Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

TiO_2 (P25) nanoparticles catalyzed C-alkylation and quinoline synthesis *via* borrowing hydrogen method[†] [‡]

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Keywords: C- alkylation, TiO_2, borrowing hydrogen; hydrogen auto-transfer; quinoline.

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[†] Supporting information is available for this paper

[‡] This paper honors the memory of our wonderful co-author, Professor M. Sasidharan, who died prematurely due to COVID-19.

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General information

The catalytic reaction's chemical components were all sourced from commercial suppliers. This was not subjected to any additional purification prior to use. Titanium dioxide (TiO_2, P25) nanoparticles (21 nm size) with 99.9% purity were purchased from Sigma-Aldrich. Benzyl alcohols, acetones, and their substituted compounds were obtained from various chemical sources, like Sigma-Aldrich, Tokyo Kasei Industries (TCI), and Avra Chemicals. Solvents (hexane, petroleum ether, and ethyl acetate) were received from Avra Chemicals. The solvents were dried using a standard procedure. C-alkylation and quinoline synthesis reactions were achieved in an Ar atmosphere. a 15-mL reaction tube made with quartz submerged in an oil bath (silicone oil), coupled with an inbuilt thermocouple that tracks temperature and a magnetic stirrer sensor to regulate stirring speed. A Bruker BBFO (500 MHz and 400 MHz) spectrometer was used to record ^{1}H and ^{13}C NMR signals. Spin-spin coupling constant (J) is mentioned in Hz, chemical shift (δ) is mentioned in ppm, and an internal standard (TMS) and solvent ($CDCl_3$) are employed in the spectrometer. An Agilent 7890-B with a 30-meter capillary column (OV-101) and equipped with a flame ionization detector (FID) was used for GC analysis, and Dodecane (30 μL) served as the external standard for the GC's product analysis.

Catalyst Characterization

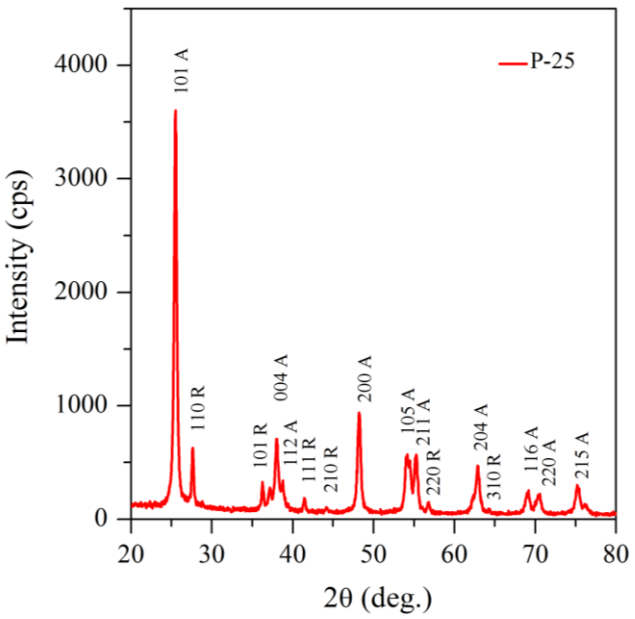


Figure. S1. XRD pattern of the commercial TiO_2.

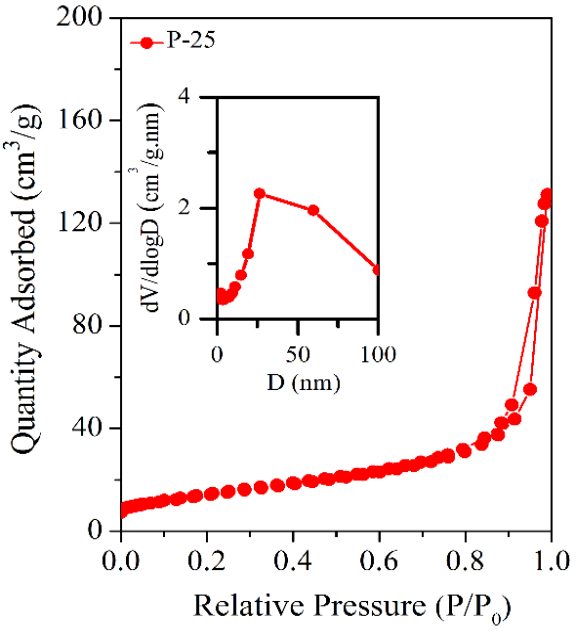


Figure. S2. BET isotherms and BJH pore-size distribution (inset) of TiO_2 catalyst.

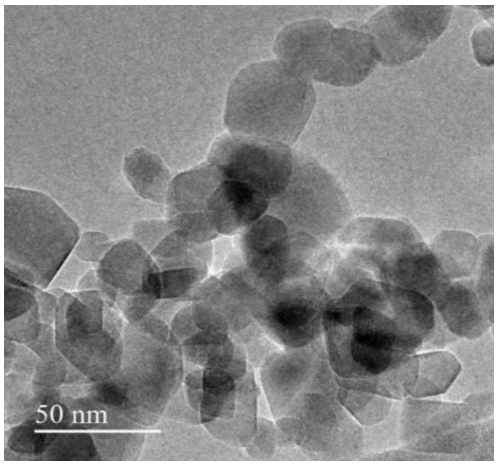


Figure. S3. TEM image of TiO_2 (P25) catalyst.

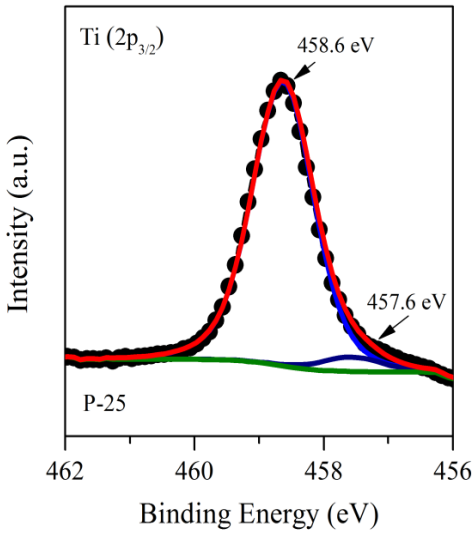


Figure.S4. Core-level XP spectra of TiO_2 (P25).

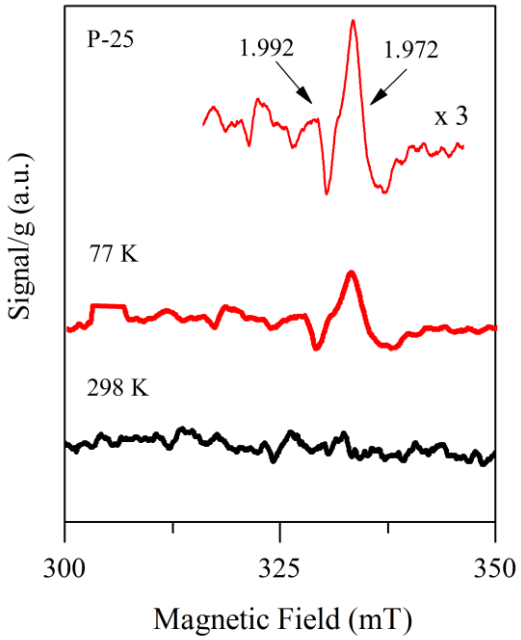


Figure. S5. EPR spectra of TiO_2 (P25).

Catalyst recyclability

The TiO_2 recovered in the first reaction run was properly washed using ethanol and milli-Q water to remove the organic products or solvent molecules clogging the catalyst's surface. It was vacuum dried at 120 °C for 2 h. Following that, the catalytic reactions were furnished with standard reaction conditions. After the reaction was completed, the reaction tube was cooled to room temperature, and the TiO_2 was centrifuged and washed properly with milli-Q water and ethanol. The recovered catalyst was vacuum dried in a vacuum oven at 120 °C for 2 hours. This complete process must be repeated each time before the next reaction run begins. This cycle of reaction was repeated six times. Silica gel column chromatography (hexane-ethyl acetate solvent method) is used to obtain the yield of pure products.

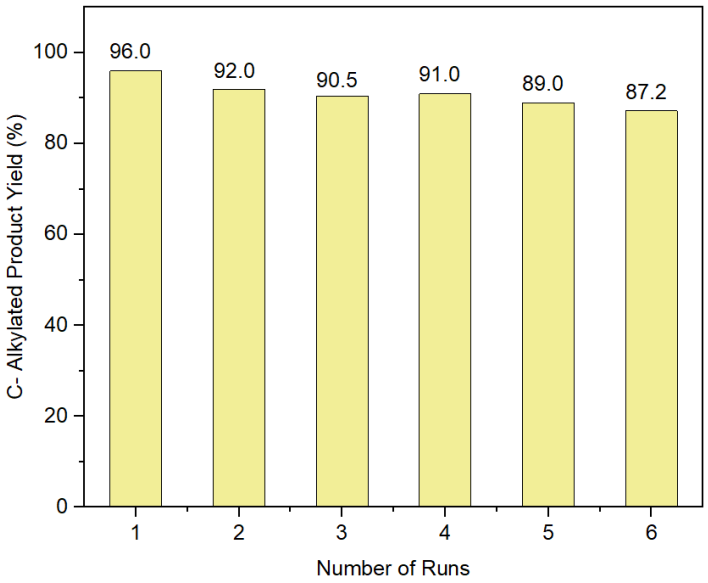
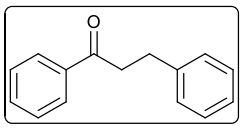
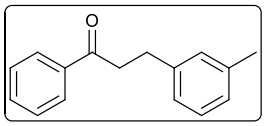
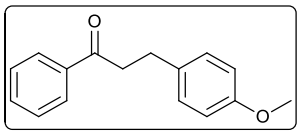
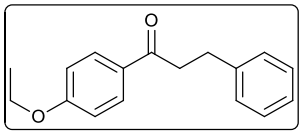
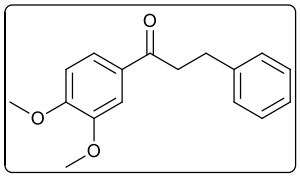
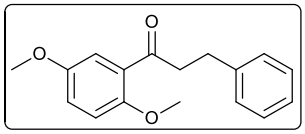
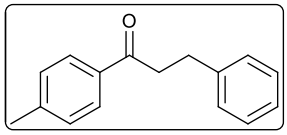
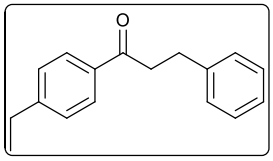
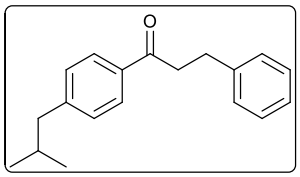
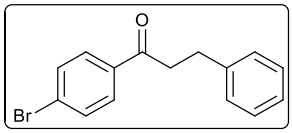
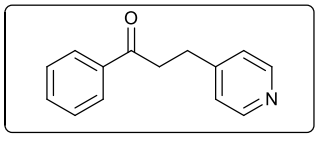


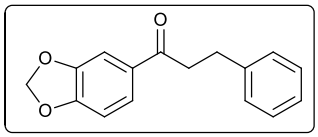
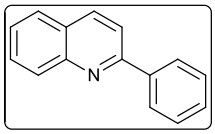
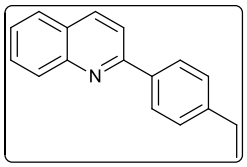
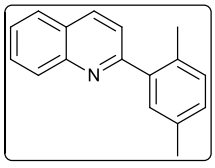
Figure. S6. Recyclability test of TiO_2 catalyst to C-Alkylation reaction.

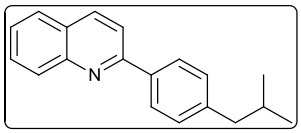
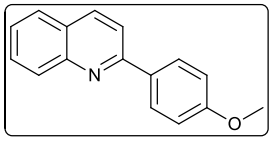
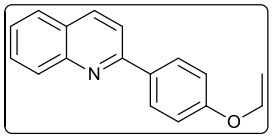
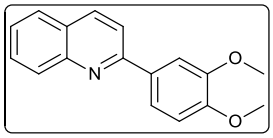
^{1}H and ^{13}C NMR data

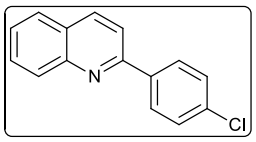
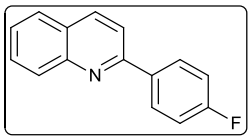
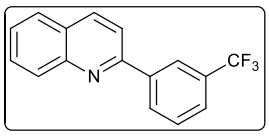
	**1,3-diphenylpropan-1-one (3aa)**[1] prepared by standard procedure with a yield of 96%, Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 7.8(d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.19 – 7.08 (m, 3H), 7.06 (t, *J* = 7.0 Hz, 1H), 3.13 (t, *J* = 7.7 Hz, 2H), 2.92 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.24, 141.40, 136.90, 133.17, 128.70, 128.64, 128.55, 128.13, 126.24, 40.51, 30.19.
	**1-phenyl-3-(m-tolyl)propan-1-one (3ba)**[2] prepared by standard procedure with a yield of 97%, white solid.**^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 7.95 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.09 – 6.95 (m, 3H), 3.33 – 3.22 (m, 2H), 3.08 – 2.92 (m, 2H), 2.32 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.37, 141.24, 138.15, 136.83, 133.09, 129.26, 128.62, 128.46, 128.07, 126.90, 125.41, 40.58, 30.07, 21.43.
	**3-(4-methoxyphenyl)-1-phenylpropan-1-one (3ca)**[2] prepared by standard procedure with a yield of 89%, Yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H), 3.30 (t, *J* = 7.7 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.43, 158.01, 136.90, 133.34, 133.09, 129.41, 128.64, 128.08, 113.96, 55.30, 40.75, 29.30.
	**1-(4-ethoxyphenyl)-3-phenylpropan-1-one (3ab)**[2] prepared by standard procedure with a yield of 81%, Yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 7.89 – 7.80 (m, 2H), 7.24 – 7.19 (m, 2H), 7.17 (dd, *J* = 6.3, 1.8 Hz, 2H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.86 – 6.77

	(m, 2H), 4.00 (m, *J* = 7.0 Hz, 2H), 3.24 – 3.09 (m, 2H), 3.05 – 2.89 (m, 2H), 1.35 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.88, 162.91, 141.52, 130.35, 129.77, 128.54, 128.47, 126.11, 114.17, 63.77, 40.14, 30.36, 14.72.
	**1-(3,4-dimethoxyphenyl)-3-phenylpropan-1-one (3ac)** prepared by standard procedure with a yield of 97%, Yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 7.60 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.32 (dd, *J* = 17.0, 9.8 Hz, 3H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.95 (d, *J* = 6.3 Hz, 6H), 3.32 – 3.24 (m, 2H), 3.12 – 3.04 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.96, 153.24, 149.01, 141.46, 130.09, 128.56, 128.48, 127.58, 126.97, 126.15, 122.70, 110.11, 56.07, 40.03, 30.46.
	**1-(2,5-dimethoxyphenyl)-3-phenylpropan-1-one (3ad)** prepared by standard procedure with a 72% yielding yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 7.29 (t, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 3H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 3.83 (t, *J* = 21.4 Hz, 6H), 3.31 (t, *J* = 7.7 Hz, 2H), 3.02 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.30, 153.45, 153.13, 141.73, 128.49, 128.42, 128.34, 125.93, 120.08, 113.94, 113.07, 56.04, 55.84, 45.46, 30.52.
	**3-phenyl-1-(p-tolyl)propan-1-one (3ae)** [2] prepared by standard procedure with a yield of 88%, Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.20 (m, 7H), 3.33 (t, *J* = 7.4 Hz, 2H), 3.22 – 3.07 (m, 2H), 2.46 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.90, 143.89, 141.49, 134.45, 129.37, 128.60, 128.52, 128.25, 126.19, 40.39, 30.27, 21.71.

	**1-(4-ethylphenyl)-3-phenylpropan-1-one (3af)**[2] prepared by standard procedure with a yield of 76%, Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.16 (m, 6H), 7.13 (t, *J* = 7.2 Hz, 1H), 3.24 – 3.15 (m, 2H), 3.03 – 2.94 (m, 2H), 2.62 (m, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.98, 150.07, 141.44, 134.59, 128.54, 128.46, 128.31, 128.14, 126.13, 40.41, 30.23, 28.97, 15.26.
	**1-(4-isobutylphenyl)-3-phenylpropan-1-one (3ag)**[2] prepared by standard procedure with a yield of 83%, Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.22 (dd, *J* = 10.1, 4.7 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.13 (dd, *J* = 10.7, 7.7 Hz, 3H), 3.29 – 3.12 (m, 2H), 3.07 – 2.91 (m, 2H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.81 (dt, *J* = 13.5, 6.8 Hz, 1H), 0.92 (s, 3H), 0.89 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.01, 147.61, 141.45, 134.64, 129.36, 128.55, 128.48, 128.35, 128.07, 126.13, 45.40, 40.41, 30.16, 22.37.
	**1-(4-bromophenyl)-3-phenylpropan-1-one (3ah)**[1] prepared by standard procedure with a yield of 55%, Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 7.0 Hz, 2H), 7.12 (dd, *J* = 35.6, 9.3 Hz, 2H), 3.19 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.23, 141.05, 135.53, 131.94, 129.59, 128.60, 128.43, 128.27, 126.26, 40.45, 30.03.
	**1-phenyl-3-(pyridin-4-yl)propan-1-one (3da)** prepared by standard procedure with a yield of 85%**,** Brown solid. **^{1}H NMR**: (500 MHz, $CDCl_3$, 25°C, TMS) δ 8.49 (dd, J=4.4 Hz, 1.8Hz, 2H), 7.93-7.95 (m, 2H), 7.53-7.57 (m, 1H), 7.43-7.46 (m, 2H), 7.16-7.18 (m, 2H), 3.31 (t, J=7.4 Hz, 2H), 3.05 (t, 7.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.23, 150.42, 149.75,

	136.57, 133.35, 128.72, 128.00, 123.94, 77.28, 77.02, 76.77, 38.85, 29.18.
	**1-(benzo[d][1,3]dioxol-5-yl)-3-phenylpropan-1-one (3ea)** prepared by standard procedure with a yield of 70%, Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.52 (d, J= 7.8Hz, 1H), 7.42 (s, 1H), 7.17-7.29 (m, 5H), 6.8 (d, J= 8.6Hz, 1H), 5.98 (s, 2H), 3.19 (t, J=7.5Hz, 2H), 3.03 (t, J=7.6Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.32, 151.73, 148.20, 141.34, 131.77, 128.53, 128.43, 126.13, 124.26, 107.90, 107.87, 101.84, 40.23, 30.36.
	**2-phenylquinoline (6aa)**[2] prepared by standard procedure with a yield of 94%, White solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 8.13 – 8.04 (m, 4H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.37 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.39, 148.33, 139.72, 136.83, 129.78, 129.72, 129.39, 128.91, 127.64, 127.53, 127.23, 126.34, 119.05.
	**2-(4-ethylphenyl)quinoline (6ab)**[2] prepared by standard procedure with a yield of 84%, white solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.99 (dd, *J* = 18.7, 8.1 Hz, 3H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 2H), 2.60 (q, *J* = 7.5 Hz, 2H), 1.16 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.42, 148.36, 145.78, 137.20, 136.70, 129.72, 129.62, 128.45, 127.62, 127.51, 127.15, 126.12, 118.94, 28.79, 15.63.
	**2-(2,5-dimethylphenyl)quinoline (6ac)**[2] prepared by standard procedure with a yield of 70%, Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 8.13 – 8.07 (m, 2H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 8.3 Hz, 1H), 7.47 (dd, *J* = 15.9, 7.8 Hz, 2H), 7.17 (s, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H).

	^{13}C NMR (126 MHz, $CDCl_3$) δ 160.46, 147.94, 140.56, 135.96, 135.49, 132.74, 130.80, 130.32, 129.61, 129.25,129.27, 127.52, 126.75, 126.36, 122.47, 20.99, 19.86.
	**2-(4-isobutylphenyl)quinoline (6ad)**[3] prepared by standard procedure with a yield of 67%, white solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 8.09 (t, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 2.47 (d, *J* = 7.1 Hz, 2H), 1.93 – 1.77 (m, 1H), 0.86 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.51, 148.31, 143.25, 137.20, 136.71, 129.70, 129.68, 127.47, 127.37, 127.11, 126.11, 118.99, 45.26, 30.31, 22.42.
	**2-(4-methoxyphenyl)quinoline (6ae)**[3] prepared by standard procedure with a yield of 93%, white solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 8.06 (t, *J* = 8.7 Hz, 4H), 7.71 (dd, *J* = 13.4, 8.4 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.83, 156.93, 148.29, 136.68, 132.25, 129.61, 129.52, 128.92, 127.47, 126.93, 125.94, 118.59, 114.25, 55.43.
	**2-(4-ethoxyphenyl)quinoline (6af)**[3] prepared by standard procedure with a yield of 95%, white solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 8.03 – 7.95 (m, 4H), 7.64 (dd, *J* = 11.1, 8.4 Hz, 2H), 7.56 (m, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.33 (m, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.90 – 6.86 (m, 2H), 3.93 (s, 2H), 1.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.24, 156.96, 148.32, 136.63, 132.06, 129.59, 129.53, 128.90, 127.47, 126.92, 125.90, 118.55, 114.77, 63.57, 14.86.
	**2-(3,4-dimethoxyphenyl)quinoline (6ag)** prepared by standard procedure with a yield of 98%, white solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 8.19 (t, *J* = 9.4 Hz, 2H), 7.89 (dd, *J* = 16.5, 5.3 Hz, 2H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.74 (m, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.68

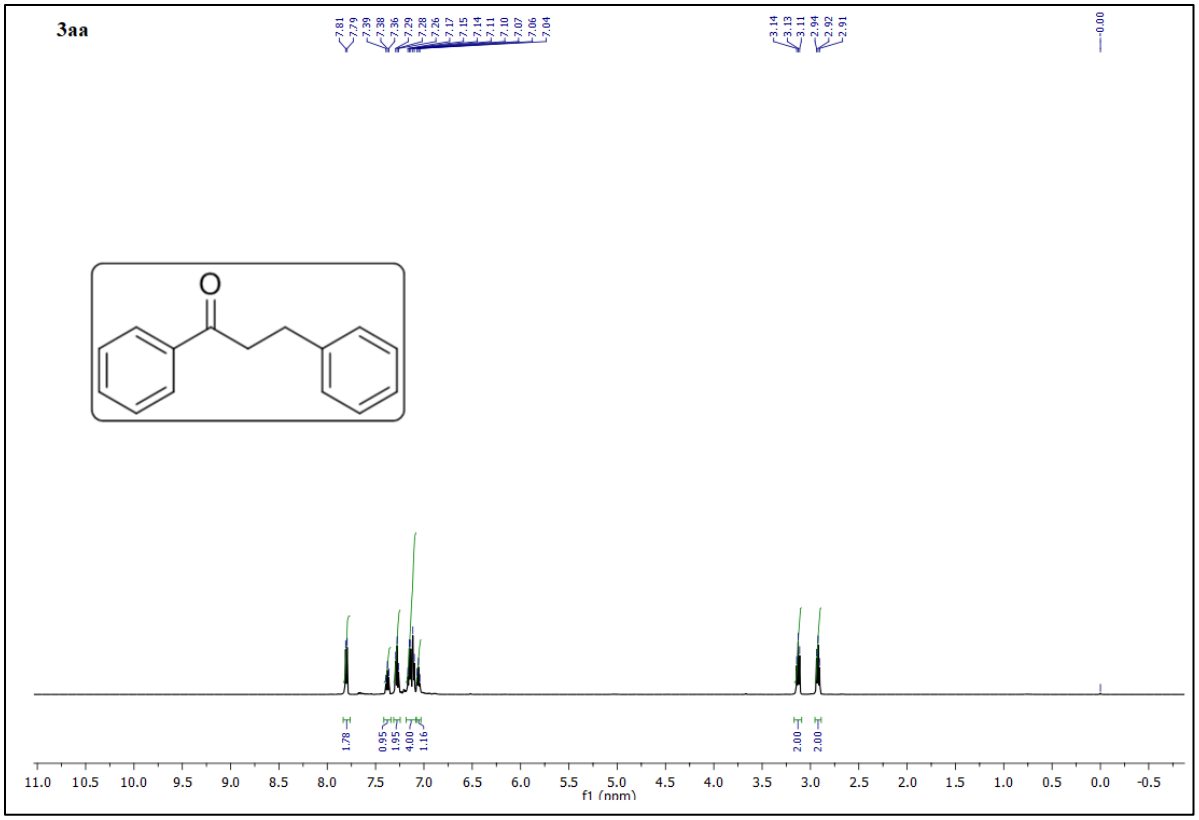
	(dd, *J* = 8.4, 2.1 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 4.07 (s, 3H), 3.98 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.86, 150.38, 149.39, 148.21, 136.69, 132.53, 129.65, 129.49, 127.47, 126.99, 126.03, 120.27, 118.67, 111.02, 110.40, 56.03.
	**2-(4-chlorophenyl)quinoline (6ah)**[3] prepared by standard procedure with a yield of 77%, white solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 8.24 (d, *J* = 8.6 Hz, 1H), 8.14 (m, *J* = 15.2, 8.5 Hz, 3H), 7.88 – 7.81 (m, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.05, 148.24, 138.07, 137.02, 135.56, 129.89, 129.69, 129.05, 128.85, 127.51, 127.24, 126.54, 118.62.
	**2-(4-fluorophenyl)quinoline (6ai)**[1] prepared by standard procedure with a 62% yielding white solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 8.23 (d, *J* = 8.6 Hz, 1H), 8.20 – 8.13 (m, 3H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.22 (t, *J* = 8.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.81, 162.83, 156.32, 148.18, 137.02, 129.87, 129.57, 129.50, 129.43, 127.52, 127.10, 126.41, 118.73.
	**2-(3-(trifluoromethyl)phenyl)quinoline (6aj)**[3] prepared by standard procedure with a yield of 98%, white solid. **^{1}H NMR** (500 MHz, $CDCl_3$, 25°C, TMS) δ 8.42 (s, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.85 – 7.75 (m, 2H), 7.74 – 7.63 (m, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.58, 148.25, 140.37, 137.19, 130.72, 130.01, 129.82, 129.33, 127.54, 127.40, 126.80, 125.92, 125.89, 124.45, 124.42, 118.59.

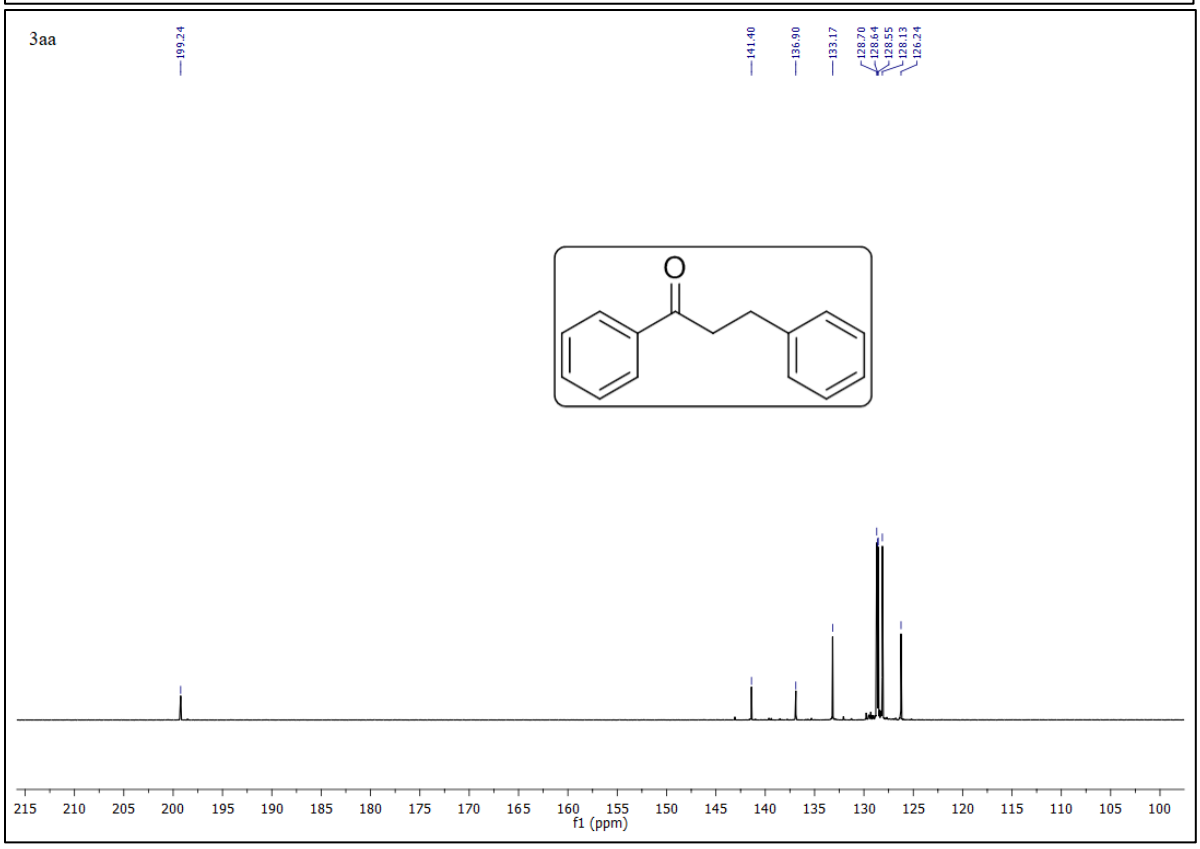
References:

1. R. Sharma, A. Mondal, A. Samanta, N. Biswas, B. Das, D. Srimani, *Adv. cat 364* (2022) 2429–2437.

2. M. Nallagangula, C. Sujatha, V. T. Bhat, K. Namitharan, *chem. commun 55* (2019) 8490–8493.

3. R. Pothikumar, V. T. Bhat, K. Namitharan, *Chem. Commun, 56* (2020) 13607– 13610.


3aa
7.81
7.79
7.39
7.38
7.36
7.29
7.28
7.26
7.17
7.15
7.14
7.11
7.10
7.07
7.06
7.04
3.14
3.13
3.11
2.94
2.92
2.91
0.00
O
1.78
0.95
1.95
4.00
1.16
2.00
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


3aa
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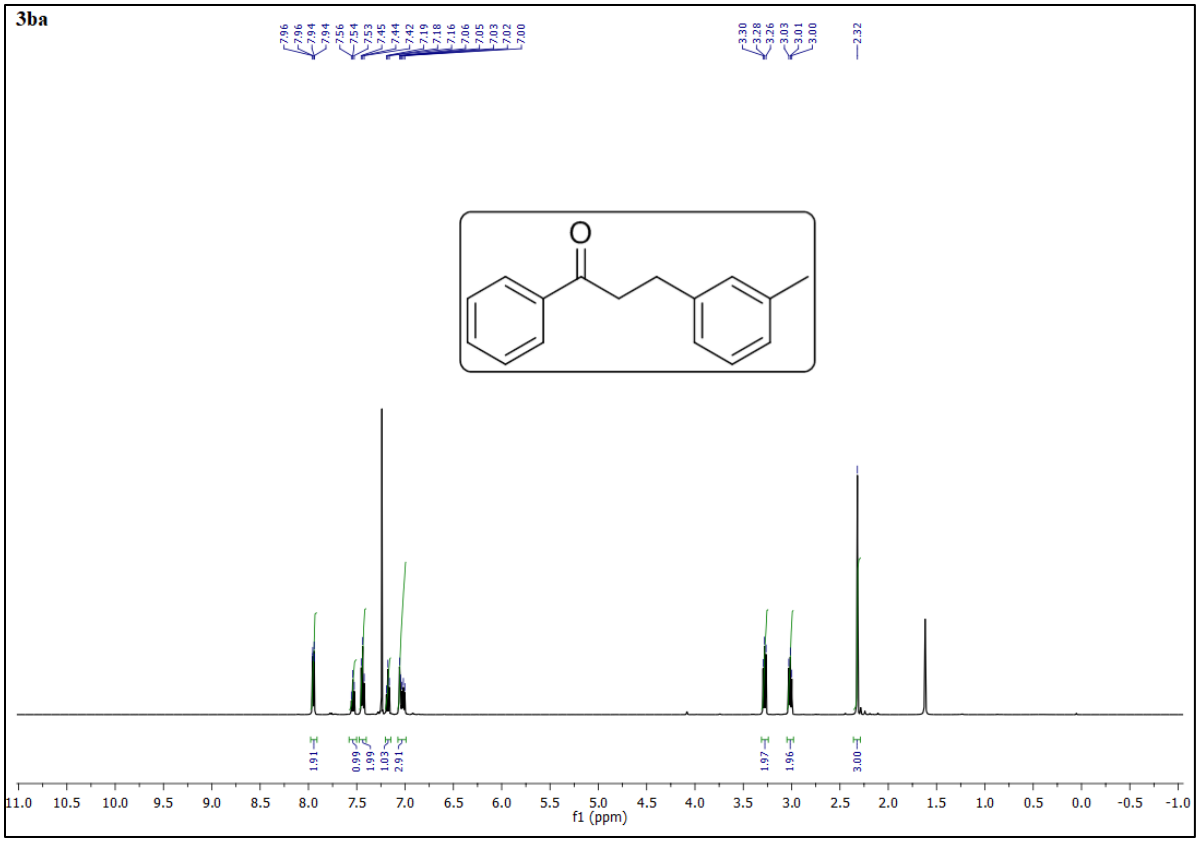
141.40
136.90
133.17
128.70
128.64
128.55
128.13
126.24
O
215 210 205 200 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100
f1 (ppm)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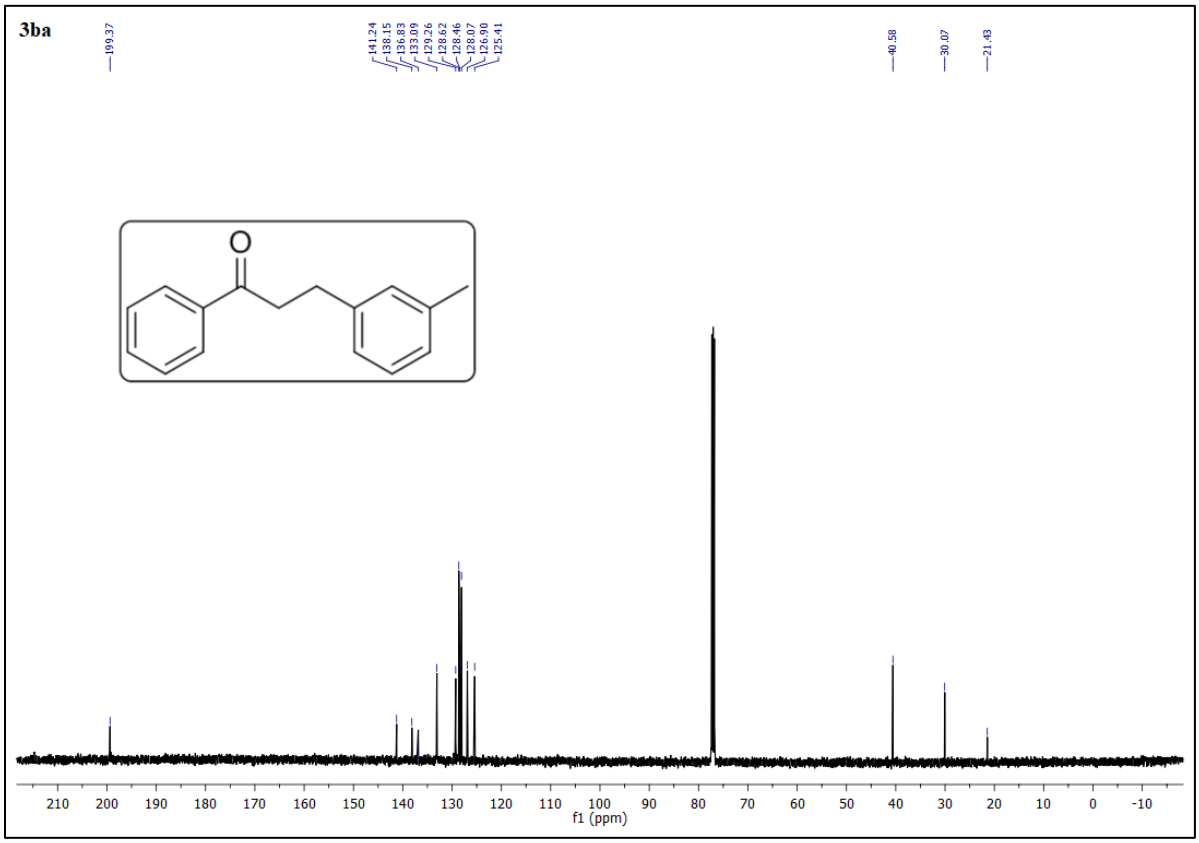
7.96
7.94
7.94
7.56
7.54
7.53
7.45
7.44
7.42
7.19
7.18
7.16
7.06
7.05
7.03
7.02
7.00
3.30
3.28
3.26
3.03
3.01
3.00
2.32
O
1.91
0.89
1.99
1.03
2.91
1.97
1.96
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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141.24
138.15
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133.09
129.26
128.62
128.46
128.07
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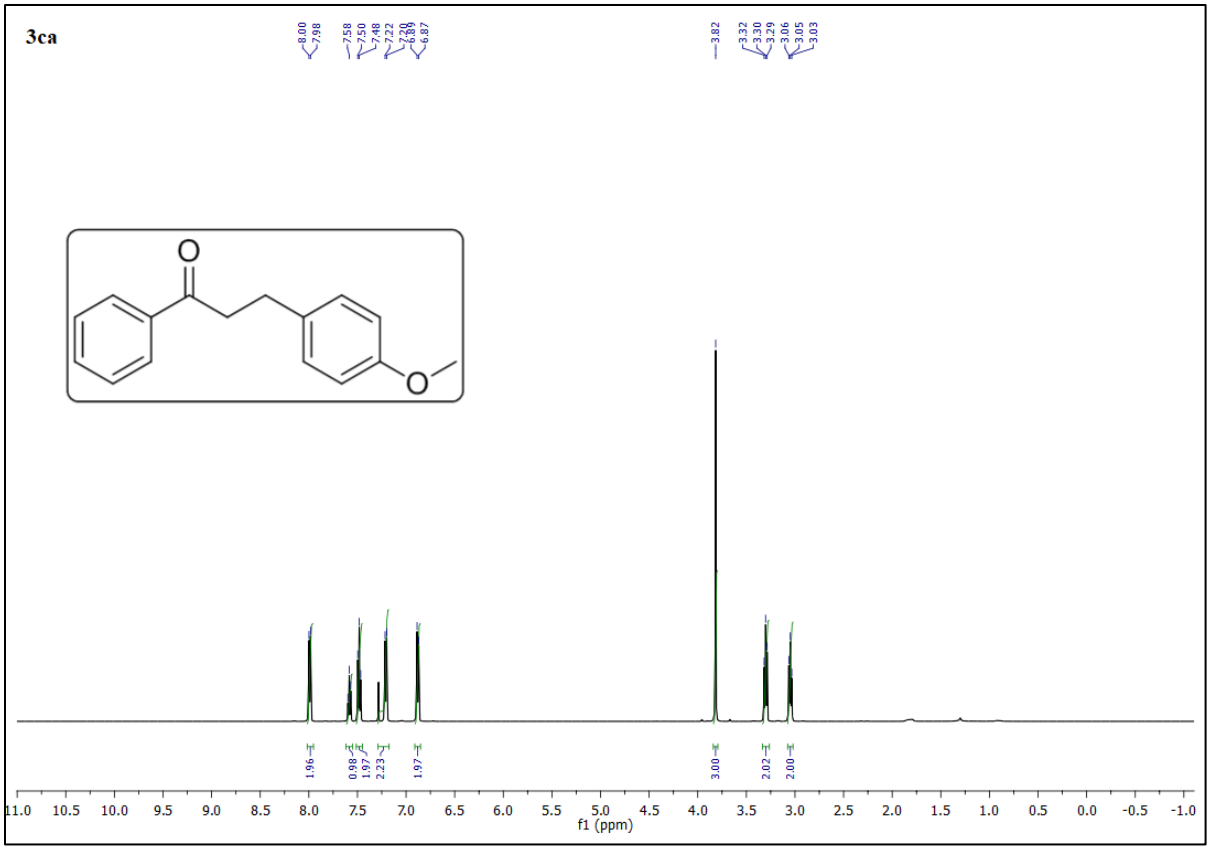
125.41
40.58
30.07
21.43
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.98
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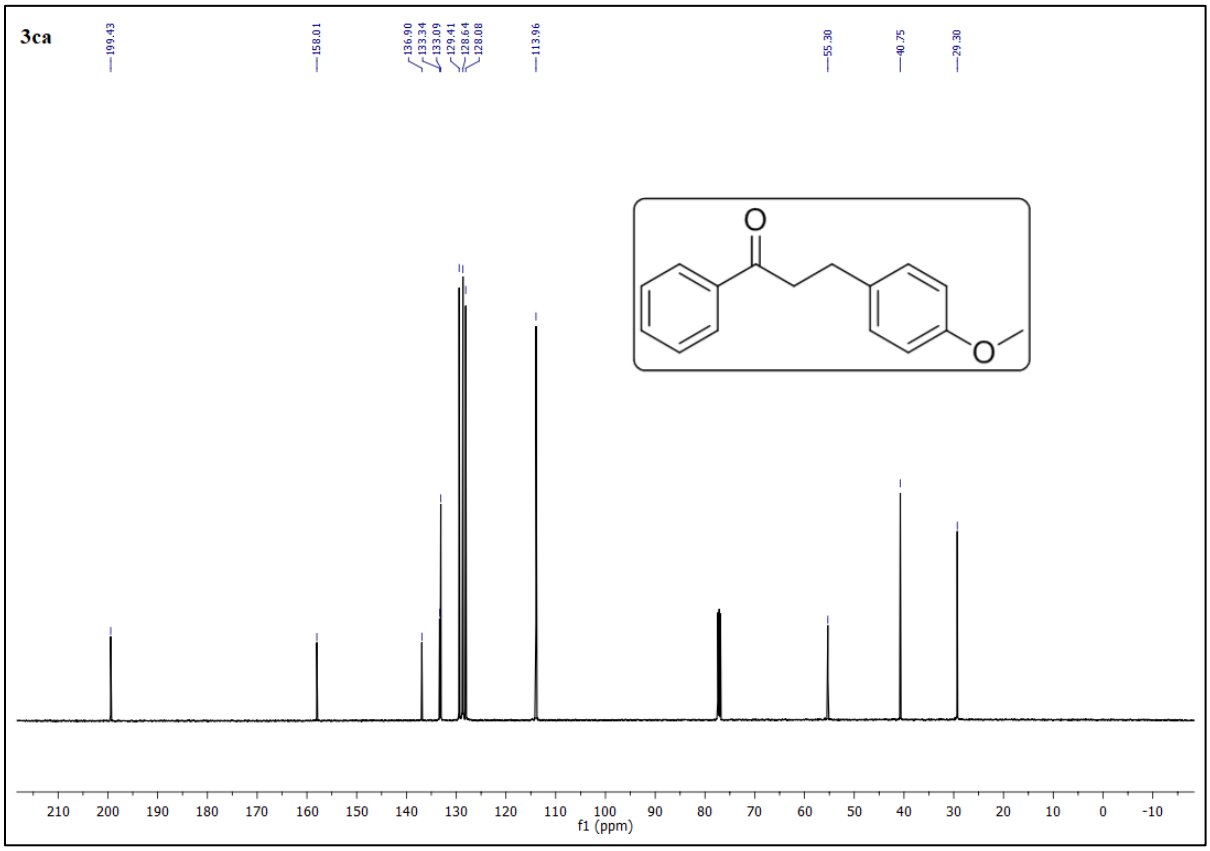
7.48
7.22
7.20
6.87
3.82
3.32
3.30
3.29
3.06
3.05
3.03
O
O
1.96
0.98
1.97
2.23
1.97
3.00
2.02
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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133.09
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128.08
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40.75
29.30
O
O
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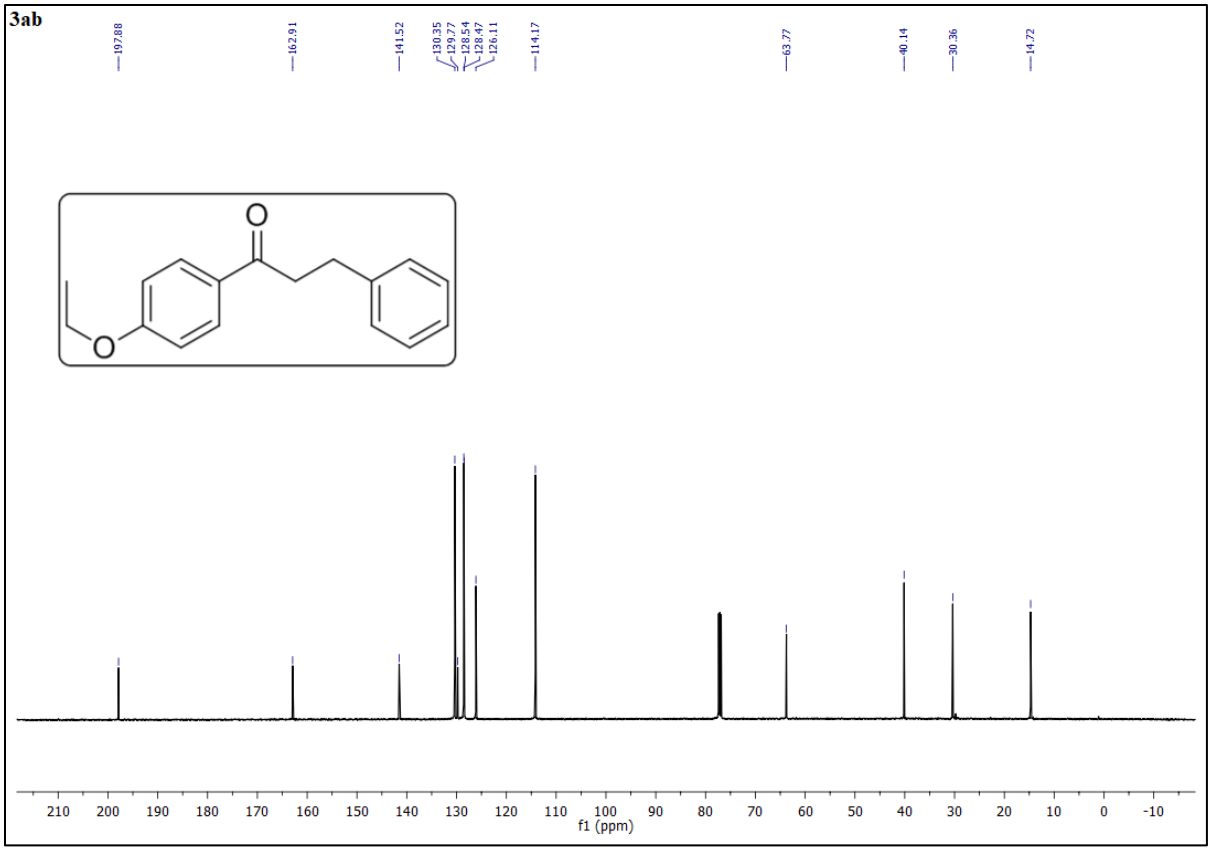
f1 (ppm)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114.17
63.77
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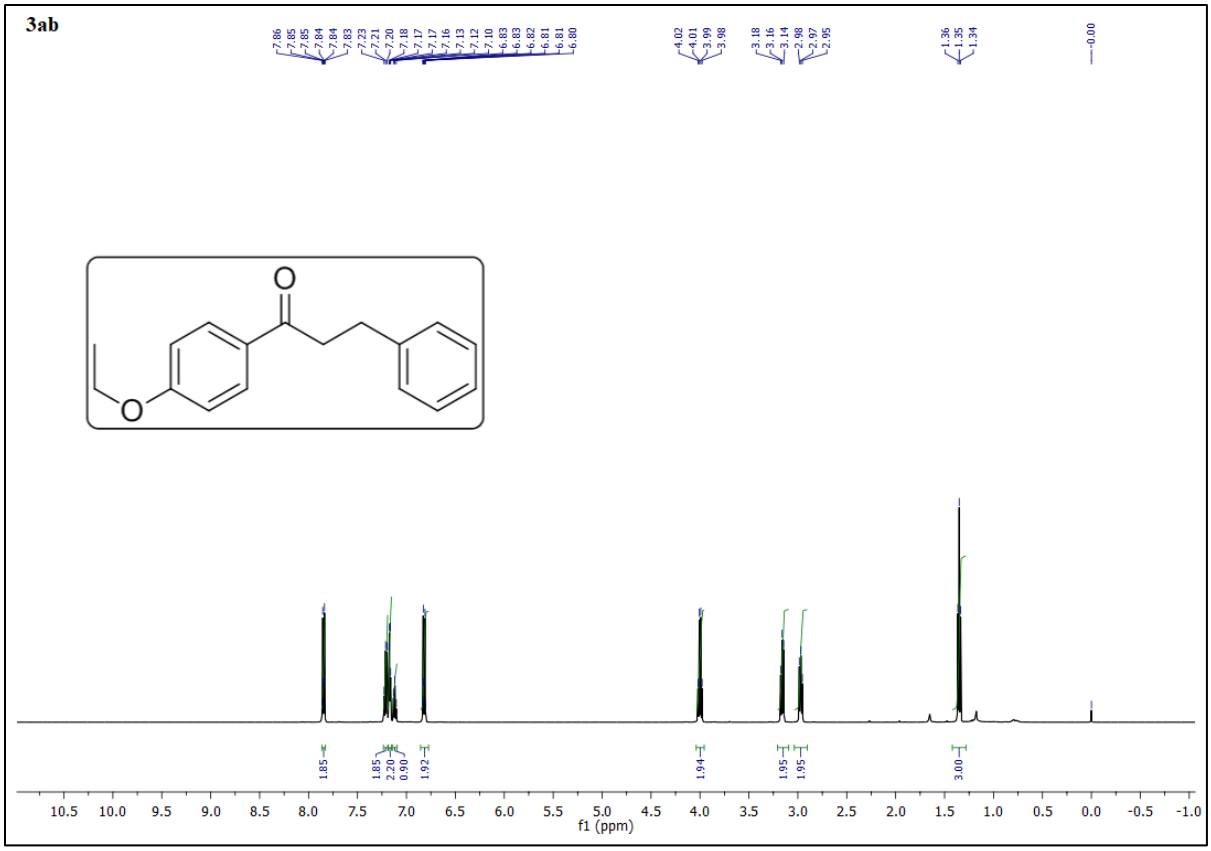
30.36
14.72
O
O
f1 (ppm)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7.85
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7.84
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7.23
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7.20
7.18
7.17
7.17
7.16
7.13
7.12
7.10
6.83
6.83
6.82
6.81
6.81
6.80
4.02
4.01
3.99
3.98
3.18
3.16
3.14
2.98
2.97
2.95
1.36
1.35
1.34
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1.92
1.94
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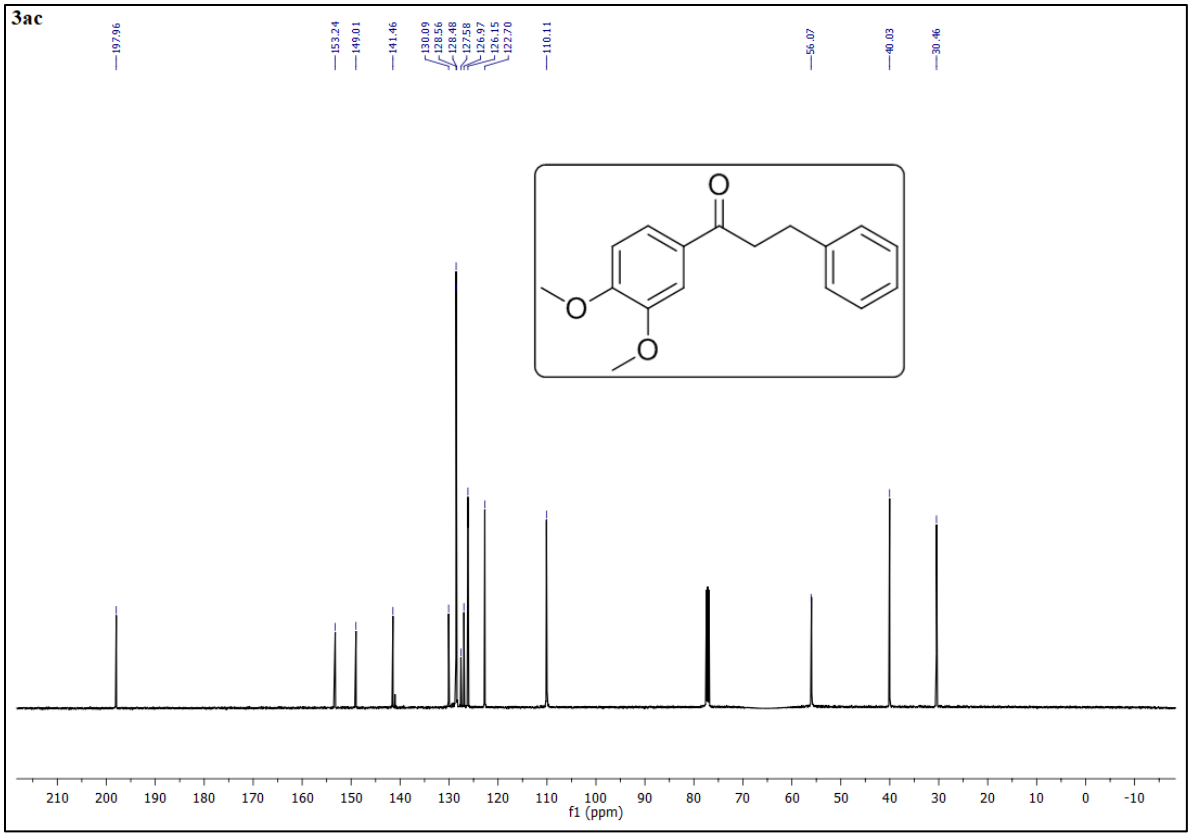
3.00
O
O
f1 (ppm)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128.48
127.58
126.97
126.15
122.70
110.11
56.07
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30.46
O
O
O
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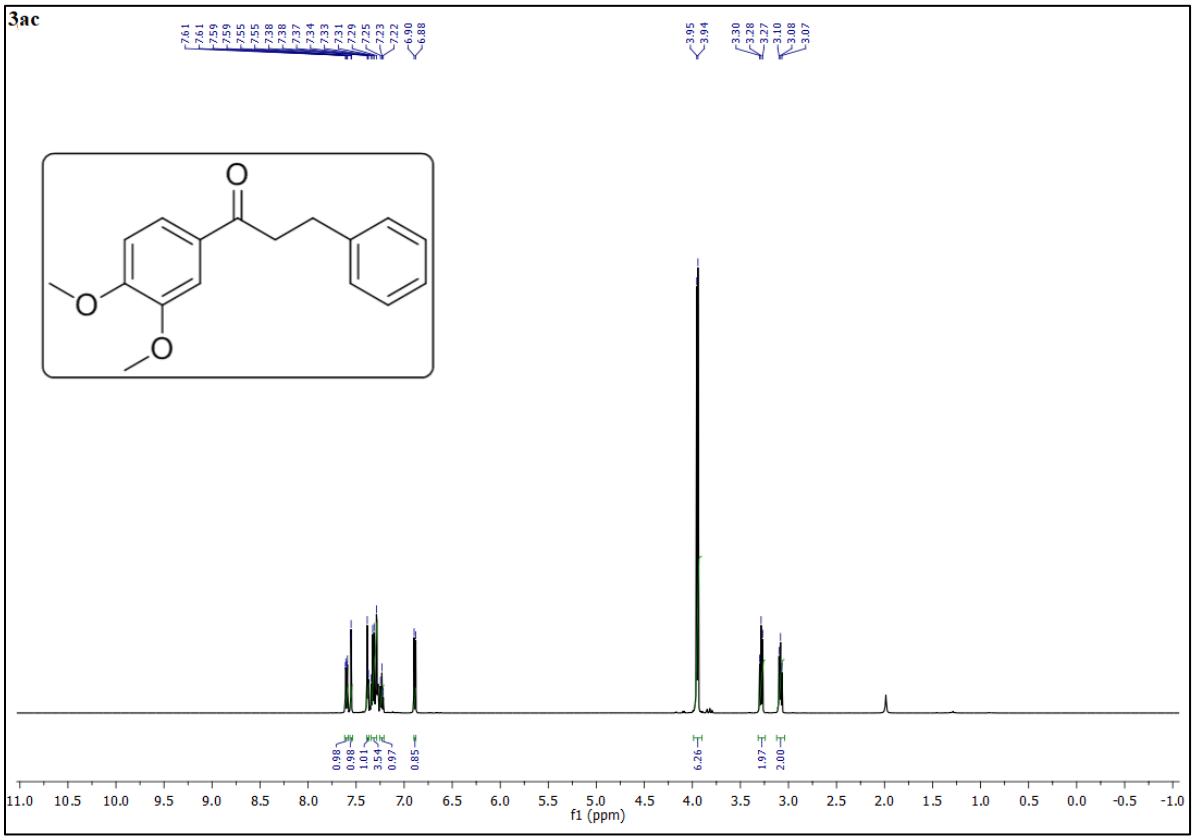
f1 (ppm)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7.61
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7.59
7.55
7.55
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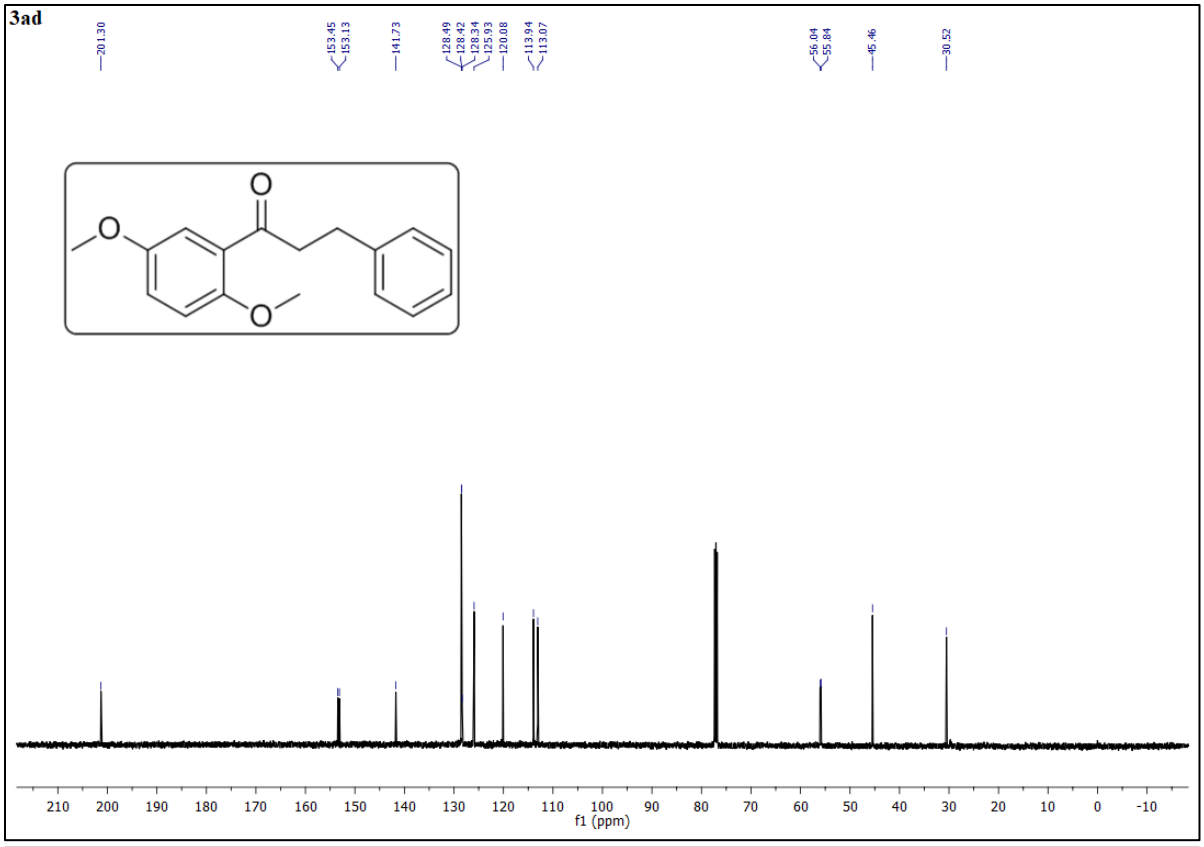
7.37
7.34
7.33
7.31
7.29
7.25
7.23
7.22
6.90
6.88
3.95
3.94
3.30
3.28
3.27
3.10
3.08
3.07
O
O
O
0.98
0.98
1.01
3.54
0.97
0.85
6.26
1.97
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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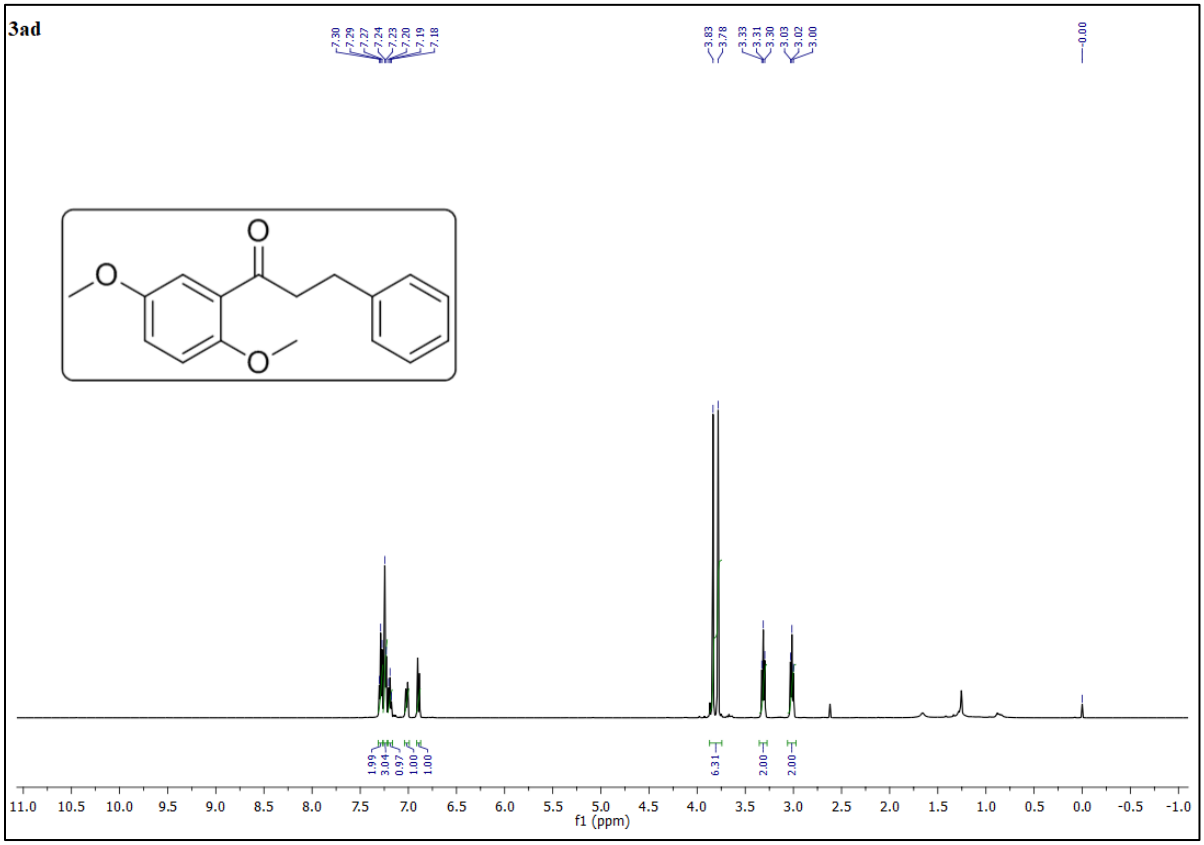
45.46
30.52
f1 (ppm)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3.31
3.30
3.03
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0.97
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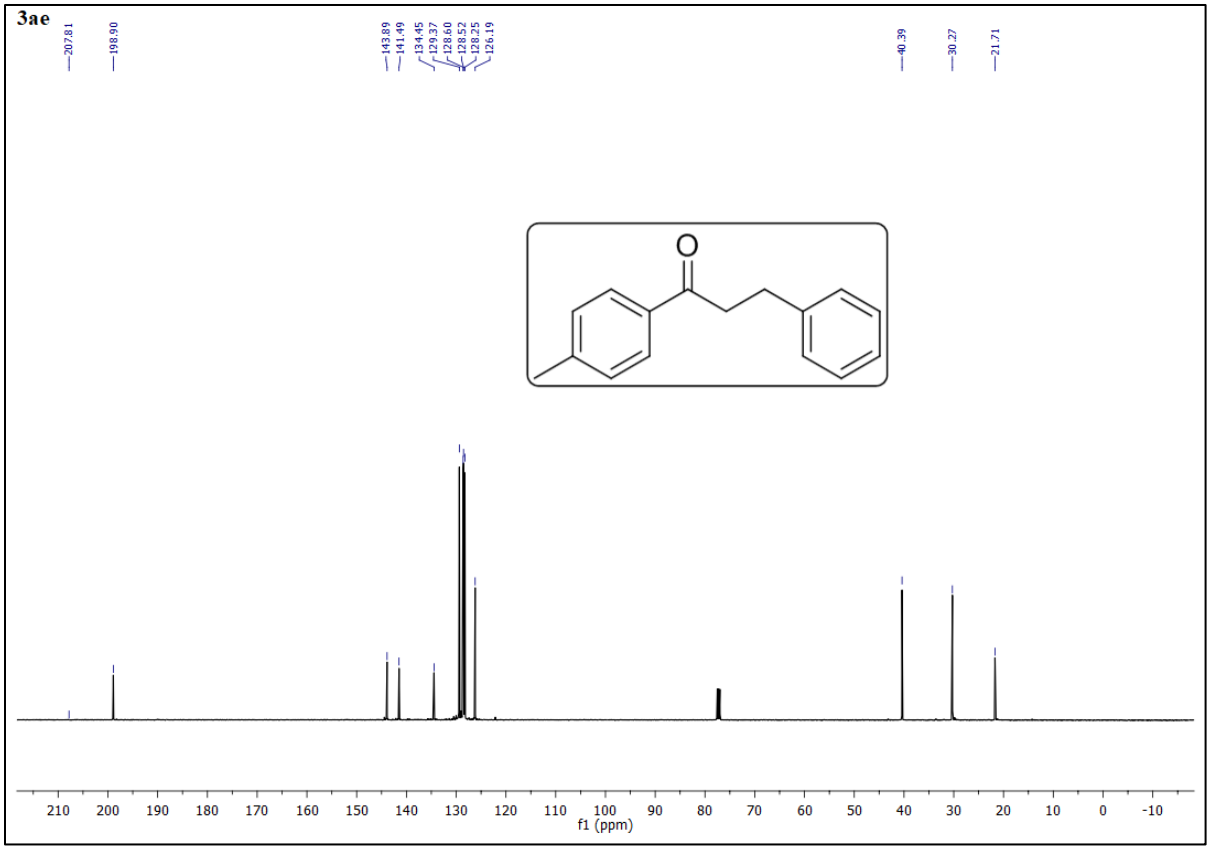
2.00
f1 (ppm)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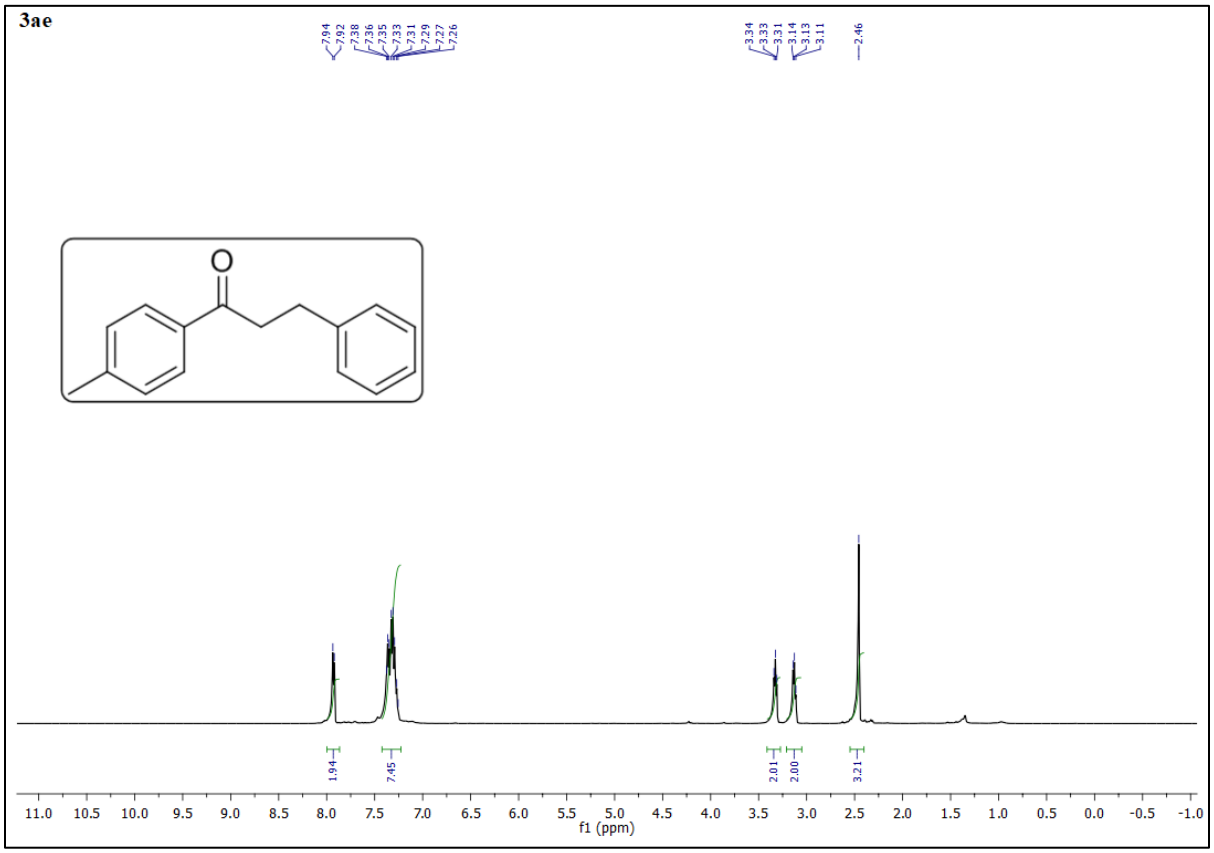
30.27
21.71
O
f1 (ppm)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7.36
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7.27
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3.33
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2.01
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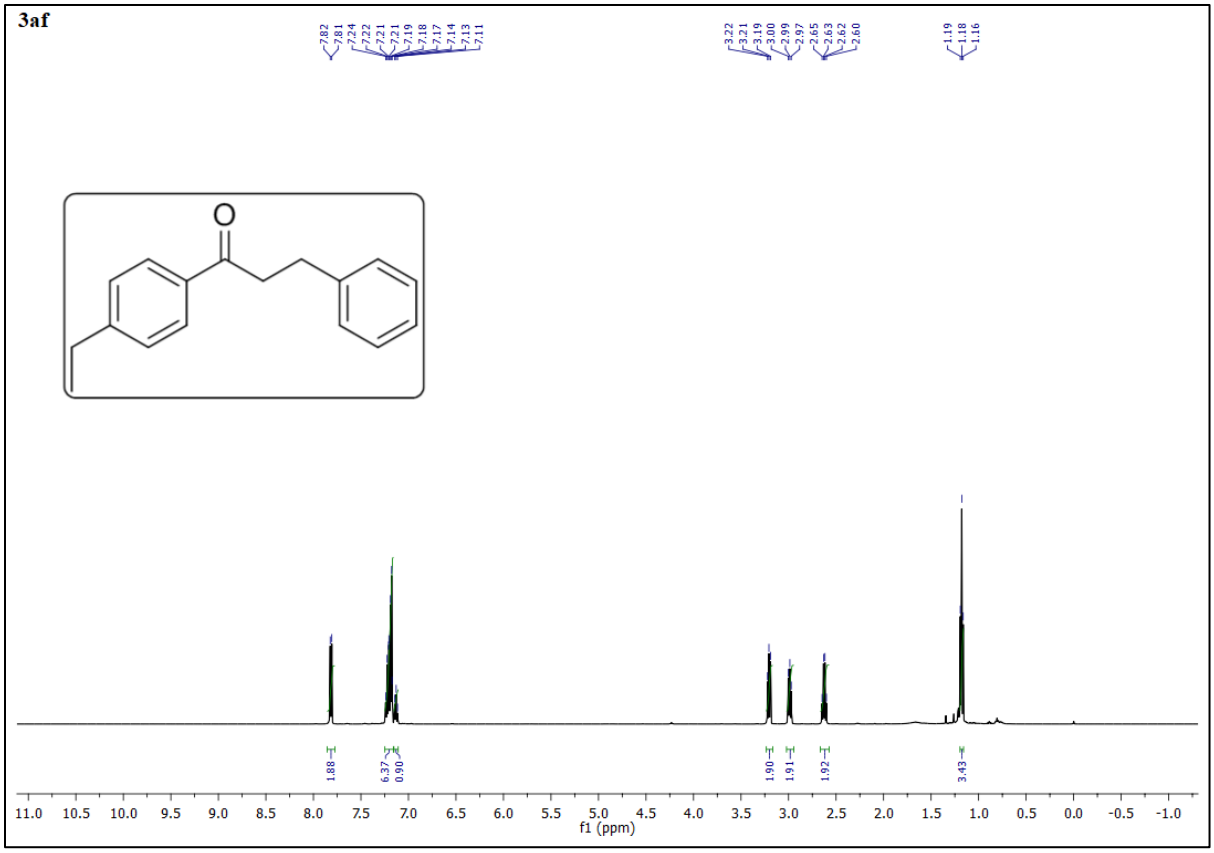
3.21
f1 (ppm)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7.21
7.19
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7.17
7.14
7.13
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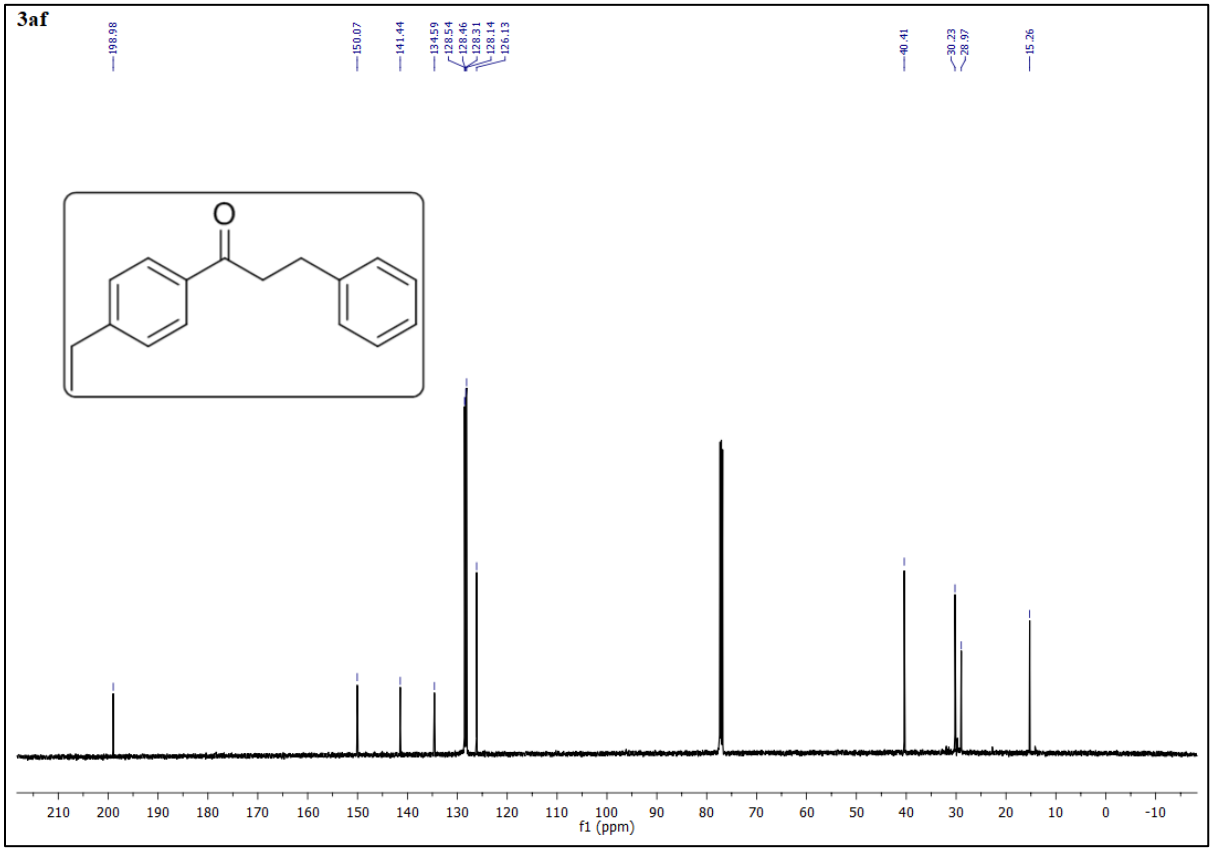
3.22
3.21
3.19
3.00
2.99
2.97
2.65
2.63
2.62
2.60
1.19
1.18
1.16
O
1.88
6.37
0.90
1.90
1.91
1.92
3.43
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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128.46
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128.14
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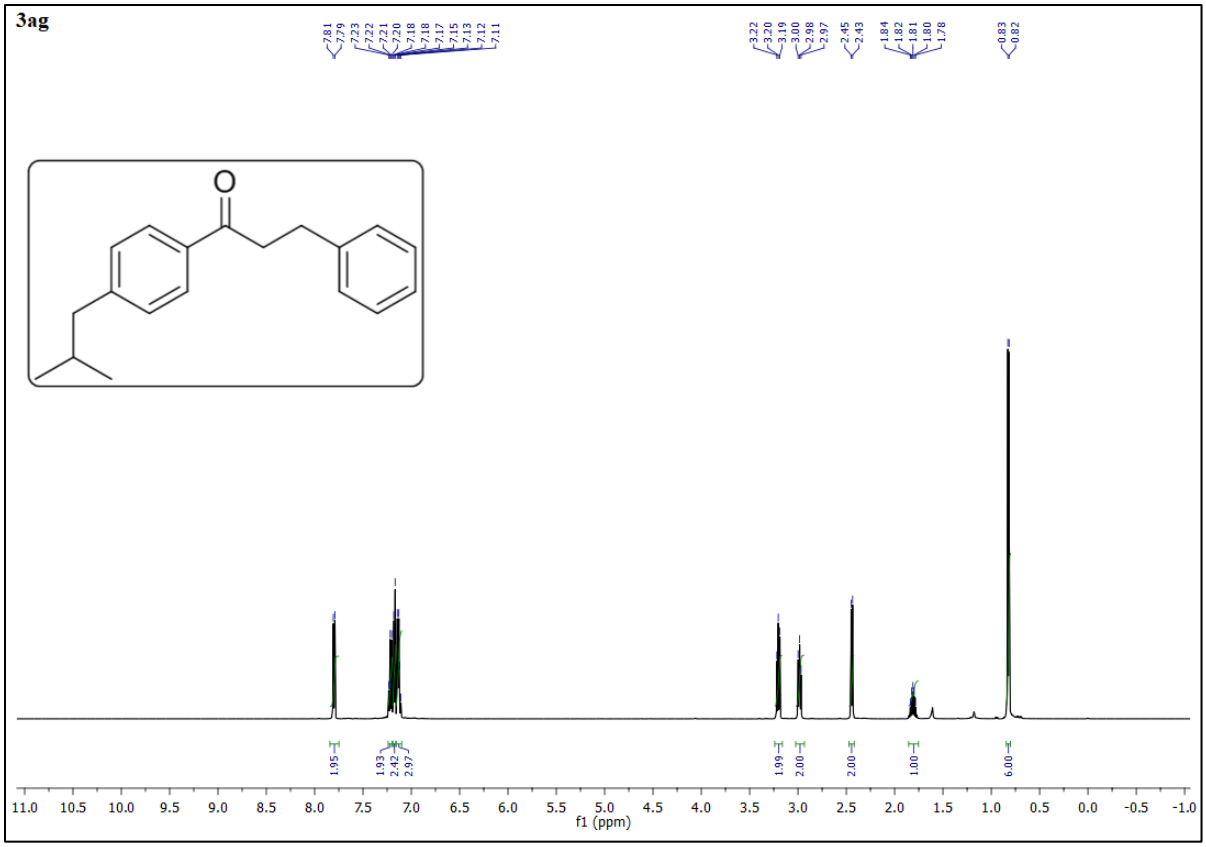
28.97
15.26
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.20
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7.17
7.15
7.13
7.12
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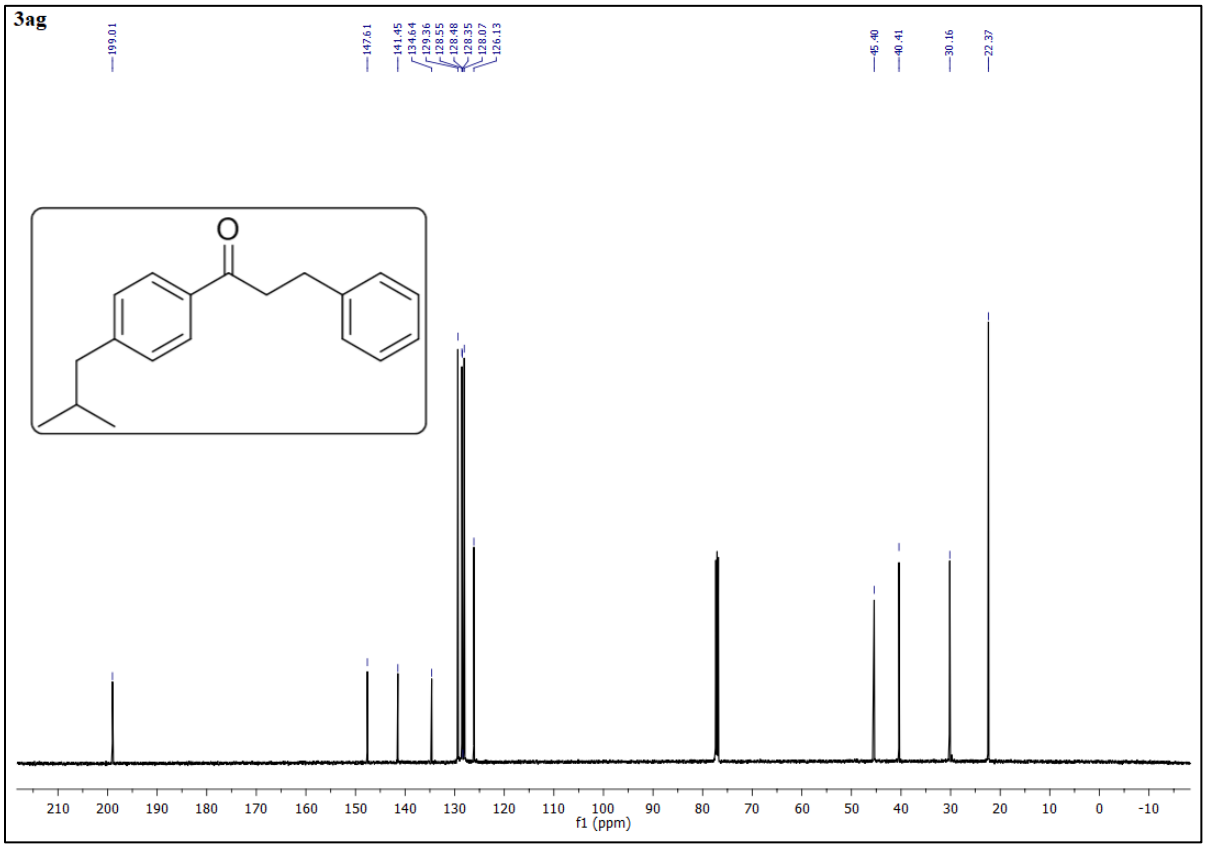
3.22
3.20
3.19
3.00
2.98
2.97
2.45
2.43
1.84
1.82
1.81
1.80
1.78
0.83
0.82
O
1.95
1.93
2.42
2.97
1.99
2.00
2.00
1.00
6.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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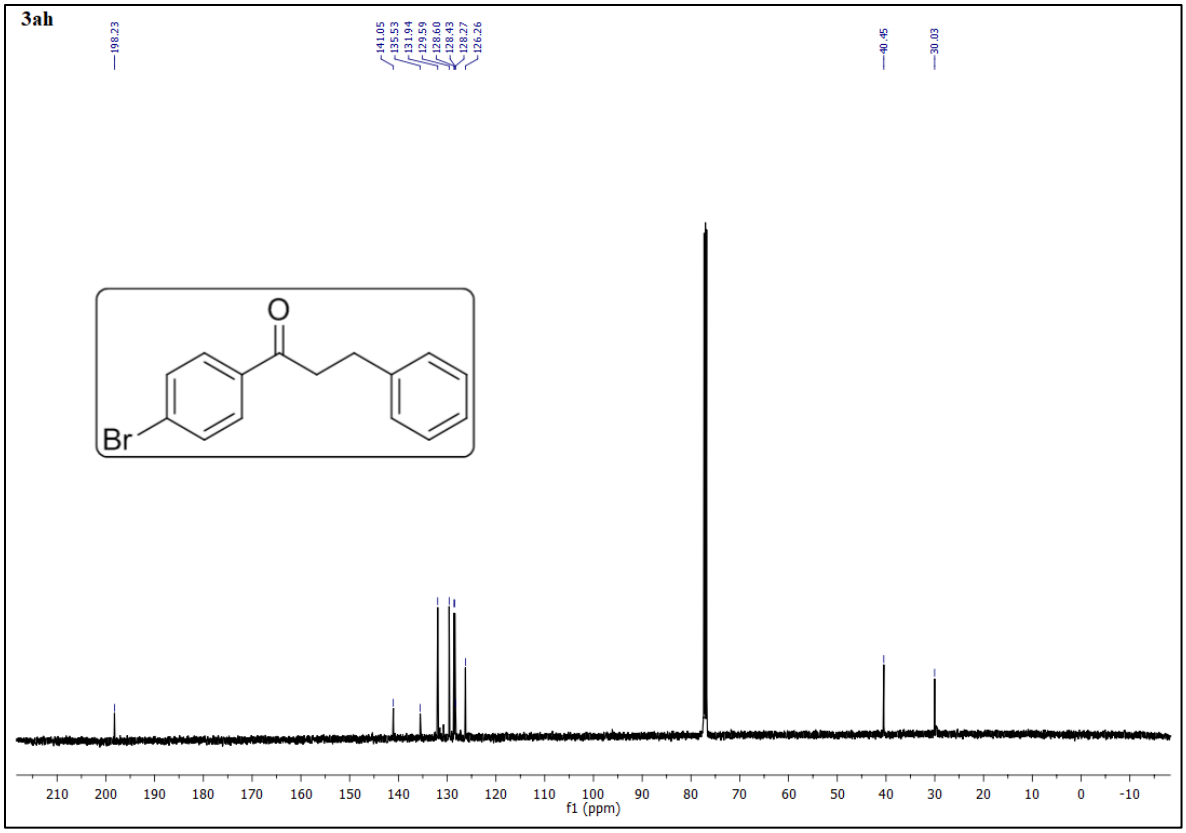
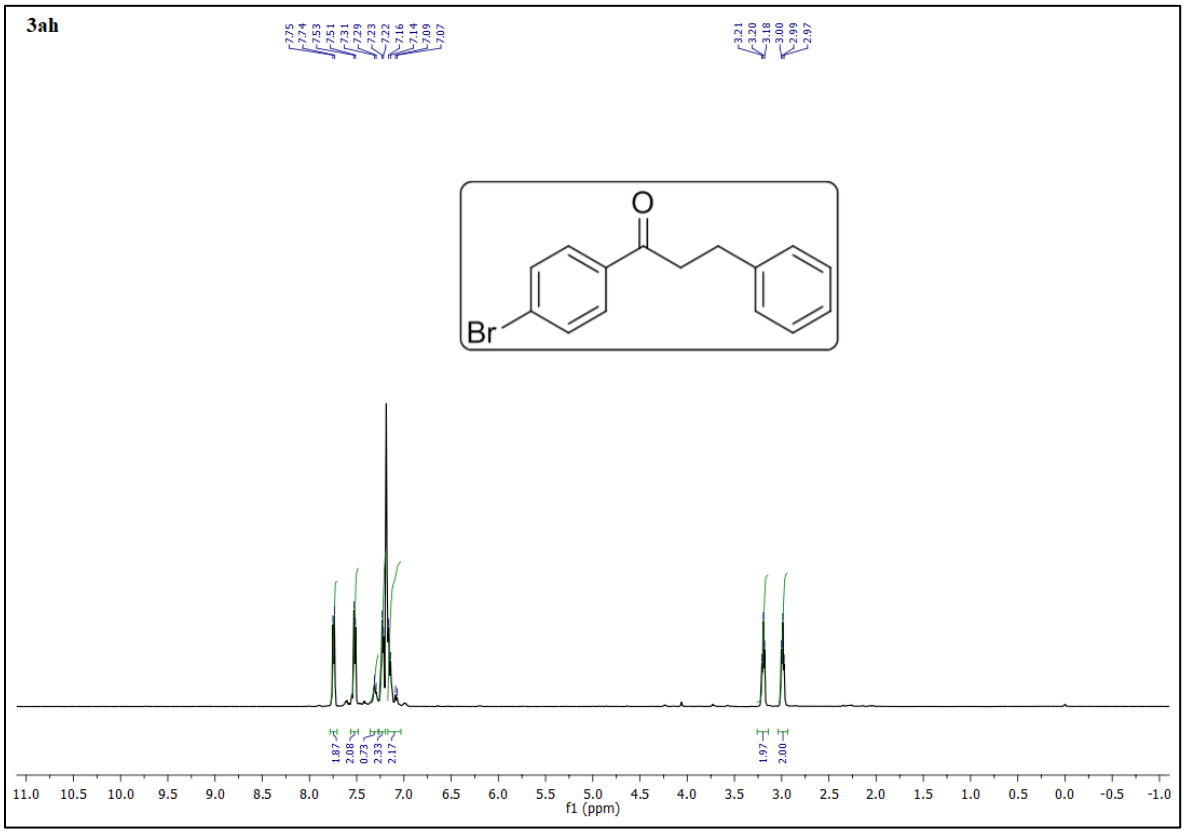
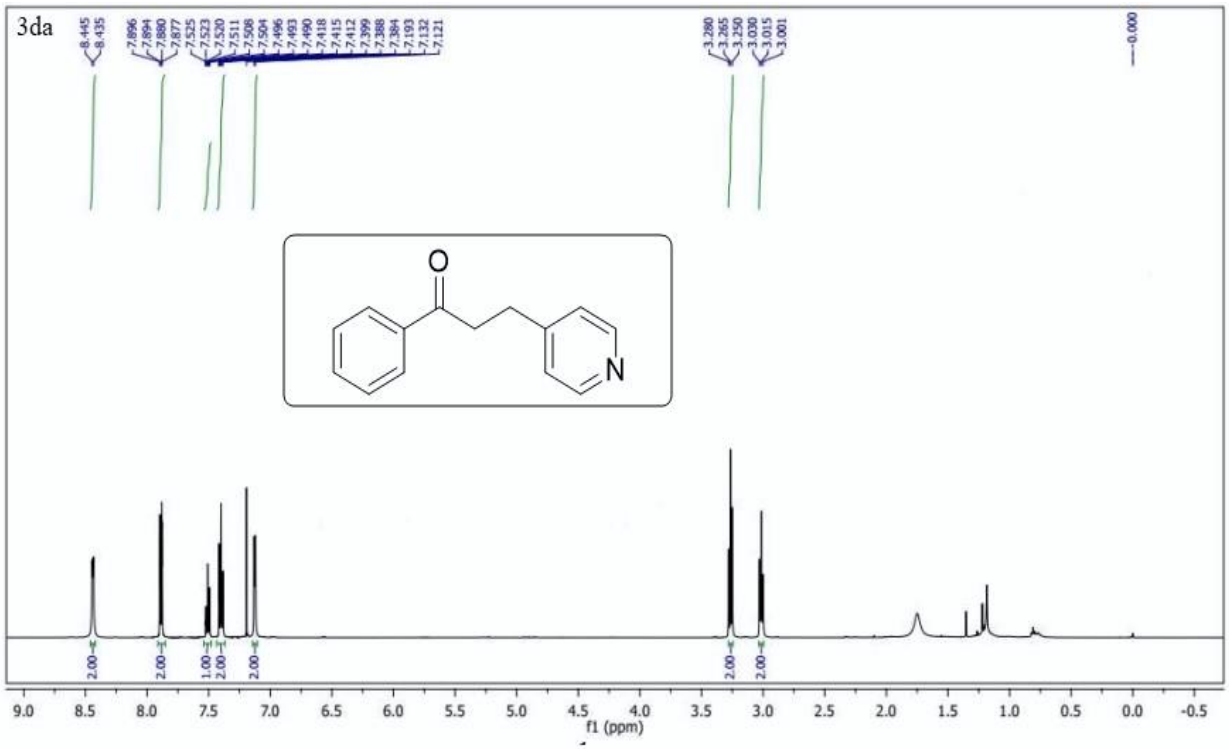
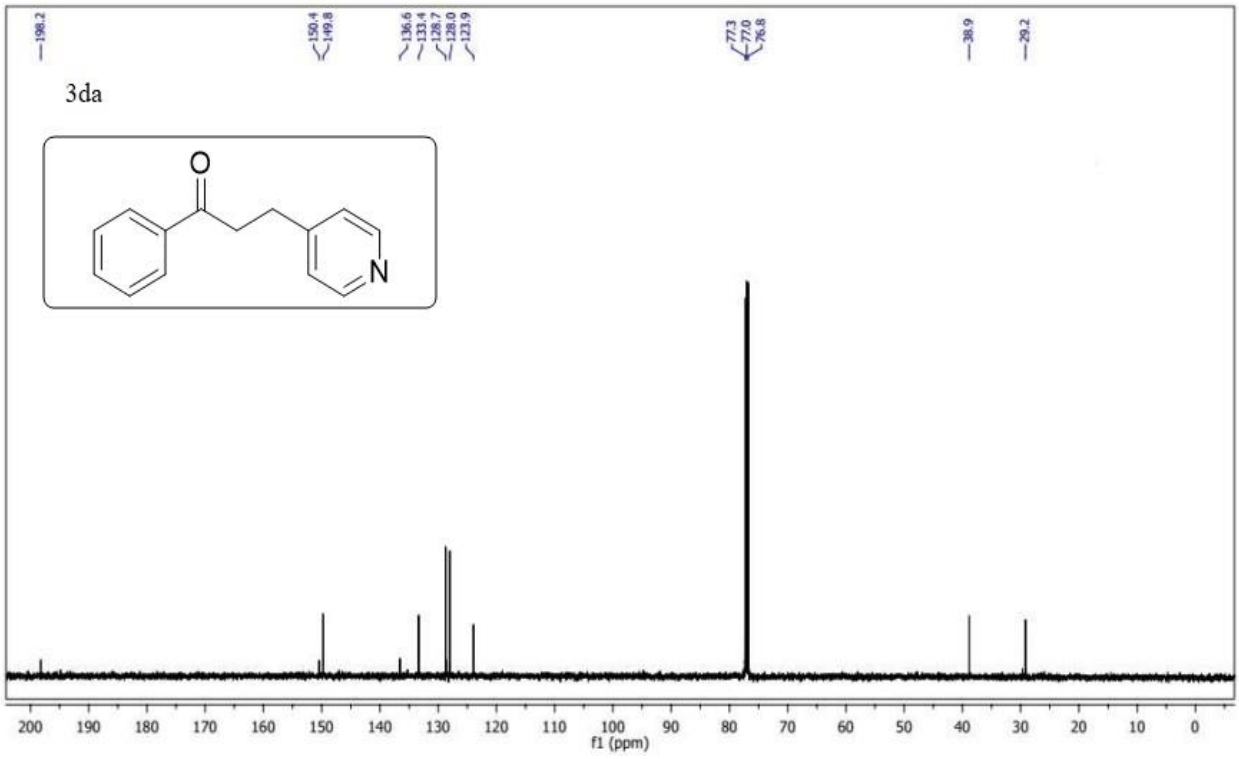
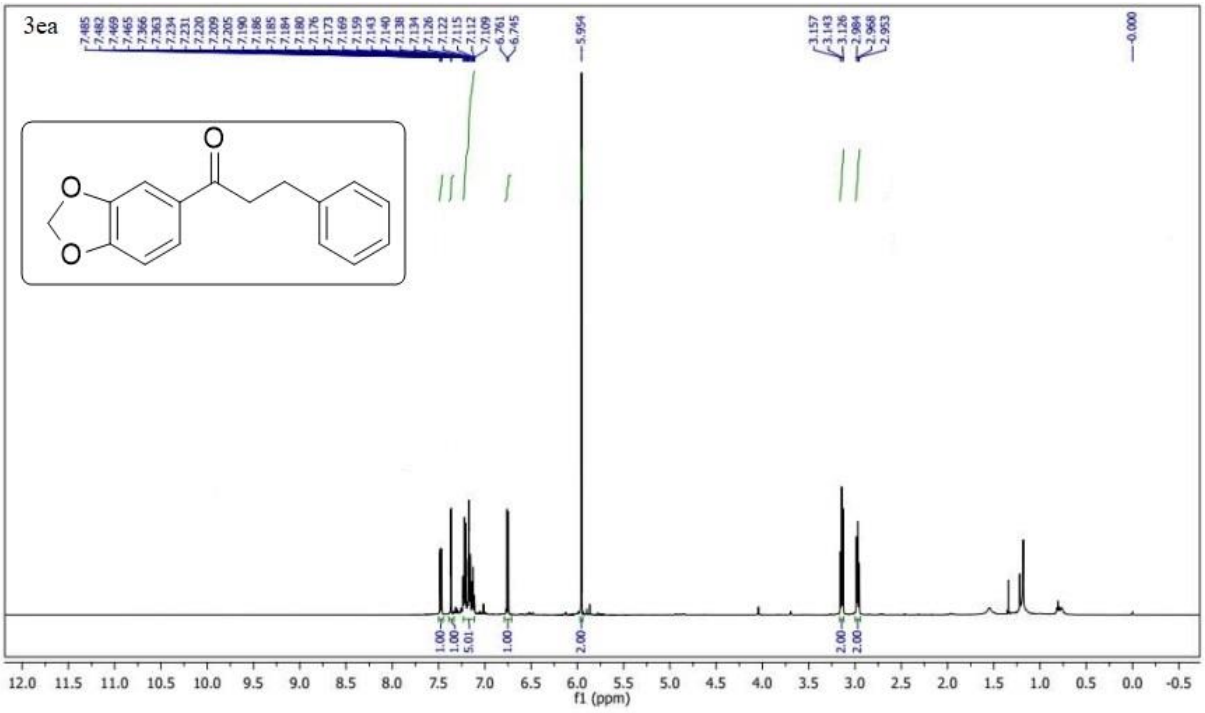
45.40
40.41
30.16
22.37
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

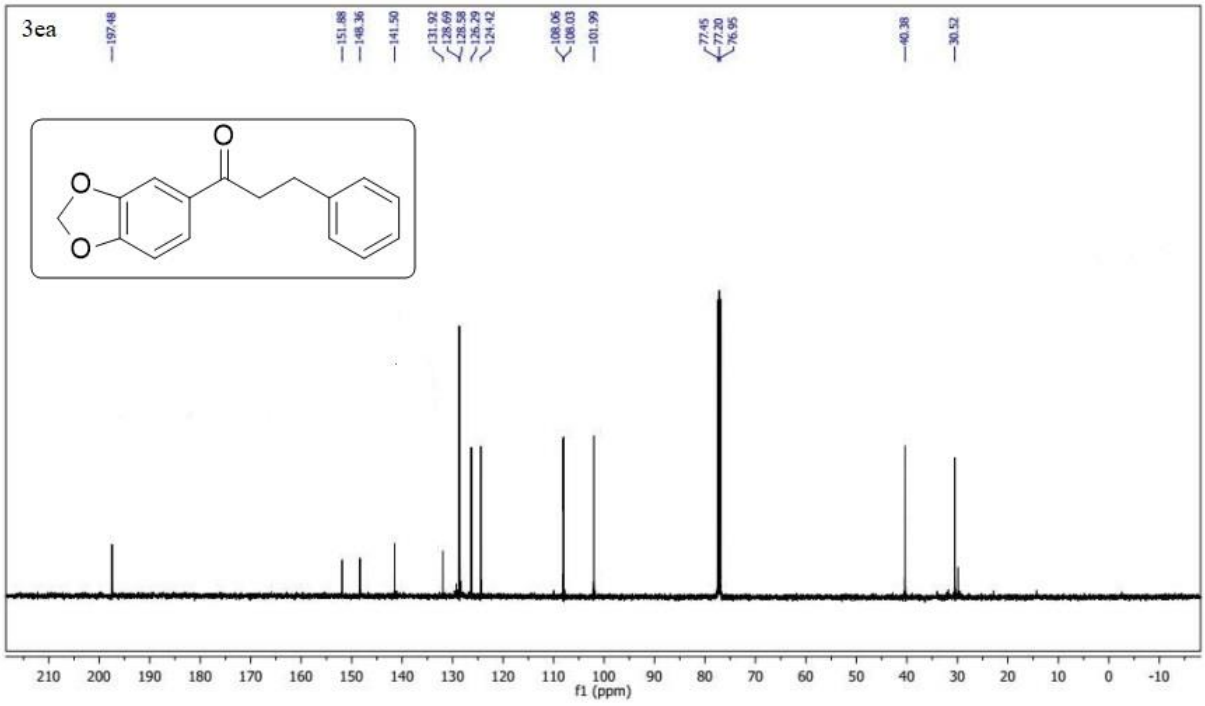

3ah
198.23
141.05
135.53
131.94
129.59
128.60
128.43
128.27
126.26
40.45
30.03
O
Br
f1 (ppm)

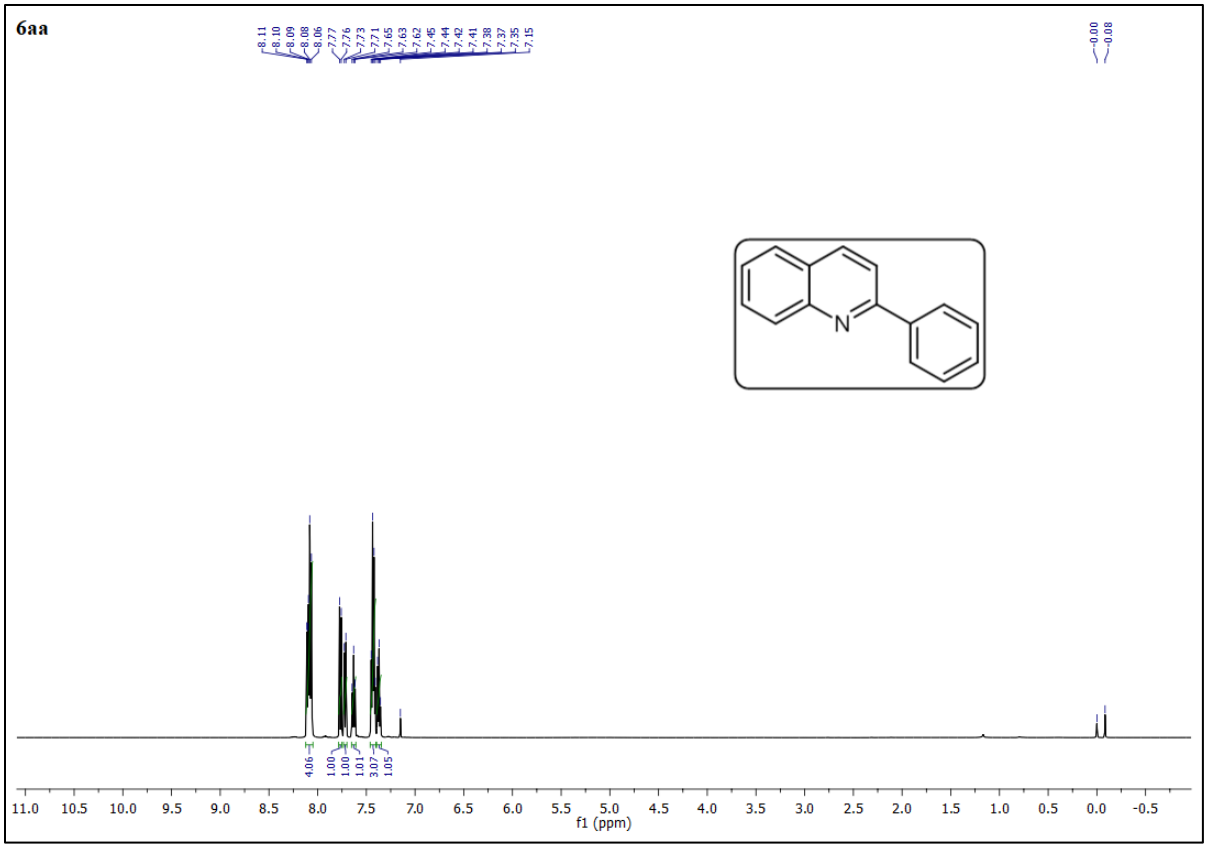

3ah
7.75
7.74
7.53
7.51
7.31
7.29
7.23
7.22
7.16
7.14
7.09
7.07
3.21
3.20
3.18
3.00
2.99
2.97
O
Br
1.87
2.08
0.73
2.33
2.17
1.97
2.00
f1 (ppm)

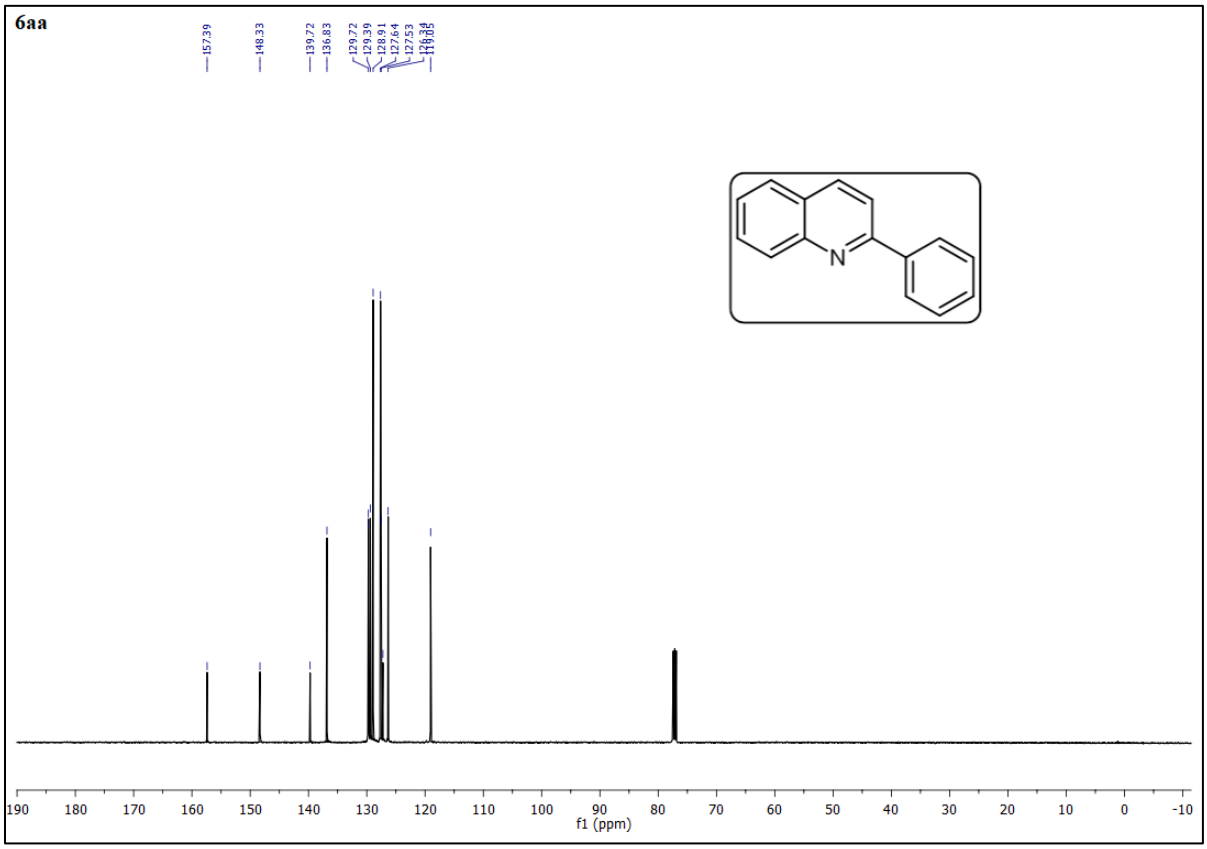

3da
8.445
8.435
7.896
7.894
7.880
7.877
7.525
7.523
7.520
7.511
7.508
7.504
7.496
7.493
7.490
7.418
7.415
7.412
7.399
7.388
7.384
7.193
7.132
7.121
3.280
3.265
3.250
3.030
3.015
3.001
0.000
O
N
2.00
2.00
1.00
2.00
2.00
2.00
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

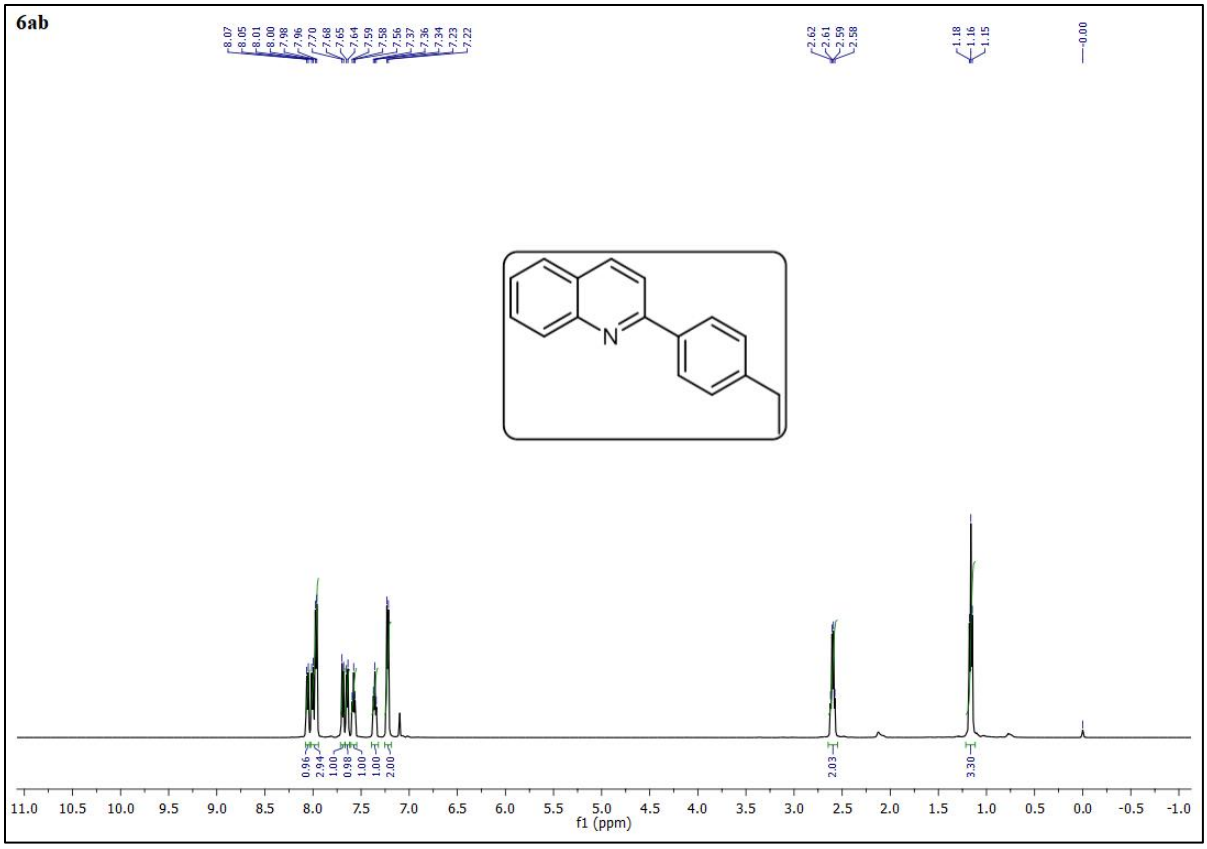

198.2
150.4
149.8
136.6
133.4
128.7
128.0
123.9
77.3
77.0
76.8
38.9
29.2
3da
O
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

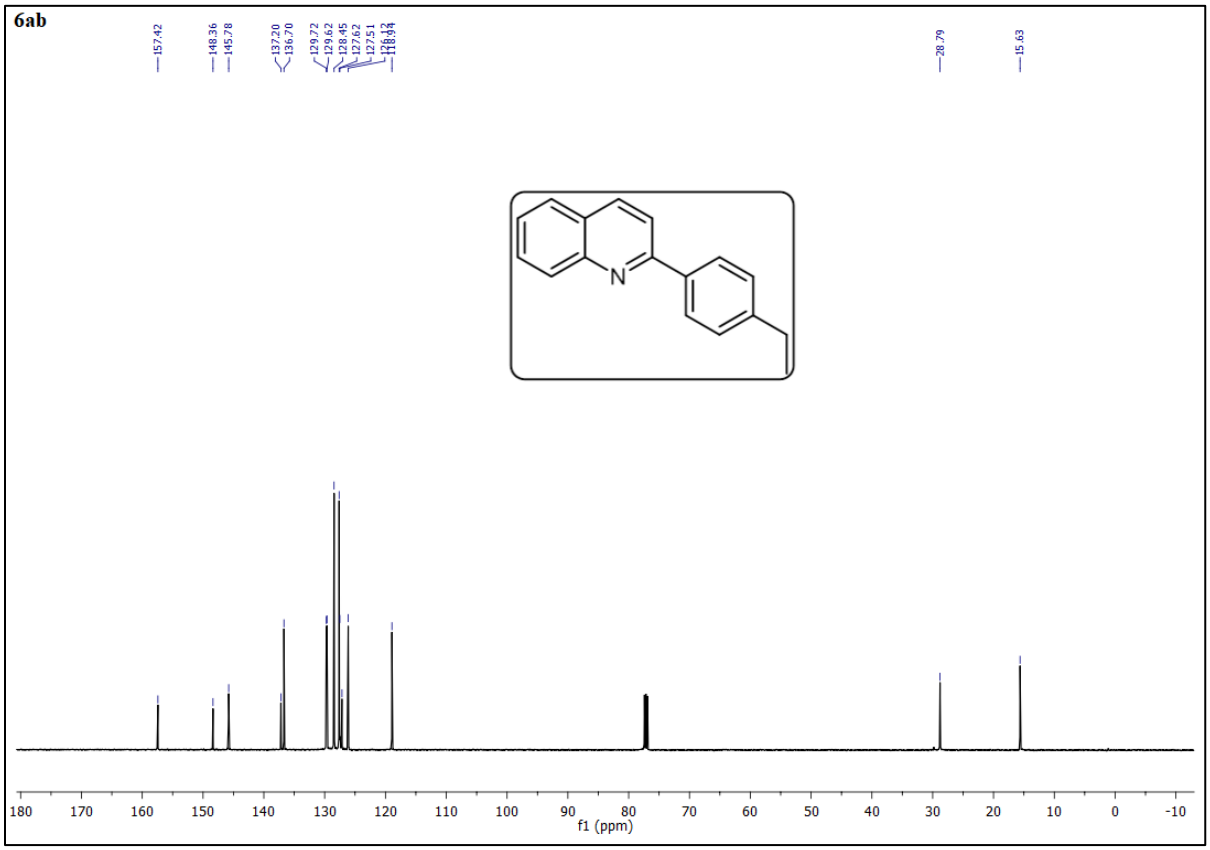

3ea
f1 (ppm)


3ea
f1 (ppm)

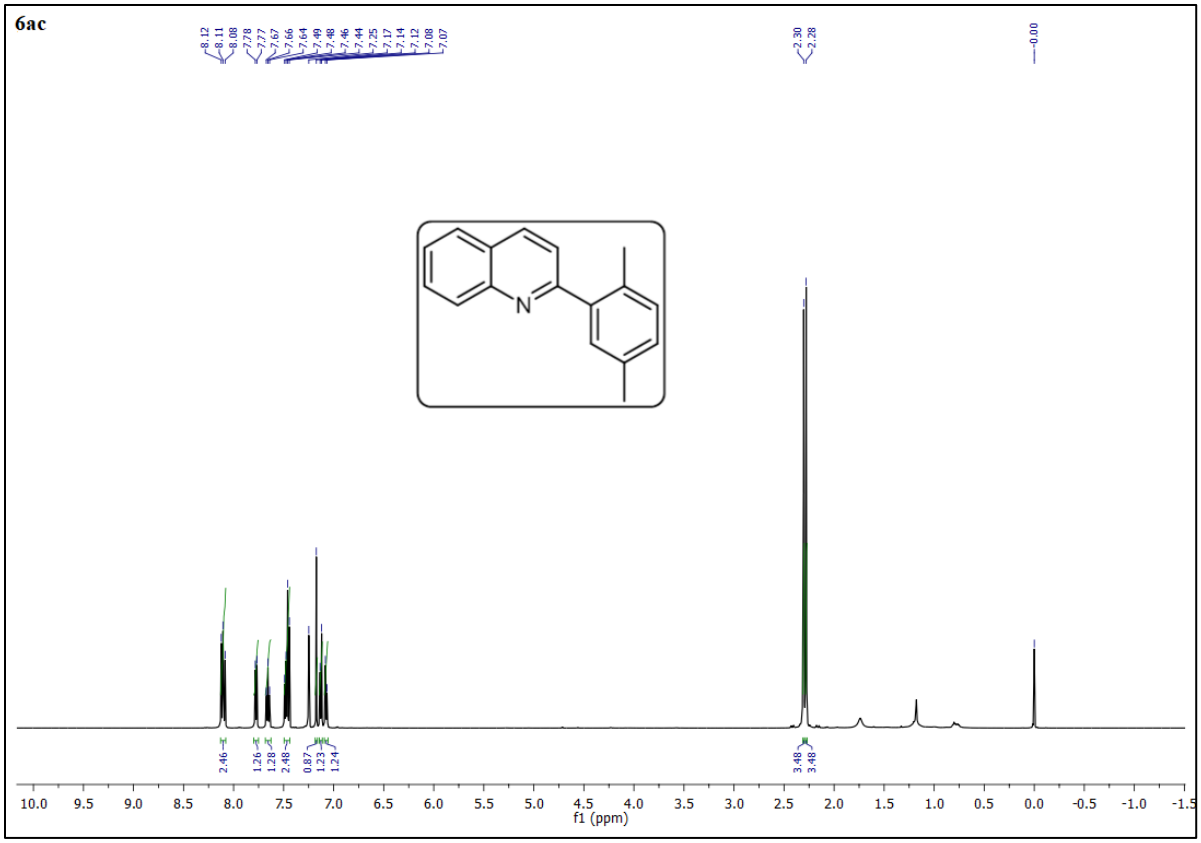

баа
8.11
8.10
8.09
8.08
8.06
7.77
7.76
7.73
7.71
7.65
7.63
7.62
7.45
7.44
7.42
7.41
7.38
7.37
7.35
7.15
0.00
-0.08
N
4.06
1.00
1.00
1.01
3.07
1.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


баа
157.39
148.33
139.72
136.83
129.72
129.39
128.91
127.64
127.53
126.34
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

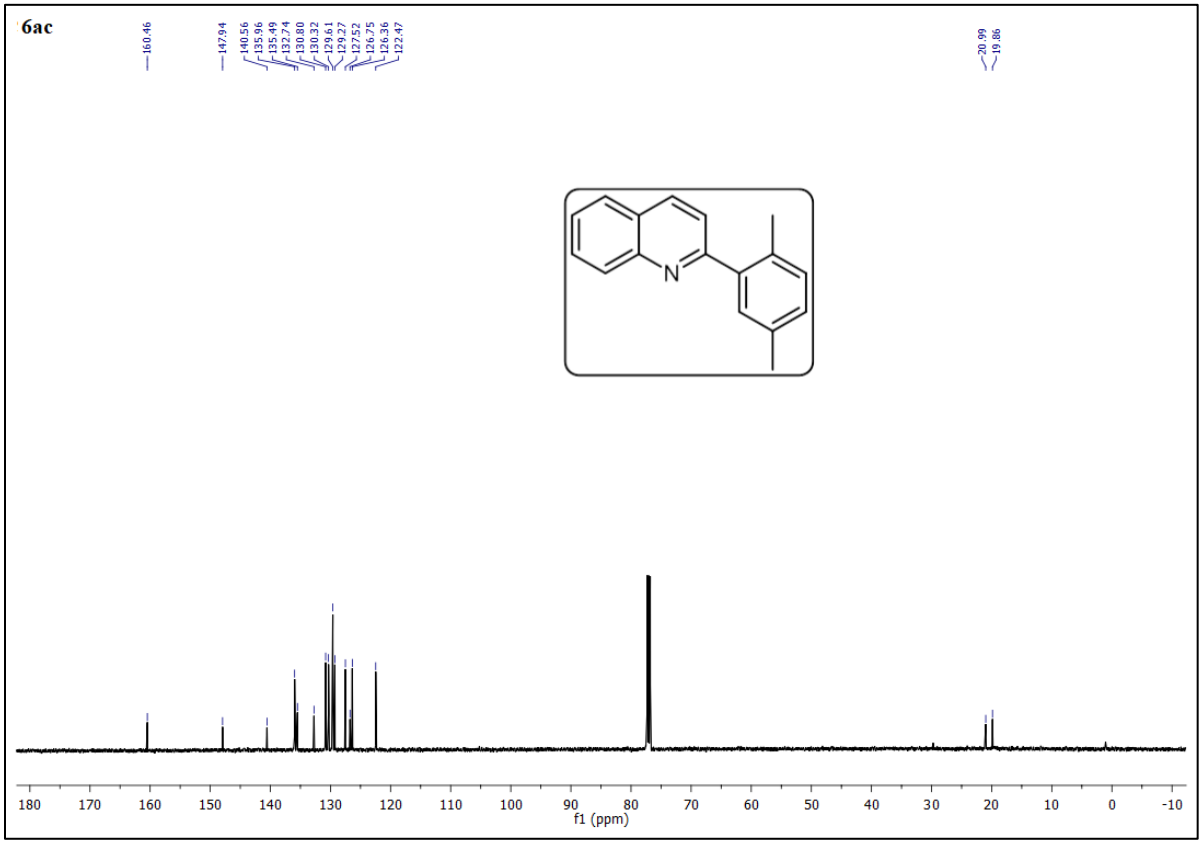

6ab
8.07
8.05
8.01
8.00
7.98
7.96
7.70
7.68
7.65
7.64
7.59
7.58
7.56
7.37
7.36
7.34
7.23
7.22
2.62
2.61
2.59
2.58
1.18
1.16
1.15
0.00
N
0.96
2.94
1.00
0.98
1.00
1.00
2.00
2.03
3.30
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

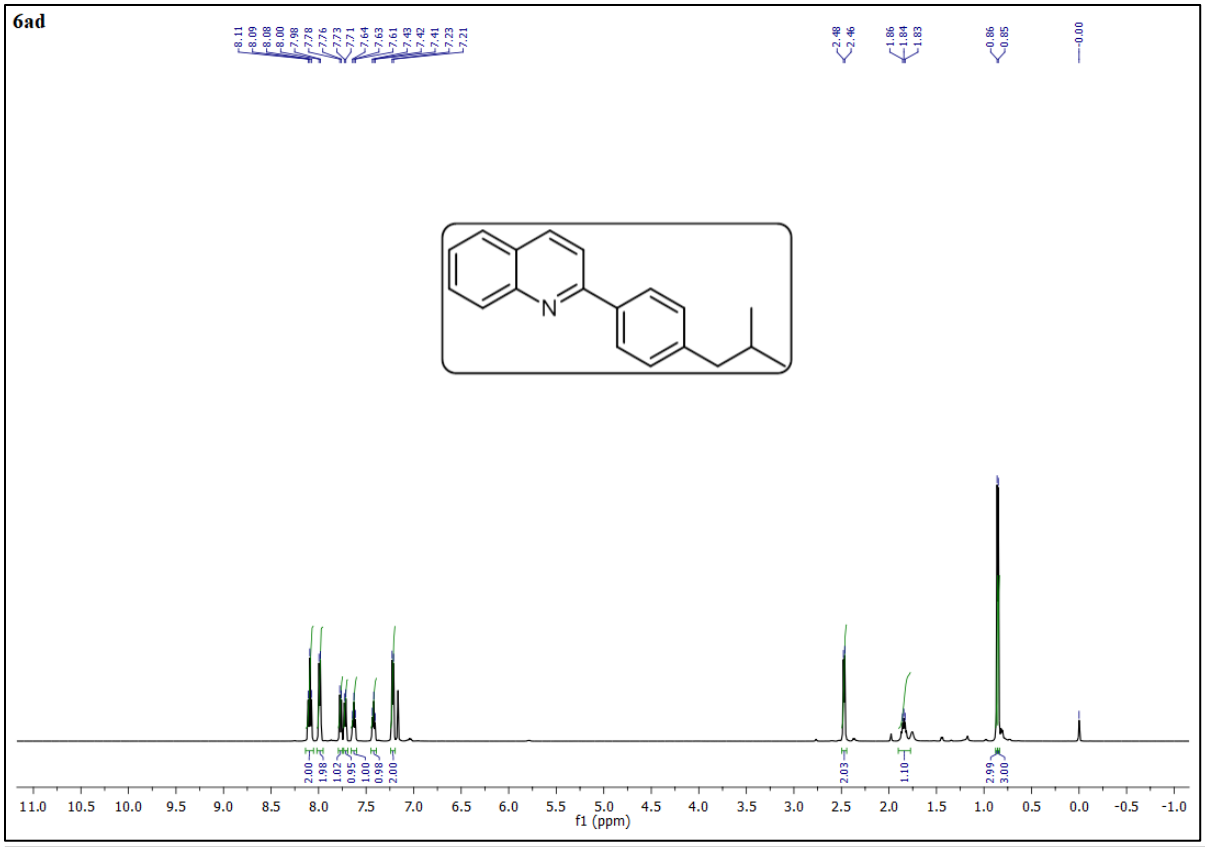

6ab
157.42
148.36
145.78
137.20
136.70
129.72
129.62
128.45
127.62
127.51
28.79
15.63
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

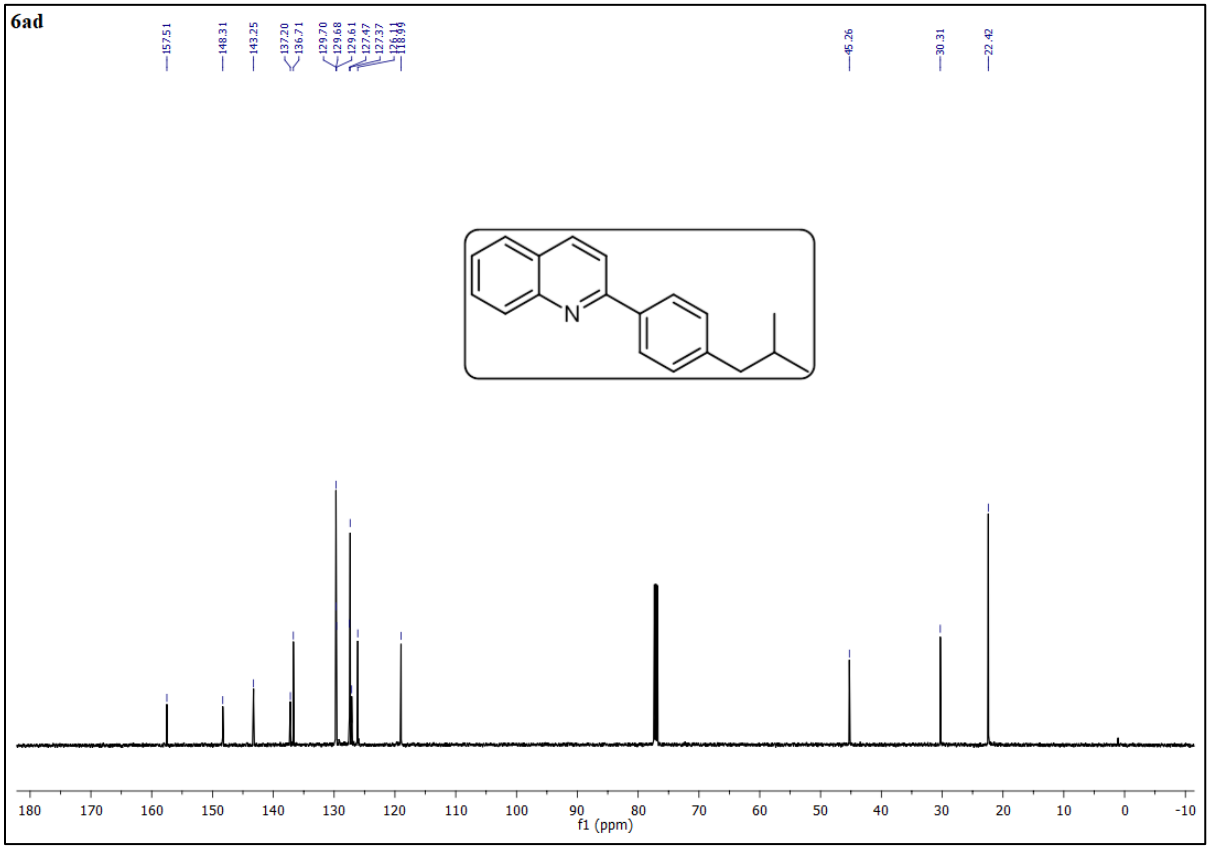
6ac


8.12
8.11
8.08
7.78
7.77
7.67
7.66
7.64
7.49
7.48
7.46
7.44
7.25
7.17
7.14
7.12
7.08
7.07
2.30
2.28
0.00
2.46
1.26
1.28
2.48
0.87
1.23
1.24
3.48
3.48
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

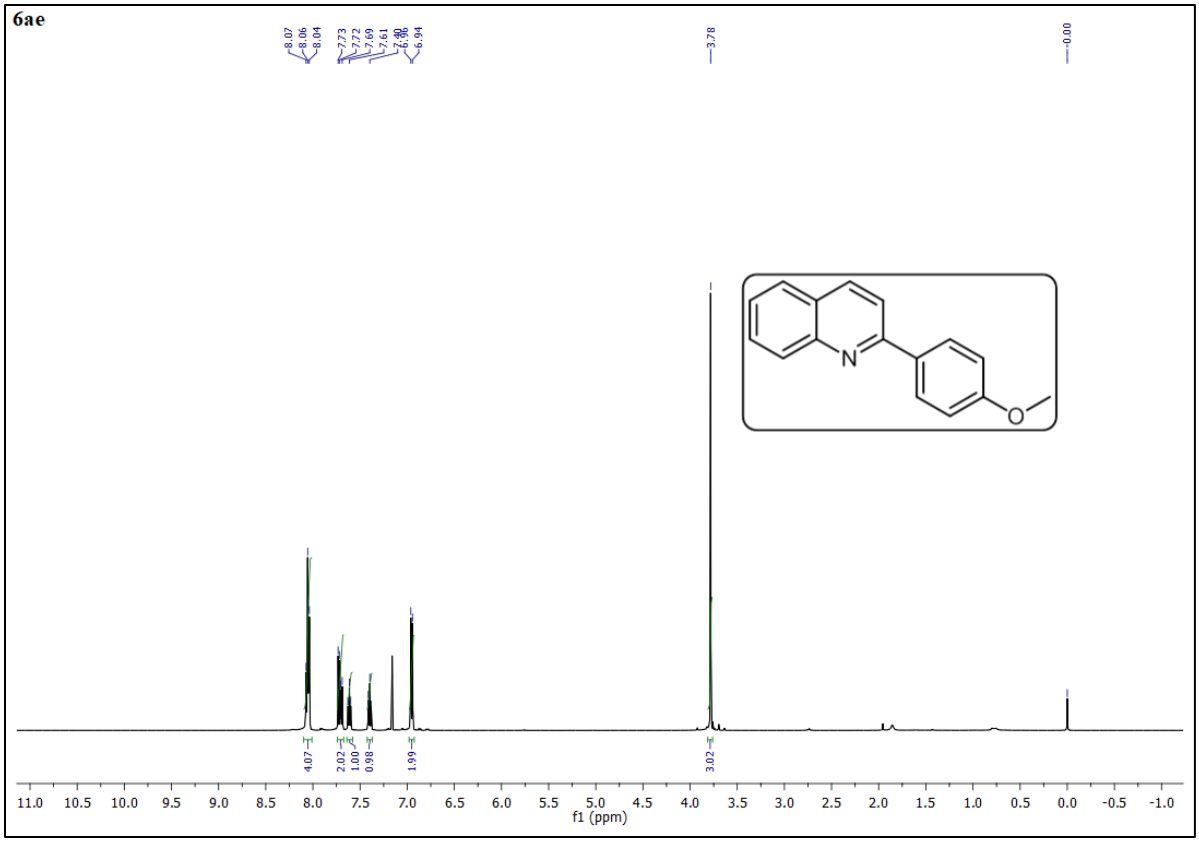
6ac


160.46
147.94
140.56
135.96
135.49
132.44
130.80
130.32
129.61
129.27
127.52
126.75
126.36
122.47
20.99
19.86
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

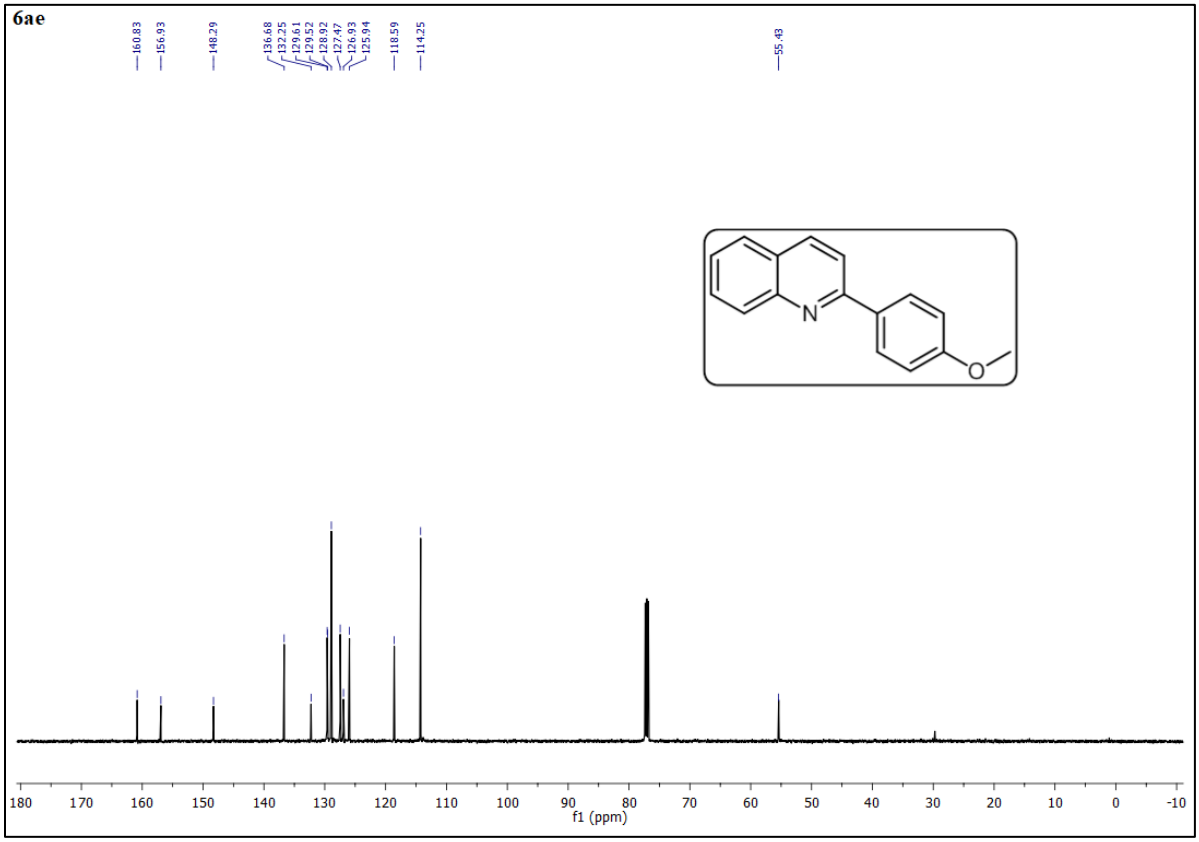

6ad
8.11
8.09
8.08
8.00
7.98
7.78
7.76
7.73
7.71
7.64
7.63
7.61
7.43
7.42
7.41
7.23
7.21
2.48
2.46
1.86
1.84
1.83
0.86
0.85
0.00
N
2.00
1.98
1.02
0.95
1.00
0.98
2.00
2.03
1.10
2.99
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


6ad
157.51
148.31
143.25
137.20
136.71
129.70
129.68
129.61
127.47
127.37
126.11
118.99
45.26
30.31
22.42
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

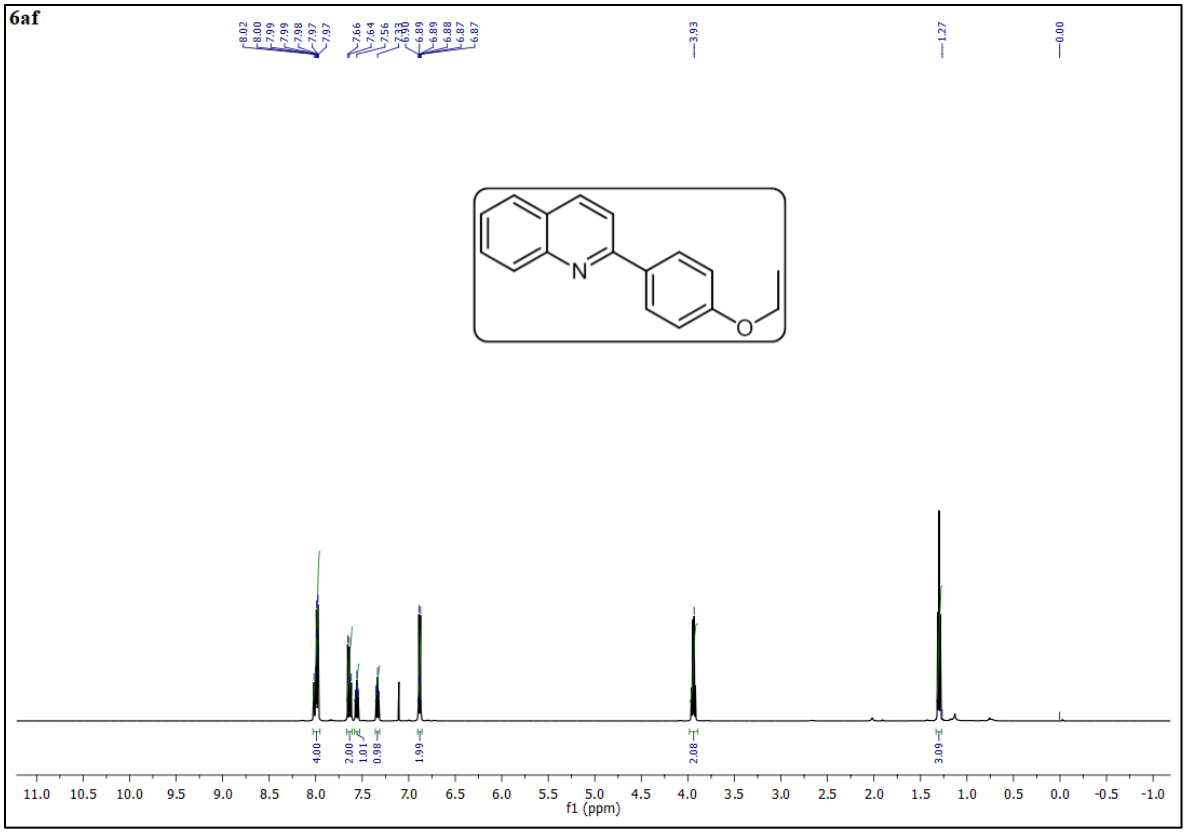
6ae


8.07
8.06
8.04
7.73
7.72
7.69
7.61
6.96
6.94
3.78
0.00
4.07
2.02
1.00
0.98
1.99
3.02
N
O
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

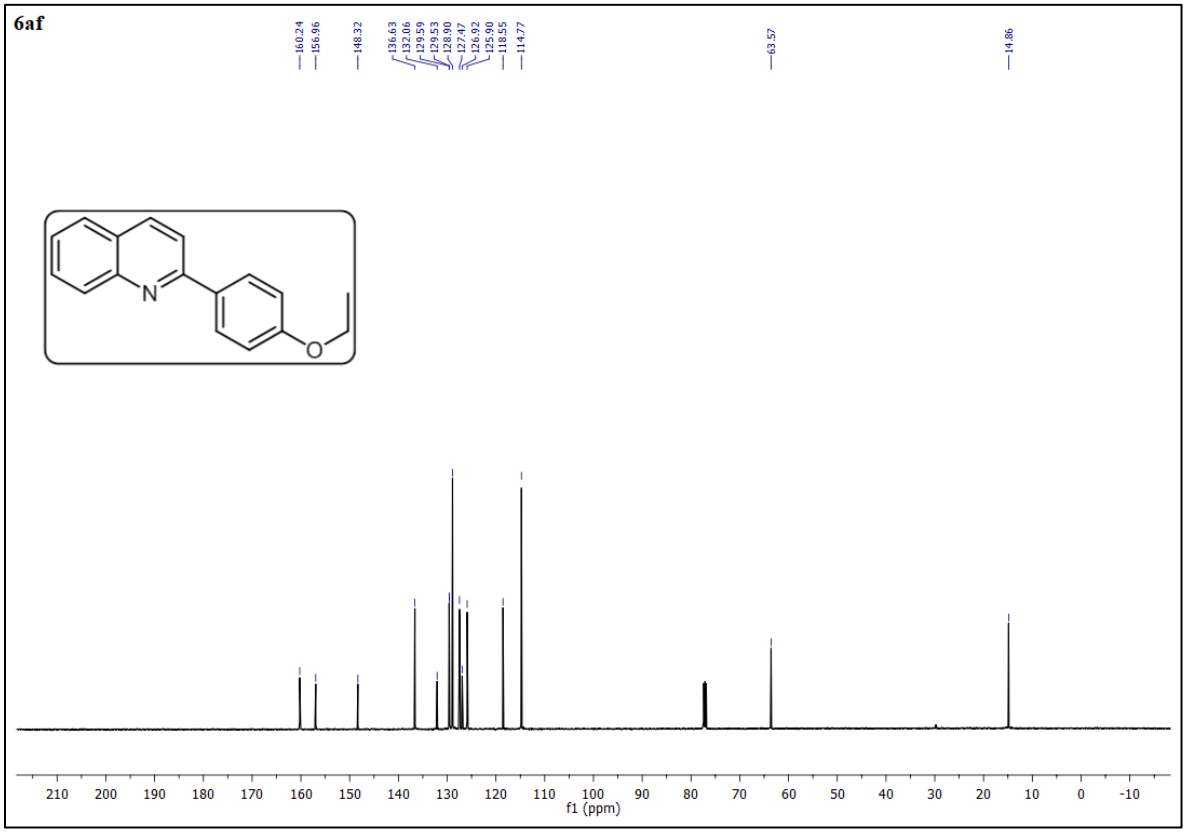
6ae

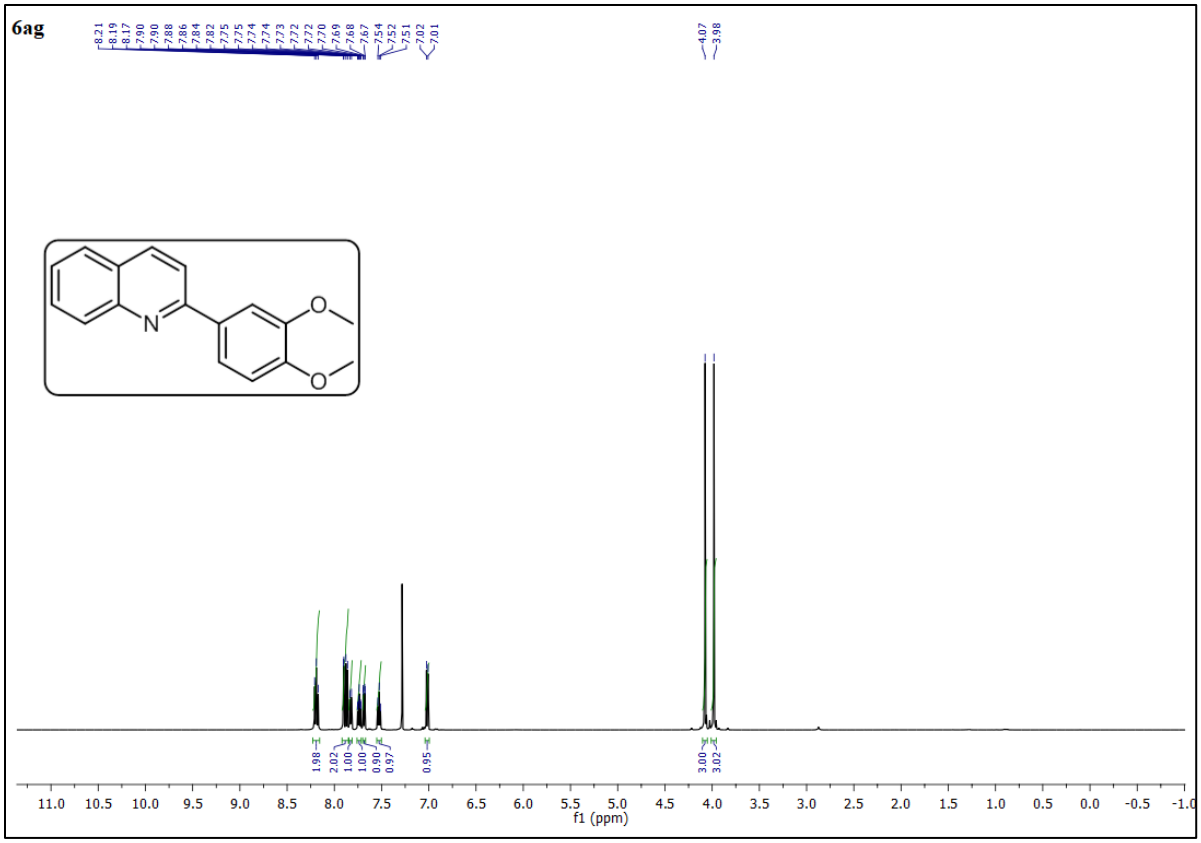

160.83
156.93
148.29
136.68
132.25
129.61
129.52
128.92
127.47
126.93
125.94
118.59
114.25
55.43
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

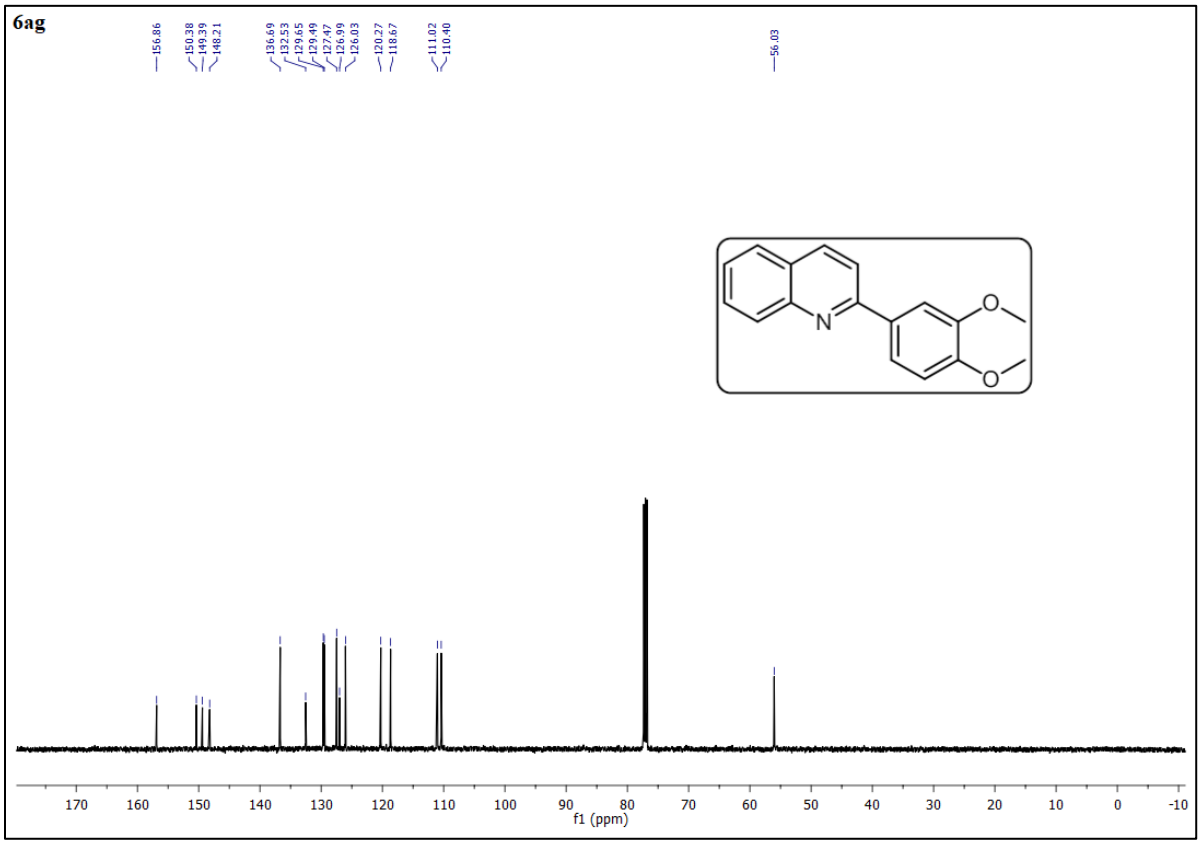
6af

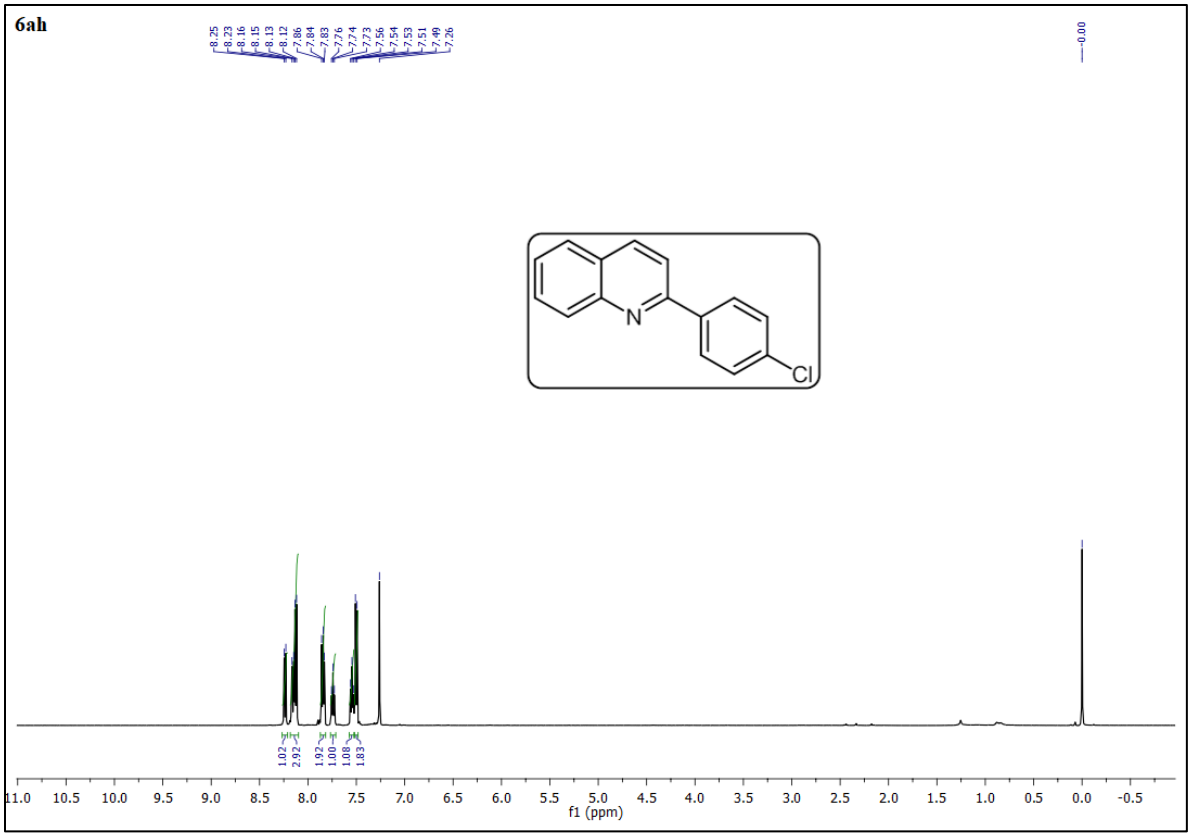

8.02
8.00
7.99
7.99
7.98
7.97
7.97
7.66
7.64
7.56
7.33
6.90
6.89
6.89
6.88
6.87
6.87
3.93
1.27
0.00
4.00
2.00
1.01
0.98
1.99
2.08
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

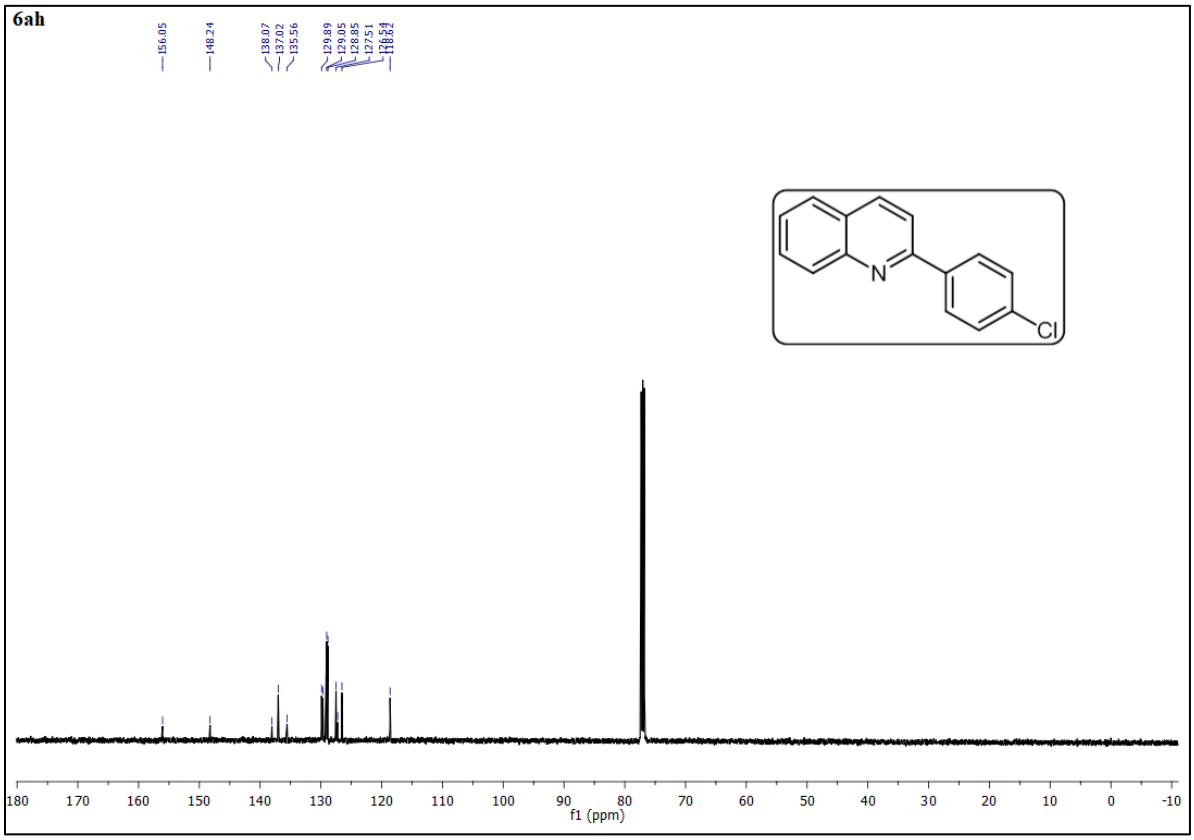
6af

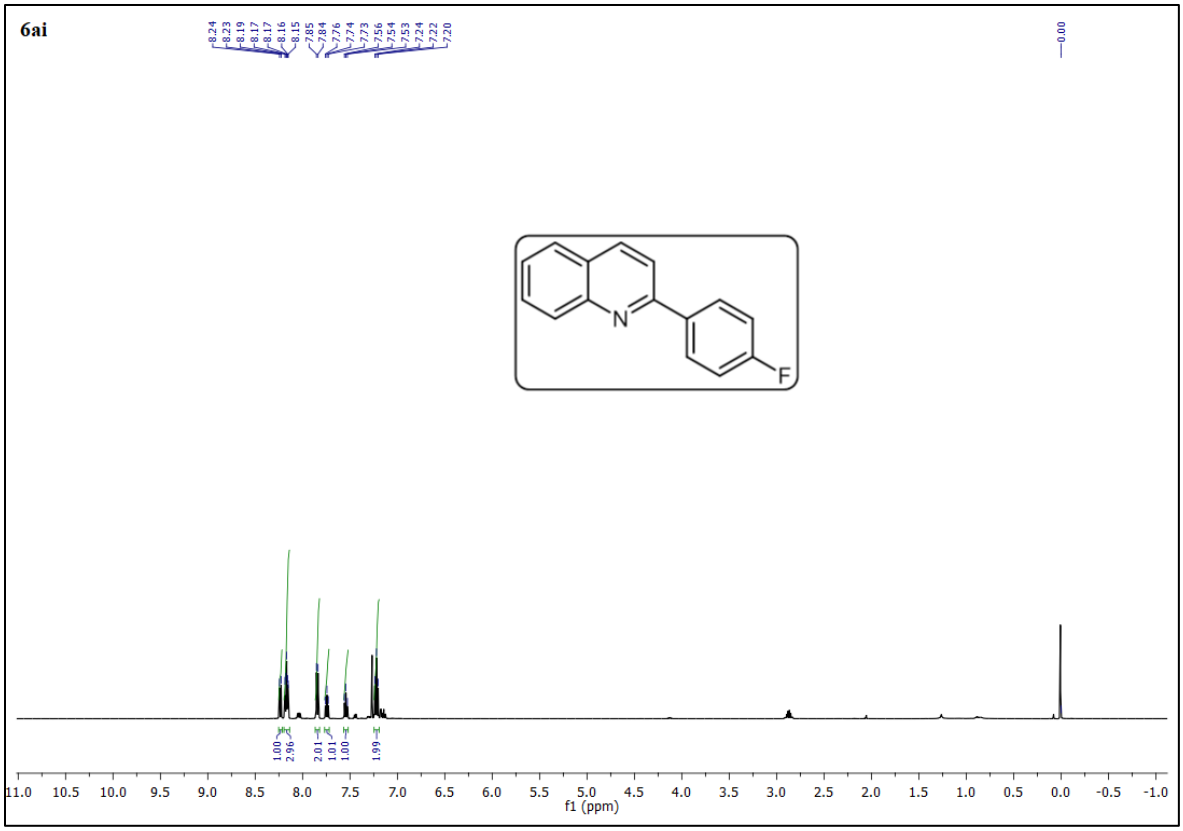

160.24
156.96
148.32
136.63
132.06
129.59
129.53
128.90
127.47
126.92
125.90
118.55
114.77
63.57
14.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

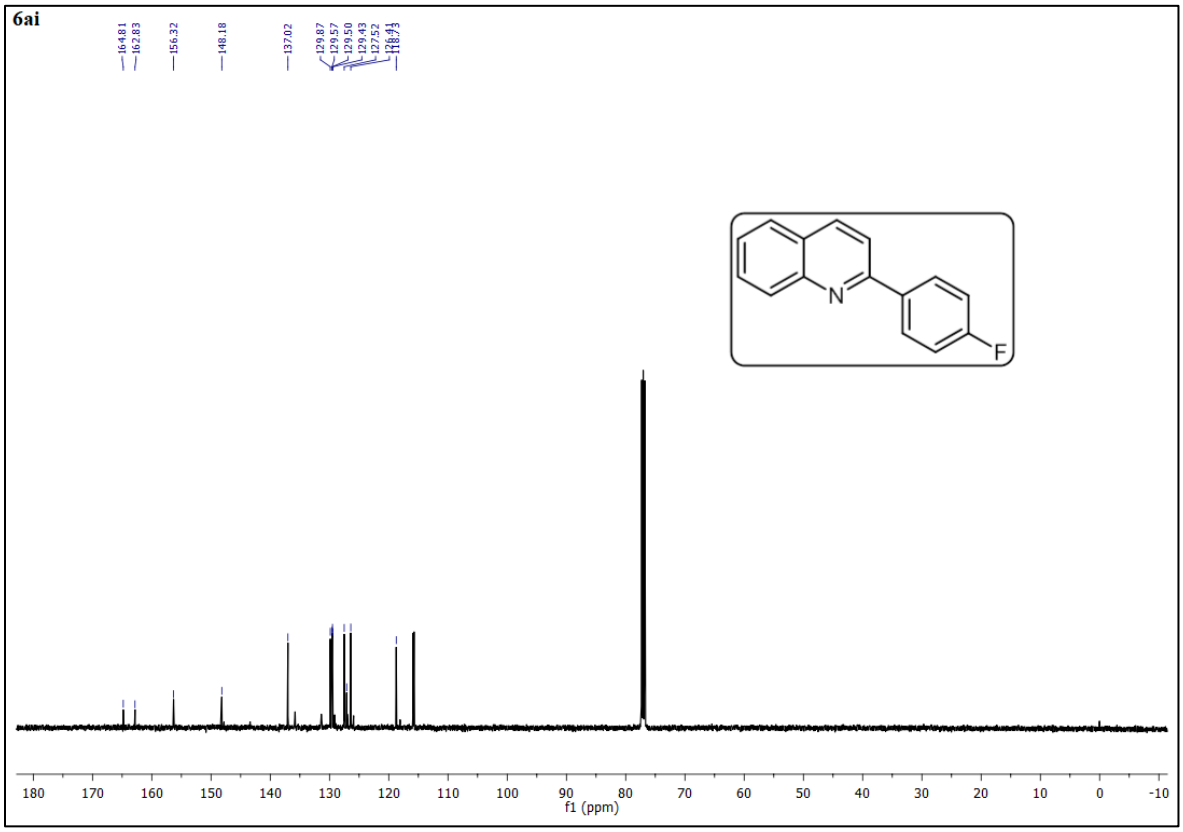

6ag
8.21
8.19
8.17
7.90
7.90
7.88
7.86
7.84
7.82
7.75
7.75
7.74
7.74
7.73
7.72
7.72
7.70
7.69
7.68
7.67
7.54
7.52
7.51
7.02
7.01
4.07
3.98
O
N
O
1.98
2.02
1.00
1.00
0.90
0.97
0.95
3.00
3.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


6ag
156.86
150.38
149.39
148.21
136.69
132.53
129.65
129.49
127.47
126.99
126.03
120.27
118.67
111.02
110.40
56.03
O
N
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

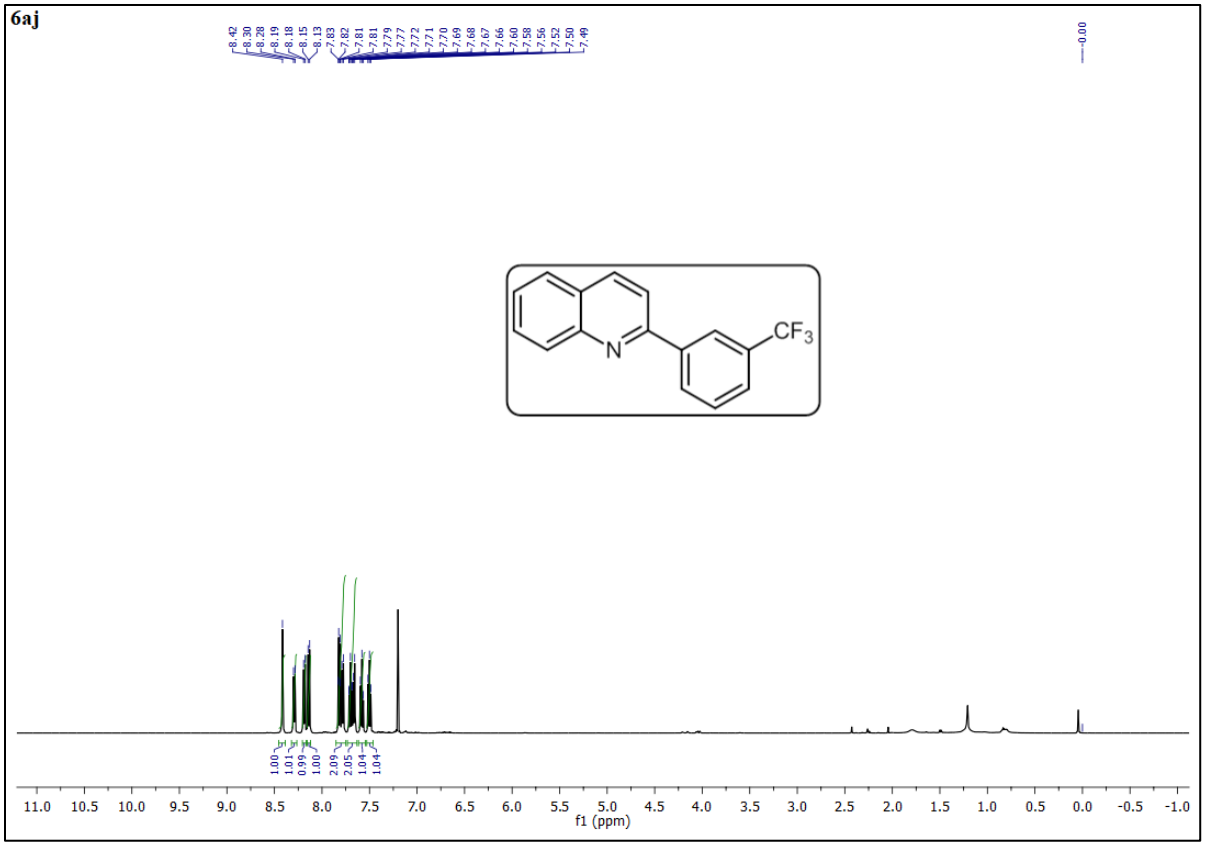

6ah
8.25
8.23
8.16
8.15
8.13
8.12
7.86
7.84
7.83
7.76
7.74
7.73
7.56
7.54
7.53
7.51
7.49
7.26
0.00
N
Cl
1.02
2.92
1.92
1.00
1.08
1.83
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


6ah
156.05
148.24
138.07
137.02
135.56
129.89
129.05
128.85
127.51
126.54
118.62
N
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

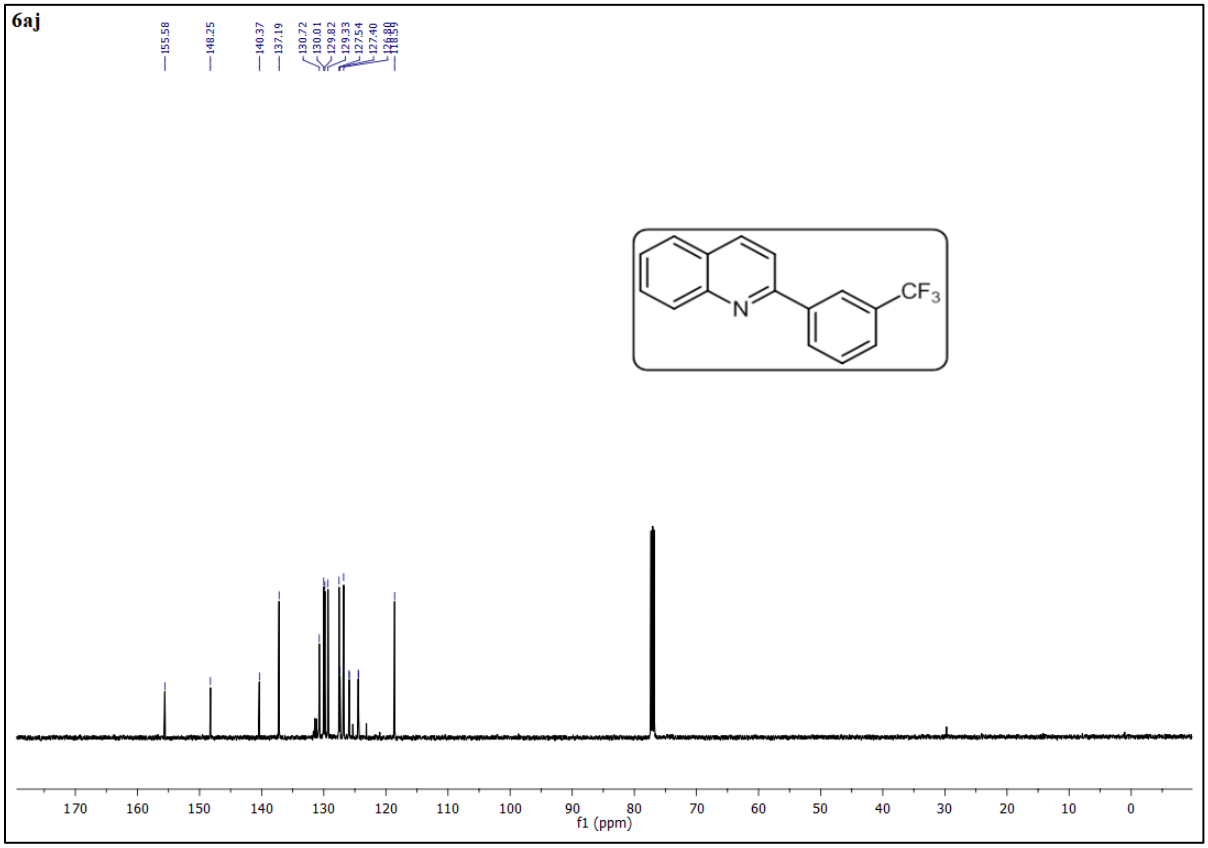

6ai
8.24
8.23
8.19
8.17
8.17
8.16
8.15
7.85
7.84
7.76
7.74
7.73
7.56
7.54
7.53
7.24
7.22
7.20
0.00
N
F
1.00
2.96
2.01
1.01
1.00
1.99
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


6ai
164.81
162.83
156.32
148.18
137.02
129.87
129.57
129.50
129.43
127.52
N
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

6aj


8.42
8.30
8.28
8.19
8.18
8.15
8.13
7.83
7.82
7.81
7.81
7.79
7.77
7.72
7.71
7.70
7.69
7.68
7.67
7.66
7.60
7.58
7.56
7.52
7.50
7.49
0.00
CF3
N
1.00
1.01
0.99
1.00
2.09
2.05
1.04
1.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

6aj


155.58
148.25
140.37
137.19
130.72
130.01
129.82
129.33
127.54
127.40
CF3
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)