Supporting Information (SI)

Oxalic acid as a dual C1 surrogate for heterogeneous palladium-catalyzed tandem four-component quinazolinones synthesis

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Contents:

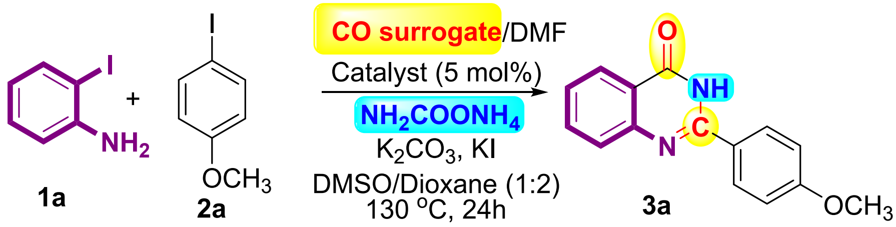
General Information:

High-quality reagents were purchased from Sigma Aldrich, Tokyo Chemical Industry (TCI), Loba Chemie, SD Fine-chem Ltd and Alfa Aesar. Pd/C and Pd/Al_2O_3 have been purchased from Sd fine Chem Ltd. and TCI Chemicals respectively. Analytical grade solvents were used. Reactions were monitored by thin layer chromatography which was performed using precoated silica gel plates 60F254 (Merck) in a UV light detector. Silica gel (60-120 and 230-400 mesh size) for column chromatography was purchased from SD Fine-chem Ltd. ESI-MS spectra were recorded using a Waters micro mass Q-TOF Ultima Spectrometer. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance 600 spectrometer operating at 600 MHz (^1H) and 150 MHz (^{13}C), JNM ECX -500 spectrometer operating at 500 MHz (^1H) and 125 (^{13}C). All the Spectra were recorded at 25 °C in DMSO-d_6 [residual DMSO-d_6 (δH 2.50, 3.39ppm) or DMSO-d_6 (δC 39.51 ppm)] with TMS as the internal standard. Chemical shifts were recorded in δ (ppm) relative to the TMS and NMR solvent signal. Coupling constants (J) are given in Hz and multiplicities of signals are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet; q, quartet. All the reactions were carried out by using a double-layer vial system (DLV) consisting of an inner vial (diameter = 12 mm, height = 32 mm) placed inside an outer vial (diameter = 20 mm, height = 65 mm) tightened with solid PTFE cap.

Optimization studies:

To check the effect of catalyst, various homogeneous and heterogeneous metal catalysts were further screened, however, no significant enhancement in desired product yield was observed (Table 1S entries 1-4). The implementation of formic acid as well as paraformaldehyde as CO surrogate or decreasing the equivalency (eq.) of $(CO_2H)_2$ also resulted in decreased desired product yield (Table 1S, entries 5-7) and $(CO_2H)_2$ (7 eq.) in DMF in outer vial of DLV system was found to the best-suited condition. Finally, the reaction temperature, as well as time, were also optimized (Table 1S, entries 1-9) and 130 °C for 24 h delivered the highest desired product yield. In addition, no desired product formation was observed in the absence of either base, $(CO_2H)_2$ or NH_2COONH_4, whereas the elimination of KI from the standard reaction condition resulted in lower desired product yield (Table 1S, entries 10-13). Hence, **1a** (1 eq.), **2a** (1.5 eq.), 5 wt% Pd/C (5 mol%), ammonium carbamate (3 eq.), K_2CO_3 (3.5 eq.), KI (2 eq.) in DMSO/Dioxane (1:2) in an inner vial and $(COOH)_2$ (7 eq.) in DMF in the outer vial were turned out to be the most suited conditions for the synthesis of targeted product **3a**.

Table 1S. Optimization studies for 2-aryl quinazolinones synthesis[a]

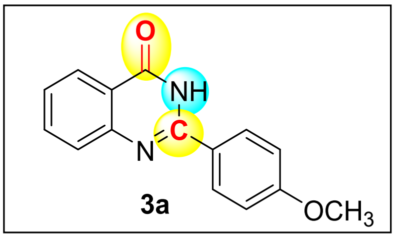


S.No.	Catalyst	CO surrogates	yield (%)[b]
1.	Pd@PS (5 mol%)	$(COOH)_2$ (7 eq.)	53
2.	Pd/Al_2O_3 (5 mol%)	$(COOH)_2$ (7 eq.)	59
3.	$Pd(OAc)_2$ (5 mol%)	$(COOH)_2$ (7 eq.)	48
4.	Pd/C (8 mol%)	$(COOH)_2$ (7 eq.)	70
5.	Pd/C (5 mol%)	Paraformaldehyde (7 eq.)	nd
6.	Pd/C (5 mol%)	HCOOH (7 eq.)	traces
7.	Pd/C (5 mol%)	$(COOH)_2$ (5 eq.)	59
8.[c]	Pd/C (5 mol%)	$(COOH)_2$ (7 eq.)	67
9.[d]	Pd/C (5 mol%)	$(COOH)_2$ (7 eq.)	65
10.[e]	Pd/C (5 mol%)	$(COOH)_2$ (7 eq.)	nd
11.	Pd/C (5 mol%)	-	nd
12.[f]	Pd/C (5 mol%)	$(COOH)_2$ (7 eq.)	nd
13.[g]	Pd/C (5 mol%)	$(COOH)_2$ (7 eq.)	52

[a]**1a** (0.23 mmol, 1 eq.), **2a** (1.5 eq.), 5 wt% Pd/C (5 mol%), NH_2COONH_4 (3 eq.), K_2CO_3 (3.5 eq.), KI (2 eq.) in DMSO/Dioxane (1:2) (1.5 mL) in an inner vial and $(COOH)_2$ (7 eq.) in DMF (0.5 mL) in outer vial at 130 °C for 24 h; [b]Isolated yield; [c]30 h; [d]140 °C; [e]Without K_2CO_3; [f]Without NH_2COONH_4; [g]Without KI.

Typical Experimental procedure and characterization:

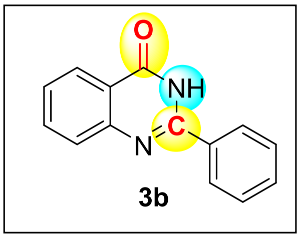
2-(4-methoxyphenyl)quinazolin-4(3H)-one



With the DLV system, 2-iodoaniline (50 mg, 0.23 mmol), 1-iodo-4-methoxybenzene (80.1 mg, 0.34mmol), 5 wt% of Pd/C (5 mol%), ammonium carbamate (53.4 mg, 0.68 mmol), K_2CO_3 (110 mg, 0.80 mmol) and KI (75.78 mg, 0.47 mmol) in dioxane/DMSO (2:1) solvent system were taken in the inner vial and this vial was placed inside the outer reaction vial containing oxalic acid (1.60 mmol, 143.8 mg) and 0.5 mL of DMF. The 5 mL reaction vessel was tightened under air with solid PTFE cap and stirred on a heating metal block at 130 ^{o}C for 24 h. The progress of the reaction was monitored with the help of TLC. After the completion of the reaction, the inner vial was taken out. The reaction was quenched with water and the organic layer was extracted with ethyl acetate. The extracted organic layer was dried over anhydrous sodium sulphate and concentrated over a rotary evaporator. The crude mixture was further purified by column chromatography using hexane: ethyl acetate (80:20) as eluent, afforded compound **3a** as white solid (39.3 mg); yield: 68%; ^{1}H (600 MHz, DMSO-d_6) δ (ppm) = 12.40 (brs, 1H), 8.19 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 7.8 Hz, 1H), 7.82 - 7.80 (m, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.49 - 7.47 (m, 1H), 7.09 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) = 162.27, 161.85, 151.84, 148.92, 134.52, 129.43, 127.27, 126.10, 125.80, 124.79,120.68,113.98, 55.44.

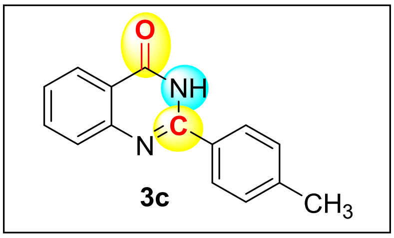
ESI-MS(M+H)$^+$ calculated for $C_{15}H_{13}N_2O_2^+$ is 253.0972 and observed is 253.0973.

2-phenylquinazolin-4(3H)-one



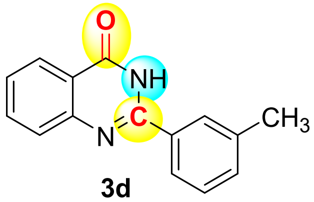
Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and iodobenzene (70 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3b** as white solid (37.5 mg); yield: 74%; ^{1}H (600 MHz, DMSO-d_6) δ (ppm) = 12.54 (brs, 1H), 8.19 - 8.15 (m, 3H), 7.85 - 7.83 (m, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.61 - 7.51 (m, 4H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) = 162.20, 152.29, 148.72, 134.58, 132.70, 131.37, 128.58, 127.74, 127.49, 126.57,125.83, 120.97.
ESI-MS(M+H)$^+$ calculated for $C_{14}H_{11}N_2O^+$ is 223.0866 and observed is 223.0866.

2-(p-tolyl)quinazolin-4(3H)-one



Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-iodo-4-methylbenzene (74.7 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3c** as white solid (41.2 mg); yield: 76%; ^{1}H (600 MHz, DMSO-d_6) δ (ppm) = 12.45 (brs, 1H), 8.15 (dd, $J_{1\text{-}3}$ = 7.9 Hz, $J_{1\text{-}2}$ = 1.2 Hz, 1H), 8.09 (d, J = 8.2 Hz, 2H), 7.83 -7.80 (m, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.51 - 7.49 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) = 162.29, 152.25, 148.81, 141.44, 134.54, 129.89, 129.17, 127.67, 127.36, 126.36, 125.83, 120.88, 20.97. ESI-MS$(M+H)^+$ calculated for $C_{15}H_{13}N_2O^+$ is 237.1022 and observed is 237.1029.

2-(m-tolyl)quinazolin-4(3H)-one

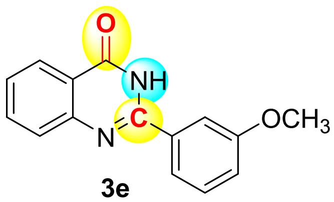


3d

Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-iodo-3-methylbenzene (74.7 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3d** as white solid (39.7 mg); yield: 74%; ^{1}H (600 MHz, DMSO-d_6) δ (ppm) = 12.47 (brs, 1H), 8.15 (d, J = 7.86 Hz, 1H), 8.02 (s, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.85 - 7.82 (m, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.53 - 7.51 (m, 1H), 7.44 - 7.39 (m, 2H), 2.41 (s, 3H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) =162.21, 152.40, 148.78, 137.94, 134.62, 132.65, 132.02, 128.52, 128.29, 127.49, 126.56, 125.85, 124.89, 120.98, 20.97.

ESI-MS$(M+H)^+$ calculated for $C_{15}H_{13}N_2O^+$ is 237.1022 and observed is 237.1025.

2-(3-methoxyphenyl)quinazolin-4(3H)-one

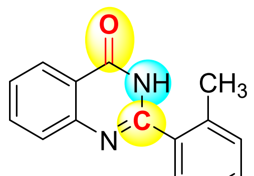


3e

Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-iodo-3-methoxybenzene (80.1 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (80:20) **3e** as white solid (36.4 mg); yield:

63%; ^{1}H (600 MHz, DMSO-d_6) δ (ppm) = 12.53 (brs, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.84 - 7.73 (m, 4H), 7.53 - 7.50 (m, 1H), 7.46 - 7.43 (m, 1H), 7.14 (d, J = 8.1 Hz, 1H), 3.86 (s, 3H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) = 162.31, 159.35, 152.09, 148.61, 134.58, 134.04, 129.73, 127.46, 126.60, 125.85, 121.01, 120.13, 117.58, 112.54, 55.38.
ESI-MS(M+H)$^+$ calculated for $C_{15}H_{13}N_2O_2^+$ is 253.0972 and observed is 253.0975.

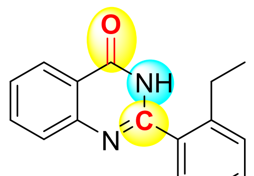
2-(o-tolyl)quinazolin-4(3H)-one



3f

Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-iodo-2-methylbenzene (74.7 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3f** as white solid (32.1 mg); yield: 60%; ^{1}H (600 MHz, DMSO-d_6) δ (ppm) = 12.45 (brs, 1H), 8.18 (dd, $J_{1\text{-}3}$ = 7.9 Hz, $J_{1\text{-}2}$ = 1.1 Hz, 1H), 7.84 - 7.81 (m, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.55 - 7.50 (m, 2H), 7.44 - 7.41 (m, 1H), 7.35 - 7.31 (m, 2H), 2.39 (s, 3H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) = 161.79, 154.38, 148.75, 136.13, 134.45, 134.24, 130.53, 129.88, 129.12, 127.37, 126.63, 125.79, 125.69, 120.99. 19.56.
ESI-MS(M+H)$^+$ calculated for $C_{15}H_{13}N_2O^+$ is 237.1022 and observed is 237.1024.

2-(2-ethylphenyl)quinazolin-4(3H)-one

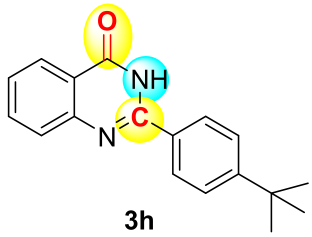


3g

Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-ethyl-2-iodobenzene (79.5 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3g** as white solid (29.3 mg); yield: 51%; ^{1}H (600 MHz, DMSO-d_6) δ (ppm) = 12.48 (brs, 1H), 8.17 (dd, $J_{1\text{-}3}$ = 7.9 Hz, $J_{1\text{-}2}$ = 1.3 Hz, 1H), 7.85 - 7.82 (m, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.56 - 7.53 (m, 1H), 7.48 - 7.46 (m, 2H), 7.39 (d, J = 7.4 Hz, 1H), 7.35 - 7.32 (m, 1H), 2.76 - 2.72 (m, 2H), 1.13 - 1.10 (m, 3H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) = 161.72, 154.36, 148.63, 142.16, 134.48, 133.84, 129.98, 129.11, 128.94, 127.35, 126.63, 125.77, 125.65, 120.95, 25.71, 15.40.

ESI-MS(M+H)+ calculated for $C_{16}H_{15}N_2O^+$ is 251.1179 and observed is 251.1179.

2-(4-(tert-butyl)phenyl)quinazolin-4(3H)-one

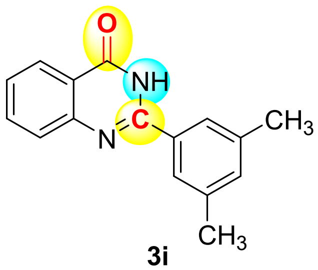


3h

Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-(tert-butyl)-4-iodobenzene (89.1mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3h** as a white solid (35.4 mg); yield: 66%; ^{1}H (500 MHz, DMSO-d_6) δ (ppm) = 12.42 (s, 1H), 8.16 - 8.12 (m, 3H), 7.84 - 7.81 (m, 1H), 7.73 (d, J = 7.75 Hz, 1H), 7.58 - 7.55 (m, 2H), 7.52 - 7.49 (m, 1H), 1.33 (s, 9H); ^{13}C (125 MHz, DMSO-d_6) δ (ppm) = 162.15, 154.25, 152.12, 148.78, 134.46, 129.89, 127.48, 127.36, 126.31, 125.76, 125.33, 120.86, 34.59, 30.83.

ESI-MS(M+H)+ calculated for $C_{18}H_{19}N_2O^+$ is 279.1492 and observed is 279.1492.

2-(3,5-dimethylphenyl)quinazolin-4(3H)-one

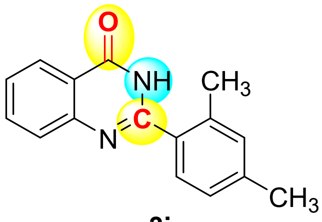


3i

Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-iodo-3,5-dimethylbenzene (79.5mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3i** as white solid (40.7 mg); yield: 71%; ^{1}H (600 MHz, DMSO-d_6) δ (ppm) = 12.39 (brs, 1H), 8.15 (d, J = 7.8 Hz, 1H), 7.84 - 7.81 (m, 3H), 7.74 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.20 (s, 1H), 2.36 (s, 6H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) = 162.15, 152.45, 148.79, 137.74, 134.54, 132.71, 132.57, 127.43, 126.44, 125.83, 125.47, 120.96, 20.85.

ESI-MS(M+H)+ calculated for $C_{16}H_{15}N_2O^+$ is 251.1179 and observed is 251.1179.

2-(2,4-dimethylphenyl)quinazolin-4(3H)-one

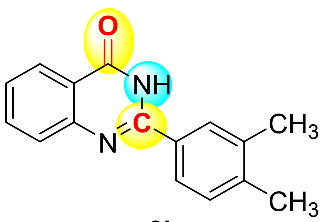


3j

Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-iodo-2,4-dimethylbenzene (79.5 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3j** as white solid (34.2 mg); yield: 60%; ^{1}H (500 MHz, DMSO-d_6) δ (ppm) = 12.37 (brs, 1H), 8.17 (dd, $J_{1\text{-}3}$ = 7.95 Hz, $J_{1\text{-}2}$ = 1.55 Hz, 1H), 7.84 - 7.81 (m, 1H), 7.68 – 7.67 (m, 1H), 7.54 – 7.51 (m, 1H), 7.41 (d, J = 7.75 Hz, 1H), 7.16 - 7.12 (m, 2H), 2.37 (d, J = 12.3 Hz, 6H); ^{13}C (125 MHz, DMSO-d_6) δ (ppm) = 161.85, 154.39, 148.79, 139.47, 136.06, 134.42, 131.41, 131.19, 129.17, 127.32, 126.50, 126.23, 125.75, 120.89, 20.84, 19.58.

ESI-MS(M+H)$^+$ calculated for $C_{16}H_{15}N_2O^+$ is 251.1179 and observed is 251.1177

2-(3,4-dimethylphenyl)quinazolin-4(3H)-one

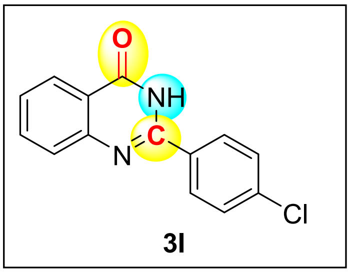


3k

Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 4-iodo-1,2-dimethylbenzene (79.5 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3k** as white solid (47.9 mg); yield: 84%; ^{1}H (500 MHz, DMSO-d_6) δ (ppm) = 12.39 (brs, 1H), 8.15 (d, J = 8.3 Hz, 1H), 8.0 (s, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.31 (d, J = 8.3 Hz, 1H), 2.32 (d, J = 7.6 Hz, 6H); ^{13}C (125 MHz, DMSO-d_6) δ (ppm) = 162.33, 152.40, 148.79, 140.23,136.58, 134.52, 130.17, 129.68, 128.61, 127.28, 126.30, 125.83, 125.16, 120.87, 19.40.

ESI-MS(M+H)$^+$ calculated for $C_{16}H_{15}N_2O^+$ is 251.1179 and observed is 251.1182.

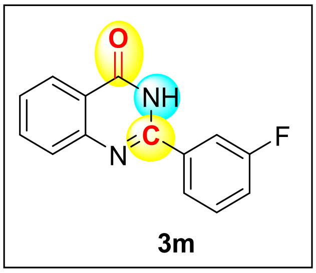
2-(4-chlorophenyl)quinazolin-4(3H)-one



Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-chloro-4-iodobenzene (81.7 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3l** as white solid (35.2 mg); yield: 60%; ^{1}H (600 MHz, DMSO-d_6) δ (ppm) = 12.61 (brs, 1H), 8.21 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 7.6 Hz, 1H), 7.86 - 7.84 (m, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.5 Hz, 2H), 7.55 - 7.53 (m, 1H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) = 162.59, 151.75, 148.69, 136.52, 134.94, 131.79, 129.82, 128.92, 127.60, 127.04, 126.08, 121.09.

ESI-MS$(M+H)^+$ calculated for $C_{14}H_{10}ClN_2O^+$ is 257.0476 and observed is 257.0476.

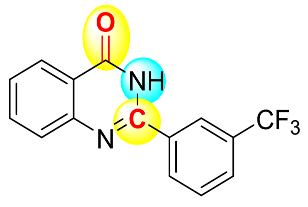
2-(3-fluorophenyl)quinazolin-4(3H)-one



Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-fluoro-3-iodobenzene (76.0 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3m** as white solid (30.3 mg); yield: 55%; ^{1}H (600 MHz, DMSO-d_6) δ (ppm) = 12.58 (brs, 1H), 8.16 - 8.14 (m, 1H), 8.04 (d, J = 7.9 Hz, 1H), 8.00 - 7.98 (m, 1H), 7.85 - 7.82 (m, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.61 - 7.57 (m, 1H), 7.54 - 7.52 (m, 1H), 7.44 - 7.41 (m, 1H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) = 162.92, 162.18, 161.31, 151.06, 148.46, 135.05, 135.00, 134.69, 130.78, 130.73, 127.60, 126.92, 125.90, 123.95, 123.93, 121.12, 118.33, 118.19, 114.63, 114.47; ^{19}F (DMSO-d_6, 471 MHz) δ *(ppm)* -112.24 (s).

ESI-MS$(M+H)^+$ calculated for $C_{14}H_{10}FN_2O^+$ is 241.0772 and observed is 241.0770.

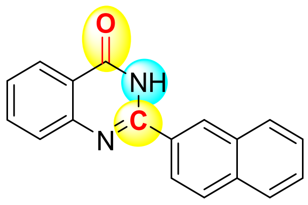
2-(3-(trifluoromethyl)phenyl)quinazolin-4(3H)-one



3n

Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-iodo-3-(trifluoromethyl)benzene (93.1 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3n** as a white solid (54.7 mg); yield: 83%; ^{1}H (500 MHz, DMSO-d_6) δ (ppm) = 12.72 (brs, 1H), 8.55 – 8.54 (m, 1H), 8.50 – 8.48 (m, 1H), 8.18 – 8.16 (m, 1H), 7.95 (dd, $J_{1\text{-}3}$ = 7.75 Hz, $J_{1\text{-}2}$ = 1.8 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.81 – 7.78 (m, 2H), 7.57 – 7.53 (m, 1H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) = 162.05, 150.94, 148.36, 134.58, 133.68, 131.68, 129.75, 129.52, 129.25, 127.71, 127.55, 126.90, 125.80, 125.00, 124.40, 122.83, 121.11; ^{19}F (DMSO-d_6, 471 MHz) δ *(ppm)* -61.12 (s). ESI-MS$(M+H)^+$ calculated for $C_{15}H_{10}F_3N_2O^+$ is 291.0740 and observed is 291.0744.

2-(naphthalen-1-yl)quinazolin-4(3H)-one

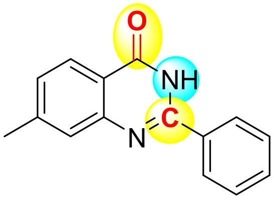


3o

Prepared as the general procedure described for **3a** starting from 2-iodoaniline (50 mg, 0.23 mmol) and 1-iodonaphthalene (87.0 mg, 0.34 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3o** as white solid (33.1 mg); yield: 53%; ^{1}H (600 MHz, DMSO-d_6) δ (ppm) = 12.66 (brs, 1H), 8.22 (dd, $J_{1\text{-}3}$ = 8.0 Hz, $J_{1\text{-}2}$ = 1.3 Hz, 1H), 8.17 – 8.16 (m, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.06 -m8.04 (m, 1H), 7.88 – 7.86 (m, 1H), 7.79 (d, $J_{1\text{-}3}$ = 7.0 Hz, $J_{1\text{-}2}$ = 1.0 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.66 – 7.64 (m, 1H), 7.61 – 7.57 (m, 3H); ^{13}C (150 MHz, DMSO-d_6) δ (ppm) = 161.90, 153.67, 148.72, 134.53, 133.13, 131.72, 130.37, 130.25, 128.33, 127.67, 127.46, 127.07, 126.80, 126.36, 125.85, 125.19, 125.07, 121.23.

ESI-MS$(M+H)^+$ calculated for $C_{18}H_{13}N_2O^+$ is 273.1022 and observed is 273.1020.

7-methyl-2-phenylquinazolin-4(3H)-one

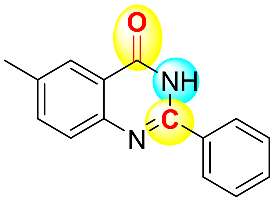


3p

Prepared as the general procedure described for **3a** starting from 2-iodo-5-methylaniline (50 mg, 0.22 mmol) and iodobenzene (65.7 mg,0.32 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3p** as white solid (30.9 mg); yield: 61%; ^{1}H (500 MHz, DMSO-d_6) δ (ppm) = 12.44 (brs, 1H), 8.18 - 8.16 (m, 2H), 8.04 (d, J = 8.04 Hz, 1H), 7.60 - 7.52 (m, 4H), 7.35 - 7.33 (m 1H), 2.47 (s, 3H); ^{13}C (125 MHz, DMSO-d_6) δ (ppm) = 162.10, 152.31, 148.86, 145.07, 132.78, 131.32, 128.59, 128.02, 127.69, 127.15, 125.70, 118.59, 21.35.

ESI-MS$(M+H)^+$ calculated for $C_{15}H_{13}N_2O^+$ is 237.1022 and observed is 237.1029.

6-methyl-2-phenylquinazolin-4(3H)-one

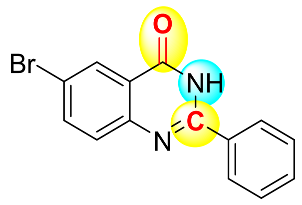


3q

Prepared as the general procedure described for **3a** starting from 2-iodo-4-methylaniline (50 mg, 0.22 mmol) and iodobenzene (65.7 mg,0.32 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3q** as white solid (24.2 mg); yield: 48%; ^{1}H (500 MHz, DMSO-d_6) δ (ppm) = 12.45 (brs, 1H), 8.18 - 8.15 (m, 2H), 7.96 - 7.95 (m, 1H), 7.67 - 7.63 (m, 2H), 7.60 - 7.52 (m, 3H), 2.46 (s, 3H); ^{13}C (125 MHz, DMSO-d_6) δ (ppm) = 162.14, 151.46, 146.74, 136.30, 135.87, 132.78, 131.22, 128.58, 127.63, 127.38, 125.23, 120.72, 20.83.

ESI-MS$(M+H)^+$ calculated for $C_{15}H_{13}N_2O^+$ is 237.1022 and observed is 273.1026.

6-bromo-2-phenylquinazolin-4(3H)-one

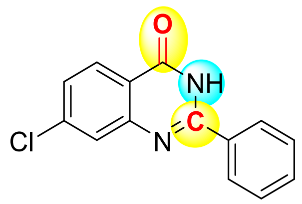


3r

Prepared as the general procedure described for **3a** starting from 4-bromo-2-iodoaniline (50 mg, 0.17 mmol) and iodobenzene (51.4 mg, 0.25 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3r** as white solid (21.4 mg); yield: 42%; ^{1}H (400 MHz, DMSO-d_6) δ (ppm) = 12.71 (brs, 1H), 8.23 (d, J = 2.32 Hz, 1H), 8.19 – 8.16 (m, 2H), 7.98 (dd, $J_{1\text{-}3}$ = 8.8 Hz, $J_{1\text{-}2}$ = 2.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.63 – 7.54 (m, 3H);^{13}C (100 MHz, DMSO-d_6) δ (ppm) = 161.72, 153.48, 148.16, 137.91, 132.90, 132.11, 130.34, 129.13, 128.45, 128.30, 123.00, 119.42.

ESI-MS$(M+H)^+$ calculated for $C_{14}H_{10}BrN_2O^+$ is 300.9971 and observed is 300.9973.

7-chloro-2-phenylquinazolin-4(3H)-one

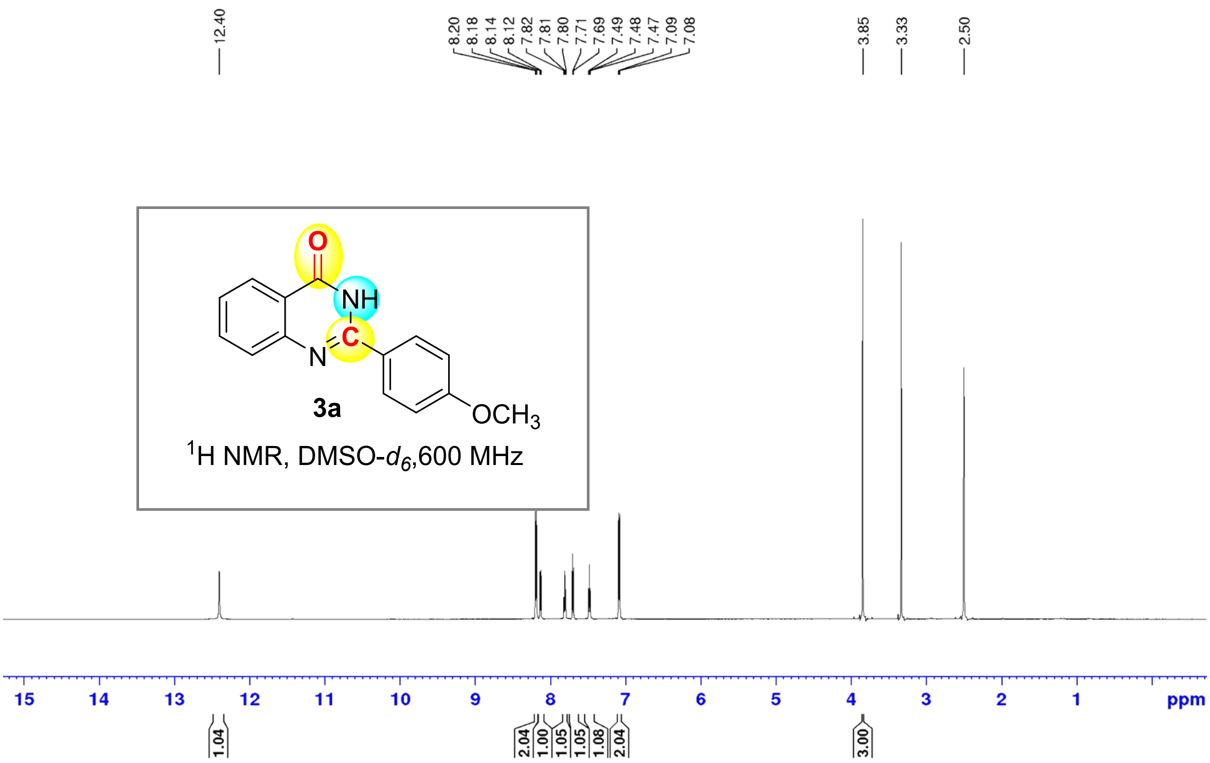


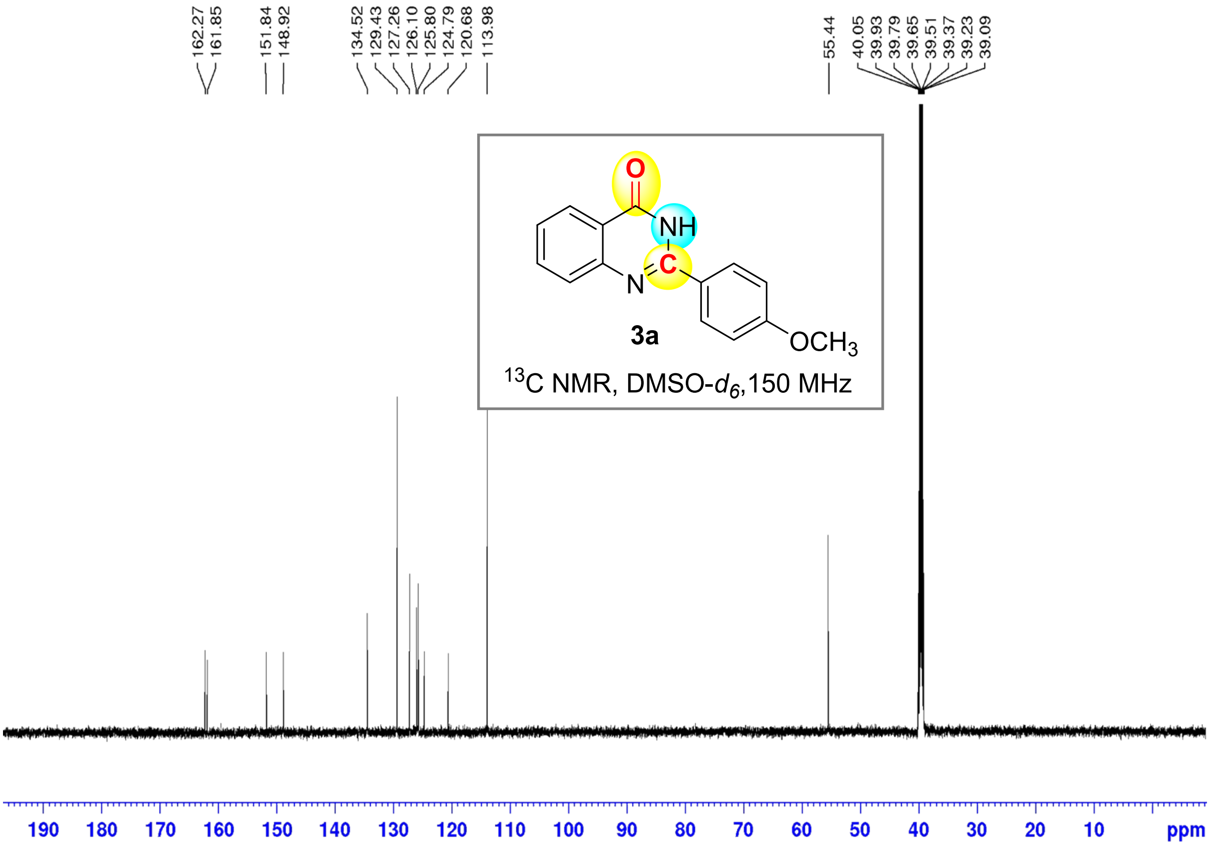
3s

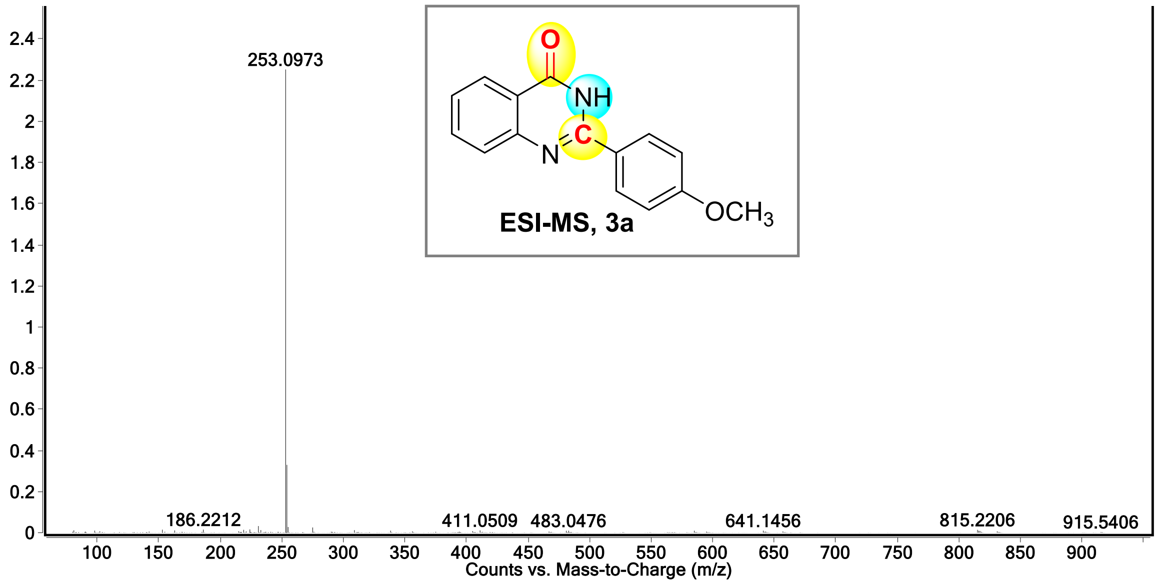
Prepared as the general procedure described for **3a** starting from 5-chloro-2-iodoaniline (50 mg, 0.20 mmol) and iodobenzene (60.4 mg, 0.30 mmol), gave after purification with silica gel column chromatography in hexane: ethyl acetate (85:15) **3s** as white solid (28.7 mg); yield: 57%; ^{1}H (500 MHz, DMSO-d_6) δ (ppm) = 12.66 (brs, 1H), 8.19 – 8.13 (m, 3H), 7.80 – 7.78 (m, 1H), 7.63 – 7.53 (m, 4H); ^{13}C (125 MHz, DMSO-d_6) δ (ppm) = 161.69, 153.81, 139.16, 132.39, 131.70, 128.63, 127.95, 127.91, 126.79, 126.54, 119.81.

ESI-MS$(M+H)^+$ calculated for $C_{14}H_{10}ClN_2O^+$ is 257.0476 and observed is 257.0471.

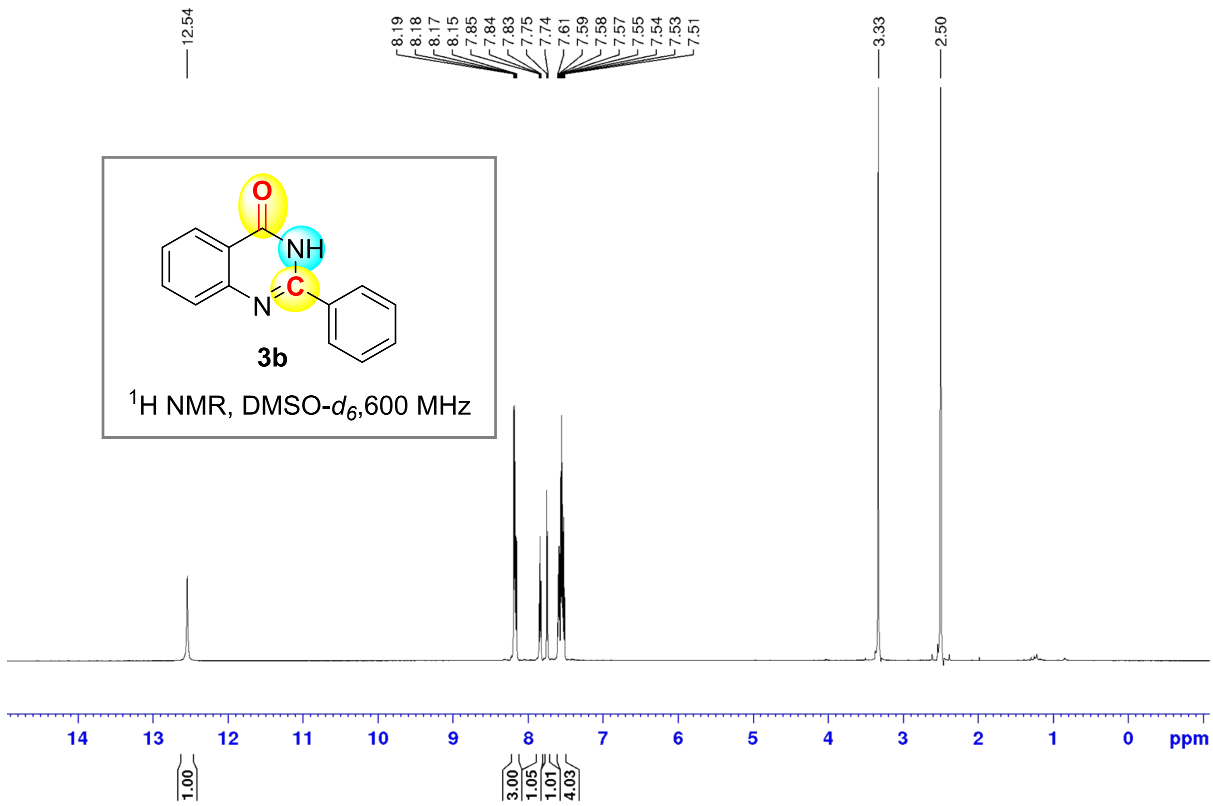
^{1}H, ^{13}C NMR and ESI-MS spectra



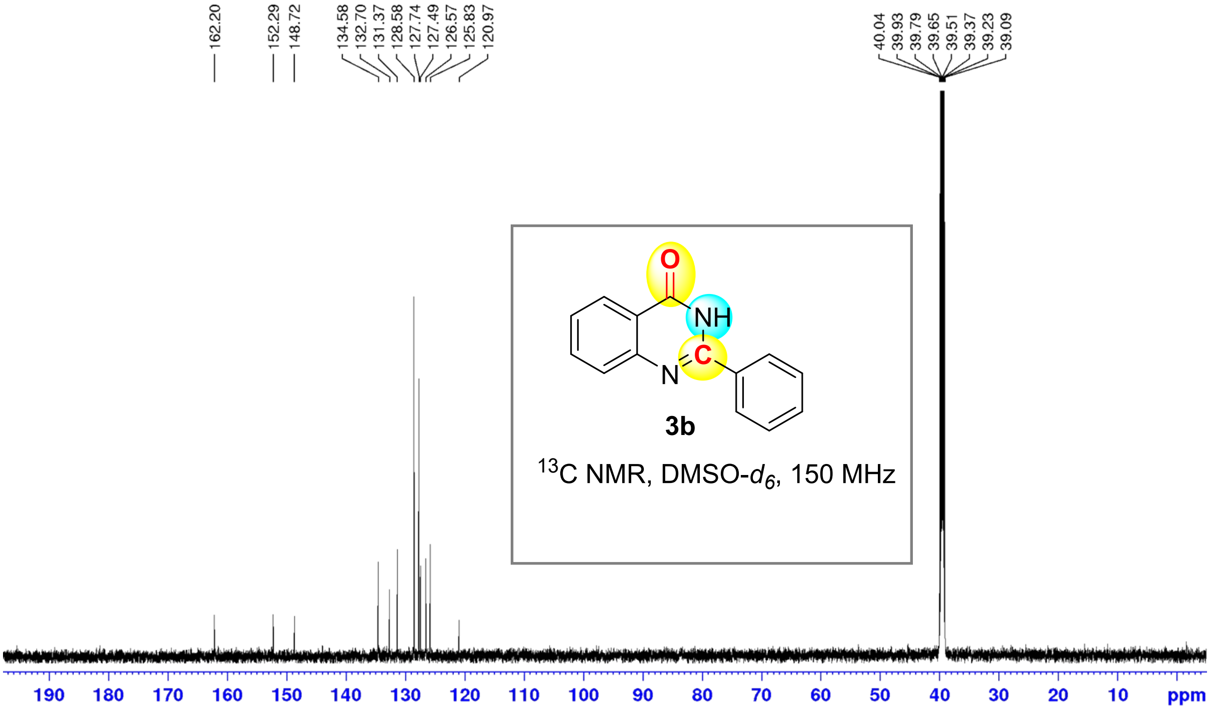




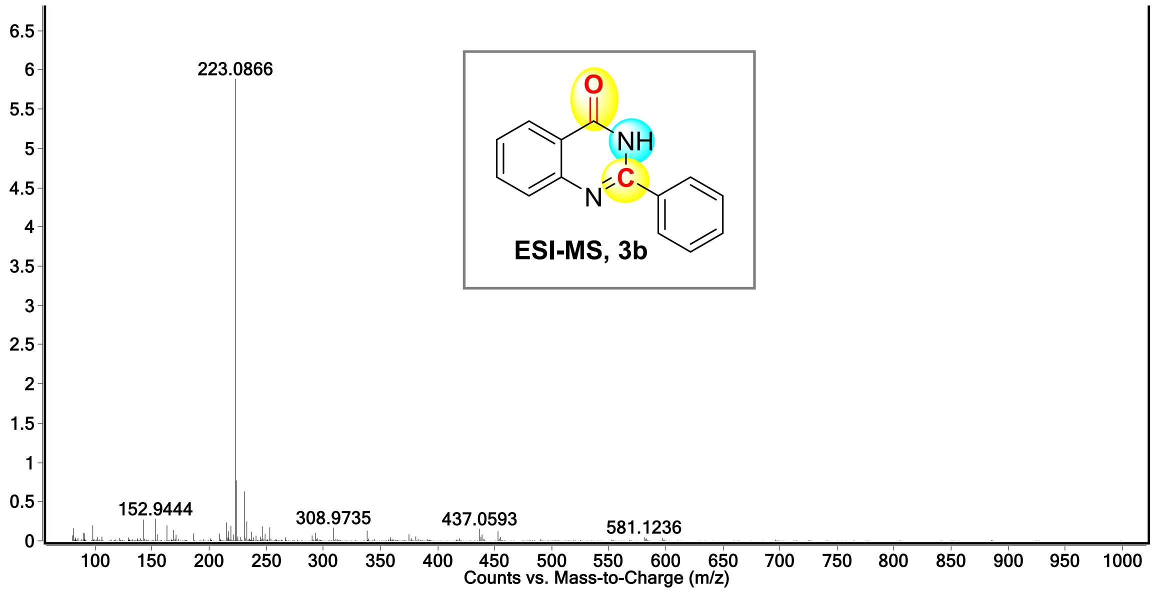
253.0973
186.2212
411.0509
483.0476
641.1456
815.2206
915.5406
Counts vs. Mass-to-Charge (m/z)
O
NH
C
N
OCH3
ESI-MS, 3a



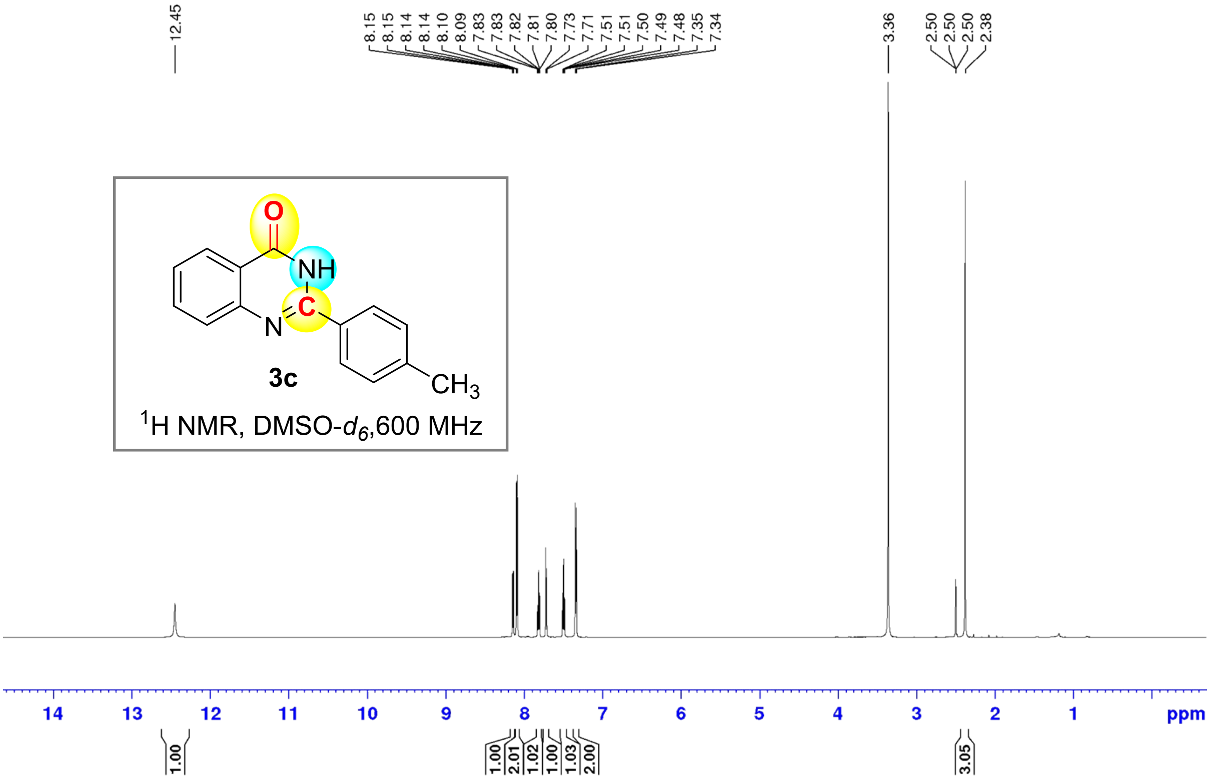
12.54
8.19 8.18 8.17 8.15 7.85 7.84 7.83 7.75 7.74 7.61 7.59 7.58 7.57 7.55 7.54 7.53 7.51
3.33
2.50
O
NH
C
N
3b
1H NMR, DMSO-d6,600 MHz
ppm
1.00
3.00
1.05
1.01
4.03

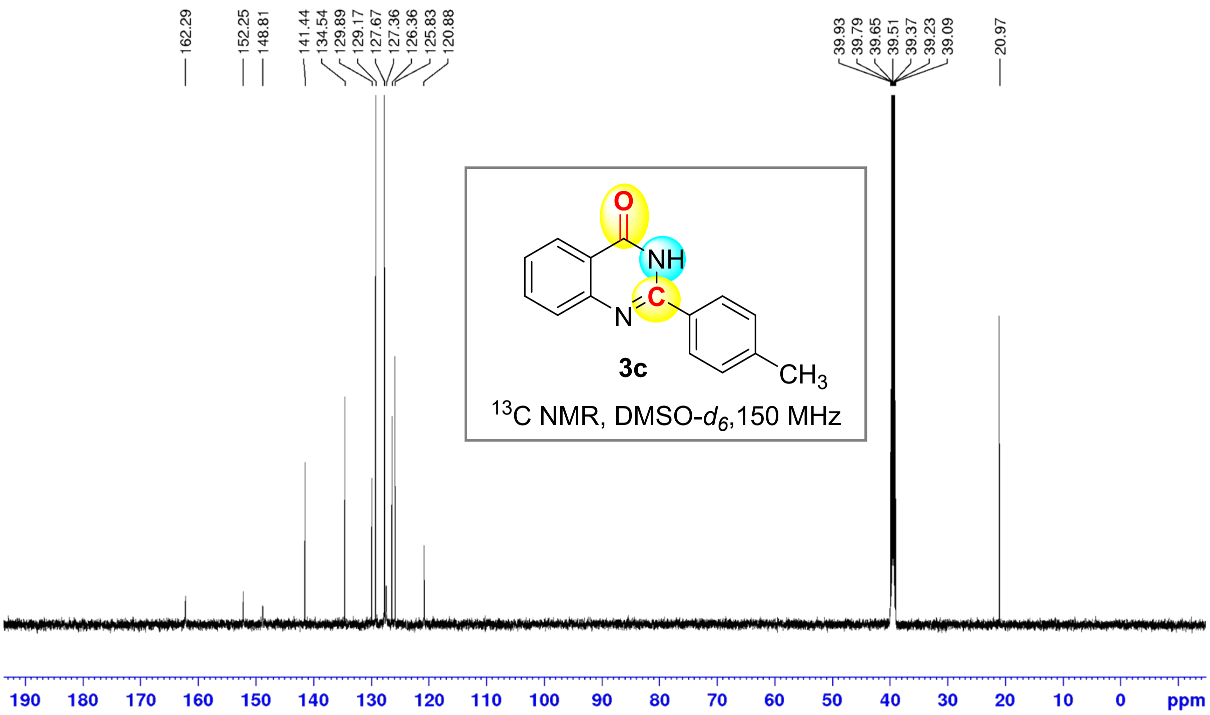


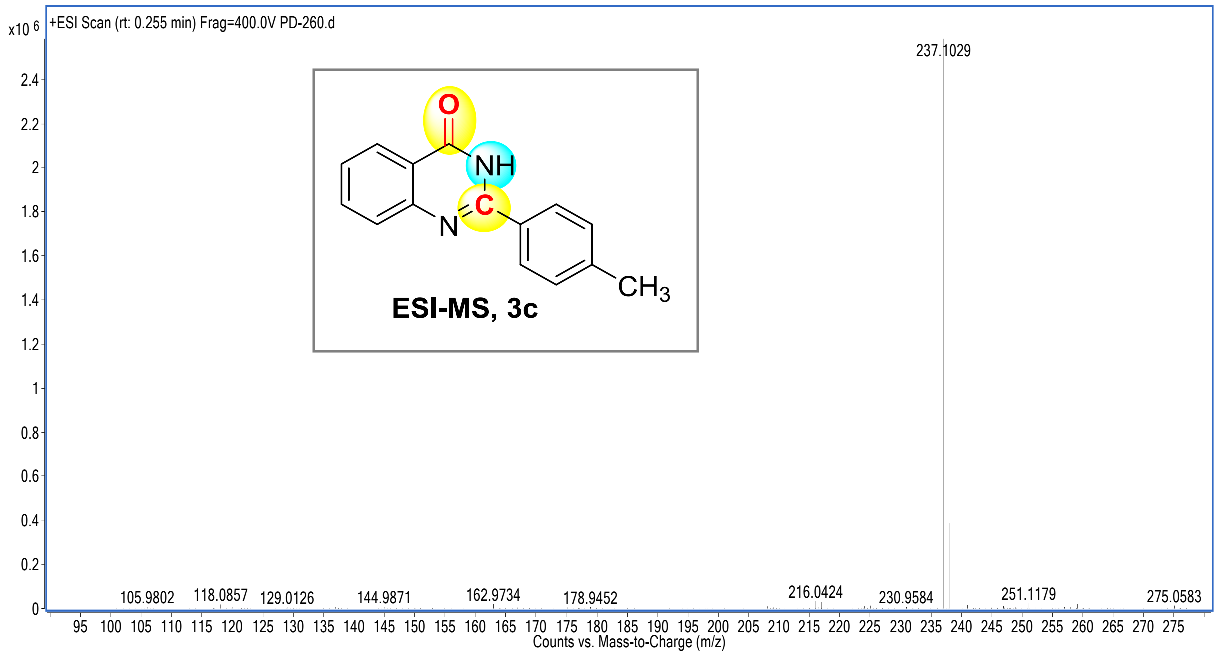
162.20
152.29
148.72
134.58
132.70
131.37
128.58
127.74
127.49
126.57
125.83
120.97
40.04
39.93
39.79
39.65
39.51
39.37
39.23
39.09
O
NH
N
C
3b
13C NMR, DMSO-d6, 150 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



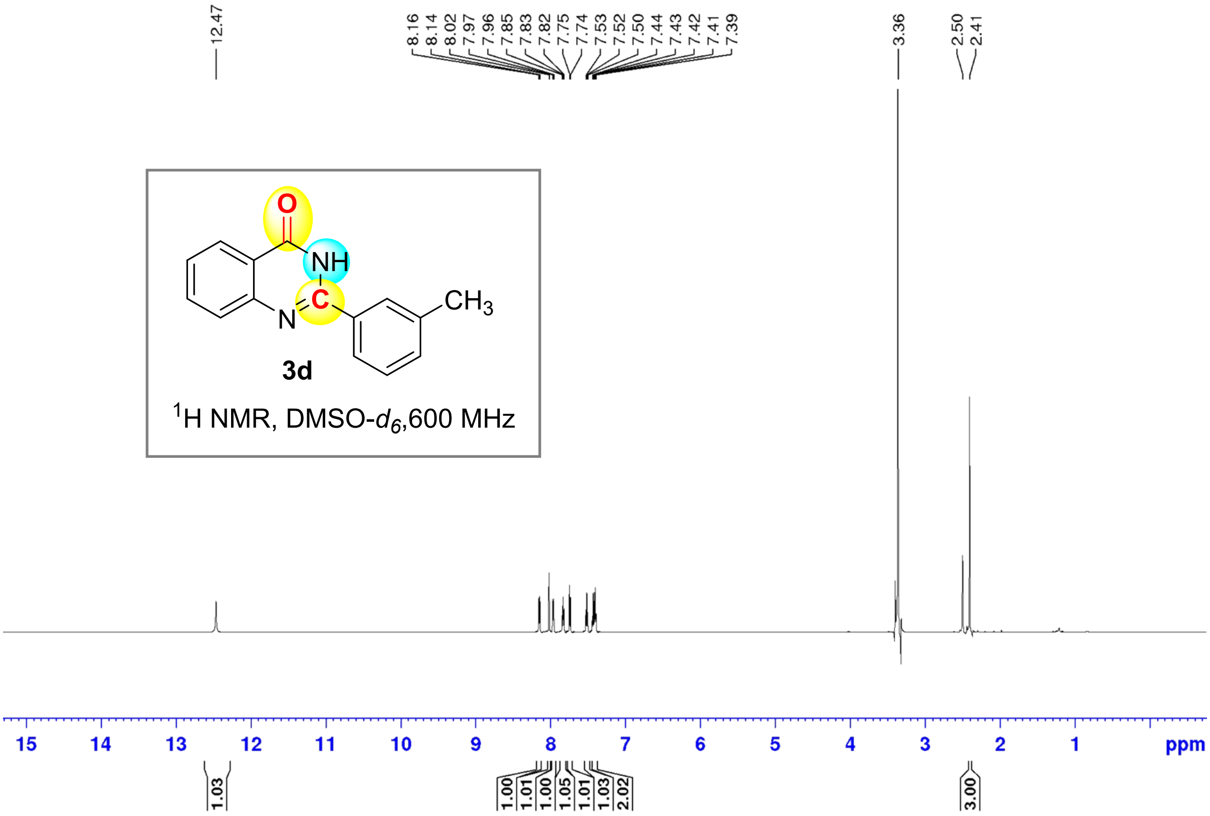
223.0866
152.9444
308.9735
437.0593
581.1236
O
NH
N
C
ESI-MS, 3b
6.5 6 5.5 5 4.5 4 3.5 3 2.5 2 1.5 1 0.5 0
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
Counts vs. Mass-to-Charge (m/z)


12.45
8.15 8.15 8.14 8.14 8.10 8.09 7.83 7.83 7.82 7.81 7.80 7.73 7.71 7.51 7.51 7.50 7.49 7.48 7.35 7.34
3.36
2.50 2.50 2.50 2.38
O
NH
C
N
CH3
3c
1H NMR, DMSO-d6,600 MHz
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.00 2.01 1.02 1.00 1.03 2.00
3.05

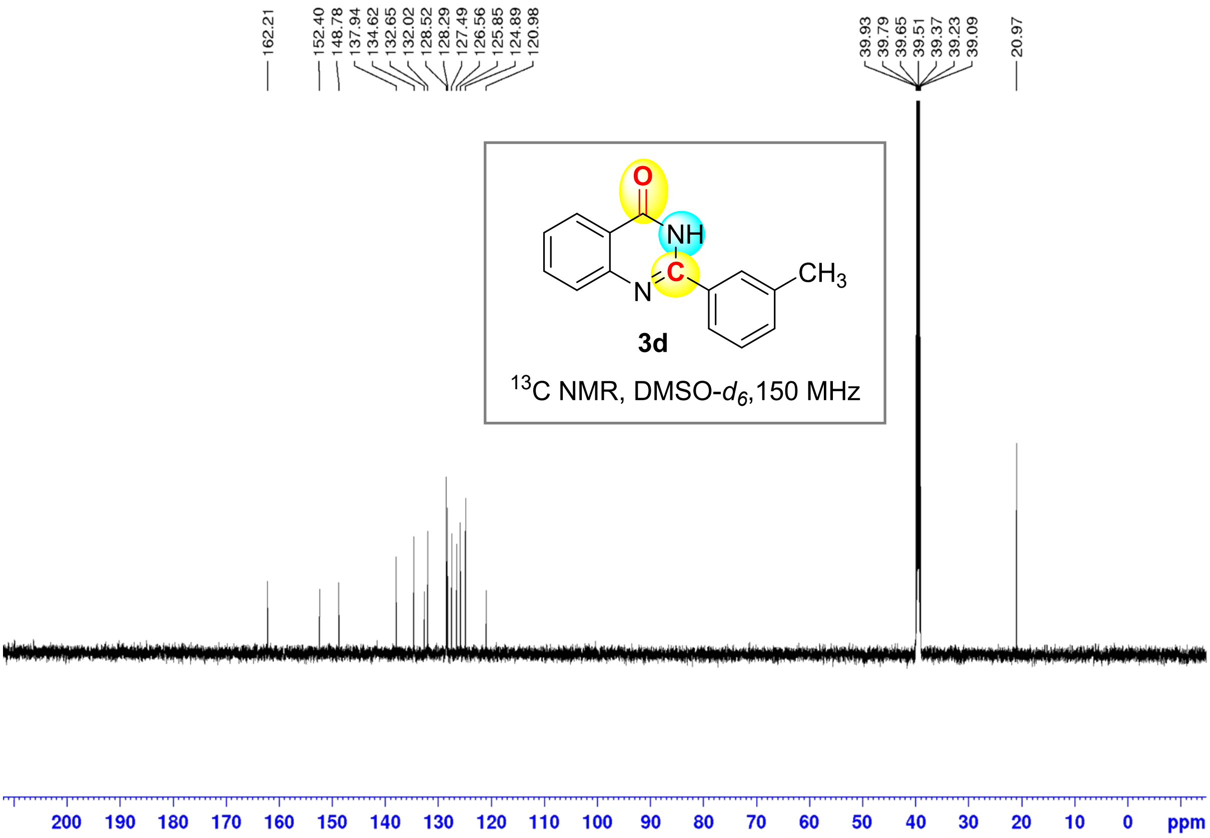

162.29
152.25 148.81
141.44 134.54 129.89 129.17 127.67 127.36 126.36 125.83 120.88
39.93 39.79 39.65 39.51 39.37 39.23 39.09
20.97
O
NH
C
N
CH3
3c
13C NMR, DMSO-d6,150 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

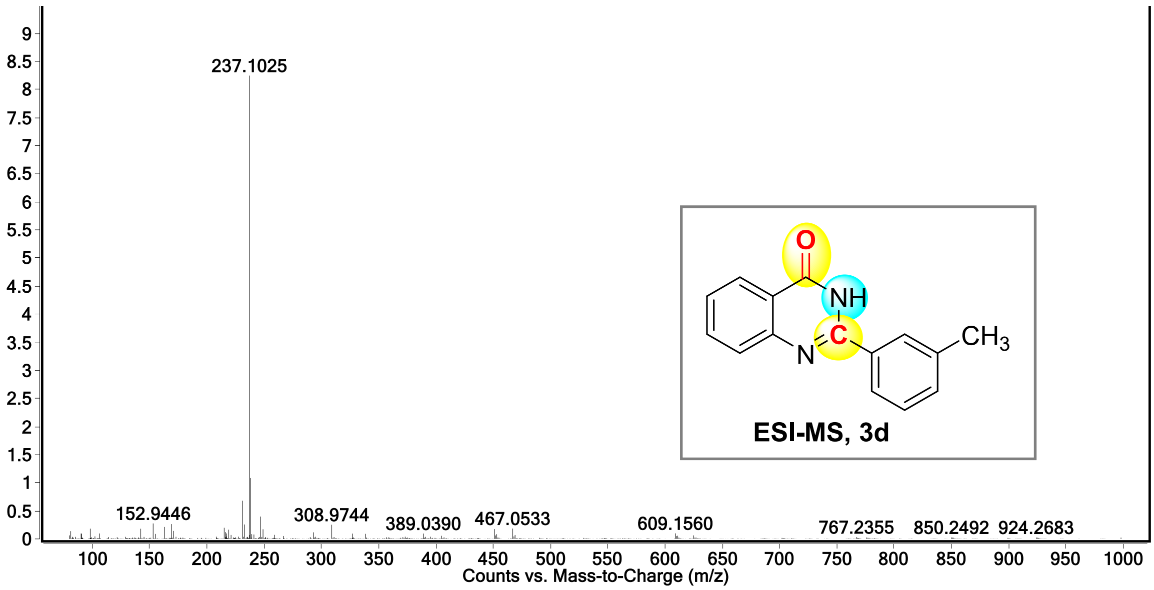


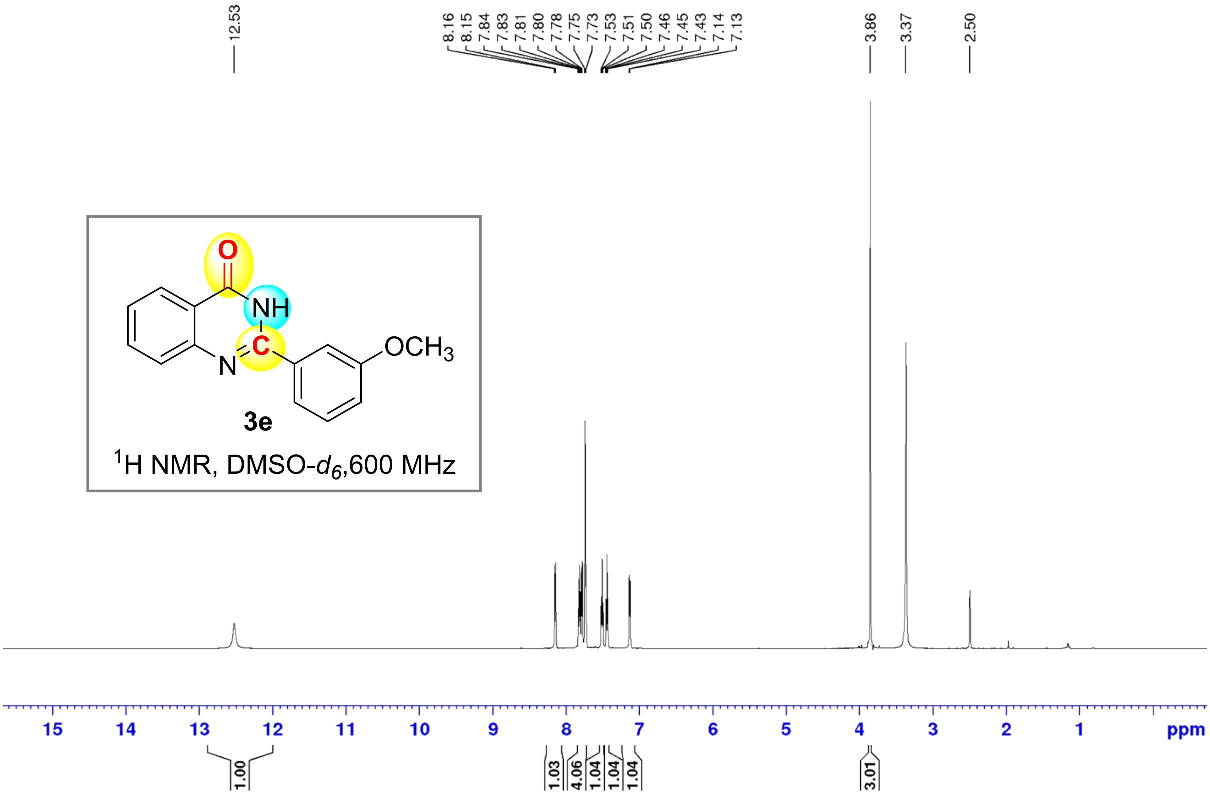
x10 6
+ESI Scan (rt: 0.255 min) Frag=400.0V PD-260.d
237.1029
105.9802
118.0857
129.0126
144.9871
162.9734
178.9452
216.0424
230.9584
251.1179
275.0583
Counts vs. Mass-to-Charge (m/z)
ESI-MS, 3c



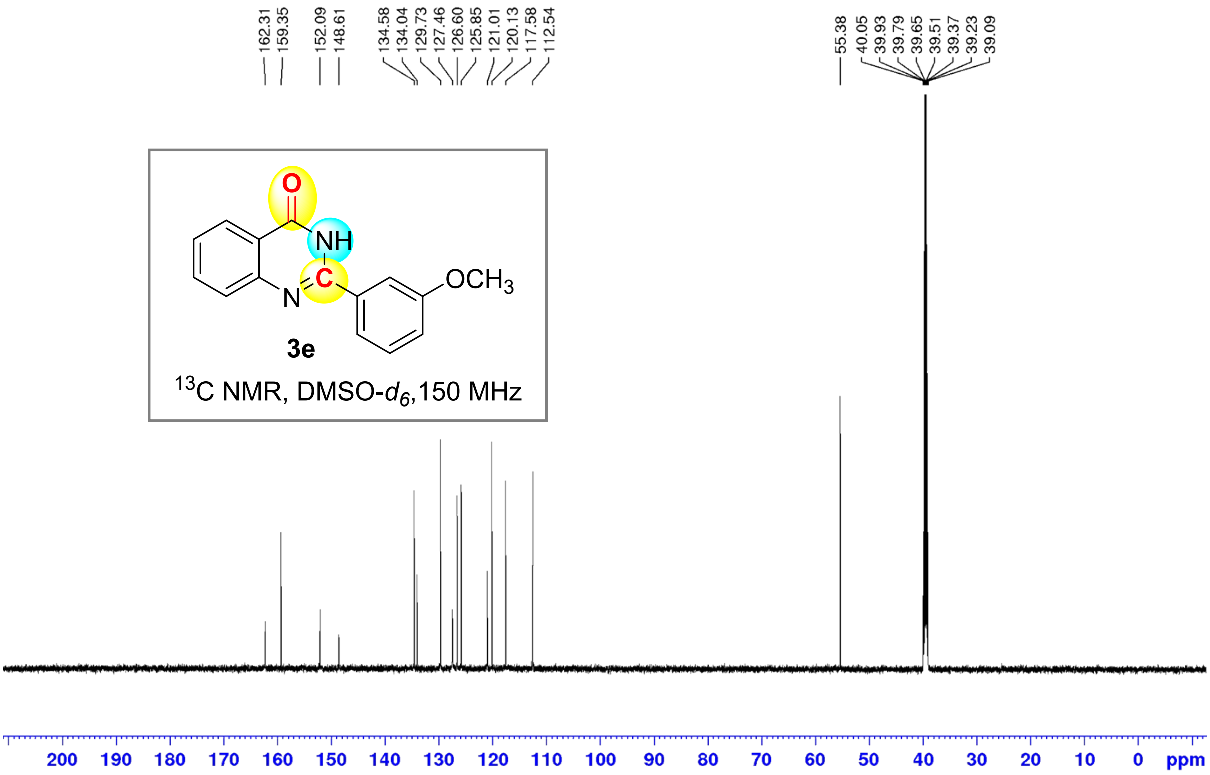
12.47
8.16 8.14 8.02 7.97 7.96 7.85 7.83 7.82 7.75 7.74 7.53 7.52 7.50 7.44 7.43 7.42 7.41 7.39
3.36
2.50 2.41
3d
1H NMR, DMSO-d6,600 MHz
ppm
1.03
1.00 1.01 1.00 1.05 1.01 1.03 2.02
3.00


162.21
152.40
148.78
137.94
134.62
132.65
132.02
128.52
128.29
127.49
126.56
125.85
124.89
120.98
39.93
39.79
39.65
39.51
39.37
39.23
39.09
20.97
O
NH
C
N
CH3
3d
13C NMR, DMSO-d6,150 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

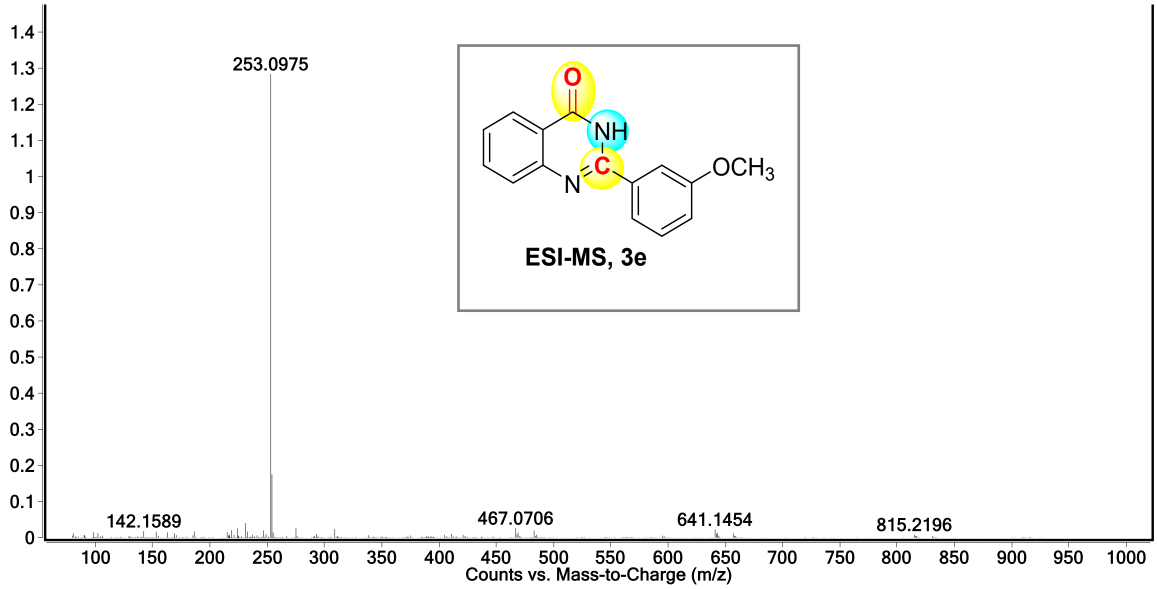

9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
237.1025
152.9446
308.9744
389.0390
467.0533
609.1560
767.2355
850.2492
924.2683
O
NH
C
N
CH3
ESI-MS, 3d
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
Counts vs. Mass-to-Charge (m/z)

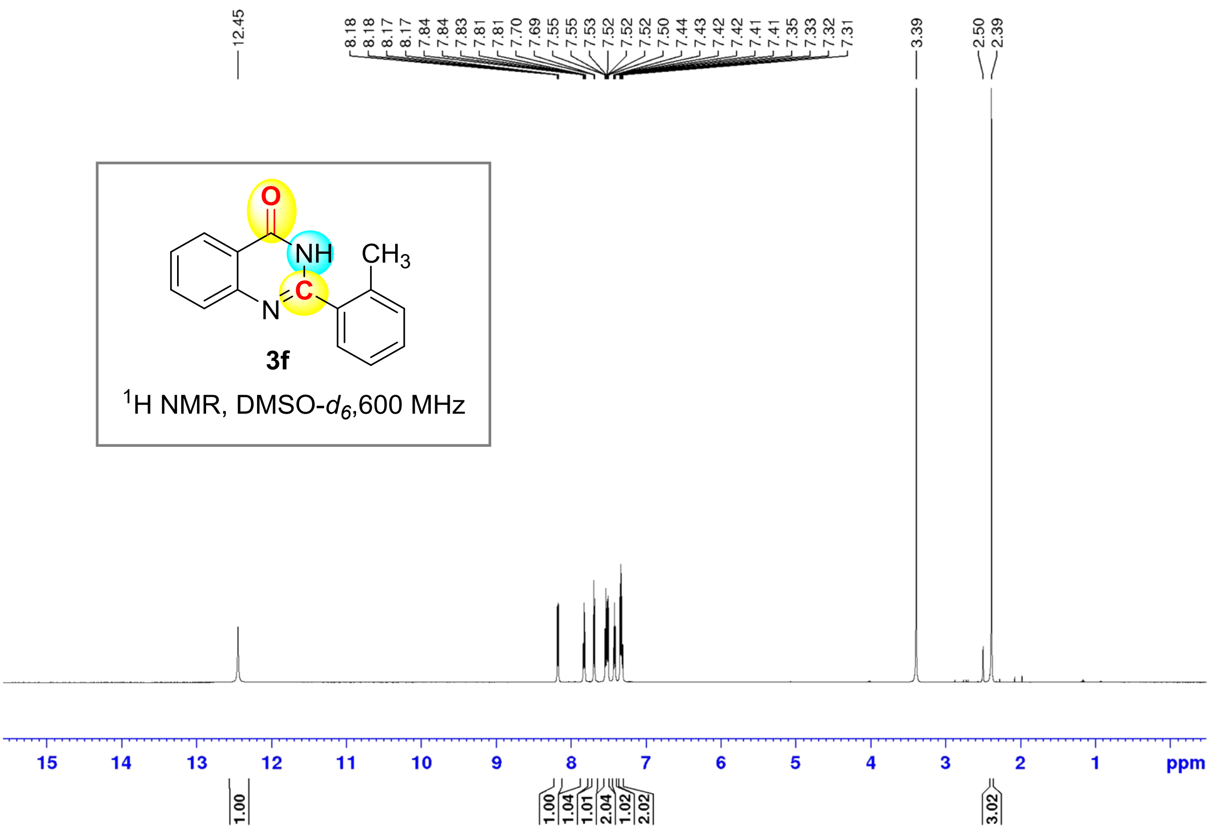


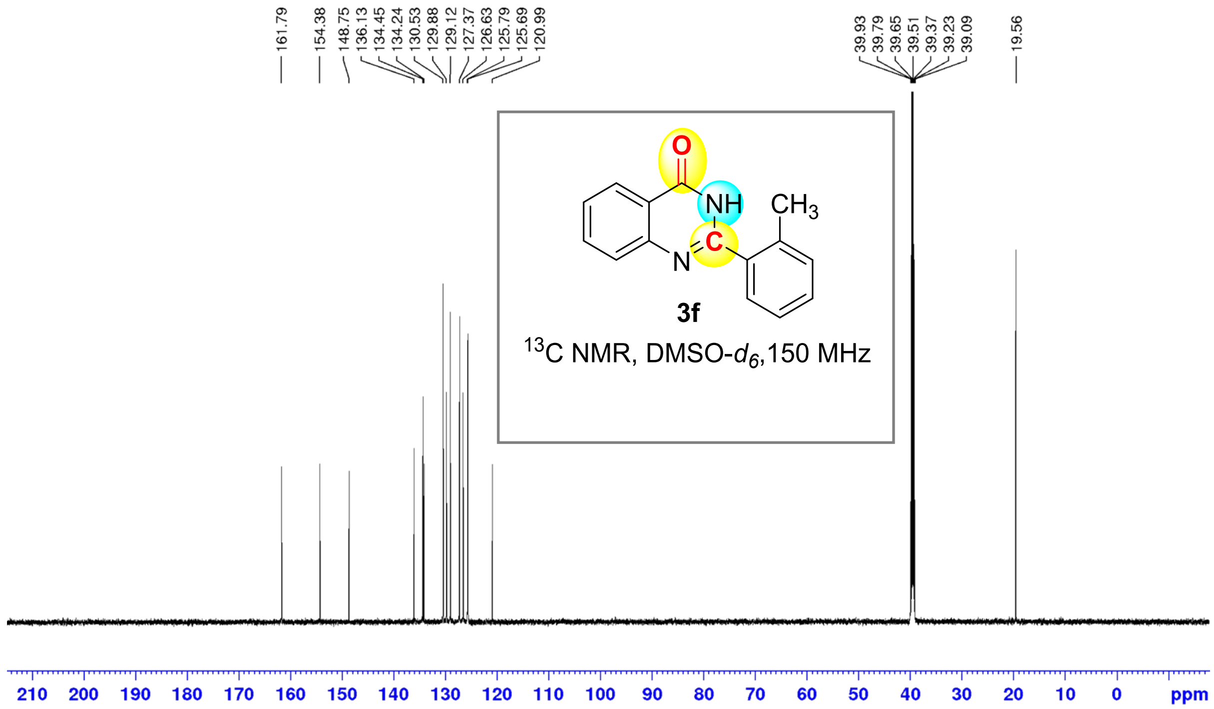
12.53
8.16
8.15
7.84
7.83
7.81
7.80
7.78
7.75
7.73
7.53
7.51
7.50
7.46
7.45
7.43
7.14
7.13
3.86
3.37
2.50
O
NH
C
N
OCH3
3e
1H NMR, DMSO-d6,600 MHz
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
4.06
1.04
1.04
1.04
3.01

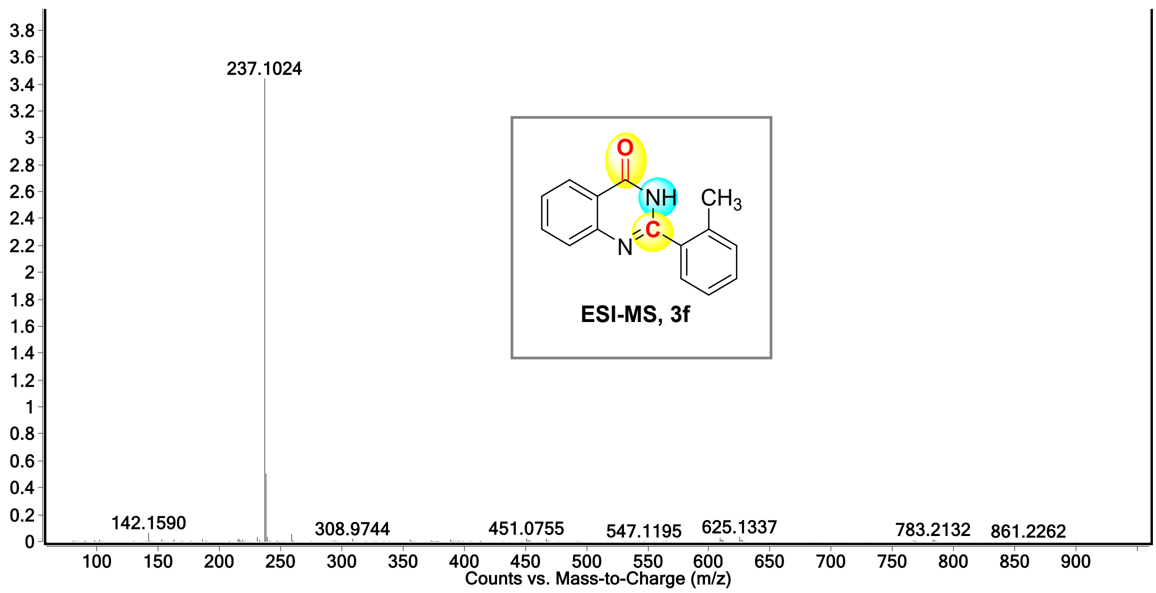


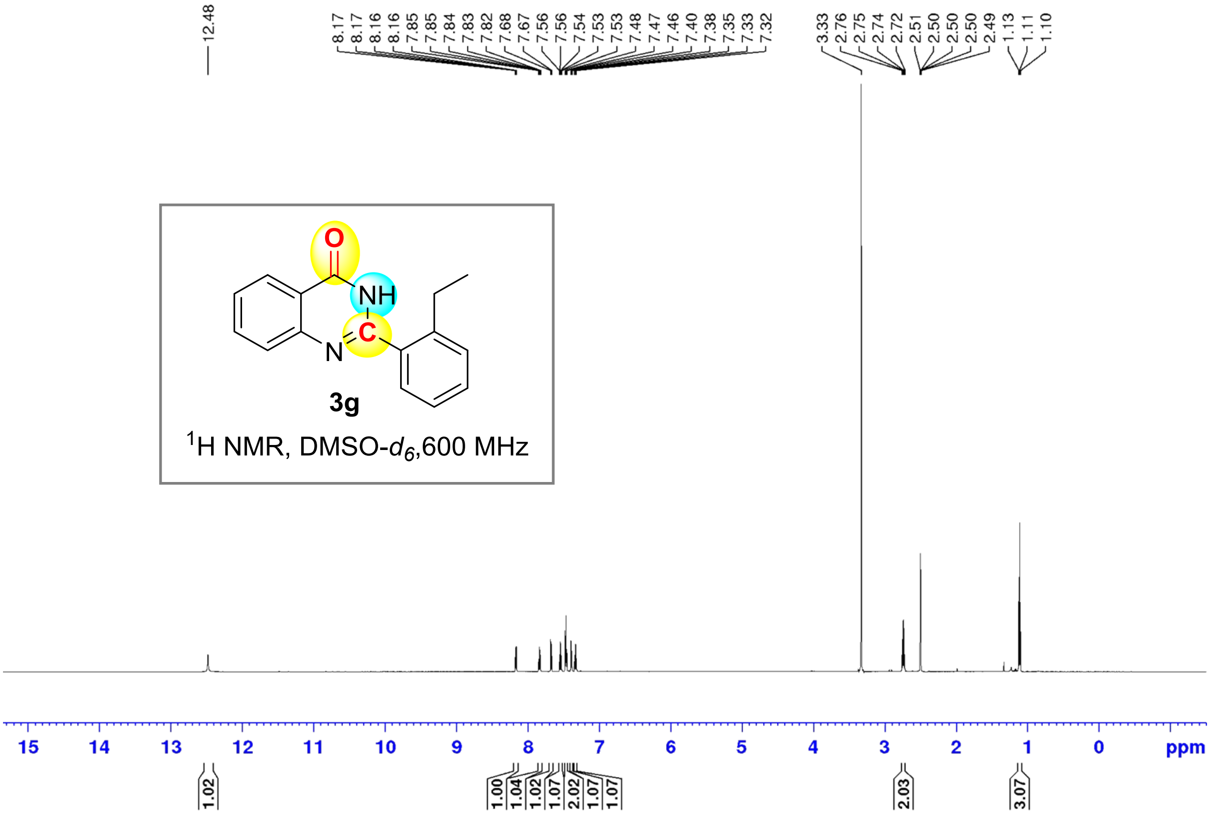
162.31
159.35
152.09
148.61
134.58
134.04
129.73
127.46
126.60
125.85
121.01
120.13
117.58
112.54
55.38
40.05
39.93
39.79
39.65
39.51
39.37
39.23
39.09
O
NH
C
N
OCH3
3e
13C NMR, DMSO-d6,150 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


253.0975
142.1589
467.0706
641.1454
815.2196
Counts vs. Mass-to-Charge (m/z)
O
NH
C
N
OCH3
ESI-MS, 3e

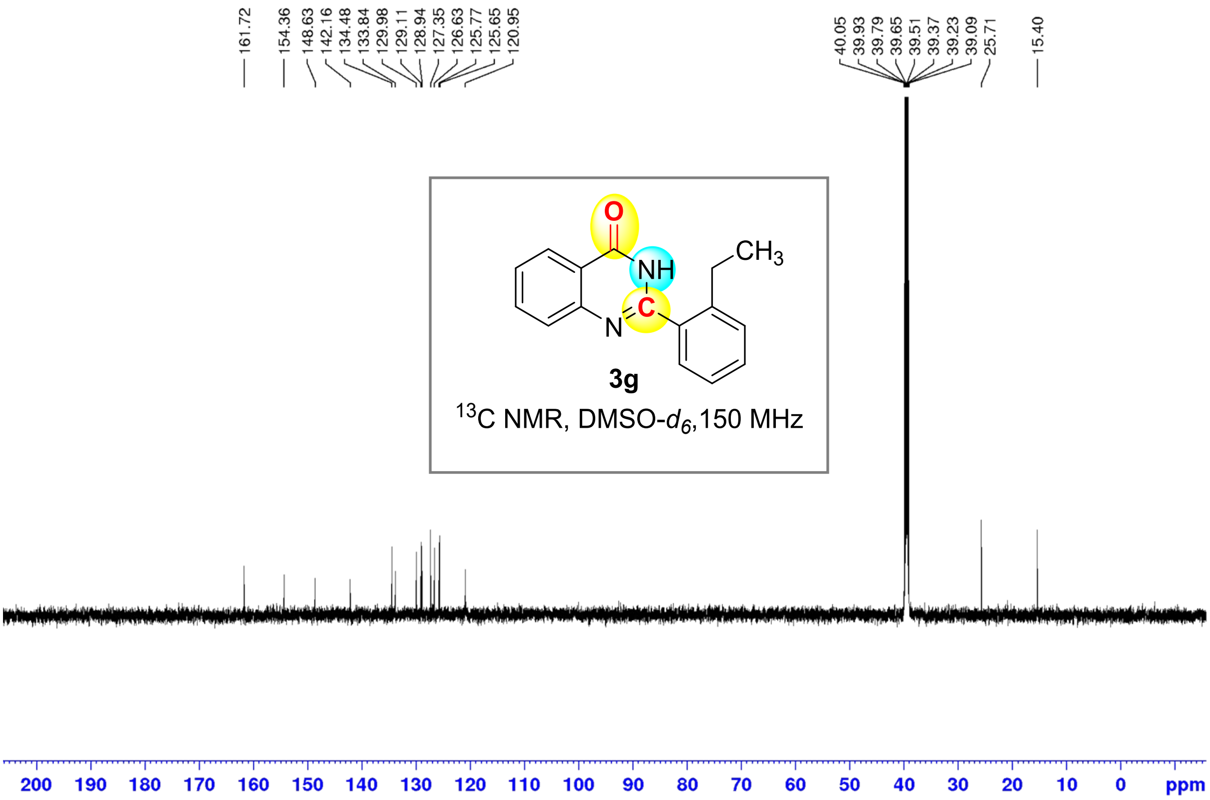

12.45
8.18
8.18
8.17
8.17
7.84
7.84
7.83
7.81
7.81
7.70
7.69
7.55
7.55
7.53
7.52
7.52
7.52
7.50
7.44
7.43
7.42
7.42
7.41
7.41
7.35
7.33
7.32
7.31
3.39
2.50
2.39
O
NH
CH3
C
N
3f
1H NMR, DMSO-d6,600 MHz
ppm
1.00
1.00
1.04
1.01
2.04
1.02
2.02
3.02


161.79
154.38
148.75
136.13
134.45
134.24
130.53
129.88
129.12
127.37
126.63
125.79
125.69
120.99
39.93
39.79
39.65
39.51
39.37
39.23
39.09
19.56
O
NH
CH3
C
N
3f
13C NMR, DMSO-d6,150 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

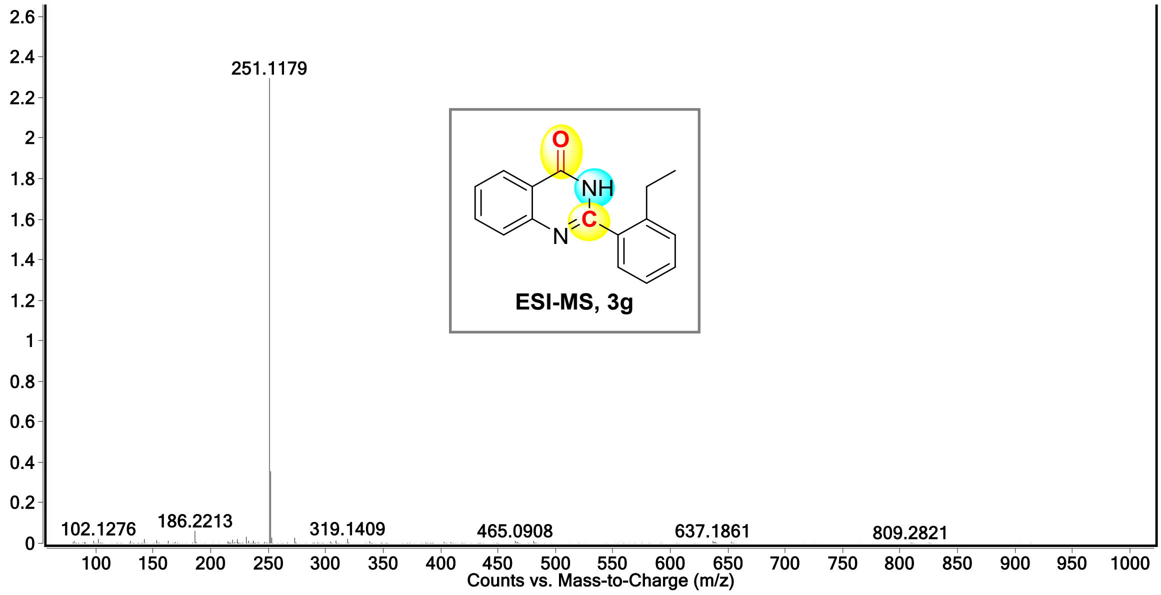

3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
237.1024
142.1590
308.9744
451.0755
547.1195
625.1337
783.2132
861.2262
O
NH
CH3
C
N
ESI-MS, 3f
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900
Counts vs. Mass-to-Charge (m/z)



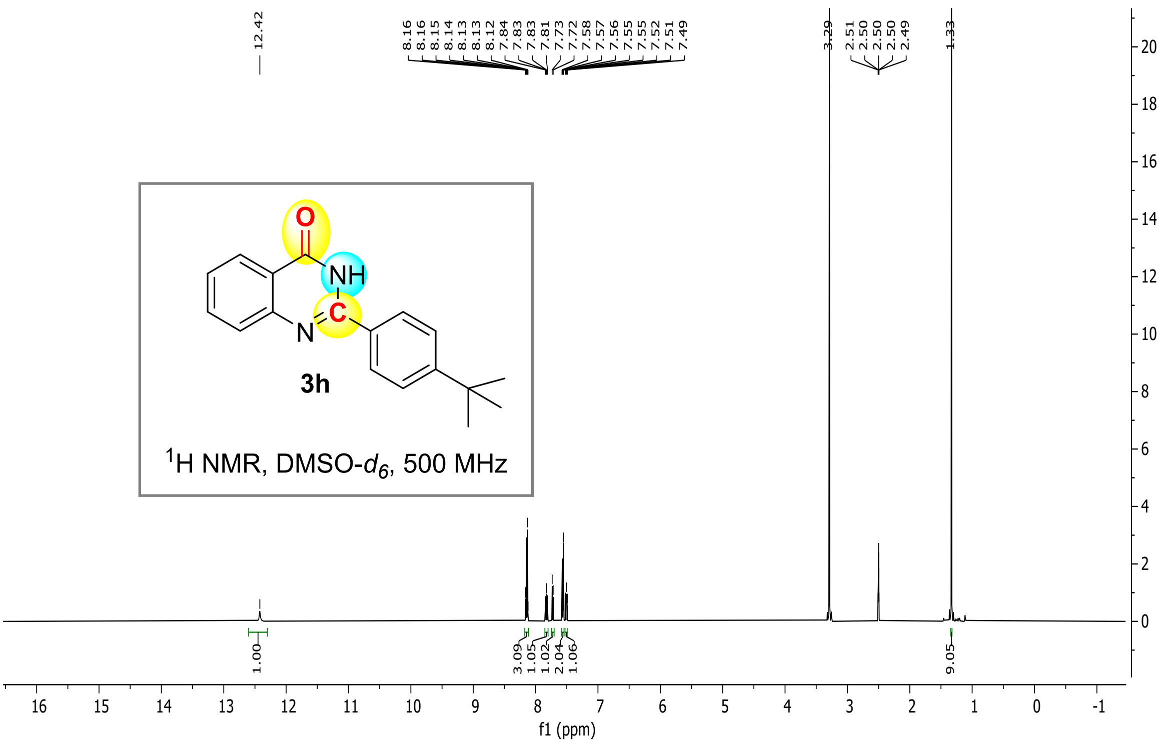
12.48
8.17
8.17
8.16
8.16
7.85
7.85
7.84
7.83
7.82
7.68
7.67
7.56
7.56
7.54
7.53
7.53
7.48
7.47
7.46
7.40
7.38
7.35
7.33
7.32
3.33
2.76
2.75
2.74
2.72
2.51
2.50
2.50
2.50
2.49
1.13
1.11
1.10
O
NH
C
N
3g
¹H NMR, DMSO-d6,600 MHz
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.02
1.00
1.04
1.02
1.07
2.02
1.07
1.07
2.03
3.07



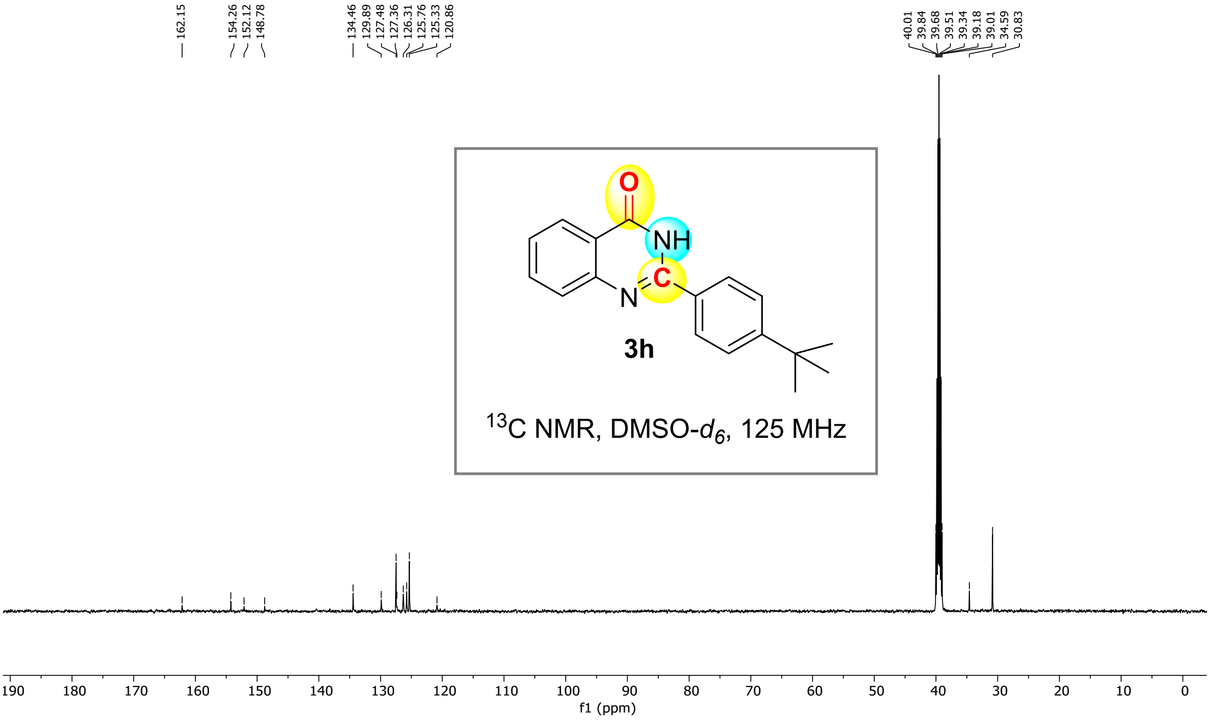
161.72
154.36
148.63
142.16
134.48
133.84
129.98
129.11
128.94
127.35
126.63
125.77
125.65
120.95
40.05
39.93
39.79
39.65
39.51
39.37
39.23
39.09
25.71
15.40
O
NH
CH3
C
N
3g
¹³C NMR, DMSO-d6,150 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



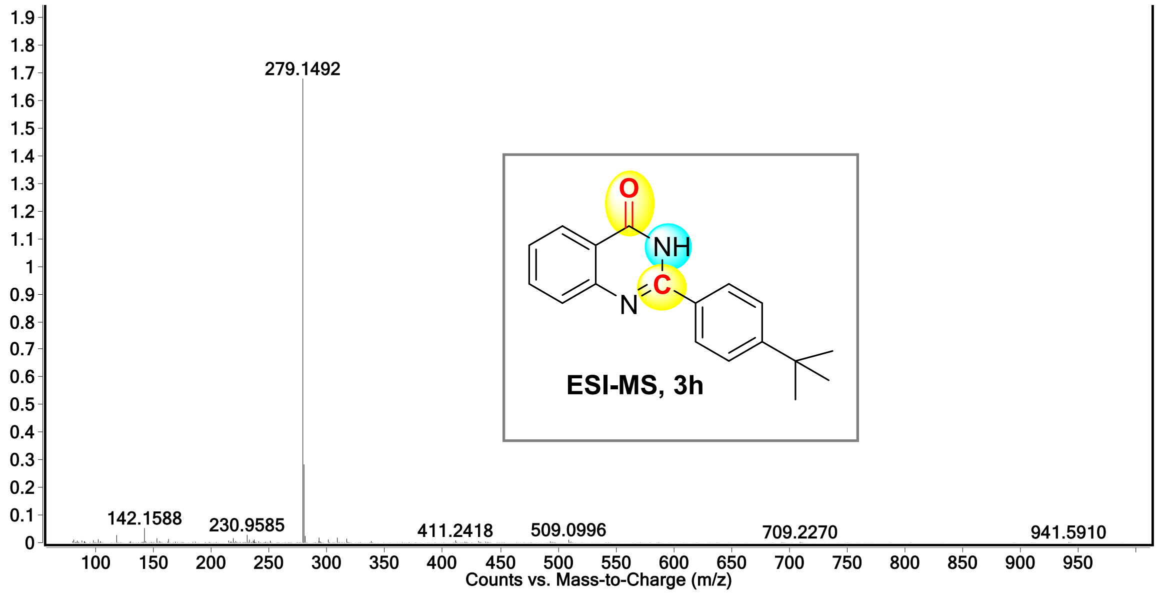
251.1179
102.1276
186.2213
319.1409
465.0908
637.1861
809.2821
Counts vs. Mass-to-Charge (m/z)
O
NH
C
N
ESI-MS, 3g



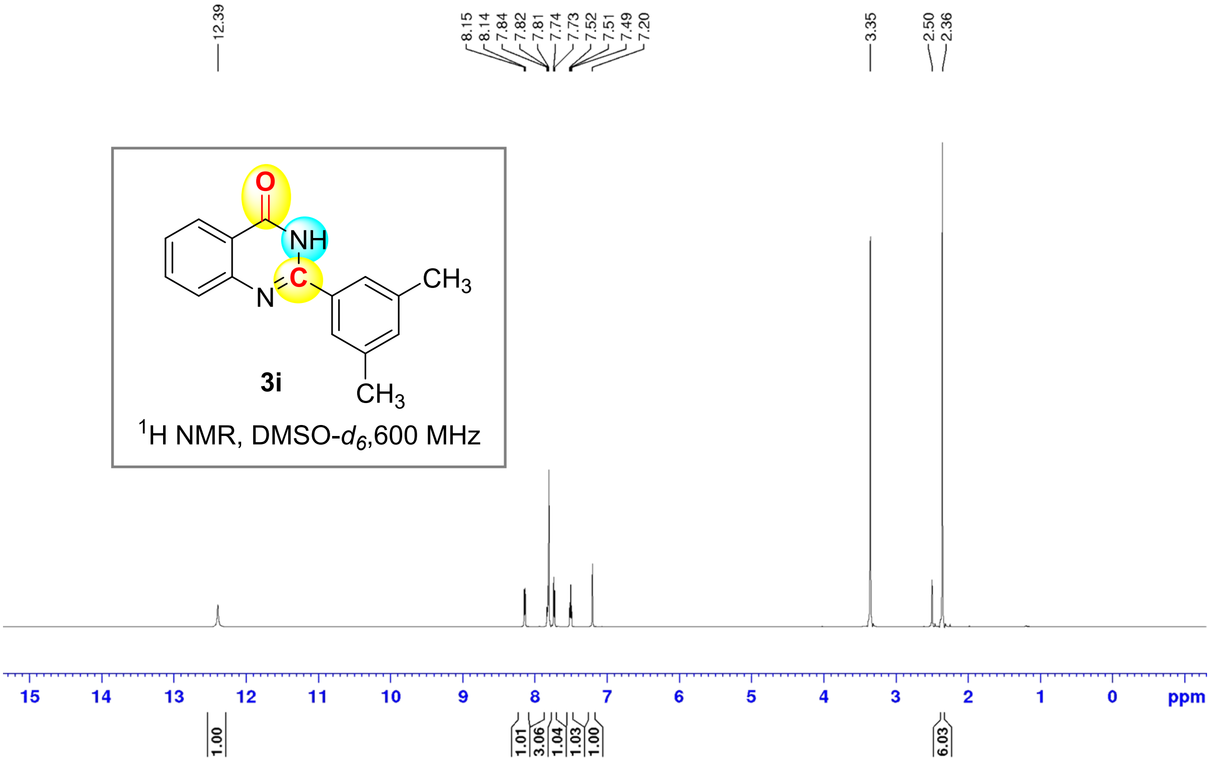
12.42
8.16
8.16
8.15
8.14
8.13
8.13
8.12
7.84
7.83
7.83
7.81
7.73
7.72
7.58
7.57
7.56
7.55
7.55
7.52
7.51
7.49
3.29
2.51
2.50
2.50
2.50
2.49
1.33
O
NH
C
N
3h
^{1}H NMR, DMSO-d_6, 500 MHz
1.00
3.09
1.05
1.02
2.04
1.06
9.05
f1 (ppm)

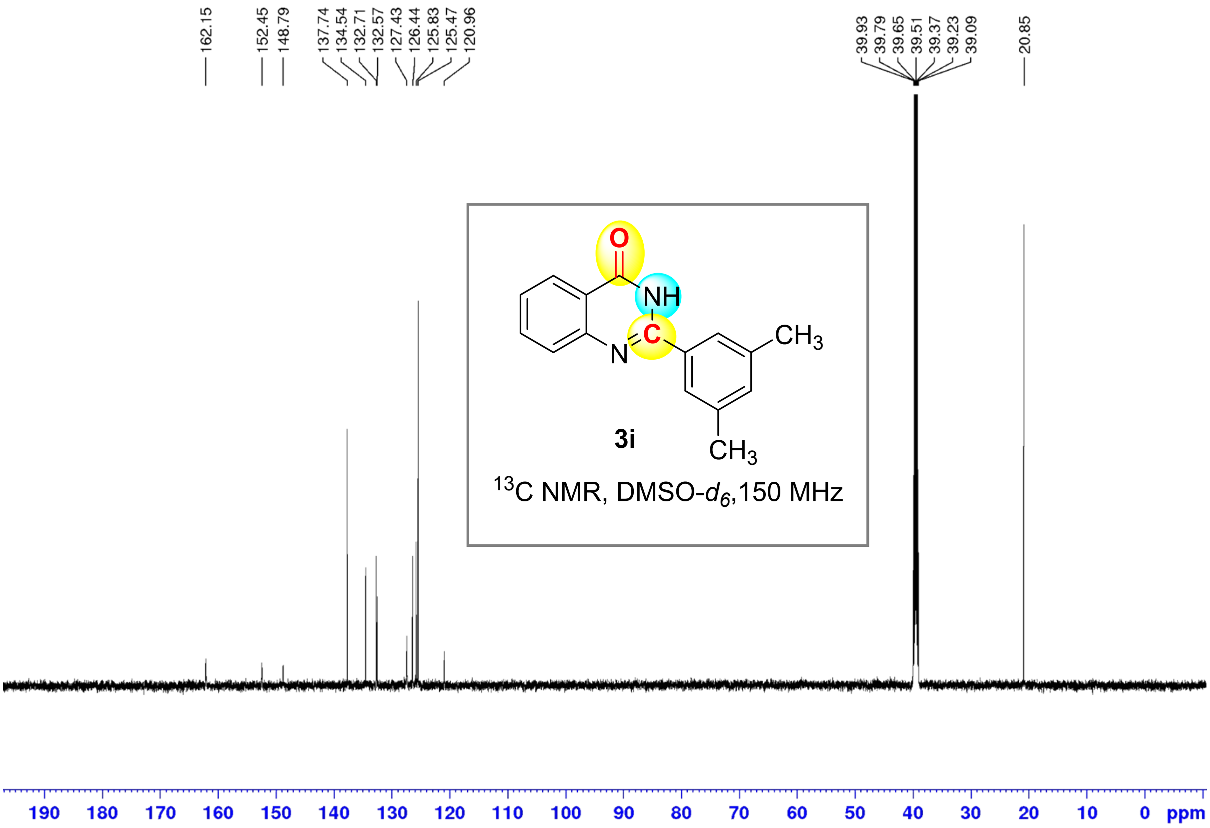


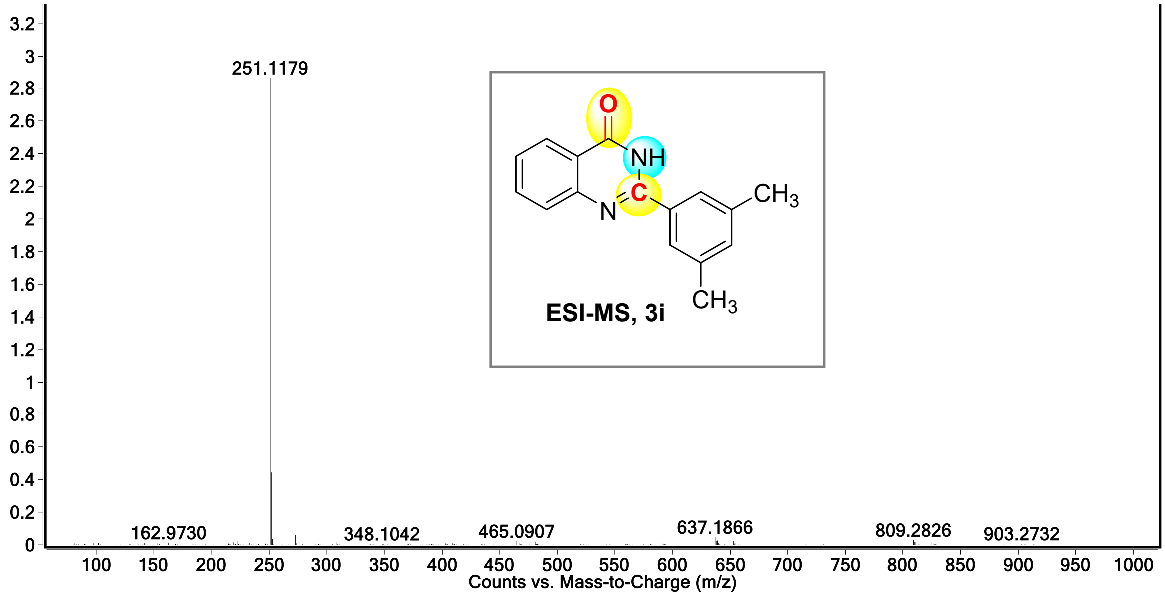
162.15
154.26
152.12
148.78
134.46
129.89
127.48
127.36
126.31
125.76
125.33
120.86
40.01
39.84
39.68
39.51
39.34
39.18
39.01
34.59
30.83
O
NH
C
N
3h
^{13}C NMR, DMSO-d_6, 125 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

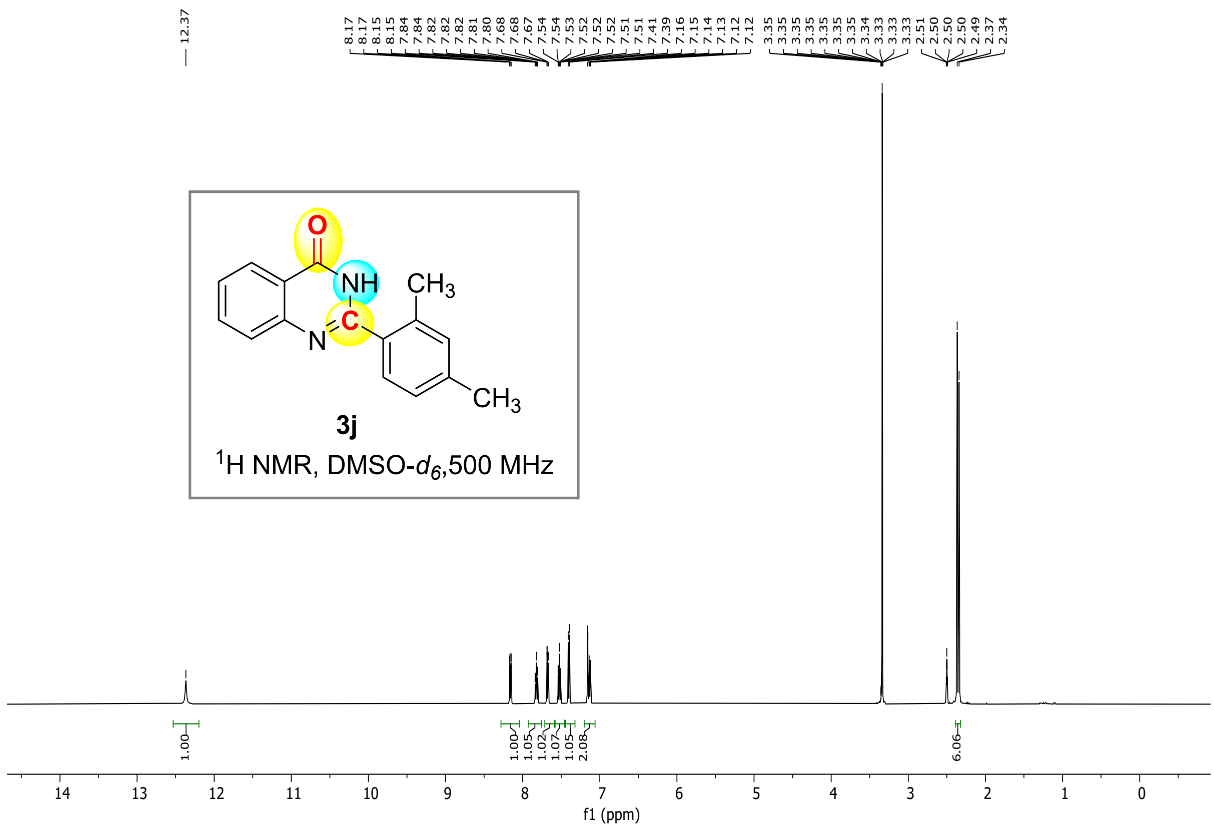


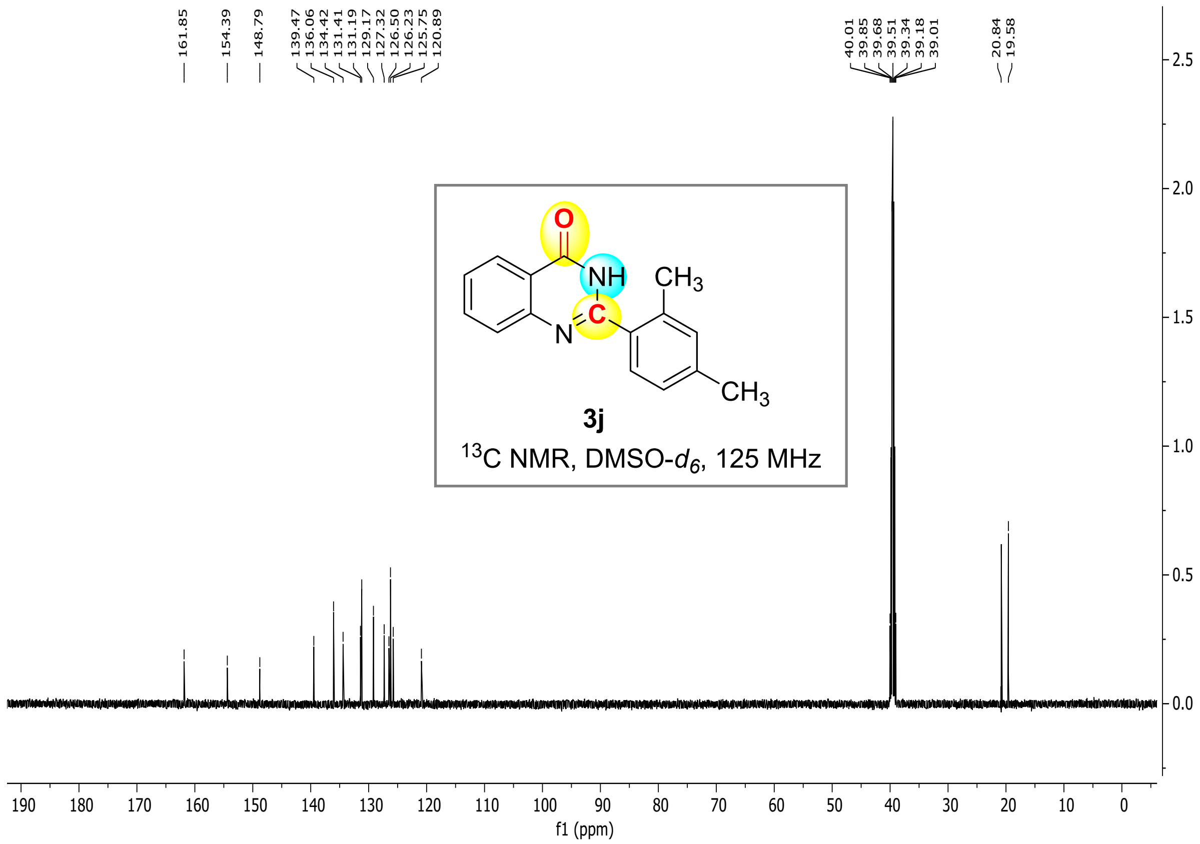
1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
279.1492
142.1588
230.9585
411.2418
509.0996
709.2270
941.5910
O
NH
C
N
ESI-MS, 3h
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950
Counts vs. Mass-to-Charge (m/z)


12.39
8.15
8.14
7.84
7.82
7.81
7.74
7.73
7.52
7.51
7.49
7.20
3.35
2.50
2.36
O
NH
C
N
CH3
CH3
3i
1H NMR, DMSO-d6,600 MHz
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
3.06
1.04
1.03
1.00
6.03

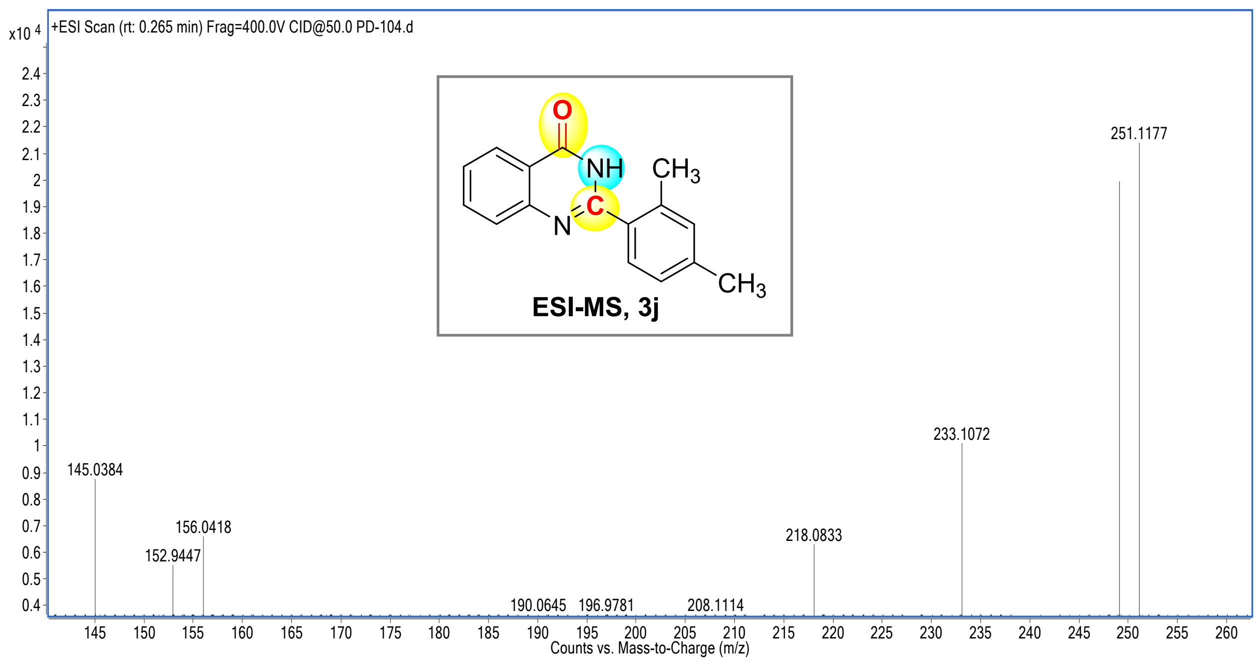

162.15
152.45
148.79
137.74
134.54
132.71
132.57
127.43
126.44
125.83
125.47
120.96
39.93
39.79
39.65
39.51
39.37
39.23
39.09
20.85
O
NH
C
N
CH3
CH3
3i
13C NMR, DMSO-d6,150 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


251.1179
162.9730
348.1042
465.0907
637.1866
809.2826
903.2732
Counts vs. Mass-to-Charge (m/z)
ESI-MS, 3i

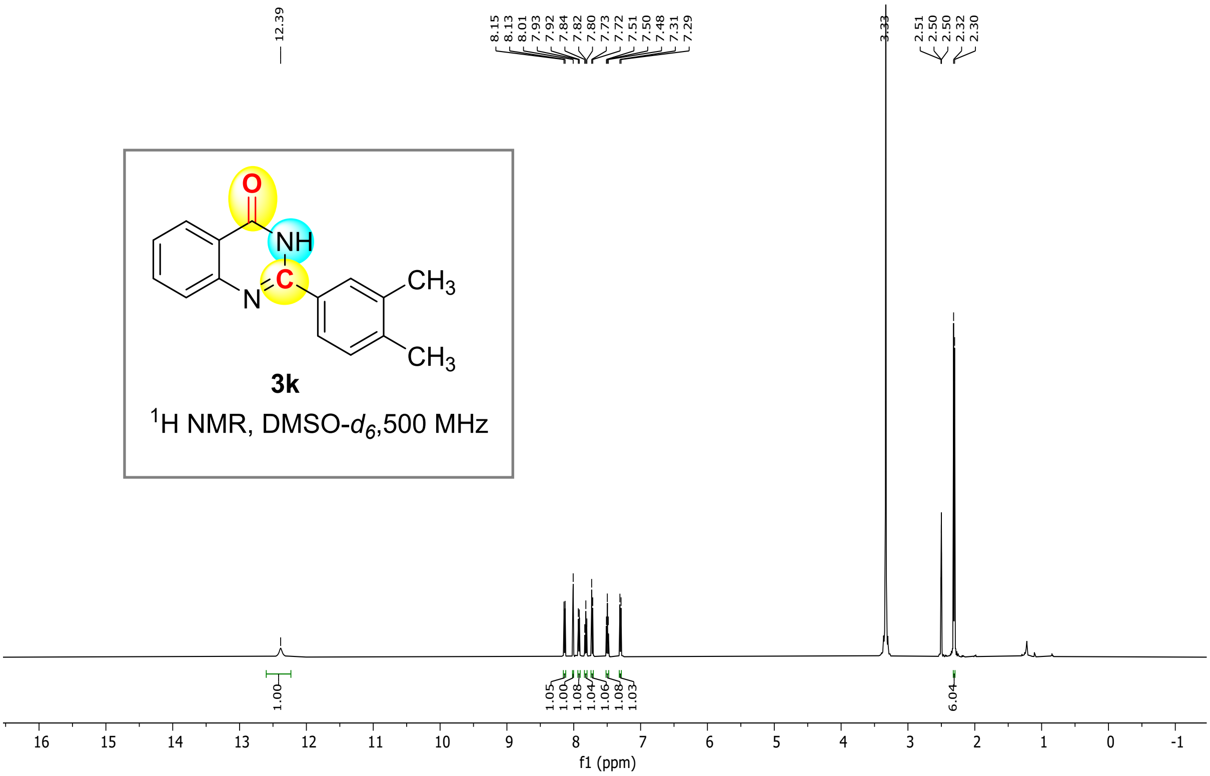

12.37
8.17 8.17 8.15 8.15 7.84 7.84 7.82 7.82 7.82 7.81 7.80 7.68 7.67 7.54 7.54 7.53 7.52 7.52 7.52 7.51 7.51 7.41 7.39 7.16 7.15 7.14 7.13 7.12 7.12
3.35 3.35 3.35 3.35 3.35 3.35 3.34 3.33 3.33 3.33 3.33 2.51 2.50 2.50 2.50 2.49 2.37 2.34
3j
^{1}H NMR, DMSO-d_6,500 MHz
1.00 1.00 1.05 1.02 1.07 1.05 2.08 6.06
f1 (ppm)

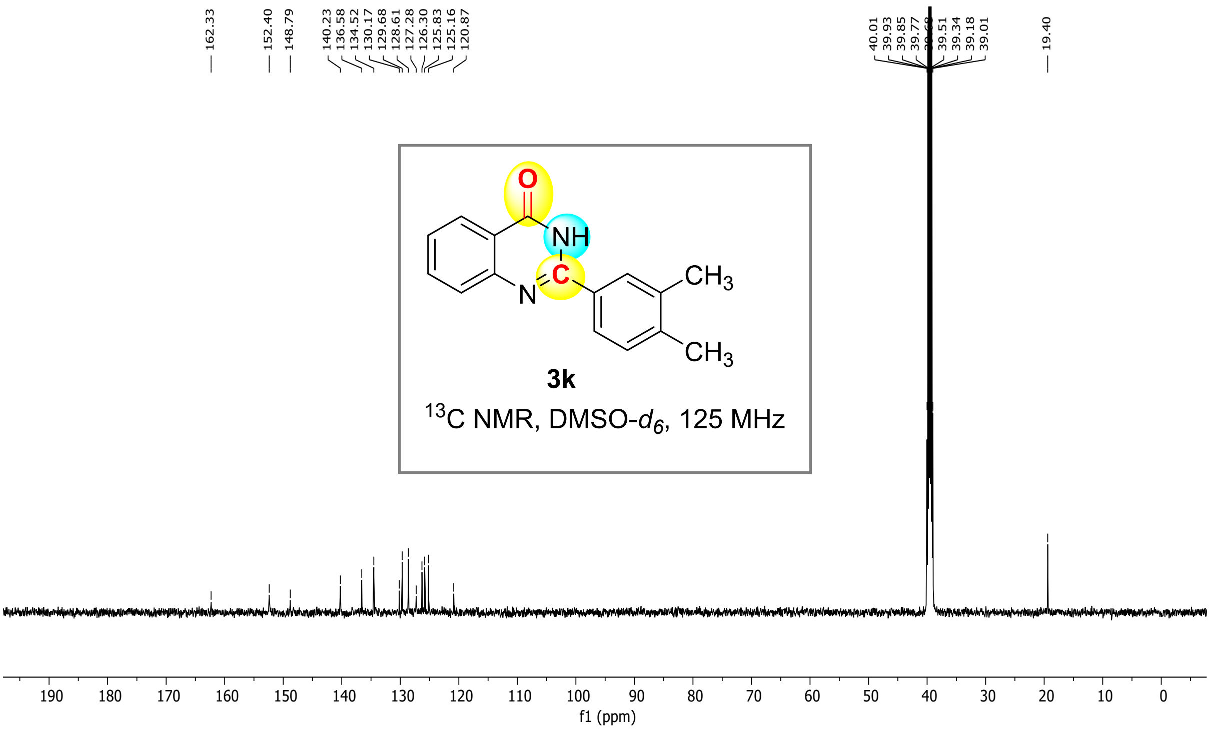


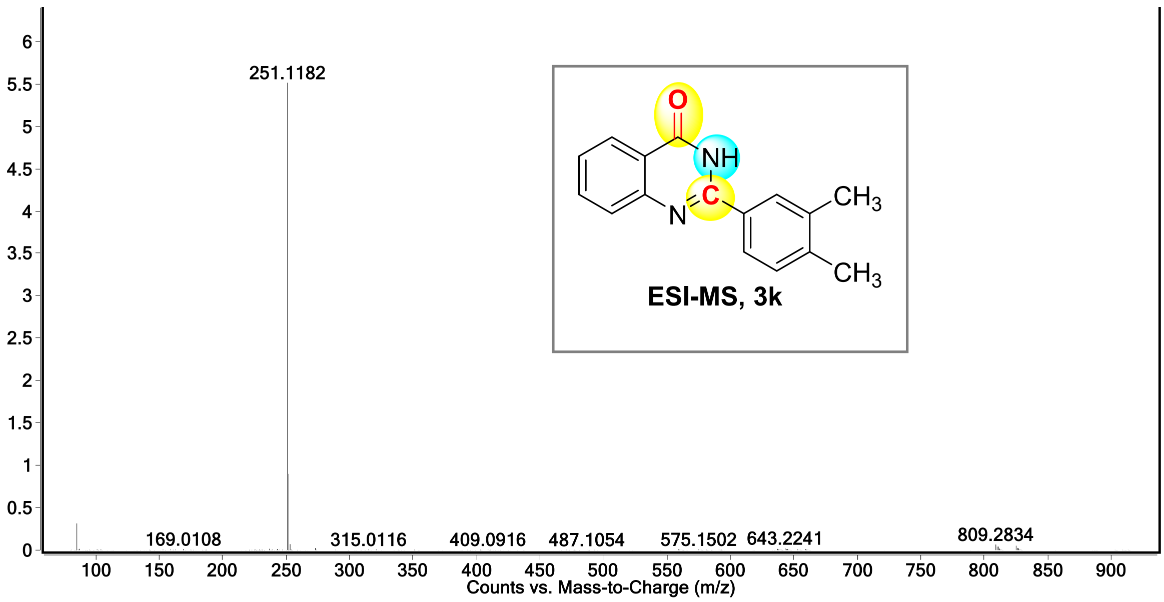
161.85
154.39
148.79
139.47
136.06
134.42
131.41
131.19
129.17
127.32
126.50
126.23
125.75
120.89
40.01
39.85
39.68
39.51
39.34
39.18
39.01
20.84
19.58
O
NH
CH3
N
C
CH3
3j
13C NMR, DMSO-d6, 125 MHz
f1 (ppm)

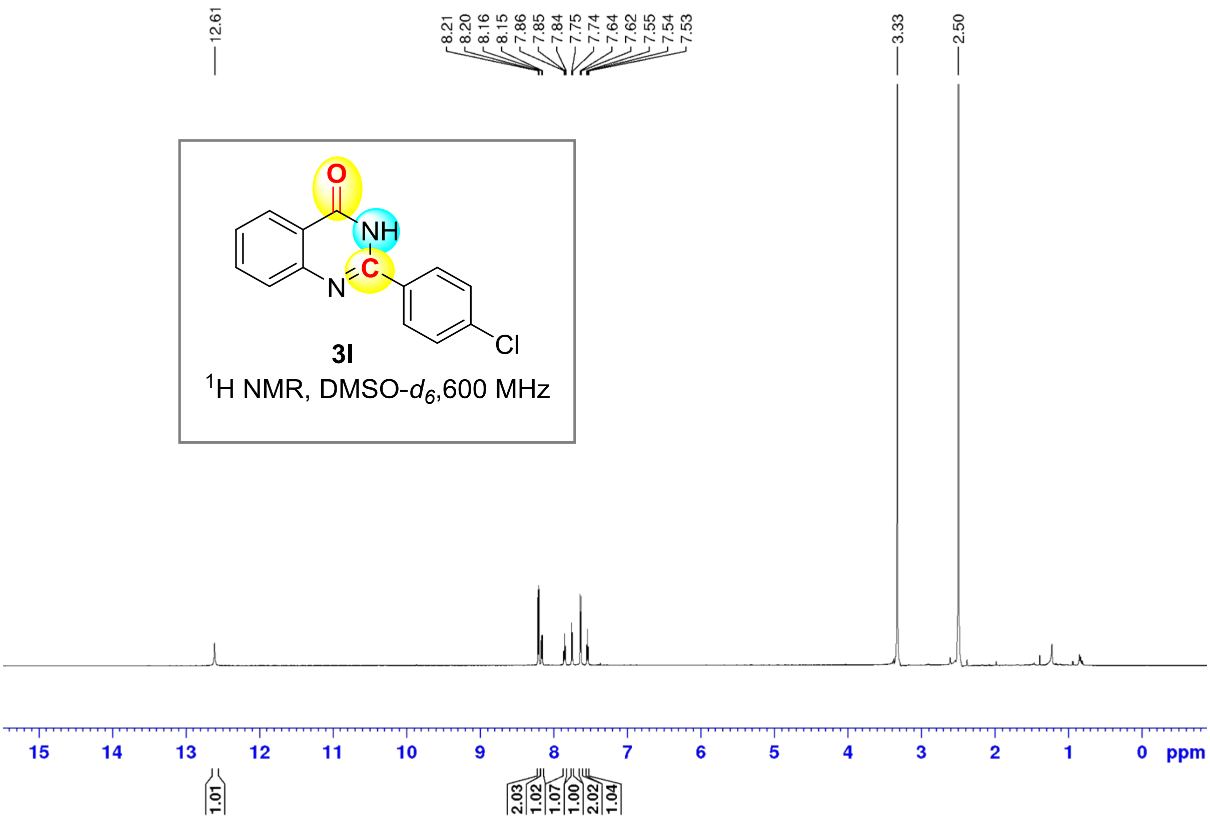


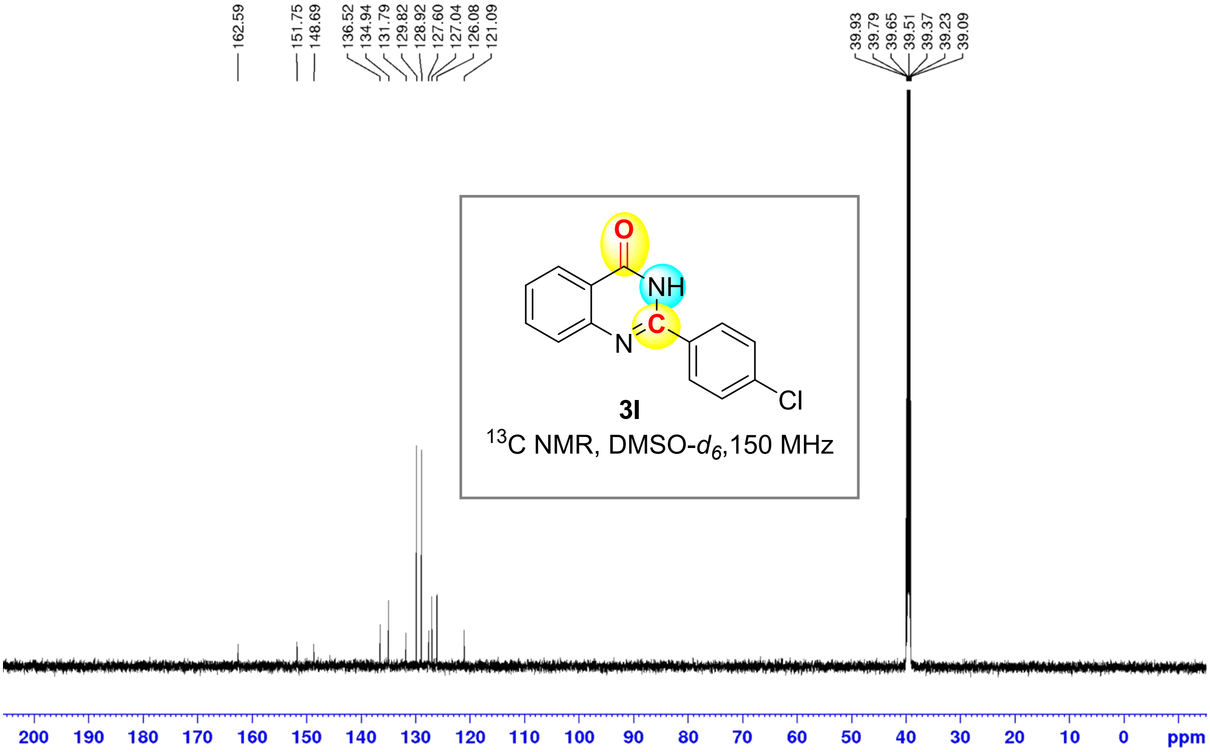
+ESI Scan (rt: 0.265 min) Frag=400.0V CID@50.0 PD-104.d
x10 4
O
NH
CH3
N
C
CH3
ESI-MS, 3j
251.1177
233.1072
218.0833
145.0384
156.0418
152.9447
190.0645
196.9781
208.1114
Counts vs. Mass-to-Charge (m/z)

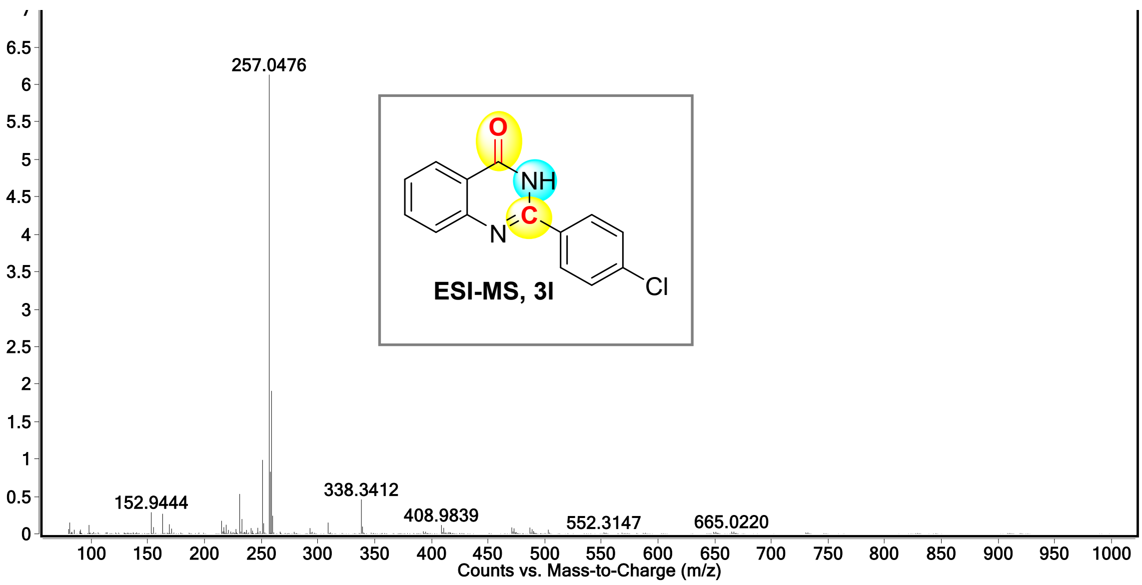

12.39
8.15
8.13
8.01
7.93
7.92
7.84
7.82
7.80
7.73
7.72
7.51
7.50
7.48
7.31
7.29
3.33
2.51
2.50
2.50
2.32
2.30
O
NH
C
N
CH_3
CH_3
3k
^{1}H NMR, DMSO-d_6,500 MHz
1.00
1.05
1.00
1.08
1.04
1.06
1.08
1.03
6.04
f1 (ppm)

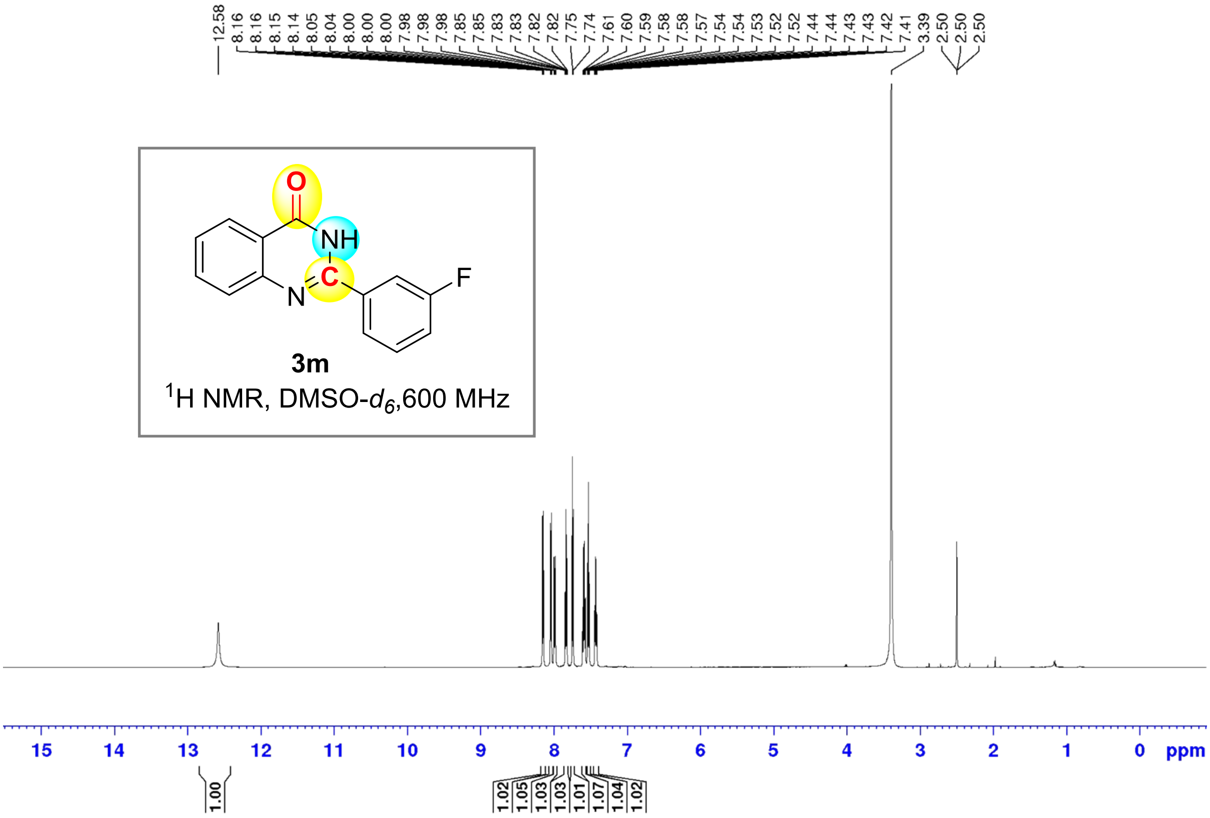

162.33
152.40
148.79
140.23
136.58
134.52
130.17
129.68
128.61
127.28
126.30
125.83
125.16
120.87
40.01
39.93
39.85
39.77
39.51
39.34
39.18
39.01
19.40
O
NH
C
N
CH_3
CH_3
3k
^{13}C NMR, DMSO-d_6, 125 MHz
f1 (ppm)

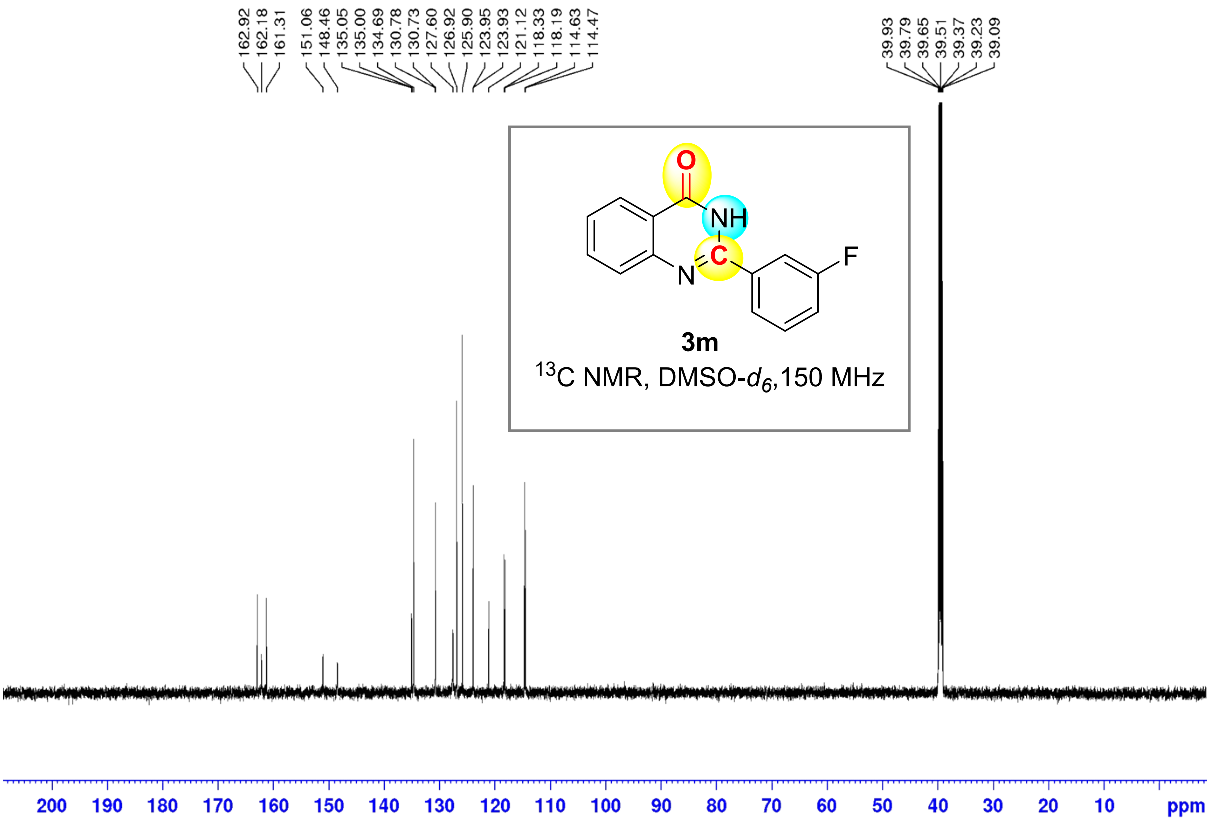

251.1182
169.0108
315.0116
409.0916
487.1054
575.1502
643.2241
809.2834
Counts vs. Mass-to-Charge (m/z)
ESI-MS, 3k

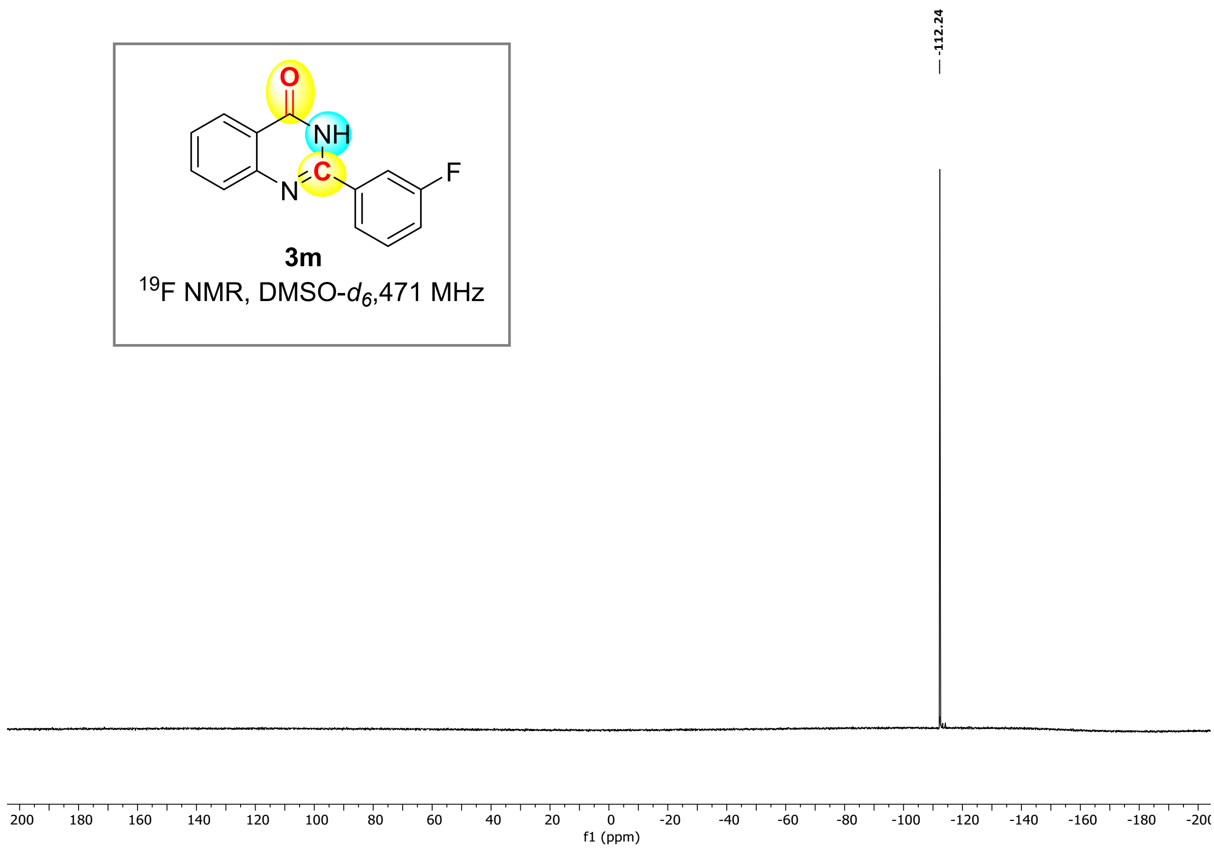

12.61
8.21
8.20
8.16
8.15
7.86
7.85
7.84
7.75
7.74
7.64
7.62
7.55
7.54
7.53
3.33
2.50
3l
¹H NMR, DMSO-d6,600 MHz
ppm
1.01
2.03
1.02
1.07
1.00
2.02
1.04

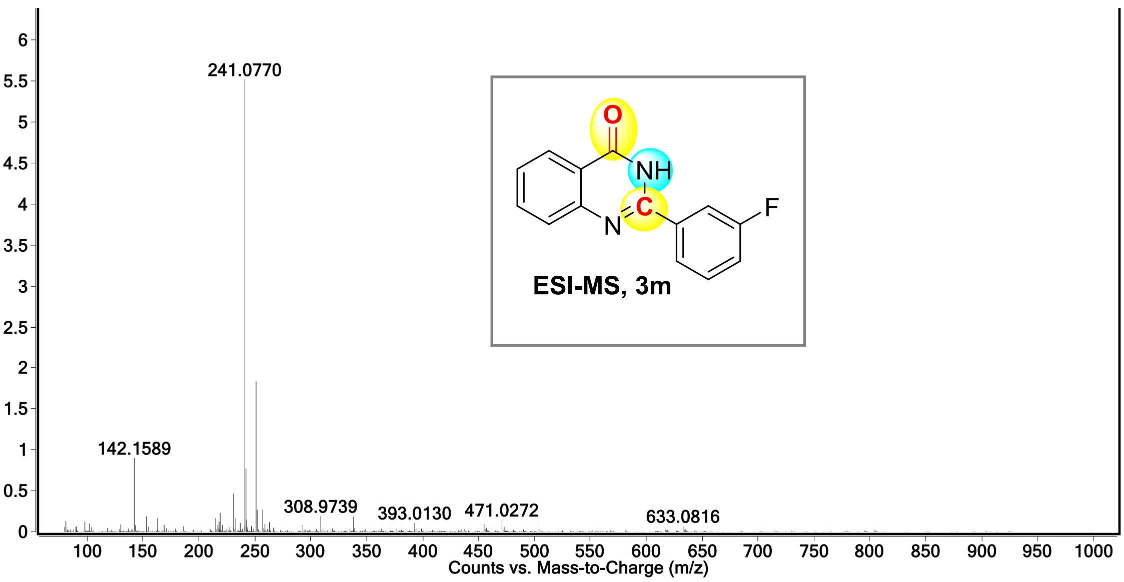

162.59
151.75
148.69
136.52
134.94
131.79
129.82
128.92
127.60
127.04
126.08
121.09
39.93
39.79
39.65
39.51
39.37
39.23
39.09
O
NH
C
N
Cl
3l
^{13}C NMR, DMSO-d_6,150 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

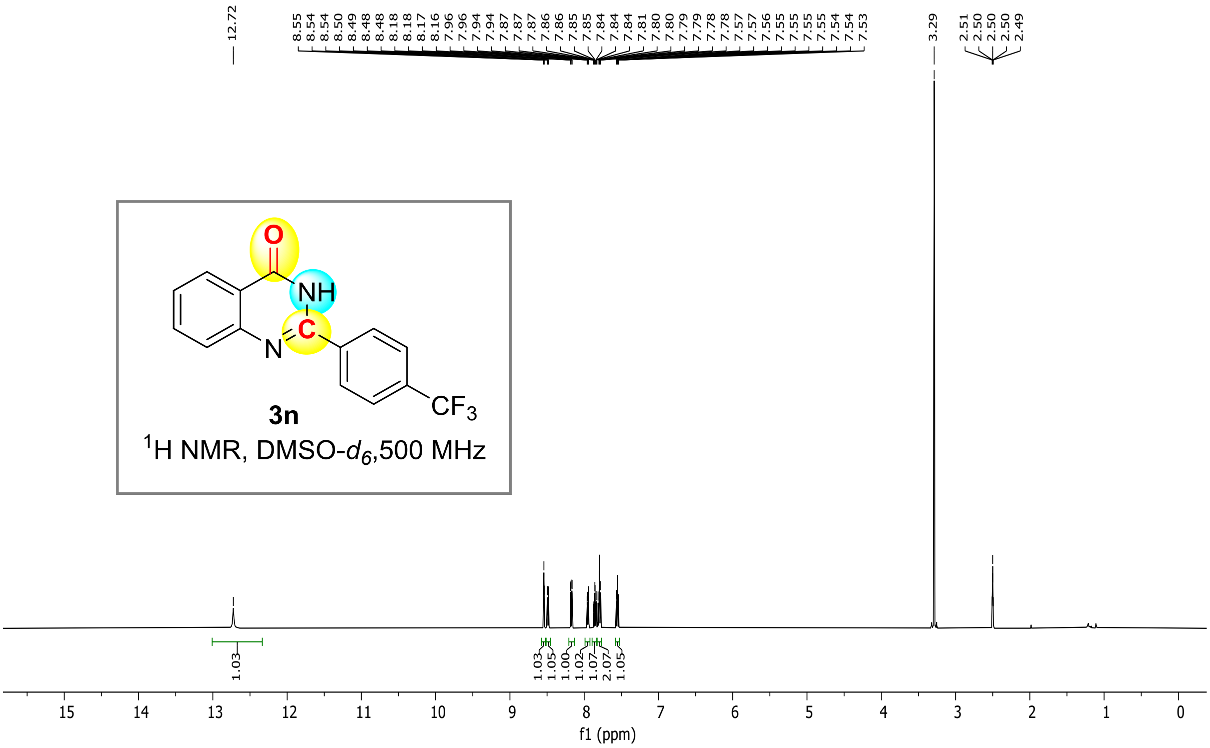

6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
257.0476
152.9444
338.3412
408.9839
552.3147
665.0220
O
NH
C
N
Cl
ESI-MS, 3l
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
Counts vs. Mass-to-Charge (m/z)

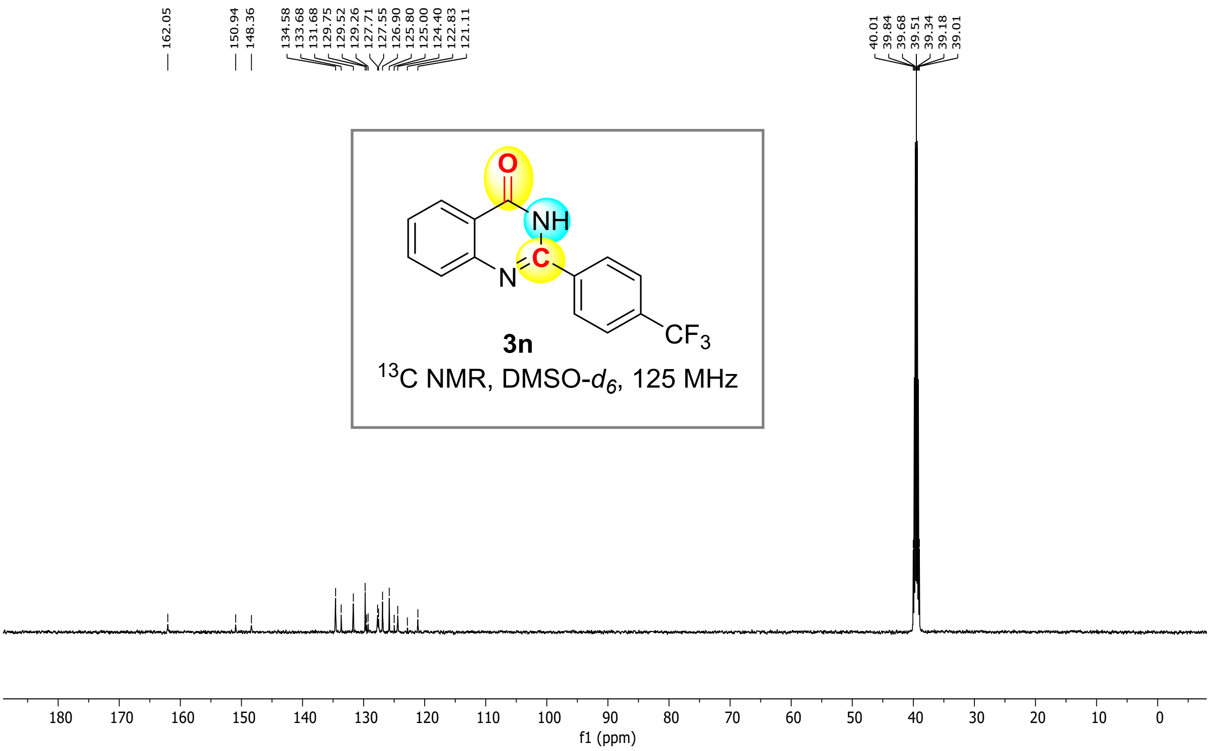

12.58
8.16
8.16
8.15
8.14
8.05
8.04
8.00
8.00
8.00
7.98
7.98
7.98
7.85
7.85
7.83
7.83
7.82
7.82
7.75
7.74
7.61
7.60
7.59
7.58
7.58
7.57
7.54
7.54
7.53
7.52
7.52
7.44
7.44
7.43
7.42
7.41
3.39
2.50
2.50
2.50
3m
¹H NMR, DMSO-d6,600 MHz
1.00
1.02
1.05
1.03
1.03
1.01
1.07
1.04
1.02
ppm

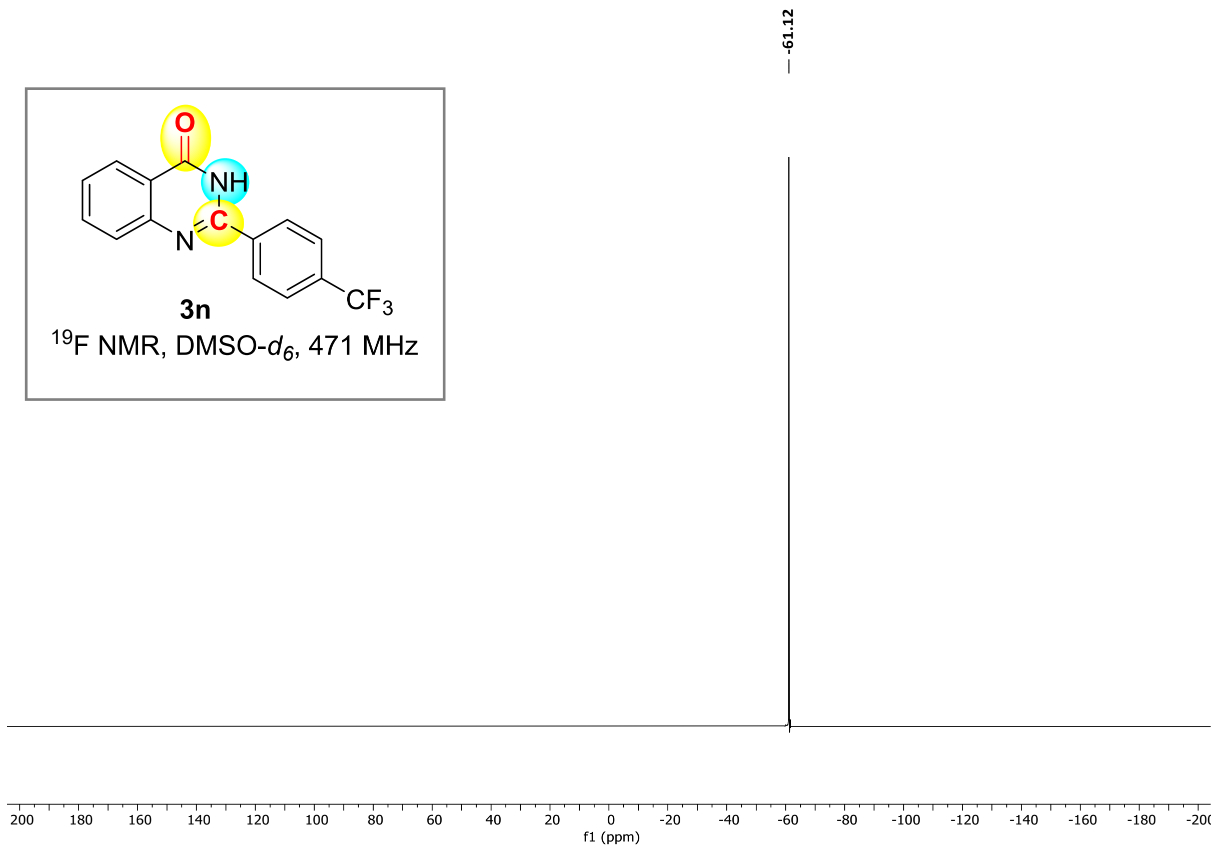

162.92
162.18
161.31
151.06
148.46
135.05
135.00
134.69
130.78
130.73
127.60
126.92
125.90
123.95
123.93
121.12
118.33
118.19
114.63
114.47
39.93
39.79
39.65
39.51
39.37
39.23
39.09
3m
¹³C NMR, DMSO-d6,150 MHz
ppm

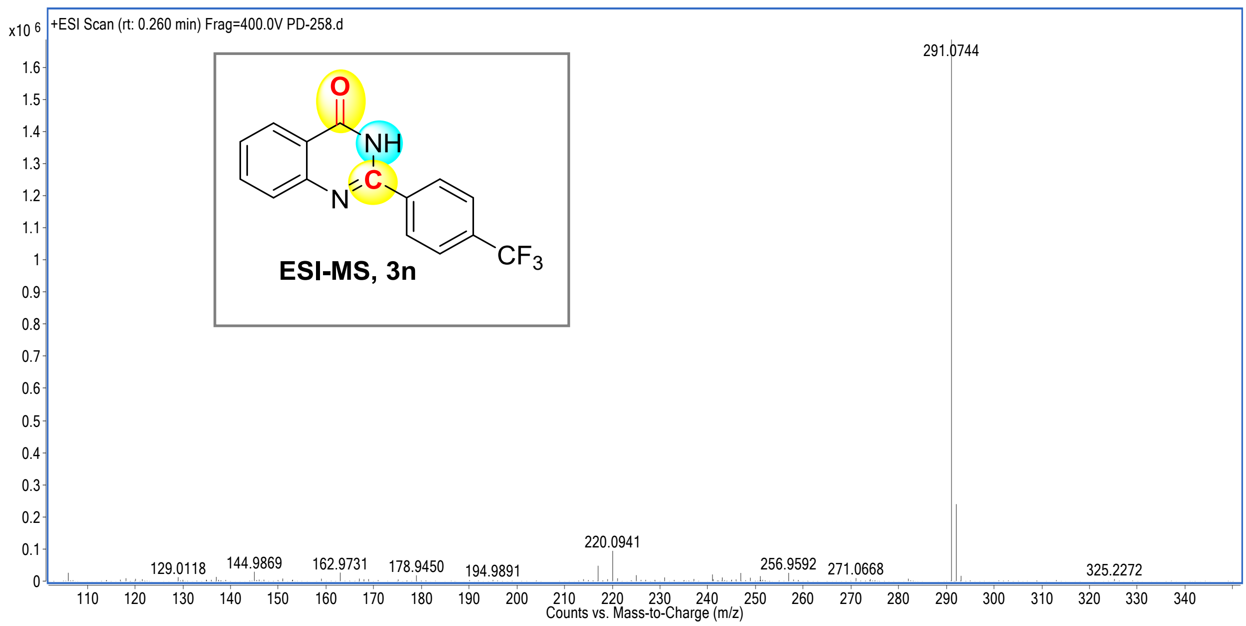

-112.24
O
NH
C
N
F
3m
19F NMR, DMSO-d6,471 MHz
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

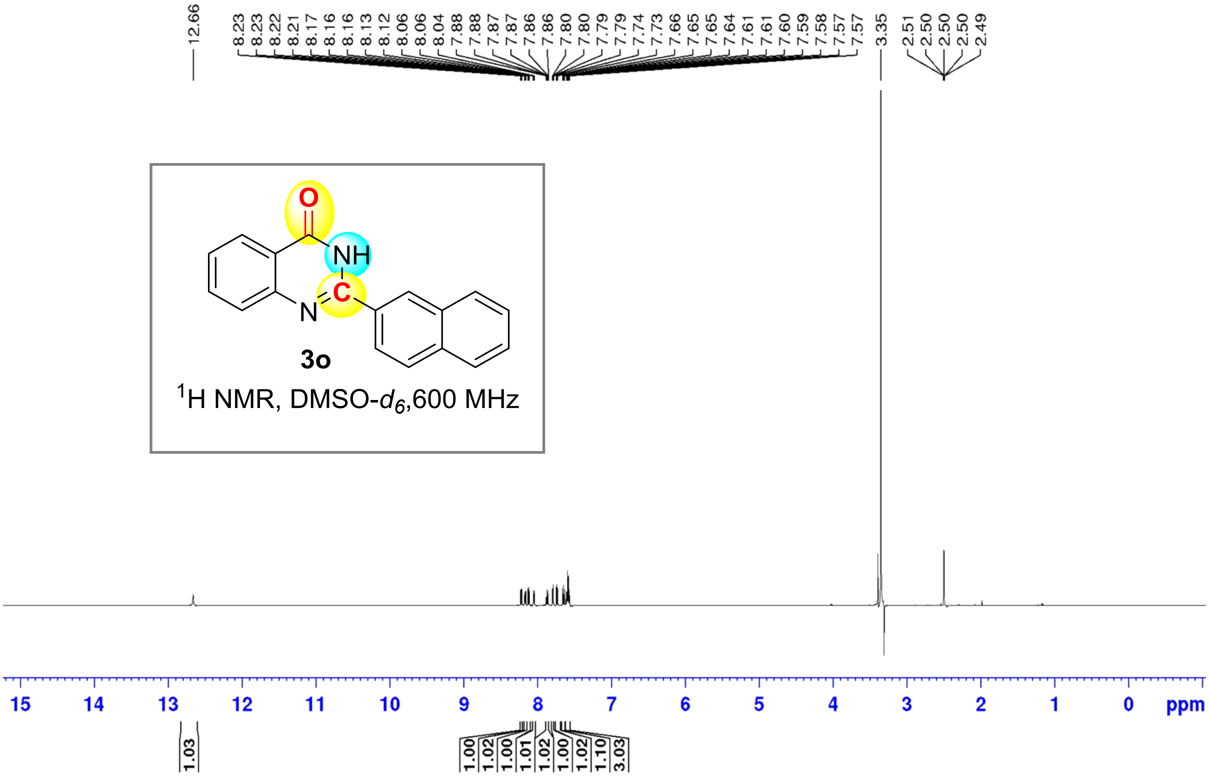

6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
241.0770
142.1589
308.9739
393.0130
471.0272
633.0816
O
NH
C
N
F
ESI-MS, 3m
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
Counts vs. Mass-to-Charge (m/z)

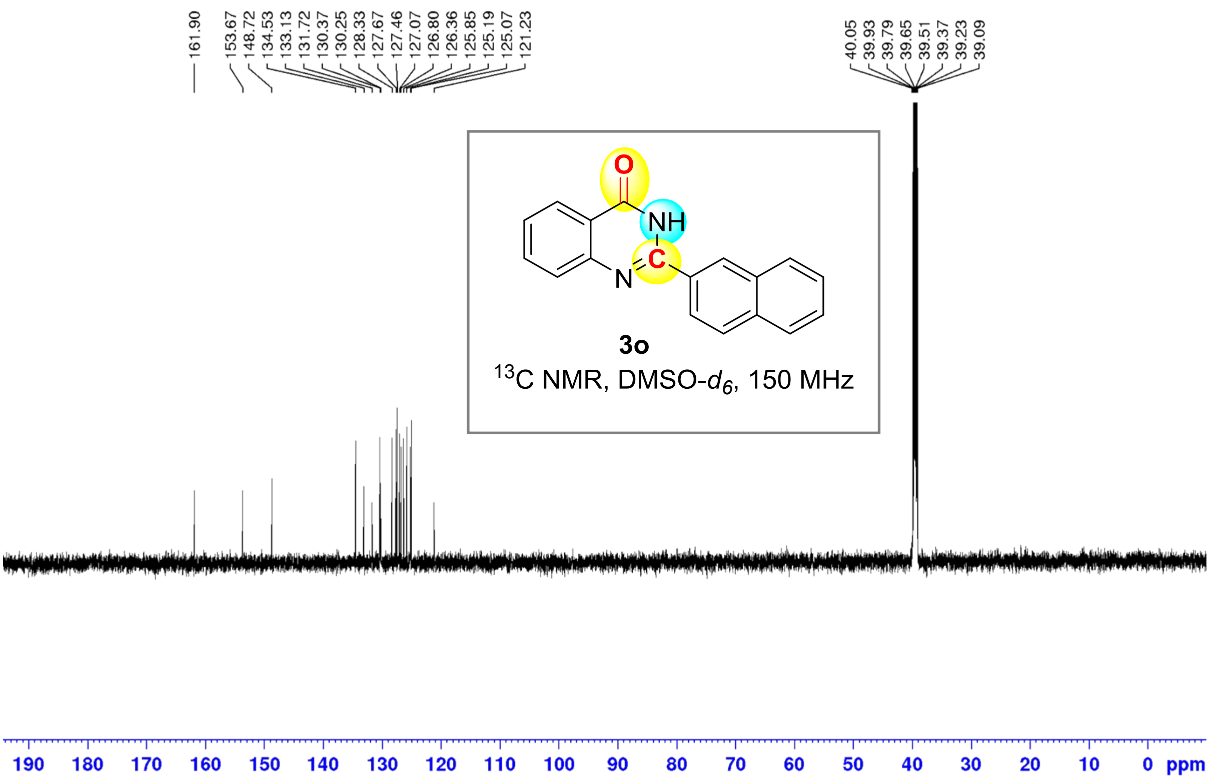

O
NH
C
N
CF3
3n
1H NMR, DMSO-d6,500 MHz
f1 (ppm)

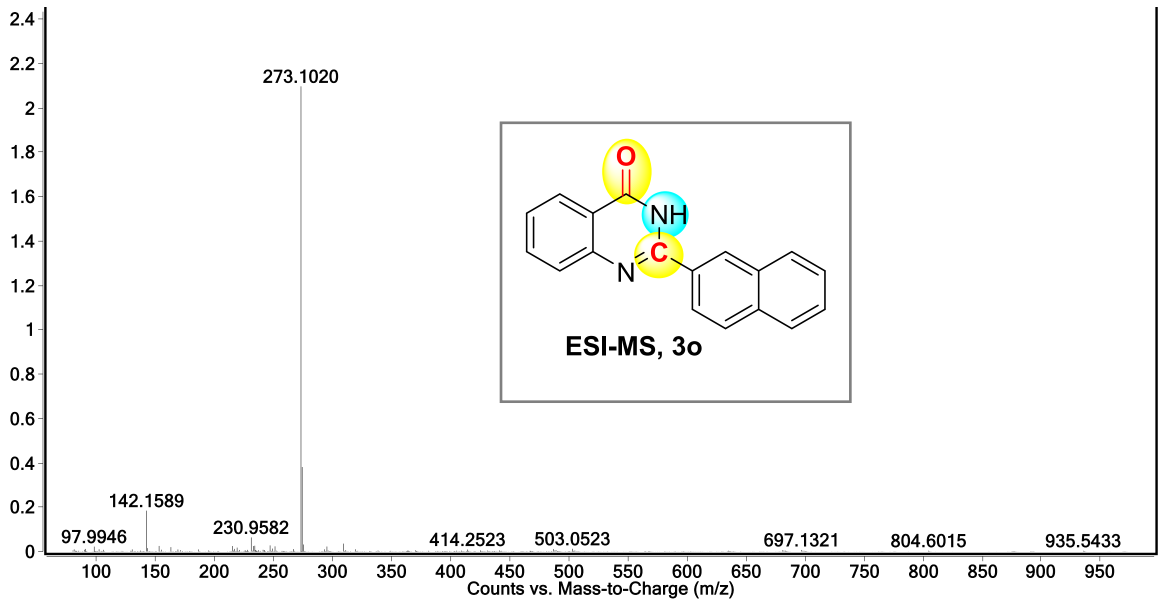

O
NH
C
N
CF3
3n
13C NMR, DMSO-d6, 125 MHz
f1 (ppm)

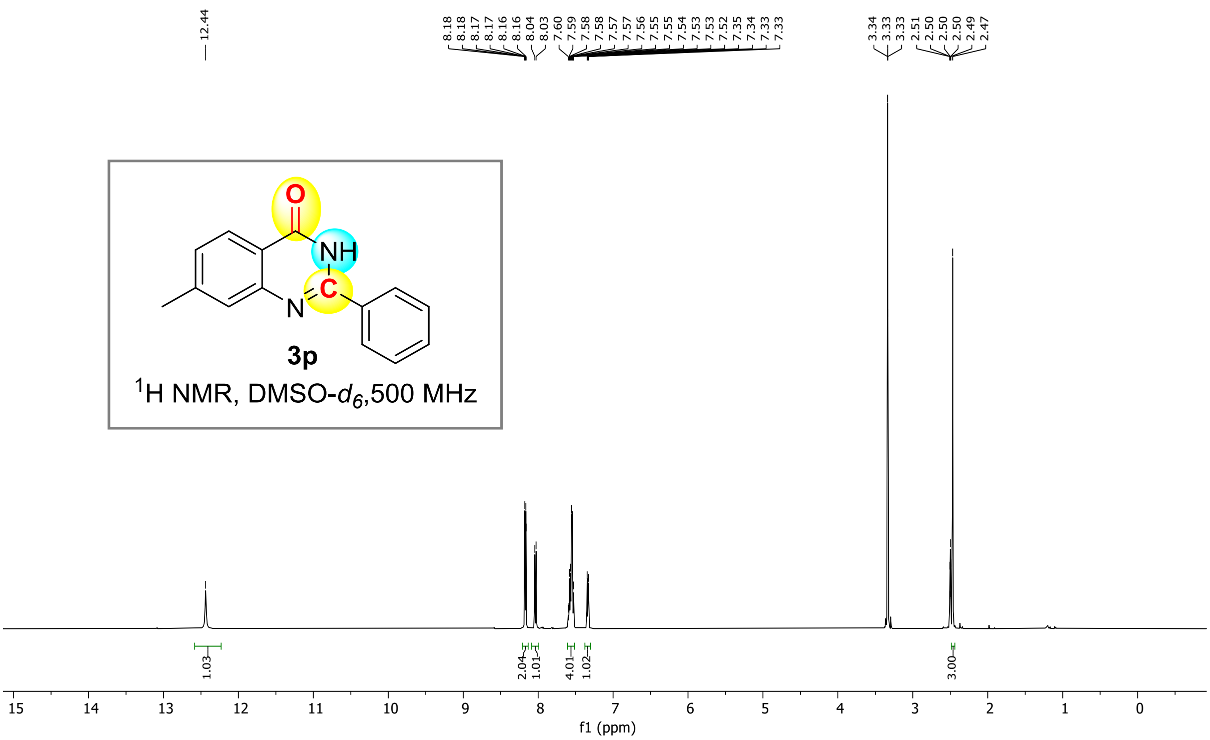

-61.12
3n
19F NMR, DMSO-d6, 471 MHz
f1 (ppm)

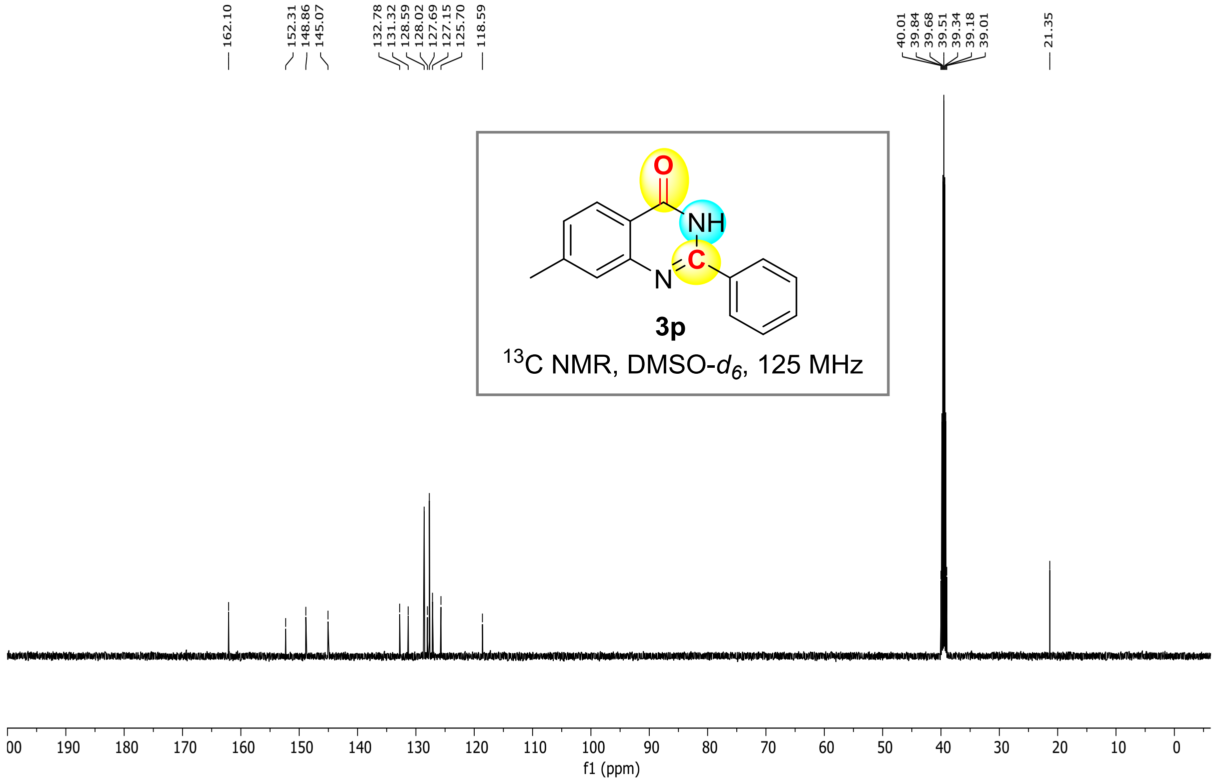

+ESI Scan (rt: 0.260 min) Frag=400.0V PD-258.d
x10 6
291.0744
220.0941
129.0118
144.9869
162.9731
178.9450
194.9891
256.9592
271.0668
325.2272
ESI-MS, 3n
Counts vs. Mass-to-Charge (m/z)

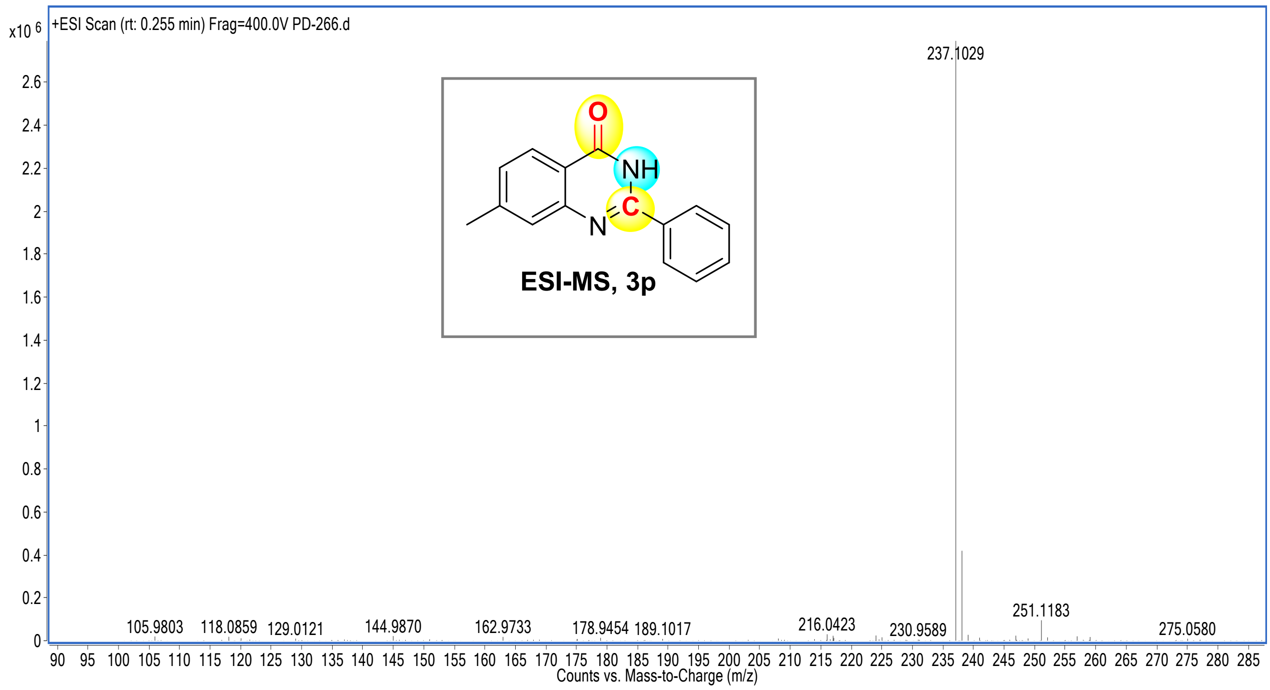

3o
^{1}H NMR, DMSO-d_6,600 MHz
ppm

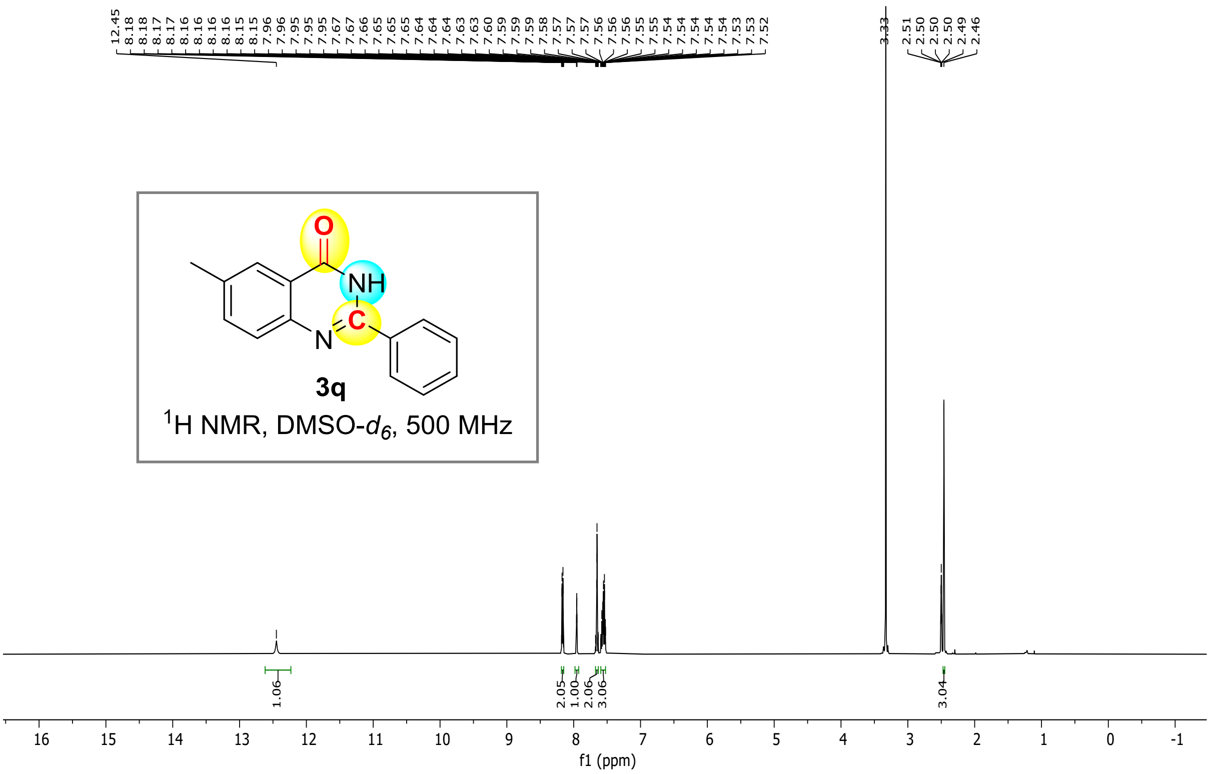

3o
^{13}C NMR, DMSO-d_6, 150 MHz
ppm


273.1020
142.1589
97.9946
230.9582
414.2523
503.0523
697.1321
804.6015
935.5433
ESI-MS, 3o
Counts vs. Mass-to-Charge (m/z)

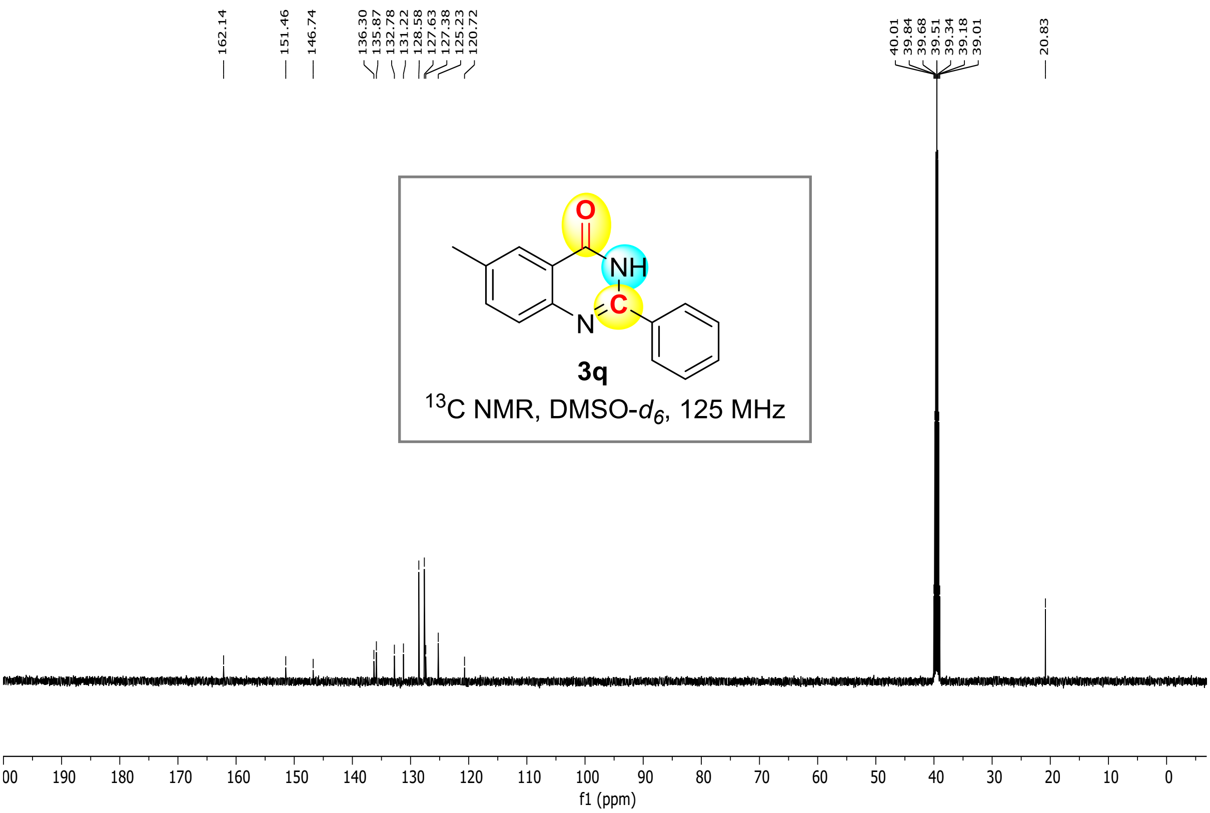

3p
1H NMR, DMSO-d6,500 MHz
f1 (ppm)


162.10
152.31
148.86
145.07
132.78
131.32
128.59
128.02
127.69
127.15
125.70
118.59
40.01
39.84
39.68
39.51
39.34
39.18
39.01
21.35
O
NH
C
N
3p
^{13}C NMR, DMSO-d_6, 125 MHz
f1 (ppm)

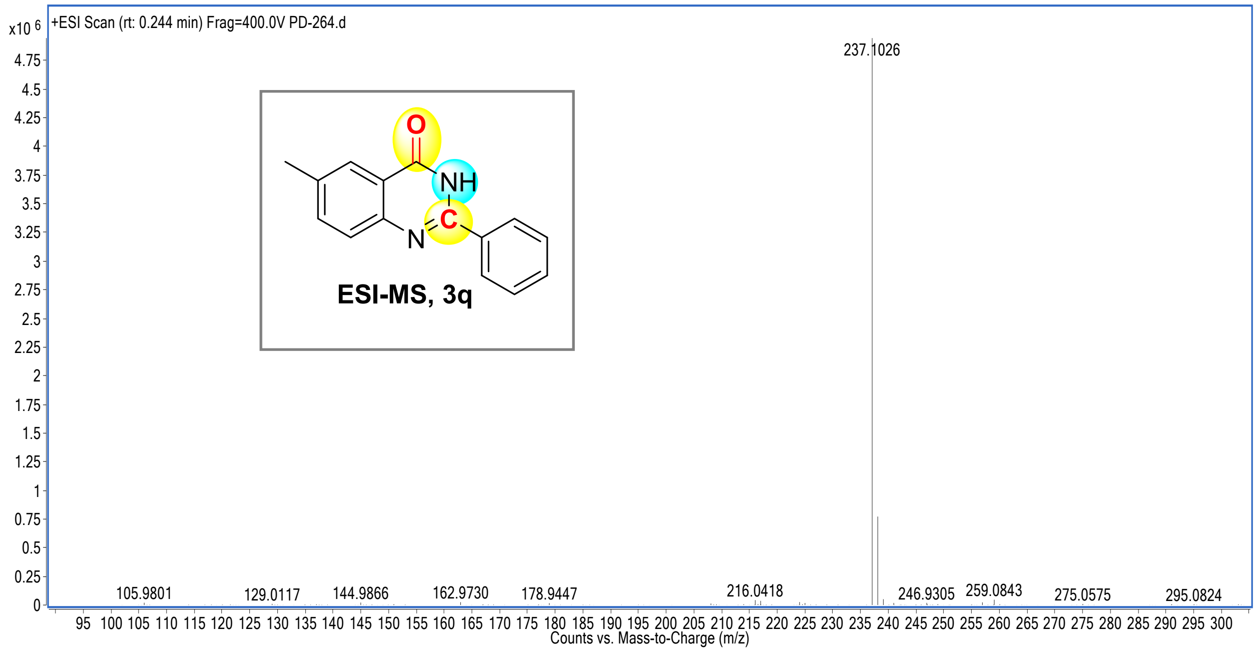

x10 6
+ESI Scan (rt: 0.255 min) Frag=400.0V PD-266.d
237.1029
105.9803
118.0859
129.0121
144.9870
162.9733
178.9454
189.1017
216.0423
230.9589
251.1183
275.0580
O
NH
C
N
ESI-MS, 3p
Counts vs. Mass-to-Charge (m/z)

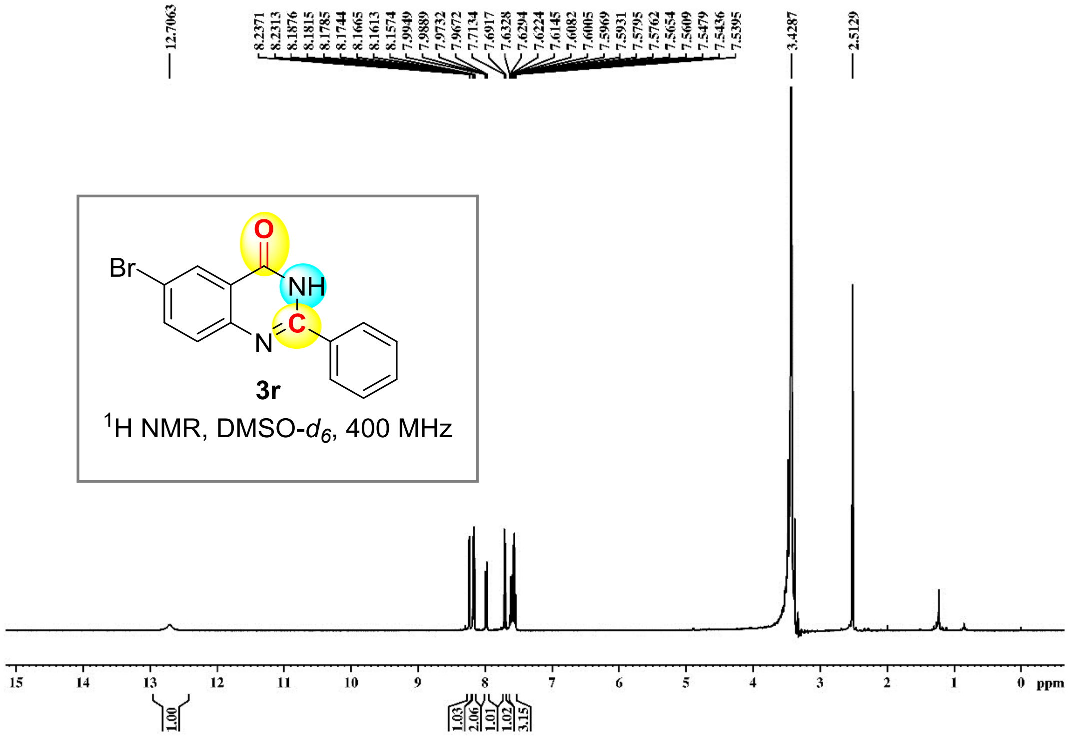


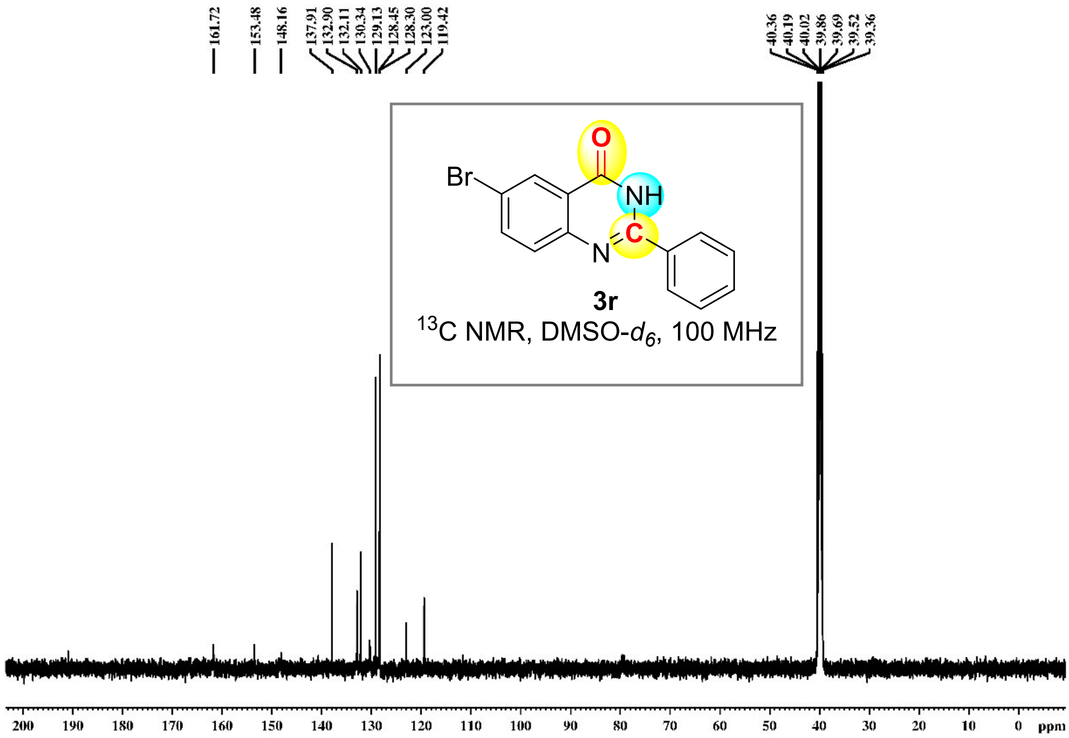
O
NH
C
N
3q
¹H NMR, DMSO-d6, 500 MHz
f1 (ppm)

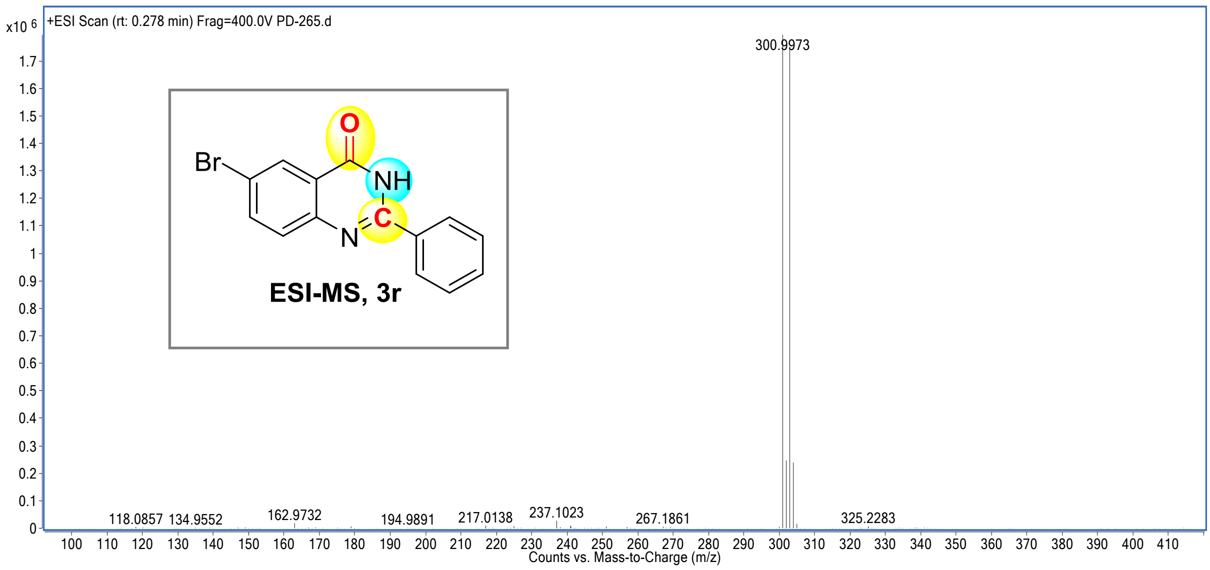


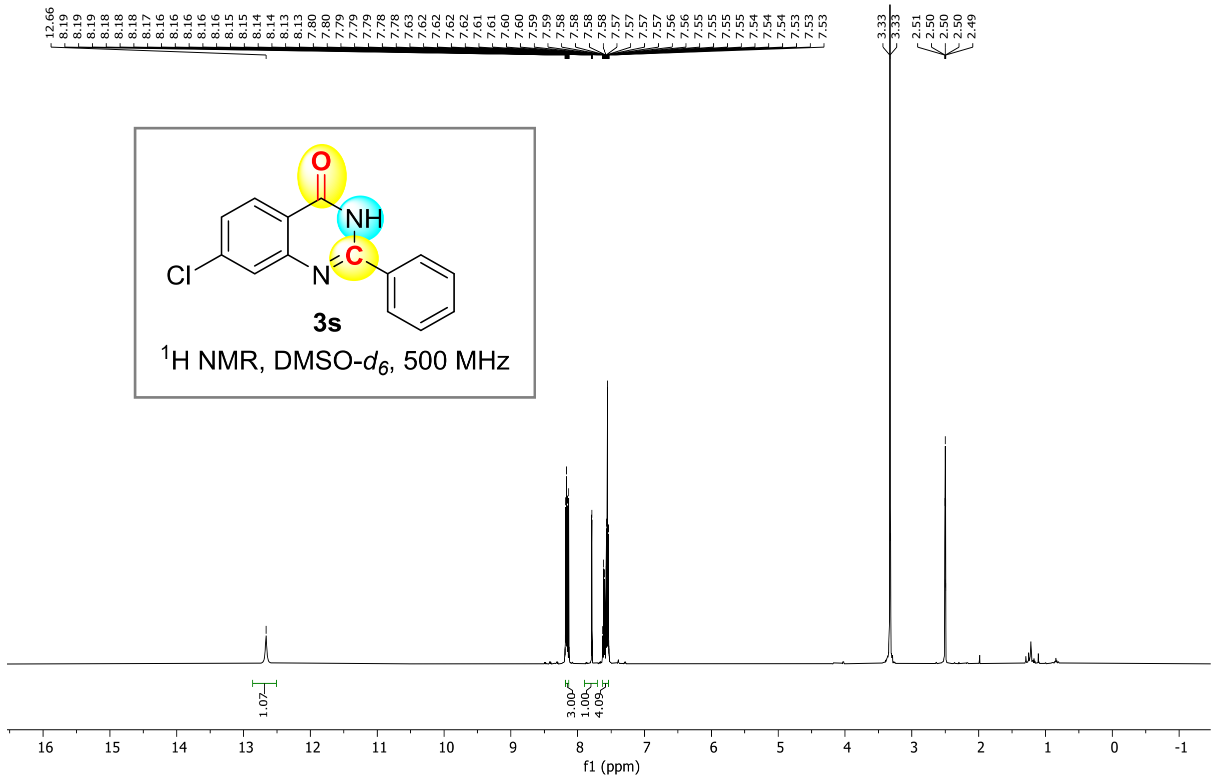
O
NH
C
N
3q
¹³C NMR, DMSO-d6, 125 MHz
f1 (ppm)

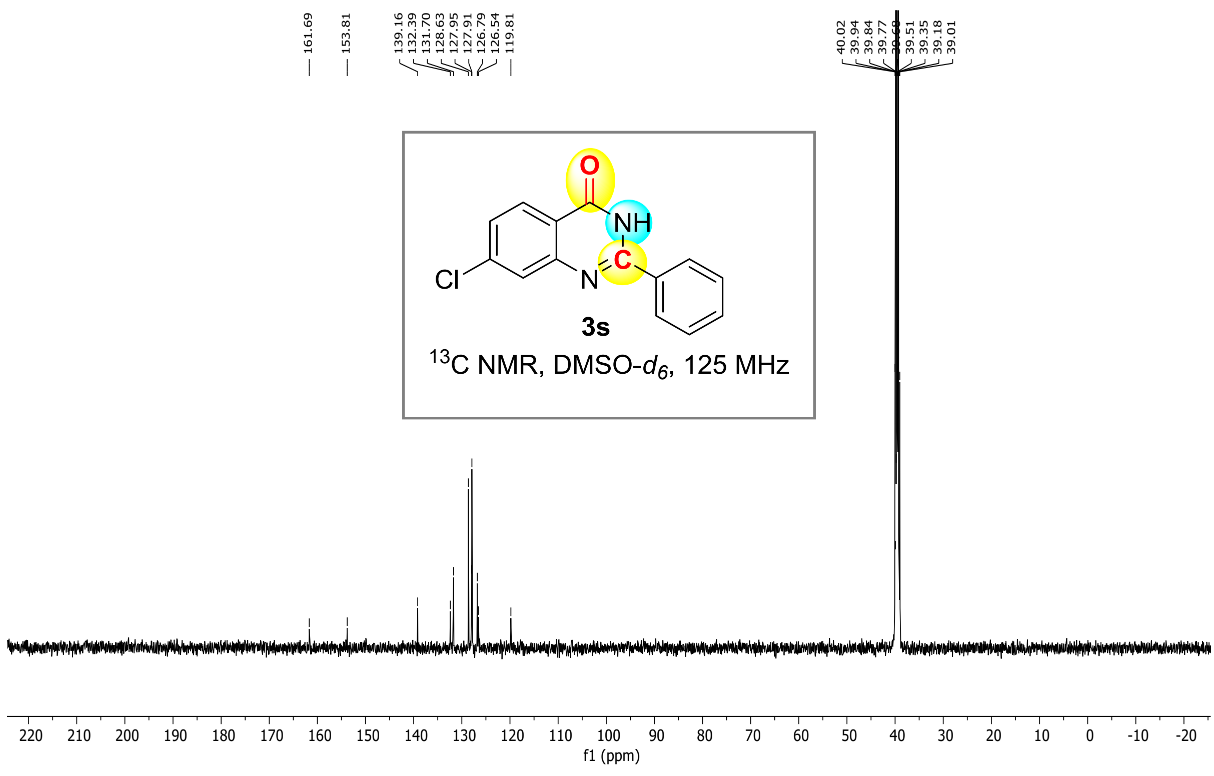

+ESI Scan (rt: 0.244 min) Frag=400.0V PD-264.d
x10 6
237.1026
105.9801
129.0117
144.9866
162.9730
178.9447
216.0418
246.9305
259.0843
275.0575
295.0824
Counts vs. Mass-to-Charge (m/z)
ESI-MS, 3q

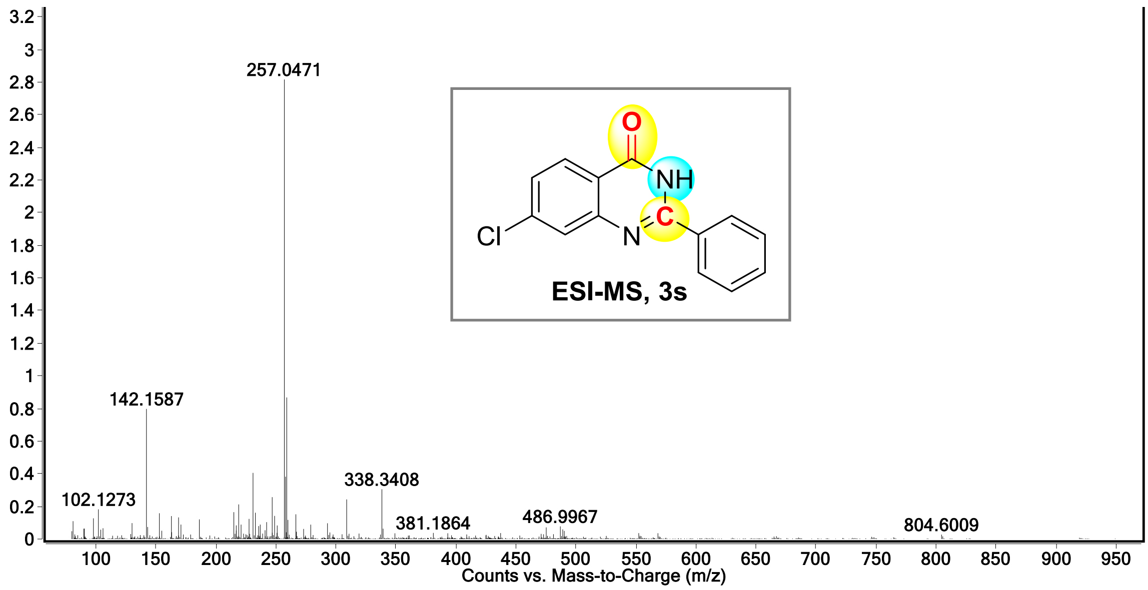

12.7063
8.2371
8.2313
8.1876
8.1815
8.1785
8.1744
8.1665
8.1613
8.1574
7.9949
7.9889
7.9732
7.9672
7.7134
7.6917
7.6328
7.6294
7.6224
7.6145
7.6082
7.6005
7.5969
7.5931
7.5795
7.5762
7.5654
7.5609
7.5479
7.5436
7.5395
3.4287
2.5129
Br
3r
^{1}H NMR, DMSO-d_6, 400 MHz
ppm
1.00
1.03
2.06
1.01
1.02
3.15


161.72
153.48
148.16
137.91
132.90
132.11
130.34
129.13
128.45
128.30
123.00
119.42
40.36
40.19
40.02
39.86
39.69
39.52
39.36
Br
O
NH
C
N
3r
13C NMR, DMSO-d6, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


x10 6
+ESI Scan (rt: 0.278 min) Frag=400.0V PD-265.d
300.9973
Br
O
NH
C
N
ESI-MS, 3r
118.0857
134.9552
162.9732
194.9891
217.0138
237.1023
267.1861
325.2283
Counts vs. Mass-to-Charge (m/z)


3s
^{1}H NMR, DMSO-d_6, 500 MHz
f1 (ppm)


161.69
153.81
139.16
132.39
131.70
128.63
127.95
127.91
126.79
126.54
119.81
3s
^{13}C NMR, DMSO-d_6, 125 MHz
f1 (ppm)



Recyclability experiments for Pd/C Catalyst:

The recyclability experiment of Pd/C (5 wt%) catalyst was further performed under the developed reaction conditions employing 2-iodoaniline (**1a**) and iodobenzene (**2b**) as a model substrate (Figure S1). After completion of the reaction, the given reaction mixture was left aside for some time and the cooled reaction mixture was then subjected to centrifugation to separate the Pd/C catalyst from the reaction mixture. The catalyst was then washed properly with distilled water followed by acetone and was dried completely under reduced pressure for further use. The Pd/C catalyst showed high recyclability up to five cycles with a small decrease in desired product yield.

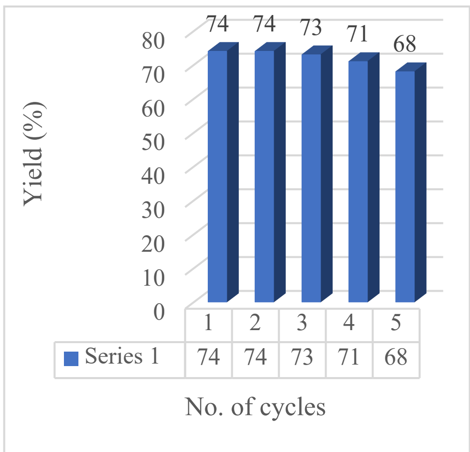


Figure S1. Recyclability experiment of Pd/C (5 wt%) catalyst

Hot Filtration Test for Pd/C Catalyst:

The reaction between 2-iodoaniline (1a) and iodobenzene (2b) was carried out under standard reaction conditions and after 22% of the product (3b) formation, the solid catalyst (Pd/C) was filtered off, and the reaction was further continued with the addition of 5 equiv. of oxalic acid to realize the total time of 24 h. There is no increase in the yield of the product was observed, hence indicating the absence of catalytic active species in the solution for fruitful conversion. While the same reaction when performed unperturbed under standard reaction conditions, gave **3b** in 74% yield. On the basis of these experiments, we concluded that the reaction takes place in truly heterogeneous manner and the catalytically active species involved in the reaction is Pd(0).

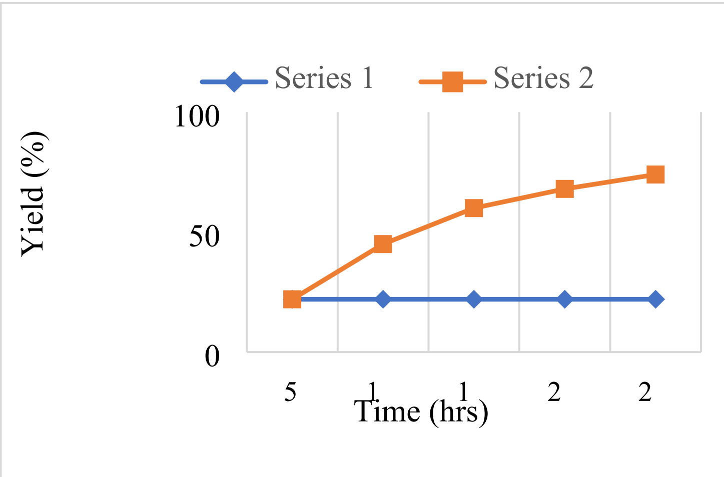
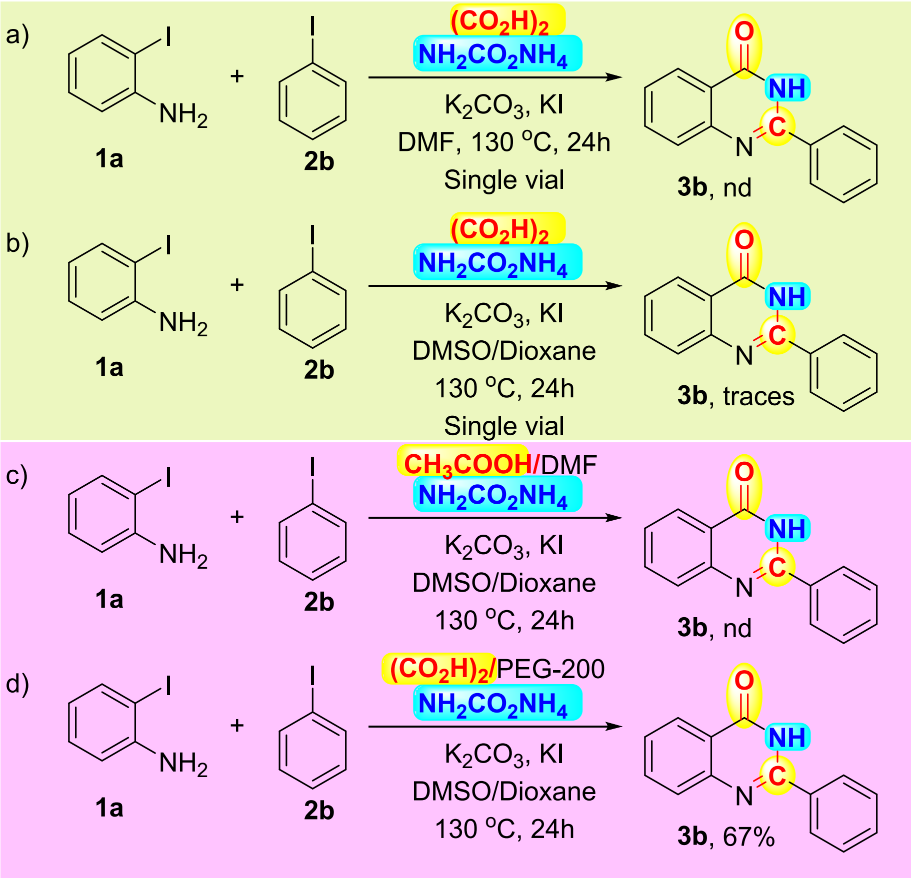


Figure S2. Hot filtration test for Pd/C catalyst.

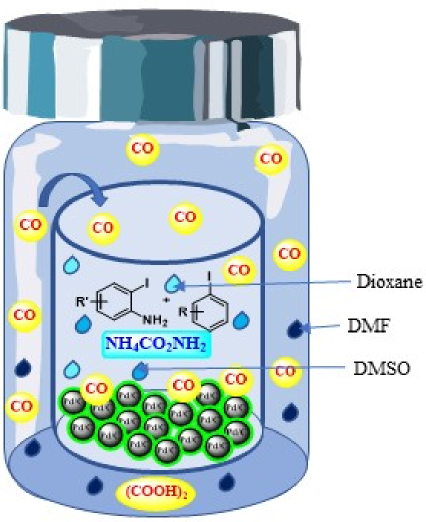
Control Experiments:

Further, several other control experiments were also performed to depict the utility of DLV system as well as the role of $(COOH)_2$ as C1 surrogate. Herein, no product formation was detected under single vial system with DMF as solvent, whereas traces of **3b** were obtained on employing DMSO/dioxane (1:2) solvent system (Scheme 1Sa-1Sb). These control experiments clearly indicates the essential need of DLV system in carrying out given transformation. Thereafter, to confirm the role of oxalic acid the given reaction was also carried out under acetic acid conditions, wherein the oxalic acid in the outer vial of DLV system was replaced with acetic acid, however, no desired product formation was obtained under these conditions (Scheme 1Sc). It clearly indicates the role of oxalic acid as a CO surrogate rather than just as an acid additive to facilitate the DMF decomposition. Furthermore, the desired product formation was also observed in 67% yield with PEG-200 as external solvent and hence eliminating the possibility of DMF acting as CO surrogate (Scheme 1Sd).



Scheme 1S. Control experiments

Schematic Diagram of Double Layer Vial (DLV) System



Time-based study of the reaction between 2-iodoaniline and iodobenzene:

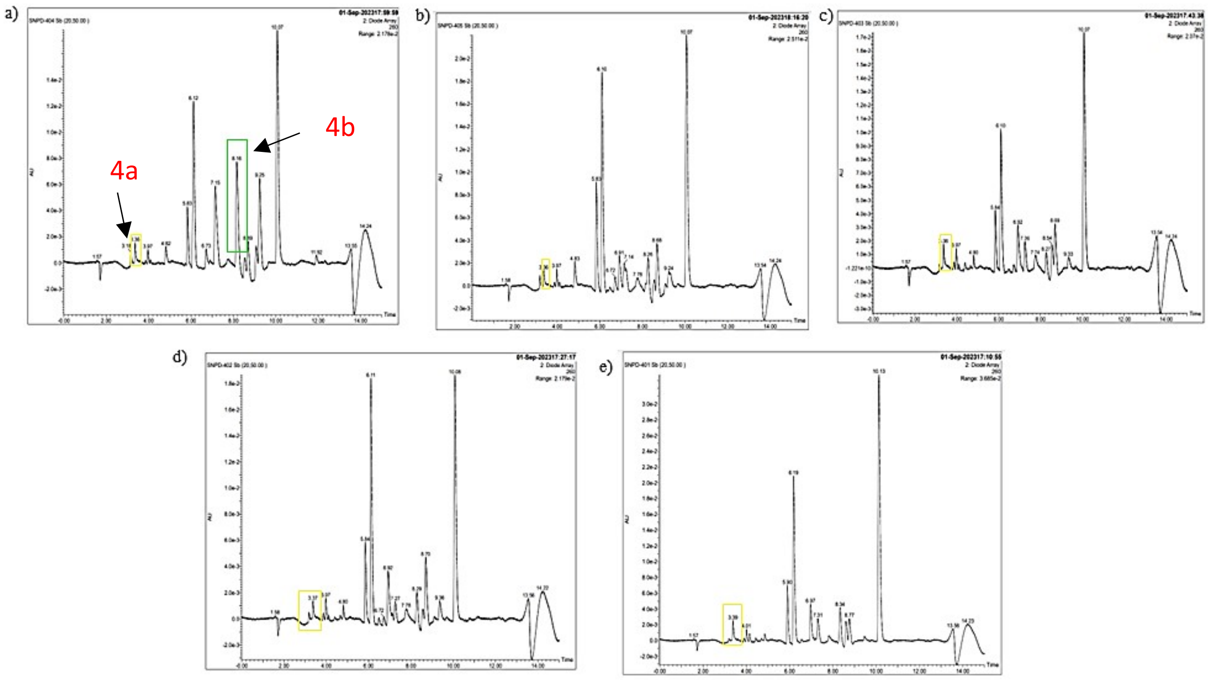


Figure S3. LCMS chromatogram for the reaction between 2-iodoaniline and iodobenzene a) after 5h; b) after 10h; c) after 15h; d) after 20h; e) after 24h.

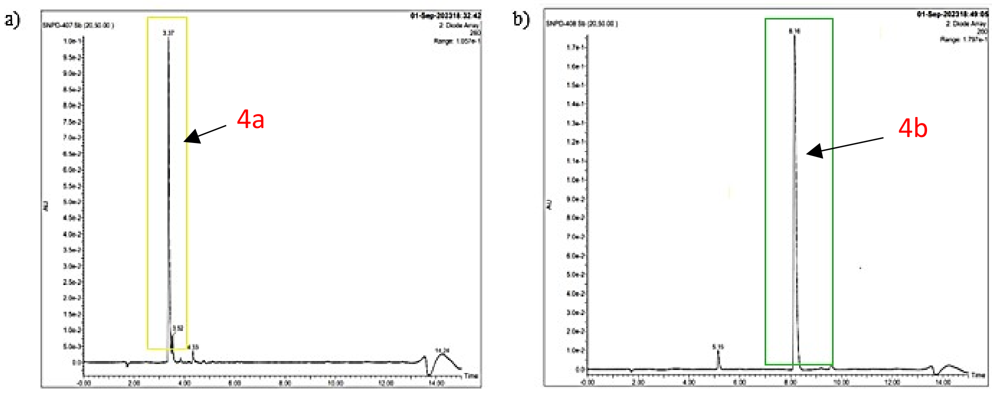
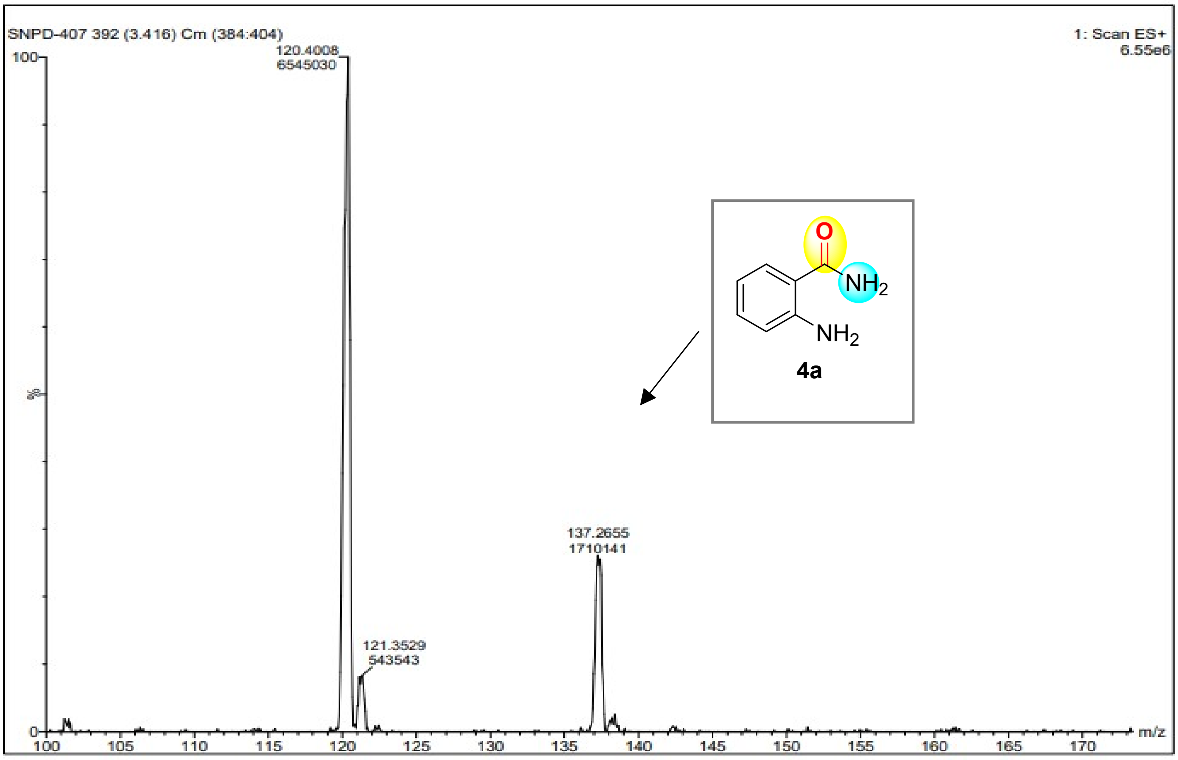
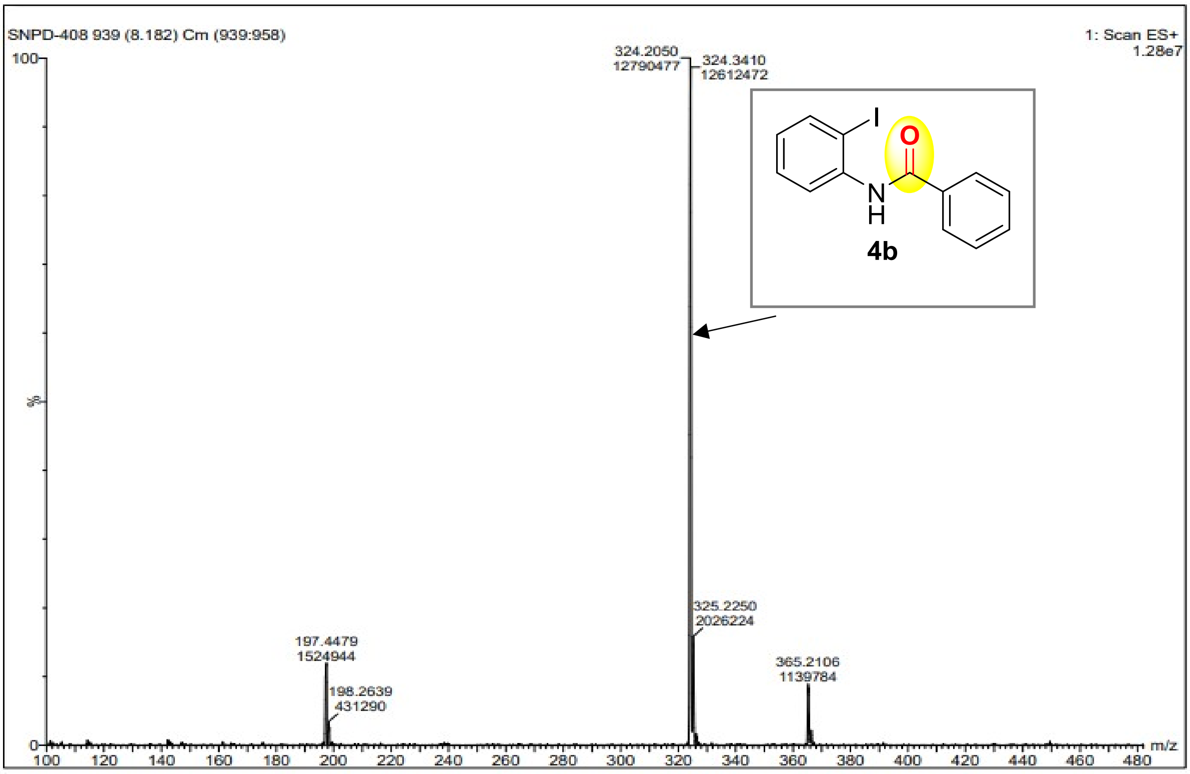


Figure S4. LCMS chromatogram for a) intermediate 4a; b) intermediate 4b.

a) Mass spectra for intermediate 4a:



b) Mass spectra for intermediate 4b:



Computational Details

All calculations were performed using the ORCA 5.0.3 software.[1,2] The density functional theoretical method was used in conjunction with the PBE0 functional,[3] with the dispersion corrections based on tight binding partial charges (D4)[4,5] and the balanced polarized double zeta basis set of Ahlrichs and coworkers.[6] The RIJCOSX[7] approximation was utilized throughout to expedite the computations. Transition states were computed using the nudged-elastic-band method.[8] Additionally, to further refine the outcome, the single point-energy of the entire system was computed using the PBE0 functional and a higher valance polarised triple zeta basis set (def2-tzvp). Using the same degree of theory, all of the minima and transition states on the potential energy surface were confirmed. The conductor-like polarizable continuum model[9] was used to describe the solute-solvent interaction. The dielectric constant and refractive index of the solvent were taken as 17.0585 and 1.4437, respectively.

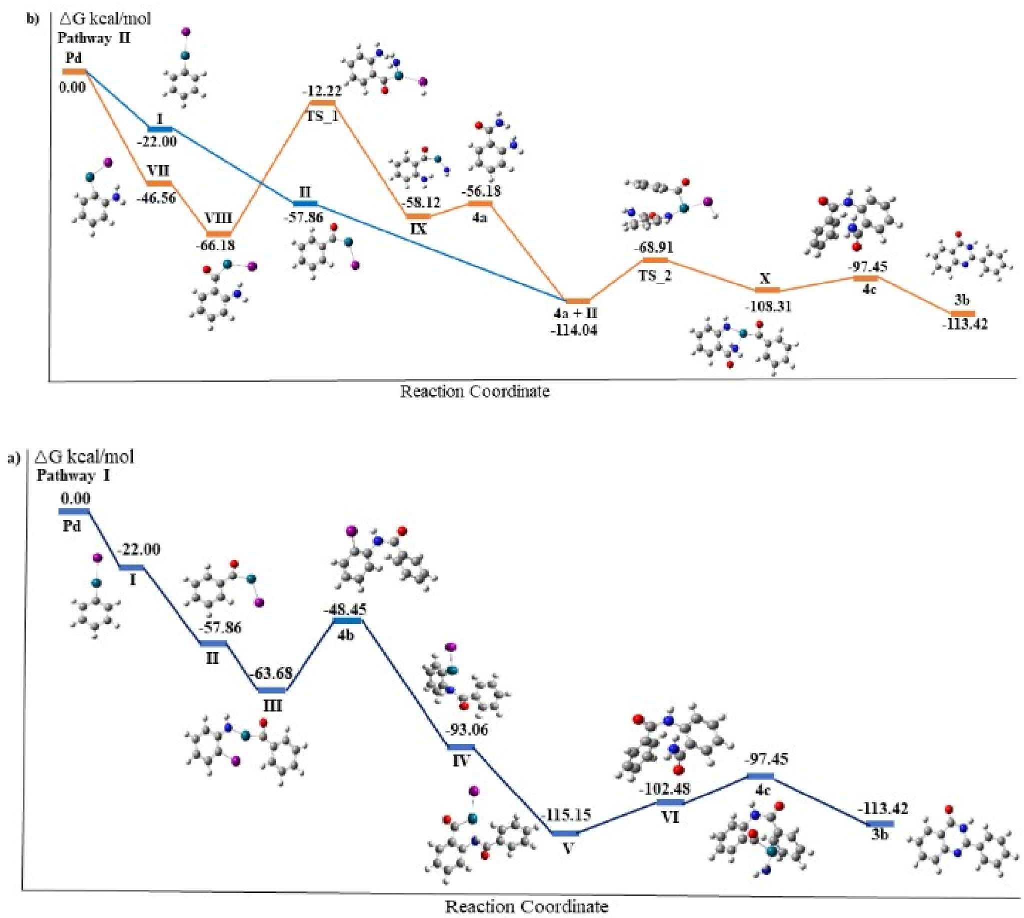


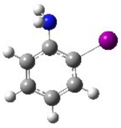
Figure S5. DFT calculations for desired product formation a) via the formation of N-(2-iodophenyl)benzamide as reaction intermediate b) via the formation of 2-aminobenzamide as reaction intermediate

Energies

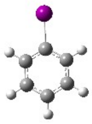
All energies are in hartee

SPECIES	E_{elec}	G_{solv}	H_{solv}
1a	-584.50339424	-584.44476791	-584.38391352
2b	-529.18466560	-529.14014464	-529.08293974
3b	-723.75496374	-723.60111653	-723.52073929
4a	-456.00037233	-455.90450615	-455.83866658
4b	-928.65667167	-928.51926719	-928.43329321
4c	-800.14213161	-799.96755717	-799.87811921
CO	-113.23209685	-113.25420004	-113.22253277
I	-657.09514938	-657.05598408	-656.99323136
II	-770.41247375	-770.36733415	-770.29391287
III	-1056.55482419	-1056.42431468	-1056.33001816
IV	-1056.60538200	-1056.47113321	-1056.37827562
V	-1169.90177925	-1169.76054233	-1169.66121985
VI	-928.02293570	-927.85634803	-927.75805658
VII	-712.45106865	-712.39974356	-712.32742005
VIII	-825.74435952	-825.68522296	-825.60683739
IX	-583.87545267	-583.78838512	-583.71265876
X	-928.03497171	-927.86563450	-927.76860278
TS2_1	-882.19583981	-882.11227957	-882.02269469
TS2_2	-1226.36851758	-1226.19991152	-1226.09229312
KI	-897.58676182	-897.62272010	-897.58098942
$KHCO_3$	-864.09839042	-864.11336225	-864.06099355
K_2CO_3	-1463.308014018	-1463.33902444	-1463.27984468
Pd	-127.85736603	-127.88077320	-127.85417426
NH_3	-56.52138052	-56.51305582	-56.48184992
H_2O	-76.38778668	-76.39189549	-76.36136048

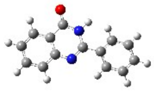
Optimized geometries



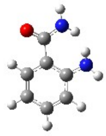
1a



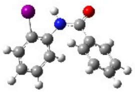
2b



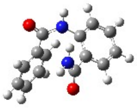
3b



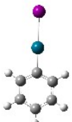
4a



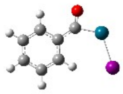
4b



4c



I



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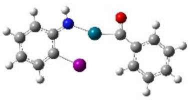

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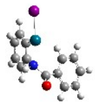

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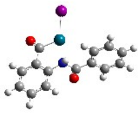

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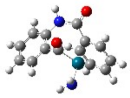

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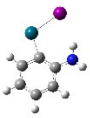
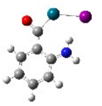
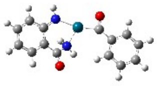


VII

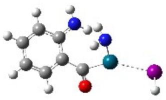


VIII

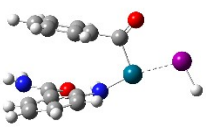
IX



X



TS_2_1



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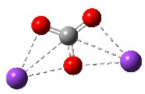

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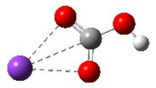
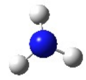
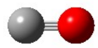


$KHCO_3$

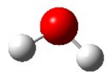
KI



NH_3



CO



H_2O

Coordinates

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2b

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N	1.12280532031339	1.57594022736924	0.08861198725693
O	0.32825163963556	5.52658515699408	-0.47672720409655
H	2.52034139919352	4.44331525311427	-0.40519785348674

4a

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C	-0.23858845113881	3.82875481220255	0.13689272728374
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H	-2.13721777895596	0.53227617064838	-0.58146238389943
H	0.30409240142361	0.51390073785524	-0.32741543032430
H	-2.15302803597485	4.75220634193633	0.14040624769029
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N	1.85385809361551	2.54890629200189	0.11749680227399
H	2.21008708715986	1.61449378562569	0.24917260055095
H	2.29494634649911	3.21067562148375	0.73802549452319
C	0.37928111605417	5.16579228399796	0.37286861034235
O	-0.22945317475759	6.05457357671313	0.96167026478864
N	1.62364556573562	5.36178538354740	-0.10510714562737
H	2.01523489651692	6.28756579710751	-0.04217656628826
H	2.05464388013944	4.70239753124369	-0.73211794318643

4b

C	-1.15013730196404	-0.15342600926163	0.51991299176207
C	0.00293156684930	-0.02204605938403	1.27981269362877

C	1.16574905541721	0.51571416590941	0.72874062245658
C	1.14460862580434	0.92253272624720	-0.60298080428864
C	0.00603298663904	0.76693708796476	-1.37242066228649
C	-1.14491684501969	0.23219524887936	-0.81135948422460
H	-2.04583736027580	-0.57039268904920	0.96304192861236
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N	2.32580678240349	0.67214978813502	1.50320357973962
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C	4.36618927126267	-2.33277510448522	-2.05255100742835
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C	4.87019183198823	-0.30967375643771	-0.85897905920156
C	3.82099863808303	-0.56458131296373	0.01779663091241
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H	2.24962463867628	-1.93012202701110	0.55841158763161
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4c

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C	0.48750453829993	-1.83680930079916	-1.50838949150929
C	1.32882420950545	-0.83440801725667	-2.00209207177944

C	0.98827590913578	0.50226868979400	-1.81642693785007
C	-0.16194206794513	0.85162898082094	-1.13222258568486
C	-0.97513639515721	-0.13756355433665	-0.59586411855659
H	-1.26868290885610	-2.25264929966598	-0.37834432010316
H	1.65440037165688	1.26637820096254	-2.20119275377253
H	-0.41088396309703	1.89820363798726	-1.00033776248318
H	-1.86845404562018	0.12607253015600	-0.04239189373610
N	2.52324575554963	-1.10995084608577	-2.69856156534248
C	3.55386076201765	-1.93008624975513	-2.35825214019274
O	4.44466002797072	-2.16444257572641	-3.16347375970286
C	3.38754764159993	-2.31020552667834	1.40326975702678
C	3.78691047777610	-3.63197861706773	1.54494824121891
C	4.10204837024647	-4.38724802053375	0.42230027380071
C	4.01672310863052	-3.82112597833159	-0.83815461415992
C	3.58950464958591	-2.50487042683459	-0.98576680479730
C	3.28057380868114	-1.74815814803794	0.14078090004948
H	3.15614403185402	-1.71416106189463	2.27842509161452
H	3.85775162857092	-4.07330364410819	2.53265682368080
H	4.41720193909492	-5.41854732075632	0.53129041497896
H	4.26694179595271	-4.39768279413461	-1.72077627363109
H	2.97023849593995	-0.71557105786807	0.03731980203384
H	2.66976533284589	-0.60458473524790	-3.56203429017483
O	0.42486777781111	-4.09603688806960	-0.79618285015648
C	0.68497845033909	-3.31058762924380	-1.69985972135965
N	1.09521531728002	-3.71508280485693	-2.91014241644171
H	1.26182092860667	-3.06956083664640	-3.66198430198636
H	1.22185863087435	-4.69947923806769	-3.07961311134804

I

C	-2.38008408694202	0.59746868859193	0.16235528431595

C	-0.98660257352311	0.57913402010683	0.12199455732453
C	-0.34758251248669	1.79697453411509	0.09537067478072
C	-0.97807750629806	3.01954543435974	0.10004019311242
C	-2.37164570521223	3.01163155440471	0.14065119450813
C	-3.06146212726286	1.80712427761604	0.17181600637446
H	-2.92225400697500	-0.34108831450099	0.18609930331712
H	-0.43827842727767	-0.35948399648825	0.11313882345183
H	-0.42323661382391	3.95402611519776	0.07451735555792
H	-2.90735454171559	3.95415859204855	0.14747590716550
H	-4.14487623644823	1.81117332460810	0.20363056002540
Pd	1.54874820683493	1.79098861031719	0.06641505827608
I	4.27665653113044	1.78924412962329	0.02606363178992

II

C	-1.76971692125370	0.45985724043777	0.11216684621434
C	-0.54396486239969	1.09952976115776	0.12979256525011
C	-0.49975645884489	2.49028295756057	0.16073390618123
C	-1.67870819383435	3.24533326683810	0.17272719254785
C	-2.89664315579992	2.59636944759526	0.15113495348821
C	-2.94128385245174	1.20599327749302	0.12145083777231
H	-1.81276156112652	-0.62228525934448	0.09014528309032
H	0.38136544744000	0.53604078842576	0.12144624832244
H	-1.62188931587015	4.32678812602345	0.19703594278008
H	-3.81467631828721	3.17133919779737	0.15770881658833
H	-3.90013779377968	0.70068953641875	0.10523559109017
Pd	2.56618542637248	2.74676512161871	0.12775130643432
I	3.17874954638409	0.27634859082792	-0.05213821080272
C	0.75384686466447	3.21352339400635	0.18513702161047
O	0.97902613878683	4.39284406314366	0.25333350943252

III

C	-2.04435042411077	0.08186179830407	0.22263043827165
C	-0.70982250993823	0.41796894111373	0.10486521952189
C	-0.19361496626782	1.72377989565948	0.23399429178929
C	-1.18344696795923	2.70634300431997	0.50350656724726
C	-2.51897361772664	2.38922777342531	0.62526238919748
C	-2.97324953751253	1.07690728827191	0.48705375849371
H	-2.36021415221552	-0.94958105790416	0.11124319632165
H	-0.85514411263042	3.73526685265475	0.61693647657609
H	-3.22867243257867	3.18282193134823	0.83521249740152
H	-4.02343068118158	0.83218866258576	0.58453606918409
I	0.70477680410194	-1.08191021176489	-0.27985243026620
N	1.11557142941880	1.99506854505960	0.11172259840816
Pd	2.61640310687169	0.60571118891355	-0.23009091731202
C	4.32093258616486	-0.18119428193799	-0.47738360739818
O	4.81971331514910	0.92526052442560	-0.35292749466369
C	4.96583315156540	-3.80366774144062	-1.11920499897058
C	6.35440794358490	-3.82622226944817	-1.09090397926044
C	7.07643491794255	-2.65888373277361	-0.86442827460577
C	6.41084224419140	-1.46435448350644	-0.66847251292354
C	5.01241426231055	-1.44030463570572	-0.69275012264822
C	4.29386463281534	-2.61166920888298	-0.91607471210857
H	4.40970493169257	-4.71601140531648	-1.29753951320228
H	6.88026817582226	-4.76153572171750	-1.24608741902471
H	8.15949031358618	-2.68533174970082	-0.84233891653199
H	6.95705843882512	-0.54561742383363	-0.49134722085329
H	3.21173305504052	-2.58204277678873	-0.93871942306805
H	1.31432169303812	2.97734532463980	0.24003050042479

IV

C	-0.82170501707284	-0.20325741083154	0.28993670363414
C	0.30982405247040	-0.12668822079185	1.07438422219036
C	1.33092936060828	0.74980333833334	0.78015683052132
C	1.28711876840623	1.59907683980297	-0.30431079369846
C	0.15134217077414	1.53529803089212	-1.10583662894559
C	-0.88102369149672	0.65250047747591	-0.81037658354495
H	-1.62790752769275	-0.89163284695083	0.50460666932417
H	2.10277431069000	2.27907487791759	-0.52380134705147
H	0.07042175327538	2.18261559582925	-1.97069863976478
H	-1.75698934033071	0.62320965393507	-1.44902080580785
N	2.39456905460483	0.63298547925378	1.76534829615398
C	3.73647363384654	0.41129275684320	1.38790681047313
O	4.61941968635378	0.90592044386954	2.05078226254582
C	3.57469108076961	-2.28035641753685	-1.26784038456436
C	4.65523436319222	-1.91159287269965	-2.05781088217223
C	5.41738770955619	-0.80059298138940	-1.72016491017880
C	5.10082947633365	-0.06194536068961	-0.59317835101117
C	4.00283426325284	-0.41547540367066	0.18885947764406
C	3.24060980641600	-1.53008681138223	-0.15281161362146
H	2.98930592832417	-3.15698271259586	-1.51901793229162
H	4.90725203911031	-2.49490744902234	-2.93613454025291
H	6.26159094665111	-0.51163582763759	-2.33519869591073
H	5.69242186553149	0.80246942796824	-0.31608883735978
H	2.40198791639387	-1.83204882429756	0.46407843041194
H	2.36983646639710	1.36118637279047	2.47596947727963
Pd	1.08666724383183	-0.98760077180231	2.60067723392583
I	-0.78837767019717	-2.59285052361317	3.21985052207180

V

C	-4.87789551074117	1.70931679062413	-1.10688889458029

C	-3.88772271171601	0.74552915065379	-1.05327239410664
C	-2.63933467006861	1.08607429216809	-0.53852933011484
C	-2.39756362035384	2.37410720469473	-0.09291563868088
C	-3.38041961412812	3.34277736797299	-0.14678225202004
C	-4.62521341810292	3.00045665498940	-0.65482550394855
H	-5.85510376113429	1.45624122313230	-1.50014957554528
H	-4.06742563922903	-0.26580641328500	-1.39562244080197
H	-3.17489094597406	4.34890262658232	0.19928294304982
H	-5.40601378105584	3.75036771119728	-0.70123373833891
C	1.29825964257922	3.75287211159596	1.58760190186470
C	2.43880548115284	4.31600605006985	2.13533689608481
C	3.24760496991392	5.13948412443440	1.36475629004650
C	2.91798693122623	5.39893598947675	0.04012803550305
C	1.78062521136936	4.83857335982989	-0.51086626632193
C	0.95958259146986	4.01513918039286	0.25911420891958
H	0.69502657125881	3.10818227992324	2.21736820982709
H	2.69572369752241	4.10967309578139	3.16728405825016
H	4.13831957444005	5.58011370896619	1.79777909760058
H	3.55038845304797	6.03963918373725	-0.56279620623537
H	1.51061204104096	5.03234038915559	-1.54129411020189
C	-0.24514181505692	3.46570535394151	-0.40116432764905
O	-0.52648361813665	3.64813453688545	-1.55823168035229
N	-1.08603554795717	2.64544040159238	0.42198636301298
H	-1.12056785604349	2.96879426683676	1.38556413860927
C	-1.55173869909244	0.08072907590230	-0.45001903408445
O	-1.61095418482718	-1.03047769007122	-0.86343931398777
Pd	0.00393418546833	0.79190595096300	0.43823125366156
I	1.67929485312783	-1.17617652814372	0.68915927054007

VI

C	-0.87652691006532	-0.40546783206869	-0.13591281707711
C	0.29862537684183	-0.22365138572791	0.58191287031359
C	0.92136407253392	1.02339739599506	0.60303697568745
C	0.32776883238273	2.09560199121924	-0.04932946155421
C	-0.86109419144518	1.91928731693917	-0.73838571025724
C	-1.45939227238757	0.66705691637894	-0.79065134524634
H	-1.33649641725420	-1.38671706352457	-0.16589721179482
H	0.81312081663348	3.06446510378086	-0.01756537693490
H	-1.31490342310425	2.76155100757553	-1.24709982448823
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N	2.11987748582608	1.21832179483065	1.32082434105163
C	3.26340054646108	0.49211476568101	1.27224520717119
O	4.12855147172599	0.62109806302189	2.12386128630166
C	3.72714364681705	-0.73259319197202	-2.28411650390043
C	4.49231935041712	-1.88151733263862	-2.06400347869154
C	4.76897750331865	-2.30102413726974	-0.77605387355144
C	4.28880604148374	-1.57067246950773	0.32149885640577
C	3.49500171325868	-0.42549940802776	0.10611680335481
C	3.22345362514846	-0.01810131338312	-1.21931465145480
H	3.52596788142219	-0.40077107394721	-3.29540259516011
H	4.87505499379900	-2.44354936718291	-2.90765166298319
H	5.37238860810735	-3.18369760004798	-0.60287471626683
H	4.60925874599678	-1.81367151463906	1.32697817834818
H	2.64178234009565	0.87812023363221	-1.39519844219605
H	2.11535802479546	1.93432557151848	2.03527826754292
Pd	2.11384521548552	-2.28636380730394	0.17646370804517
O	0.68608686502223	-1.62617194003472	2.47748316774632
C	0.89997138750379	-1.36803479189151	1.33121999877747
N	0.90024645625346	-3.84755070842528	-0.05361627280325
H	0.02470051854334	-3.57603130393234	-0.49439758128237

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VII

C -2.08837809745776 1.69665353016232 -0.07150945962216

C -0.71207583432087 1.56612636126978 -0.10645039196522

C 0.14935416297314 2.67832241719085 -0.09326868698413

C -0.49434385110740 3.91124770279119 -0.03065765686702

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C -2.69487512766574 2.94639601847477 -0.01979125797589

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N 1.50636653682624 2.51931886088395 -0.19590883018240

H 1.86539873010663 1.62201952641448 0.08905300339581

H 2.06827457708802 3.30137542843275 0.10961748756246

I 2.47069884363518 5.91491303126650 0.04850528139655

VIII

C -2.26128025161057 1.13744096009969 -0.28317752695884

C -0.89828424697375 1.22800663551254 -0.19276708107206

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C -3.08504176731988 2.26237313103111 -0.10819565862537

H -2.71048559669272 0.17288826743861 -0.49293823767950

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Pd	0.94159951499595	5.97253556179156	0.19677947804842
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H	1.60662326011123	1.66394550150954	0.01680520947753
H	1.57349355783206	3.36098586593534	0.28648596696152
I	3.15537733316424	5.27982301437508	-0.89148444414186
C	-0.61227810005447	4.92023508205244	0.42983828958039
O	-1.15540310906072	5.93700357931553	0.80266839372464

IX

C	-2.18962946768218	1.10839160561112	-0.12833119667159
C	-0.83365745496437	1.29528380056603	-0.18875020530157
C	-0.26522371737345	2.58373415658399	-0.07049000140597
C	-1.16078278809619	3.67327820947802	0.11183466994385
C	-2.55361931708982	3.44497653153909	0.16949327187720
C	-3.07322648428201	2.18558507708860	0.05276760532416
H	-2.58496485391731	0.10275889405677	-0.22281361975371
H	-0.16744115293336	0.45094687069027	-0.32858511238990
H	-3.20100847888113	4.30254801887410	0.31073786461204
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Pd	0.85099467239760	6.05165193341702	0.28454901318000
N	1.06392858835652	2.72856038012940	-0.13572553697486
H	1.64852331442089	1.91948988918492	-0.25174732329636
H	1.50329222809217	3.63549965787312	-0.03910365765451
C	-0.71382899621180	5.01594969029795	0.24518335894023
O	-1.33628397404693	6.05681810769501	0.40316045879111
N	2.72644538203885	5.56670873576800	0.12945206878004
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X

C	-1.54105001600362	2.90401781686214	0.05358959219867
C	-0.65080863671267	2.02291684255120	0.60561558319739
C	0.75601381351269	2.26022177794106	0.60263746879032
C	1.17199110855682	3.52375634514843	0.06565348717641
C	0.23244127985042	4.38901704772366	-0.51967617855311
C	-1.10976060478023	4.10512653547845	-0.53597868717604
H	-2.59950562374142	2.66336933779874	0.06927018694234
H	-1.00275445046383	1.09013645867856	1.03596186426956
H	0.60284327470013	5.31761763276511	-0.93933203612664
H	-1.82039536202150	4.79503405529461	-0.97341080059859
N	1.61433174230827	1.33017553021349	1.02543821312978
C	2.54379348026307	3.99244439615241	0.09421748974975
O	3.01772704515196	4.85557231296056	-0.62138755989626
N	3.39888476932787	3.41189825468186	1.09179689334275
H	4.24578553659713	3.96554481271972	1.16266045715857
H	2.94032551075163	3.37172671338081	2.00047820003820
H	1.13419491864434	0.50034730408118	1.34658162310067
Pd	3.68836970945424	1.38588183828011	0.76035842653912
C	5.48003860119315	0.92670713357509	0.39058448291032
O	5.13349350678377	-0.24699326233692	0.42459835858976
C	6.81026875709629	1.44970712278647	0.13917277633625
C	7.90947515551364	0.58579128350208	0.11769843849803
C	9.17257028842757	1.09512239854782	-0.11600159758792
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C	6.98343526700964	2.81487052006329	-0.08297623441823
H	7.76040142209073	-0.47308789780788	0.29244215645928
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CO

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O -0.65975763849655 -3.33931302887101 -1.87385190832991

O -2.63762880043350 -2.30538768760391 -1.67867719795976

O -0.77177027884143 -1.12934829333895 -1.53028184922959

K -2.75192532780158 -4.87665220155334 -2.02760534058960

H 0.17846151399320 -1.29354030222623 -1.57045133044493

KI

K -0.62905577247081 0.88047080000000 0.15021488000000

I -3.85308104752919 0.88047080000000 0.15021488000000

NH_3

N -2.65325919493804 1.65262589713872 0.00000000544584

H -2.26296039075569 0.71642965138457 -0.00000002368020

H -2.26294312183103 2.12072898467791 0.81081084729601

H -2.26294312247524 2.12072894679880 -0.81081082906166

H_2O

O	0.15538994557158	0.67750594663781	-0.01134225000000
H	1.11626213424527	0.72102173918645	-0.01134225000000
H	-0.12436121981685	1.59781884417574	-0.01134225000000

TS_2_1

C	-2.67572578338311	0.20963343480272	-1.24072297678278
C	-1.52891008578300	-0.55336937495675	-1.28380069838287
C	-0.33082772536552	-0.09668201386944	-0.72236701213879
C	-0.26234870328321	1.18764823232672	-0.14471472468245
C	-1.43877262418249	1.95297592238101	-0.11977229543907
C	-2.61682033268436	1.47098963355924	-0.64835089743916
H	-3.60134090137423	-0.16395631316606	-1.66055392597077
H	-1.53928390232957	-1.53991723433388	-1.73309340699303
H	-1.40151411062705	2.94438280657206	0.31919492378482
H	-3.50594169099212	2.09047701282091	-0.60632970765571
N	0.88729897531223	1.70453323091818	0.37185452760971
C	0.80174100865704	-1.01973752363005	-0.75486247632717
O	1.09568428362022	-1.73456083274064	-1.68960850855504
Pd	2.06875249597706	-1.50275883498584	0.57566358060456
I	4.64530322690139	-2.86096898037693	0.86059027723438
N	1.26107303297239	-0.81300633528997	2.25762349353773
H	3.98227094100915	-4.31478023344535	1.09711135199022
H	1.17953990814519	0.19847908748448	2.17702189560063
H	0.29195626143523	-1.12712516999344	2.27550477480339
H	1.76527433202800	1.26977923373132	0.14358426421438
H	0.92259139394678	2.69796425219172	0.52602754098702

TS_2_2

C	-2.35605866544069	-1.43818309862714	-0.19111759305887
C	-2.32894006282837	-0.68191801067101	0.97060040170377
C	-1.95628653110907	0.65443769277006	0.92572034959909
C	-1.61375149129965	1.22637813173226	-0.29241789849045
C	-1.62537416764791	0.47129802905592	-1.45925805906549
C	-2.00491631048720	-0.85918542228864	-1.40455101624130
H	-2.64172959666548	-2.48307111984337	-0.15201645846312
H	-2.59305176577624	-1.13207732755960	1.92069320106666
H	-1.93069433765222	1.24909145891918	1.83141974340508
H	-1.33253805947445	0.92148763200346	-2.40070460865761
H	-2.01834233114983	-1.44921370710160	-2.31352820979179
I	0.07112293607802	5.69962753968511	0.25090042440877
Pd	0.62982684528626	3.11977468130052	-0.20209509505514
C	-1.24578158233722	2.66624747362758	-0.34334628779292
O	-2.04433931403927	3.55402106685118	-0.45106908203979
C	1.52085526014278	-1.90536565251088	2.05126729069044
C	1.43295499560343	-0.59308789050599	2.52208541230297
C	1.53568799063343	-2.11908751849625	0.68934665823999
C	1.47522672161795	-1.06857756759761	-0.23318549120977
C	1.43042296955252	0.27491340347623	0.24190380701532
C	1.38582383390232	0.45987480519143	1.64299802922528
N	1.44705203120584	1.35396382372472	-0.57376642760949
H	1.32011243946808	1.48019907933398	2.00833633980385
H	1.40779418333756	-0.39929951890908	3.58931879824644
H	1.58200209599708	-2.73982488522302	2.73899121570187
H	1.62260729110434	-3.13797193315409	0.32897091810051
H	1.53135146709339	6.30960904401505	0.59882245704835
H	1.43731743447668	1.05797137103672	-1.54488733458827
C	1.43914400424290	-1.35631001435425	-1.68201190782308
O	1.72704401117678	-0.51593978608078	-2.54251353128881

N	1.08529874990465	-2.60510531379191	-2.05605892105103
H	0.62362549931585	-3.23621473644563	-1.42614968422661
H	0.98653345576770	-2.77846172956256	-3.04269744010481

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