

SUPPLEMENTARY INFORMATION

Photo Catalytic Activity of Rose Bengal Encapsulated on Zeolitic Imidazolate Framework-8 (RB@ZIF-8): A Innovative Approach for the One Pot Synthesis of Highly Functionalized Tetrahydropyridines and Study of their Anti-tubercular Activity.

Munmee Goswami a, Pooja Paul a, Chayan Pandya b, Ridahunlang Nongkhlaw a, Arup Dutta a, Jyothi Kumari c, Dharmarajan Sriram c, Akella Sivaramakrishna b, Rishanlang Nongkhlaw a,*

a Centre for Advanced Studies in Chemistry, North Eastern Hill University, Shillong 793022, India

b Department of Chemistry, Vellore Institute of Technology (VIT), Vellore Tamil Nadu 632014, India

c Department of Pharmacy, BITS Pilani, Hyderabad Campus, 500078, India

*Corresponding author E-mail address: rlnongkhlaw@gmail.com

Sl. No.	Table of Contents	Page No.
I	General Information	S2
II	Preparation of RB@ZIF-8 composite photocatalyst	S2
III	Characterization of RB@ZIF-8 composite photocatalyst	S3-S5
IV	General methods of compound synthesis	S5
V	Recycling Experiment	S5-6
VI	Calculation of Green Chemistry matrices	S6-S8
VII	Analytical and spectroscopic data of the synthesized compounds	S8-S27
VIII	^1H & ^{13}C NMR Spectra of the synthesized compounds	S27-S67
IX	Evaluation of Anti-tubercular activities	S67
X	References	S68

I. General Information

All the chemicals were bought from Alfa Aesar, Spectrochem, Sigma-Aldrich & Merck and were used without any further purification. The purity of the prepared compounds were confirmed by using FT-IR, ¹H-NMR, ¹³C-NMR. The HR-MS data for novel derivatives also provided. FT-IR spectra were recorded in KBr pellets on a Bruker ALPHA II spectrometer and the frequencies are expressed in cm⁻¹. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance II-400 spectrometer in CDCl₃ solvent. Mass spectral data of the newly synthesized compounds were recorded on Waters, Xevo G2-XS QToF Mass Spectrometer. Powder XRD analysis was conducted using Powder XRD Make: Rigaku (Model: SmartLab SE). All reactions were monitored by thin layer chromatography (TLC) using pre-coated aluminum sheets (silica gel 60 F 254 0.2 mm thickness) and developed in an iodine and UV-light chamber. Melting points were recorded in capillary tubes using OPTICS Technology. TEM were conducted using a transmission electron microscope of JEM-2100 make (JEOL). SEM and EDX analyses were carried out using Zeiss, model: Sigma 300 make scanning electron microscope and Gemini 500 FE-SEM. TGA analysis was conducted on a Perkin Elmer STA-6000. 24 W LED light was used as visible light source

II. Preparation of RB@ZIF-8 photocatalyst

Preparation of ZIF-8 and RB@ZIF-8 NPs

ZIF-8 nanoparticles (ZIF-8 NPs) were prepared on the word of a previously published protocol [S1]. Briefly, in 300 mL methanol, 4.5 gm of Zn (NO₃)₂·6H₂O (15 mmol) and 9.9 gm of 2-methylimidazole (2-MI)(0.12 mol) were dissolved (solution prepared separately in 150 ml methanol each) and the solution was stirred at room temperature. The resulting solid precipitate was collected through centrifugation, washed with methanol and dried in a vacuum oven at 40 °C for 12 hour. Similarly, RB@ZIF-8 NPs were also prepared with a minor modification. 4.5 gm of Zn (NO₃)₂·6H₂O (15 mmol) was dissolved in 150 mL methanol, followed by adding 150 mL of methanol containing 9.9 gm of 2-MI (0.12 mol) and 200 mg of RB (0.19 mmol) and stirred at room temperature. Afterwards, the suspension was centrifuged at 12000 rpm for 8 min to obtain RB@ZIF-8 NPs, which were washed with methanol, dried in vacuum and stored at dry environment [S2].

III. Characterization of RB@ZIF-8 NPs

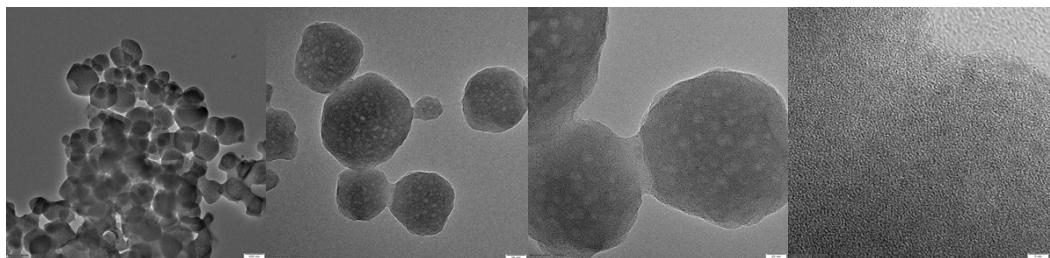


Figure S1. TEM mages of the prepared RB@ZIF-8

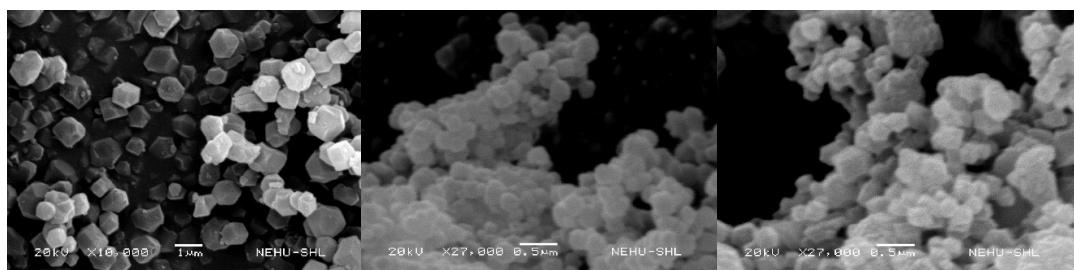


Figure S2. SEM images of (A) ZIF-8, (B) RB@ZIF-8 and (C) Recovered RB@ZIF-8

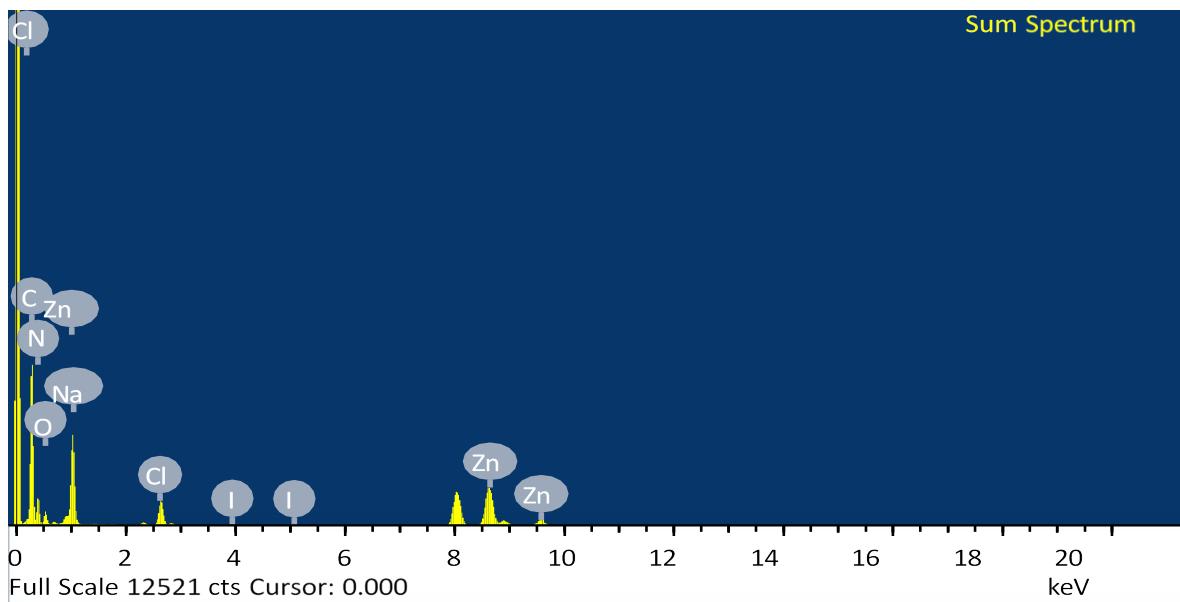


Figure S3. EDS peaks of the prepared RB@ZIF-8

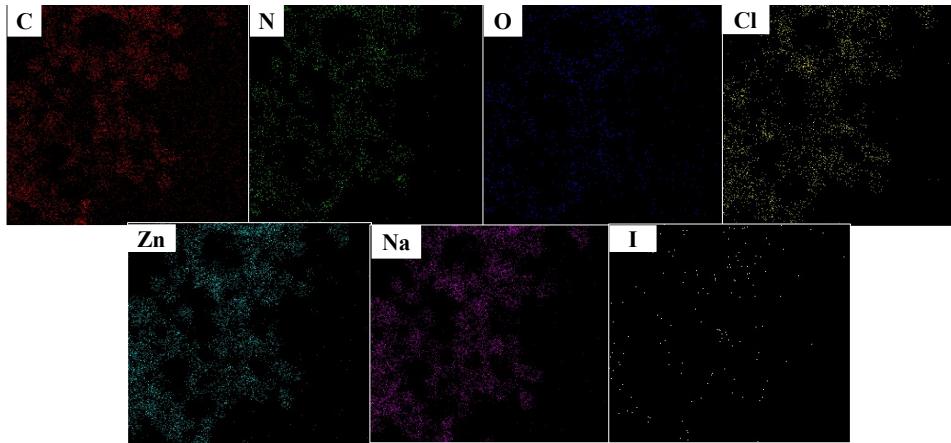


Figure S4. Elementary mapping of the prepared RB@ZIF-8

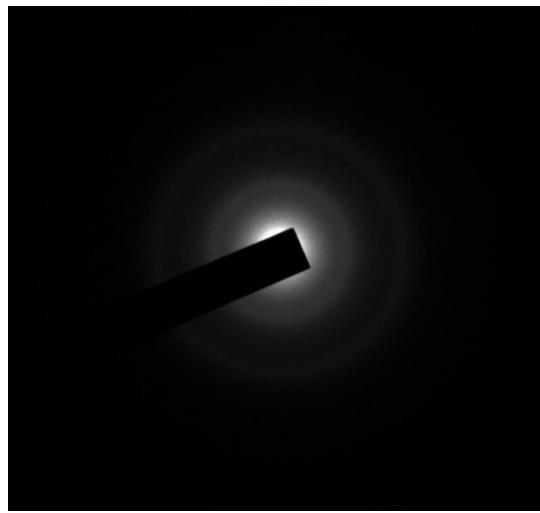


Figure S5. SAED pattern of recovered catalyst

The band gap of the catalyst is calculated by using Tauc method [S3] as given below

$$\alpha = \frac{A(hv - E_g)^n}{hv} \quad \text{or} \quad (\alpha hv)^{\frac{1}{n}} = A^{\frac{1}{n}} hv - A^{\frac{1}{n}} E_g$$

$$\alpha = \frac{\ln(1/T)}{x}$$

Where, α = absorption coefficient, T = Transmittance, x = thickness of the sample, E_g = band gap of the material, $n = 2, 1/2, 2/3$ and $1/3$ for direct allowed, indirect allowed, direct forbidden and indirect forbidden.

By plotting a graph of $(\alpha hv)^{\frac{1}{n}}$ vs hv , we got slope as $A^{\frac{1}{n}}$ and y intercept as $A^{\frac{1}{n}} E_g$. Dividing y intercept by A^n , we can estimate the band gap.

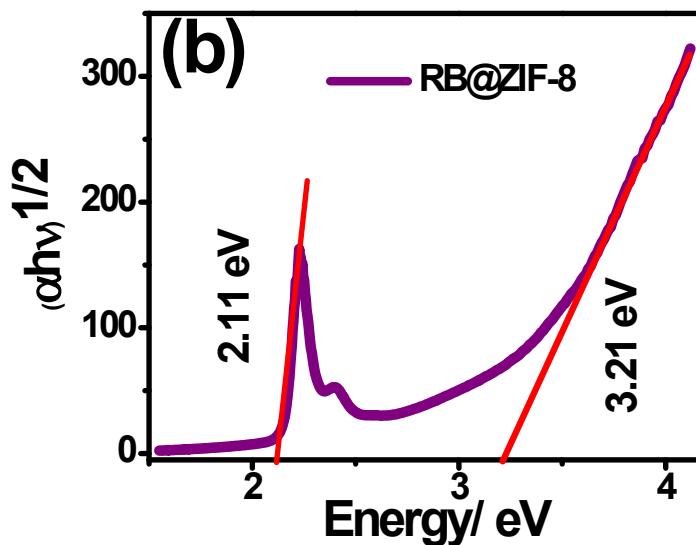


Figure S6. Tauc plot of RB@ZIF-8 for Band Gap energy calculation

IV. General methods of compound synthesis

General method for the synthesis of tetrahydropyridine derivatives

In a round bottom flask, a mixture of methyl acetoacetate (1 mmol), aniline (2 mmol), benzaldehyde (2 mmol) and RB@ZIF-8 (25 mg) in 5 mL of ethanol was magnetically stirred under 24W LED light for required times. The progress of the reaction was monitored by TLC. After completion, the catalyst was recovered by simple centrifugation and washed with ethanol and dried it for next run and the pure product was obtained by washing with ethanol or recrystallization from hot ethanol wherever it's needed.

V. Recycling experiments

In a round bottom flask, a mixture of methylacetoacetate (1 mmol), benzaldehyde (2 mmol) and aniline (2 mmol)) in 5 mL of ethanol was stirred under 24W LED light in presence of RB@ZIF-8 for 10 min at room temperature. After completion of the reaction, simple centrifugation method was used to separate the RB@ZIF-8 from the reaction system. The recovered RB@ZIF-8 was washed three times with ethanol. The ethanol solution was combined with reaction solution and

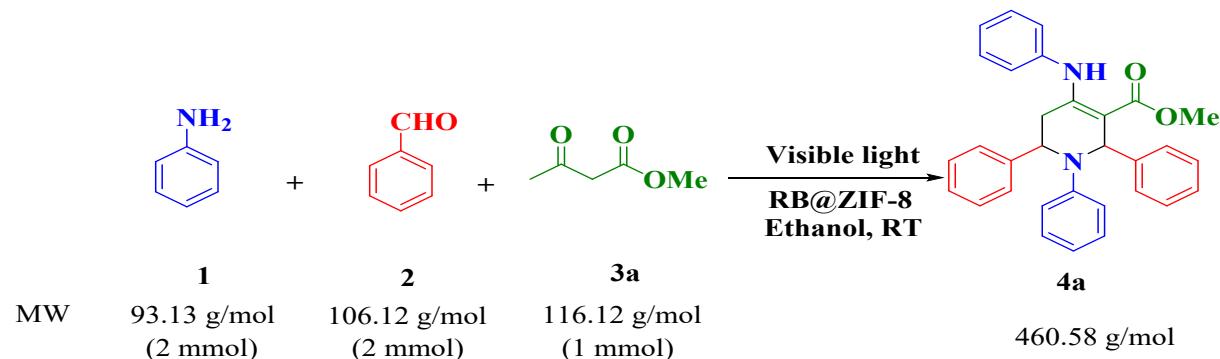
evaporated to dry the solvent. The remaining residue was mixed with internal standard and the mixture was subjected for ^1H NMR quantification. The washed RB@ZIF-8 was then dried in an oven and used for the next round of photocatalysis. The catalyst can be reused up to six times without significant loss of the catalytic activity.



Figure S5. Recyclability of RB@ZIF-8 in the synthesis of **4a**

VI. Green chemistry matrix calculations for **4a:** Green chemistry matrix has been calculated for the reaction on the basis of following parameters below.

- (i) Atom economy (AE)
- (ii) Reaction mass efficiency (RME)
- (iii) Environmental factor (E-factor)
- (iv) Product mass intensity (PMI)



- (i) Atom economy (AE) for **4a**:** Atom economy define the efficacy of a chemical reaction with regard to how many atoms from the starting materials reside within the product.

Higher the value of AE, greener is the reaction. The ideal value of AE factor is 100% which indicates that all atoms from the starting materials reside in the product.

$$\text{AE} = \frac{\text{MW of the Product}}{\sum (\text{MW of stoichiometric reactants})} \times 100$$

$$= \frac{460.58}{(93.13 \times 2) + (106.12 \times 2) + (116.12 \times 1)} \times 100$$

$$= \frac{460.58}{514.62} \times 100$$

$$= 89 \%$$

(ii) Reaction mass efficiency (RME) for 4a: Reaction mass efficiency is calculated by following equation,

$$\text{RME} = \frac{\text{Mass of the Product}}{\sum (\text{MW of stoichiometric reactants})} \times 100$$

$$= \frac{442.15}{(93.13 \times 2) + (106.12 \times 2) + (116.12 \times 1)} \times 100$$

$$= \frac{442.15}{514.62} \times 100$$

$$= 85.9 \%$$

(iii) E-factor or environmental factor for 4a: E-factor implies the total amount of waste generated during a chemical reaction. The ideal value of E-factor is zero

$$\text{E-factor} = \frac{\text{Mass of waste}}{\text{Mass of Product}}$$

Where, mass of waste = (total mass of raw materials) – (the total mass of product)

$$E - \text{Factor} = \frac{[(93.13 \times 2) + (106.12 \times 2) + (116.12 \times 1)] - 442.15 \text{ mg}}{442.15 \text{ mg}}$$

$$\begin{aligned}
 & \frac{[186.26 + 212.24 + 116.12) - 442.15] \text{ mg}}{442.15 \text{ mg}} \\
 &= \frac{72.47}{442.15} \\
 &= 0.16
 \end{aligned}$$

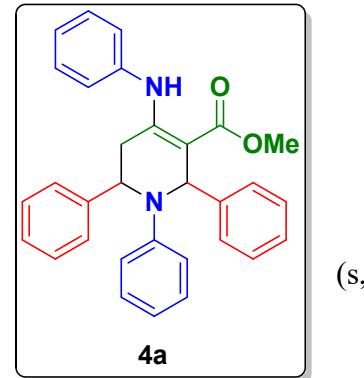
(iv) **Product mass intensity (PMI) for 4a:** PMI can be calculated by the following equation,

$$\begin{aligned}
 \text{PMI} &= \frac{\Sigma (\text{mass of stoichiometric reactants} + \text{solvent})}{\text{mass of product}} \\
 &= \frac{(93.13 \times 2) + (106.12 \times 2) + (116.12 \times 1) + 46.06}{442.15} \\
 &= \frac{512.62 + 46.06}{442.15} \\
 &= 1.26
 \end{aligned}$$

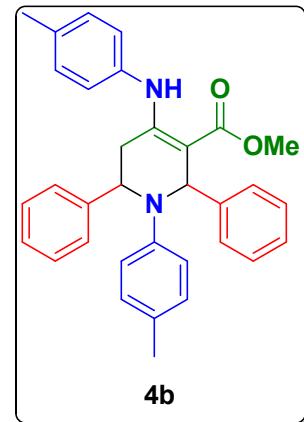
VII. Analytical and spectroscopic data of the synthesized compounds

Methyl-1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate, 4a

White solid. Melting point: 194-196 °C. IR (KBr): ν_{max} 3251, 3025, 2949, 2867, 1661, 1587, 1500, 1451, 1377, 1323, 1256, 1186, 1078, 982, 929, 752, 699 cm⁻¹: ¹H NMR (400 MHz, CDCl₃) δ 10.23 (s, 1H), 7.29 (t, *J* = 6.5 Hz, 3H), 7.25-7.18 (m, 4H), 7.17-7.11 (m, 2H), 7.10 – 7.01 (m, 6H), 6.58 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 8.3 Hz, 2H), 6.43 (s, 1H), 6.29 – 6.23 (m, 2H), 5.13 (d, *J* = 3.9 Hz, 1H), 3.91 (3H), 2.85 (dd, *J* = 15.1, 5.7 Hz, 1H), 2.74 (dd, *J* = 15.1, 2.4 Hz, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 168.7, 156.4, 147.0, 144.0, 142.8, 137.9, 129.0, 128.9, 128.7, 128.3, 127.2, 126.7, 126.5, 126.4, 125.9, 125.9, 116.2, 113.0, 98.0, 58.3, 55.2, 51.1, 33.7 ppm.

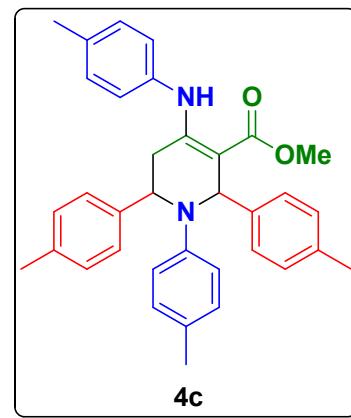


White solid. Melting Point: 220-222 °C. IR (KBr): ν_{max} 3258, 3025, 2945, 2862, 1656, 1594, 1516, 1451, 1318, 1257, 1076, 832, 700 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.17 (s, 1H), 7.33 - 7.16 (m, 10H), 6.90-6.83 (m, 4H), 6.42 (d, $J = 4.1$ Hz, 3H), 6.15 (d, $J = 7.9$ Hz, 2H), 5.12 (s, 1H), 3.93 (s, 3H), 2.85-2.72 (m, 2H), 2.26 (s, 3H), 2.16 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 168.6, 156.6, 144.8, 144.2, 143.0, 135.6, 135.1, 129.4, 129.4, 128.6, 128.2, 127.0, 126.6, 126.4, 126.2, 126.0, 125.0, 112.8, 97.4, 58.2, 55.1, 50.9, 33.5, 20.9, 20.1 ppm.



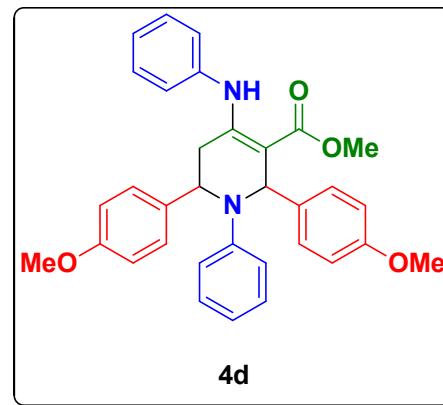
Methyl-4-(p-tolylamino)-1,2,5,6-tetrahydro-1,2,6-trip-tolylpyridine-3-carboxylate, 4c

White solid. Melting point: 204-206 °C. IR (KBr): ν_{max} 3251, 3022, 2919, 2855, 1906, 1657, 1596, 1457, 1369, 1259, 1182, 1021, 948, 793, 661 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.17 (s, 1H), 7.20 (d, $J = 7.9$ Hz, 2H), 7.09-7.04 (m, 6H), 6.89 (d, $J = 8.0$ Hz, 2H), 6.87 (d, $J = 8.5$ Hz, 2H), 6.43 (d, $J = 8.5$ Hz, 2H), 6.36 (s, 1H), 6.18 (d, $J = 8.0$ Hz, 2H), 5.08 (s, 1H), 3.91 (s, 3H), 2.82 (dd, $J = 15.1$, 5.6 Hz, 1H), 2.73 (d, $J = 15.0$, 2.4 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 2.27 (s, 3H), 2.16 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 168.6, 156.6, 144.9, 141.2, 139.9, 136.5, 135.6, 135.5, 135.2, 129.4, 129.4, 129.2, 128.9, 126.5, 126.3, 125.9, 124.8, 112.8, 97.5, 57.9, 55.0, 50.9, 33.5, 21.1, 21.0, 20.9, 20.1 ppm.



Methyl-1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)-1-phenyl-4-phenylamino)pyridine-3-carboxylate, 4d

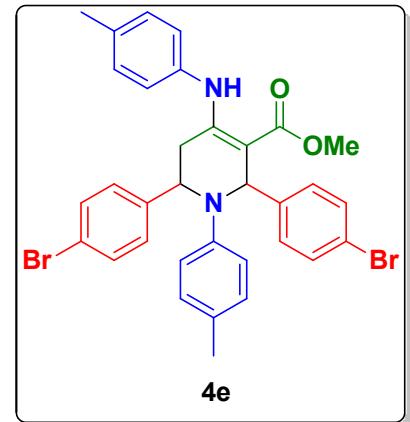
White solid. Melting point: 187-189 °C. IR (KBr): ν_{max} 3243, 3062, 2951, 2838, 1654, 1593, 1505, 1454, 1372, 1250, 1185, 1072, 1034, 830, 760, 698 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.27 (s, 1H), 7.22 (d, $J = 8.6$ Hz, 2H), 7.05-7.14 (m, 7H), 6.82 (d, $J = 8.3$ Hz, 4H), 6.61 (t,



= 7.2 Hz, 1H), 6.53 (d, *J* = 8.3 Hz, 2H), 6.36 - 6.37 (m, 3H), 5.09 (s, 1H), 3.93 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 2.86 (dd, *J* = 15.0, 5.5 Hz, 1H), 2.76 (dd, *J* = 15.0, 2.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 158.8, 158.1, 156.5, 147.1, 138.0, 135.9, 134.7, 128.9, 128.9, 127.8, 127.5, 125.8, 125.7, 116.1, 114.1, 113.6, 113.0, 98.2, 57.6, 55.4, 55.3, 54.6, 51.1, 33.8 ppm.

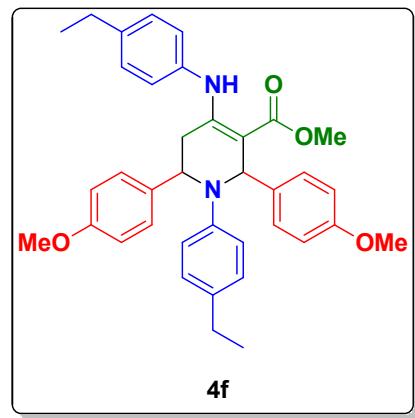
Methyl-4-(p-tolylamino)-2,6-bis(4-bromophenyl)-1,2,5,6-tetrahydro-1-p-tolylpyridine-3-carboxylate, 4e

White solid. M.P. 195-197 °C. IR (KBr): ν_{max} 3232, 3085, 2922, 2857, 1656, 1624, 1516, 1314, 1252, 1138, 1071, 1013, 925, 794, 536 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.15 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 4H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.98 (dd, *J* = 16.0, 8.2 Hz, 4H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 8.6 Hz, 2H), 6.28 (d, *J* = 7.9 Hz, 3H), 5.04 (s, 1H), 3.90 (s, 3H), 2.77 (dd, *J* = 15.2, 5.4 Hz, 1H), 2.69 (dd, *J* = 15.2, 2.5 Hz, 1H), 2.29 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 156.3, 144.2, 143.2, 141.73, 136.0, 134.91, 131.69, 131.30, 129.6, 128.4, 128.2, 125.9, 125.8, 120.8, 120.1, 120.0, 112.9, 96.9, 57.3, 54.8, 51.1, 33.5, 20.9, 20.1 ppm.



Methyl-4-(4-ethylphenylamino)-1-(4-ethylphenyl)-1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)pyridine-3-carboxylate, 4f

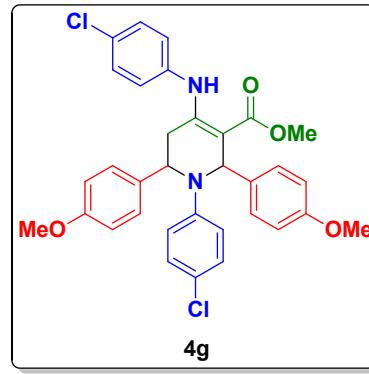
White solid. Melting Point: 202-206 °C. IR (KBr): ν_{max} 3256, 3065, 2960, 2866, 1654, 1611, 1512, 1458, 1374, 1248, 1189, 1073, 1032, 981, 812 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.20 (s, 1H), 7.24 – 7.20 (m, 2H), 7.11 – 7.05 (m, 2H), 6.92 (dd, *J* = 15.3, 8.5, 1.9 Hz, 4H), 6.82 (dd, *J* = 8.6, 3.6, 1.8 Hz, 4H), 6.49 – 6.42 (m, 2H), 6.35 – 6.31 (m, 1H), 6.29 – 6.22 (m, 2H), 5.06 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 2.82



(dd, $J = 15.1, 5.1$ Hz, 1H), 2.73 (d, $J = 15.0$ Hz, 1H), 2.57 (q, $J = 7.5$ Hz, 2H), 2.47 (q, $J = 7.5$ Hz, 2H), 1.19 (t, $J = 7.6$ Hz, 3H), 1.13 (t, $J = 7.5$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 158.0, 156.8, 145.2, 136.3, 135.5, 135.1, 131.5, 128.3, 128.2, 127.8, 127.6, 126.0, 114.0, 113.6, 113.0, 97.7, 57.6, 55.4, 55.3, 54.8, 51.0, 33.8, 28.3, 27.7, 15.7, 15.5 ppm. HRMS (ESI): calcd Exact Mass: 576.2988; found 576.2985

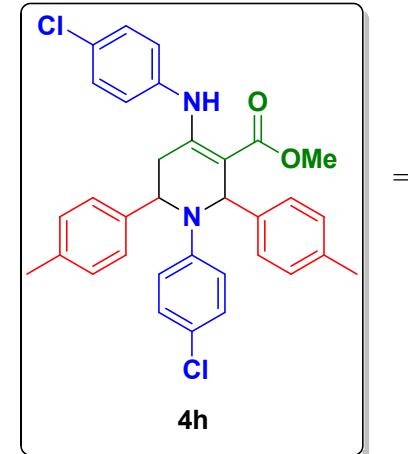
Methyl-4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)pyridine-3-carboxylate, 4g

White solid. Melting point: 194-196 °C. IR (KBr): ν_{max} 3239, 3000, 2947, 1661, 1608, 1501, 1447, 1375, 1252, 1181, 1073, 978, 760, 1012, 812 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.21 (s, 1H), 7.17 (d, $J = 8.5$ Hz, 2H), 7.09-6.98 (m, 6H), 6.82 (dd, $J = 8.5, 4.4$ Hz, 4H), 6.43 (d, $J = 9.0$ Hz, 2H), 6.27 (t, 3H), 5.05 (s, 1H), 3.93 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 2.83 (dd, $J = 15.1, 5.6$ Hz, 1H), 2.68 (dd, $J = 14.8, 1.8$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 158.9, 158.2, 155.6, 145.5, 136.4, 135.0, 134.0, 131.3, 129.0, 128.6, 127.5, 127.3, 127.0, 121.1, 114.1, 114.0, 114.0, 113.7, 113.6, 98.6, 57.6, 55.3, 55.2, 54.7, 33.6 ppm.



Methyl-4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-dip-tolylpyridine-3-carboxylate, 4h

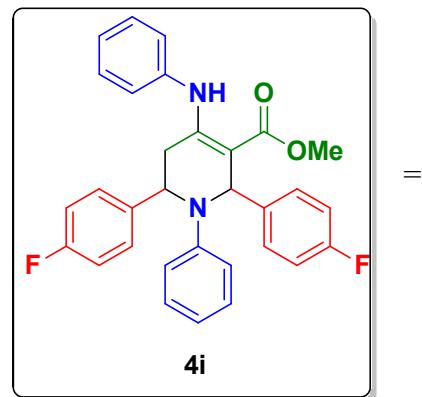
White solid; Melting point: 184-186 °C. IR (KBr): ν_{max} 3260, 2954, 2858, 1650, 1604, 1497, 1375, 1264, 1084, 929, 852, 757, 652 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.19 (s, 1H), 7.21 – 6.94 (m, 12H), 6.43 (d, $J = 8.8$ Hz, 2H), 6.32 (s, 1H), 6.19 (d, $J = 8.3$ Hz, 2H), 5.07 (s, 1H), 3.93 (s, 3H), 2.85 (dd, $J = 15.1, 5.5$ Hz, 1H), 2.69 (d, $J = 14.9$ Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 168.6, 155.6, 145.6, 140.2, 139.2, 137.1, 136.5, 136.2, 131.4, 129.5, 129.1, 129.0, 128.7,



127.1, 126.5, 126.2, 121.1, 114.0, 98.6, 58.1, 55.1, 51.2, 33.6, 21.2, 21.1 ppm.

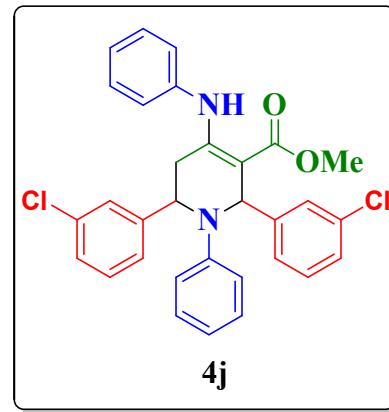
Methyl-2,6-bis(4-fluorophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate, 4i

White solid. Melting point: 182-184 °C. IR (KBr): ν_{max} 3258, 3046, 2949, 2860, 1658, 1593, 1469, 1369, 1267, 1196, 1074, 1013, 829, 793, 694 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.27 (s, 1H), 7.28 (s, 1H), 7.24 (s, 1H), 7.19-7.05 (m, 7H), 6.96 (t, *J* = 8.6 Hz, 4H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 8.5 Hz, 2H), 6.39 (dd, *J* = 9.5, 2.7 Hz, 3H), 5.12 (s, 1H), 3.93 (s, 3H), 2.84 (dd, *J* = 15.1, 5.5 Hz, 1H), 2.75 (dd, *J* = 15.1, 2.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 163.3, 162.8, 160.8, 160.4, 156.2, 146.7, 139.4, 138.2, 137.7, 129.1, 128.3, 128.2, 128.0, 127.9, 126.1, 125.8, 116.7, 115.7, 115.5, 115.2, 115.0, 113.0, 97.8, 57.4, 54.7, 51.2, 33.9 ppm.



Methyl-2,6-bis(3-chlorophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate, 4j

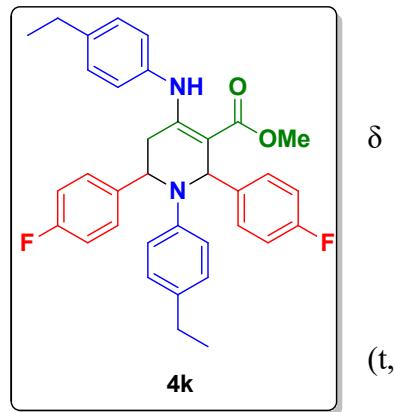
White solid. Melting point: 130-132 °C. IR (KBr): ν_{max} 3242, 3062, 2948, 2869, 1656, 1598, 1521, 1399, 1266, 1180, 1072, 1012, 859, 747, 695 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.25 (s, 1H), 7.24 (s, 5H), 7.20 – 7.03 (m, 8H), 6.65 (t, *J* = 7.1 Hz, 1H), 6.43 (dd, *J* = 19.4, 7.6 Hz, 4H), 6.36 (s, 1H), 5.10 (s, 1H), 3.92 (s, 3H), 2.83 (dd, *J* = 15.1, 5.4 Hz, 1H), 2.74 (d, *J* = 13.7 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 156.1,



146.5, 142.4, 141.0, 137.6, 132.9, 132.2, 129.1, 129.1, 128.9, 128.5, 128.1, 127.8, 126.1, 125.8, 116.8, 113.0, 97.6, 57.4, 54.8, 51.3, 33.7 ppm.

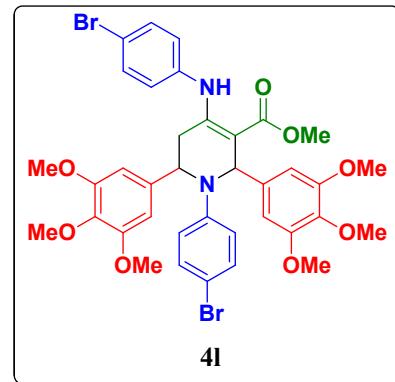
Methyl-4-(4-ethylphenylamino)-1-(4-ethylphenyl)-2,6-bis(4-fluorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate, 4k

White solid; Melting point: 220-222 °C. IR (KBr): ν_{max} 3260, 3052, 2962, 2866, 1654, 1595, 1455, 1374, 1255, 1230, 1226, 1189, 1073, 1017, 979, 826, 668 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.19 (s, 1H), 7.25 (s, 1H), 7.11 (s, 2H), 6.93 (dd, $J = 19.7, 6.9$ Hz, 9H), 6.40 (d, $J = 7.8$ Hz, 2H), 6.33 (s, 1H), 6.28 (d, $J = 7.4$ Hz, 2H), 5.08 (s, 1H), 3.91 (s, 3H), 2.75 (dd, 2H), 2.57 (q, $J = 6.8$ Hz, 2H), 2.47 (q, $J = 6.7$ Hz, 2H), 1.19 (t, $J = 7.3$ Hz, 3H), 1.12 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 156.3, 144.4, 142.0, 134.9, 131.8, 128.1, 128.1, 127.9, 127.9, 127.7, 127.7, 125.7, 115.3, 115.1, 114.8, 114.6, 112.7, 97.0, 57.1, 54.5, 50.8, 33.5, 28.0, 27.4, 15.4, 15.2 ppm. HRMS (ESI): calcd 552.2588; found 552.2598



Methyl-4-(4-bromophenylamino)-1-(4-bromophenyl)-1,2,5,6-tetrahydro-2,6-bis(3,4,5-trimethoxyphenyl)pyridine-3-carboxylate, 4l

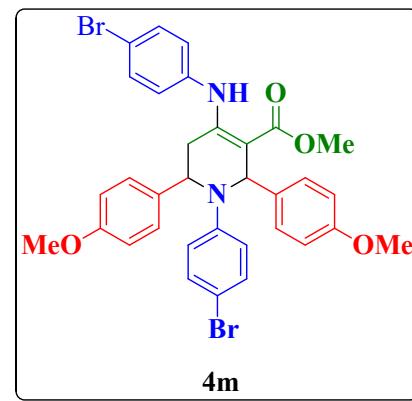
White solid; Melting point: 136-138 °C. IR (KBr): ν_{max} 3252, 3069, 2994, 2833, 1657, 1590, 1496, 1373, 1255, 1186, 1073, 1038, 960, 779, 698 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.17 (s, 1H), 7.28 (s, 1H), 7.16 (d, $J = 8.7$ Hz, 2H), 6.49 – 6.38 (m, 4H), 6.33 – 6.21 (m, 6H), 4.98 (s, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.74 (s, 6H), 3.70 (s, 6H), 2.93 (dd, $J = 14.9, 5.2$ Hz, 1H), 2.70 (d, $J = 14.6$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 156.2, 153.5, 153.2, 145.9, 138.8, 137.6,



137.2, 136.9, 136.8, 132.0, 131.6, 127.8, 119.7, 114.7, 108.9, 103.8, 103.0, 97.9, 61.0, 60.9, 58.4, 56.1, 56.1, 55.7, 51.2, 33.7 ppm. HRMS (ESI): calcd 796.0995; found 796.0978.

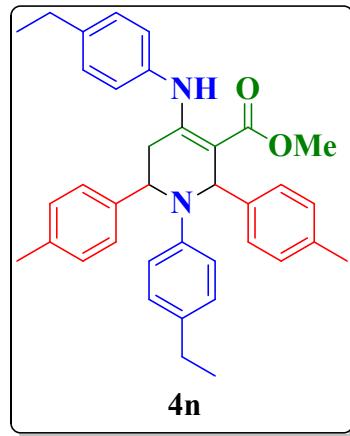
Methyl-4-(4-bromophenylamino)-1-(4-bromophenyl)-1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)pyridine-3-carboxylate, 4m

White solid. Melting point: 178-180 °C. IR (KBr): ν_{max} 3240, 3062, 2996, 2835, 1659, 1607, 1494, 1374, 1251, 1179, 1071, 1034, 807, 756 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.21 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.14 (dd, *J* = 15.9, 8.8 Hz, 4H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.82 (dd, *J* = 8.6, 3.9 Hz, 4H), 6.39 (d, *J* = 9.0 Hz, 2H), 6.28 (s, 1H), 6.20 (d, *J* = 8.5 Hz, 2H), 5.03 (s, 1H), 3.93 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 2.83 (dd, *J* = 15.1, 5.6 Hz, 1H), 2.69 (dd, *J* = 15.0, 2.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 168.6, 159.0, 158.3, 155.6, 165.0, 137.0, 135.0, 134.0, 132.1, 131.6, 127.6, 127.4, 127.3, 114.7, 114.2, 113.8, 108.4, 98.8, 57.6, 55.4, 55.3, 54.7, 51.3, 33.6 ppm.



Methyl-4-(4-ethylphenylamino)-1-(4-ethylphenyl)-1,2,5,6-tetrahydro-2,6-dip-tolylpyridine-3-carboxylate, 4n

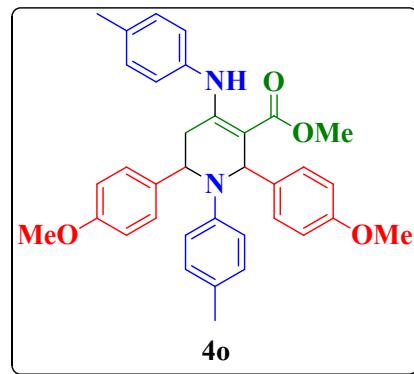
White solid. Melting point: 178-180 °C. IR (KBr): ν_{max} 3262, 3089, 2960, 2865, 1655, 1595, 1454, 1372, 1254, 1186, 1073, 1022, 786, 690 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.17 (s, 1H), 7.20 (d, *J* = 7.1 Hz, 2H), 7.12 – 7.03 (m, 6H), 6.90 (t, *J* = 7.4 Hz, 4H), 6.45 (d, *J* = 7.7 Hz, 2H), 6.35 (s, 1H), 6.19 (d, *J* = 7.3 Hz, 2H), 5.08 (s, 1H), 3.90 (s, 3H), 2.82 (dd, *J* = 14.7, 4.5 Hz, 1H), 2.73 (d, *J* = 14.7 Hz, 1H), 2.56 (d, *J* = 7.3 Hz, 2H), 2.46 (d, *J* = 7.3 Hz, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H) ppm. ¹³C NMR (100 MHz,



CDCl_3) δ 168.7, 156.8, 145.2, 141.4, 140.1, 136.6, 135.5, 131.4, 129.3, 128.9, 128.2, 126.6, 126.4, 126.1, 112.9, 97.6, 58.0, 55.1, 51.0, 33.7, 28.3, 27.7, 21.2, 21.1, 15.8, 15.6 ppm.

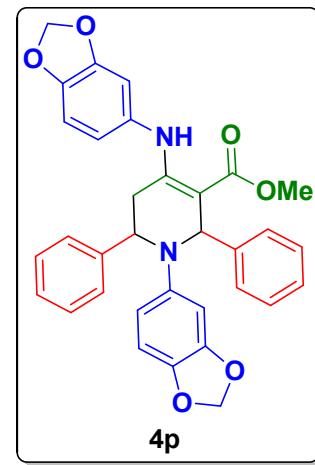
Methyl-4-(p-tolylamino)-1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)-1-p-tolylpyridine-3-carboxylate, 4o

White solid. Melting point: 175-177 $^{\circ}\text{C}$. IR (KBr): ν_{max} 3241, 3095, 2949, 2856, 1656, 1609, 1512, 1459, 1370, 1248, 1176, 1069, 1034, 799, 760 690 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.19 (s, 1H), 7.21 (d, $J = 8.6$ Hz, 2H), 7.07 (d, $J = 8.6$ Hz, 2H), 6.90 (dd, $J = 17.3, 8.3$ Hz, 4H), 6.81 (dd, $J = 8.8, 2.3$ Hz, 4H), 6.44 (d, $J = 8.7$ Hz, 2H), 6.32 (s, 1H), 6.24 (d, $J = 8.2$ Hz, 2H), 5.05 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 2.81 (dd, $J = 14.7, 5.2$ Hz, 1H), 2.72 (dd, $J = 15.0, 2.6$ Hz, 1H), 2.27 (s, 3H), 2.16 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 158.7, 158.1, 156.8, 144.9, 135.6, 135.3, 135.0, 129.5, 129.5, 127.8, 127.6, 126.0, 125.0, 114.0, 113.6, 113.0, 97.6, 57.5, 55.4, 55.3, 54.7, 51.0, 33.7, 21.0, 20.2 ppm.



Methyl-1-(benzo[d][1,3]dioxol-5-yl)-4-(benzo[d][1,3]dioxol-6-ylamino)-1,2,5,6-tetrahydro-2,6-diphenylpyridine-3-carboxylate, 4p

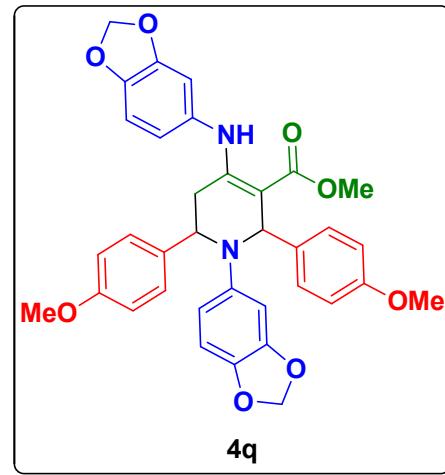
White solid. Melting point: 166-168 $^{\circ}\text{C}$. IR (KBr): ν_{max} 3212, 3064, 2946, 2864, 1660, 1589, 1485, 1399, 1288, 1230, 1185, 1071, 1010, 790, 697 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.02 (s, 1H), 7.28 (d, $J = 6.5$ Hz, 1H), 7.25-7.13 (m, 7H), 6.49 (dd, $J = 12.3, 8.4$ Hz, 2H), 6.27 (s, 1H), 6.14 (d, $J = 2.4$ Hz, 1H), 5.88 (d, $J = 7.5$ Hz, 3H), 5.73 (d, $J = 5.1$ Hz, 3H), 5.67 (d, $J = 1.9$ Hz, 1H), 5.02 (s, 1H), 3.88 (s, 3H), 2.77 (dd, $J = 15.1, 5.8$ Hz, 1H), 2.63 (dd, $J = 15.2, 2.4$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 168.6, 156.9, 148.2, 147.7, 146.9, 144.0, 143.2, 143.1, 138.6, 131.8, 128.8, 128.3, 127.3, 126.8,



126.5, 126.4, 120.0, 108.4, 108.1, 107.9, 105.1, 101.5, 100.5, 97.4, 96.1, 58.7, 56.1, 51.0, 33.8 ppm. HRMS (ESI): calcd 548.1947; found 548.1962

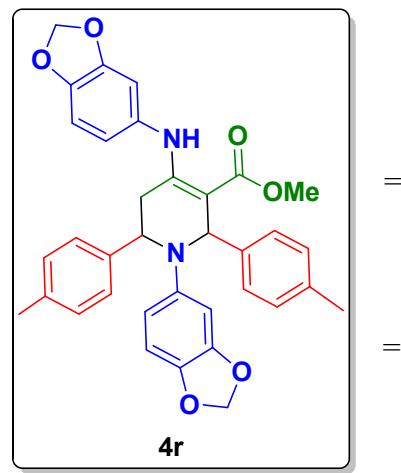
Methyl-1-(benzo[d][1,3]dioxol-5-yl)-4-(benzo[d][1,3]dioxol-6-ylamino)-1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)pyridine-3-carboxylate, 4q

White solid. Melting point: 220-222 °C. IR (KBr): ν_{max} 3274, 2989, 2946, 2894, 1656, 1586, 1488, 1351, 1291, 1222, 1185, 1098, 1036, 828, 778, 670 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.06 (s, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.82 (t, *J* = 8.1 Hz, 4H), 6.53 (dd, *J* = 8.4, 3.1 Hz, 2H), 6.20 (s, 1H), 6.17 (d, *J* = 2.4 Hz, 1H), 5.91 (dt, *J* = 8.6, 2.0 Hz, 3H), 5.84 (dd, *J* = 8.2, 1.8 Hz, 1H), 5.76 (d, *J* = 3.6 Hz, 3H), 4.97 (s, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 2.77 (dd, *J* = 15.1, 5.5 Hz, 1H), 2.63 (dd, *J* = 15.1, 2.7 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 168.7, 158.8, 158.1, 157.0, 148.1, 147.7, 145.9, 143.3, 138.5, 135.4, 134.9, 131.9, 127.8, 127.5, 119.9, 114.1, 113.6, 108.3, 108.1, 107.9, 105.3, 101.5, 100.5, 97.4, 96.3, 57.9, 55.6, 55.4, 55.3, 51.0, 33.9 ppm. HRMS (ESI): calcd 608.2159; found 608.2166.



Methyl-1-(benzo[d][1,3]dioxol-5-yl)-4-(benzo[d][1,3]dioxol-6-ylamino)-1,2,5,6-tetrahydro-2,6-dip-tolylpyridine-3-carboxylate, 4r

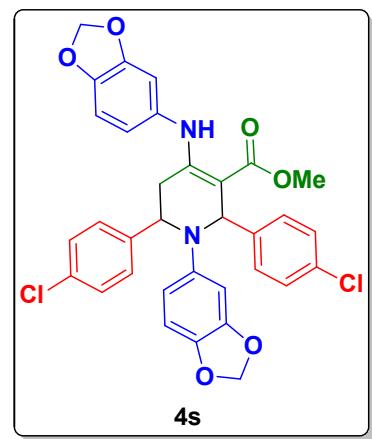
White solid. Melting point: 198-200 °C. IR (KBr): ν_{max} 3258, 2946, 2861, 1656, 1588, 1487, 1367, 1261, 1228, 1183, 1070, 1035, 840, 799, 657 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.03 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.10-7.01 (m, 6H), 6.51 (dd, *J* = 12.0, 8.4 Hz, 2H), 6.24 (s, 1H), 6.16 (d, *J* = 2.5 Hz, 1H), 5.92-5.89 (m, 3H), 5.79-5.74 (m, 3H), 5.68 (d, *J* = 2.0 Hz, 1H), 5.00 (s, 1H), 3.90 (s, 3H), 2.79 (dd, *J* = 15.1, 5.7 Hz, 1H), 2.63 (dd, *J* = 15.1, 2.6 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 156.6, 1478.8, 147.4, 145.6, 143.0, 140.7,



139.7, 138.1, 136.5, 135.5, 131.5, 129.1, 128.6, 126.4, 126.1, 119.7, 108.0, 107.8, 107.5, 104.7, 101.2, 100.1, 97.2, 97.8, 58.1, 55.5, 50.7, 33.5, 20.9, 20.8 ppm. HRMS (ESI): calcd 576.2260; found 576.2274

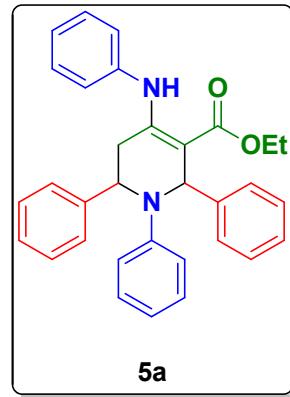
Methyl-1-(benzo[d][1,3]dioxol-5-yl)-4-(benzo[d][1,3]dioxol-6-ylamino)-2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate, 4s

White solid. Melting point: 196-198 °C. IR (KBr): ν_{max} 3256, 2998, 2946, 2873, 1661, 1590, 1487, 1359, 1261, 1226, 1184, 1096, 1035, 816, 797, 657 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.06 (s, 1H), 7.28 (d, *J* = 2.3 Hz, 2H), 7.24-7.19 (m, 4H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.56 (t, *J* = 8.8 Hz, 2H), 6.20 (s, 1H), 6.10 (d, *J* = 2.4 Hz, 1H), 5.95 (d, *J* = 4.6 Hz, 2H), 5.88-5.83 (m, 3H), 5.80 (d, *J* = 4.4 Hz, 2H), 4.99 (s, 1H), 3.90 (s, 3H), 2.75 (dd, *J* = 15.3, 5.6 Hz, 1H), 2.65 (dd, *J* = 15.3, 2.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 156.6, 148.3, 146.9, 146.2, 142.6, 142.3, 141.2, 139.1, 133.0, 132.2, 131.5, 128.9, 128.4, 128.2, 127.9, 119.9, 108.5, 108.0, 107.9, 105.4, 101.7, 100.7, 96.9, 96.3, 57.7, 55.8, 51.2, 33.8 ppm. HRMS (ESI): calcd 616.1168; found 616.1204 [M⁺], 618.1190 [M+2]



Ethyl 1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate, 5a

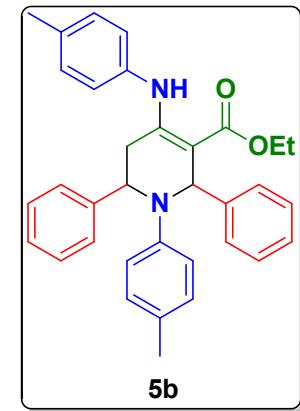
White solid. Melting point: 173-175 °C: IR (KBr): ν_{max} 3246, 3059, 2979, 2871, 1651, 1595, 1498, 1449, 1370, 1323, 1250, 1173, 1071, 1031, 916, 836, 723, 723, 697 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.29 (s, 1H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.30 - 7.28 (m, 3H), 7.25-7.16 (m, 5H), 7.12-7.04 (m, 5H), 6.62-6.59 (m, 1H), 6.53 (d, *J* = 8.2 Hz, 2H), 6.46 (s, 1H), 6.29 (d, *J* = 7.8 Hz, 2H), 5.15 (s, 1H), 4.50-4.42 (m, 1H), 4.37-4.28 (m, 1H), 2.88 (dd, *J* = 15.1, 5.7 Hz, 1H), 2.77 (dd, *J* = 15.1, 2.4 Hz, 1H), 1.47 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 168.9, 168.7, 157.7, 150.8, 147.3, 146.7, 144.4, 143.8, 143.1, 139.0, 138.2, 129.7, 129.3, 129.2, 129.1,



129.1, 129.0, 128.8, 128.6, 127.5, 127.4, 127.1, 127.0, 126.8, 126.7, 126.4, 126.1, 125.2, 124.1, 118.4, 116.5, 115.8, 113.3, 98.5, 98.3, 61.8, 60.9, 60.1, 58.6, 55.4, 36.8, 34.0, 15.2, 14.9 ppm.

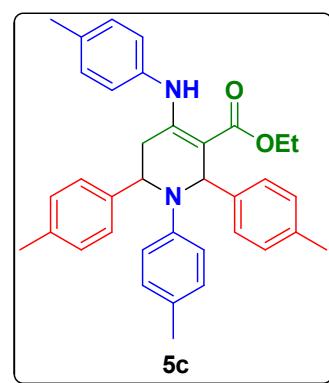
Ethyl-4-(p-tolylamino)-1,2,5,6-tetrahydro-2,6-diphenyl-1-p-tolylpyridine-3-carboxylate, 5b

White solid. Melting point: 194-196 °C: IR (KBr): ν_{max} 3239, 3059, 3025, 2919, 1650, 1615, 1594, 1515, 1449, 1315, 1250, 1074, 892, 773, 700 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 10.20 (s, 1H), 7.33 (d, *J* = 7.4 Hz, 2H), 7.29-7.26 (m, 3H), 7.25-7.14 (m, 5H), 6.88 (m, 4H), 6.43 (d, *J* = 9.0 Hz, 3H), 6.15 (d, *J* = 8.1 Hz, 2H), 5.11 (s, 1H), 4.47-4.41 (m, 1H), 4.35-4.29 (m, 1H), 2.83 (dd, *J* = 15.1, 5.7 Hz, 1H), 2.73 (dd, *J* = 15.1, 2.3 Hz, 1H), 2.25 (s, 3H), 2.15 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 156.3, 144.7, 144.2, 142.9, 135.4, 135.1, 129.3, 129.2, 128.4, 128.0, 126.9, 126.5, 126.3, 126.3, 126.0, 125.8, 124.9, 112.7, 97.6, 59.4, 58.1, 55.0, 33.4, 20.7, 20.0, 14.7 ppm.



Ethyl 4-(p-tolylamino)-1,2,5,6-tetrahydro-1,2,6-trip-tolylpyridine-3-carboxylate, 5c

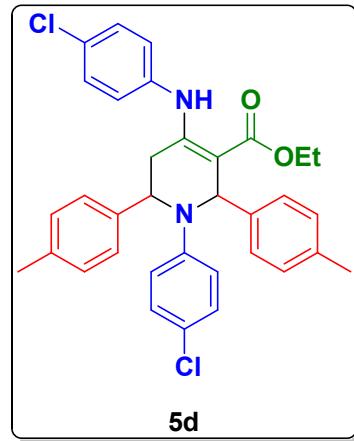
White solid. Melting point: 171-172 °C. IR (KBr): ν_{max} 3237, 3091, 3025, 2979, 2919, 2868, 1651, 1616, 1596, 1514, 1253, 1072, 795 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.20 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.08-7.03 (m, 4H), 6.87 (t, *J* = 8.1 Hz, 4H), 6.43 (d, *J* = 8.7 Hz, 2H), 6.36 (s, 1H), 6.17 (d, *J* = 8.2 Hz, 2H), 5.07 (s, 1H), 4.43 (m, 1H), 4.35-4.27 (m, 1H), 2.81 (dd, *J* = 15.1, 5.6 Hz, 1H), 2.72 (dd, *J* = 15.0, 2.6 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H), 2.15 (s, 3H), 1.44 (t, *J* = 7.1



Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) ppm: δ 168.3, 156.4, 144.9, 141.4, 139.9, 136.4, 135.6, 135.3, 129.4, 129.3, 129.2, 128.8, 126.5, 126.3, 125.9, 112.8, 97.7, 59.5, 57.9, 54.9, 33.5, 21.1, 21.0, 20.9, 20.1, 14.8 ppm.

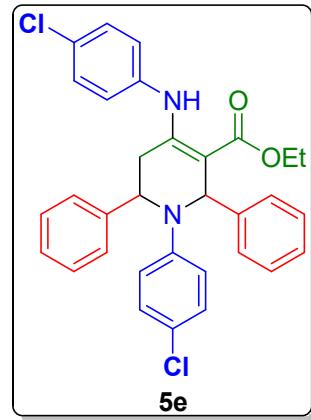
Ethyl-4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-di-*p*-tolylpyridine-3-carboxylate, 5d

White solid. Melting point: 218-220 °C. IR (KBr): ν_{max} 3234, 3090, 2979, 2859, 1646, 1604, 1498, 1448, 1319, 1254, 1073, 848, 795, 759, 683 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 10.24 (s, 1H), 7.16-6.98 (m, 12H), 6.43 (d, $J = 7.5$ Hz, 2H), 6.33 (s, 1H), 6.19 (d, $J = 7.1$ Hz, 2H), 5.07 (s, 1H), 4.52-4.44 (m, 1H), 4.34-4.27 (m, 1H), 2.85 (dd, $J = 24, 4.0$ Hz, 1H), 2.69 (d, $J = 14.7$ Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 1.46 (t, $J = 8.0$, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 168.3, 155.5, 145.7, 140.4, 139.3, 137.1, 136.6, 136.2, 131.3, 129.5, 129.1, 129.0, 128.8, 127.0, 126.5, 126.3, 121.1, 114.1, 99.0, 59.9, 58.1, 55.1, 33.6, 21.2, 21.1, 14.8 ppm.



Ethyl-4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-diphenyl pyridine-3-carboxylate, 5e

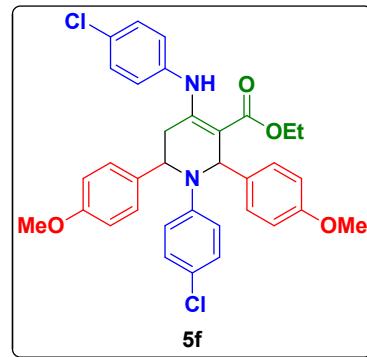
White solid. Melting point: 202-204 °C. IR (KBr): ν_{max} 3243, 3060, 2976, 2857, 1647, 1496, 1426, 1320, 1227, 1071, 941, 848, 803, 777, 698 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.21 (s, 1H), 7.26-7.20 (m, 9H), 7.12 (d, $J = 7.0$ Hz, 1H), 7.02 (d, $J = 8.2$ Hz, 2H), 6.97 (d, $J = 8.5$ Hz, 2H), 6.40 (d, $J = 8.8$ Hz, 2H), 6.36 (s, 1H), 6.15 (d, $J = 8.2$ Hz, 2H), 5.08 (s, 1H), 4.50 – 4.38 (m, 1H), 4.36 – 4.25 (m, 1H), 2.83 (dd, $J = 15.0, 5.3$ Hz, 1H), 2.67 (d, $J = 14.8$ Hz, 1H), 1.45 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.4, 156.8, 145.6, 142.4, 140.4, 137.9,



132.5, 131.5, 129.1, 128.9, 128.8, 128.5, 127.1, 126.6, 126.4, 117.9, 114.1, 98.7, 60.0, 58.3, 55.4, 33.6, 14.8 ppm.

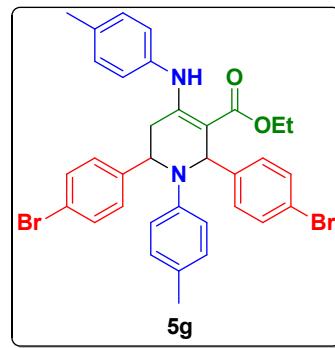
Ethyl-4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)pyridine-3-carboxylate, 5f

White solid. Melting point: 182-183 °C. IR (KBr): ν_{max} 3454, 3101, 2962, 1647, 1608, 1502, 1364, 1249, 1071, 798 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 10.25 (s, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.06 (dd, *J* = 15.4, 8.1 Hz, 4H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.86 – 6.79 (m, 4H), 6.44 (d, *J* = 8.3 Hz, 2H), 6.30 (s, 1H), 6.26 (d, *J* = 7.9 Hz, 2H), 5.04 (s, 1H), 4.50 – 4.40 (m, 1H), 4.37 – 4.27 (m, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.83 (dd, *J* = 15.6, 5.6 Hz, 1H), 2.69 (d, *J* = 14.7 Hz, 1H), 1.46 (t, *J* = 6.7 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 168.3, 159.0, 155.5, 145.7, 136.7, 135.3, 134.2, 131.3, 129.1, 128.8, 127.7, 127.5, 127.0, 121.2, 114.2, 114.2, 113.8, 99.0, 60.0, 57.7, 55.4, 55.3, 54.9, 33.7, 14.9 ppm.



Ethyl-4-(p-tolylamino)-2,6-bis(4-bromophenyl)-1,2,5,6-tetrahydro-1-p-tolylpyridine-3-carboxylate, 5g

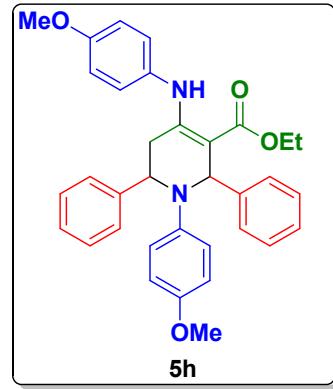
White solid. Melting point: 191-192 °C. IR (KBr): 3236, 3089, 2979, 2860, 1647, 1495, 1370, 1253, 1070, 896, 794 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 10.24 (s, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.13 – 7.10 (m, 6H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.39 (d, *J* = 8.6 Hz, 2H), 6.33 (s, 1H), 6.14 (d, *J* = 8.1 Hz, 2H), 5.07 (s, 1H), 4.49-4.43 (m, 1H), 4.36 – 4.30 (m, 1H), 2.85 (dd, *J* = 15.1, 5.3 Hz, 1H), 2.70 (d, *J* = 15.0 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 155.3, 146.1,



140.3, 139.2, 137.1, 132.0, 131.6, 129.5, 129.2, 127.3, 126.5, 126.3, 114.6, 108.4, 99.1, 60.0, 58.1, 55.1, 33.6, 21.2, 21.1, 14.8 ppm.

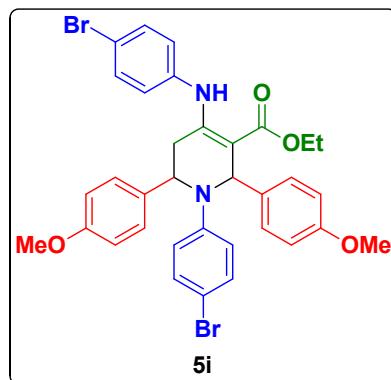
Ethyl-4-(4-methoxyphenylamino)-1,2,5,6-tetrahydro-1-(4-methoxyphenyl)-2,6-diphenylpyridine-3-carboxylate, 5h

White solid. Melting point: 173-175 °C. IR (KBr): ν_{max} 3247, 3047, 2981, 2834, 1652, 1607, 1511, 1460, 1319, 1243, 1068, 1038, 947, 845, 810, 736 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 10.14 (s, 1H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.10-7.05 (m, 6H), 6.66 (d, *J* = 9.1 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 6.46 (d, *J* = 9.0 Hz, 2H), 6.29 (s, 1H), 6.23 (d, *J* = 8.6 Hz, 2H), 5.02 (s, 1H), 4.46-4.40 (m, 1H), 4.33-4.27 (m, 1H), 3.75 (s, 3H), 3.66 (s, 3H), 2.79 (dd, *J* = 15.1, 5.6 Hz, 1H), 2.64 (dd, *J* = 15.0, 2.6 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 168.4, 156.9, 150.9, 141.8, 140.3, 136.6, 135.7, 131.0, 129.3, 128.9, 127.9, 126.8, 126.6, 114.6, 114.2, 114.0, 97.5, 59.5, 58.0, 55.7, 55.6, 55.5, 33.7, 21.2, 21.1, 14.9 ppm.



Ethyl-4-(4-bromophenylamino)-1-(4-bromophenyl)-1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)pyridine-3-carboxylate, 5i

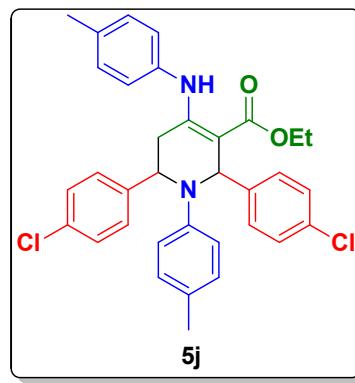
White solid. Melting point: 218-220 °C. IR (KBr): ν_{max} = 3243, 3064, 2977, 2835, 1648, 1606, 1585, 1505, 1251, 1068, 1034, 757 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.25 (s, 1H), 7.21 (dd, *J* = 17.0, 8.6 Hz, 4H), 7.13 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.82 (dd, *J* = 8.8, 2.4 Hz, 4H), 6.39 (d, *J* = 9.1 Hz, 2H), 6.29 (s, 1H), 6.20 (d, *J* = 8.6 Hz, 2H), 5.03 (s, 1H), 4.50 – 4.40 (m, 1H), 4.38 – 4.25 (m, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.84 (dd, *J* = 15.1, 5.6 Hz, 1H), 2.70 (dd, *J* = 15.1, 2.2 Hz, 1H), 1.46 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 158.7, 158.0, 155.1, 145.7,



136.8, 134.8, 133.7, 131.8, 131.3, 127.3, 127.1, 126.9, 114.4, 113.9, 113.5, 108.1, 98.8, 59.7, 57.4, 55.1, 55.0, 54.4, 33.3, 14.5 ppm.

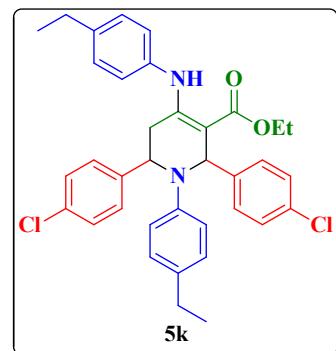
Ethyl-4-(p-tolylamino)-2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydro-1-p-tolylpyridine-3-carboxylate, 5j

White Solid. Melting Point: 238-240 °C. IR (KBr): $\nu_{\text{max}} = 3249, 3095, 3065, 3032, 2981, 2921, 1654, 1618, 1593, 1516, 1255, 1074, 804 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 10.21 (s, 1H), 7.24 – 7.20 (m, 6H), 7.06 (d, $J = 8.0 \text{ Hz}$, 2H), 6.95 (d, $J = 8.0 \text{ Hz}$, 2H), 6.88 (d, $J = 8.0 \text{ Hz}$, 2H), 6.36 (d, $J = 7.4 \text{ Hz}$, 2H), 6.30 (d, $J = 4.1 \text{ Hz}$, 2H), 6.28 (s, 1H), 5.04 (s, 1H), 4.47 – 4.40 (m, 1H), 4.35 – 4.28 (m, 1H), 2.77 (dd, $J = 15.2, 5.3 \text{ Hz}$, 1H), 2.71 (dd, $J = 15.5, 3.1 \text{ Hz}$, 1H), 2.28 (s, 3H), 2.17 (s, 3H), 1.42 (d, $J = 7.4 \text{ Hz}$, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 156.2, 144.4, 142.9, 141.3, 135.9, 135.1, 132.8, 132.1, 129.7, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 125.9, 125.8, 124.2, 113.1, 97.3, 59.8, 57.4, 54.9, 33.7, 31.0, 21.0, 20.4, 14.9 ppm.



Ethyl-4-(4-ethylphenylamino)-2,6-bis(4-chlorophenyl)-1-(4-ethylphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate, 5k

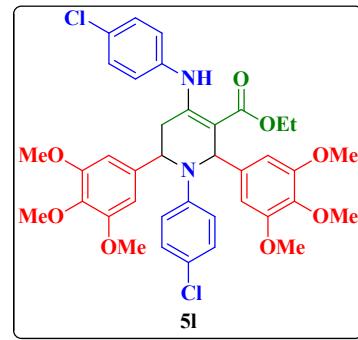
White Solid. Melting Point: 204-206 °C IR (KBr): $\nu_{\text{max}} = 3222, 3027, 3005, 2974, 2926, 2863, 1647, 1602, 1574, 1514, 1254, 1091, 1012, 813 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 10.22 (s, 1H), 7.26-7.23 (m, 6H), 7.06 (s, 2H), 6.97 (d, $J = 7.9 \text{ Hz}$, 2H), 6.92 (d, $J = 8.3 \text{ Hz}$, 2H), 6.38 (d, $J = 8.4 \text{ Hz}$, 2H), 6.32 (d, $J = 5.4 \text{ Hz}$, 2H), 6.29 (s, 1H), 5.06 (s, 1H), 4.48 – 4.38 (m, 1H), 4.36 – 4.26 (m, 1H), 2.79 (dd, $J = 15.2, 5.2 \text{ Hz}$, 1H), 2.73 (d, $J = 14.8 \text{ Hz}$, 1H), 2.58 (q, $J = 7.5 \text{ Hz}$, 2H), 2.48 (q, $J = 7.5 \text{ Hz}$, 2H), 1.44 (t, $J = 7.1 \text{ Hz}$, 3H), 1.19 (t, $J = 7.6 \text{ Hz}$, 3H), 1.13 (t, $J = 7.5 \text{ Hz}$, 3H) ppm.



¹³C NMR (101 MHz, CDCl₃) δ 169.2, 157.4, 145.8, 144.0, 143.4, 142.5, 136.4, 133.9, 133.4, 129.9, 129.5, 129.3, 129.1, 127.1, 114.2, 98.5, 60.9, 58.6, 56.0, 34.8, 29.5, 28.8, 16.9, 16.7, 16.0 ppm.

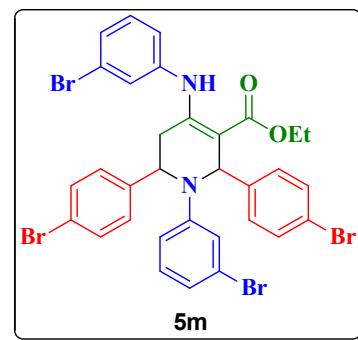
Ethyl-4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-bis(3,4,5-trimethoxyphenyl)pyridine-3-carboxylate, 5l

White Solid. Melting Point: 162-164 °C. IR (KBr): $\nu_{\text{max}} = 3217, 3067, 2984, 2837, 1724, 1610, 1541, 1516, 1261, 1061, 1035, 950, 892, 814 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 10.24 (s, 1H), 7.11 (d, $J = 8.1 \text{ Hz}$, 2H), 7.04 (d, $J = 8.5 \text{ Hz}$, 2H), 6.53 – 6.43 (m, 4H), 6.34 – 6.24 (m, 5H), 4.98 (s, 1H), 4.52 – 4.40 (m, 1H), 4.34 – 4.23 (m, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.74 (s, 6H), 3.70 (s, 6H), 2.93 (dd, $J = 15.0, 5.5 \text{ Hz}$, 1H), 2.68 (d, $J = 14.9 \text{ Hz}$, 1H), 1.43 (t, $J = 7.1 \text{ Hz}$, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 168.0, 156.2, 153.6, 153.2, 145.5, 139.0, 137.9, 136.7, 136.4, 129.0, 128.8, 127.5, 121.6, 114.1, 103.8, 103.0, 98.1, 61.0, 60.9, 59.8, 58.5, 56.1, 56.0, 55.7, 33.7, 15.1 ppm.



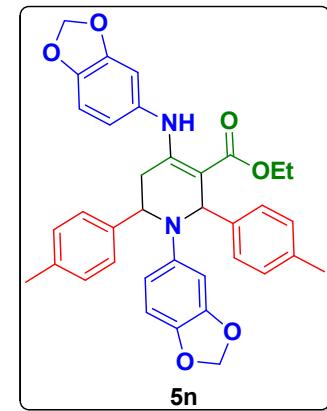
Ethyl-4-(3-bromophenylamino)-1-(3-bromophenyl)-2,6-bis(4-bromophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate, 5m

White Solid. Melting Point: 179-181 °C. IR (KBr): $\nu_{\text{max}} = 3241, 3055, 2980, 2926, 1660, 1613, 1586, 1256, 1097, 1028, 821 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 10.27 (s, 1H), 7.41 (dd, $J = 13.4, 8.3 \text{ Hz}$, 4H), 7.25 (s, 1H), 7.13 (d, $J = 8.2 \text{ Hz}$, 2H), 7.03 (t, $J = 7.9 \text{ Hz}$, 1H), 6.98 (d, $J = 8.2 \text{ Hz}$, 2H), 6.91 (t, $J = 8.1 \text{ Hz}$, 1H), 6.76 (d, $J = 7.7 \text{ Hz}$, 1H), 6.58 (s, 1H), 6.44 – 6.32 (m, 3H), 6.26 (s, 1H), 5.05 (s, 1H), 4.52 – 4.41 (m, 1H), 4.37 – 4.25 (m, 1H), 2.78 (dd, $J = 15.2, 5.4 \text{ Hz}$, 1H), 2.68 (d, $J = 13.9 \text{ Hz}$, 1H), 1.45 (t, $J = 7.1 \text{ Hz}$, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 155.3, 148.1, 142.3, 141.0, 139.3, 132.6, 132.0, 130.7, 130.7, 129.6, 129.0, 128.6, 128.3, 124.7, 123.8, 122.9, 121.9, 121.0, 120.3, 116.0, 112.0, 98.7, 60.6, 57.9, 55.2, 33.8, 15.2 ppm.



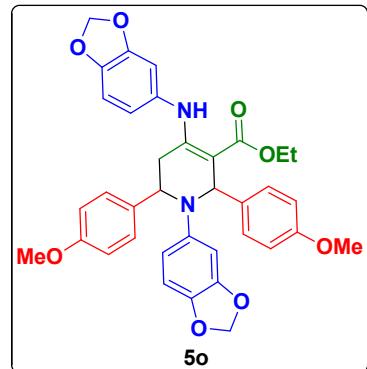
Ethyl-1-(benzo[d][1,3]dioxol-5-yl)-4-(benzo[d][1,3]dioxol-6-ylamino)-1,2,5,6-tetrahydro-2,6-dip-tolylpyridine-3-carboxylate, 5n

White Solid. Melting Point: 234-236 °C. IR (KBr): $\nu_{\text{max}} = 3247, 3083, 3048, 2879, 1655, 1632, 1592, 1488, 1367, 1255, 1067, 1037, 933, 813, 568 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 10.08 (s, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.08 (t, 4H), 7.04 (d, $J = 8.0$ Hz, 2H), 6.52 (dd, $J = 15.2, 8.4$ Hz, 2H), 6.26 (s, 1H), 6.18 (d, $J = 2.4$ Hz, 1H), 5.95 – 5.87 (m, 3H), 5.81 – 5.73 (m, 3H), 5.69 (d, $J = 2.0$ Hz, 1H), 5.01 (s, 1H), 4.49 – 4.37 (m, 1H), 4.34 – 4.24 (m, 1H), 2.80 (dd, $J = 15.1, 5.7$ Hz, 1H), 2.64 (dd, $J = 15.1, 2.5$ Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 1.45 (t, $J = 7.1$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 156.7, 148.1, 147.7, 145.8, 143.4, 141.1, 140.0, 138.4, 136.8, 135.8, 131.9, 129.4, 128.9, 126.7, 126.4, 119.9, 108.4, 108.1, 107.8, 105.0, 101.5, 100.4, 97.7, 96.1, 59.7, 58.4, 55.8, 33.8, 21.2, 21.1, 14.9 ppm. HRMS (ESI): calcd 591.2417; found 591.2563



Ethyl-1-(benzo[d][1,3]dioxol-5-yl)-4-(benzo[d][1,3]dioxol-6-ylamino)-1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)pyridine-3-carboxylate, 5o

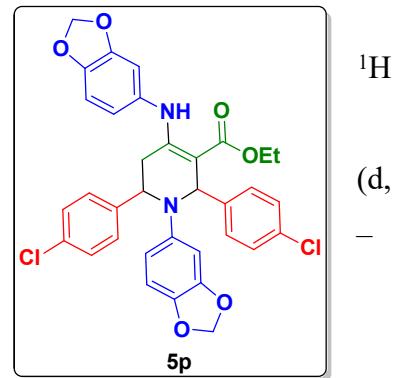
White Solid. Melting Point: 183-185 °C. IR (KBr): $\nu_{\text{max}} = 3259, 3170, 3066, 2977, 2903, 1650, 1605, 1592, 1506, 1248, 1064, 1036, 930, 811, 549 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 10.10 (s, 1H), 7.19 (d, $J = 8.6$ Hz, 2H), 7.06 (d, $J = 8.6$ Hz, 2H), 6.82 (dd, $J = 8.6, 7.1$ Hz, 4H), 6.53 (dd, $J = 8.4, 5.5$ Hz, 2H), 6.20 (s, 1H), 6.17 (d, $J = 2.5$ Hz, 1H), 5.91 (dd, 3H), 5.84 (dd, $J = 8.2, 1.9$ Hz, 1H), 5.78 – 5.75 (m, 3H), 4.96 (s, 1H), 4.46 – 4.37 (m, 1H), 4.33 – 4.24 (m, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.77 (dd, $J = 15.1, 5.5$ Hz, 1H), 2.63 (dd, $J = 15.1, 2.7$ Hz, 1H), 1.43 (t, $J = 7.1$ Hz, 3H) ppm. ^{13}C NMR (101 MHz,



CDCl_3) δ 168.0, 158.5, 157.8, 156.5, 147.8, 145.6, 138.2, 135.7, 131.7, 127.5, 127.2, 119.6, 113.8, 113.3, 108.0, 107.7, 107.6, 105.0, 101.2, 100.2, 97.4, 96.0, 59.3, 57.6, 55.3, 55.1, 55.0, 33.6, 14.6 ppm. HRMS (ESI): calcd 622.2315; found 622.2327

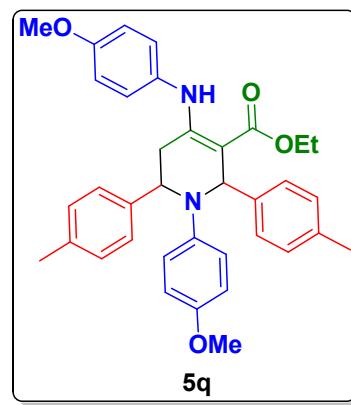
Ethyl-1-(benzo[d][1,3]dioxol-5-yl)-4-(benzo[d][1,3]dioxol-6-ylamino)-2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate, 5p

White Solid. Melting Point: 205-207 $^{\circ}\text{C}$. IR (KBr): $\nu_{\text{max}} = 3255$, 3086, 2973, 2877, 1649, 1594, 1487, 1243, 1093, 932, 818 cm^{-1} . NMR (400 MHz, CDCl_3) δ 10.09 (s, 1H), 7.25 – 7.18 (m, 5H), 7.06 (d, $J = 8.4$ Hz, 2H), 6.61 – 6.50 (m, 2H), 6.18 (s, 1H), 6.09 ($J = 2.5$ Hz, 1H), 5.93 (dd, $J = 5.6, 1.2$ Hz, 2H), 5.87 (s, 2H), 5.86, 5.83 (m, 1H), 5.82 (d, $J = 2.5$ Hz, 1H), 5.78 (dd, $J = 5.7, 1.3$ Hz, 2H), 4.96 (s, 1H), 4.46 – 4.36 (m, 1H), 4.33 – 4.23 (m, 1H), 2.74 (dd, $J = 15.3, 5.5$ Hz, 1H), 2.64 (dd, $J = 15.3, 3.0$ Hz, 1H), 1.41 (t, $J = 7.1$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 156.4, 148.3, 147.9, 142.7, 142.4, 141.2, 139.1, 133.0, 132.2, 131.6, 128.9, 128.4, 128.2, 127.9, 119.8, 108.5, 108.0, 107.9, 105.6, 101.6, 100.7, 97.1, 96.5, 59.9, 57.8, 55.9, 33.8, 14.8 ppm. HRMS (ESI): calcd 630.1324; found 630.1306.



Ethyl-4-(4-methoxyphenylamino)-1,2,5,6-tetrahydro-1-(4-methoxyphenyl)-2,6-dip-tolylpyridine-3-carboxylate, 5q

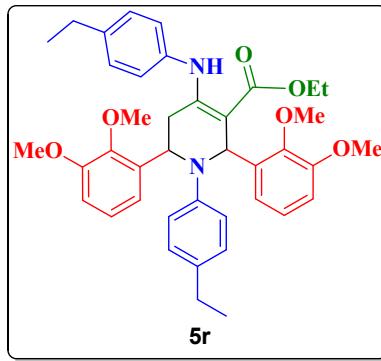
White Solid. Melting Point: 222-224 $^{\circ}\text{C}$. IR (KBr): $\nu_{\text{max}} = 3247$, 3047, 2981, 2835, 1652, 1606, 1511, 1244, 1069, 810 cm^{-1} . ¹H NMR (400 MHz, CDCl_3) δ 10.13 (s, 1H), 7.19 (d, $J = 7.2$ Hz, 2H), 7.07 (d, $J = 8.7$ Hz, 6H), 6.63 (dd, $J = 20.0, 8.2$ Hz, 4H), 6.44 (d, $J = 8.2$ Hz, 2H), 6.29 (s, 1H), 6.21 (d, $J = 7.9$ Hz, 2H), 5.01 (s, 1H), 4.48 – 4.36 (m, 1H), 4.34 – 4.25 (m, 1H), 3.75 (s, 3H), 3.66 (s, 3H), 2.77 (dd, $J = 14.8, 4.6$ Hz, 1H), 2.63 (d, $J = 14.9$ Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 1.43 (t, $J = 6.6$ Hz, 3H)



ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 156.8, 141.7, 141.4, 140.2, 136.5, 135.6, 130.8, 129.2, 128.8, 127.8, 126.7, 126.4, 114.4, 114.0, 113.8, 97.3, 59.4, 57.9, 55.6, 55.4, 55.3, 33.6, 21.1, 21.0, 14.8 ppm.

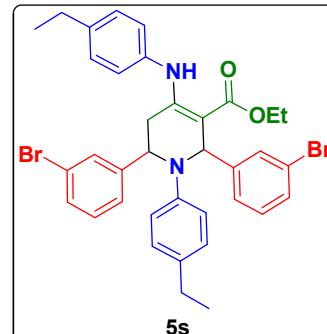
Ethyl-4-(4-ethylphenylamino)-1-(4-ethylphenyl)-1,2,5,6-tetrahydro-2,6-bis(2,3-dimethoxyphenyl)pyridine-3-carboxylate, 5r

White Solid. Melting Point: 162–164 °C. IR (KBr): $\nu_{\max} = 3252$, 2987, 2831, 1653, 1613, 1590, 1514, 1253, 1061, 1030, 942, 806 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 9.73 (s, 1H), 6.92 – 6.81 (m, 5H), 6.77 (s, 1H), 6.74 (s, 2H), 6.69 (dd, $J = 8.7, 2.6$ Hz, 1H), 6.64 – 6.60 (m, 1H), 6.40 (s, 1H), 6.35 (d, $J = 8.4$ Hz, 2H), 6.20 (d, $J = 8.0$ Hz, 2H), 5.39 (s, 1H), 4.37 – 4.22 (m, 2H), 3.78 (s, 3H), 3.64 (s, 3H), 3.61 (s, 3H), 3.56 (s, 3H), 2.91 – 2.82 (m, 2H), 2.54 (q, $J = 7.5$ Hz, 2H), 2.45 (q, $J = 7.4$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H), 1.16 (t, $J = 7.6$ Hz, 3H), 1.11 (t, $J = 7.6$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 153.7, 153.0, 151.8, 150.3, 144.9, 141.4, 136.2, 132.8, 131.4, 131.3, 128.1, 128.0, 126.2, 116.0, 113.7, 113.4, 112.8, 112.0, 110.8, 110.4, 97.4, 59.5, 56.0, 55.6, 55.3, 53.2, 29.7, 28.4, 27.7, 15.8, 14.9 ppm. HRMS (ESI): calcd 651.3434; found 651.3427



Ethyl-4-(4-ethylphenylamino)-2,6-bis(3-bromophenyl)-1-(4-ethylphenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate, 5s

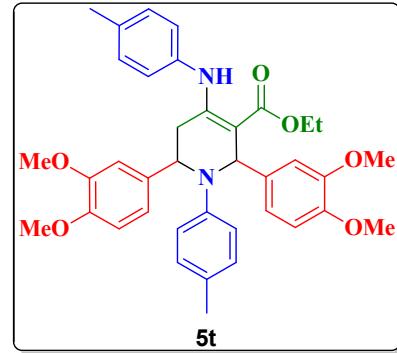
White Solid. Melting Point: 166–168 °C. IR (KBr): $\nu_{\max} = 3233$, 2963, 2928, 2871, 1651, 1595, 1514, 1253, 1091, 1026, 894, 776, 697 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 10.20 (s, 1H), 7.55 (s, 1H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 7.5$ Hz, 1H), 7.25 (s, 1H), 7.21 – 7.05 (m, 4H), 7.00 (d, $J = 7.9$ Hz, 2H), 6.92 (d, $J = 8.3$ Hz, 2H), 6.39 (d, $J = 8.4$ Hz, 2H), 6.33 (s, 1H), 6.25 (d, $J = 8.0$ Hz, 2H), 5.07 (s, 1H), 4.53 – 4.42 (m, 1H), 4.37 – 4.26 (m, 1H), 2.79 (dd, $J = 15.1, 5.3$ Hz, 1H), 2.71 (d, $J = 15.3$ Hz, 1H), 2.59 (q, $J = 7.5$ Hz, 2H), 2.48 (q, $J = 7.4$ Hz, 2H), 1.47 (t, $J = 7.0$ Hz, 3H), 1.20 (t, $J = 7.6$ Hz, 3H), 1.13 (t, $J = 7.5$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 167.9, 156.2, 145.3, 142.4, 130.2, 130.2, 129.7, 129.7, 129.5, 129.4, 128.4, 128.3, 126.3, 125.3, 125.0, 122.6,



113.0, 96.8, 59.7, 57.5, 55.1, 33.5, 28.3, 27.6, 15.6, 15.4, 14.8 ppm. HRMS (ESI): calcd 686.1144; found 686.1150

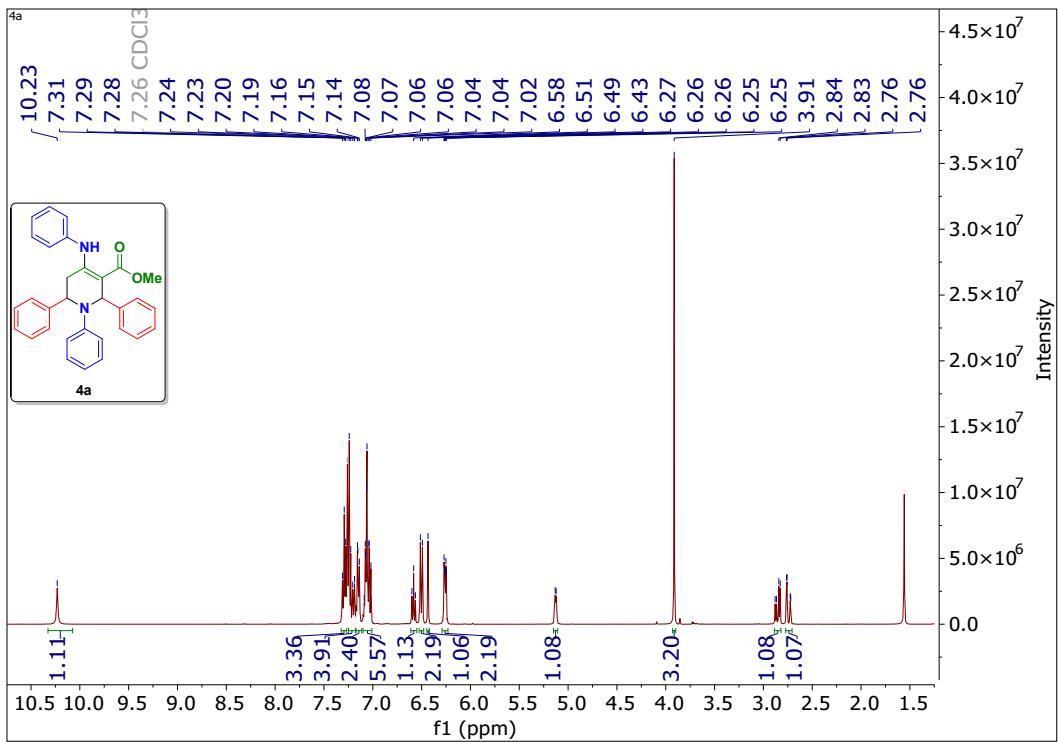
Ethyl-4-(p-tolylamino)-1,2,5,6-tetrahydro-2,6-bis(3,4-dimethoxyphenyl)-1-p-tolylpyridine-3-carboxylate, 5t

White Solid. Melting Point: 176-178 °C. IR (KBr): $\nu_{\text{max}} = 3228$, 3087, 3062, 2998, 2905, 1711, 1653, 1587, 1514, 1257, 1069, 1027, 920, 864, 630, 578 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 10.32 (s, 1H), 7.17 – 7.04 (m, 5H), 6.97 (s, 1H), 6.76 (d, *J* = 8.3 Hz, 4H), 6.63 (d, *J* = 7.3 Hz, 2H), 6.54 (d, *J* = 7.9 Hz, 2H), 6.42 – 6.32 (m, 3H), 5.06 (s, 1H), 4.56 – 4.38 (m, 1H), 4.35 – 4.21 (m, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.72 (s, 3H), 2.93 (dd, *J* = 14.8, 4.9 Hz, 1H), 2.78 (d, *J* = 14.6 Hz, 1H), 1.45 (t, *J* = 6.9 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 156.5, 149.0, 148.8, 147.9, 147.4, 137.9, 136.3, 135.1, 128.8, 128.8, 125.9, 125.7, 118.6, 118.5, 116.2, 113.0, 111.1, 110.5, 110.1, 109.2, 97.8, 59.5, 57.8, 55.9, 55.8, 55.7, 55.7, 54.9, 33.7, 14.9 ppm.

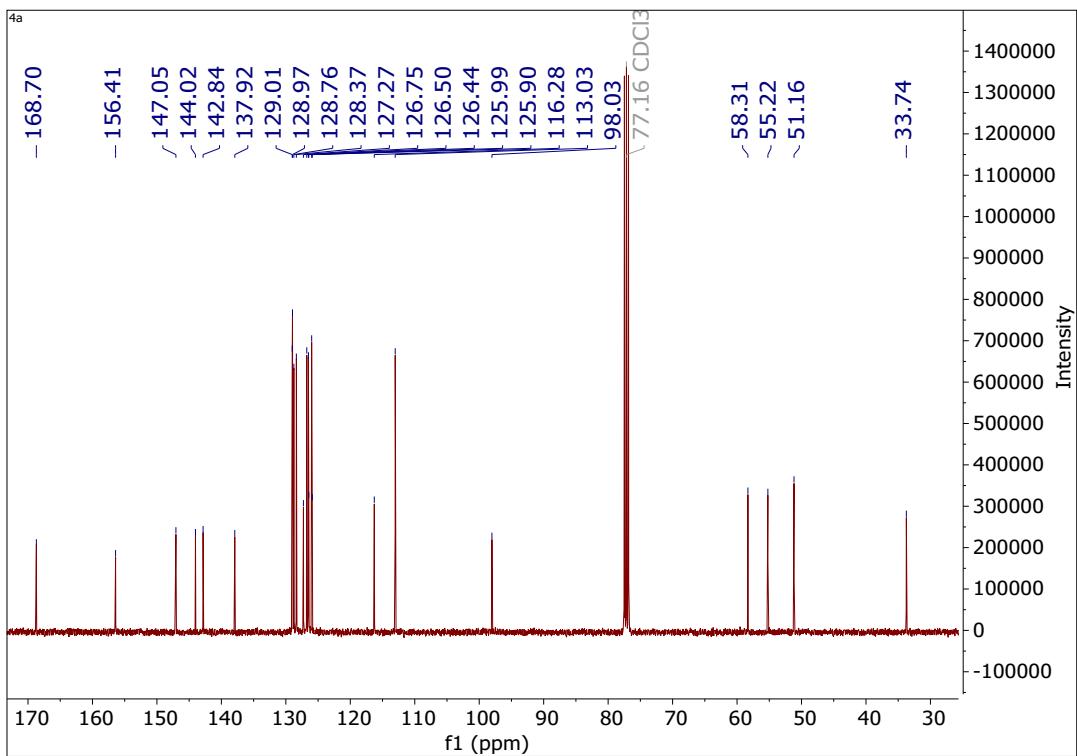


VIII. ¹H & ¹³C NMR spectra of the synthesized compounds

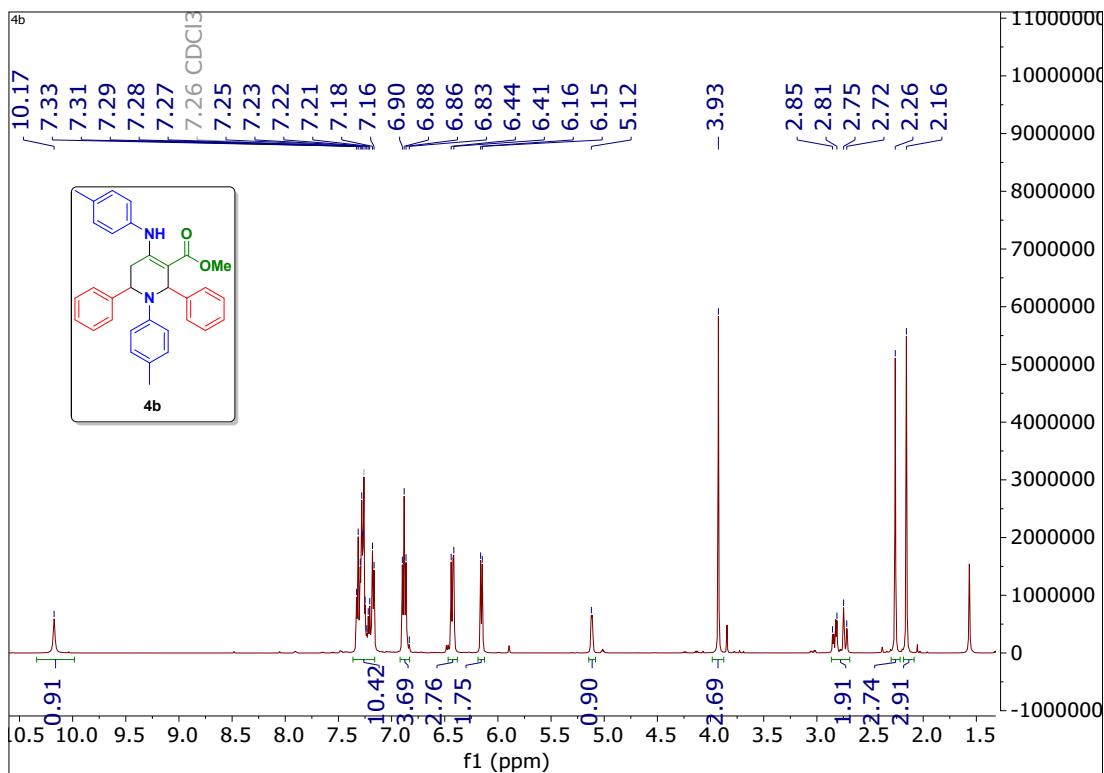
¹H NMR spectra of 4a



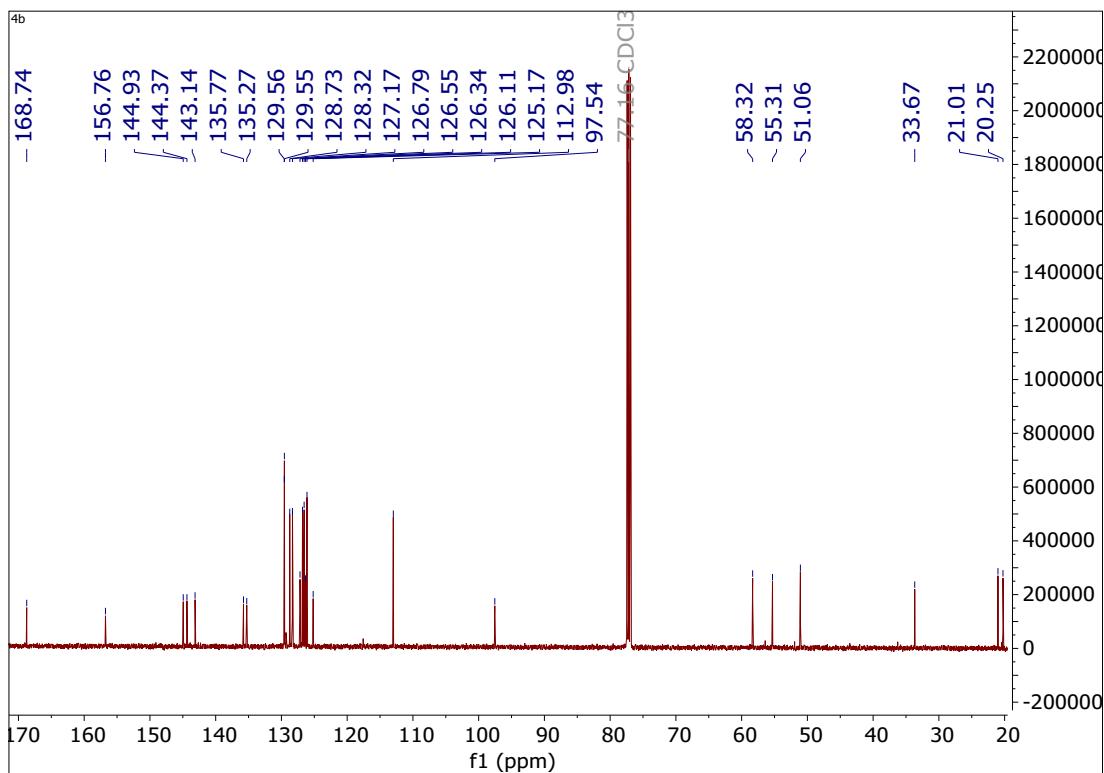
¹³H NMR spectra of 4a



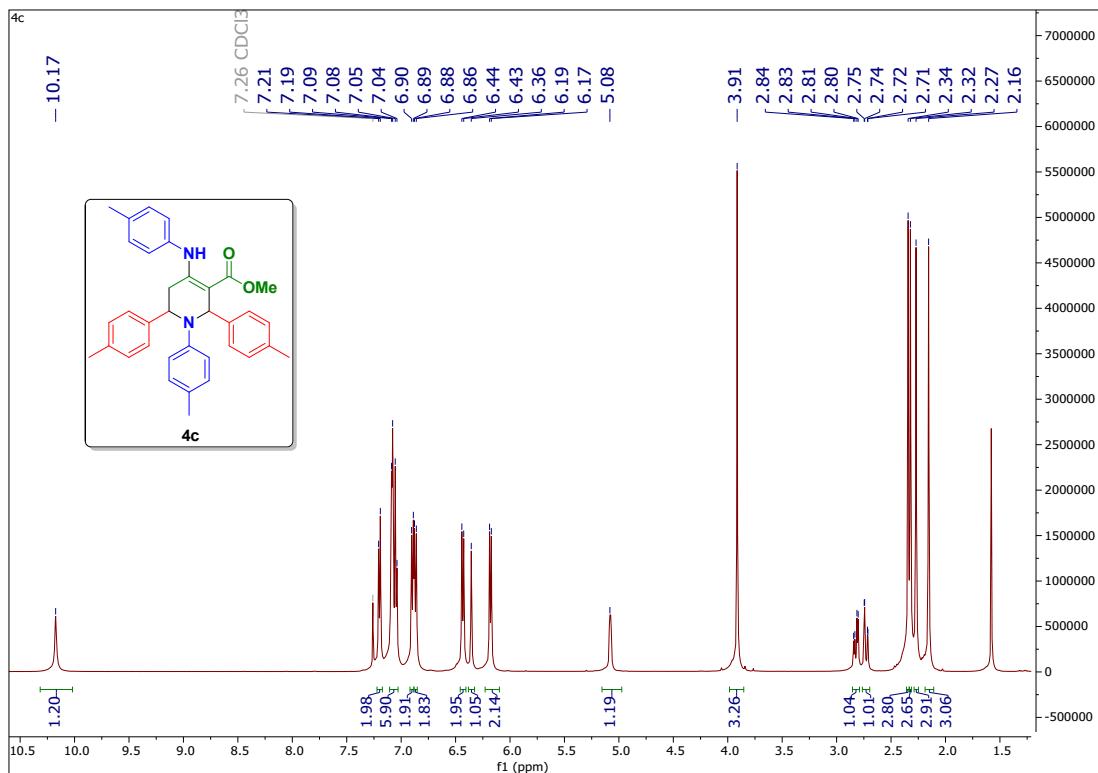
¹H NMR Spectrum of 4b



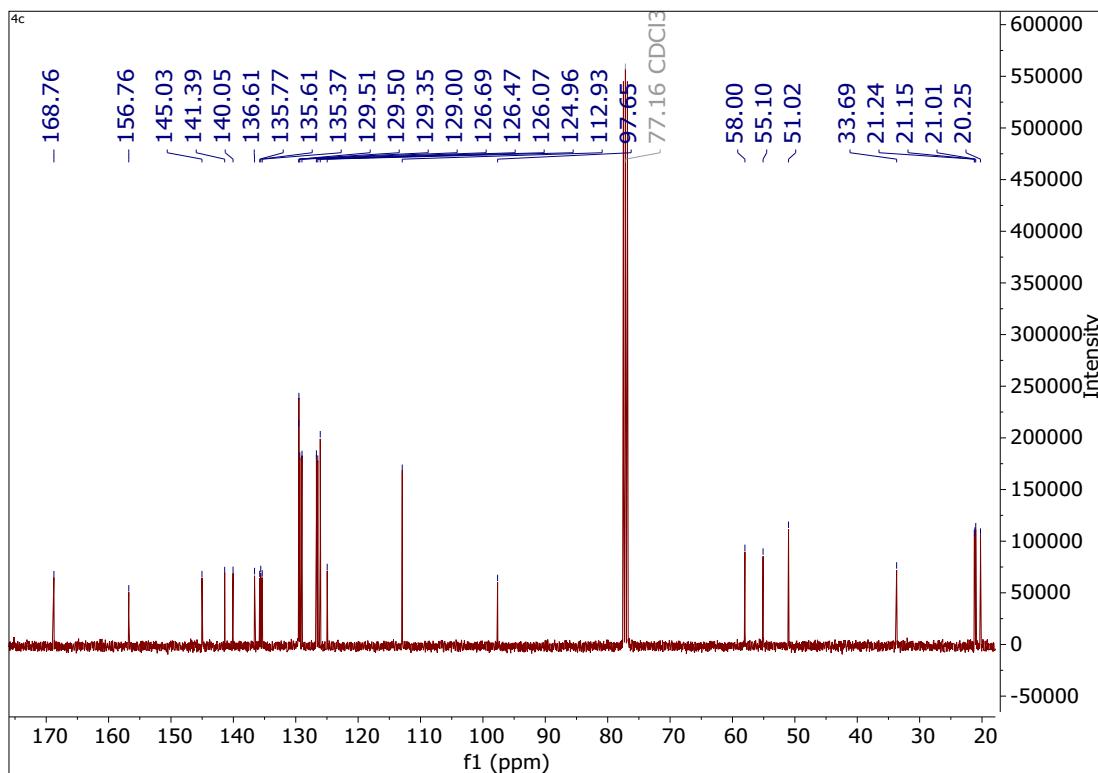
¹³C NMR Spectrum of 4b



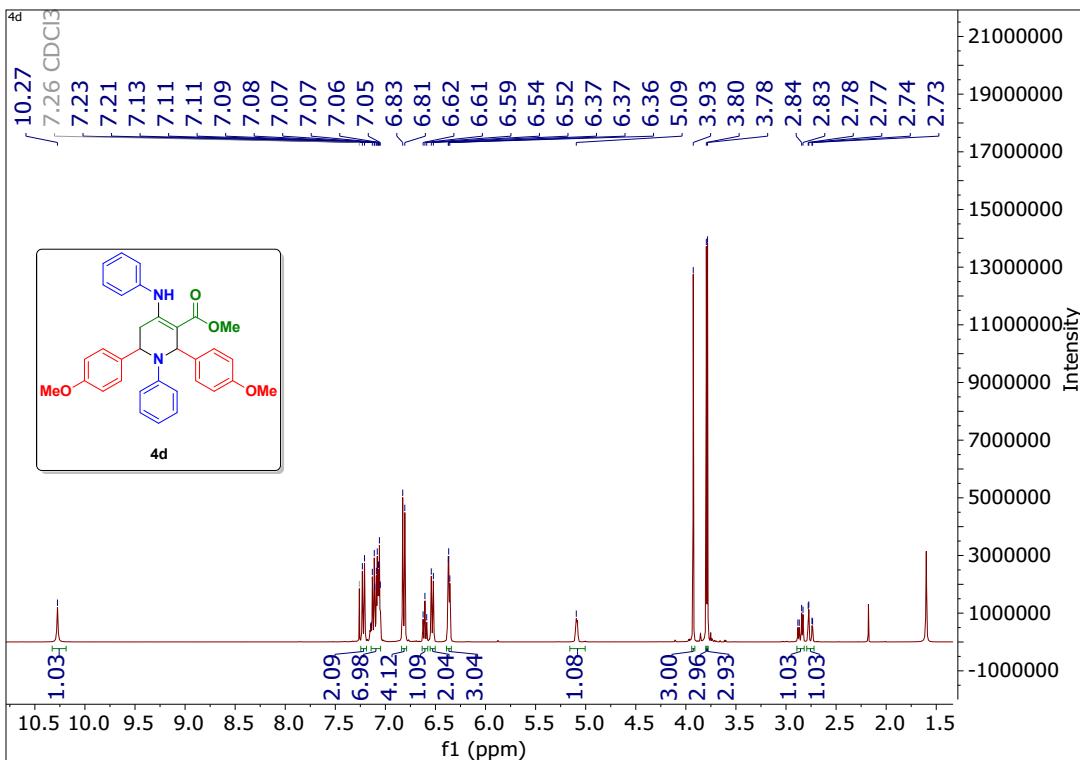
¹H NMR spectrum of 4c



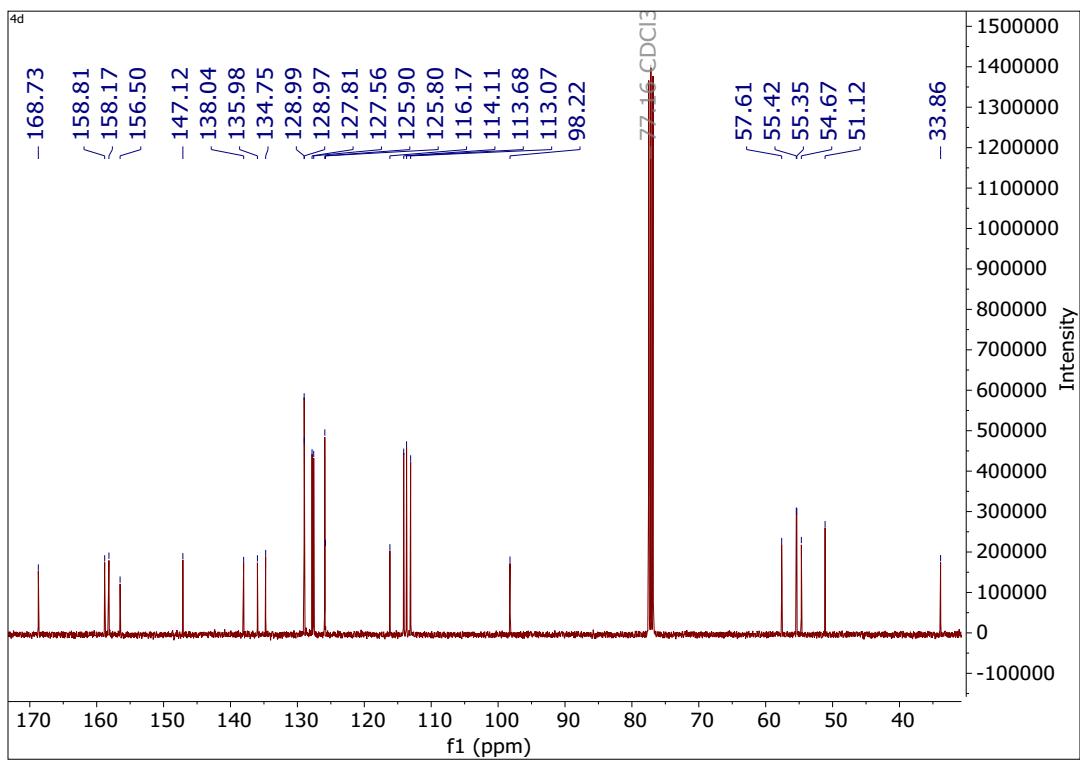
¹³C NMR spectrum of 4c



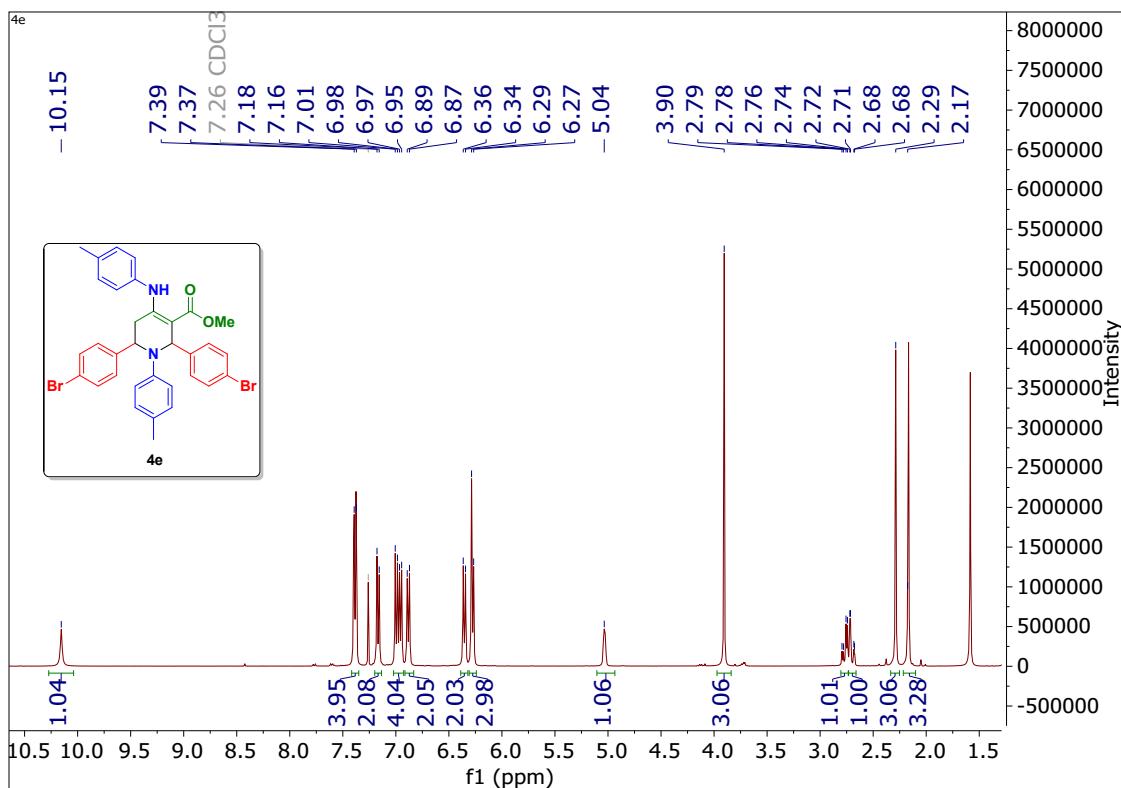
¹H NMR spectrum of 4d



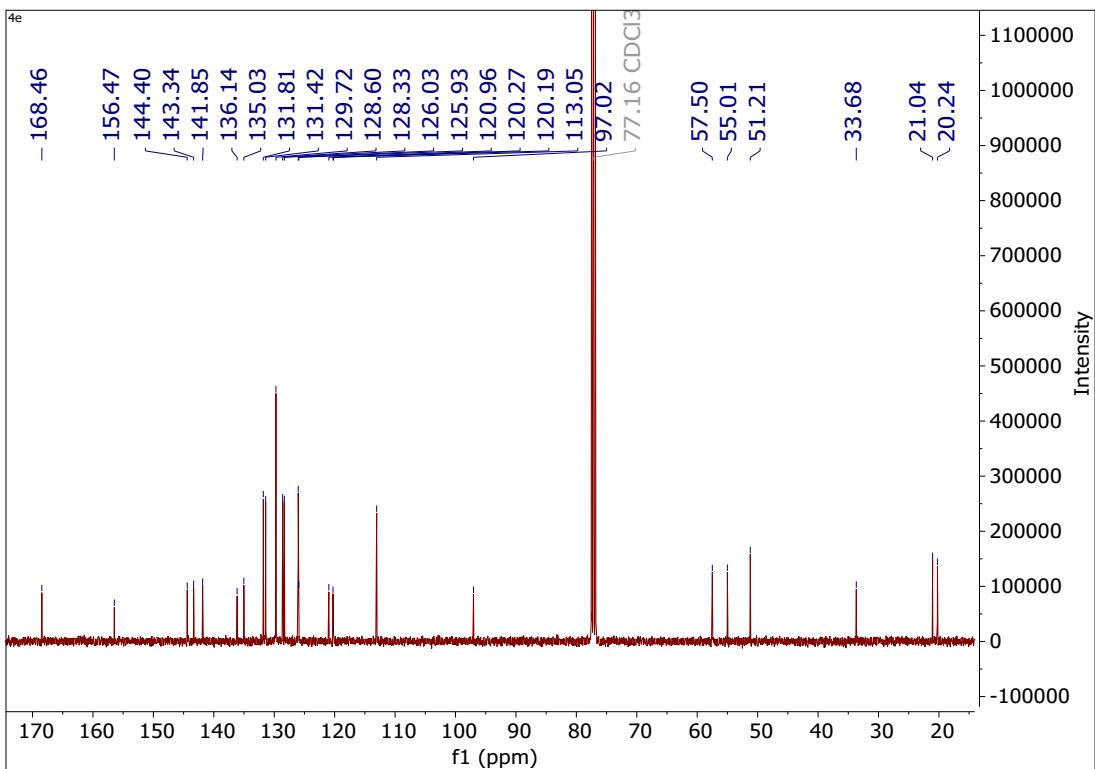
¹³C NMR spectrum of 4d



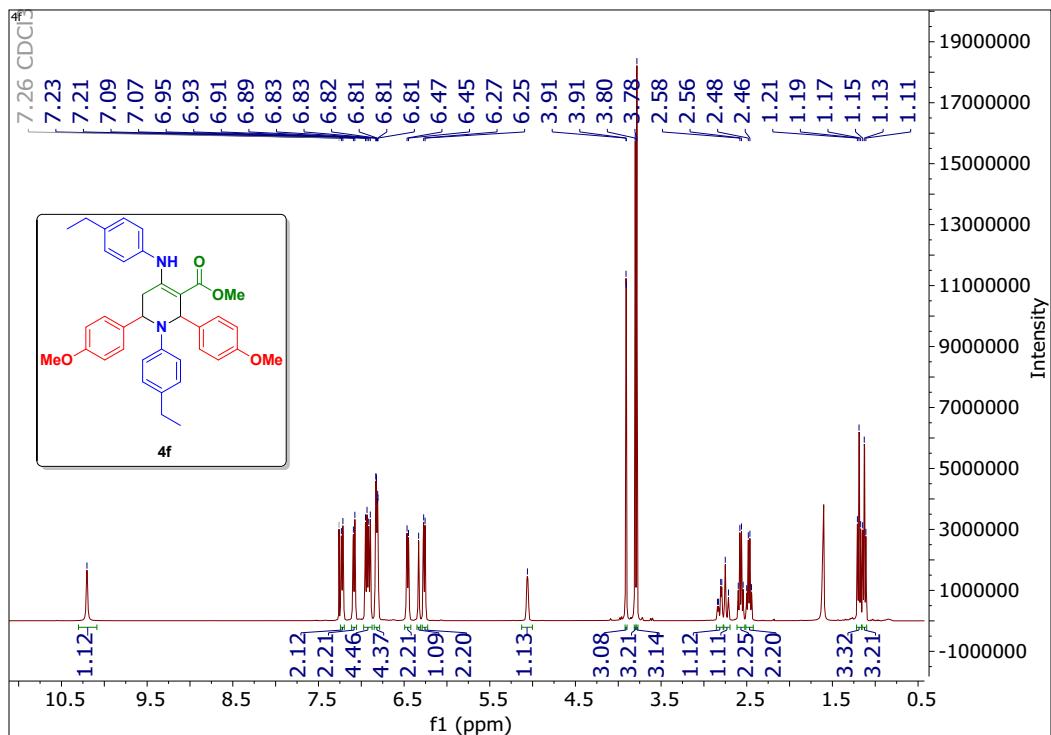
¹H NMR spectrum of 4e



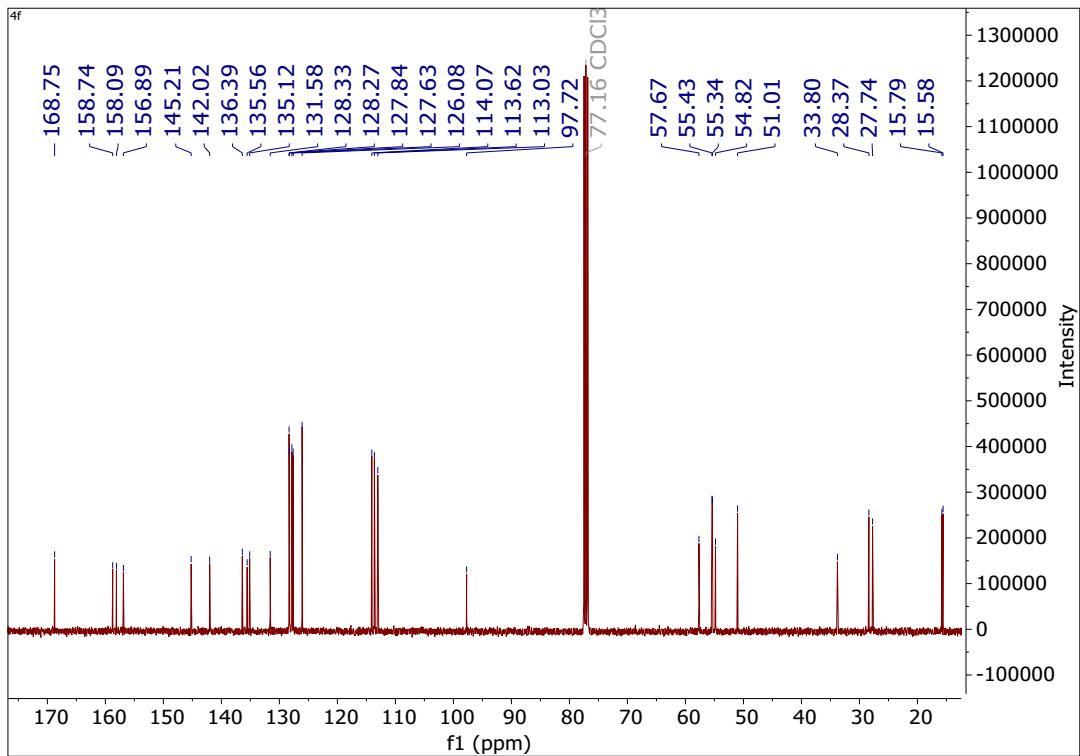
¹³C NMR spectrum of 4e



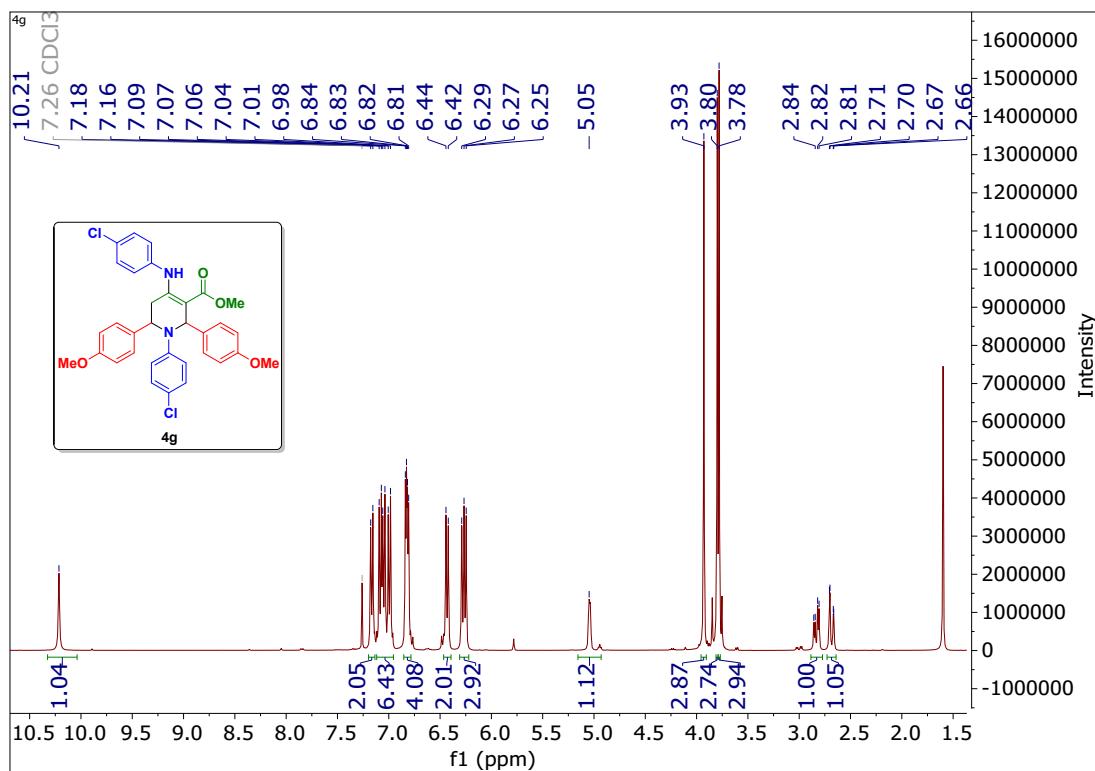
¹H NMR spectrum of 4f



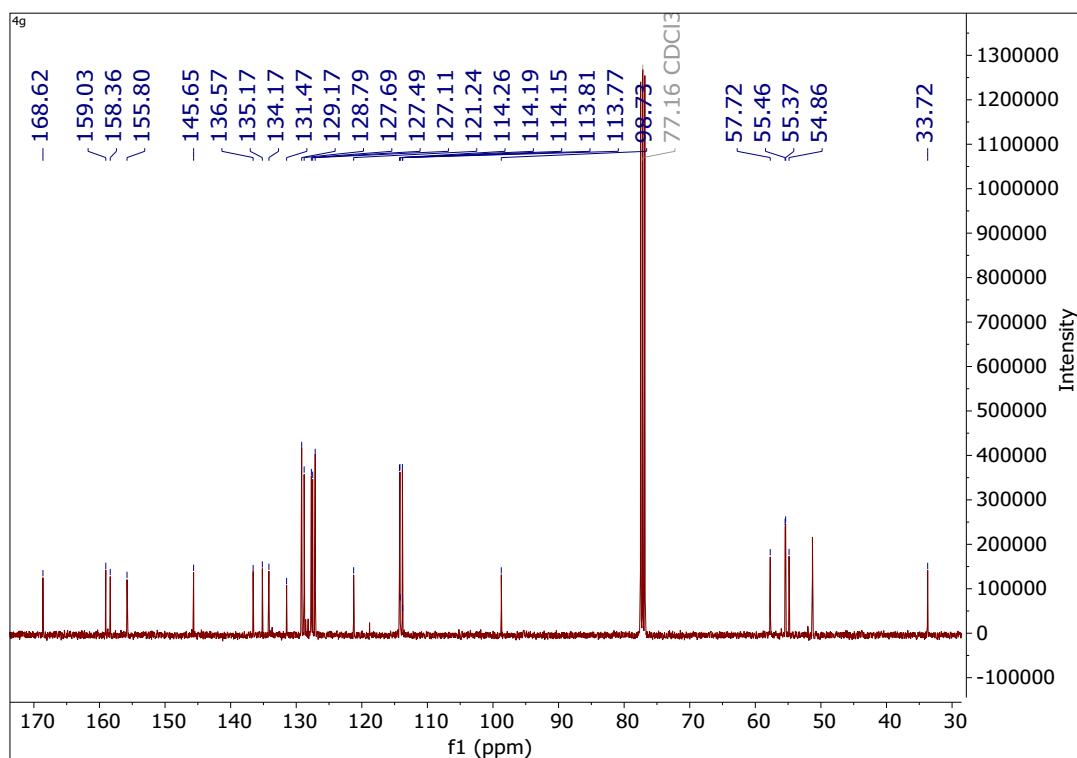
¹³C NMR Spectrum of 4f



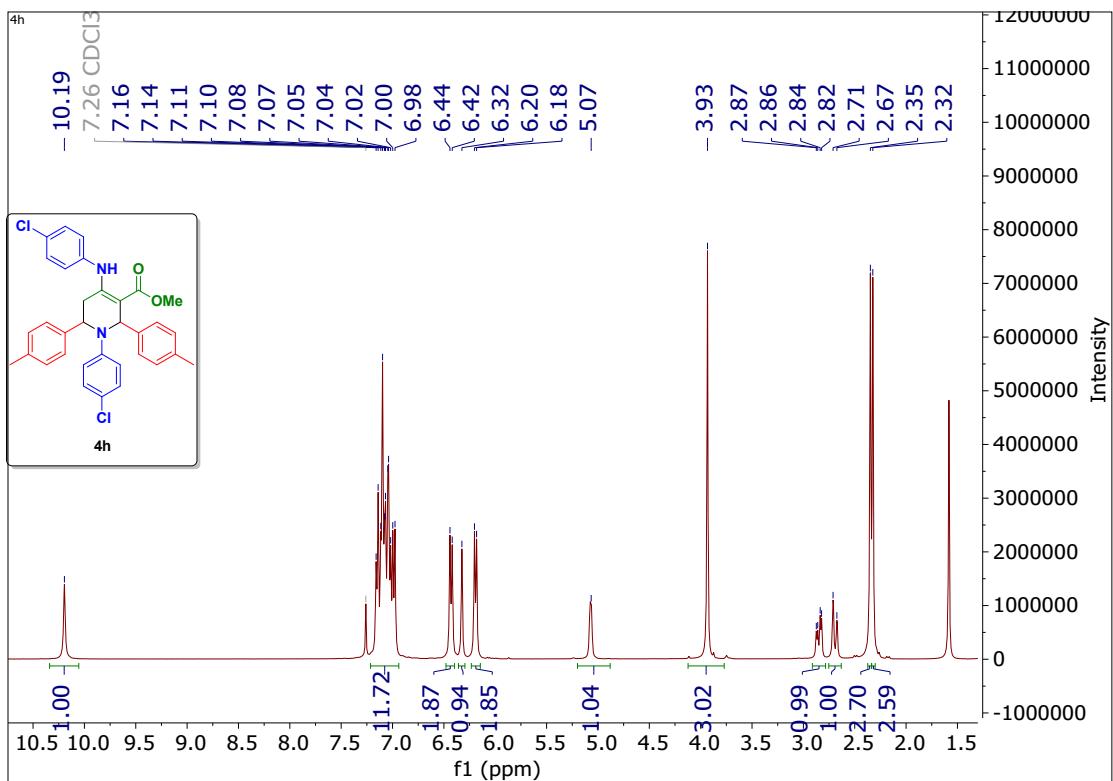
¹H NMR Spectrum of 4g



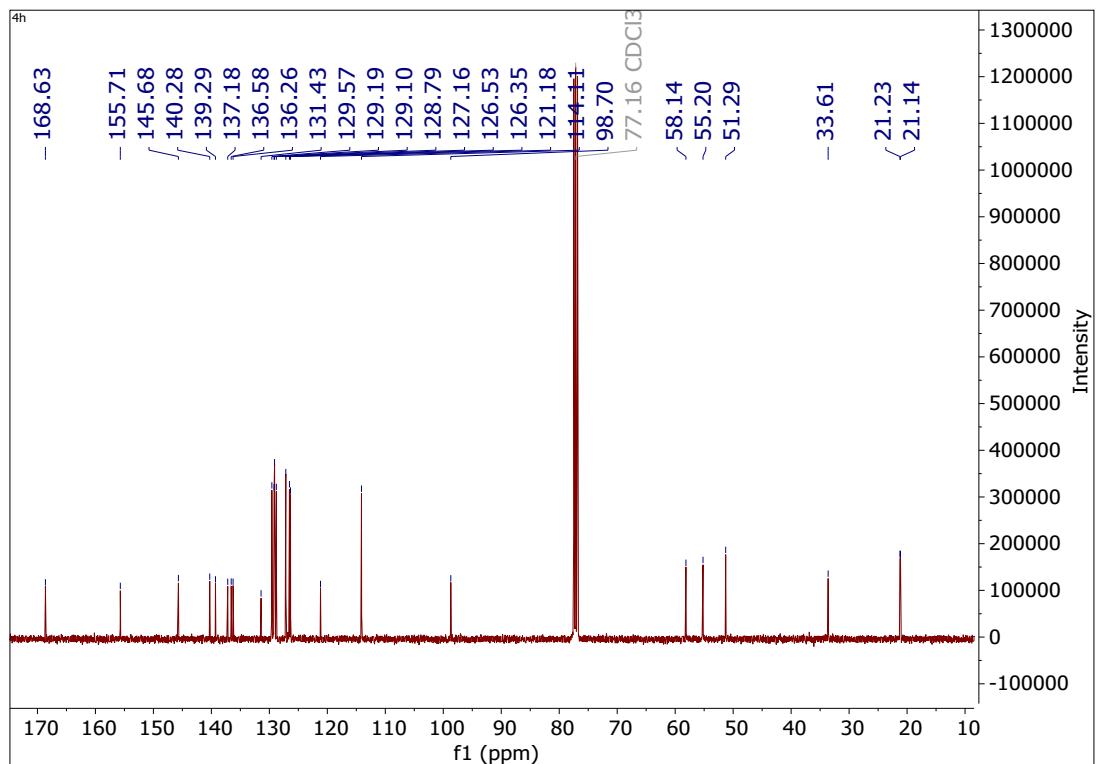
¹³C NMR Spectrum of 4g



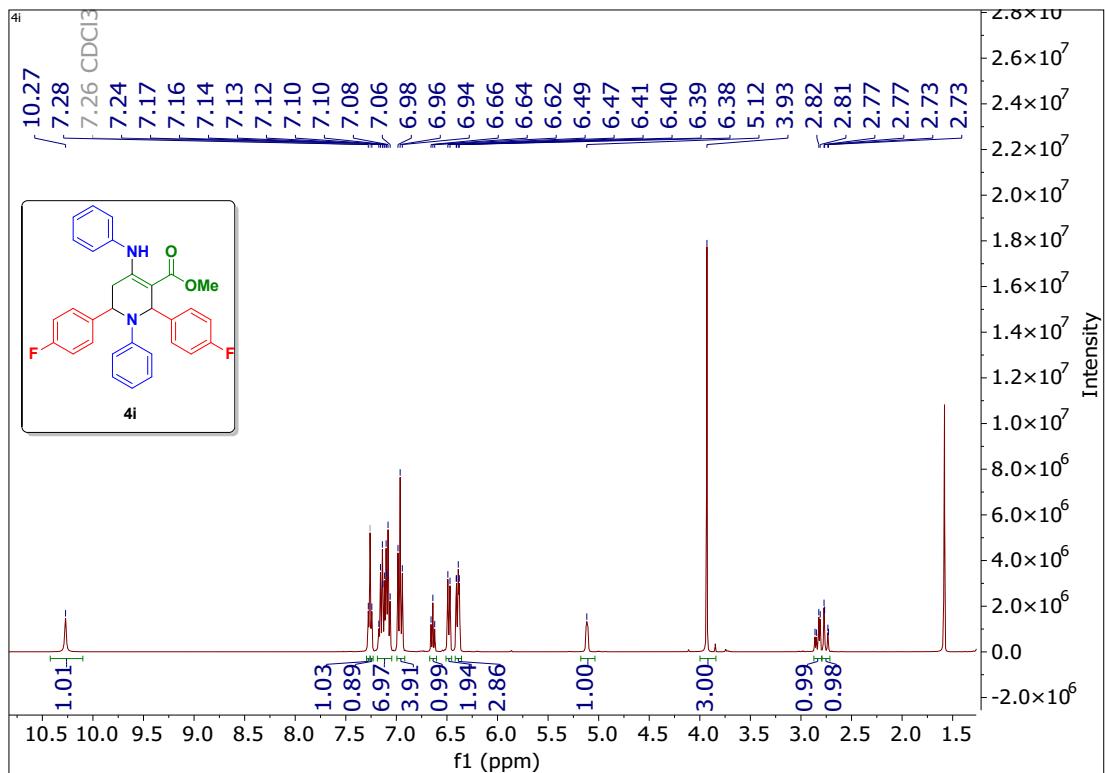
¹H NMR spectrum of 4h



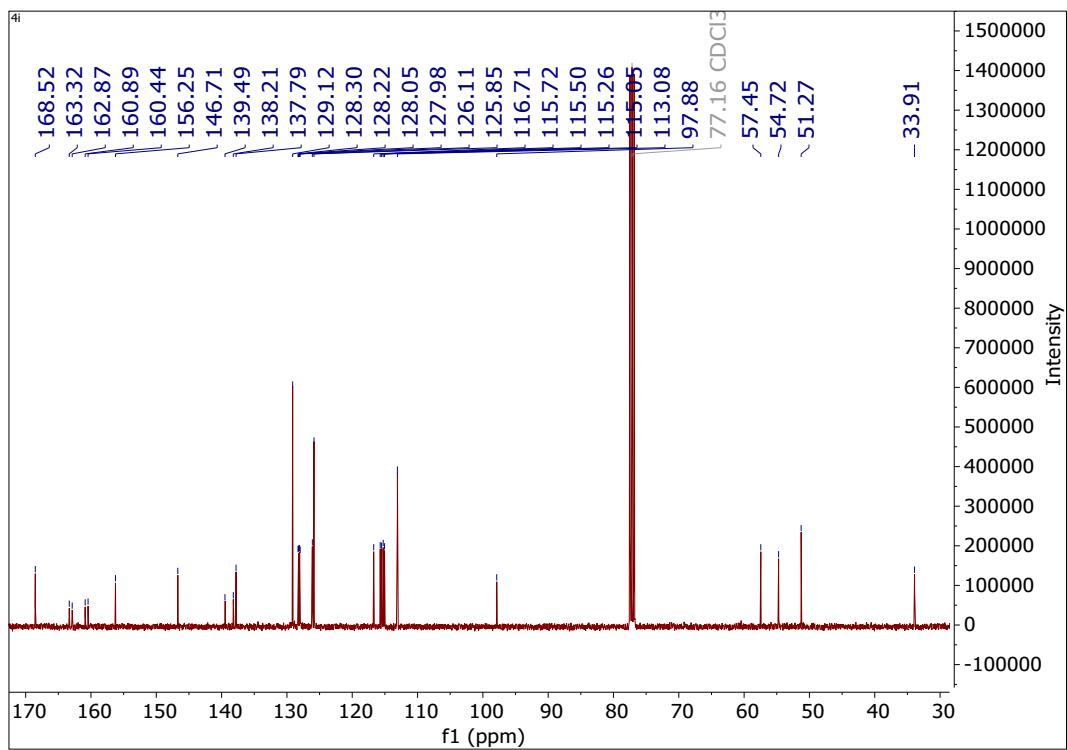
¹³C NMR spectrum of 4h



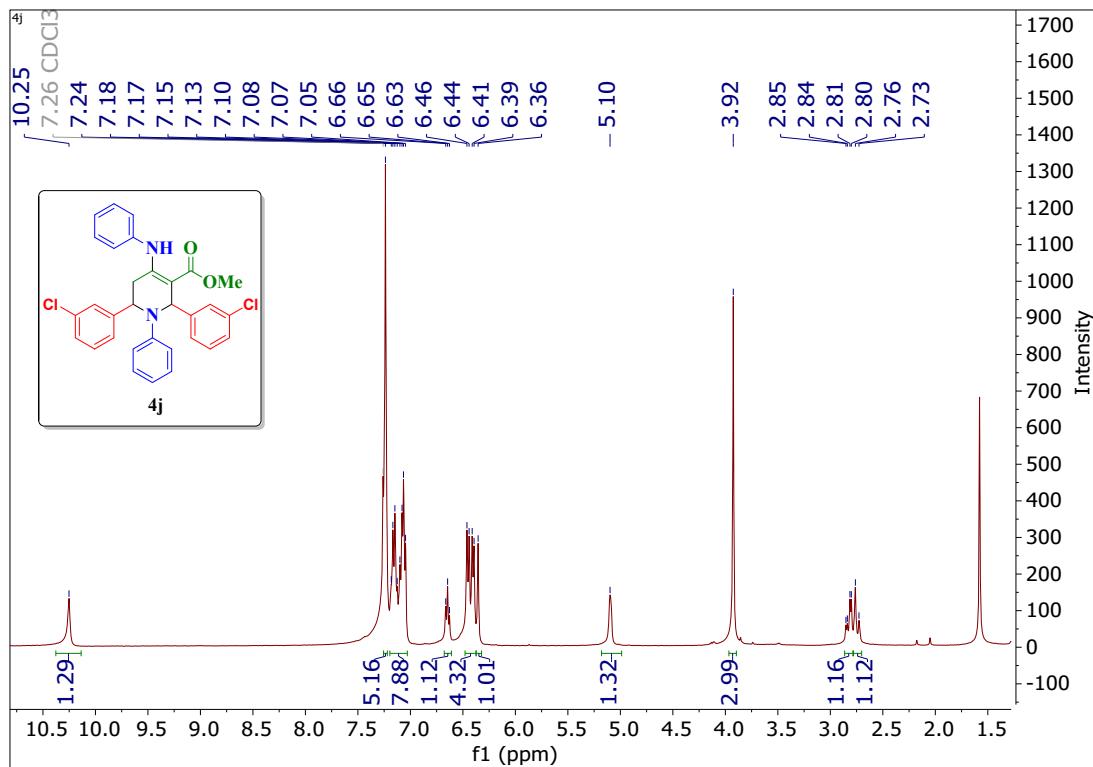
¹H NMR Spectrum of 4i



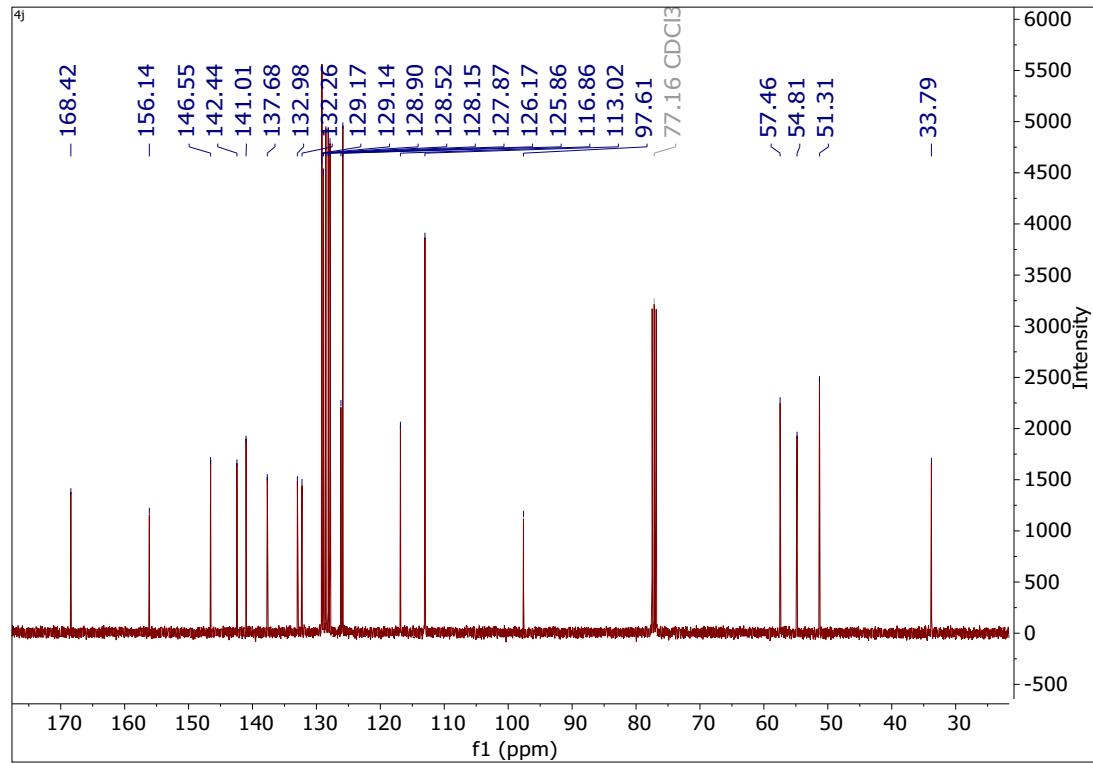
¹³C NMR spectrum of 4i



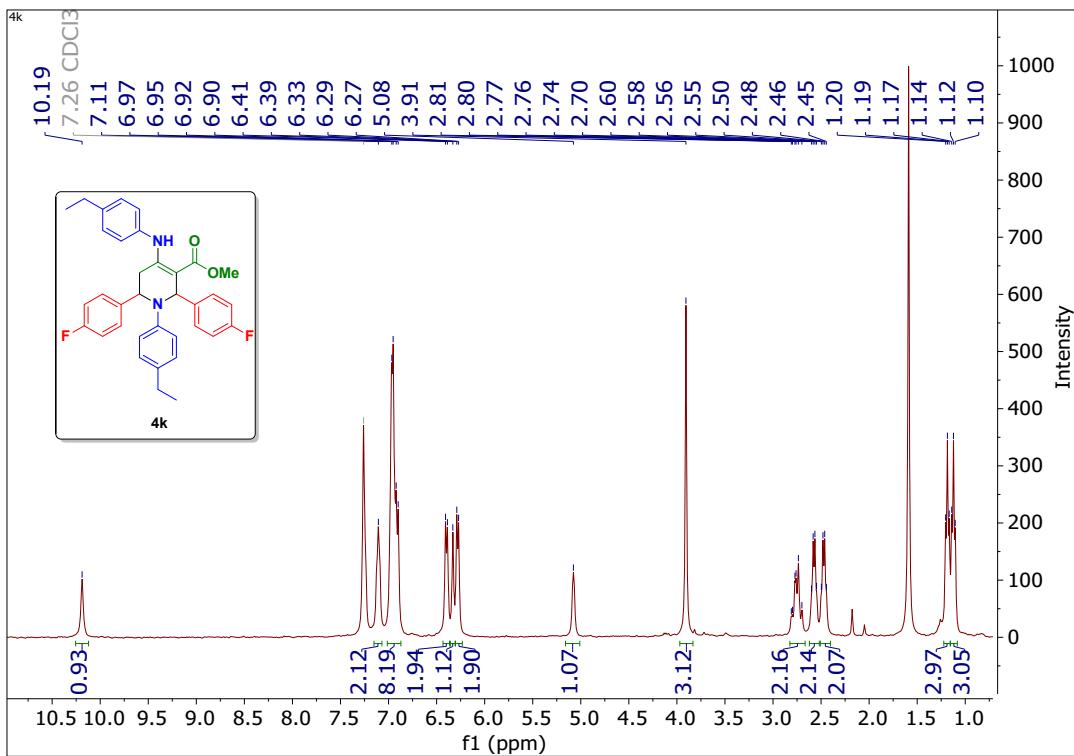
¹H NMR Spectrum of 4j



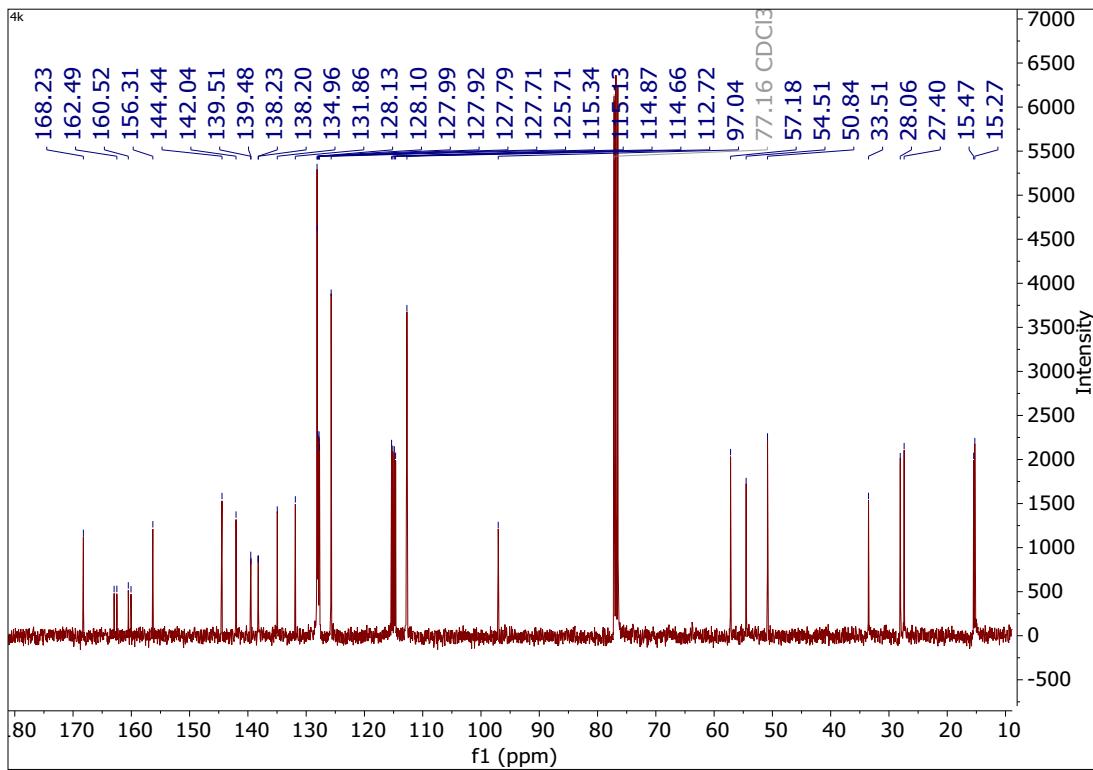
¹³C NMR spectrum of 4j



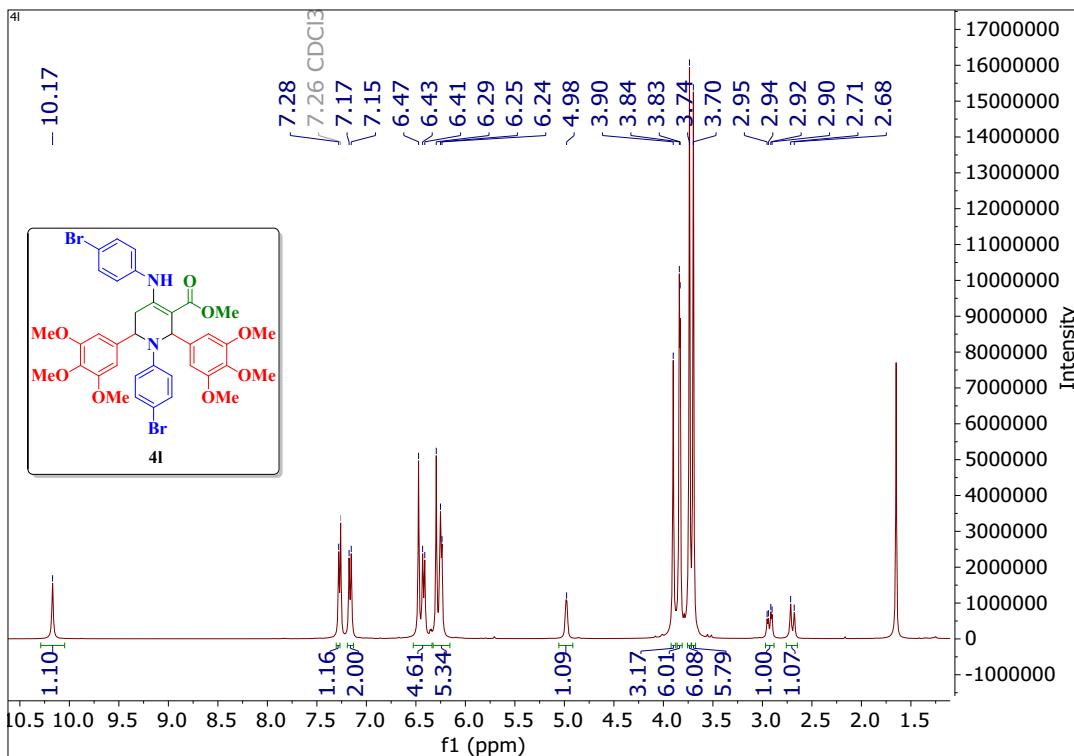
¹H NMR Spectrum of 4k



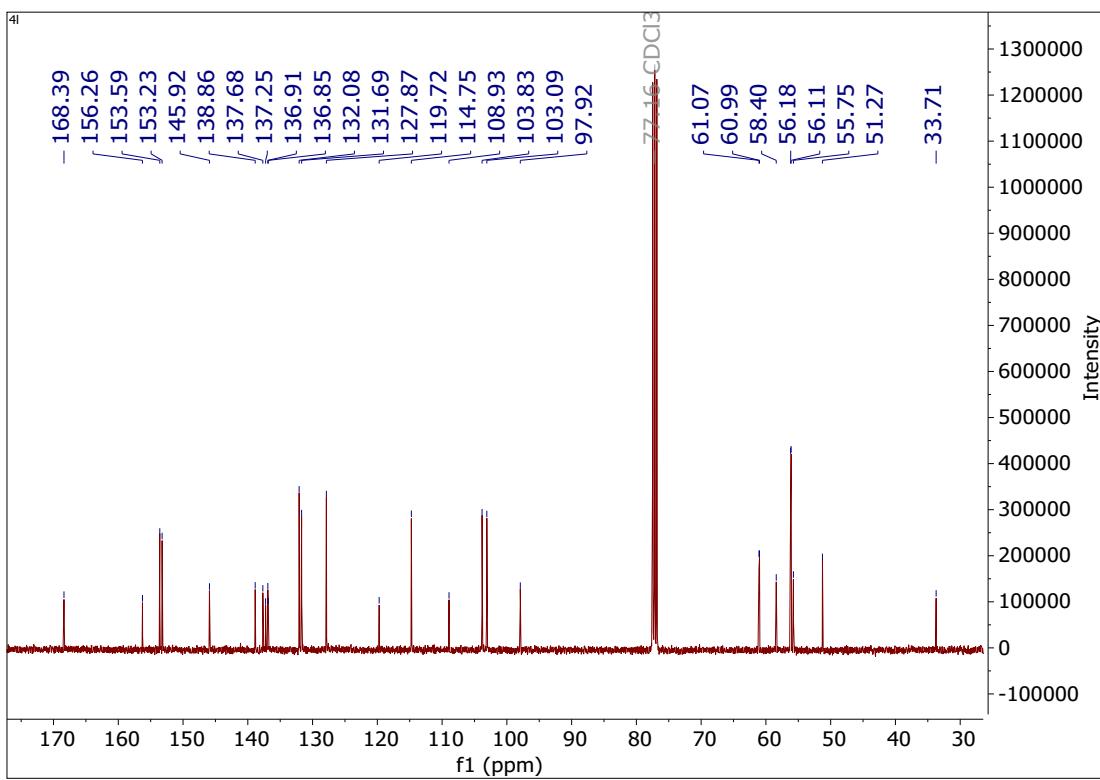
¹³C NMR spectrum of 4k



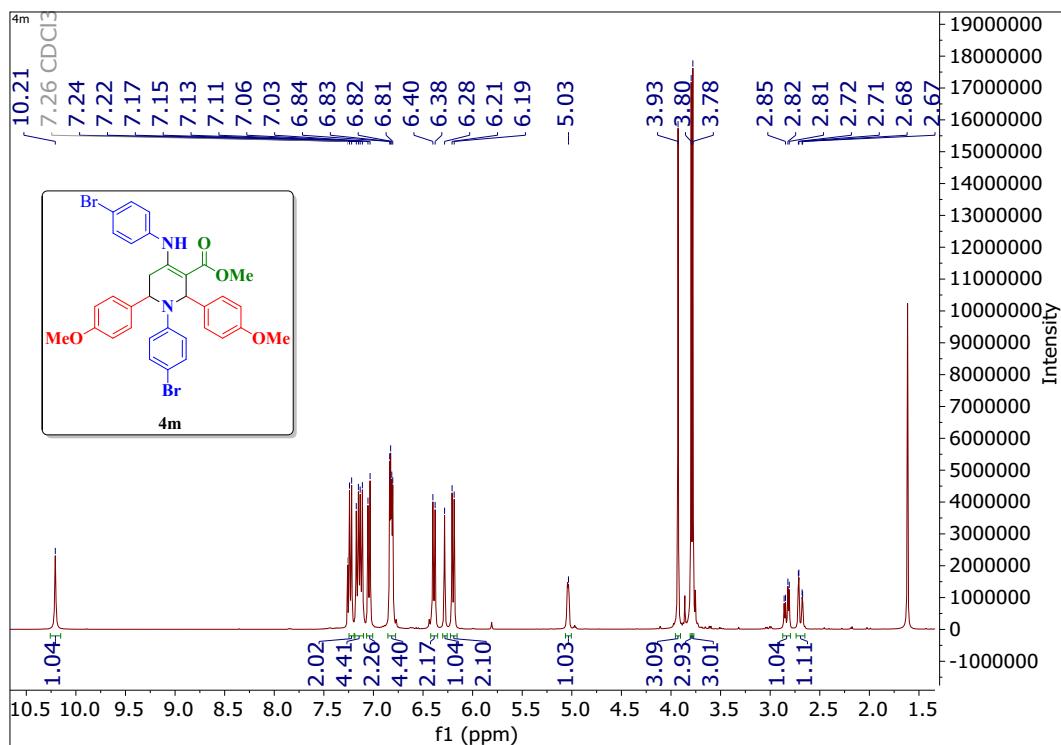
¹H NMR spectrum of 4l



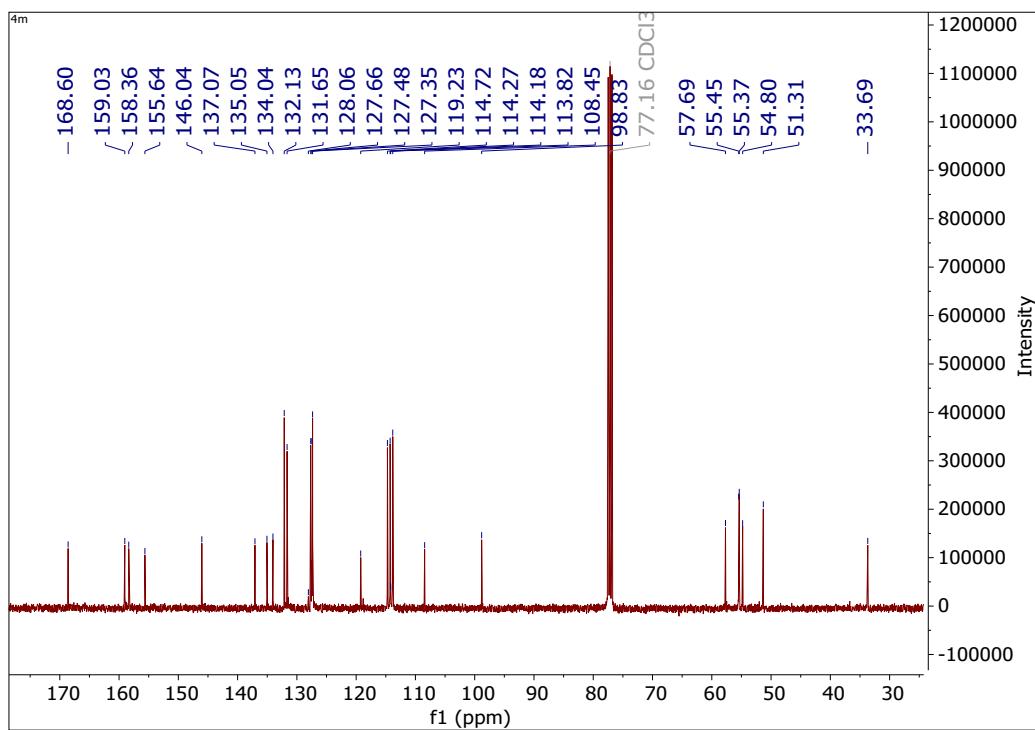
¹³C NMR Spectrum of 4l



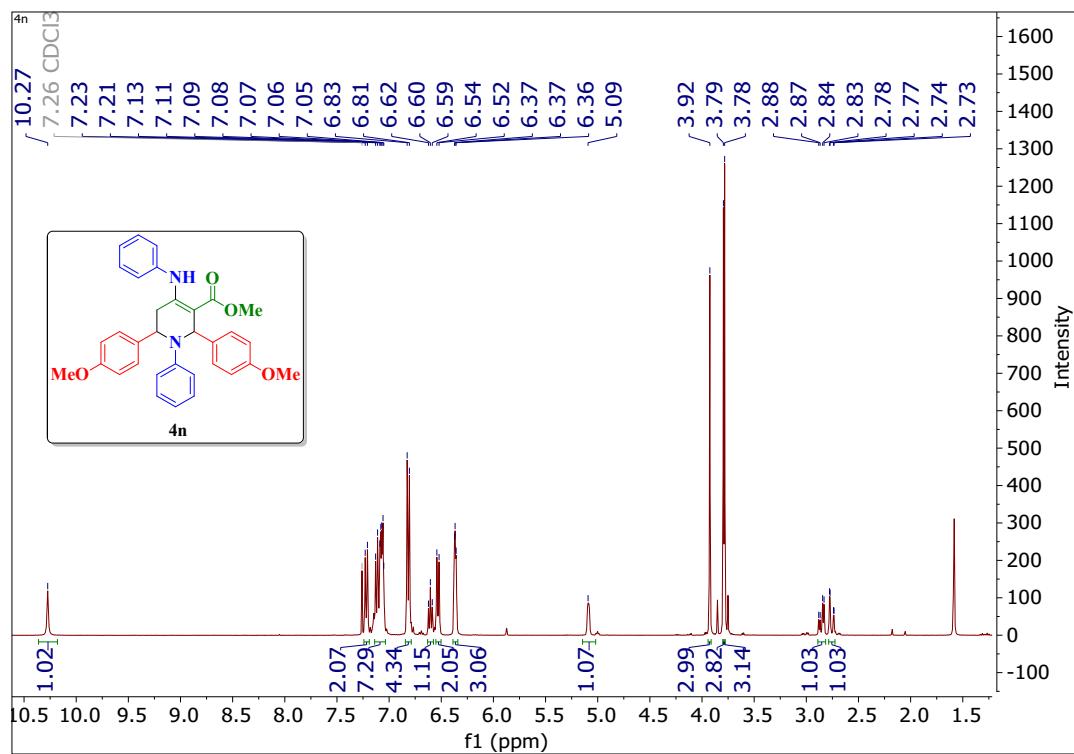
¹H NMR spectrum of 4m



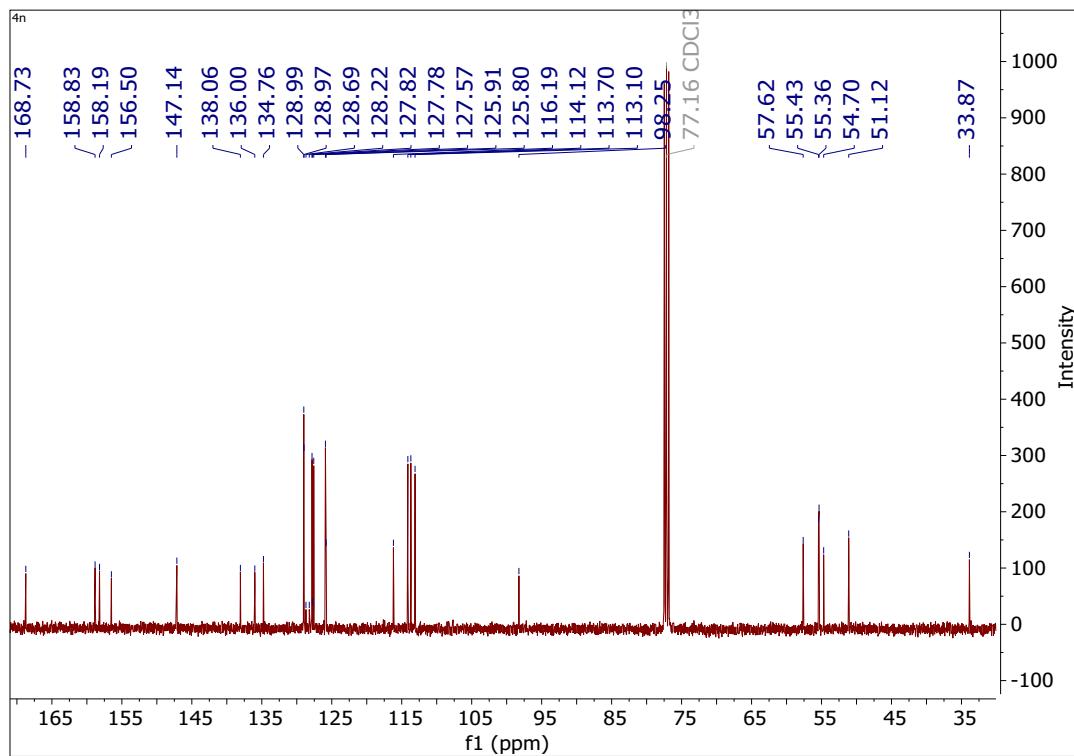
¹³C NMR spectrum of 4m



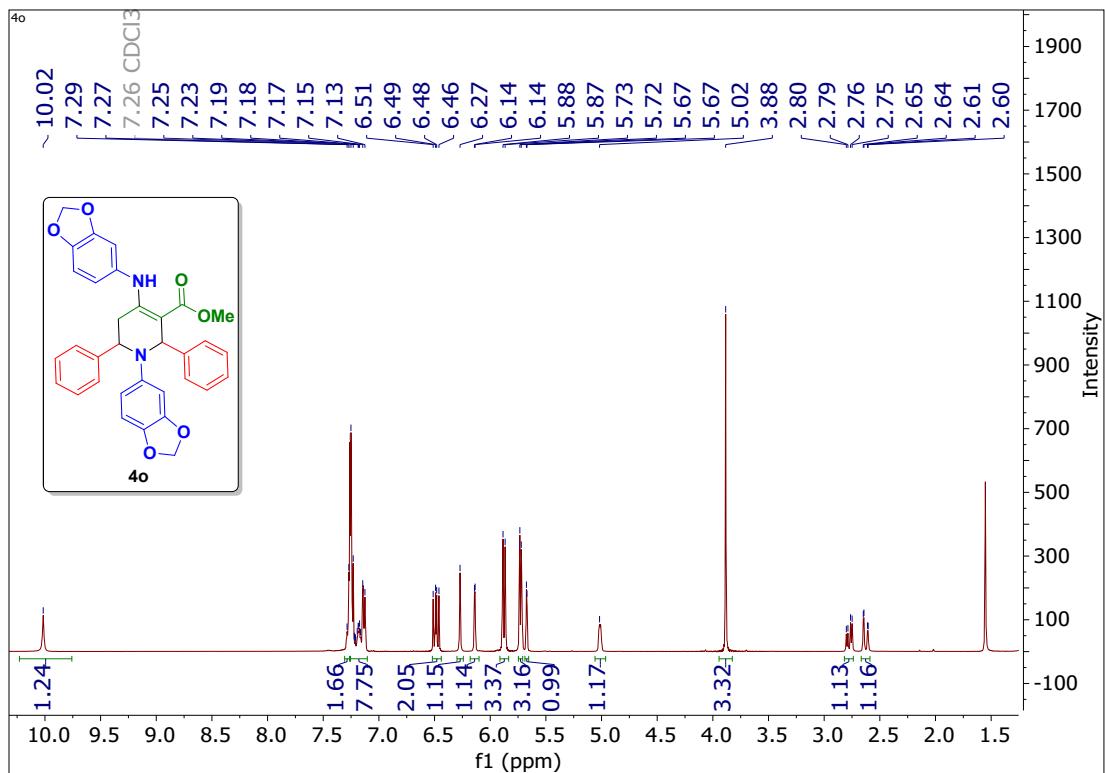
¹H NMR spectrum of 4n



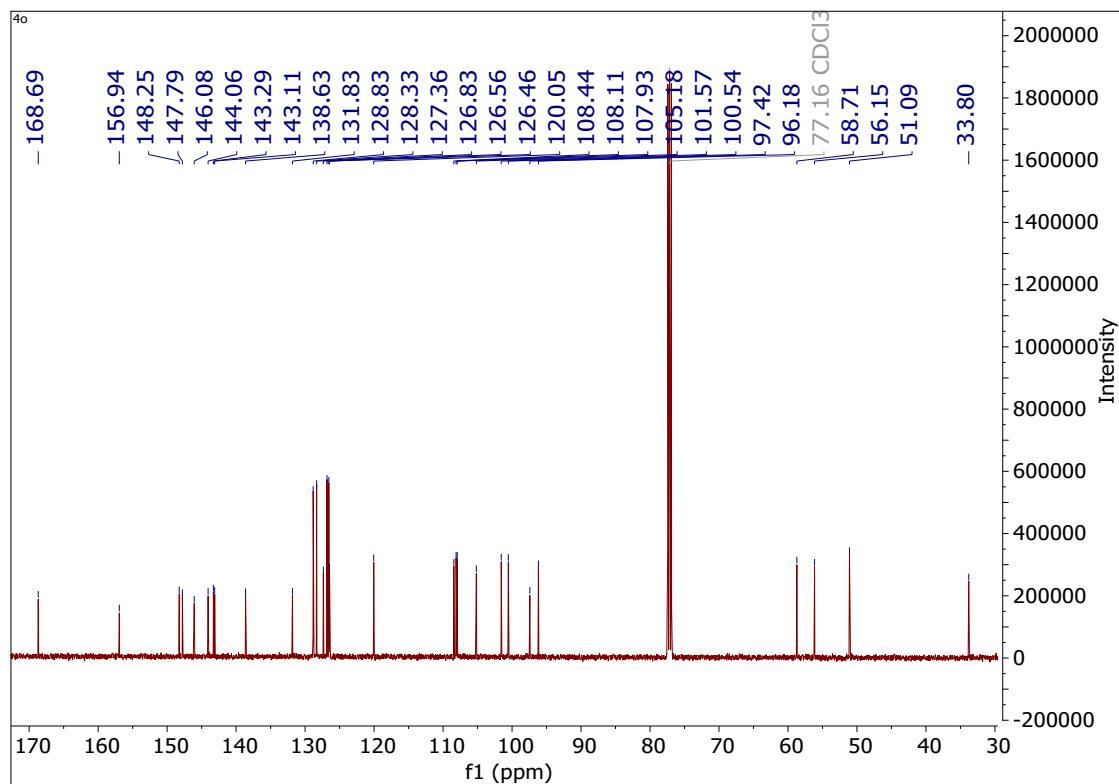
¹³C NMR Spectrum of 4n



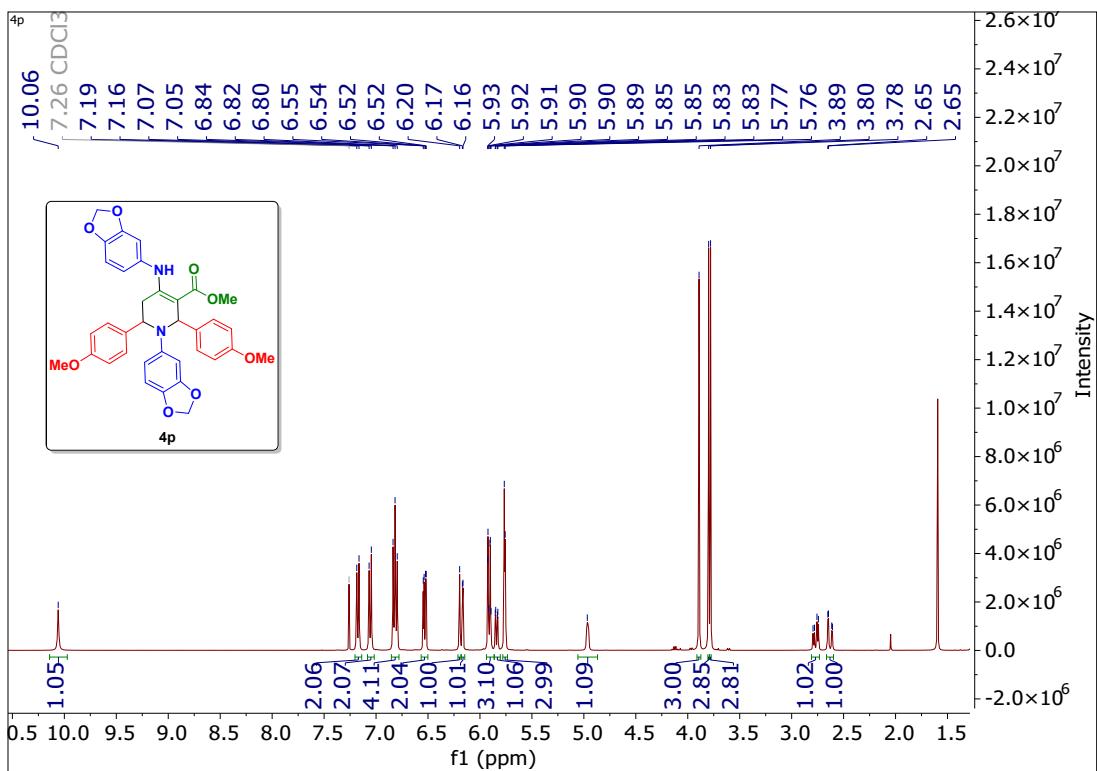
¹H NMR spectrum of 4o



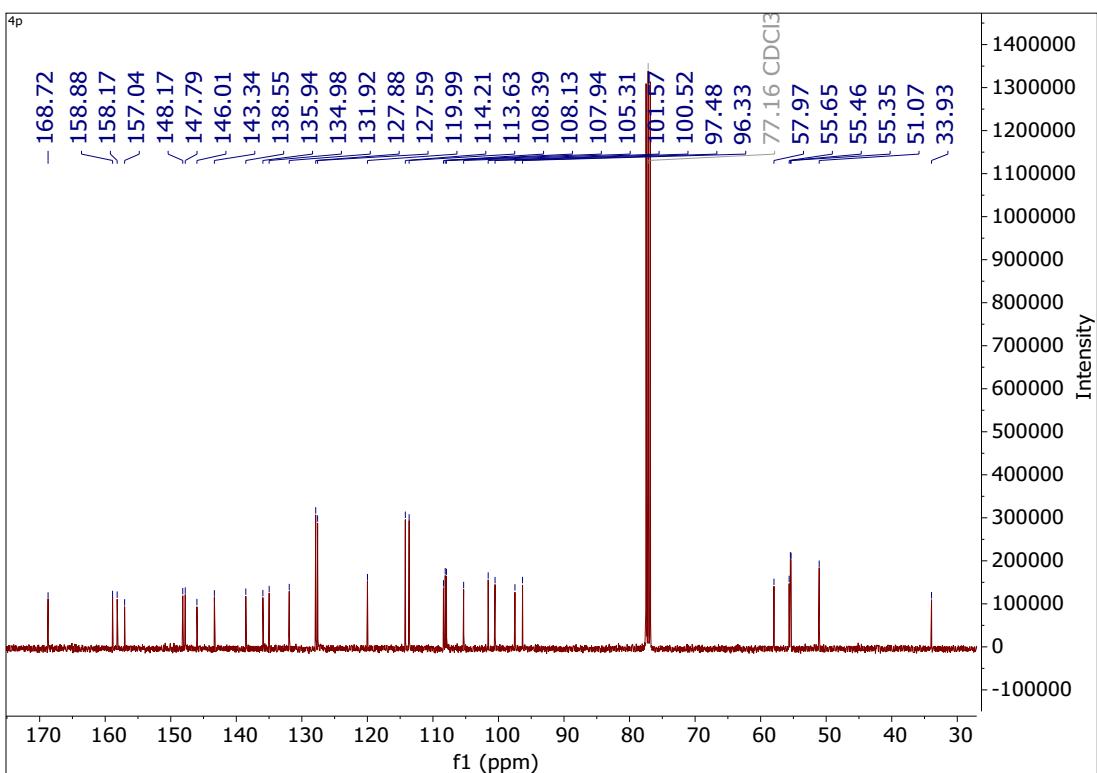
¹³C NMR spectrum of 4o



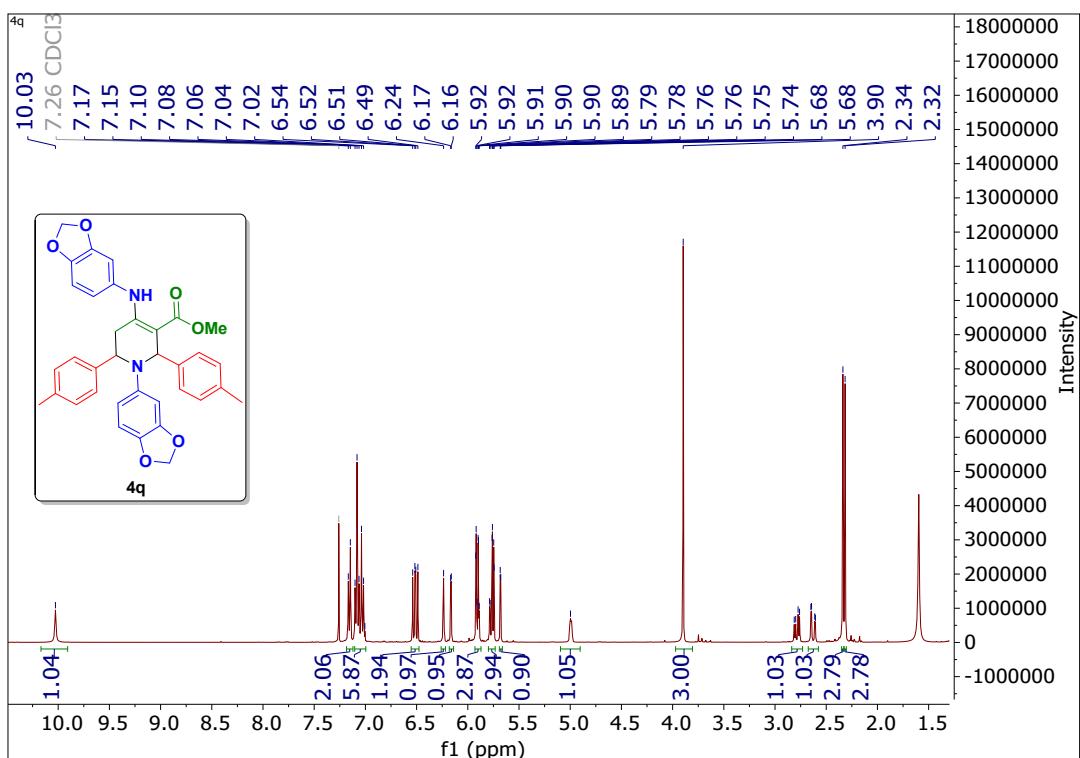
¹H NMR spectrum of 4p



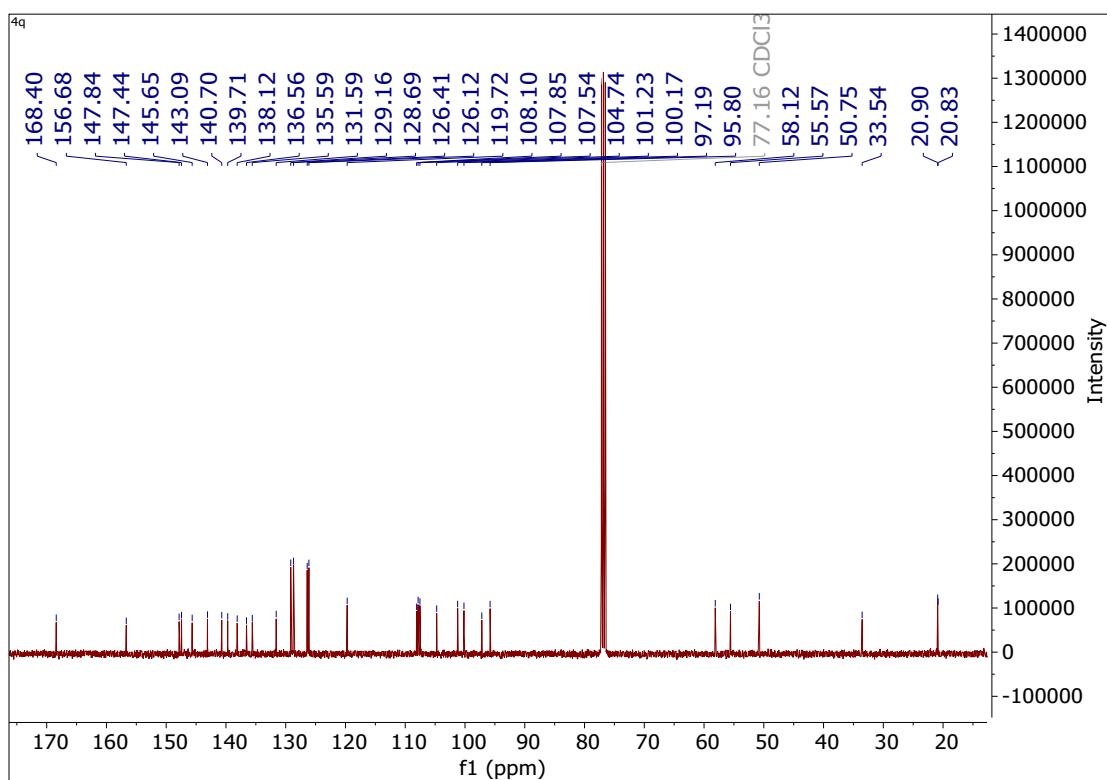
¹³C NMR spectrum of 4p



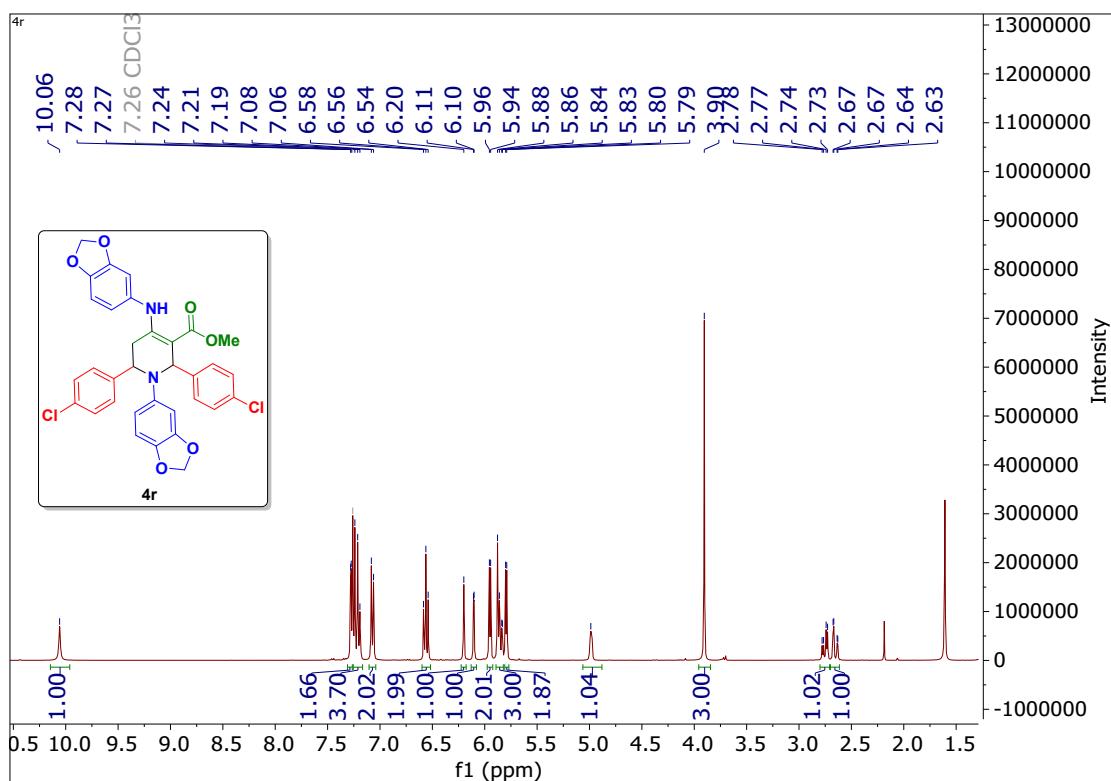
¹H NMR spectrum of 4q



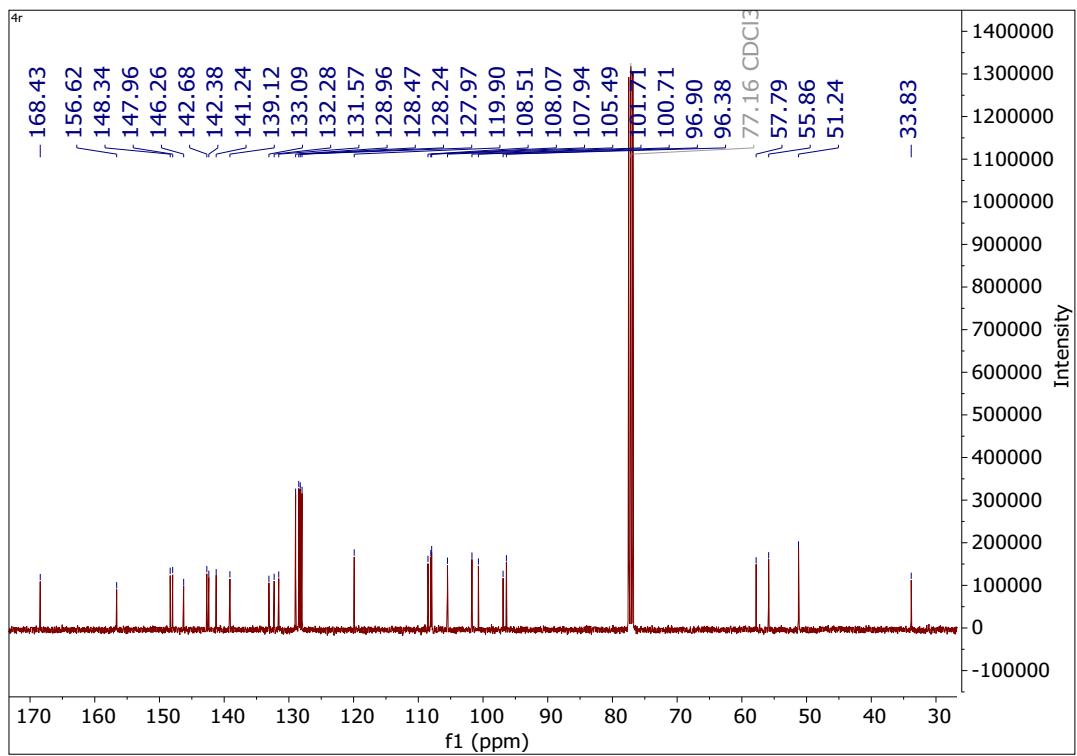
¹³C NMR spectrum of 4q



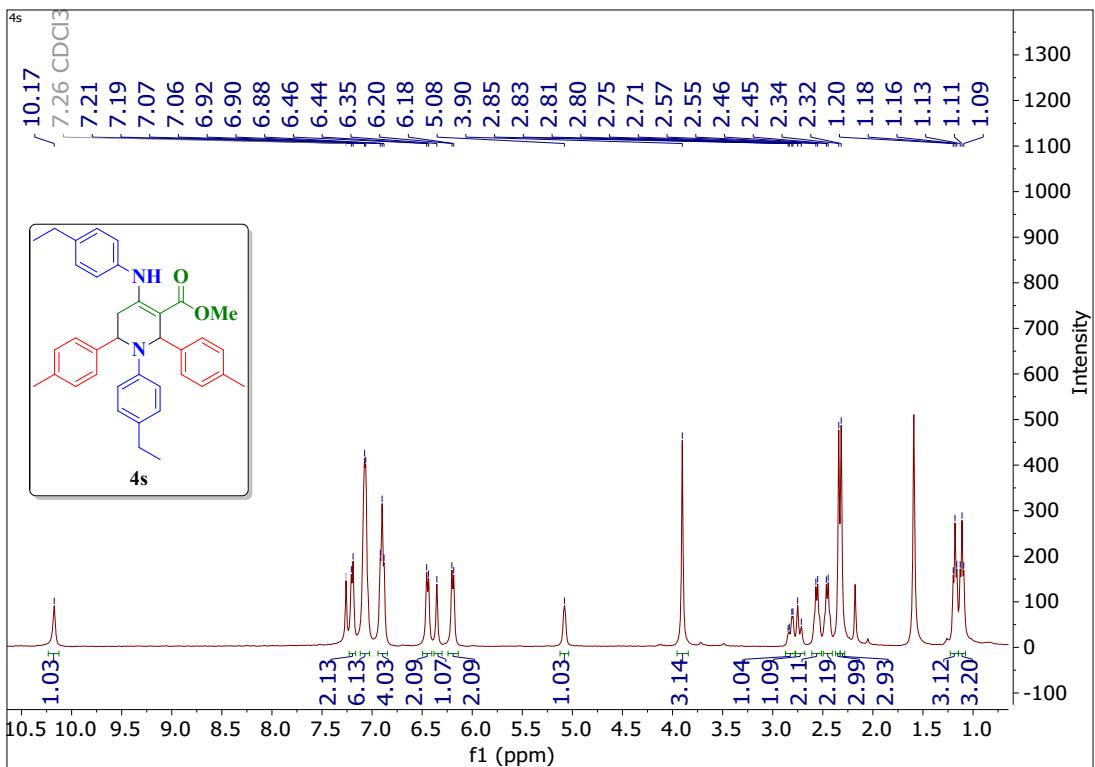
¹H NMR spectrum of 4r



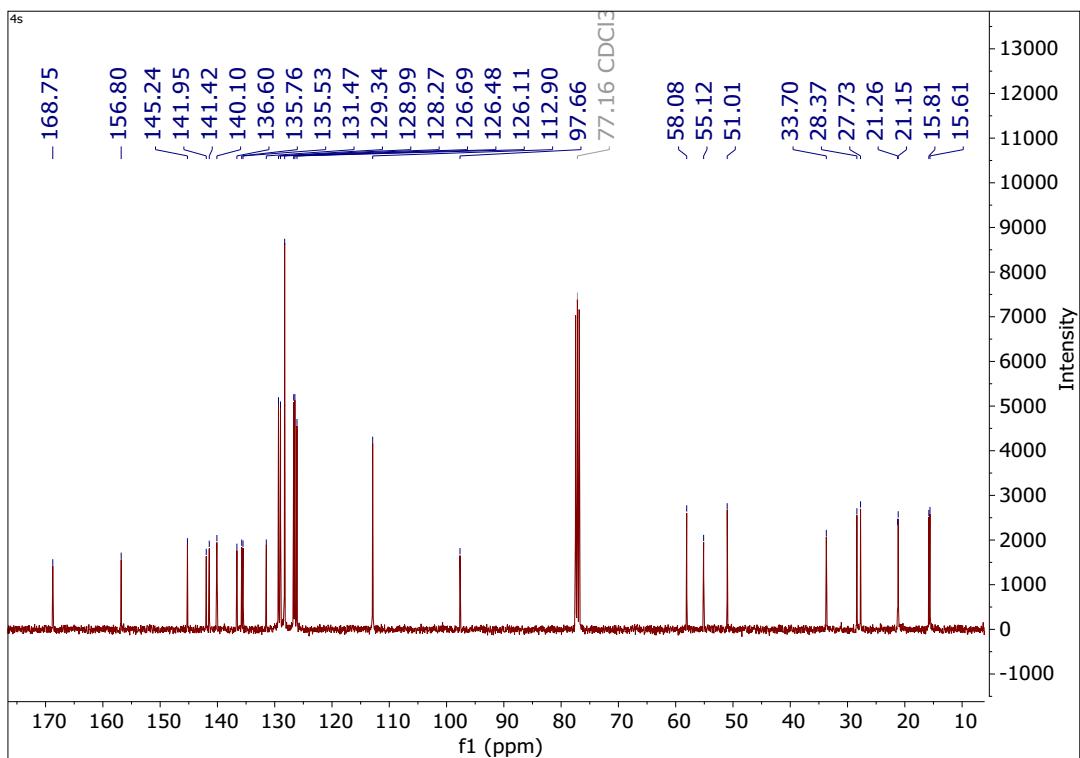
¹³C NMR spectrum of 4r



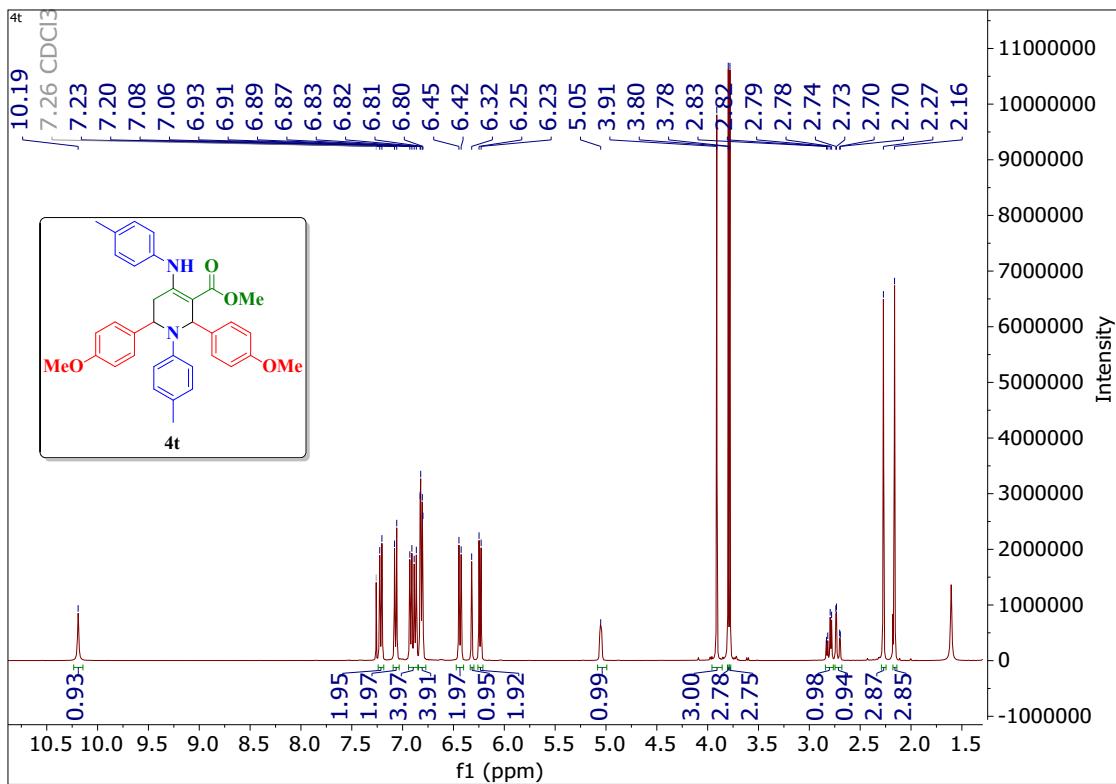
¹H NMR spectrum of 4s



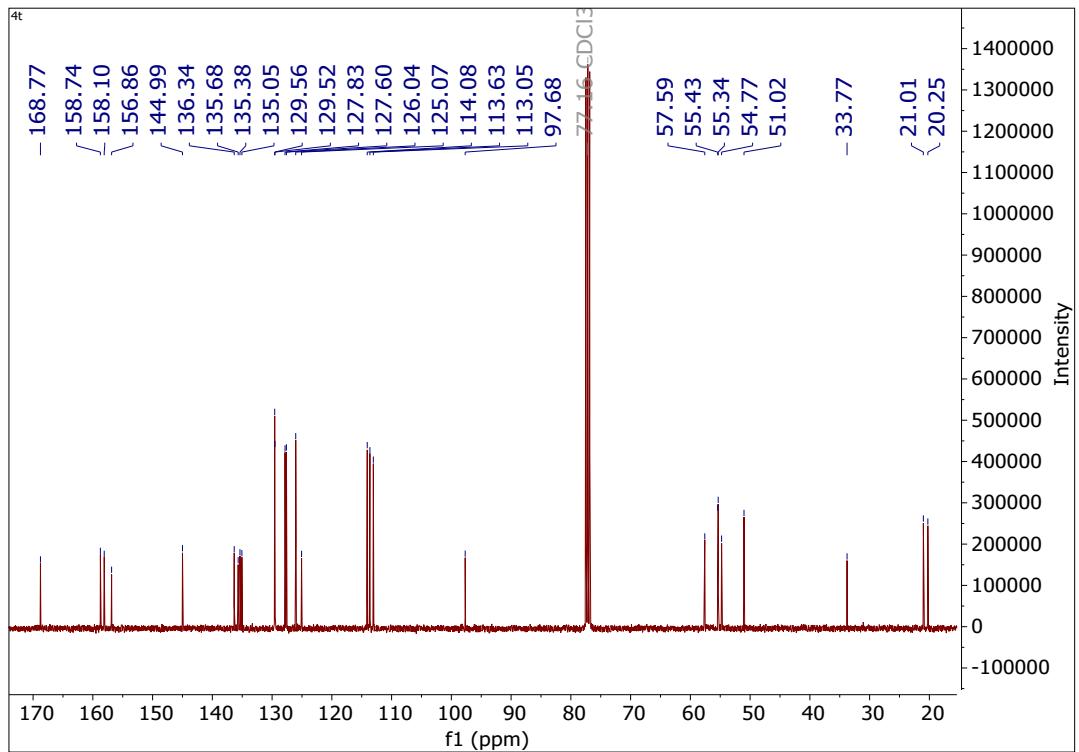
¹³C NMR spectrum of 4s



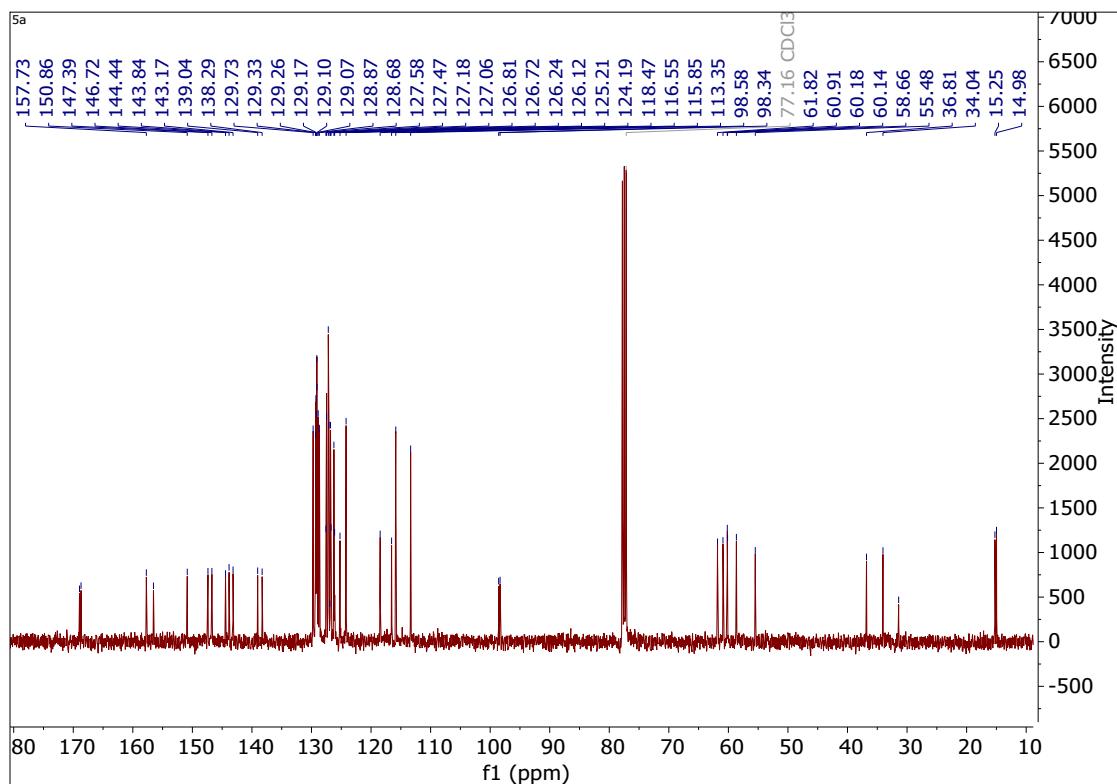
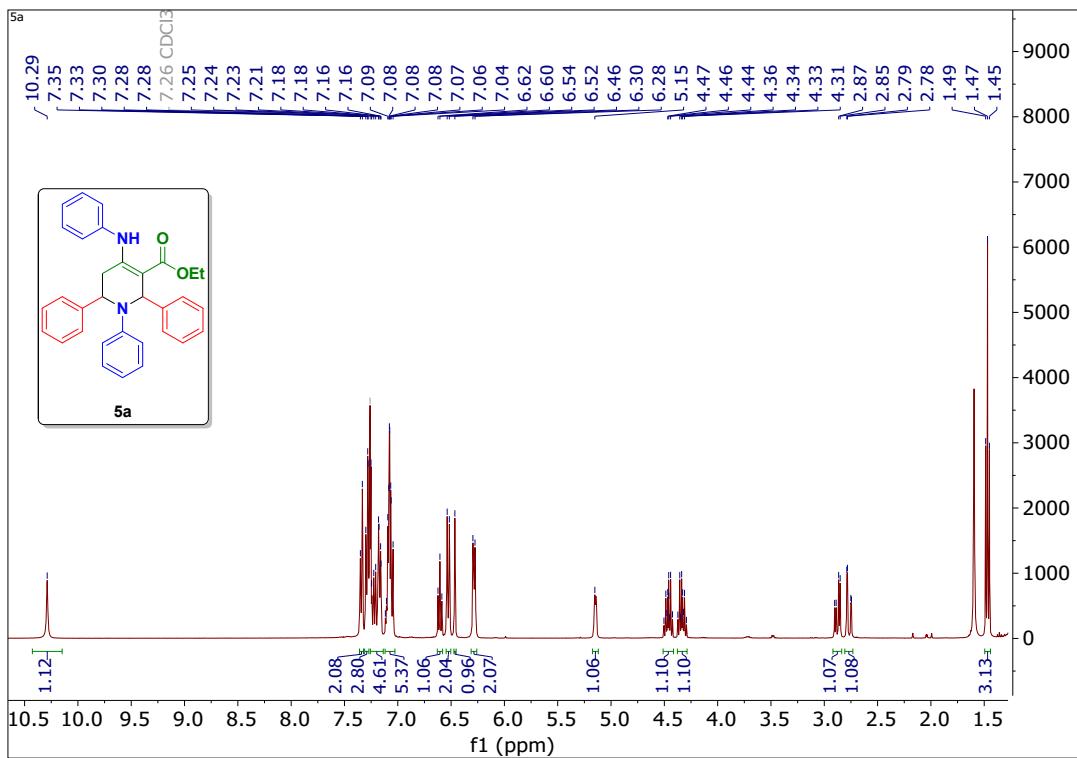
¹H NMR spectrum of 4t



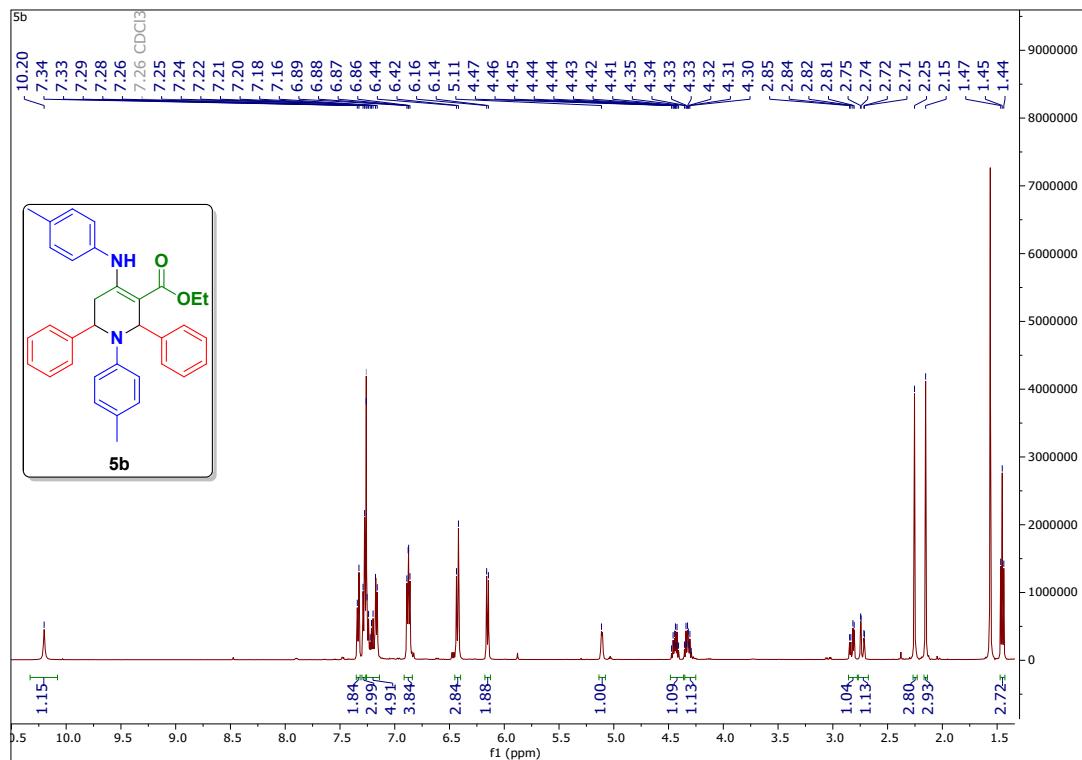
¹³C NMR spectrum of 4t



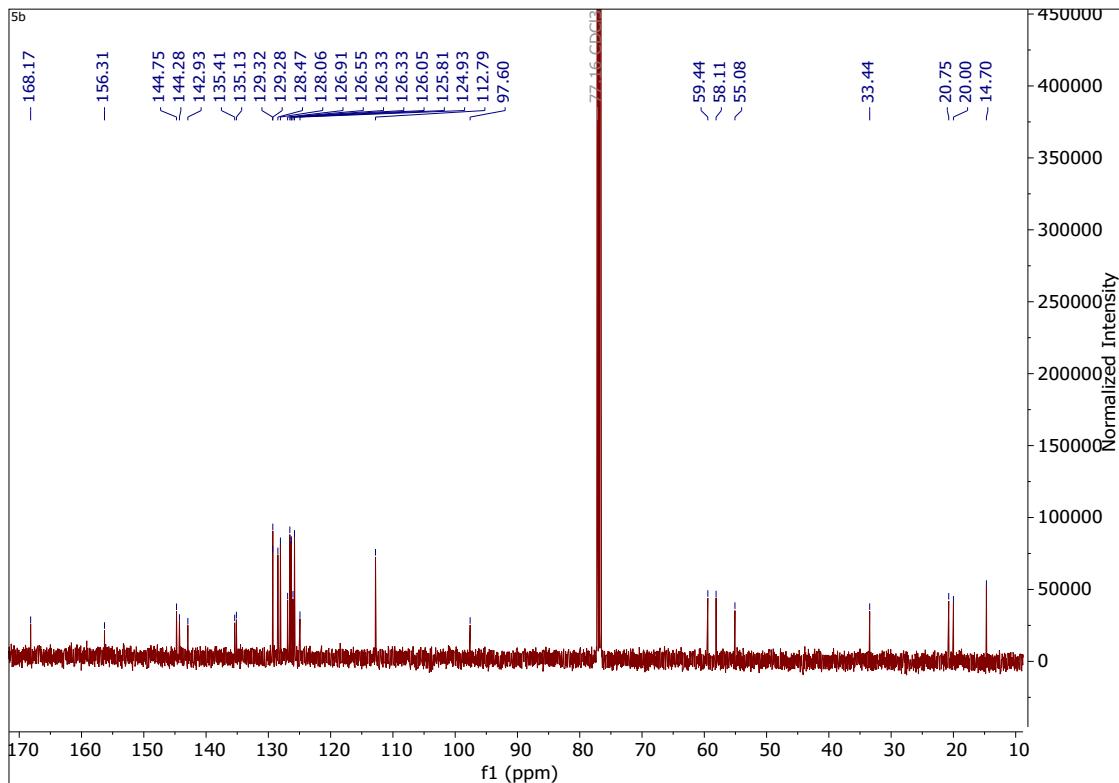
¹H NMR spectrum of 5a



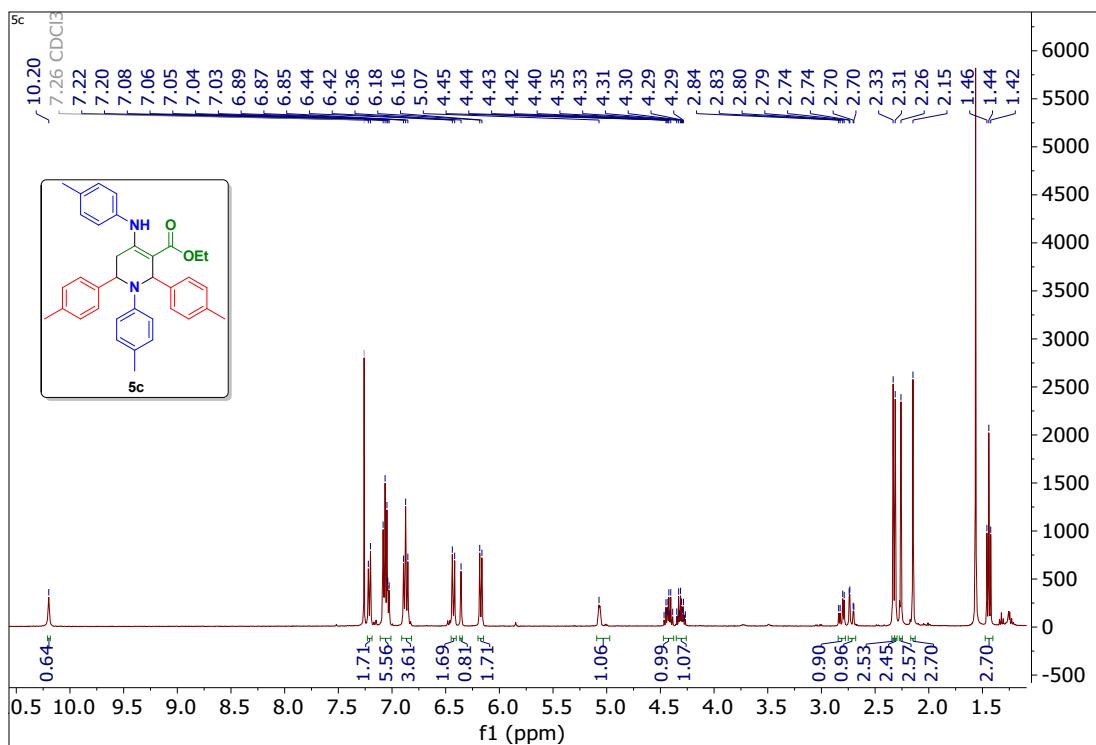
¹H NMR spectrum of 5b



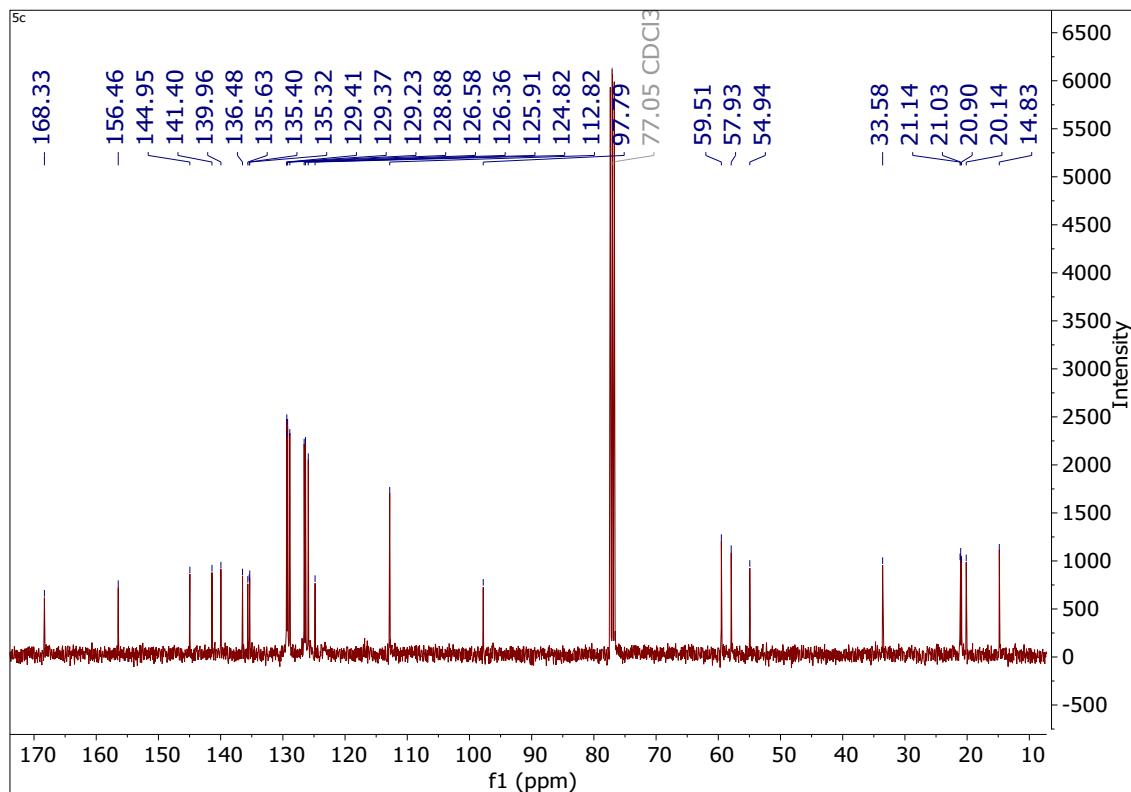
¹³C NMR spectrum of 5b



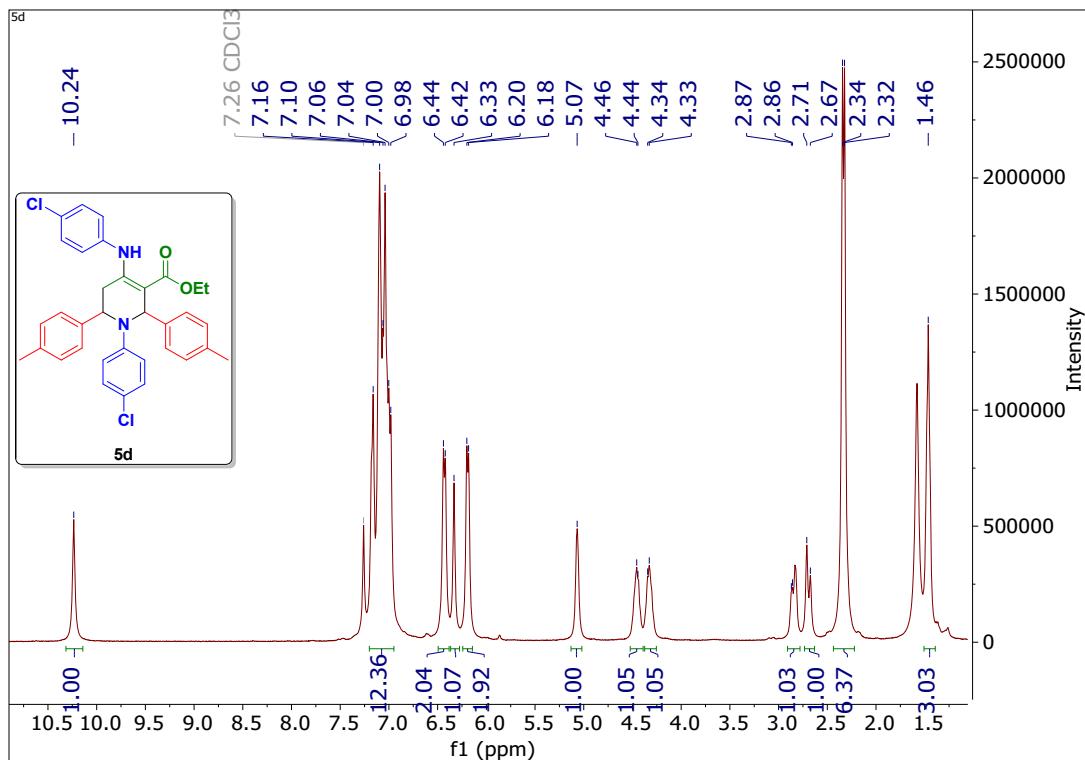
¹H NMR spectrum of 5c



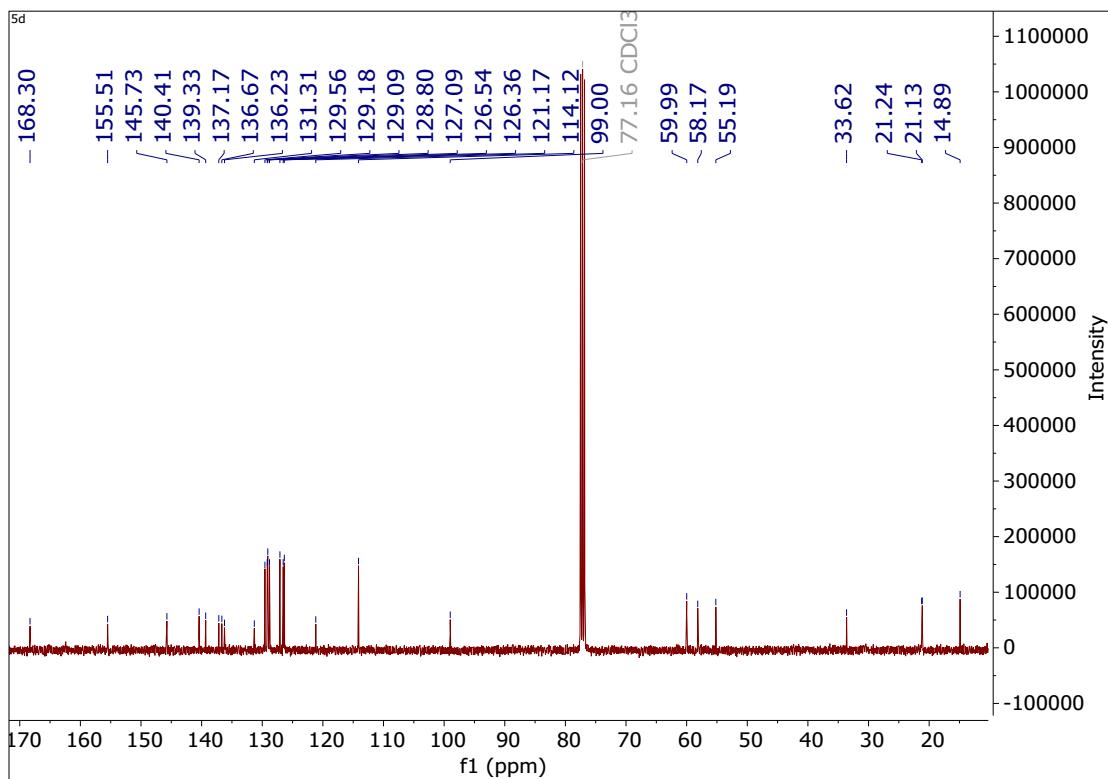
¹³C NMR spectrum of 5c



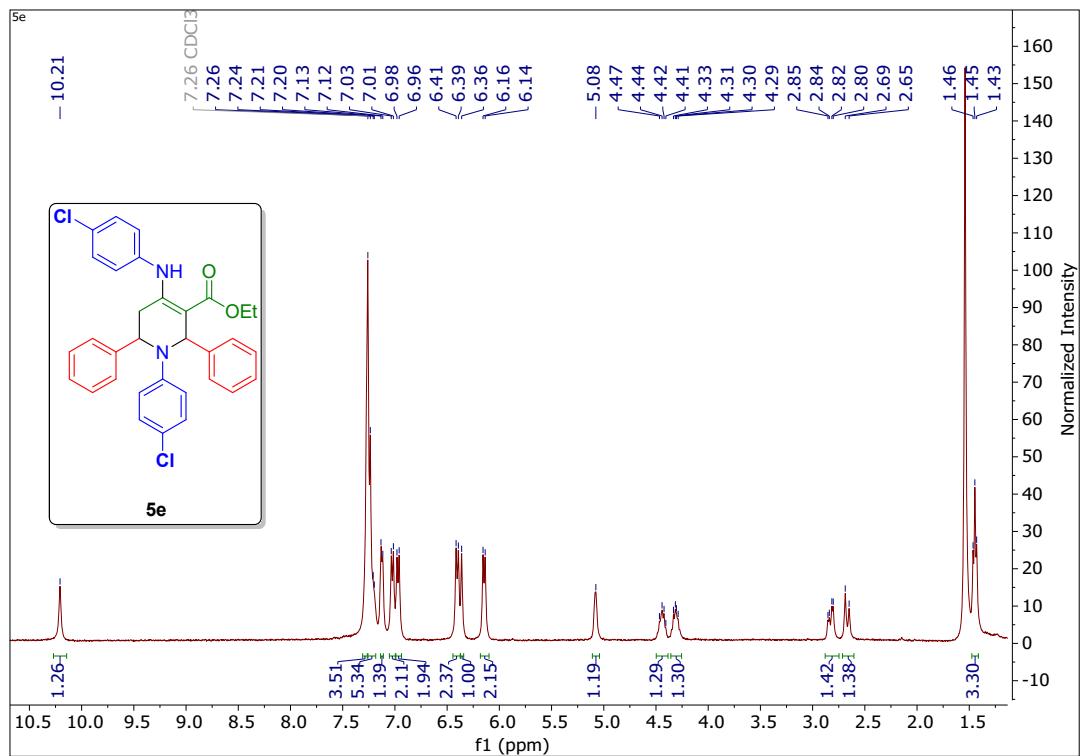
¹H NMR spectrum of 5d



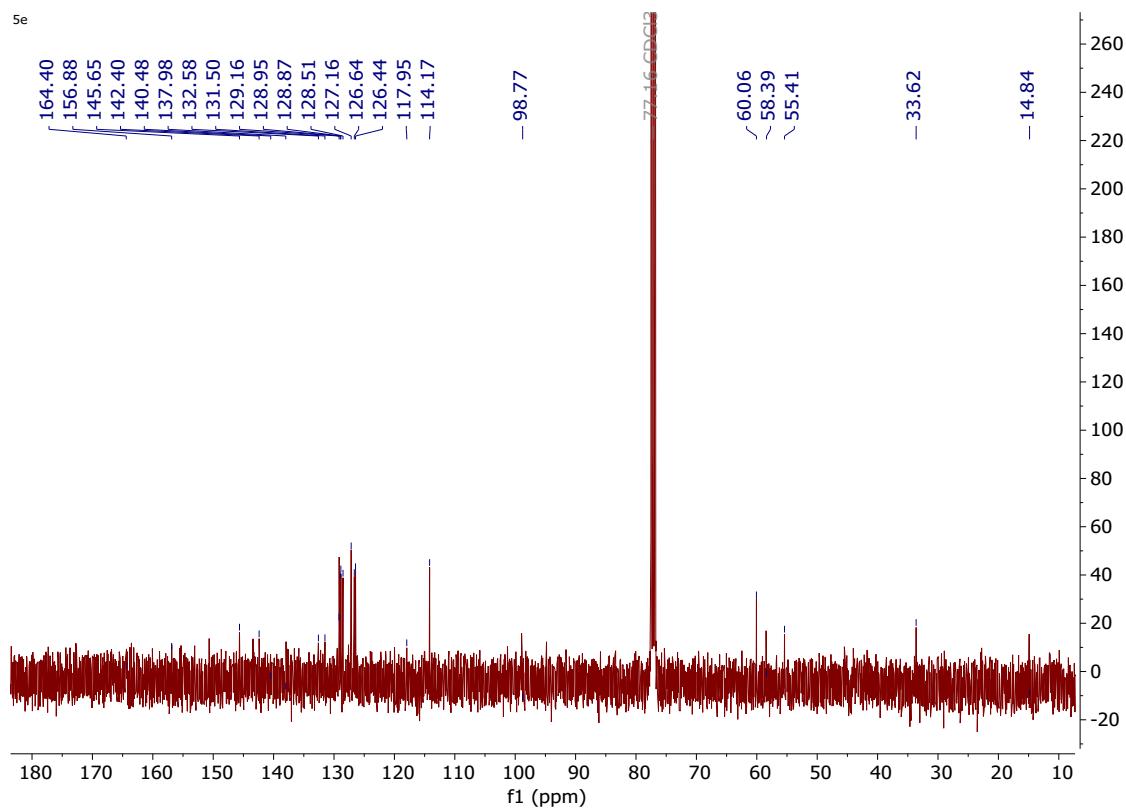
¹³C NMR spectrum of 5d



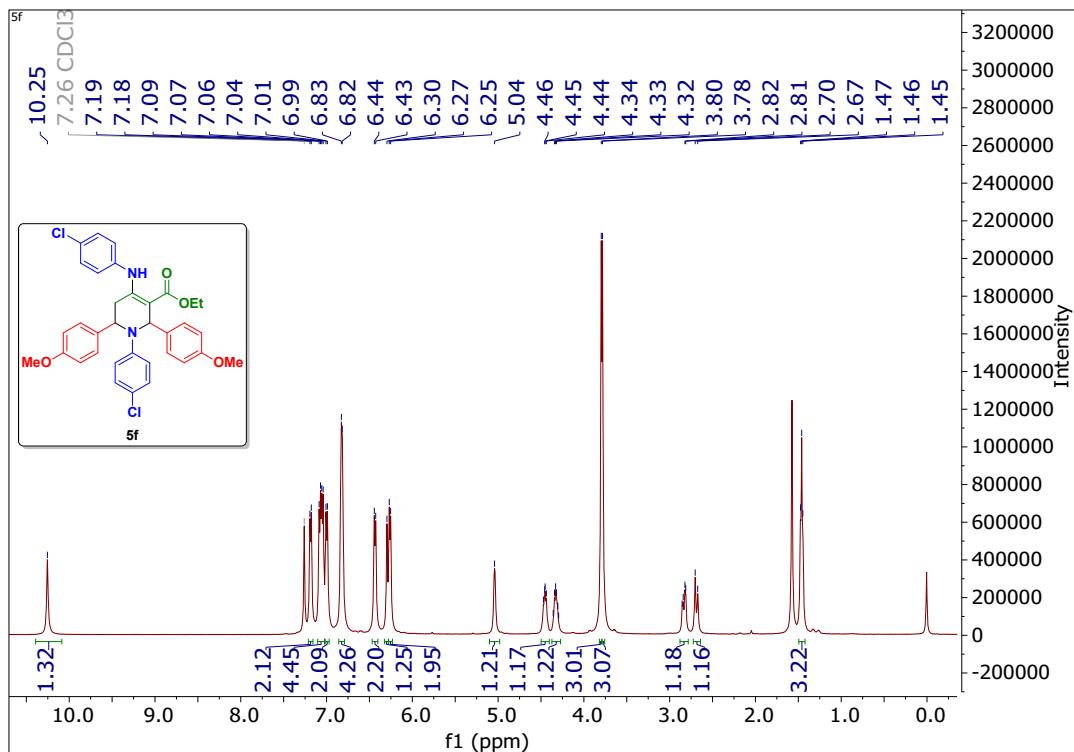
¹H NMR spectrum of 5e



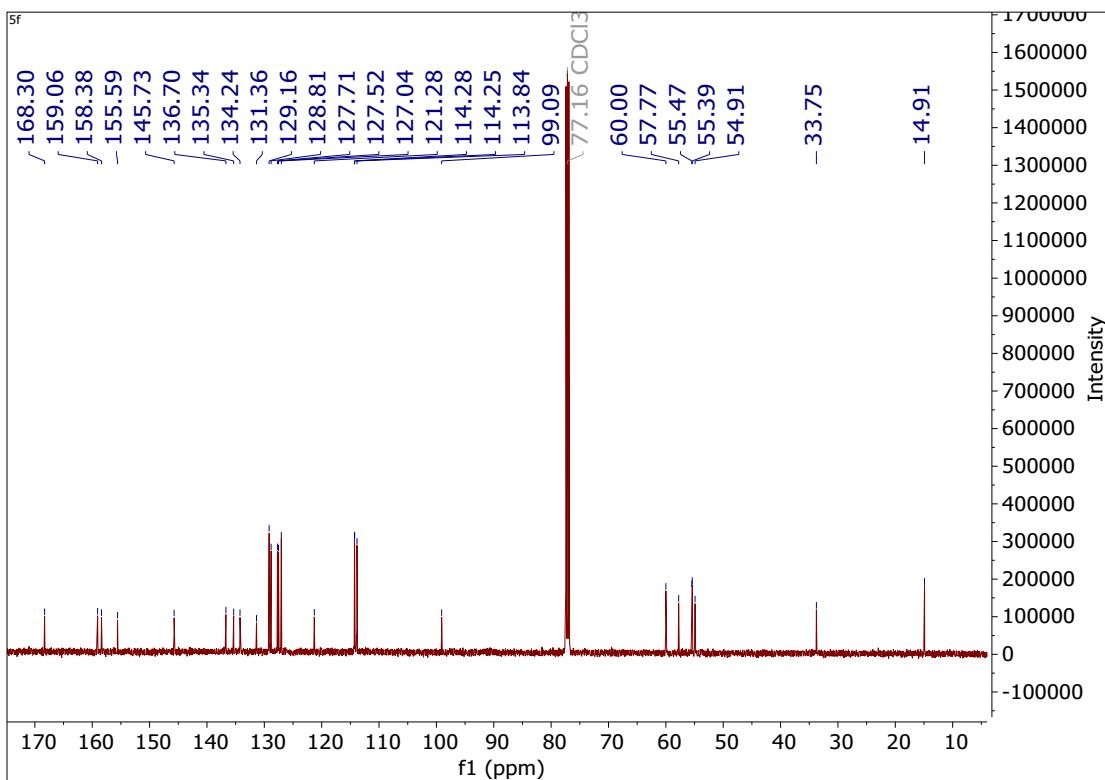
¹³C NMR spectrum of 5e



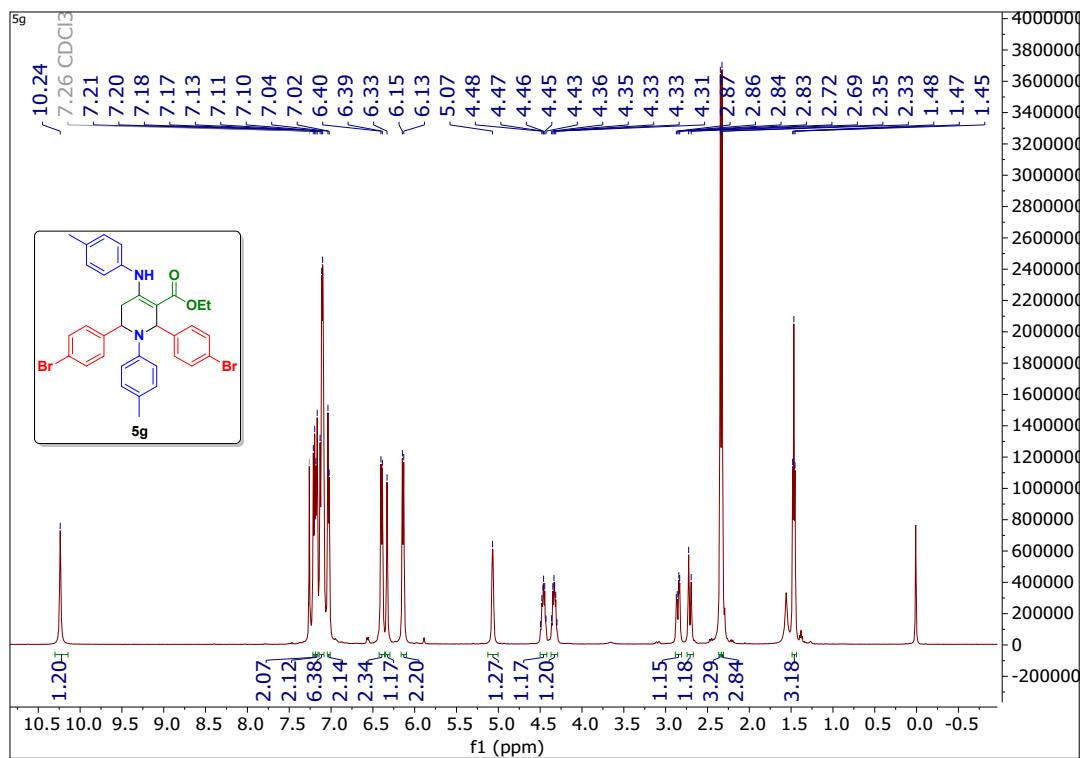
¹H NMR spectrum of 5f



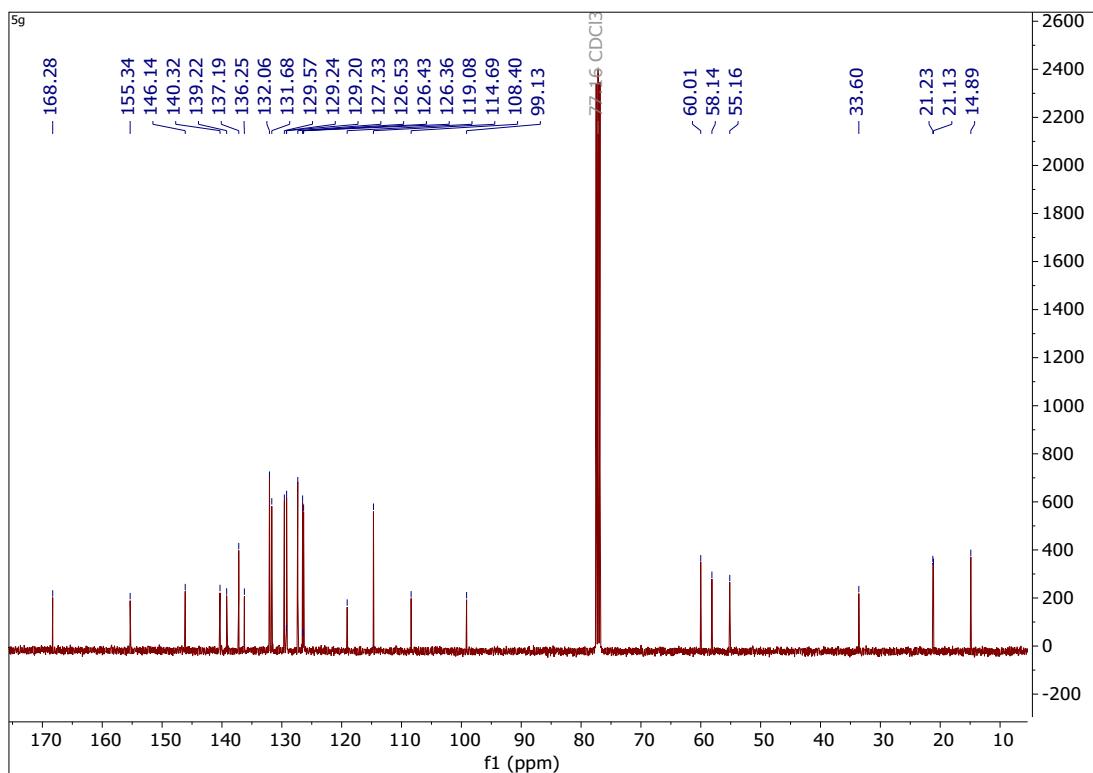
¹³C NMR spectrum of 5f



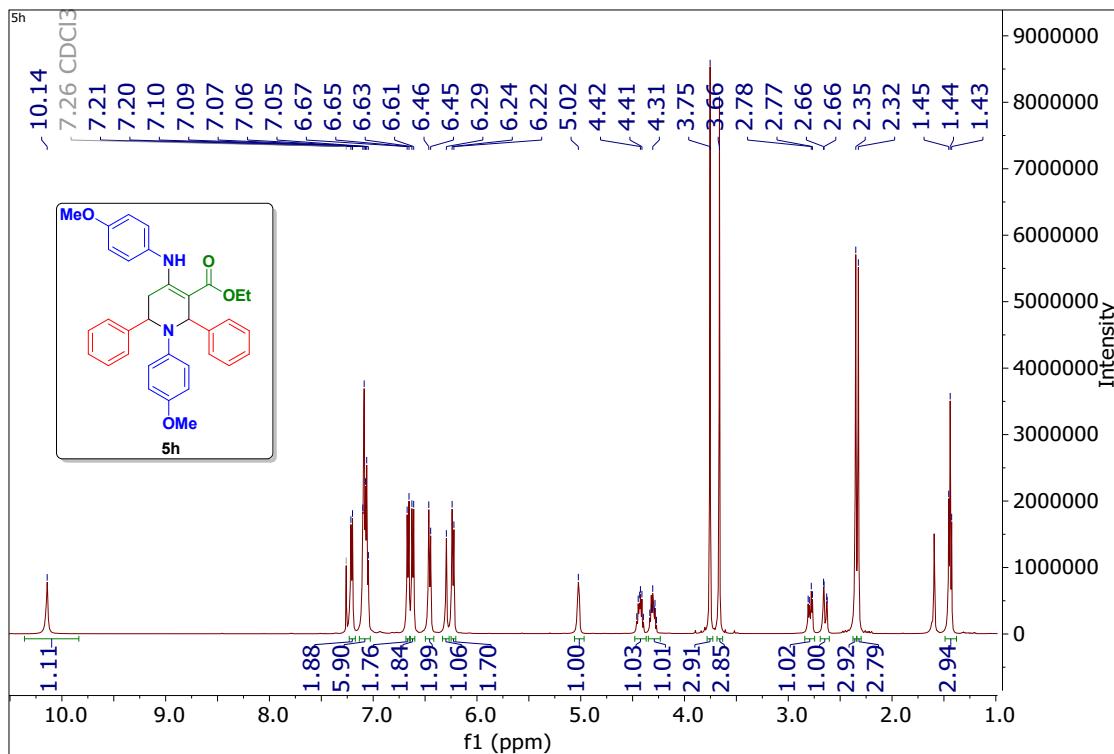
¹H NMR spectrum of 5g



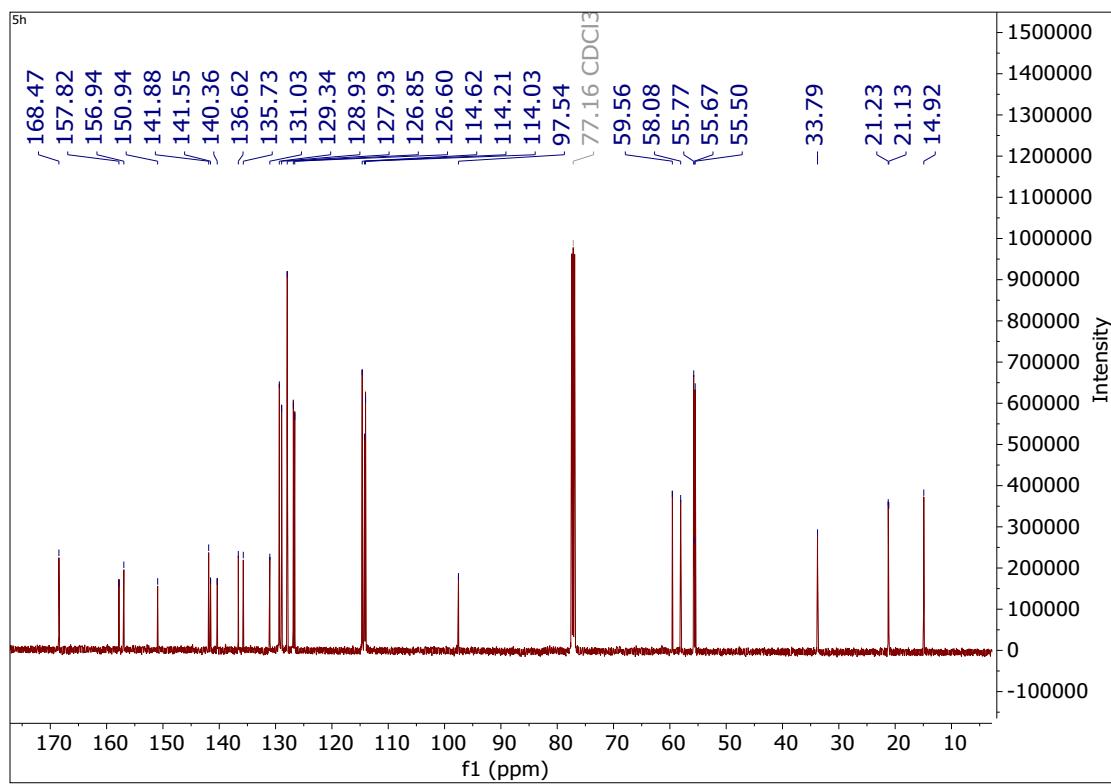
¹³C NMR spectrum of 5g



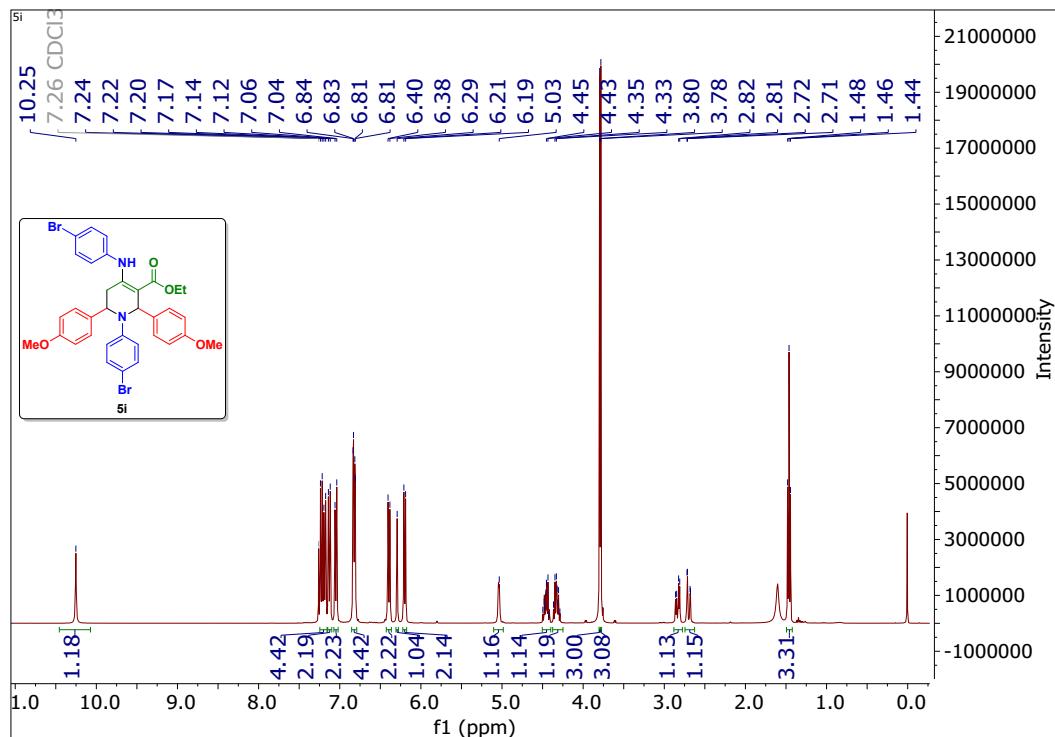
¹H NMR spectrum of 5h



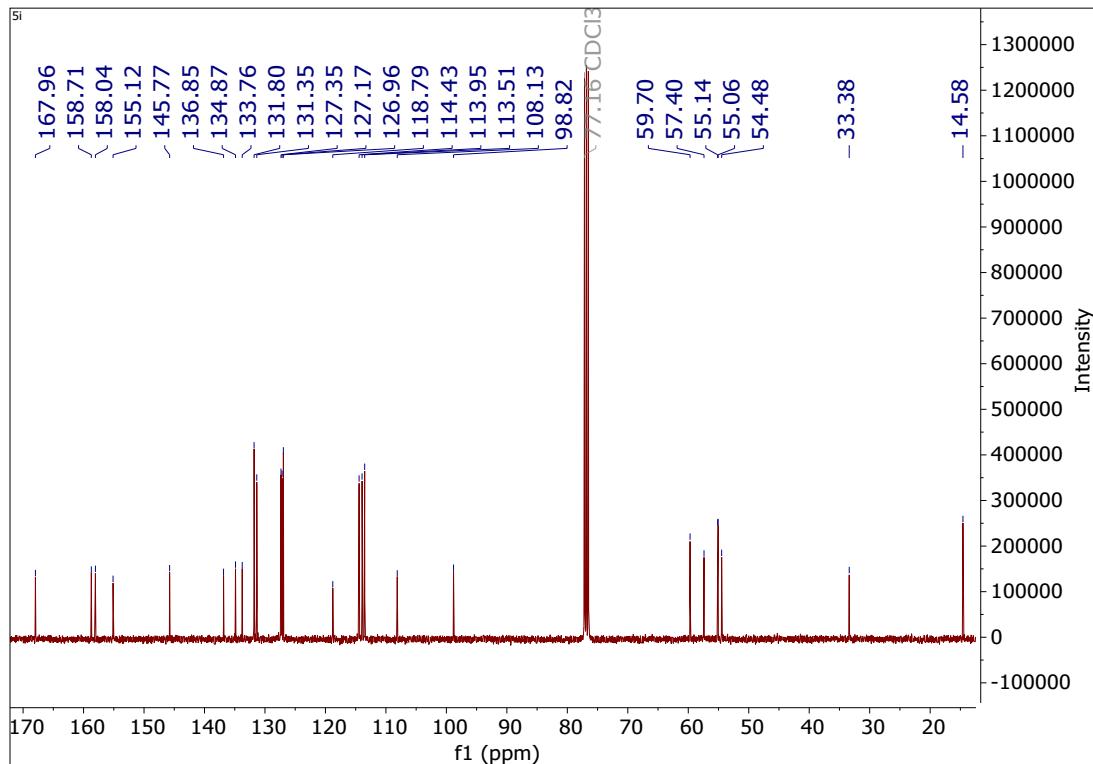
¹³C NMR spectrum of 5h



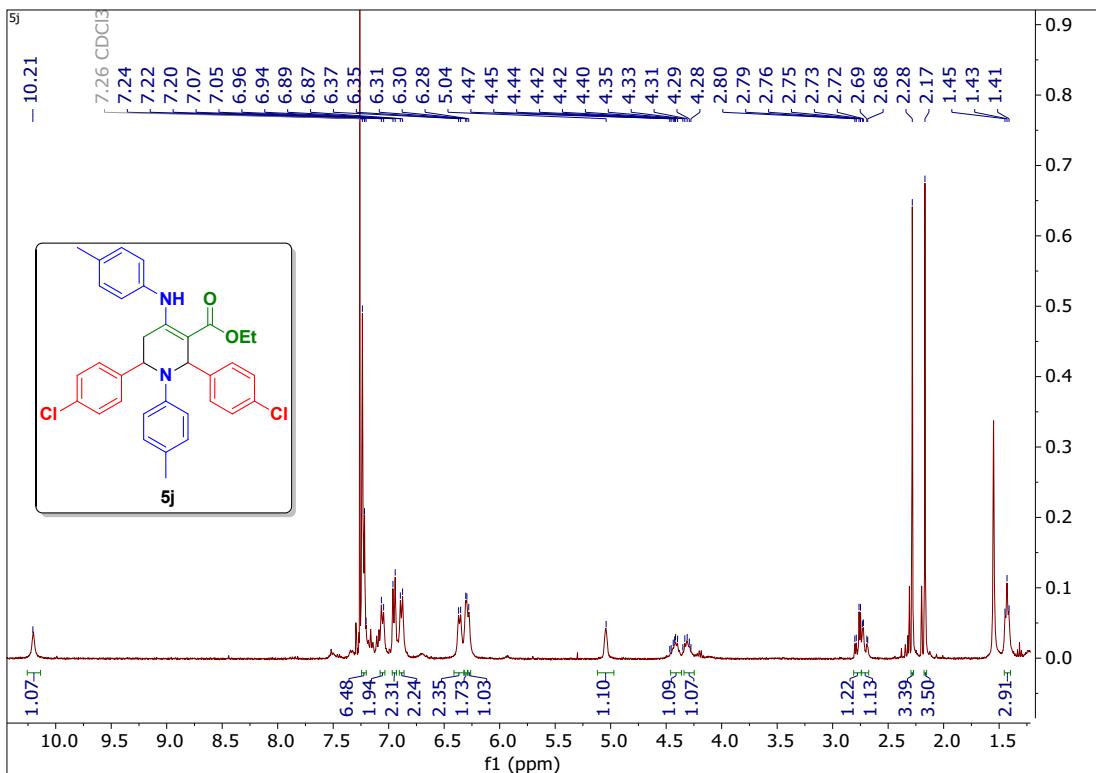
¹H NMR spectrum of 5i



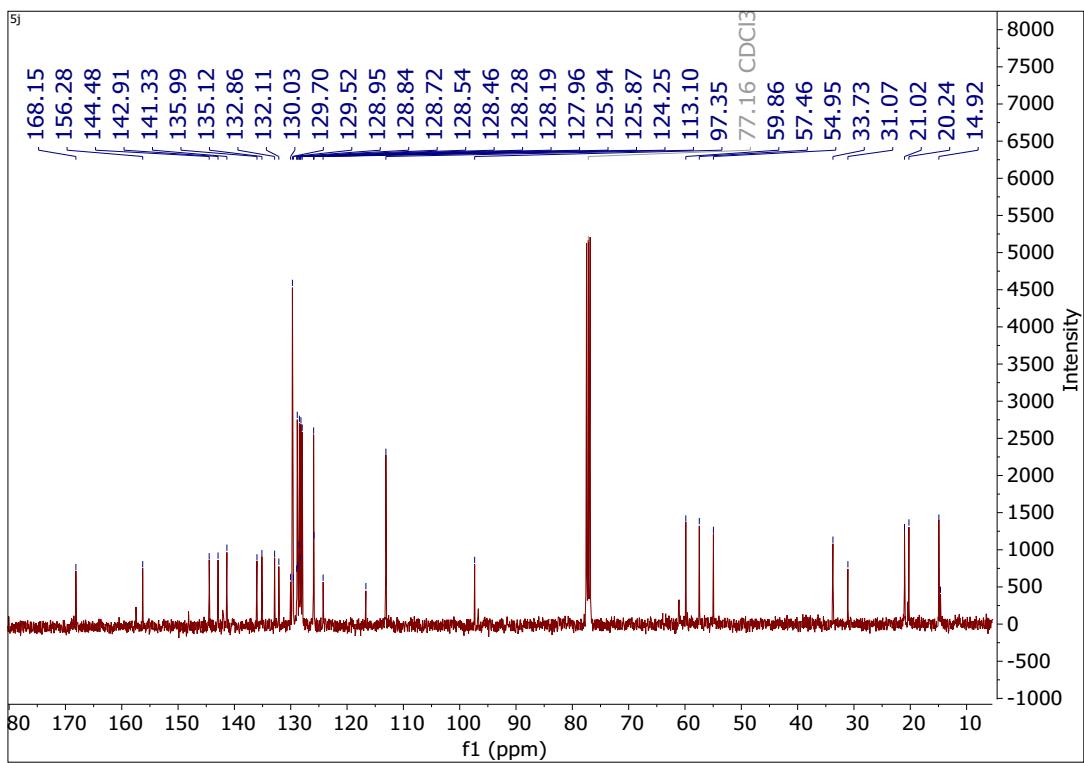
¹³C NMR spectrum of 5i



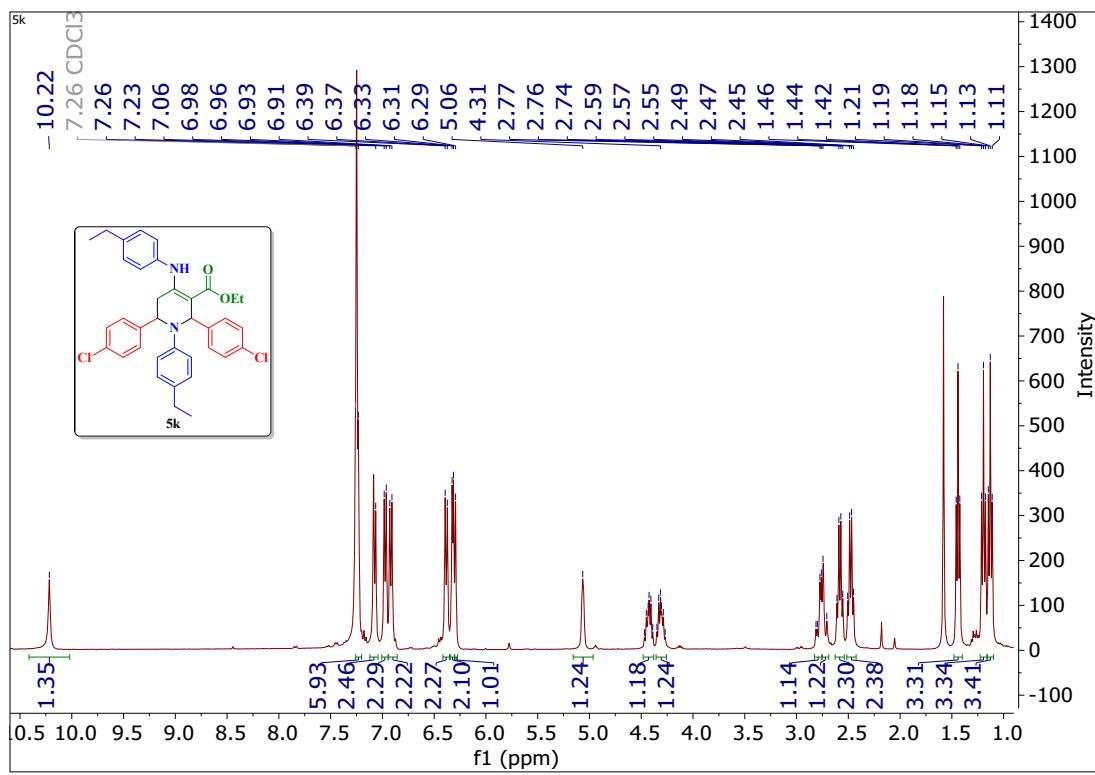
¹H NMR spectrum of 5j



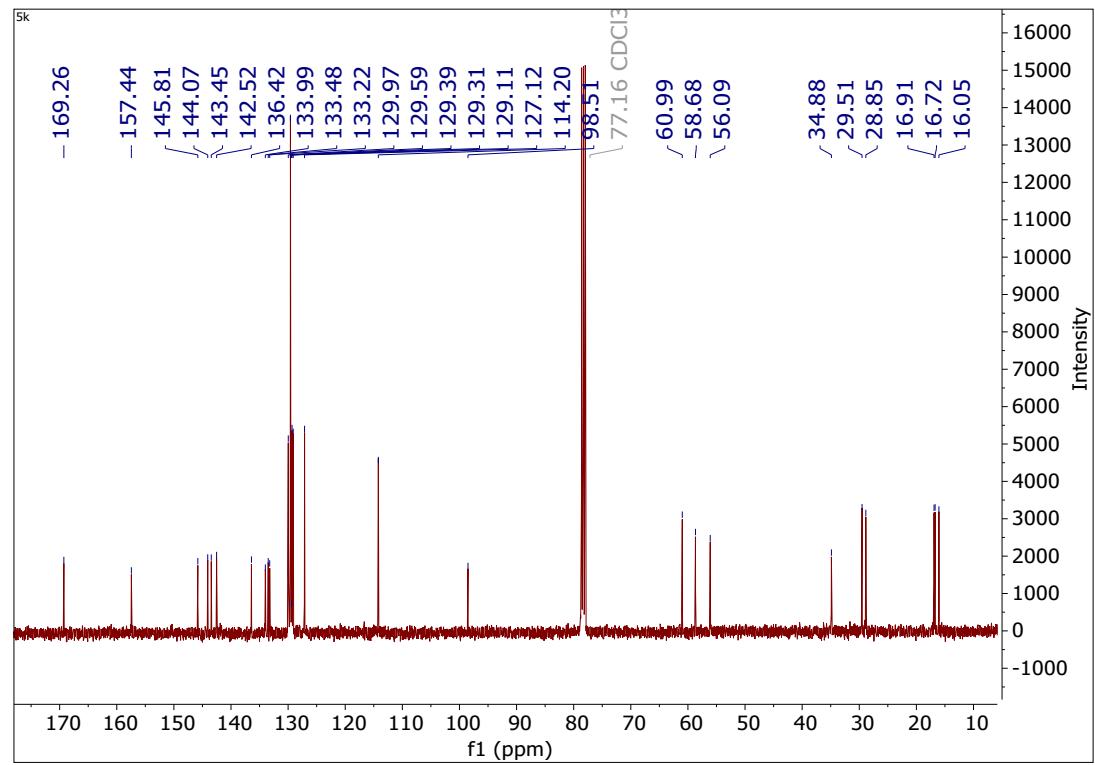
¹³C NMR spectrum of 5j



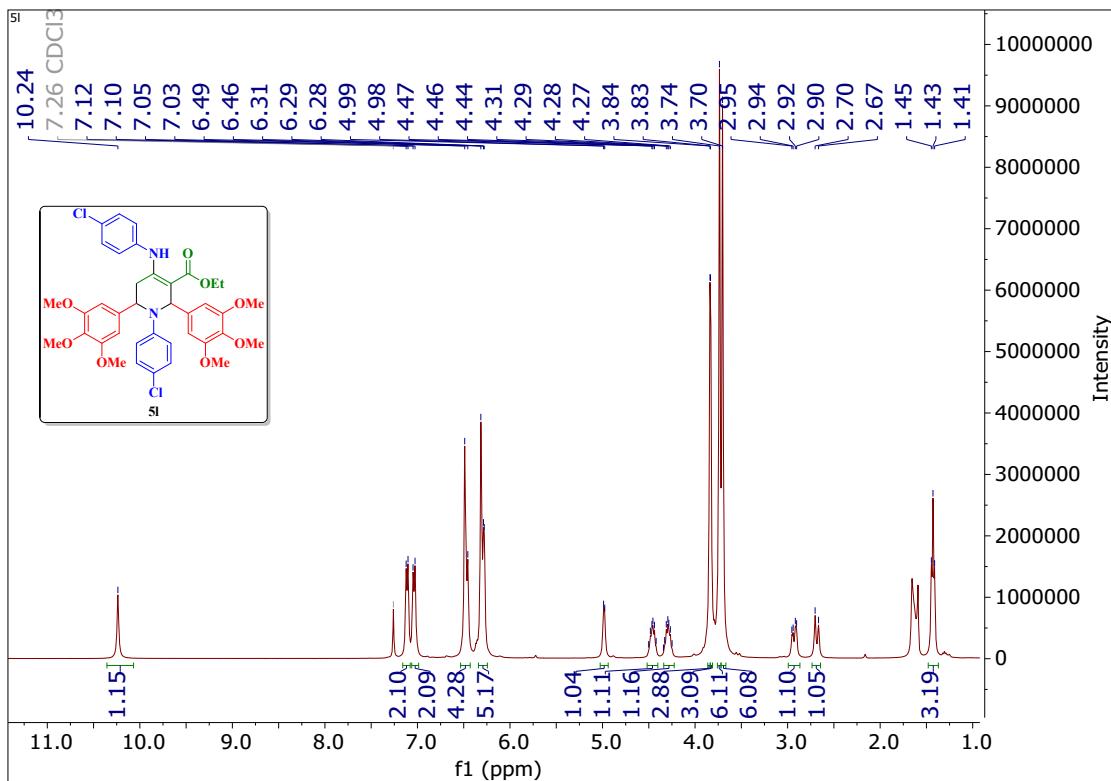
¹H NMR spectrum of 5k



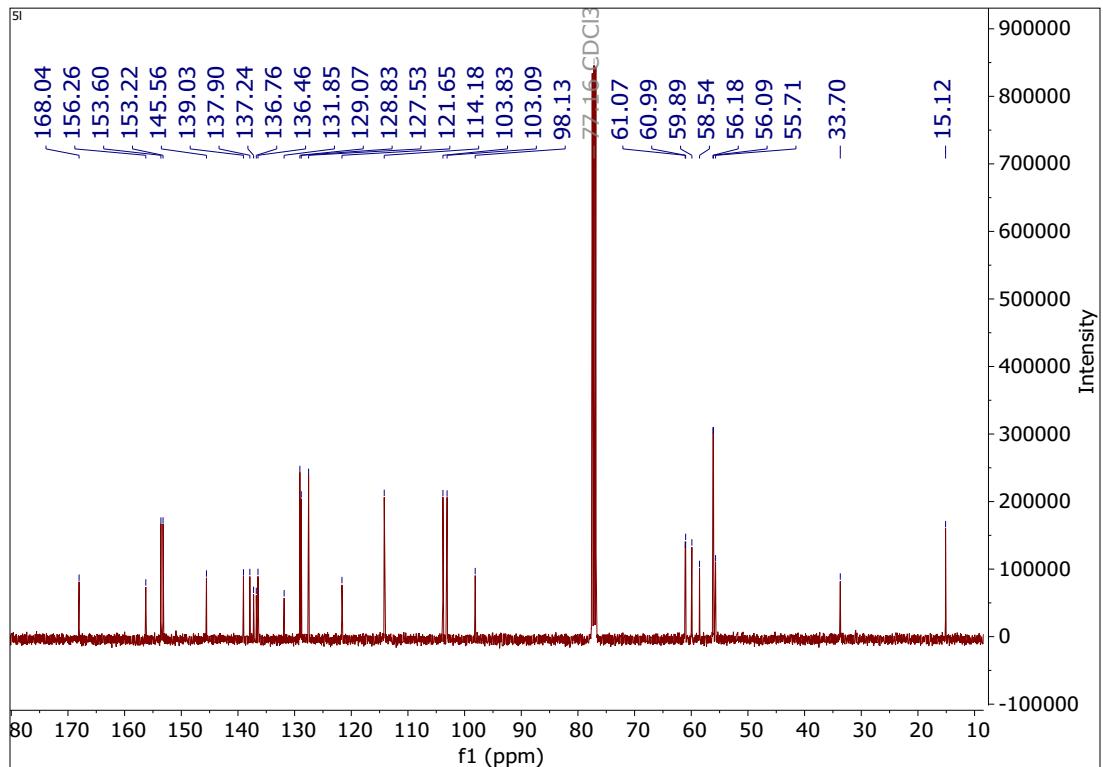
¹³C NMR spectrum of 5k



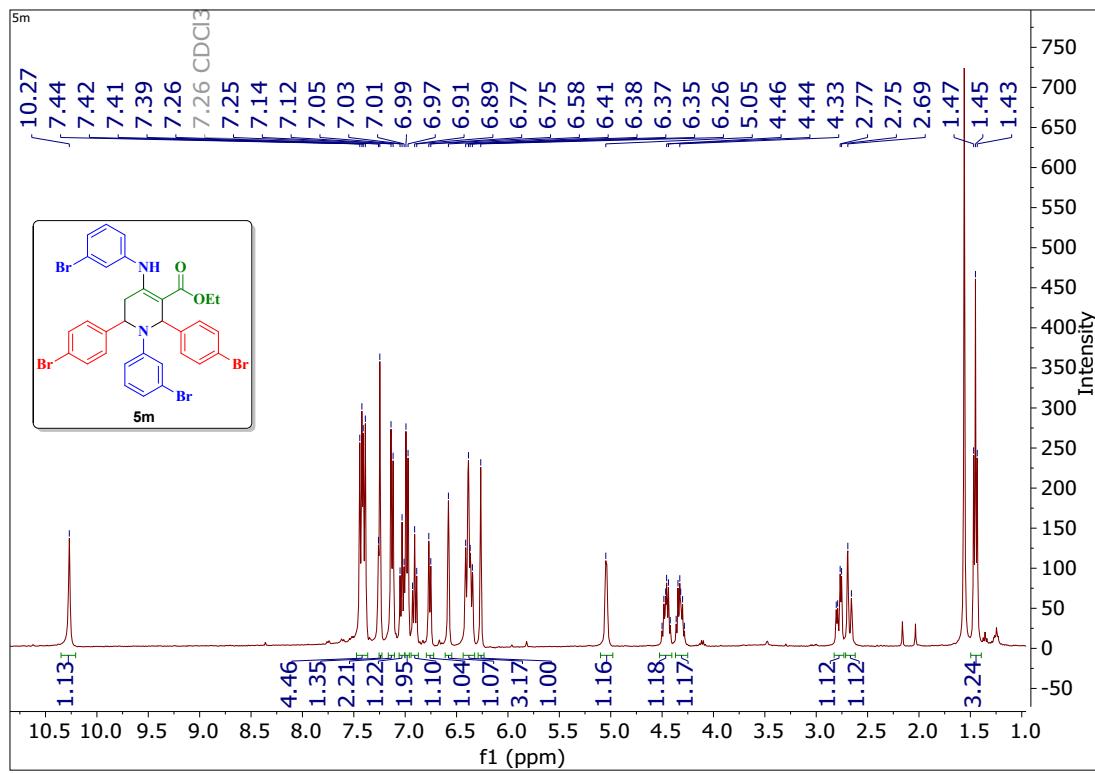
¹H NMR spectrum of 5l



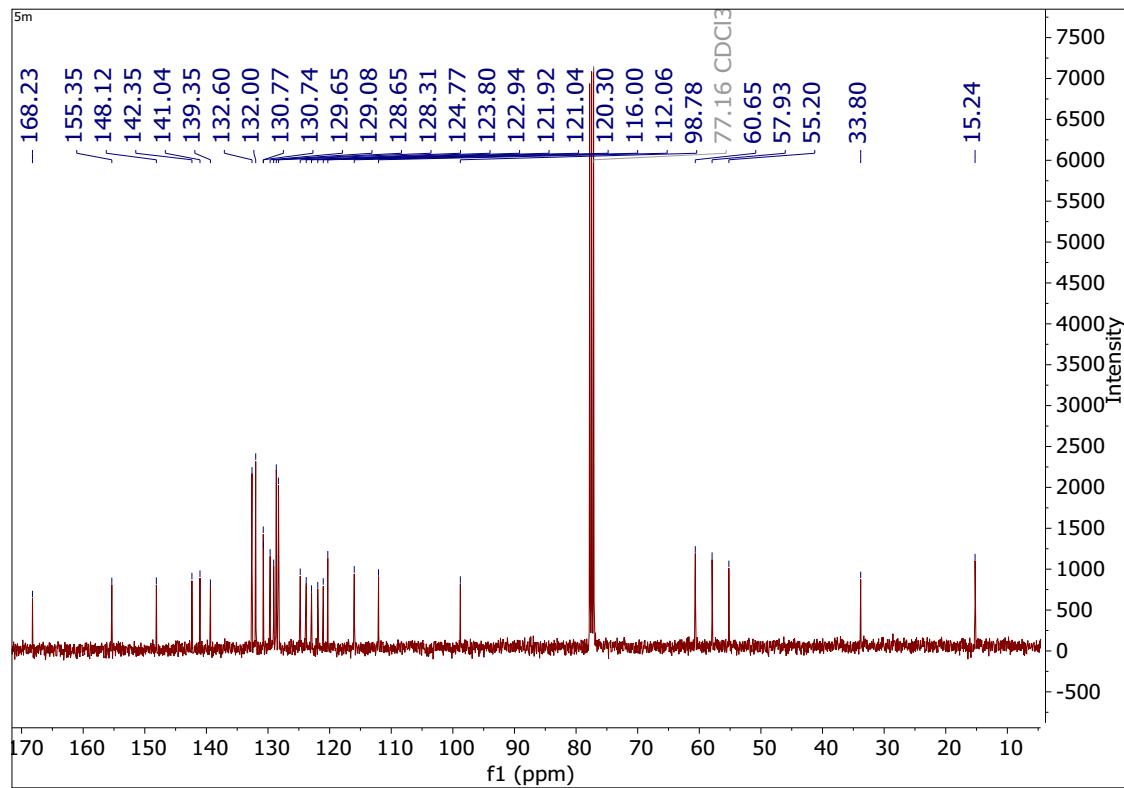
¹³C NMR spectrum of 5l



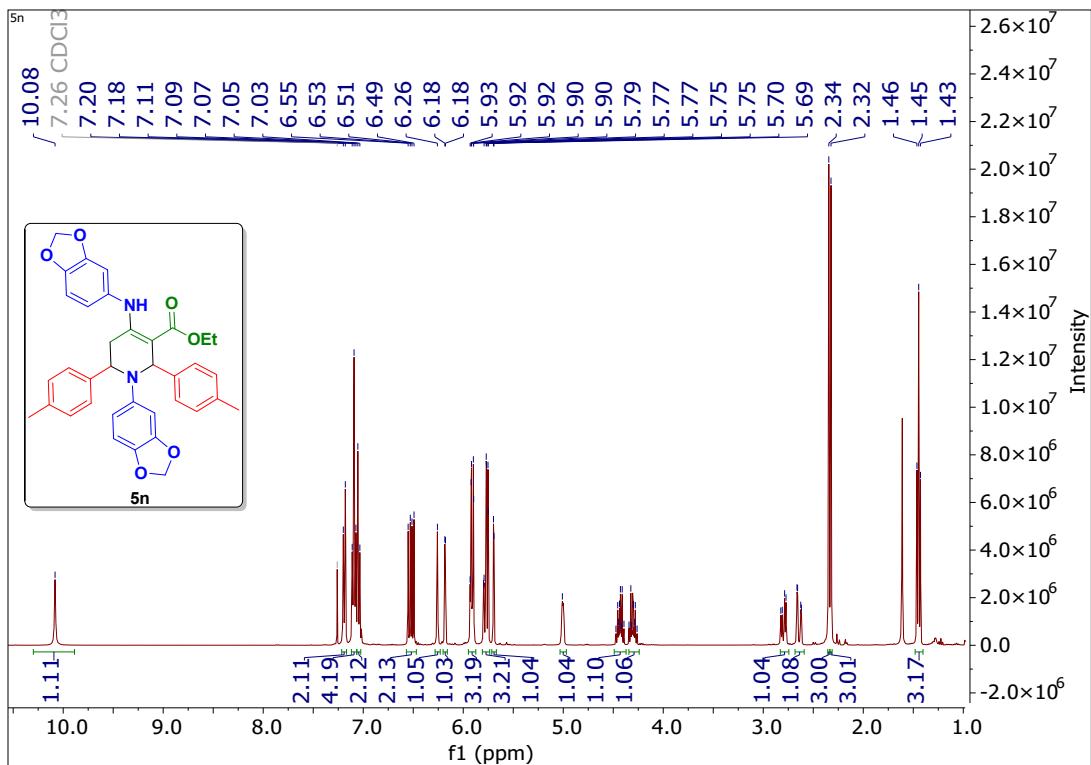
¹H NMR spectrum of 5m



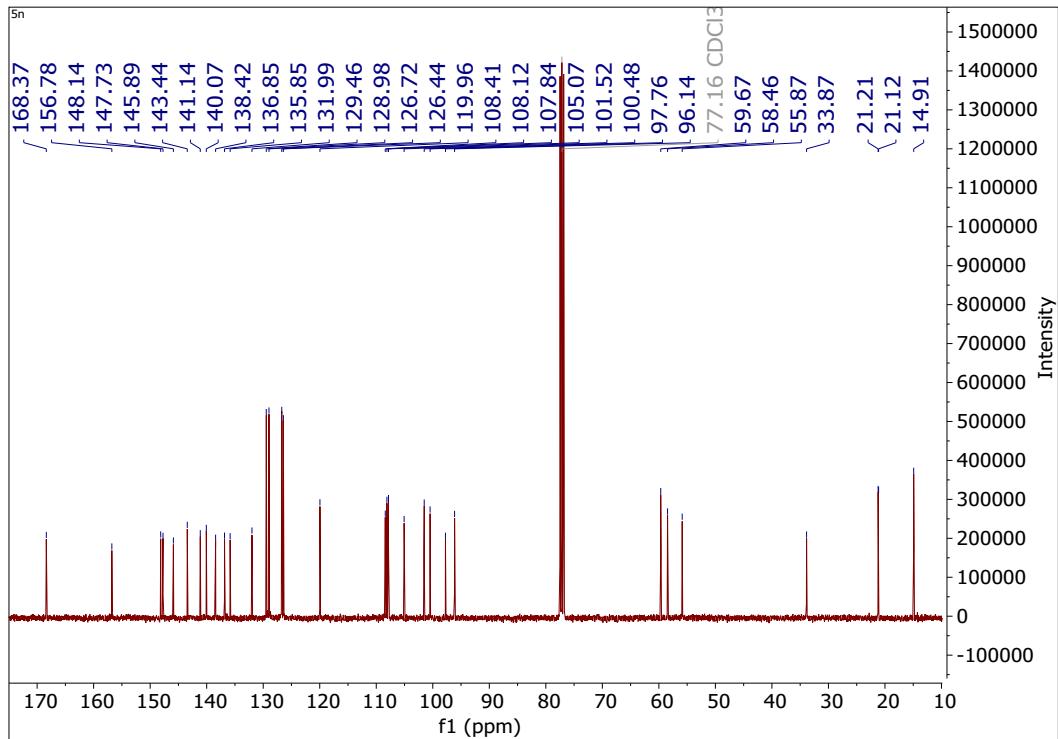
¹³C NMR spectrum of 5m



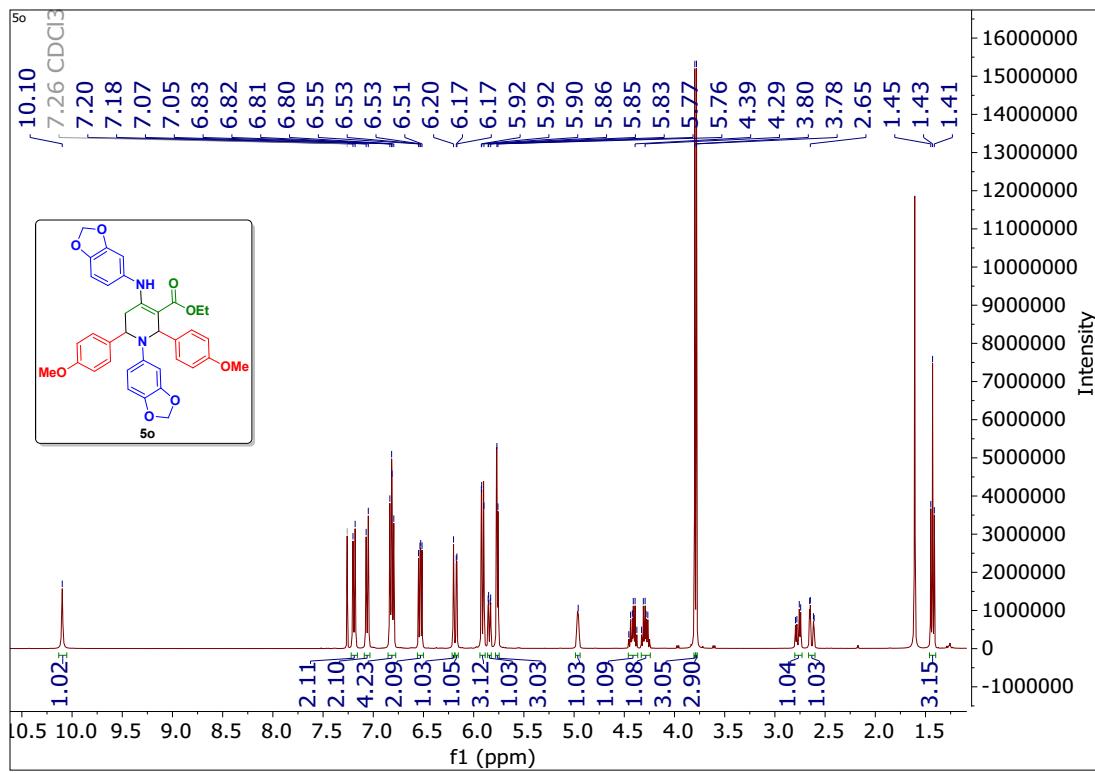
¹H NMR spectrum of 5n



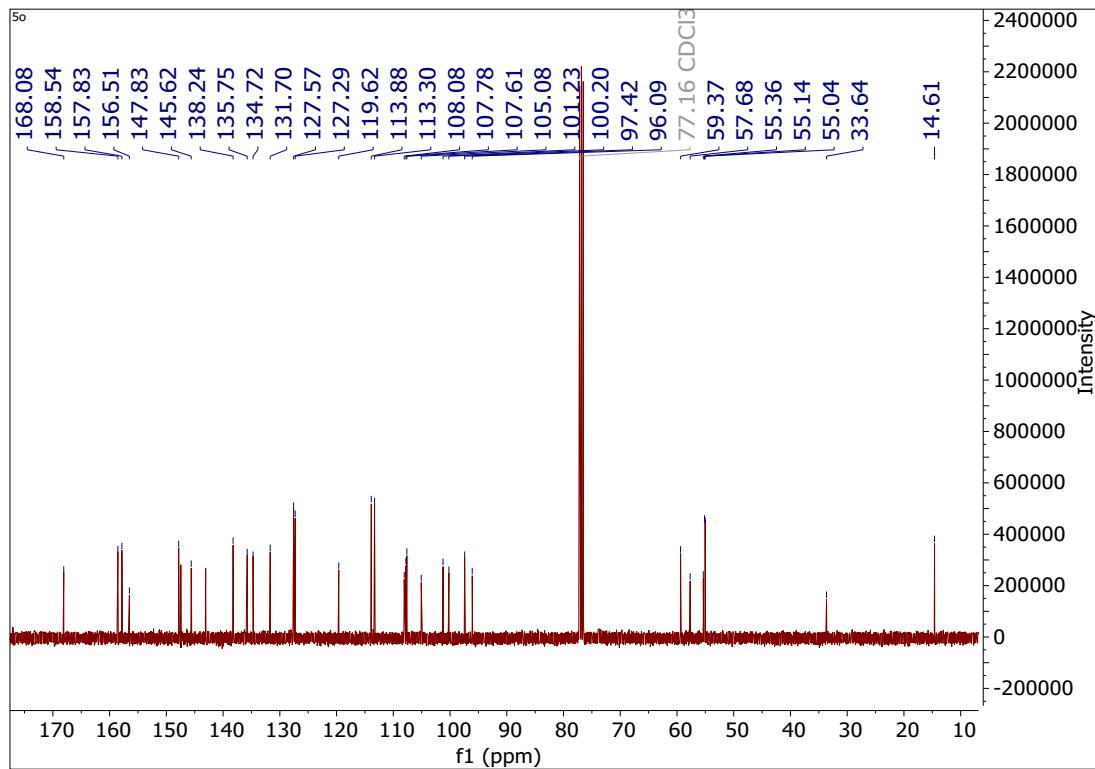
¹³C NMR spectrum of 5n



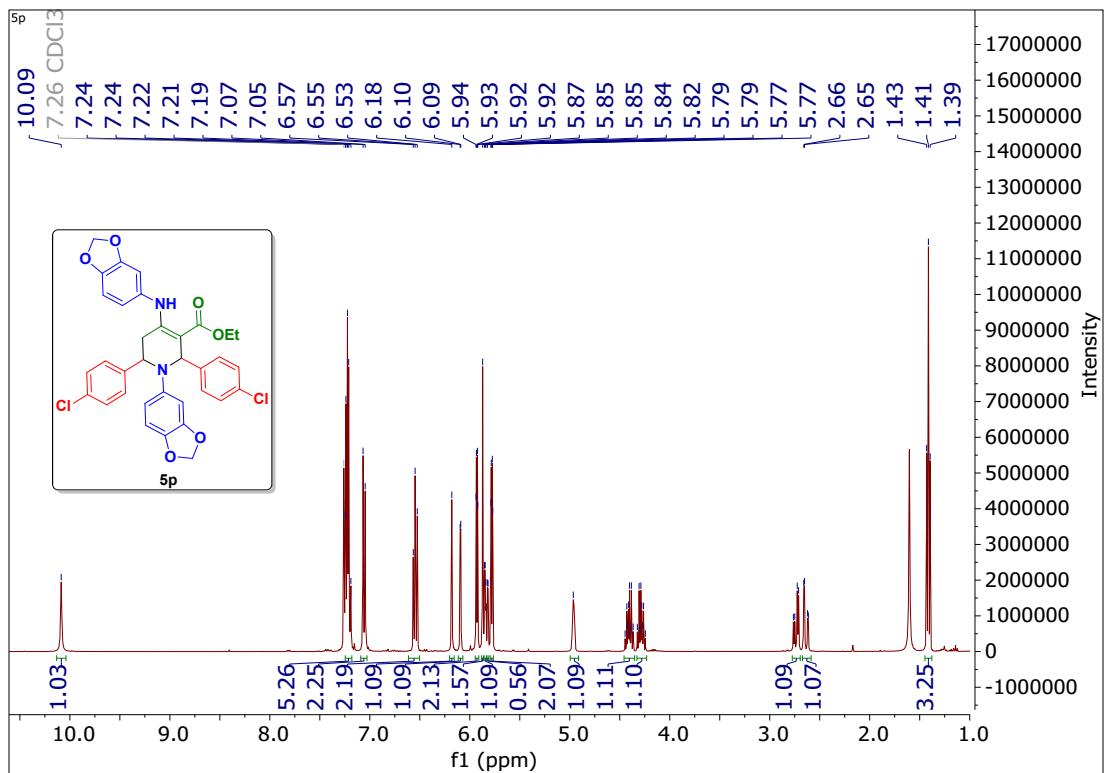
¹H NMR spectrum of 5o



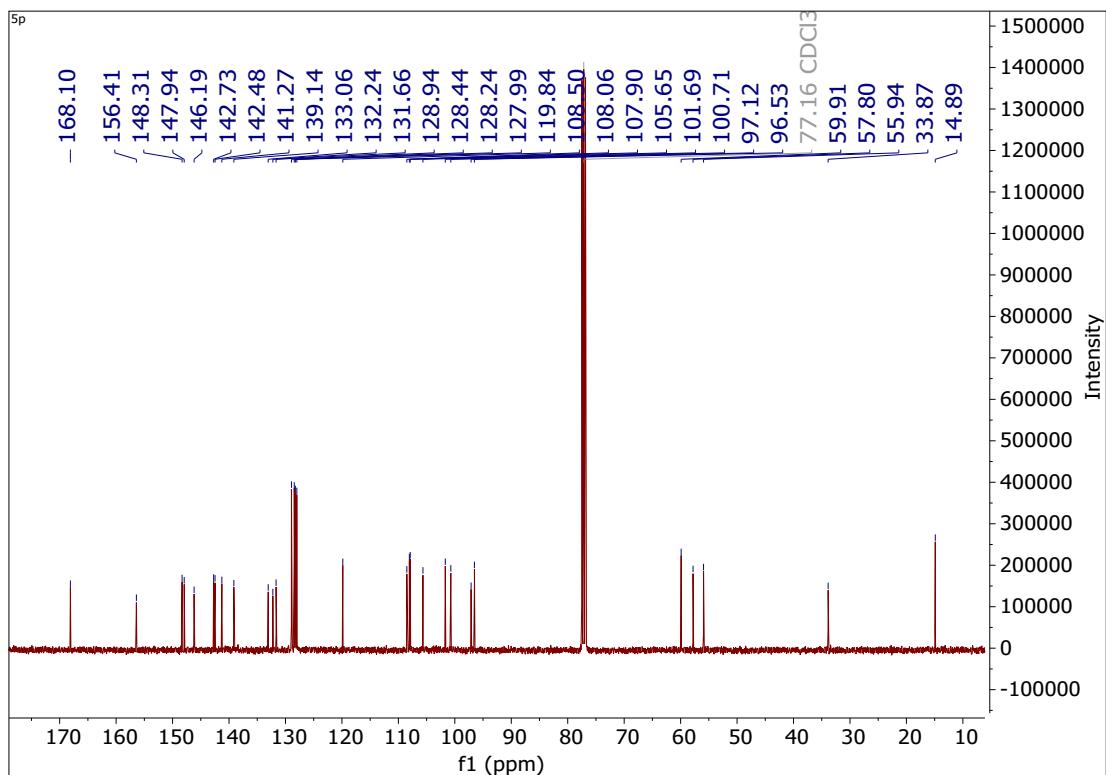
¹³C NMR spectrum of 5o



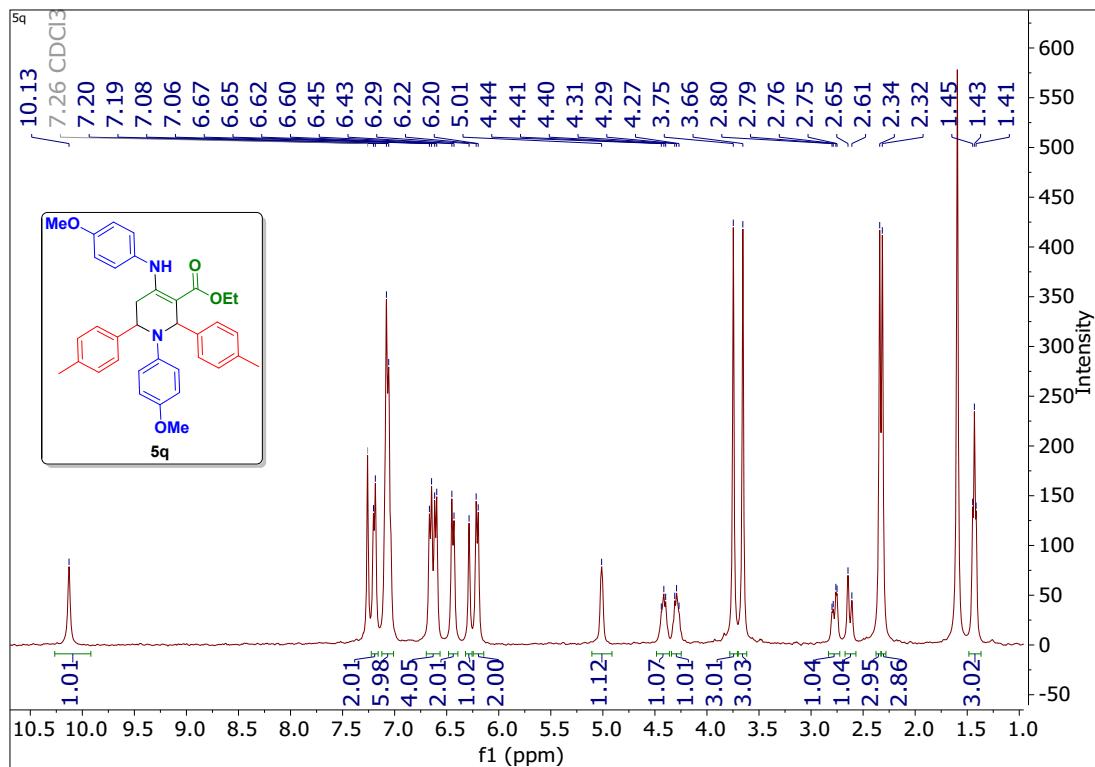
¹H NMR spectrum of 5p



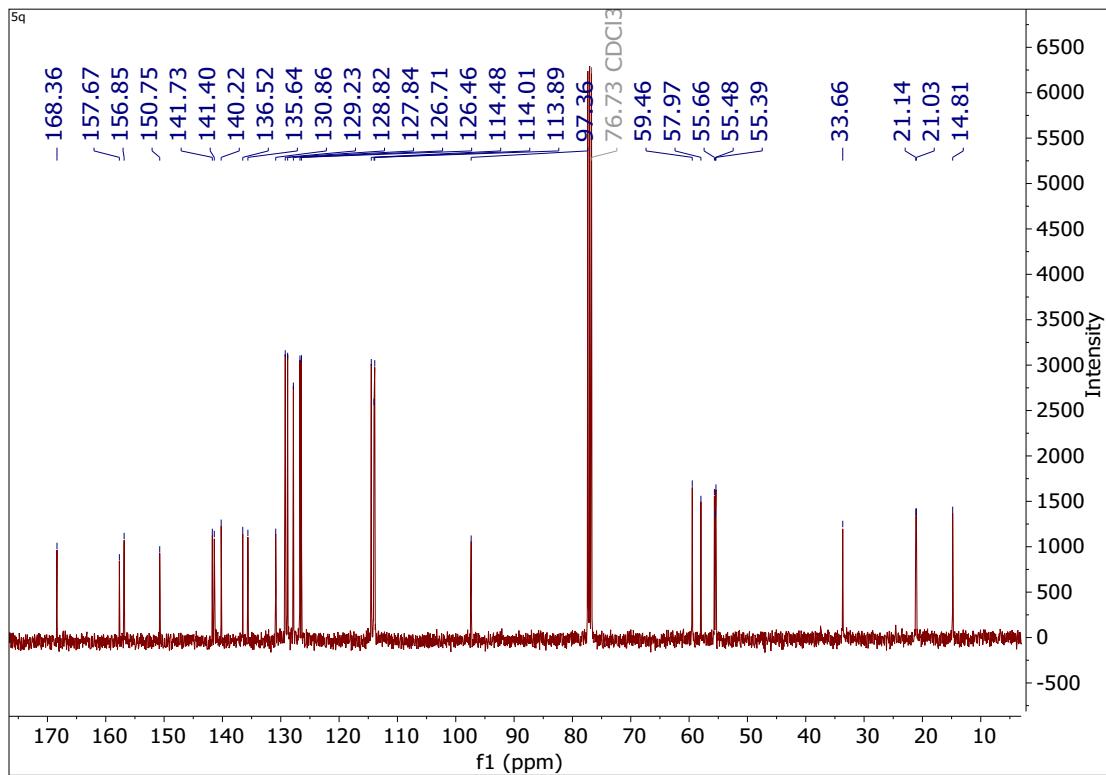
¹³C NMR spectrum of 5p



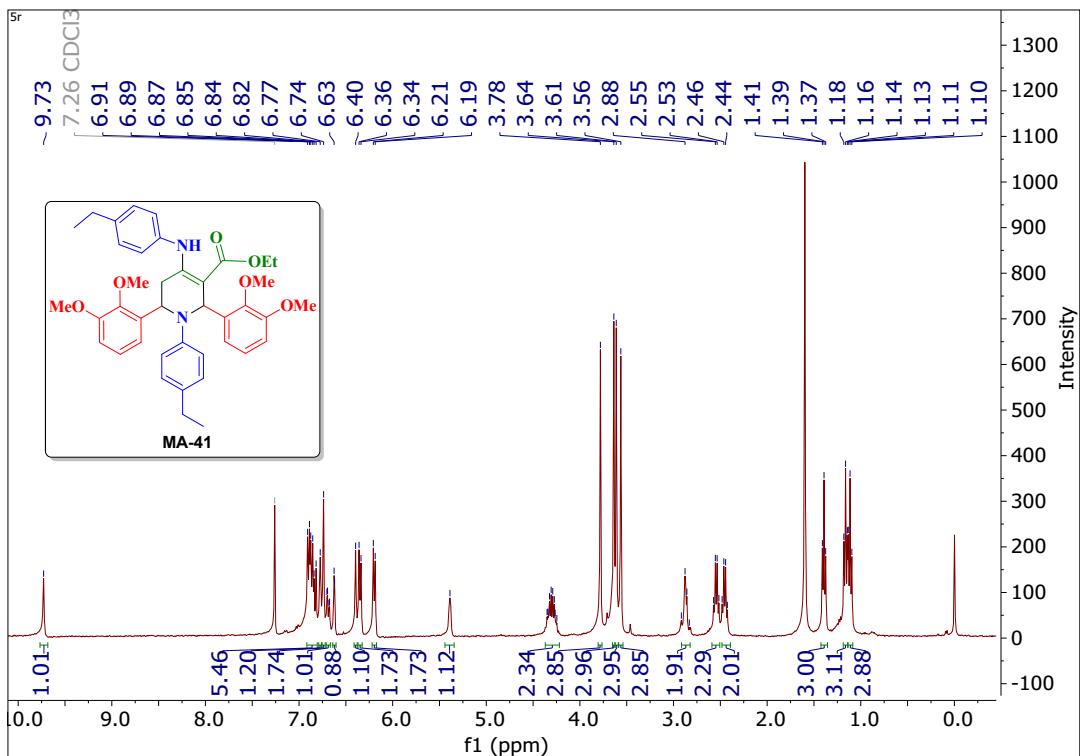
¹H NMR spectrum of 5q



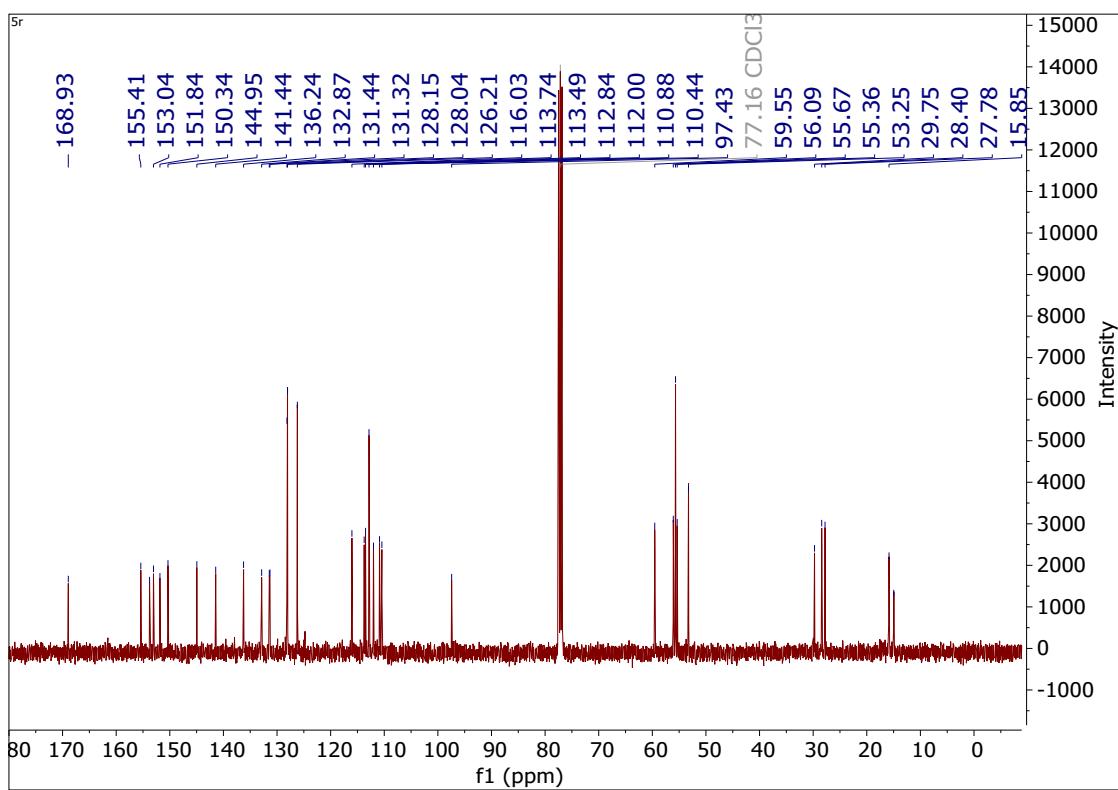
¹³C NMR spectrum of 5q



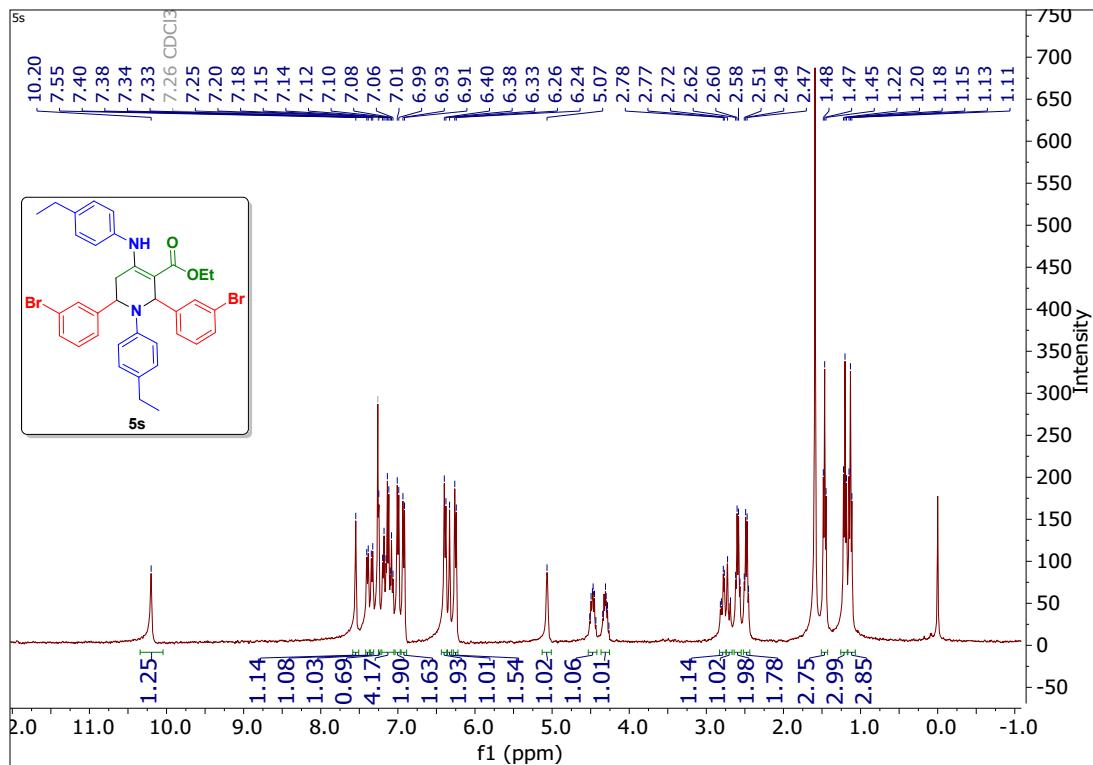
¹H NMR spectrum of 5r



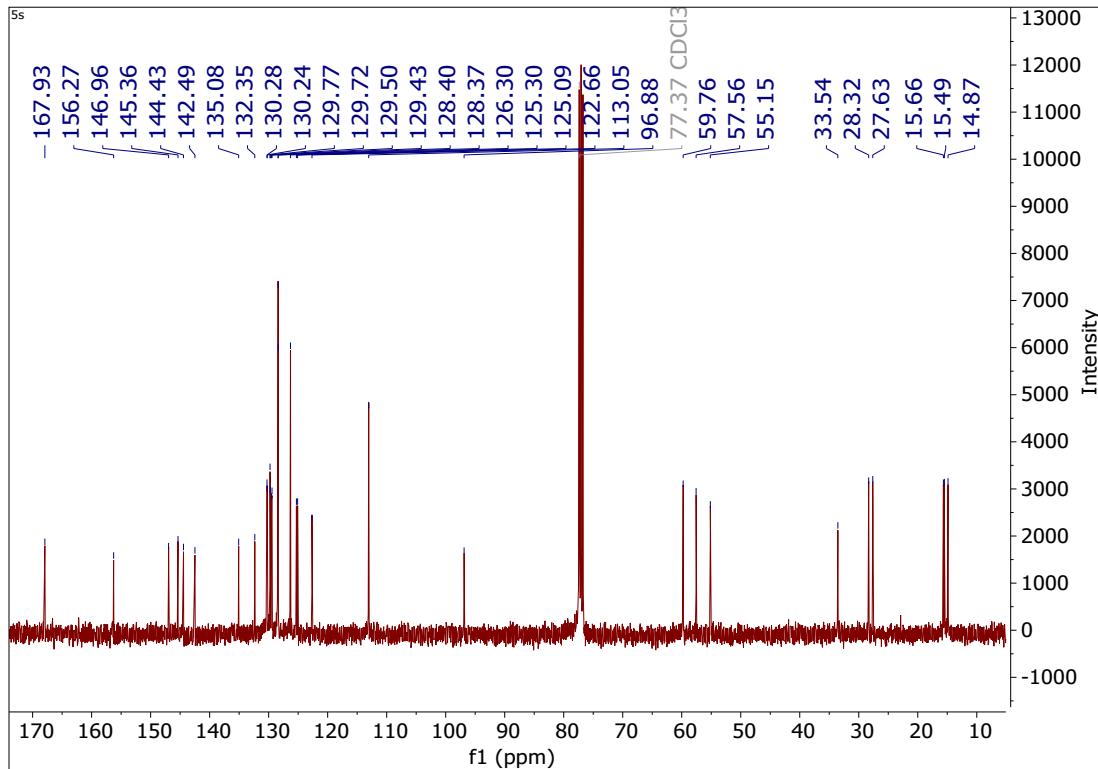
¹³C NMR spectrum of 5r



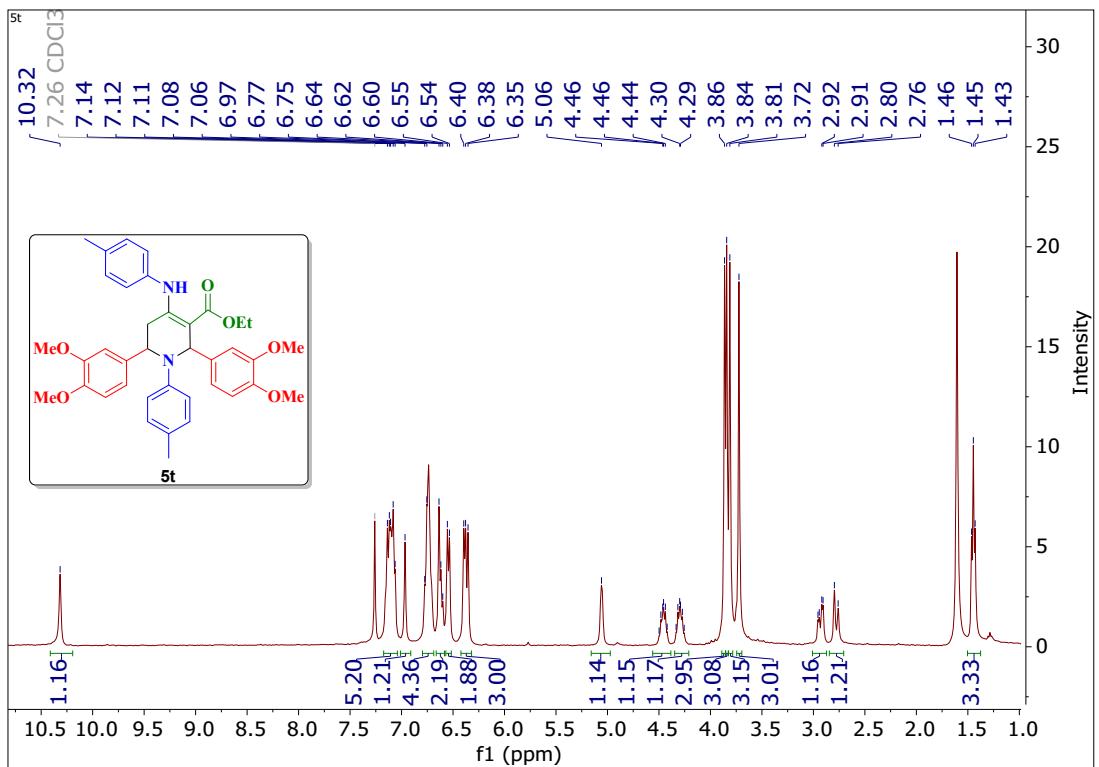
¹H NMR spectrum of 5r



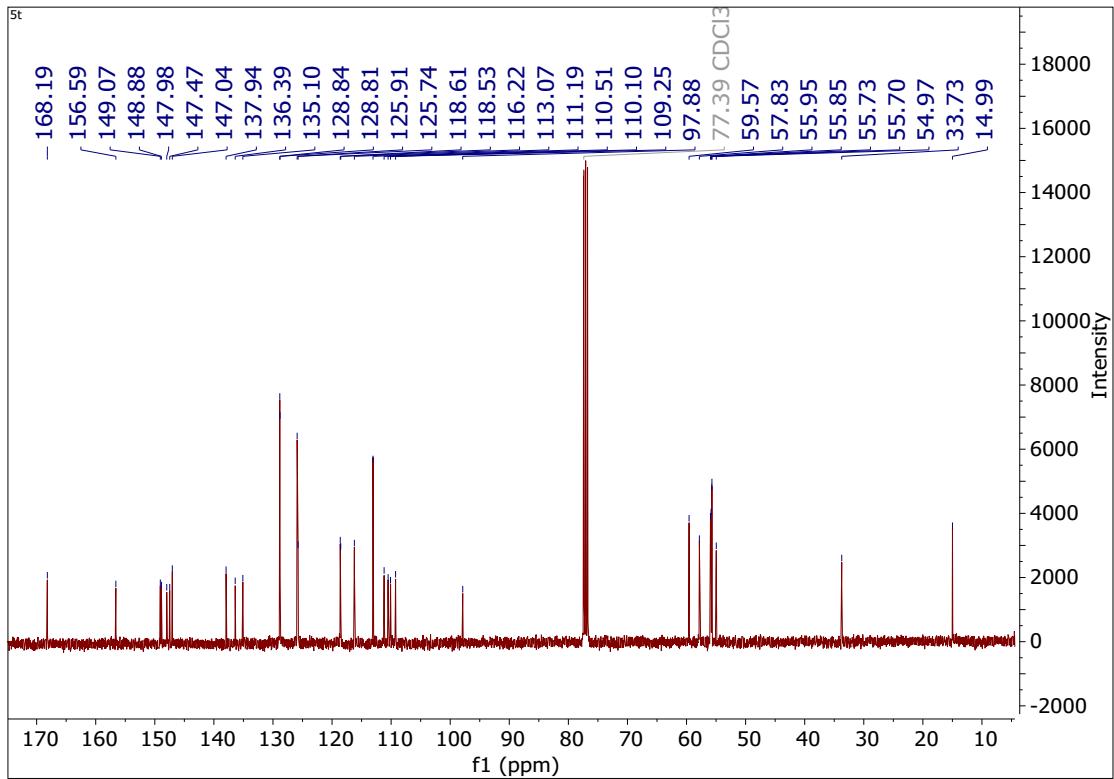
¹³C NMR spectrum of 5r



¹H NMR spectrum of 5t



¹³C NMR spectrum of 5t



IX. Evaluation of Anti-tubercular activities

In-vitro *MTB* MABA assay

Briefly, the inoculum was prepared from fresh LJ medium re-suspended in 7H9-S medium (7H9 broth, 0.1% casitone, 0.5% glycerol, supplemented oleic acid, albumin, dextrose, and catalase [OADC]), adjusted to a OD₅₉₀ 1.0, and diluted 1:20; 100 µl was used as inoculum. Each drug stock solution was thawed and diluted in 7H9-S at four-fold the final highest concentration tested. Serial two-fold dilutions of each drug were prepared directly in a sterile 96-well microtiter plate using 100 µl 7H9-S. A growth control containing no antibiotic and a sterile control were also prepared on each plate. Sterile water was added to all perimetre wells to avoid evaporation during the incubation. The plate was covered, sealed in plastic bags and incubated at 37°C in normal atmosphere. After 7 days incubation, 30 µl of alamar blue solution was added to each well, and the plate was re-incubated overnight. A change in colour from blue (oxidised state) to pink (reduced) indicated the growth of bacteria, and the MIC was defined as the lowest concentration of drug that prevented this change in colour [S4, S5]

References from supplementary information

- S1. Y. Li, N. Xu, J. Zhou, W. Zhu, L. Li, M. Dong, H. Yu, L. Wang, W. Liu and Z. Xie, *Biomater. Sci.*, 2018, **6**, 2918-2924.
- S2. S. Qiana, L. Song, L. Sun, X. Zhang, Z. Xin, J. Yin and S. Luan, *J. of Photochem. Photobiol. A: Chem.*, 2020, **400**, 112626-112652
- S3. P. Makula, M. Pacia and W. Macyk, *J. Phys. Chem. Lett.*, 2018, **9**, 6814-6817.
- S4. L. A. Collins and S. G. Franzblau, *Antimicrob. Agents Chemother.* 1997, **41**, 1004-1009.
- S5. V. S. Krishna, S. Zheng, E. M. Rekha, L.W. Guddat, and D. Sriram, *J. Comput. Mol. Des.*, 2019, **33**, 357-366.