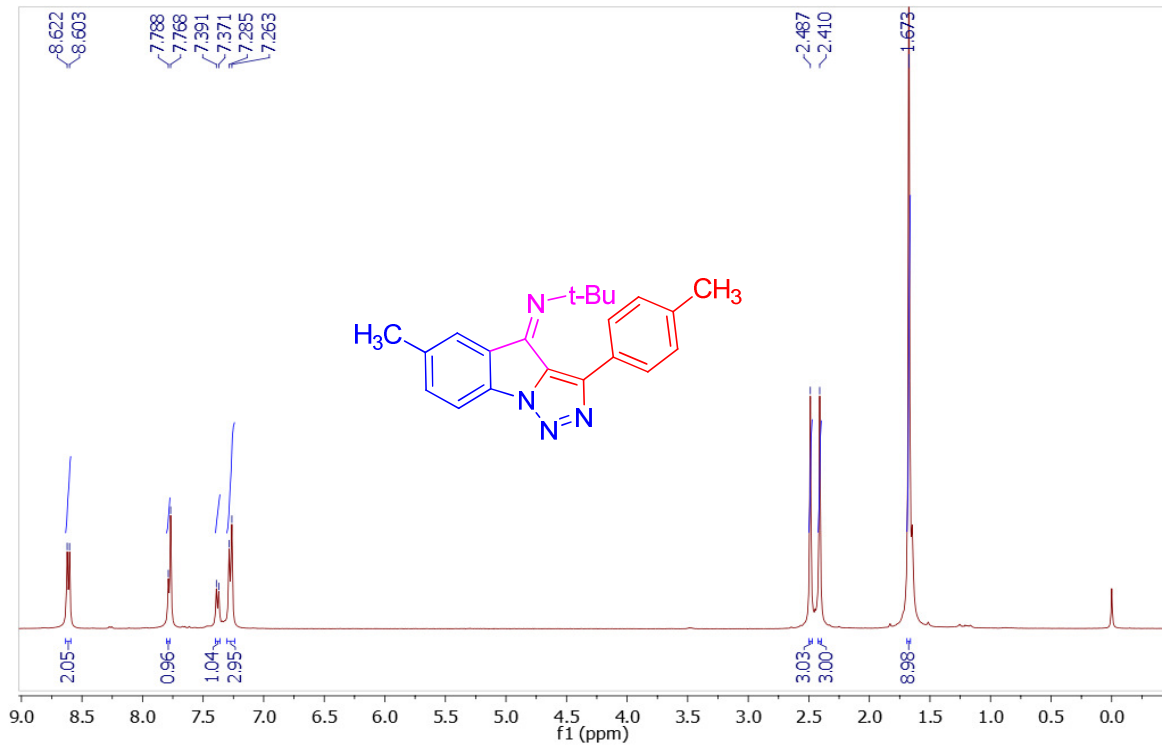
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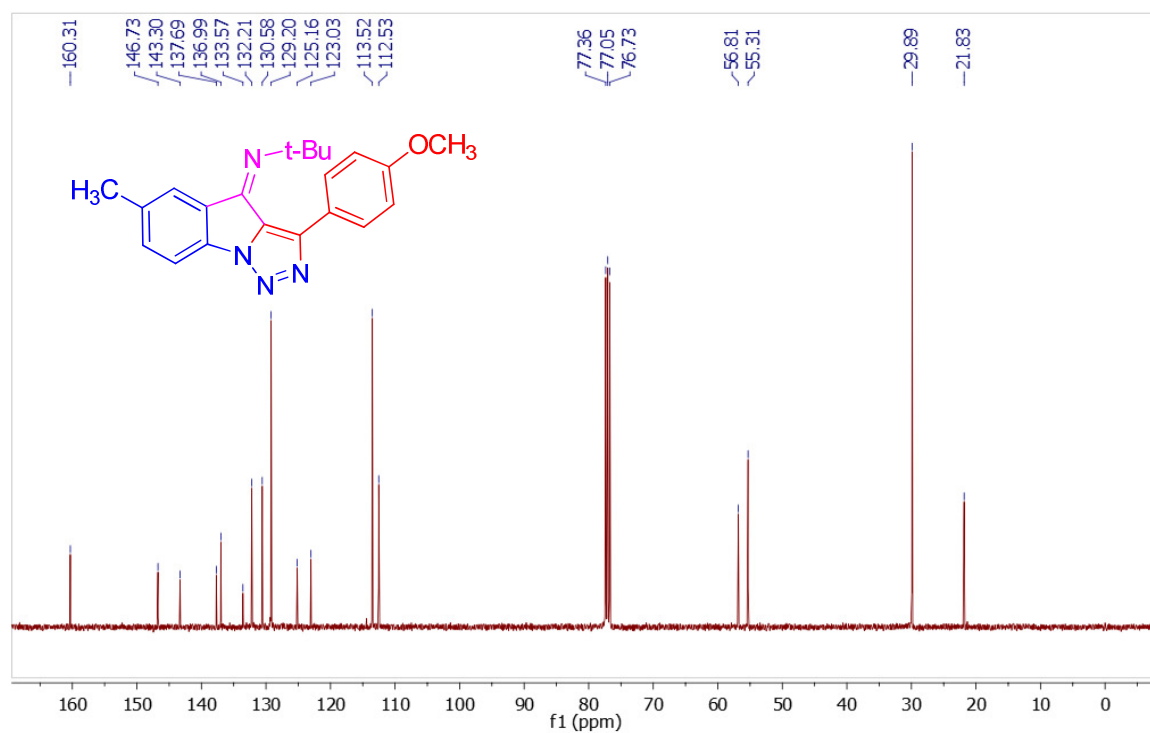
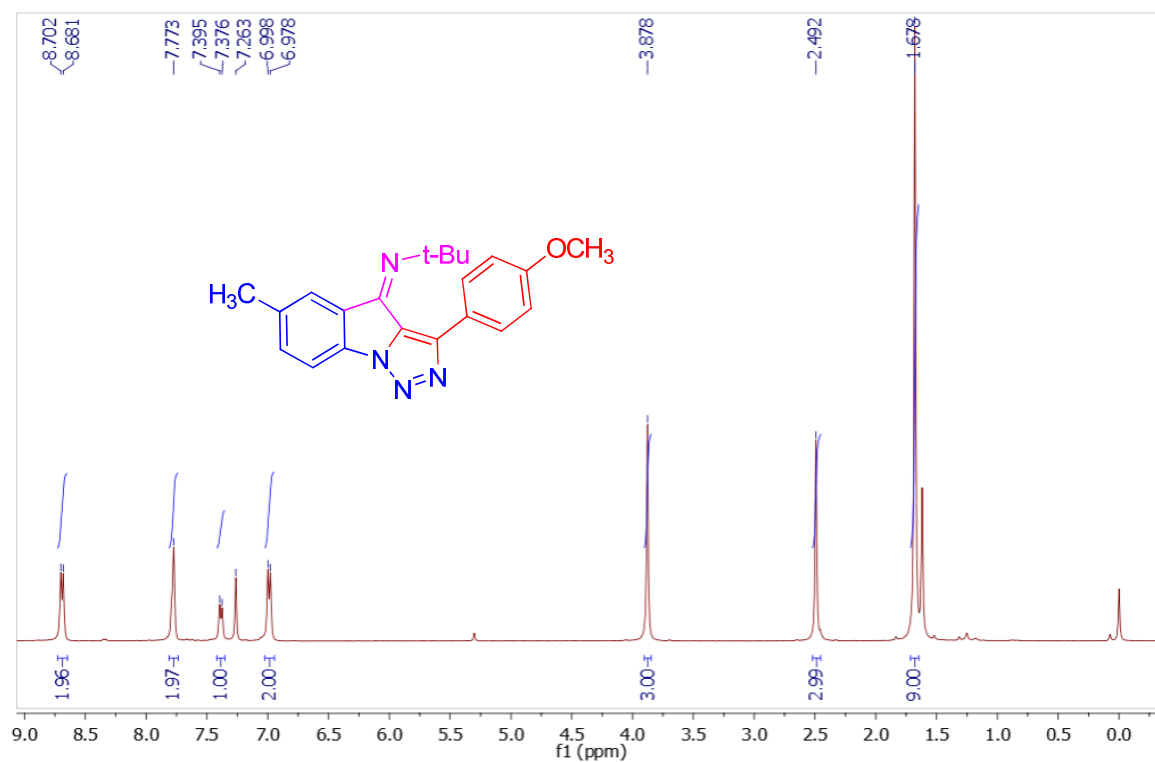
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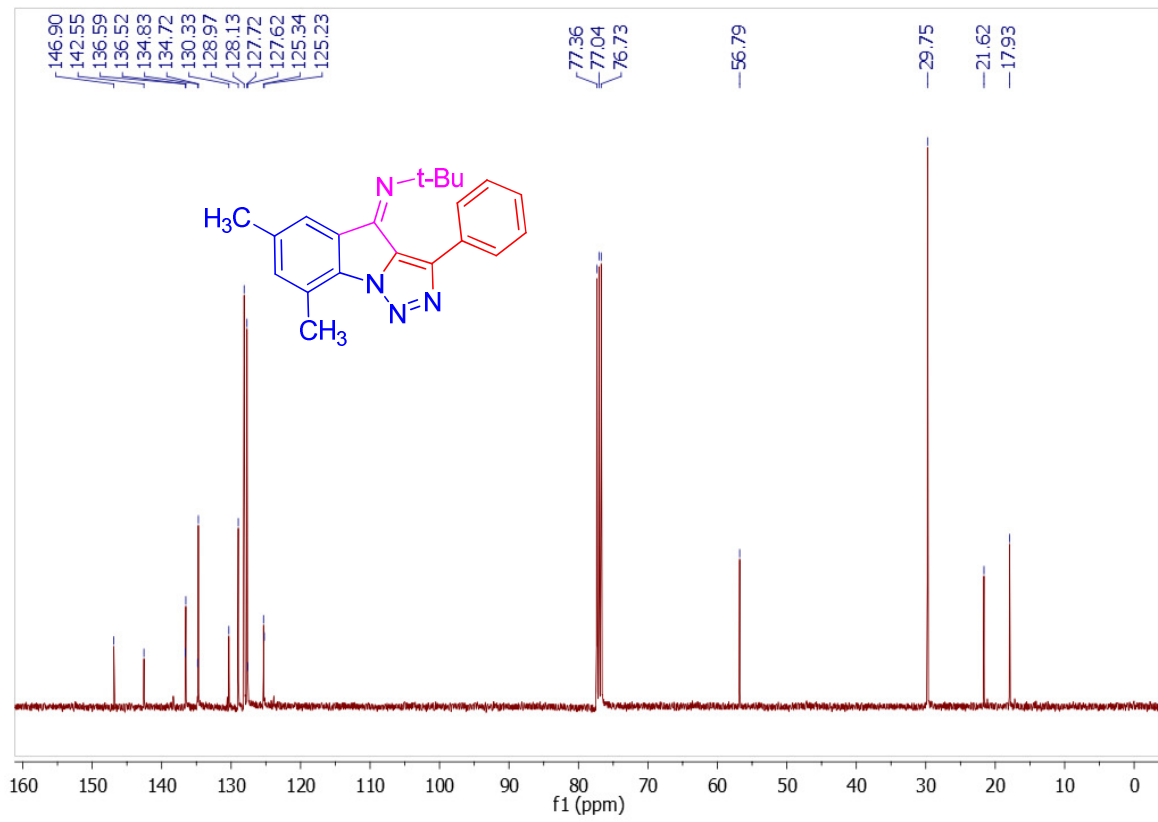
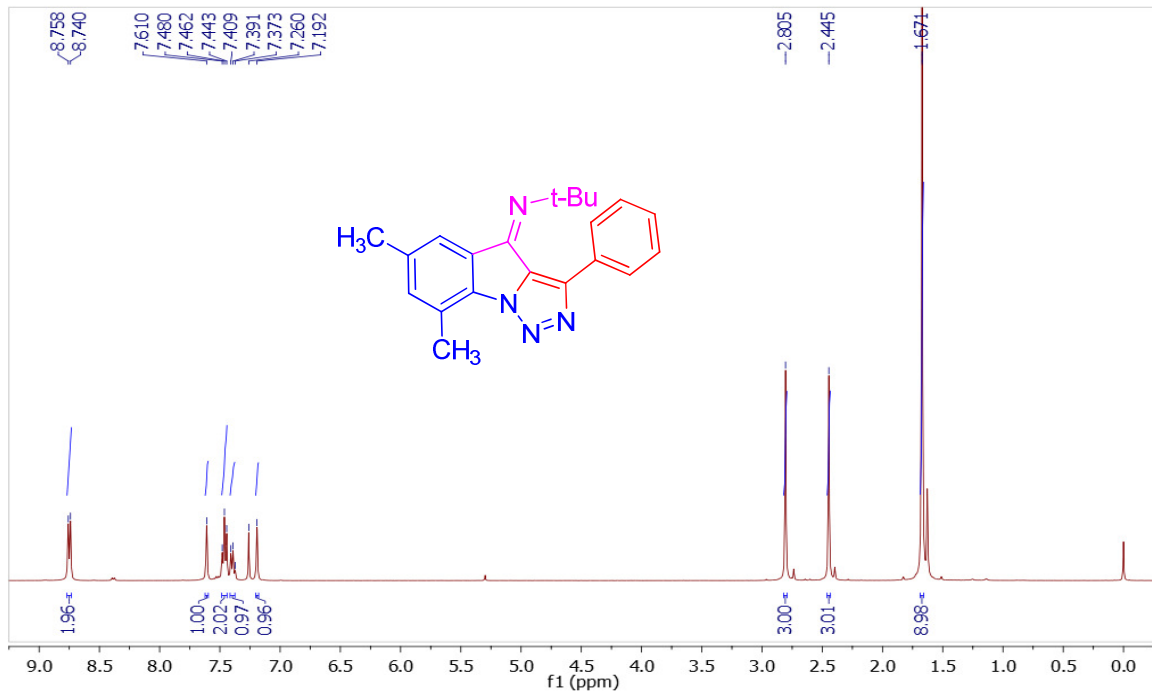
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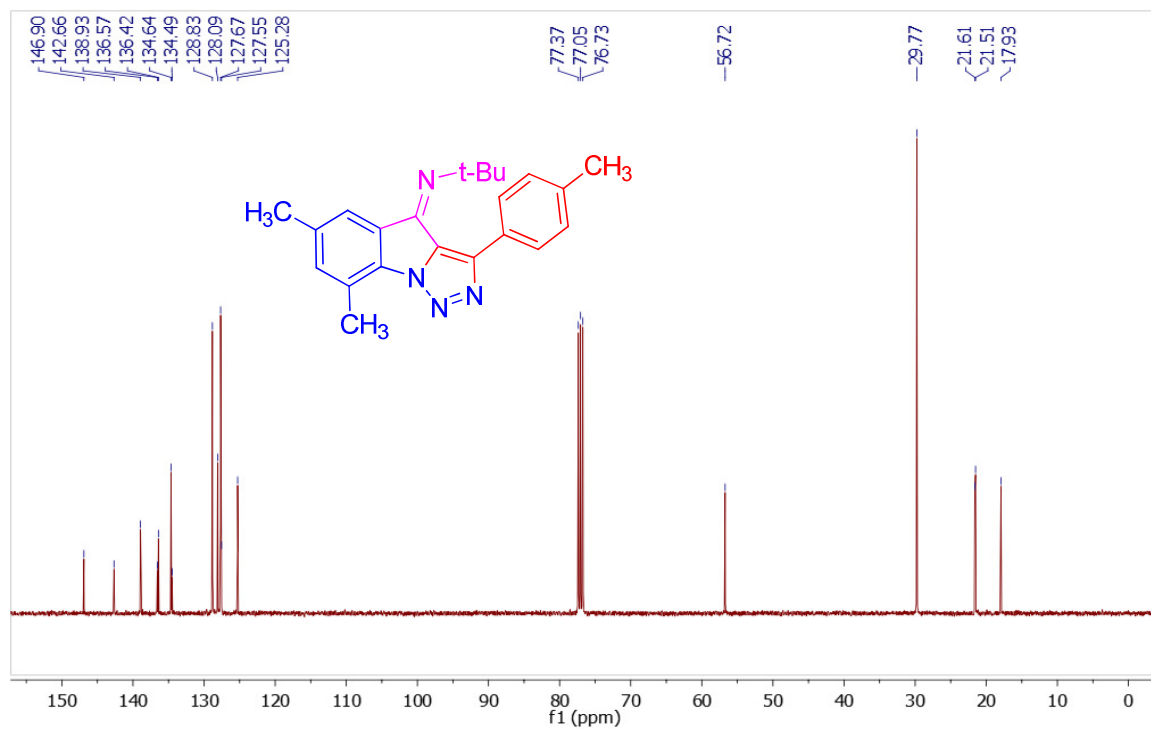
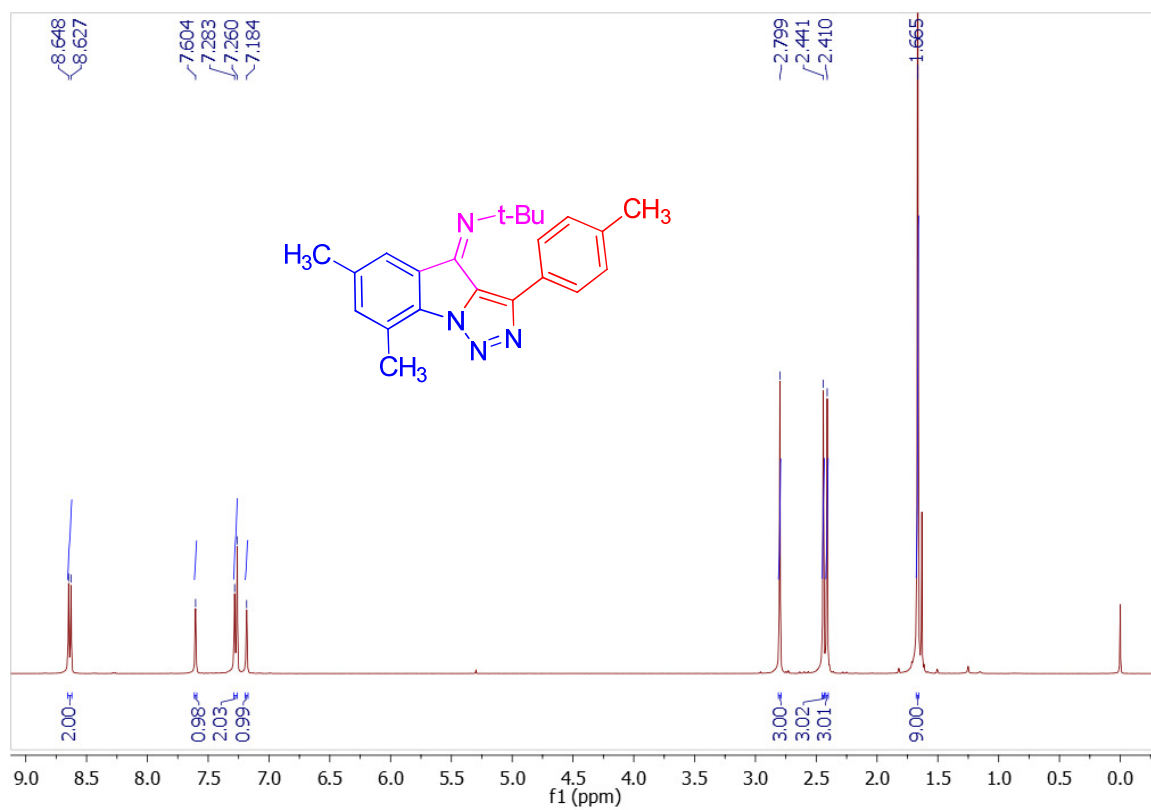
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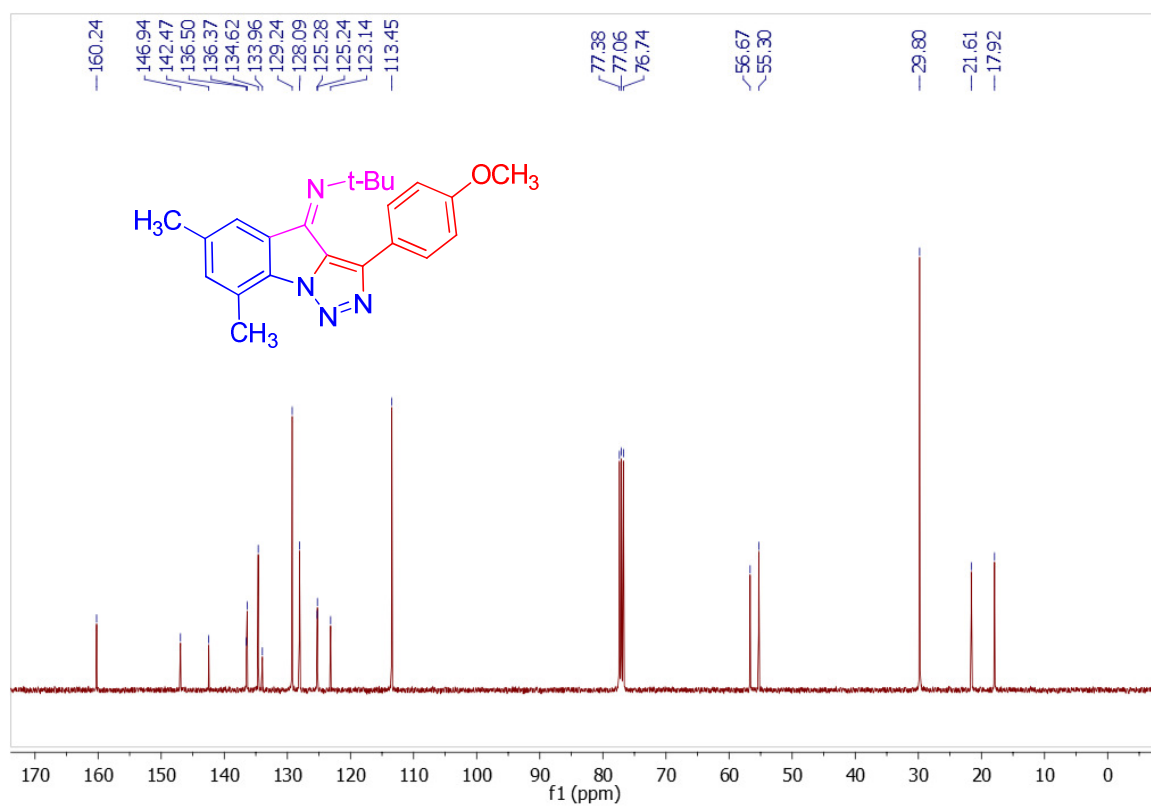
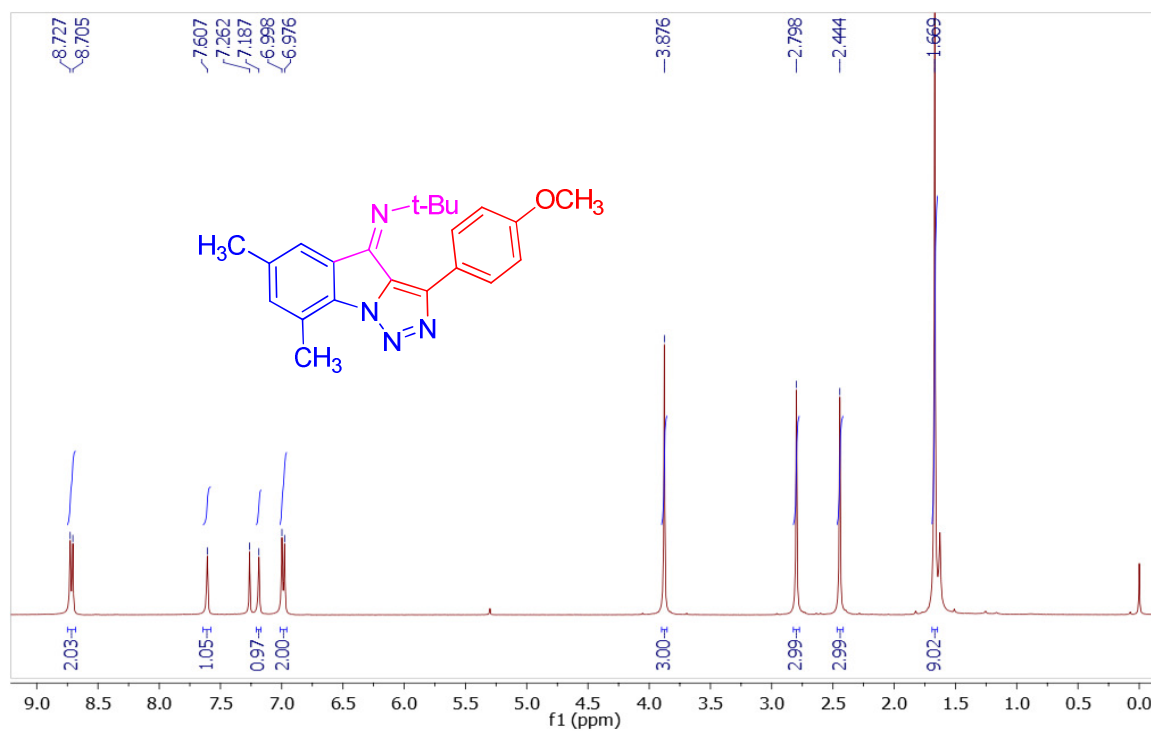
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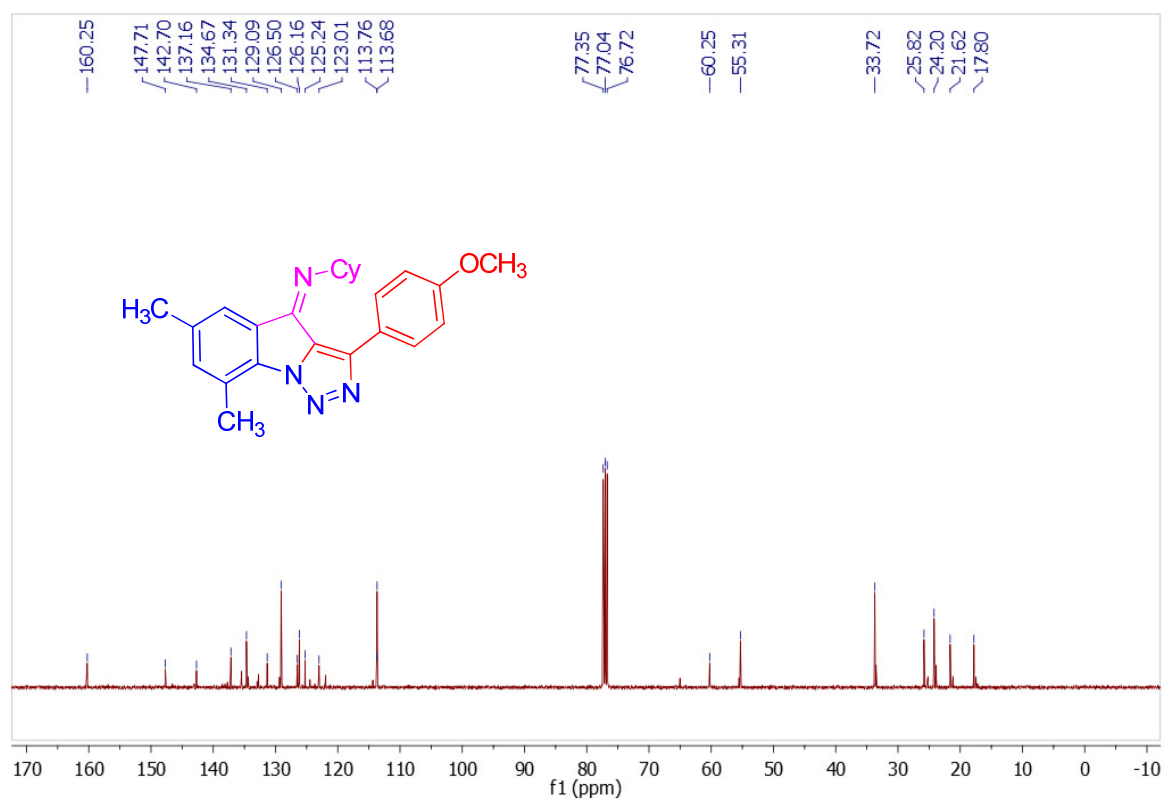
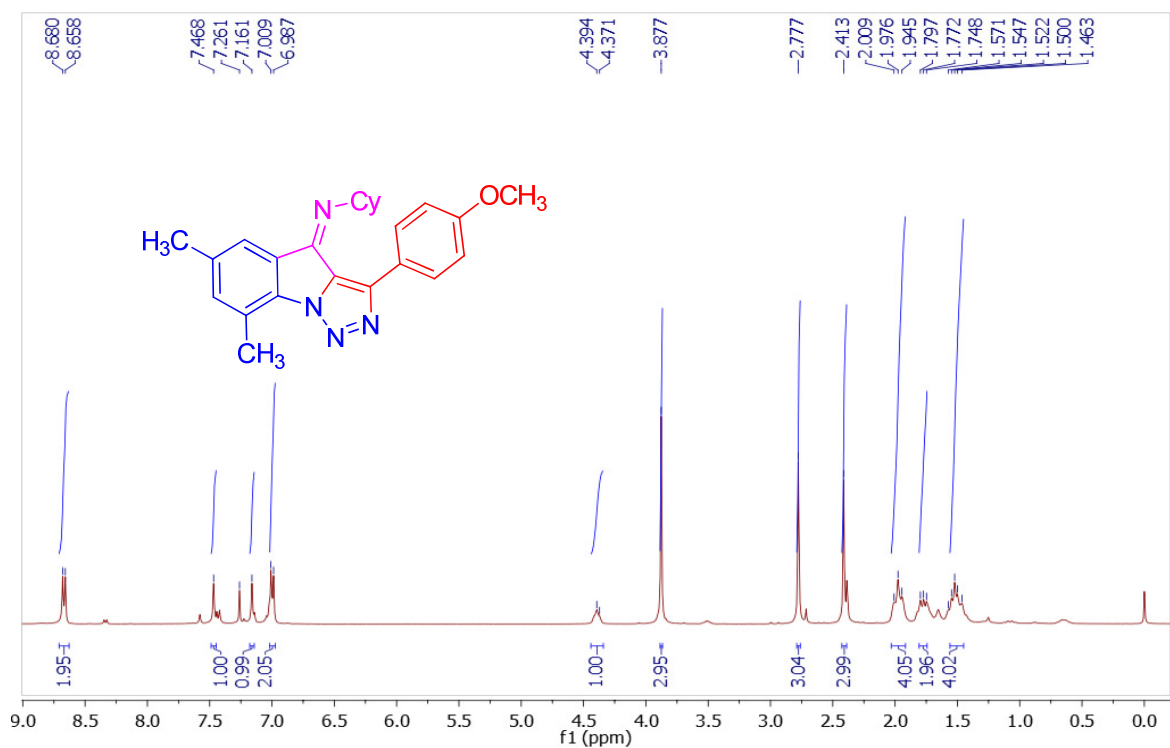
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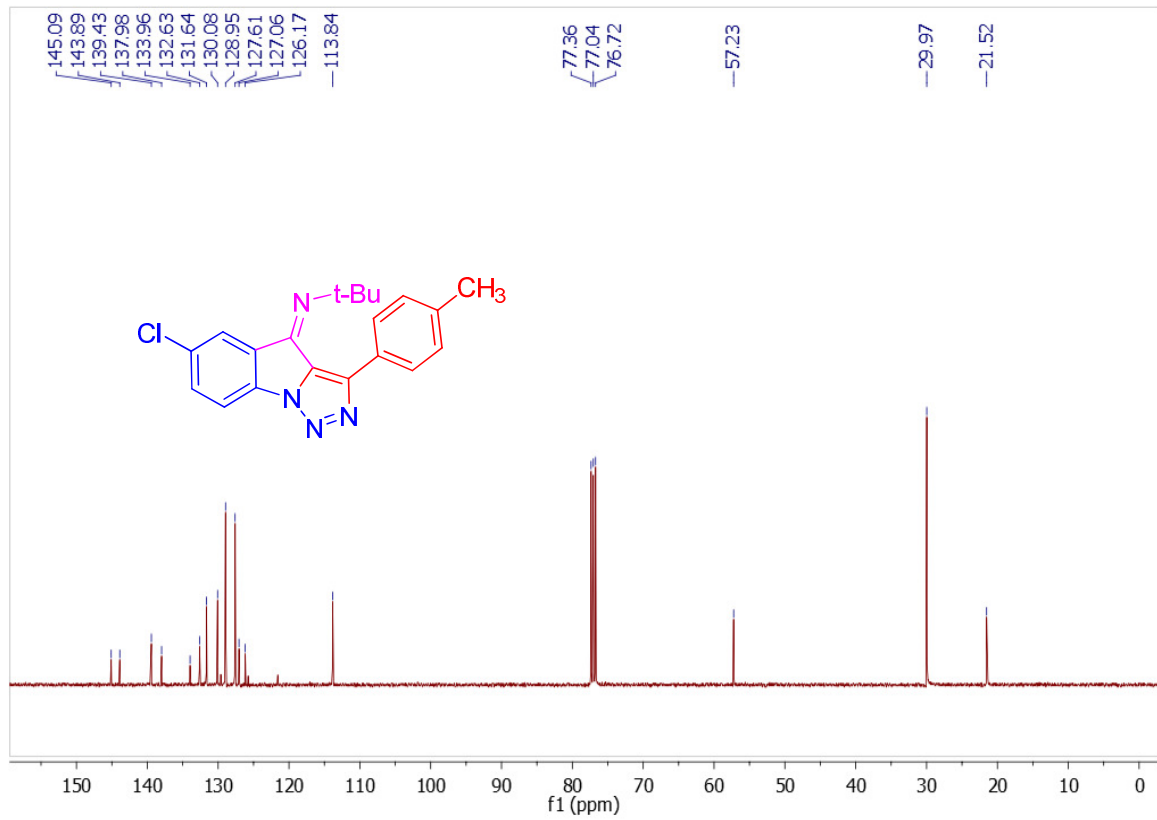
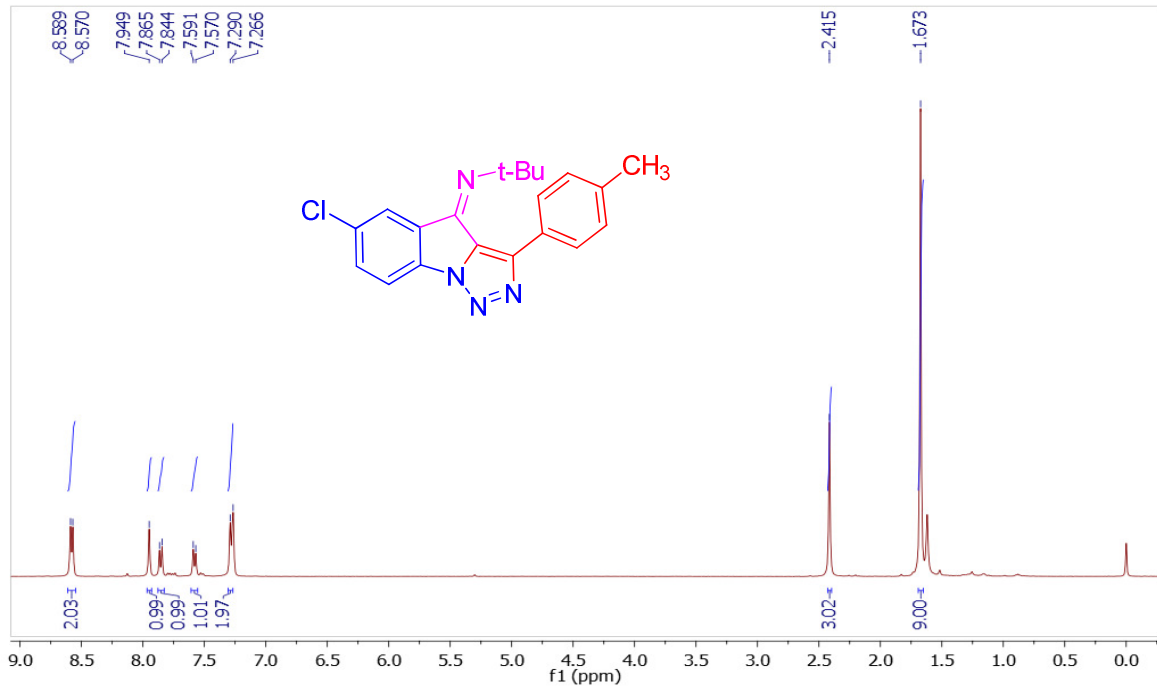
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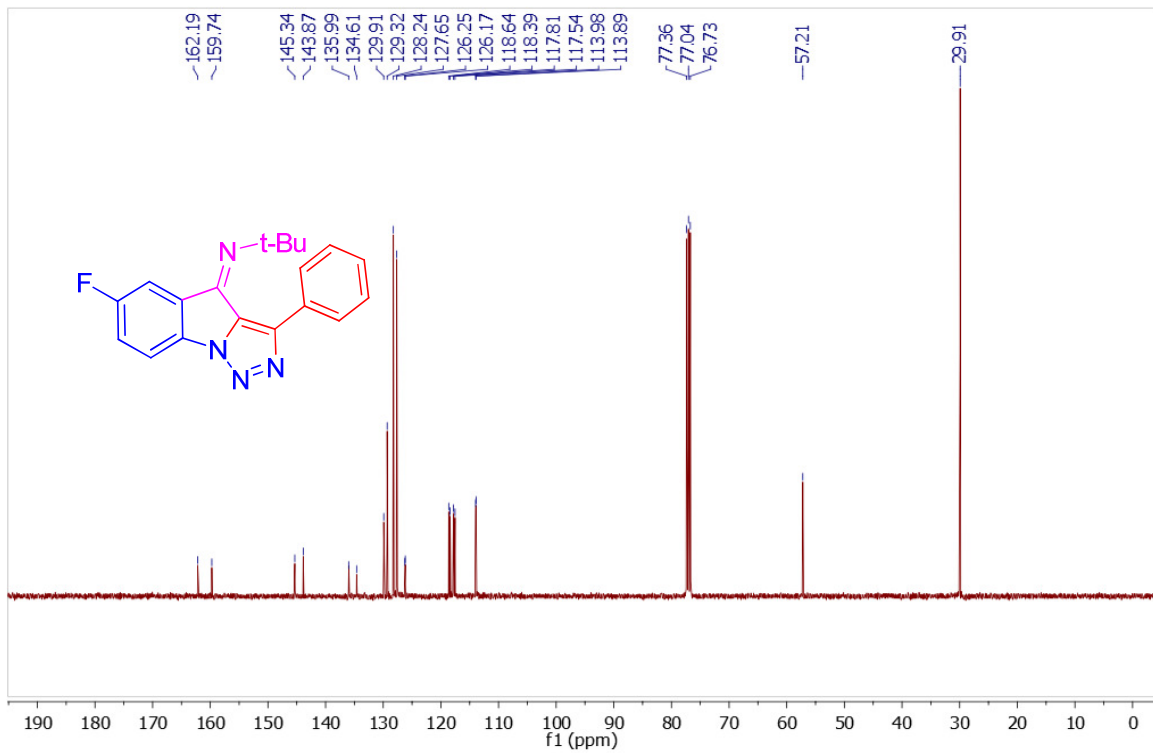
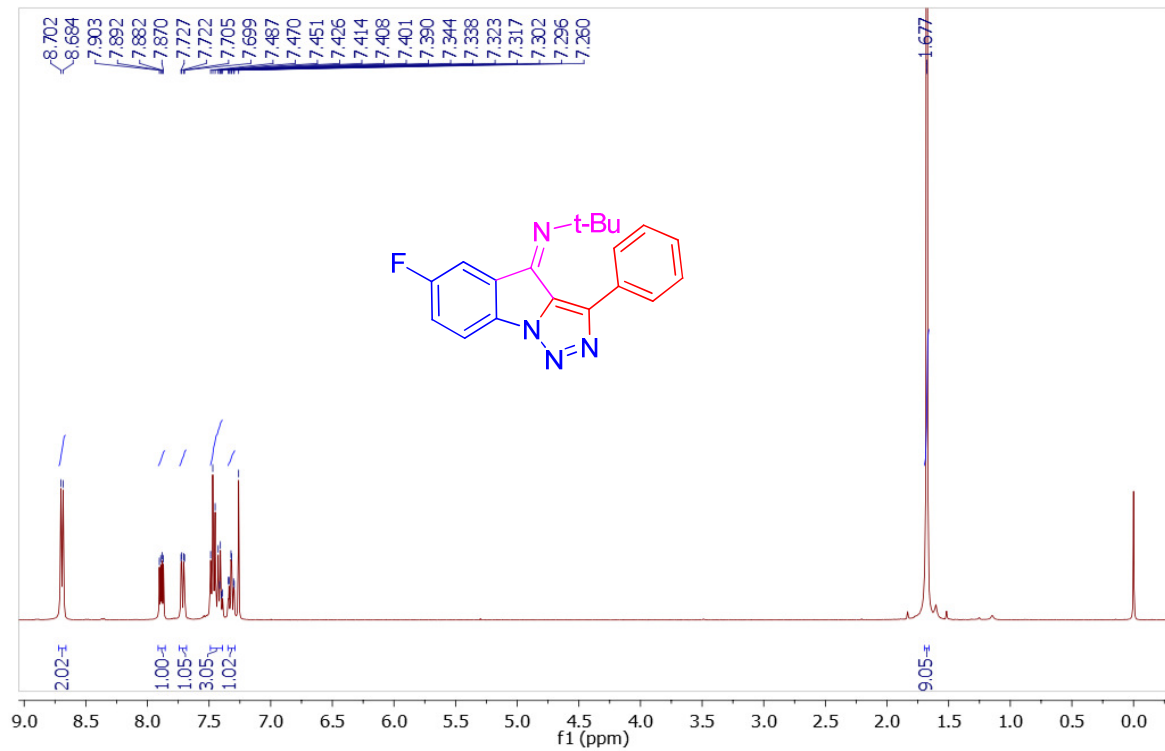
Compound-5j



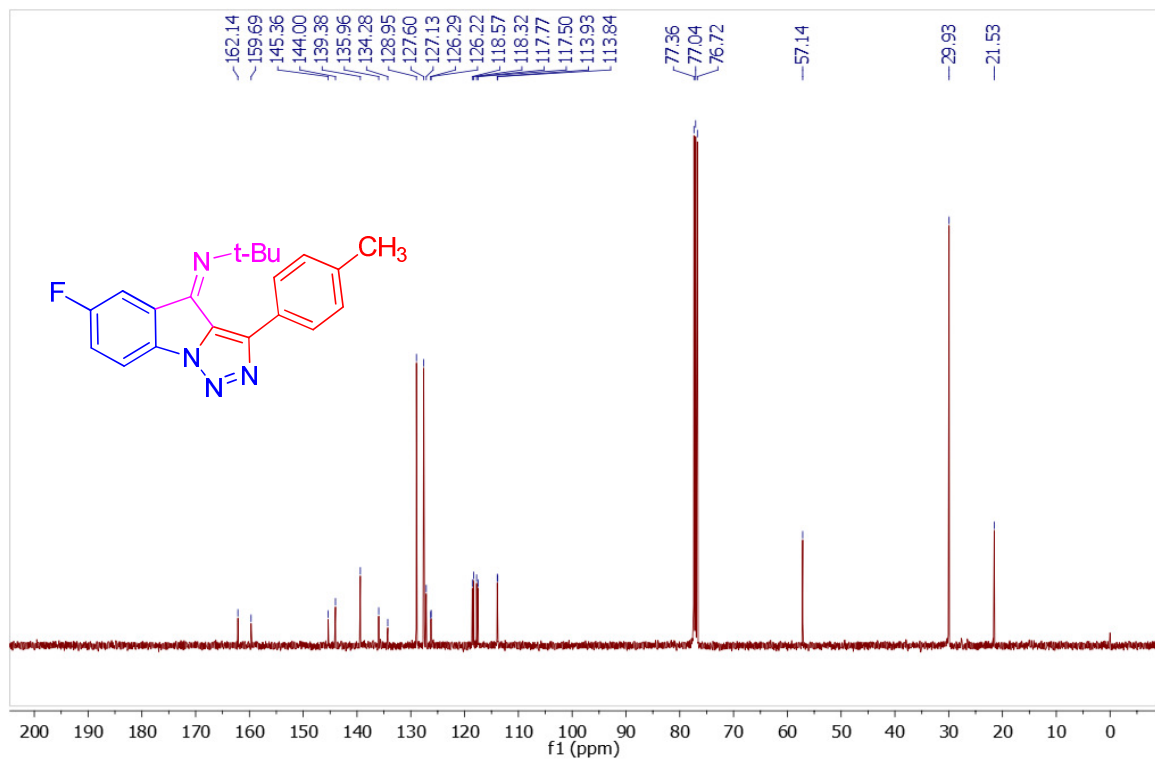
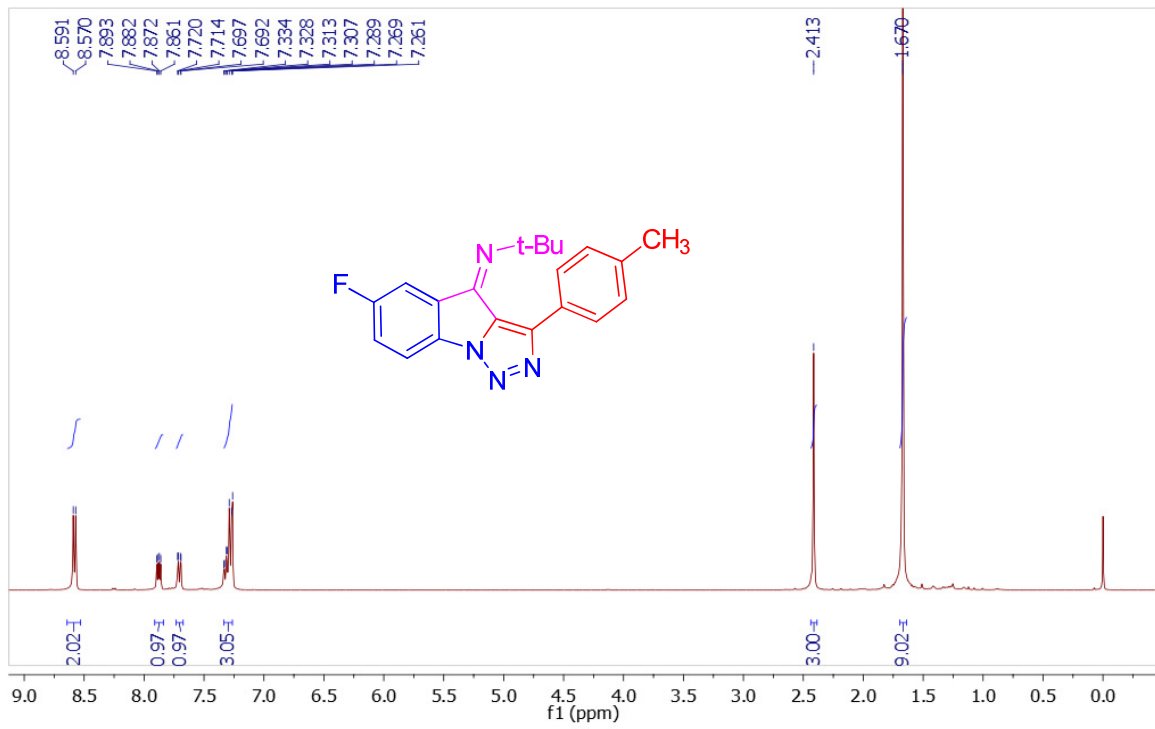
Compound-5k



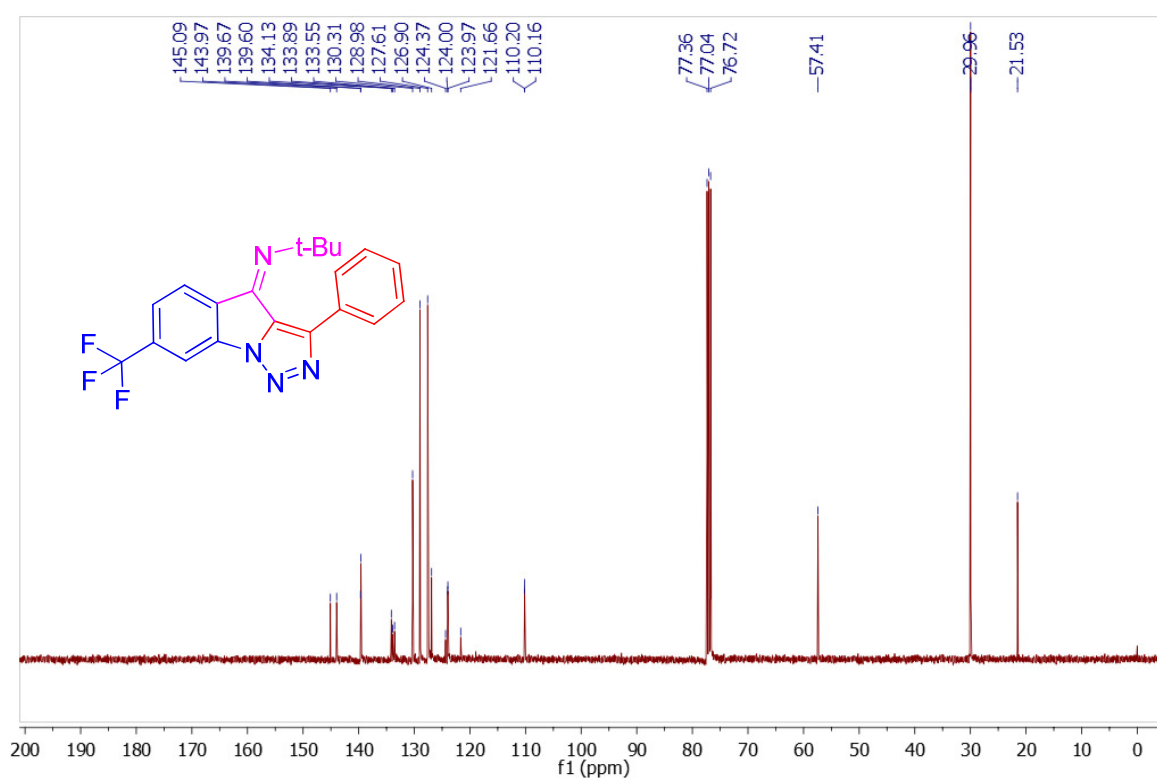
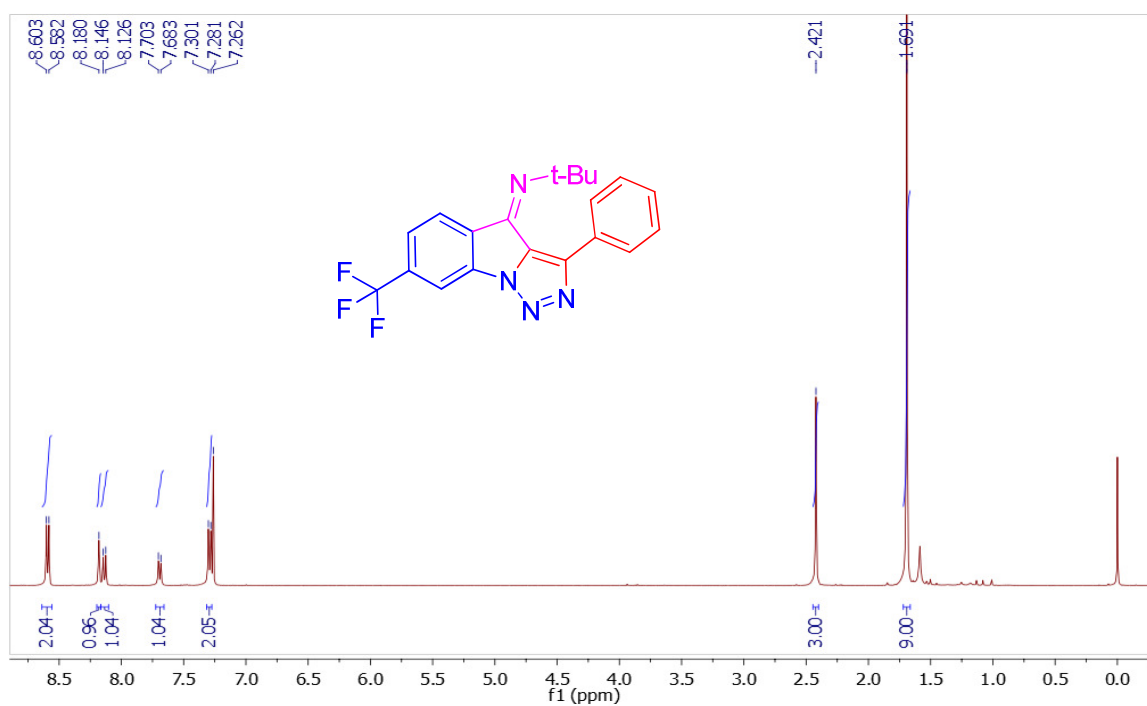
Compound-5l



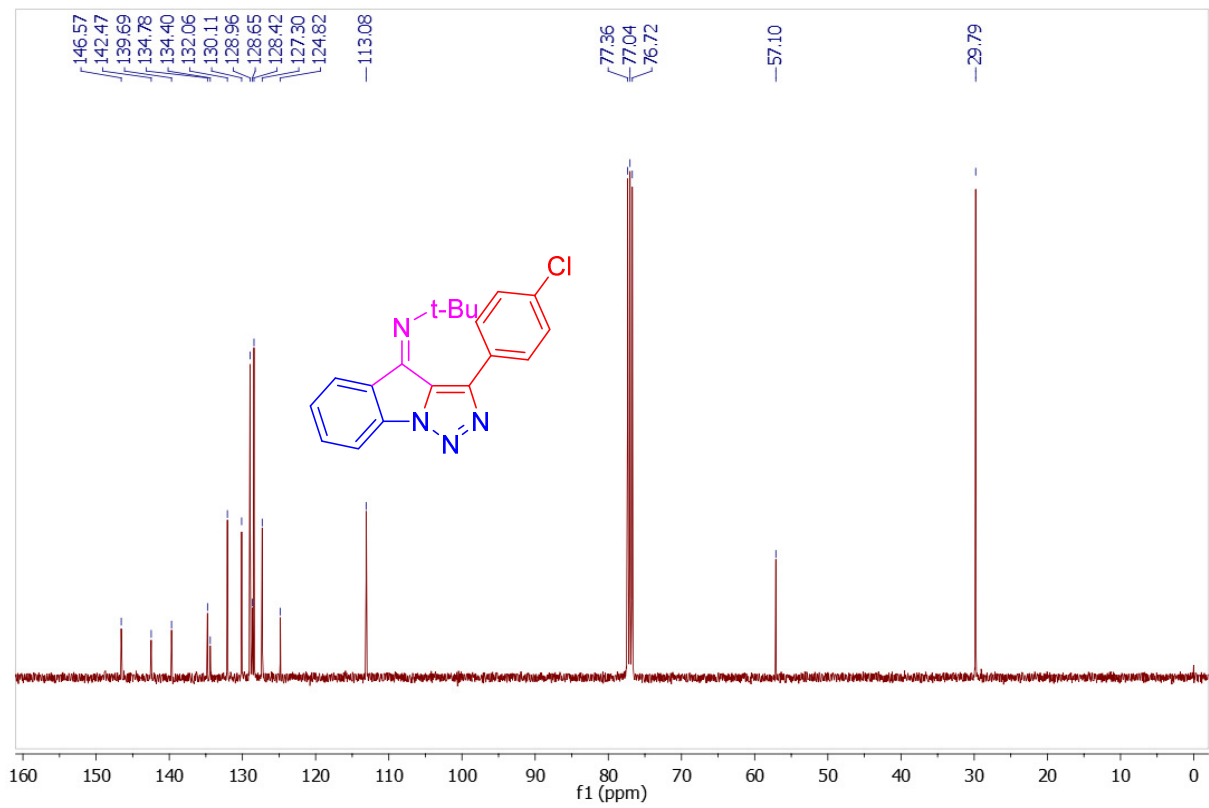
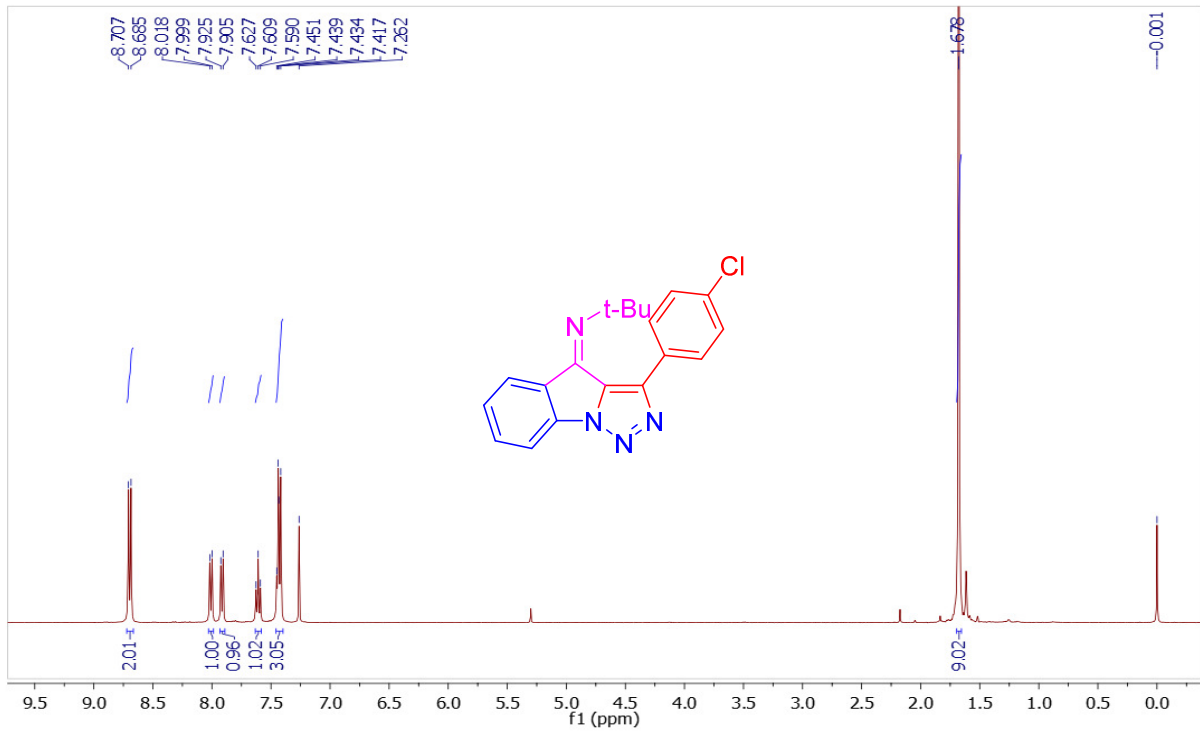
Compound-5m



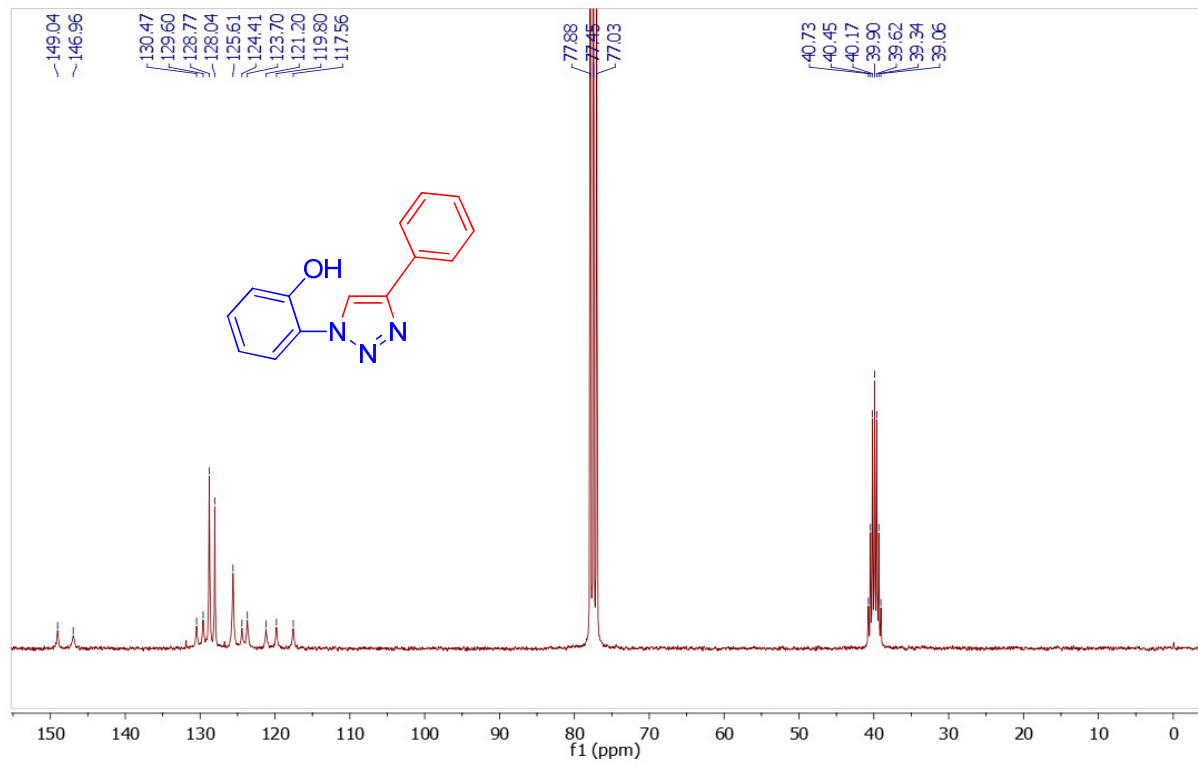
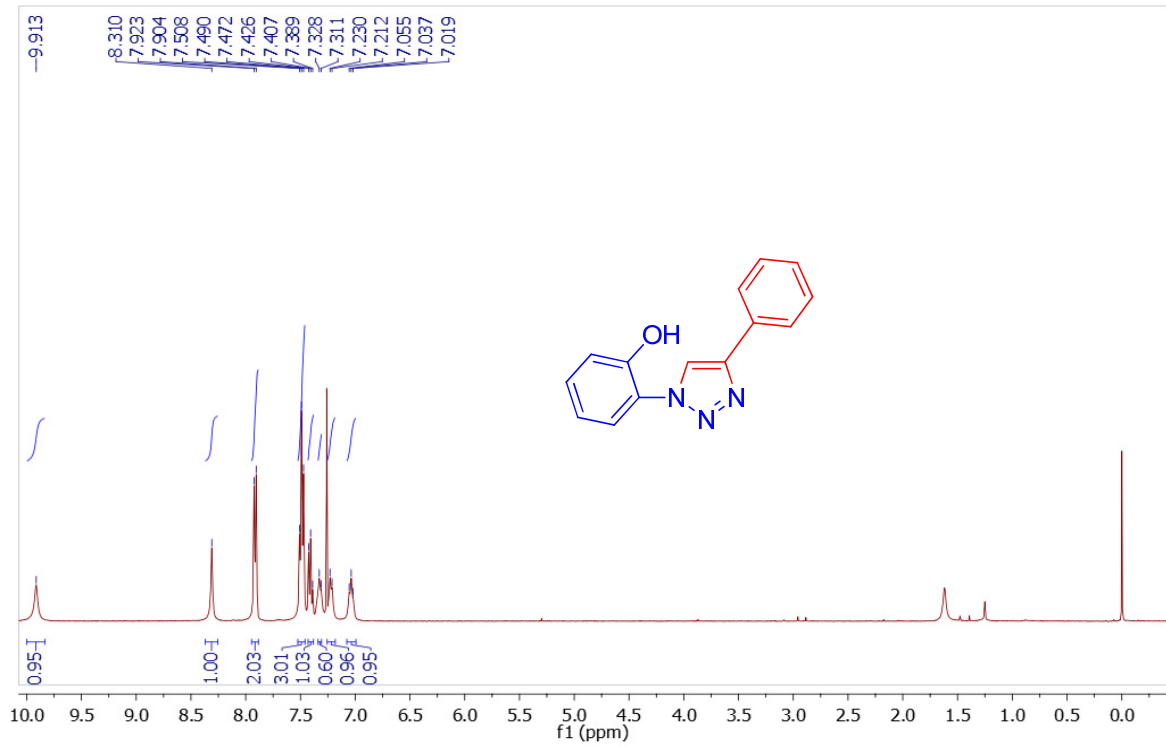
Compound-5n



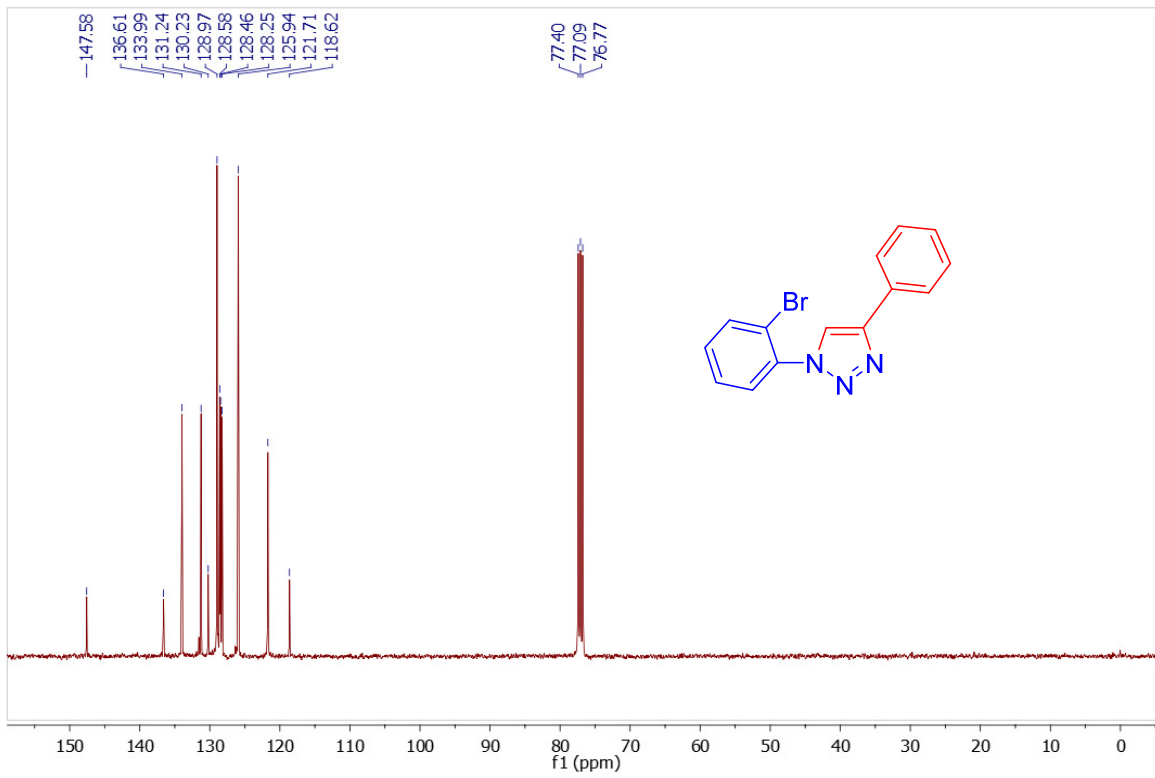
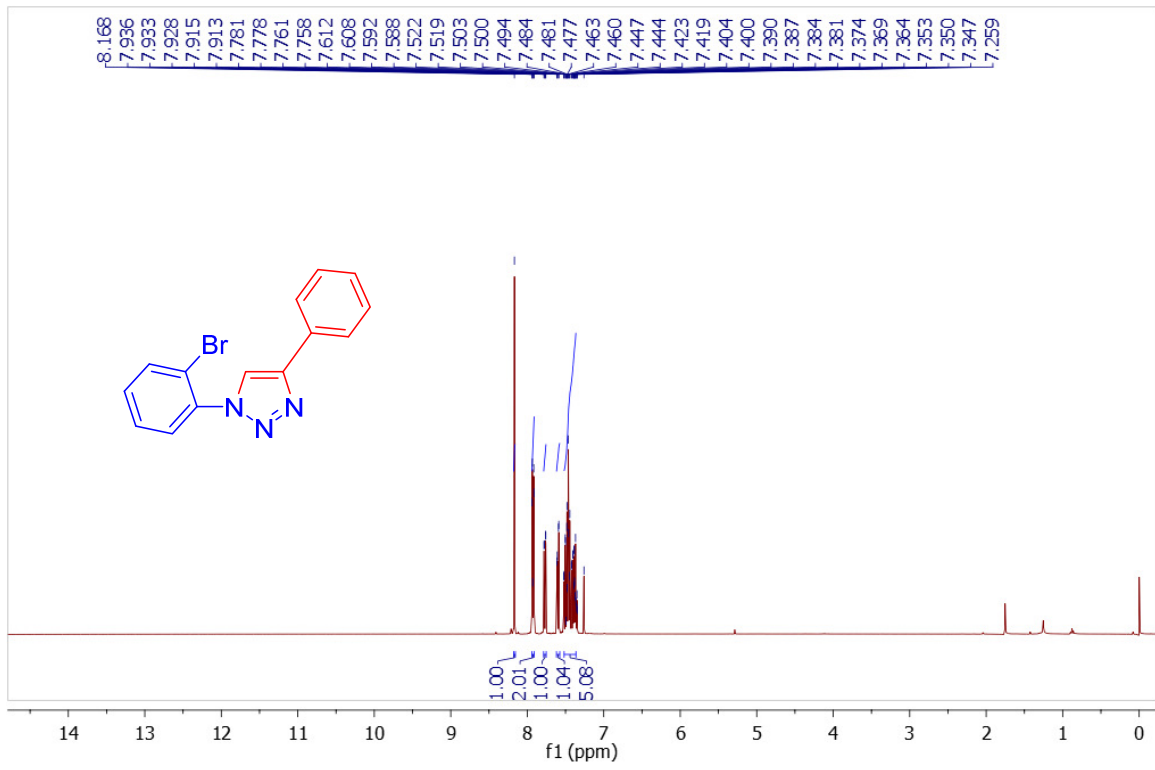
Compound-5o



Compound-Ia



Compound-IIa



Compound-1k

