Supporting Information

for

WEPA: A Bio-derived Media for Added Base, π-Acid and Ligand Free Ullmann Coupling of Aryl Halides Using $Pd(OAc)_2$

Jangam Lakshmidevi,[a] Rama Moorthy Appa,[a] Bandameeda Ramesh Naidu,[a] S. Siva Prasad,[a] Loka Subramanyam Sarma[b] and Katta Venkateswarlu*[a]

[a] Laboratory for Synthetic and Natural Products Chemistry, Department of Chemistry, Yogi Vemana University, Kadapa – 516 005, India.

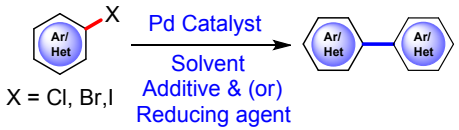
[b] Nanoelectrochemistry Laboratory, Department of Chemistry, Yogi Vemana University, Kadapa – 516 005, India.

E-mail: kvenkat@yogivemanauniversity.ac.in

Table of contents **Pages**

1. Comparative analysis of Pd catalyzed Ullmann couplings of aryl halides

Table 1. Comparative study of reported methods for Pd catalyzed homocoupling (Ullmann) reaction of aryl halides.



Sl. No.	Catalyst	Base	Solvent	Additive & (or) Reducing agent	Temperature	Time	Range of yields	Reference	Remarks
1	Pd-C	NaOH + AcONa	H_2O	Surfactant	95 °C	24h	30–65%	1	External base and surfactant were required. Low to moderate yields of products.
2	$Pd(OAc)_2$	Cs_2CO_3	DMA	Hydroquinone & ligand: $P(o\text{-}tol)_3$ or $As(o\text{-}tol)_3$	100 °C	2–48h	37–99%	2	External base, organic solvent, ligand and reducing agent were compulsory.
3	Pd-C	-	Acetone + water	Zn	Rt	0.5h	70–94%	3	10 mol% Pd and 300 mol% Zn were required.
4	$Pd(OAc)_2$	K_2CO_3 or Et_3N	DMF + water	$^nBu_4NBr$ & Isopropanol	115 °C	7–50h	42–95%	4	External base, organic solvent and TBAB are required.
5	Pd-C	-	Water	Zn + liquid CO_2	Rt	Overnight	42–92%	5	High pressure - liquid CO_2, Zn (200 mol%) was necessary.
6	Pd-C	-	Water	Zn + liquid CO_2	Rt	8–96h	78%–quantitative	6	High pressure - liquid CO_2, Zn are required.
7	$PdCl_2(PhCN)_2$	TDAE	DMF	Tetrakis(dimethylamino)ethylene (TDAE)	50 °C	2–42h	trace–98%	7	Organic solvent and external base cum reducing agent (TDAE) were required. Trace amount of yields of product was reported with aryl chlorides.
8	Sulfur-palladacycles	K_3PO_4	DMF	-	100 °C	87–143h	12–96%	8	External base, *S*-palladacycles, large reaction time and organic solvent were necessary.
9	$Pd(dba)_2$	-	DMF	TBAF	90 °C	12h	0–94%	9	300 mol% of TBAF and organic solvents were required. Only aryl iodides and aryl bromides were studied.
10	$Pd(OAc)_2$	K_2CO_3	PEG 4000	-	120 °C	4–28h	82–97%	10	Use of base and PEG 4000 was critical. Only aryl iodides and aryl bromides were studied.
11	$PdCl_2$	K_2CO_3	EtOH + water	EDTA + ascorbic acid	Reflux	4–11h	15–84%	11	External base, EDTA and ascorbic acid (100 mol%) were required.
12	$Pd_2(dba)_3$	^tBuONa	Diglyme	Phosphite ligand	130 °C	12h	10–80%	12	Phosphite based ligand, external base and organic solvent are compulsory.
13	$PdCl_2$	Et_3N or ^iPrONa	Ionic liquid	IL-$OPPh_2$ ligand	80 °C	0.25–20h	58–95%	13	Requirement of external base, IL and ligand are detrimental.

Sl. No.	Catalyst	Base	Solvent	Additive & (or) Reducing agent	Temperature	Time	Range of yields	Reference	Remarks
14	$Pd(OAc)_2$	K_2CO_3	2-Butanone	-	120 °C	5h	65–91%	14	External base, inert (N_2) atmosphere and organic solvent are obligatory.
15	$Pd_{colloids}$	$^nBu_4NAc$	$^nBu_4NAc$ (TBAA)	Aldehyde	90 °C	2–7h	81–92%	15	Added base and reducing agent were compulsory. Aryl chlorides show no reactivity.
16	$Pd(OAc)_2$	Et_3N	DMF	Biphenyl phosphine ligand	100 °C	5h	<5%–quantitative	16	Inert atmosphere, organic base & solvent and phosphine ligand were necessary. Limited examples with only aryl bromides.
17	$Pd(OAc)_2$	Cs_2CO_3	DMF or MeCN	Benzoin, PPh_3 & TBAc	120 °C	1–2h	56–96%	17	External base, organic solvent, ligand and TBAc were essential.
18	$PdCl_2$	$^nPr_3N$	IL	-	100 °C	0.5–15h	45–96%	18	Organic base and ionic liquid were necessary.
19	Pd-C	NaOH	Water	-	Microwave irradiation-150 °C	1h	20–95%	19	Base and microwave irradiation are obligatory. Hydrodehalogenation was always associates. Studies were limited only for aryl iodides.
20	Pd@poly-CN-PF_6	NaOH	Water	Ascorbic acid	100 °C	9–24h	8–95%	20	External base and reducing agent (ascorbic acid) were necessary.
21	$Pd(OAc)_2$	-	Water	Mg & paraformaldehyde	70 °C	12h	21–87%	21	Reducing agent - Mg and paraformaldehyde were detrimental. Only aryl iodides were tested.
22	$Pd(OAc)_2$	Cs_2CO_3	1,4-Butanediol	1,4-Butanediol	75 °C	1.5–24h	39–94%	22	External base and organic solvent cum reducing agent were necessarily required.
23	Hydrotalcite supported Pd-Au nanocatalyst	KOH	Isopropanol	-	40 °C	2–22h	80–97%	23	Use of base and organic solvent was necessary.
24	Au-Pd nanochain network	K_2CO_3	Water + EtOH	-	80 °C	4h	77–98%	24	External base and Au-Pd NNCs were necessary.
25	Fe_3O_4-silica functionalized Pd nano catalyst	K_2CO_3	Water	-	Rt	1–2h	52–95%	25	Synthesis of magnetic nanoparticle supported palladium and the use of external base are critical.
26	Pd-PVP/MCM-48	K_2CO_3	DMF	-	100 °C	12h	55-90%	26	Base and organic solvents were used for the limited number (only seven) of substrates.
27	**$Pd(OAc)_2$**	**-**	**Water extract of pomegranate ash (WEPA) + EtOH**	**-**	**80 °C**	**2–12h**	**25–99%**	**Present method**	**Use of novel renewable base (derived from agro waste) and benign reaction media. Exploitation of aryl iodides, aryl bromides and aryl chlorides. Avoiding the addition of base, ligand, reducing agent and toxic (organic) solvent.**

2. General information:

The aryl halides of present conversion were used without further purification was procured from Alfa-Aesar, Sigma-Aldrich, and Spectrochem. All the reactions were performed in open-air and the reaction progress was monitored by silica gel based thin-layer chromatography (TLC) (Merch - 60 F254). The purification of Ullmann coupling products was performed by column chromatography using a silica gel (60-120 mesh) packed glass columns. Ethyl acetate and n-hexane were used as eluents for column chromatography were purchased from Merck. pH of WEPA was measured by using ELICO pH meter. Brucker Avance 500 MHz and Varian 400 MHz spectrometer were employed to record ^{1}H NMR and ^{13}C NMR spectra at ambient temperature using $CDCl_3$ as solvent and tetramethylsilane (TMS) as reference standard. The chemical shift (δ) was given in parts per million (ppm) and coupling constant (*J*) in Hz. The signal patterns are: s = singlet; brs = broad singlet; d = doublet; dd = doublet of doublet; dt = doublet of triplet; dq = doublet of quartet; ddd = doublet of doublet of doublet, t = triplet; td = triplet of doublet; m = multiplet.

3. Experimental procedures and product characterization data:

3.1. Procedure for the preparation of water extract of pomegranate ash (WEPA):

Shade dried pomegranate peel was cut into small pieces was burned to obtain ash. 10 gr of ash was suspended into 100 ml of distilled water was subjected for heating at 80 °C for 50 min with constant stirring. The suspension was then filtered to obtain a light pale yellow colored extract, WEPA. The following figure (Figure 1) illustrates the preparation of WEPA.

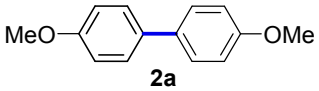
Figure 1. Representative steps in WEPA preparation.

3.2. General procedue for WEPA mediated Ullmann coupling of aryl halides:

Aryl halide (**1**) (1 mmol), WEPA (1 mL) and ethanol (0.5 mL) were taken into a round bottomed flask was added 3 mol% of $Pd(OAc)_2$ and the resultant suspension was heated in a preheated oil bath at 80 °C. Progress of the reaction was monitored by using thin layer chromatography (TLC) by dissolving a little amount of the reaction mixture in ethyl acetate in a separate vial. After the completion, as indicated by TLC, the reaction mixture was cooled to room temperature, evaporated ethanol and added distilled water (5 mL). The resultant aqueous portion was extracted with ethyl acetate (3 x 5 ml), combined ethyl acetate layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated to obtain crude residue. The residue was subjected for column chromatography using silica gel packed glass column to obtain pure biaryls (**2**). The structures of the products were settled from their ^1H NMR and ^{13}C NMR data and was found in good aggregate with the reported data.

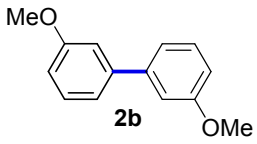
The homocoupling reaction of 7.02 gr of 4-iodoanisole (**1a**) (30 mmol), in WEPA (30 mL), 3 mol% of $Pd(OAc)_2$ and ethanol (15 mL) provided 3.05 gr 4,4'-dimethoxybiphenyl (**2a**) in 95% yield under the above conditions.

3.4. Product characterization data:



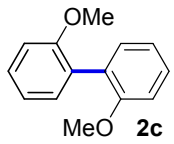
2a

3.3.1. 4,4'-Dimethoxybiphenyl (2a).[10] Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.7 Hz, 4H), 6.95 (d, *J* = 8.7 Hz, 4H), 3.84 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.7, 133.5, 127.7, 114.2, 55.3 ppm.



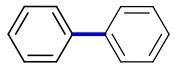
2b

3.3.2. 3,3'-Dimethoxybiphenyl (2b).[27] Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15−7.01 (m, 6H), 6.82 (d, *J* = 8.9 Hz, 2H), 3.77 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 142.6, 130.5, 123.8, 117.2, 113.1, 55.4 ppm.

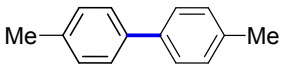


2c

3.3.2. 2,2'-Dimethylbiphenyl (2c).[9] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (td, *J* = 1.7, 7.5 Hz, 2H), 7.23 (td, *J* = 1.6, 7.5 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 131.4, 128.6, 127.8, 120.3, 111.0, 55.6 ppm.

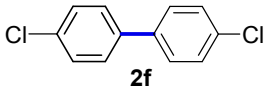

2d

3.3.3. Biphenyl (2d).[10] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 4H), 7.47−7.39 (m, 4H), 7.38−7.30 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 128.6, 127.1, 127.0 ppm.



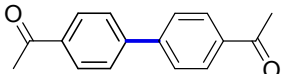
2e

3.3.4. 4,4'-Dimethylbiphenyl (2e).[10] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.8 Hz, 4H), 7.22 (d, *J* = 7.8 Hz, 4H), 2.38 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 136.7, 129.4, 126.8, 21.0 ppm.



2f

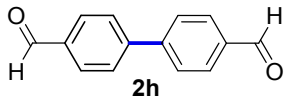
3.3.5. 4,4'-Dichlorobiphenyl (2f).[10] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.4 Hz, 4H), 7.39 (d, *J* = 8.4 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 133.7, 129.0, 128.2 ppm.



2g

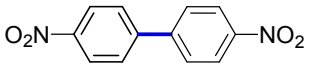
3.3.6. 4,4'-Diacetylbiphenyl (2g).[10] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.1 Hz, 4H), 7.72 (d, *J* = 8.1 Hz, 4H), 2.66 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 144.3,

136.5, 129.0, 127.4, 26.7 ppm.



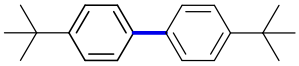
2h

3.3.7. 4,4'-Diformylbiphenyl (2h).[28] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (brs, 2H) 8.00 (d, *J* = 8.1 Hz, 4H), 7.80 (d, *J* = 8.1 Hz, 4H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 145.5, 136.0, 130.3, 128.0 ppm.

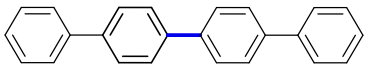


2i

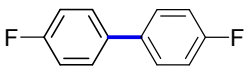
3.3.8. 4,4'-Dinitrobiphenyl (2i).[10] Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (dt, *J* = 8.8, 2.3 Hz, 4H), 7.80 (dt, *J* = 8.8, 2.3 Hz, 4H) ppm.


2j

3.3.9. 4,4'-Di-*tert*-butylbiphenyl (2j).[27] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dt, *J* = 8.6, 2.1 Hz, 4H), 7.44 (dt, *J* = 8.6, 2.1 Hz, 4H), 1.36 (s, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 138.2, 126.6, 125.6, 34.5, 31.4 ppm.

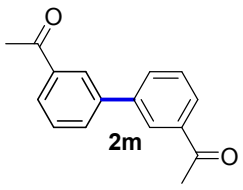

2k

3.3.10. 4,4'-Quaterphenyl (2k).[29] Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 4H), 7.53 (d, *J* = 7.8 Hz, 4H), 7.42 (t, *J* = 7.3 Hz, 4H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 8.4 Hz, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.7, 140.0, 138.0, 137.8, 129.0, 128.9, 127.7, 126.9 ppm.



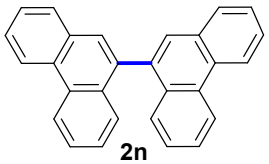
2l

3.3.11. 4,4'-Difluorobiphenyl (2l).[27] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.23 (m, 4H), 7.16−7.06 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (d, *J* = 246.5 Hz), 136.4 (d, *J* = 3.7 Hz), 128.5 (d, *J* = 8.1 Hz), 115.7 (d, *J* = 21.3 Hz) ppm.

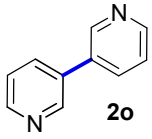


2m

3.3.12. 3,3'-Diacetylbiphenyl (2m).[30] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (t, *J* = 1.8 Hz, 2H), 7.98 (ddd, *J* = 1.3, 1.8, 7.8 Hz, 2H), 7.82 (ddd, *J* = 1.3, 2.0, 7.8 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 2H), 2.68 (s, 6H) ppm.

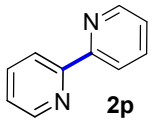

2n

3.3.13. 9,9'-Biphenanthrene (2n).[31] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (dd, *J* = 6.3 7.5 Hz, 4H), 7.92 (dd, *J* = 1.5, 7.8 Hz, 2H), 7.86 (s, 2H), 7.78−7.60 (m, 6H), 7.50 (dd, *J* = 1.5, 7.3 Hz, 2H), 7.42−7.33 (m, 2H) ppm.



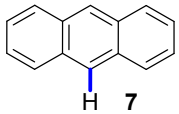
2o

3.3.14. 3,3'-Bipyridine (2o).[31] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (d, *J* = 2.1 Hz, 2H), 8.68 (dd, *J* = 1.3, 4.9 Hz, 2H), 7.93 (dt, *J* = 2.1, 7.9 Hz, 2H), 7.46 (d, *J* = 4.9, 7.9 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 147.8, 134.8, 133.6, 124.0 ppm.



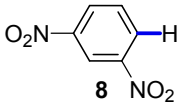
2p

3.3.15. 2,2'-Bipyridine (2p).[10] Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 4.8 Hz, 2H), 8.40 (d, *J* = 8.0 Hz, 2H), 7.83 (td, *J* = 1.8, 8.0 Hz, 2H), 7.32 (dt, *J* = 1.3, 5.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 149.2, 136.9, 123.7, 121.1 ppm.



7

3.3.16. Anthracene (7).[32] Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (s, 2H), 8.05−7.95 (m, 4H), 7.50−7.43 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.6, 128.2, 126.2, 125.4 ppm.



8

3.3.17. *m*-Dinitrobenzene (8).[32] Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (t, *J* = 2.3 Hz, 1H), 8.60 (dd, *J* = 2.3, 8.0 Hz, 2H), 7.83 (t, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 130.7, 128.9, 119.1 ppm.

4. Recyclability Tests

The reaction mixture of the homocoupling of 4-iodoanisole (**1a**), was subjected to evaporation of ethanol, extracted the product, **2a** by using EtOAc (3 x 6 mL) and added **1a** (1 mmol) and 0.5 mL of EtOH. The reaction was repeated using the same experimental conditions and found a very low yield (~30%) of **2a**. It indicates the consumption of bases that are present in the medium. However, the recyclability of the catalyst was also checked by using evaporated part of aqueous portion obtained in **Sec. 3.2** after the completion of extraction of product, **2a**. The solid mass obtained was added 1 mL of WEPA and 0.5 mL of EtOH and 1 mmol of **1a** and found the formation of biaryl with 74%, 52% and 35% was observed in 2nd, 3rd and 4th cycles of the reaction under the identical conditions as mentioned in **Sec. 3.2**. Further, it was also observed that the reduction of $Pd(OAc)_2$ into fine particles of palladium. The presence of Pd was evidenced by the EDS (**Sec. 9.2**), cyclic voltammetry (**Sec. 10**), and particle size analysis (**Sec. 11**). The decrease in the yield of the

reaction of **1a** on recycling was assumed due to the fair dispersion of fine palladium particles into organic portion during the work-up process.

5. References

1 P. Bamfield and P. M. Quan, *Synthesis*, 1978, 537−538.

2 D. D. Hennings, T. Iwama and V. H. Rawal, *Org. Lett.*, 1999, **1**, 1205−1208.

3 S. Venkatraman and C.-J. Li, *Org. Lett.*, 1999, **1**, 1133−1135.

4 V. Penalva, J. Hassan, L. Lavenot, C. Gozzi and M. Lemaire, *Tetrahedron Lett.*, 1998, **39**, 2559−2560.

5 J. Li, Y. Xie, H. Jiang and M. Chen, *Green Chem.*, 2002, **4**, 424−425.

6 J.-H. Li, Y.-X. Xie and D.-L. Yin, *J. Org. Chem.*, 2003, **68**, 9867−9869.

7 M. Kuroboshi, Y. Waki and H. Tanaka, *J. Org. Chem.*, 2003, **68**, 3938−3942.

8 P. B. Silveira, V. R. Lando, J. Dupont and A. L. Monteiro, *Tetrahedron Lett.*, 2002, **43**, 2327−2329.

9 W. M. Seganish, M. E. Mowery, S. Riggleman and P. DeShong, *Tetrahedron*, 2005, **61**, 2117−2121.

10 L. Wang, Y. Zhang, L. Liu and Y. Wang, *J. Org. Chem.*, 2006, **71**, 1284−1287.

11 R. N. Ram and V. Singh, *Tetrahedron Lett.*, 2006, **47**, 7625−7628.

12 J. Moon, H. Nam, J. Ju, M. Jeong, S. Lee, *Chem. Lett.*, 2007, **36**, 1432−1433.

13 N. Iranpoor, H. Firouzabadi and R. Azadi, *J. Organomet. Chem.*, 2008, **693**, 2469−2472.

14 L. Wang and W. Lu, *Org. Lett.*, 2009, **11**, 1079−1082.

15 V. Calò, A. Nacci, A. Monopoli and P. Cotugno, *Chem. Eur. J.*, 2009, **15**, 1272−1279.

16 S. Nadri, E. Azadi, A. Ataei, M. Joshaghani and E. Rafiee, *J. Organomet. Chem.*, 2011, **696**, 2966−2970.

17 B. R. Park, K. H. Kim, T. H. Kim and J. N. Kim, *Tetrahedron Lett.*, 2011, **52**, 4405−4407.

18 N. Iranpoor, H. Firouzabadi and Y. Ahmadi, *Eur. J. Org. Chem.*, 2012, 305−311.

19 T. M. Gädda, Y. Kawanishi and A. Miyazawa, *Synth. Commun.*, 2012, **42**, 1259−1267.

20 J. Wang, Y. Li, P. Li and G. Song, *Monatsh Chem.*, 2013, **144**, 1159−1163.

21 A. Bhattacharjya, P. Klumphu and B. H. Lipshutz, *Nat. Commun.*, 2015, **6**, 7401−7406.

22 Y. Huang, L. Liu and W. Feng, *ChemistrySelect*, 2016, **1**, 630−634.

23 J. Wang, A. Xu, M. Jia, S. Bai, X. Cheng and B. Zhaorigetu, *New J. Chem.*, 2017, **41**, 1905−1908.

24 Z.-J. Wang, X. Wang, J.-J. Lv, J.-J. Feng, X. Xu, A.-J. Wang and Z. Liang, *New J. Chem.*, 2017, **41**, 3894−3899.

25 F. M. Moghaddam, R. Pourkaveh, A. Karimi and S. E. Ayati, *Asian J. Org. Chem.*, 2018, **7**, 802−809.

26 N. Mosaddegh and I. Yavari, *Chem. Pep.*, 2018, **72**, 2013−2021.

27 A. R. Kapdi, G. Dhangar, J. L. Serrano, J. A. De Haro, P. Lozano and I. J. S. Fairlamb, *RSC Adv.*, 2014, **4**, 55305–55312.

28 S. Dwivedi, S. Bardhan, P. Ghosh and S. Das, *RSC Adv.*, 2014, **4**, 41045–41050.

29 V. Vajpayee, Y. H. Song, J. S. Ahn and K.-W. Chi, *Bull. Korean Chem. Soc.*, 2011, **32**, 2970–2972.

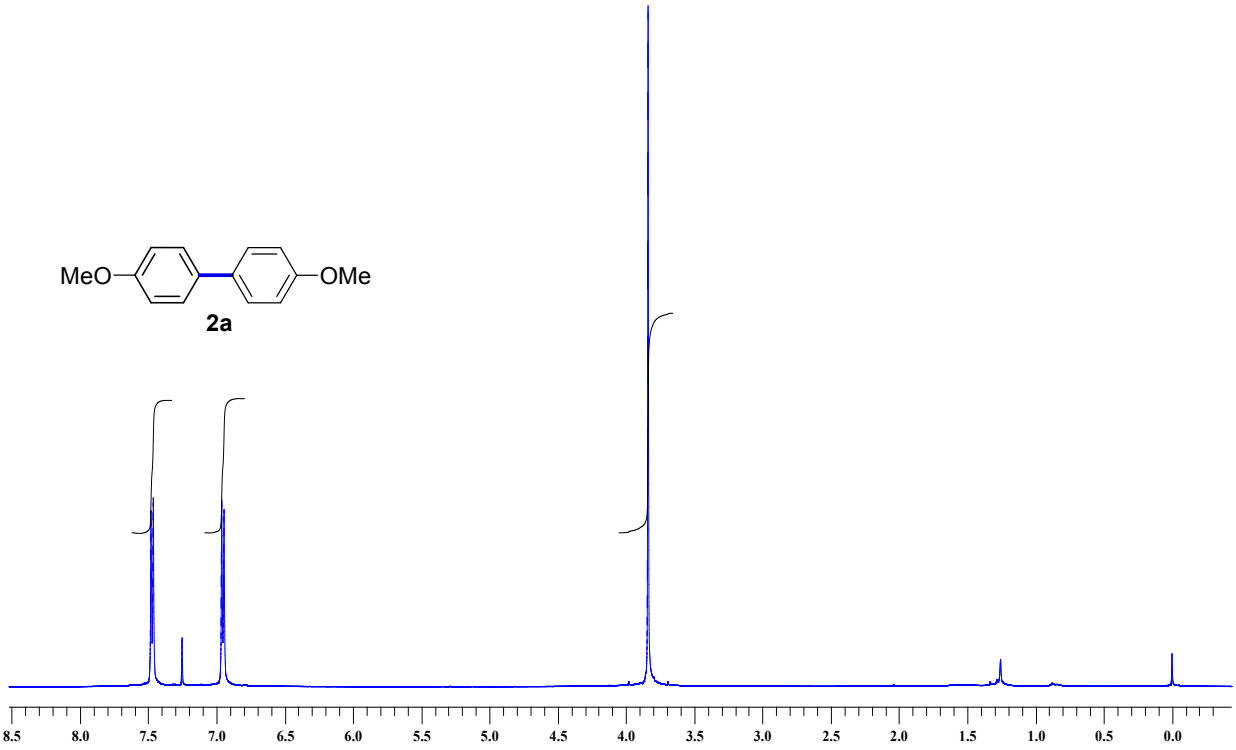
30 M. Lourak, R. Vanderesse, Y. Fort and P. Caubère, *J. Org. Chem.*, 1989, **54**, 4840−4844.

31 G. Cheng and M. Luo, *Eur. J. Org. Chem.*, 2011, 2519−2523.

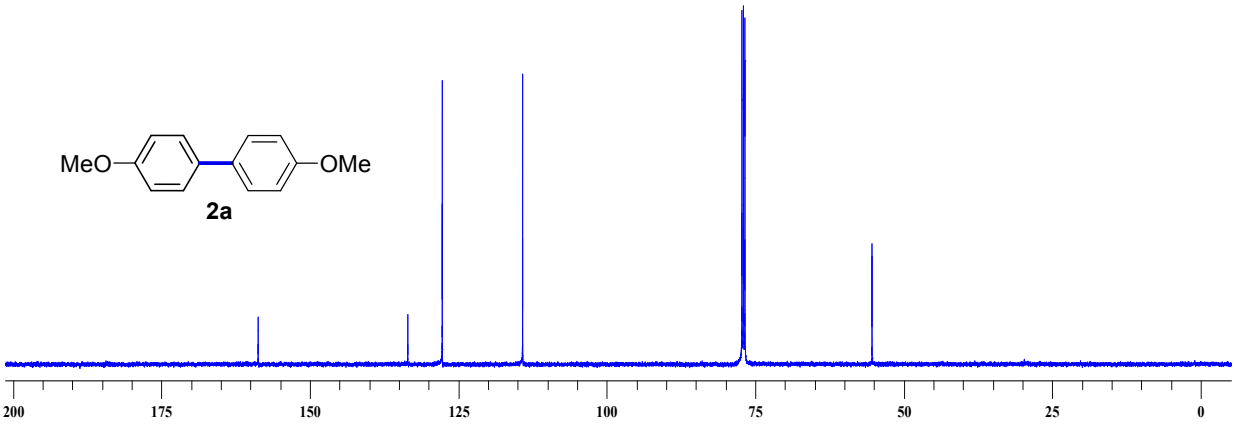
32 ^{13}C NMR and (or) ^{1}H NMR of the compound was matched with the data available with the commercially available one.

6. ^{1}H & ^{13}C NMR Spectra:

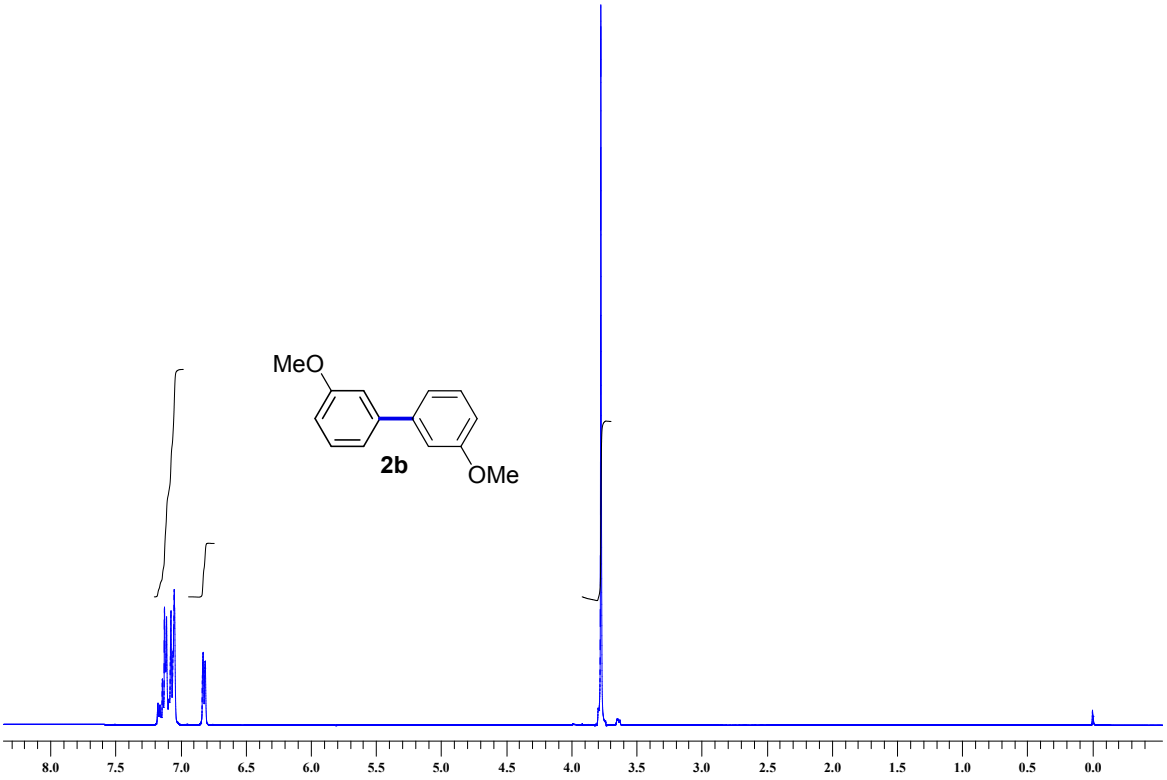
6.1. ^{1}H NMR Spectrum of **2a**



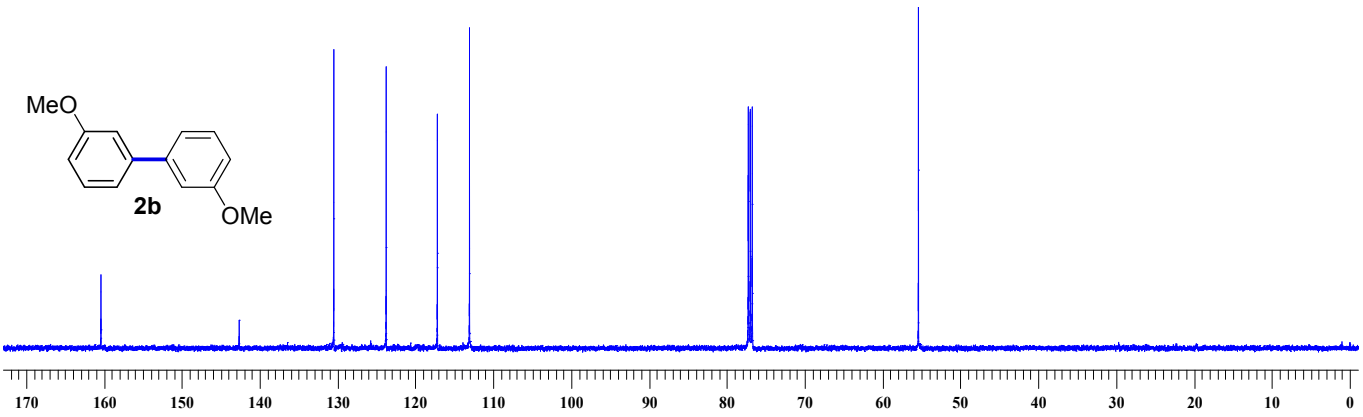
6.2. ^{13}C NMR Spectrum of **2a**



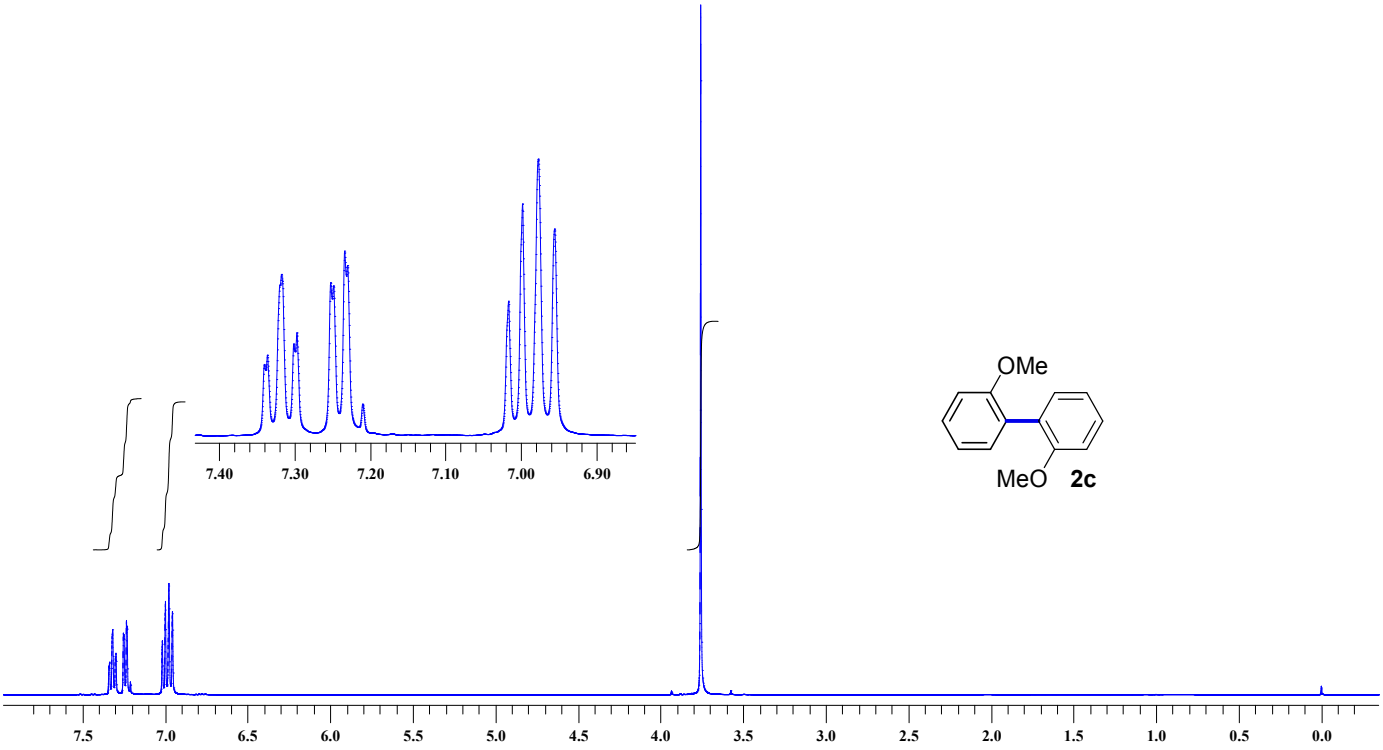
6.3. ^{1}H NMR Spectrum of **2b**



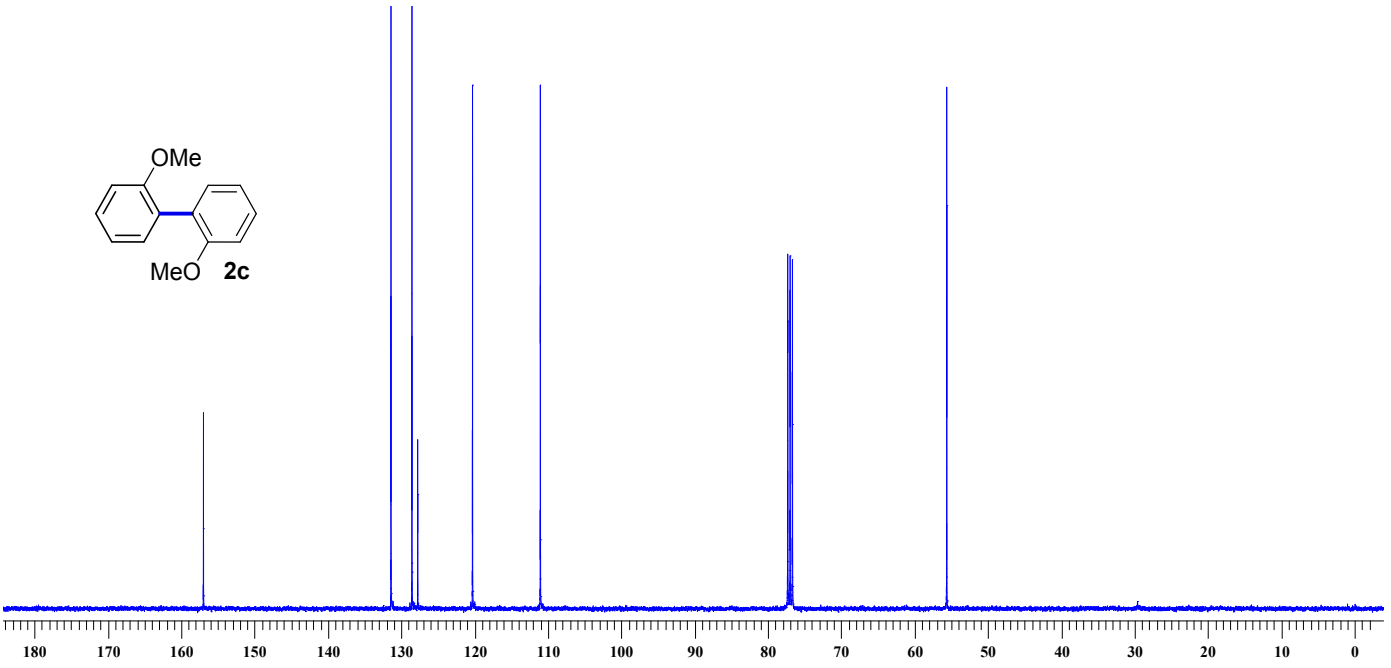
6.4. ^{13}C NMR Spectrum of **2b**



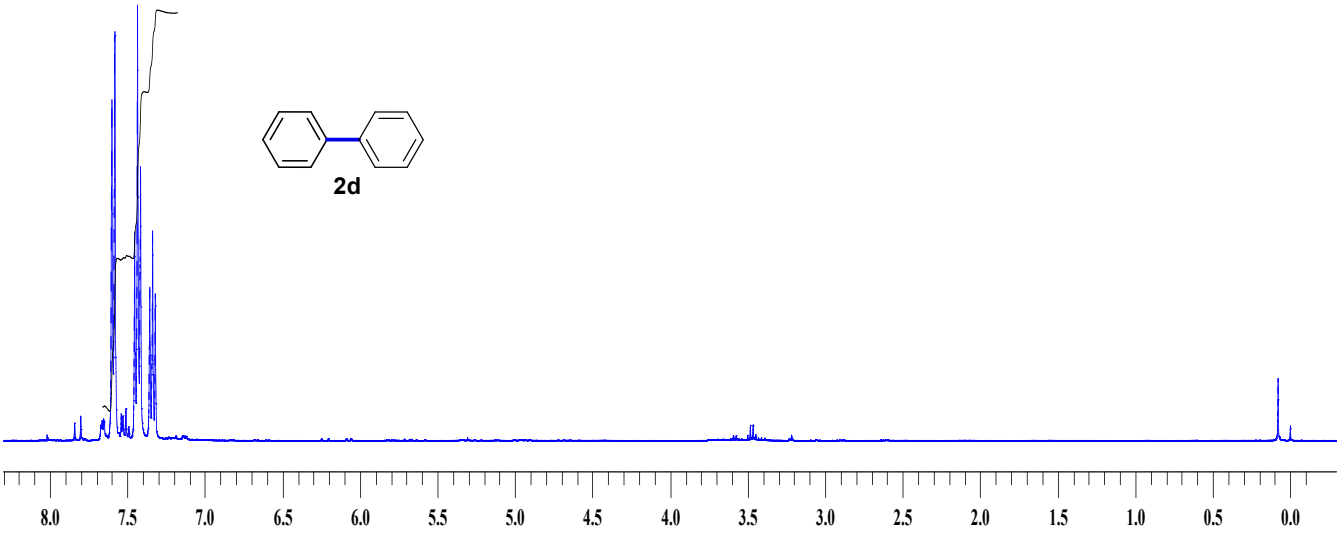
6.5. ^{1}H NMR Spectrum of **2c**



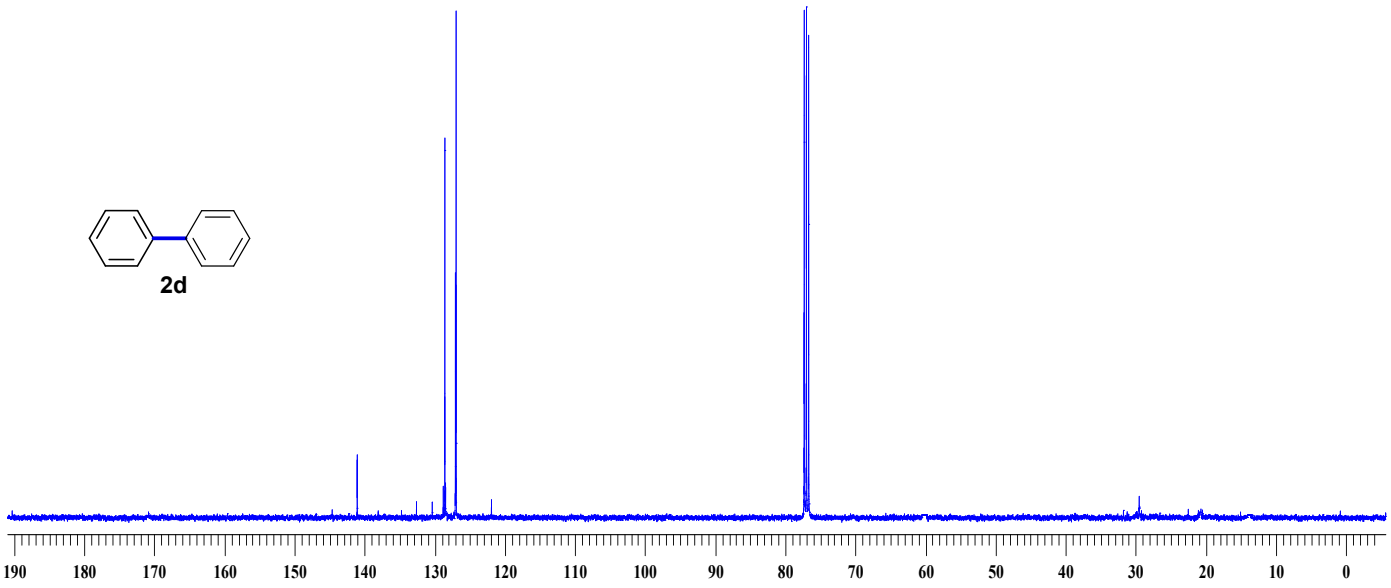
6.6. ^{13}C NMR Spectrum of **2c**



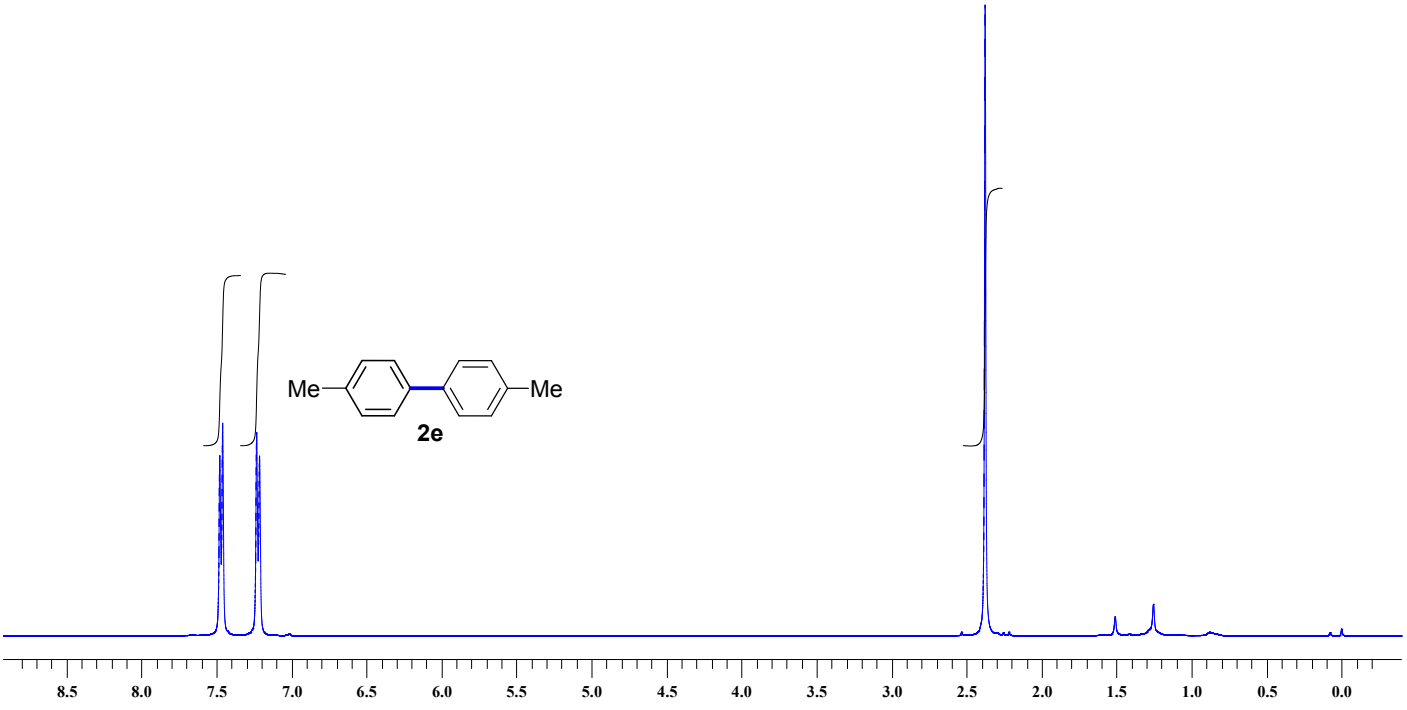
6.7. ^{1}H NMR Spectrum of **2d**



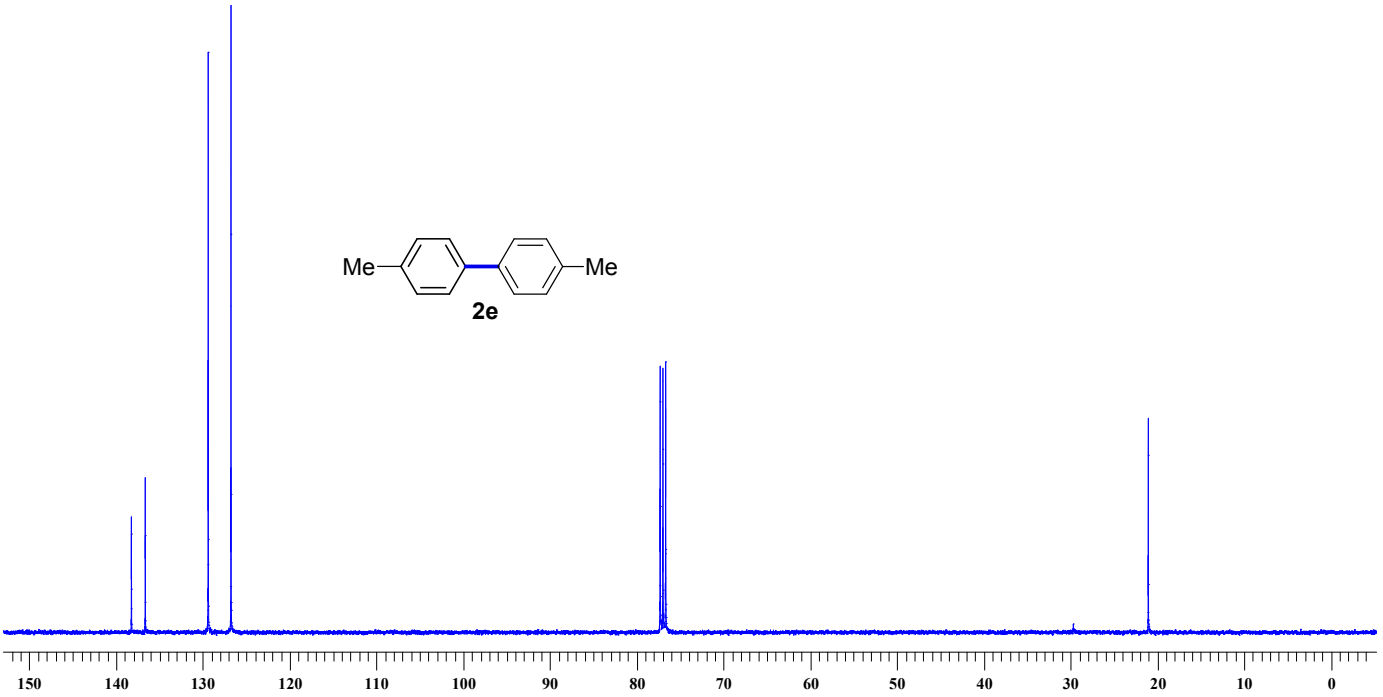
6.8. ^{13}C NMR Spectrum of **2d**



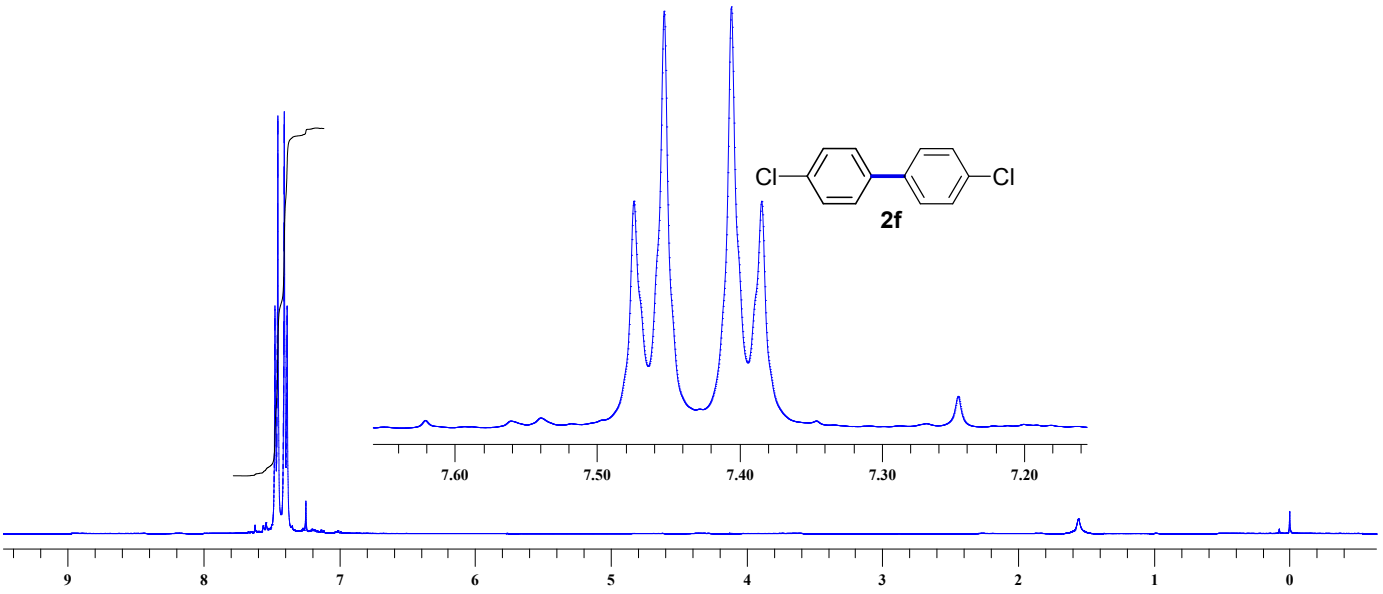
6.9. ^{1}H NMR Spectrum of **2e**



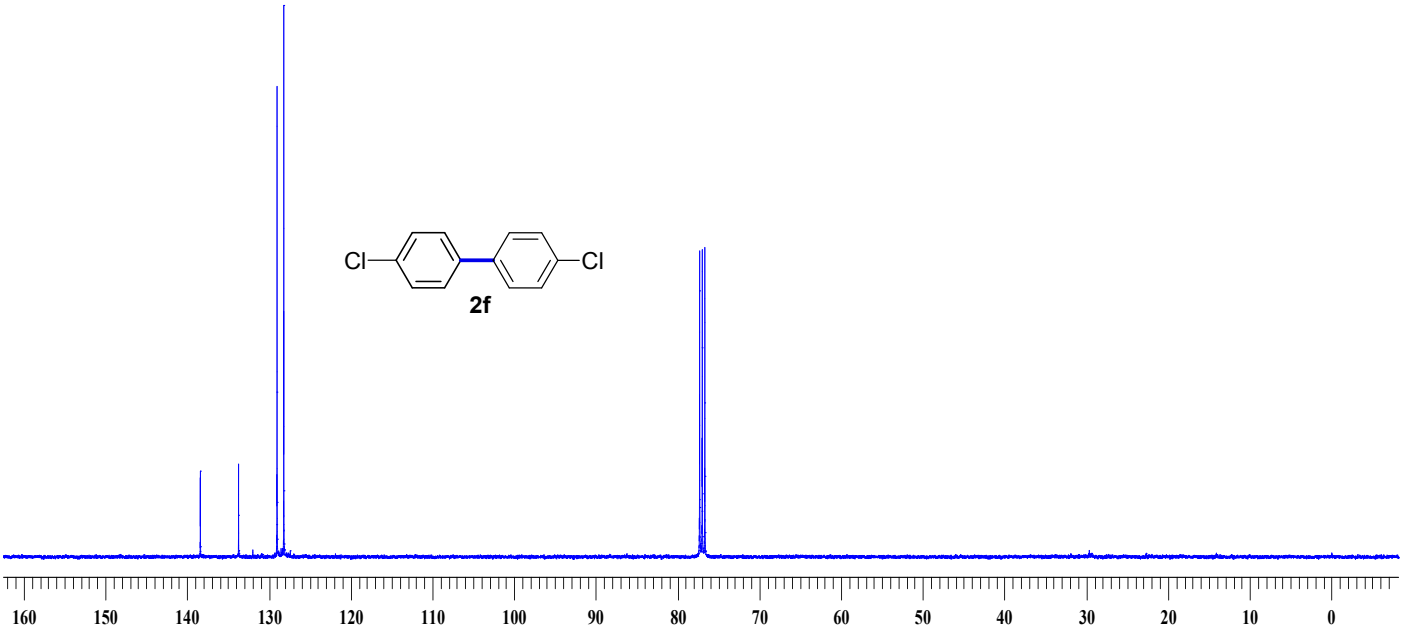
6.10. ^{13}C NMR Spectrum of **2e**



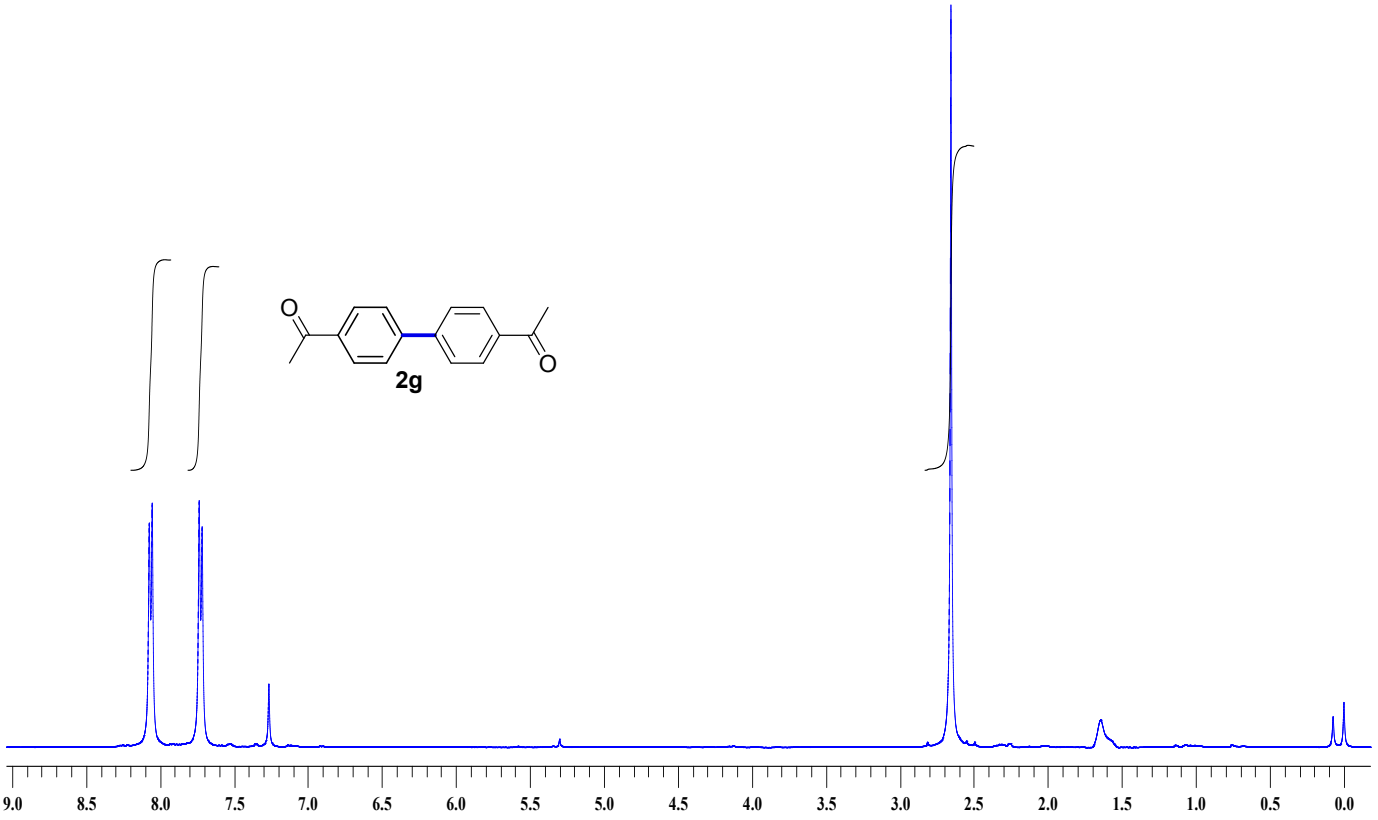
6.11. ^{1}H NMR Spectrum of **2f**



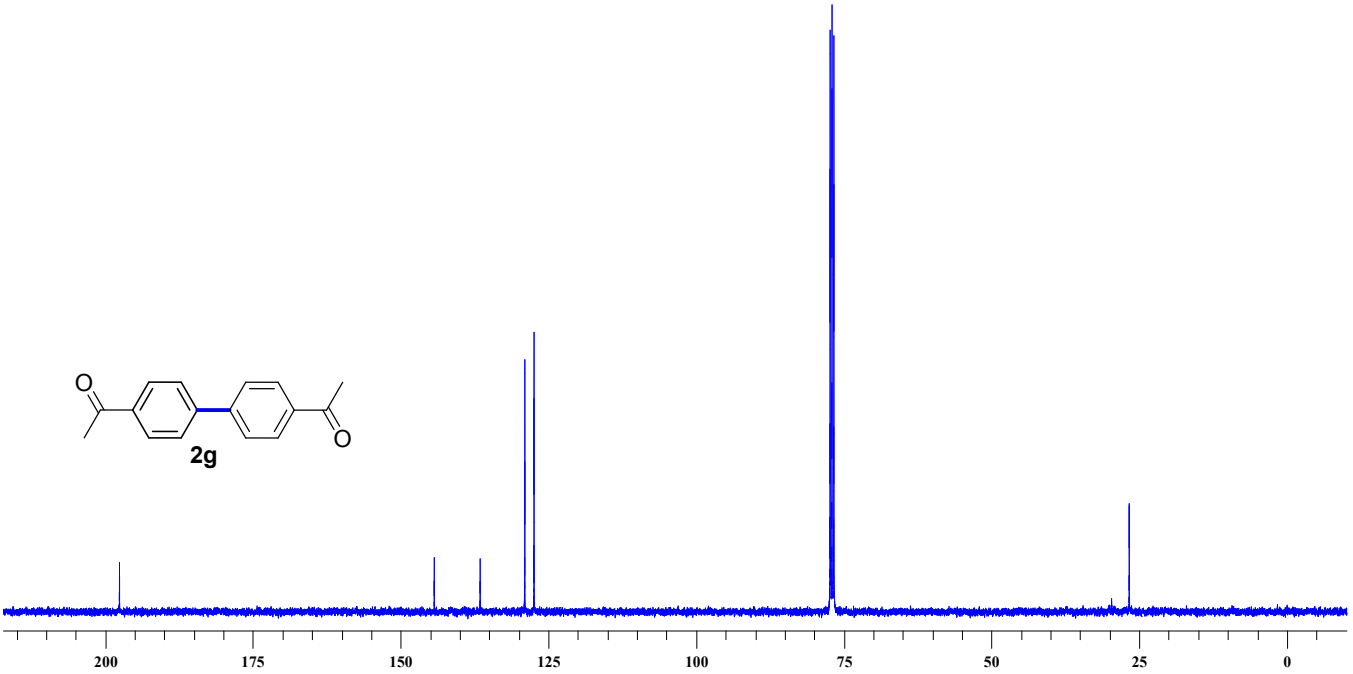
6.12. ^{13}C NMR Spectrum of **2f**



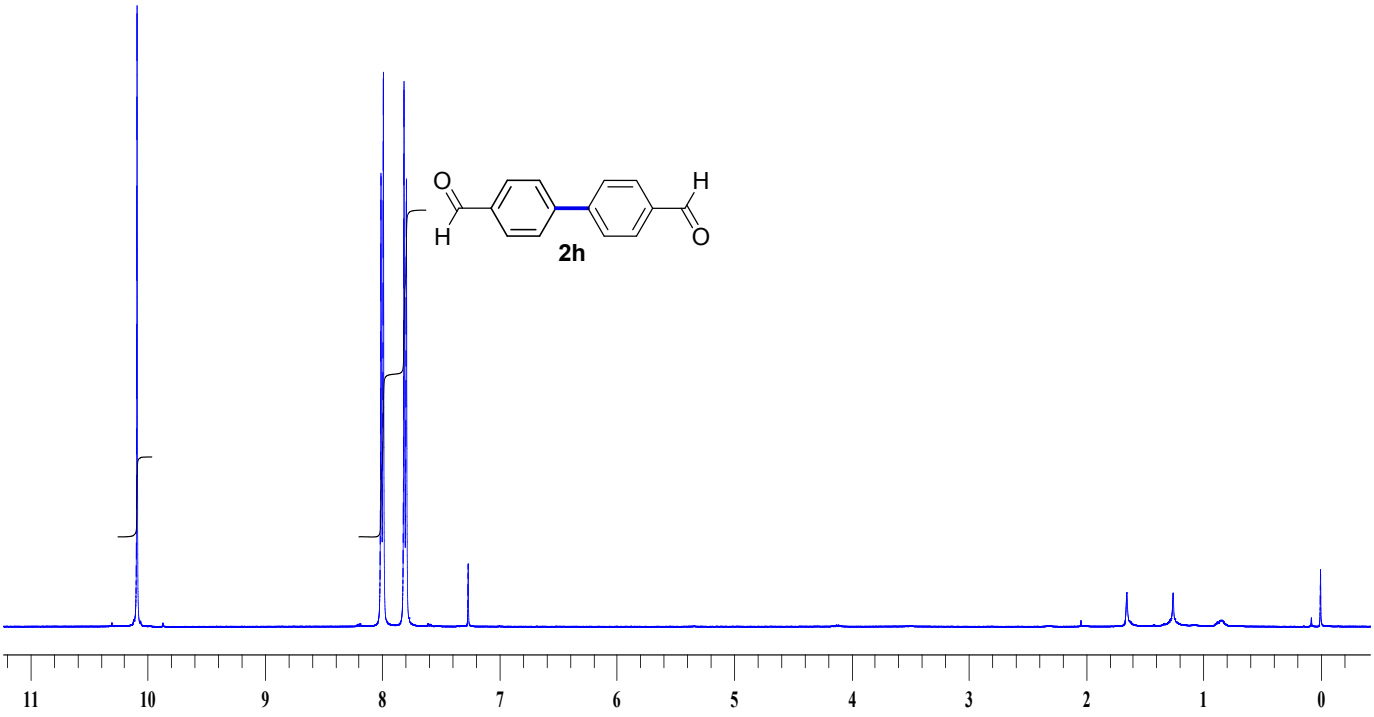
6.13. ^{1}H NMR Spectrum of **2g**



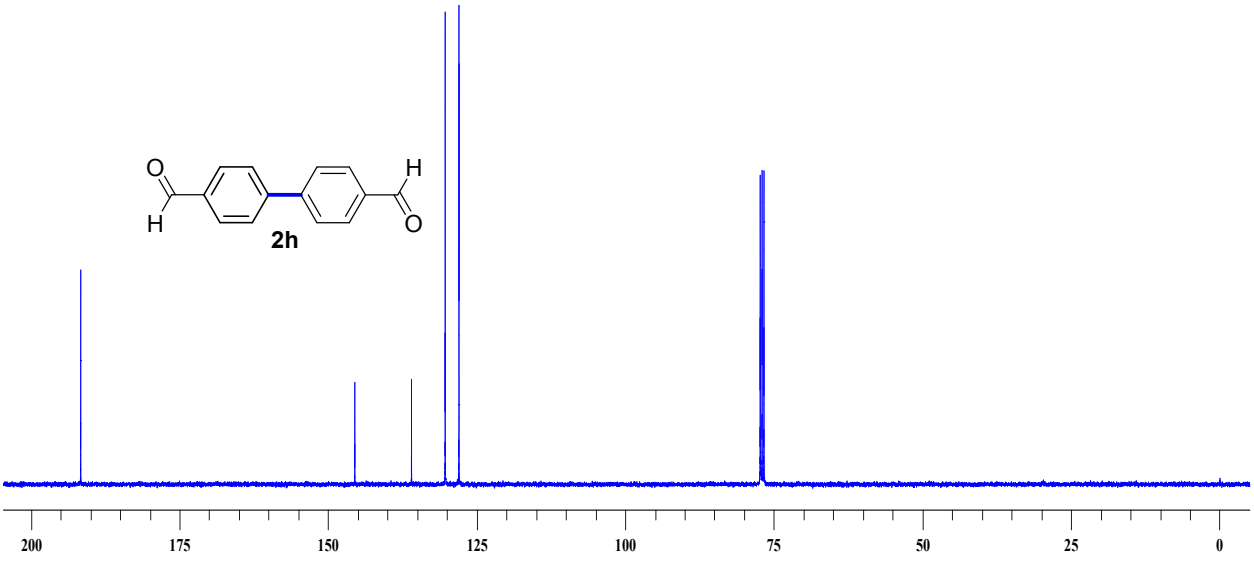
6.14. ^{13}C NMR Spectrum of **2g**



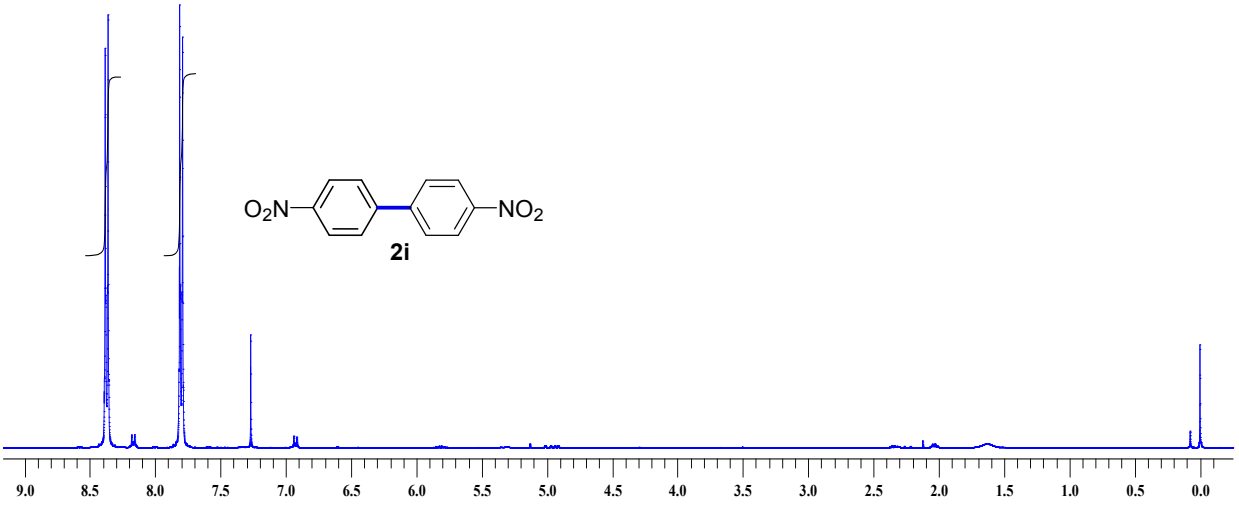
6.15. ^{1}H NMR Spectrum of **2h**



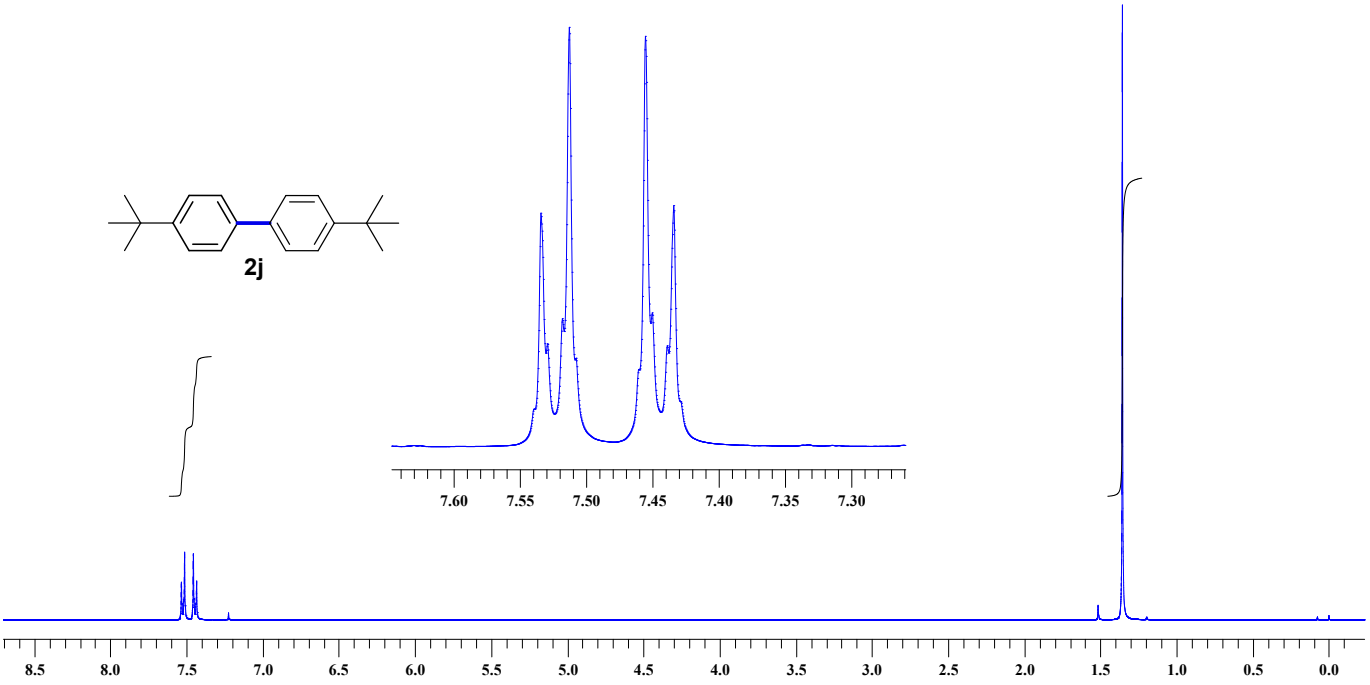
6.16. ^{13}C NMR Spectrum of **2h**



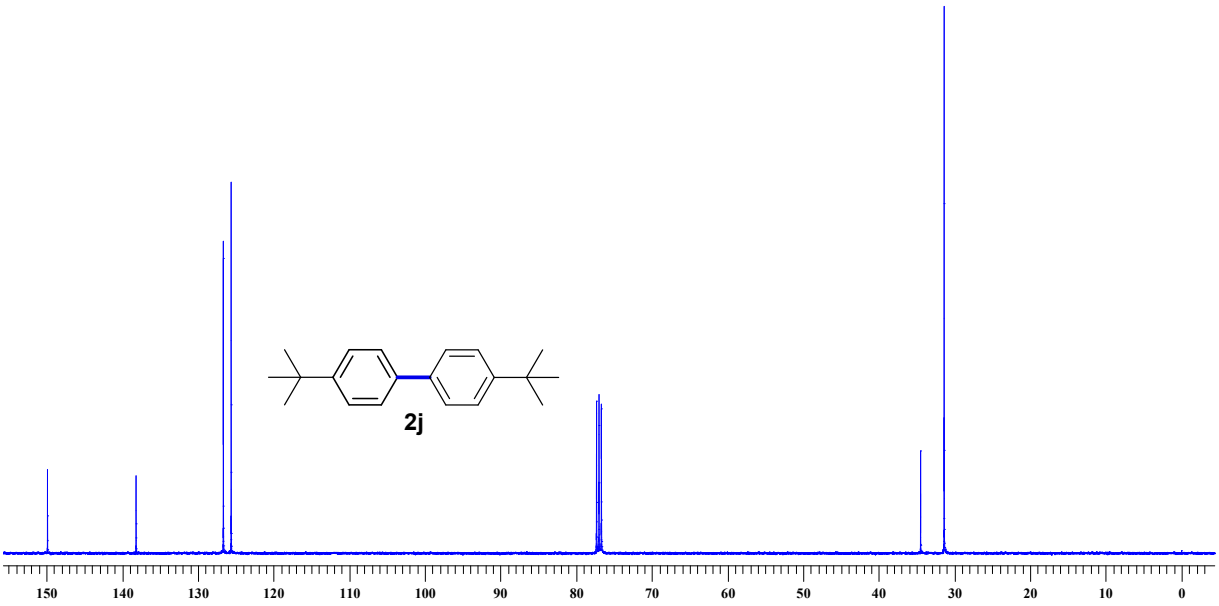
6.17. ^{1}H NMR Spectrum of **2i**



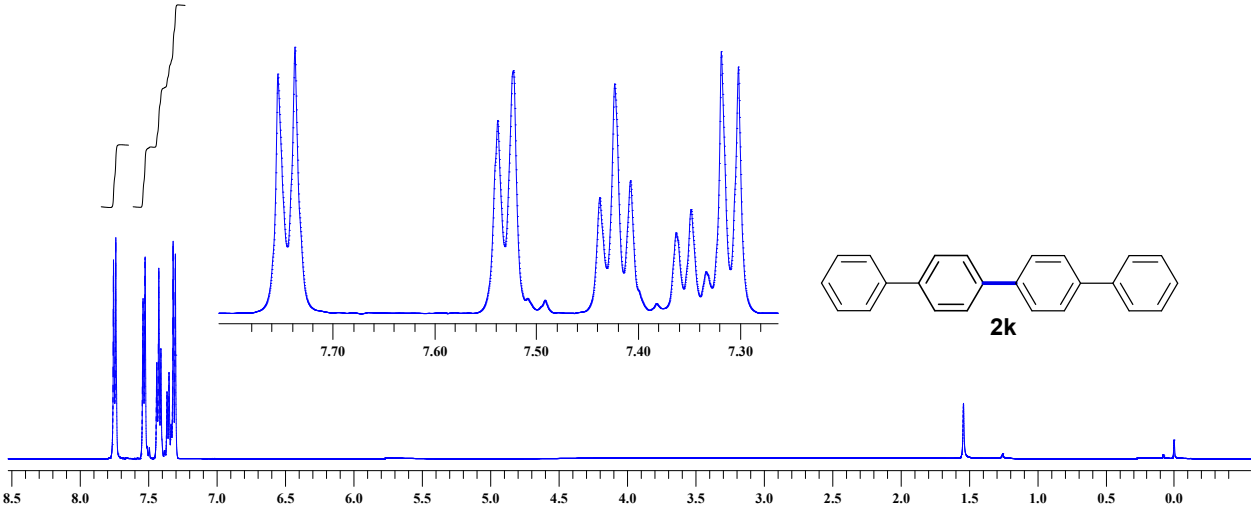
6.18. ^{1}H NMR Spectrum of **2j**



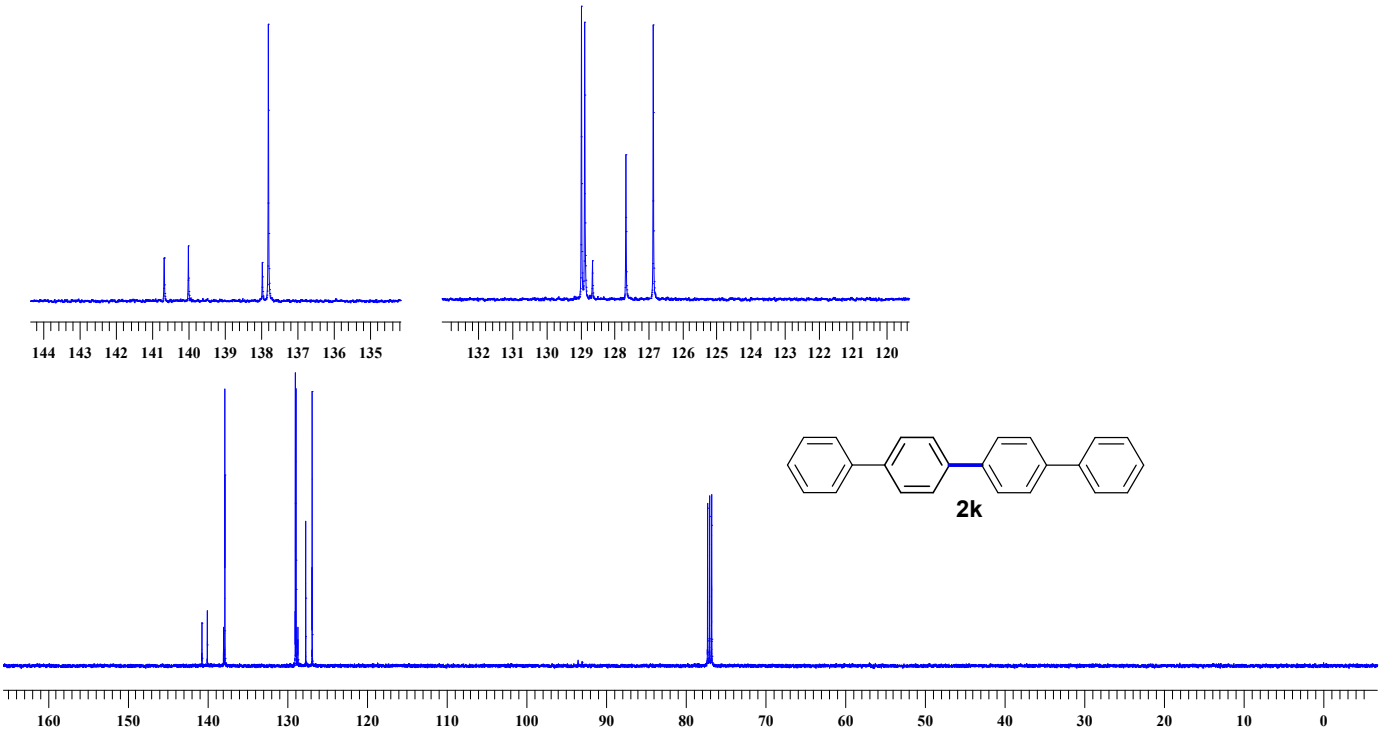
6.19. ^{13}C NMR Spectrum of **2j**



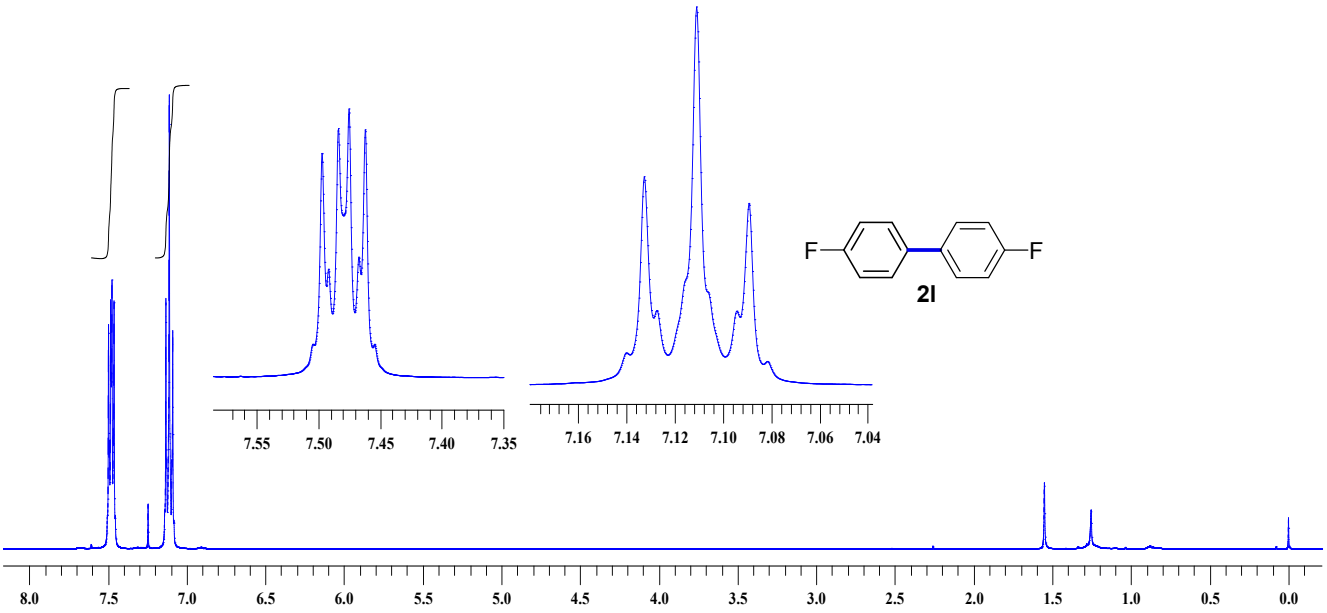
6.20. ^{1}H NMR Spectrum of **2k**



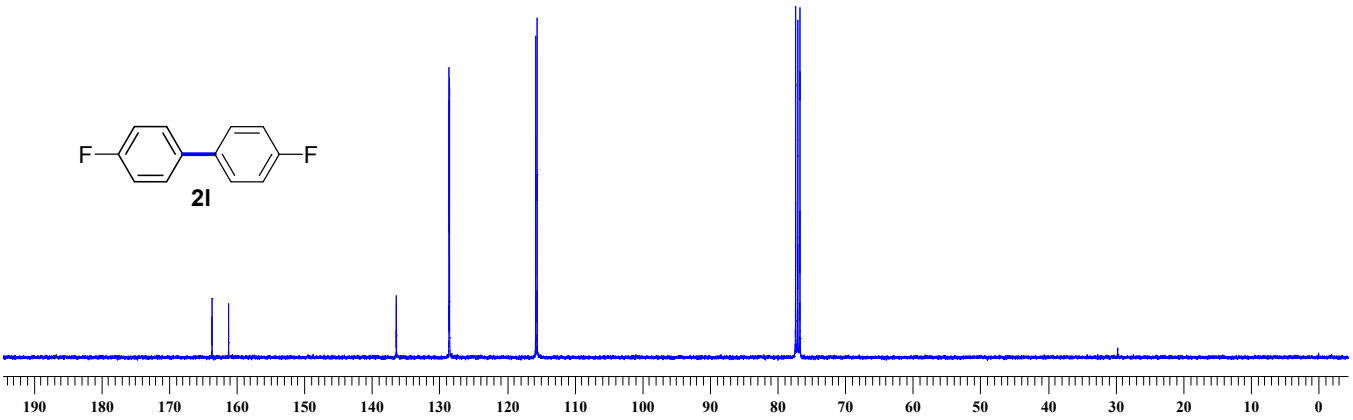
6.21. ^{13}C NMR Spectrum of **2k**



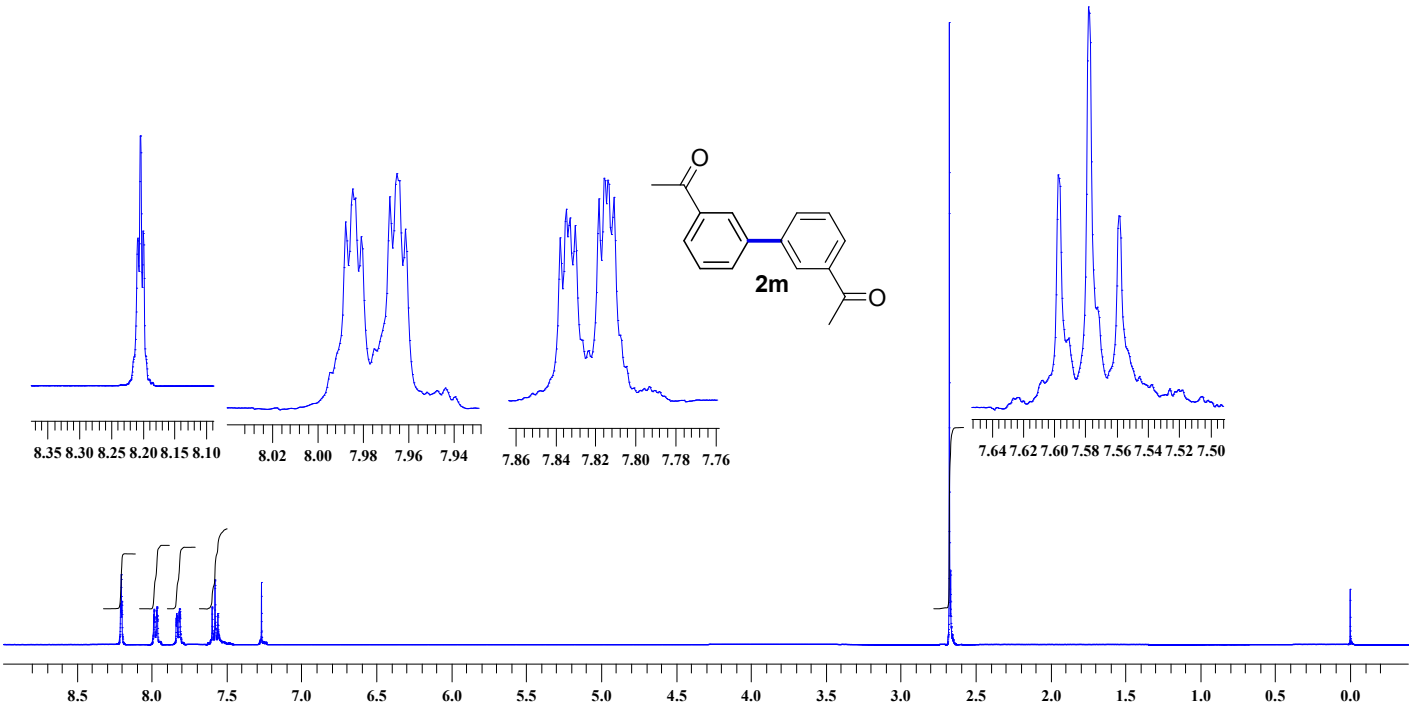
6.22. ^{1}H NMR Spectrum of **2l**



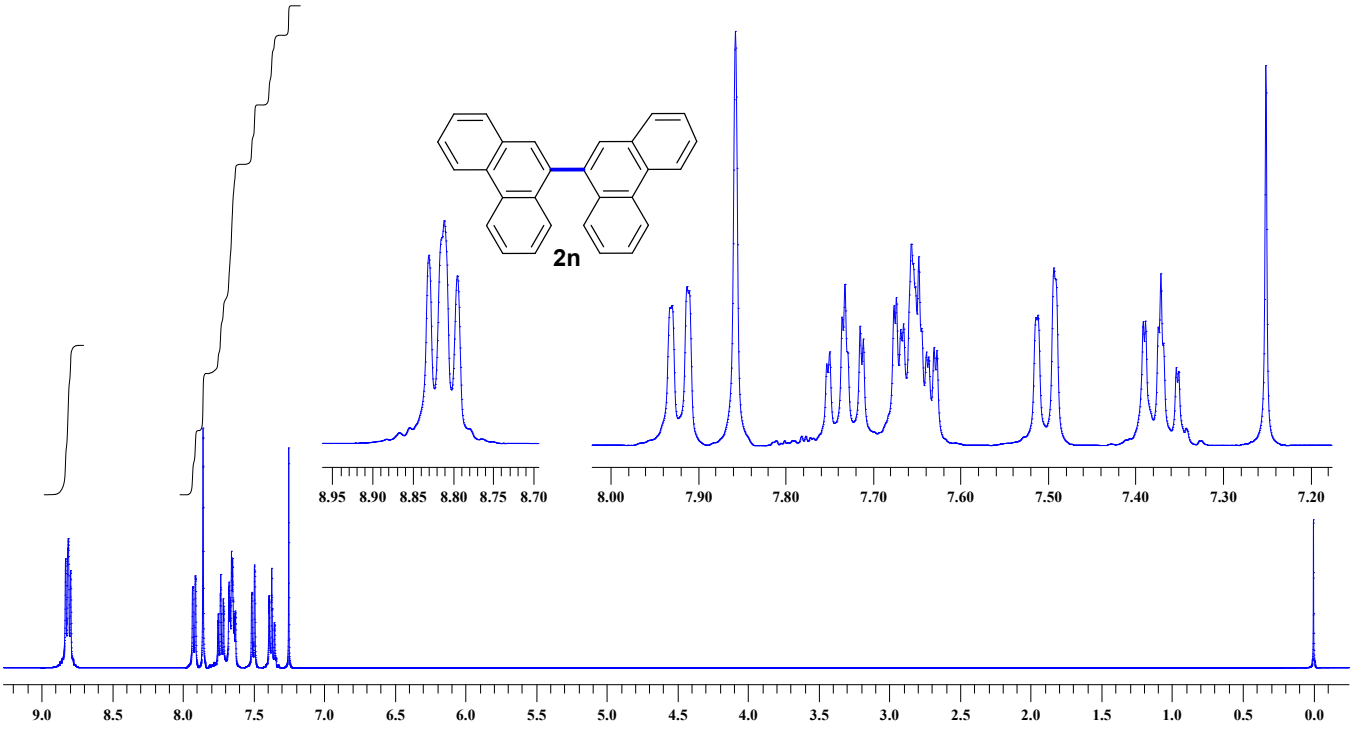
6.23. ^{13}C NMR Spectrum of **2l**



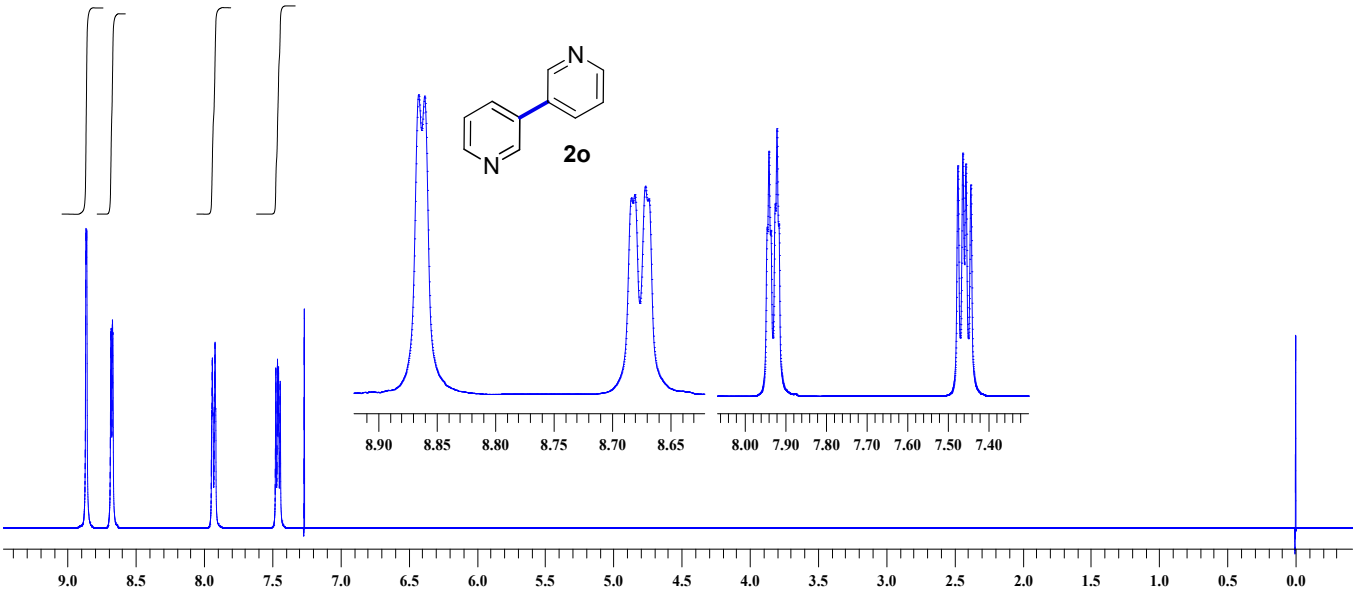
6.24. ^{1}H NMR Spectrum of **2m**



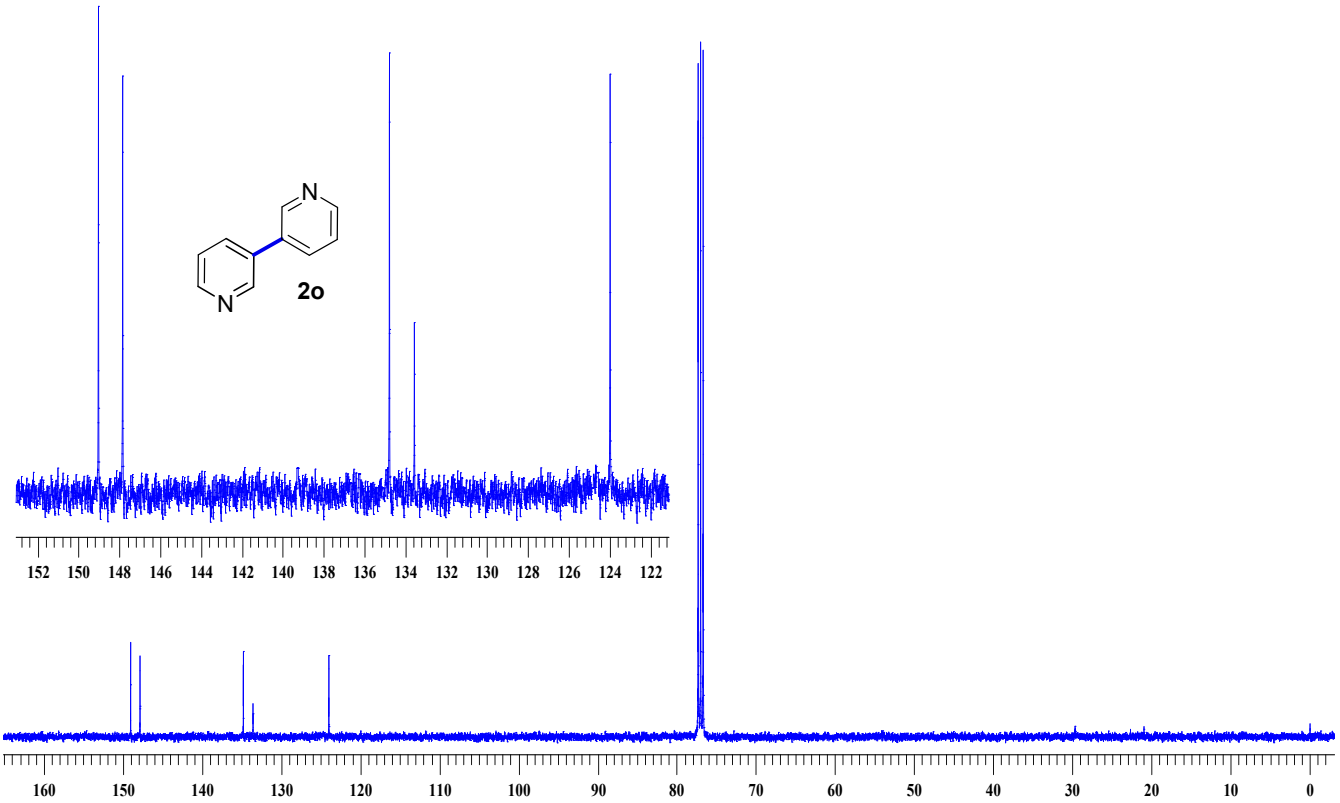
6.25. ^{1}H NMR Spectrum of **2n**



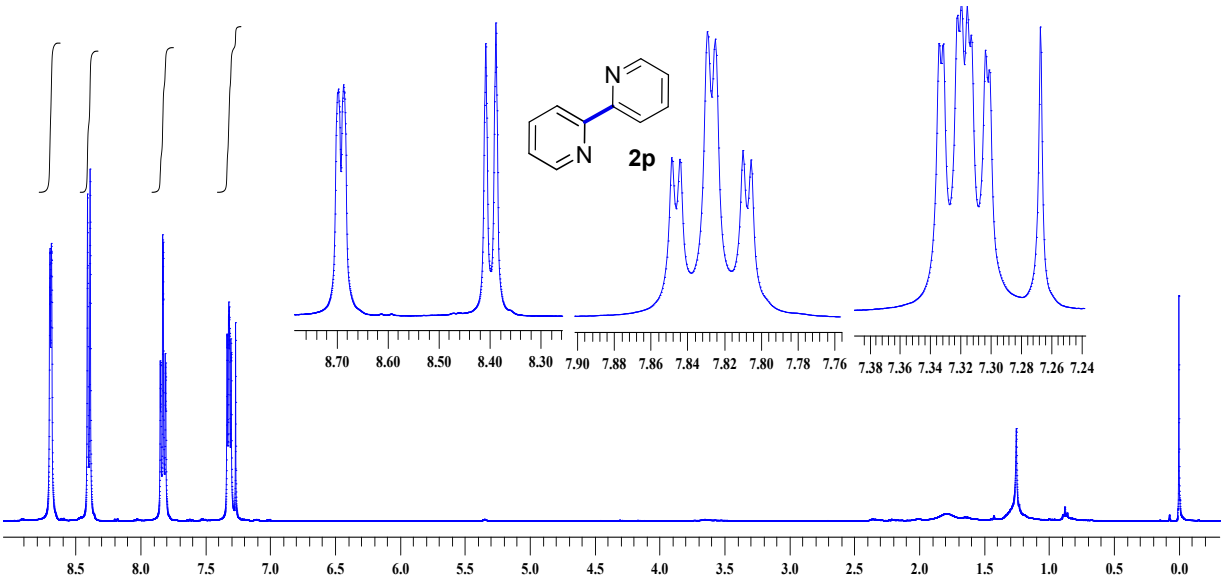
6.26. ^{1}H NMR Spectrum of **2o**



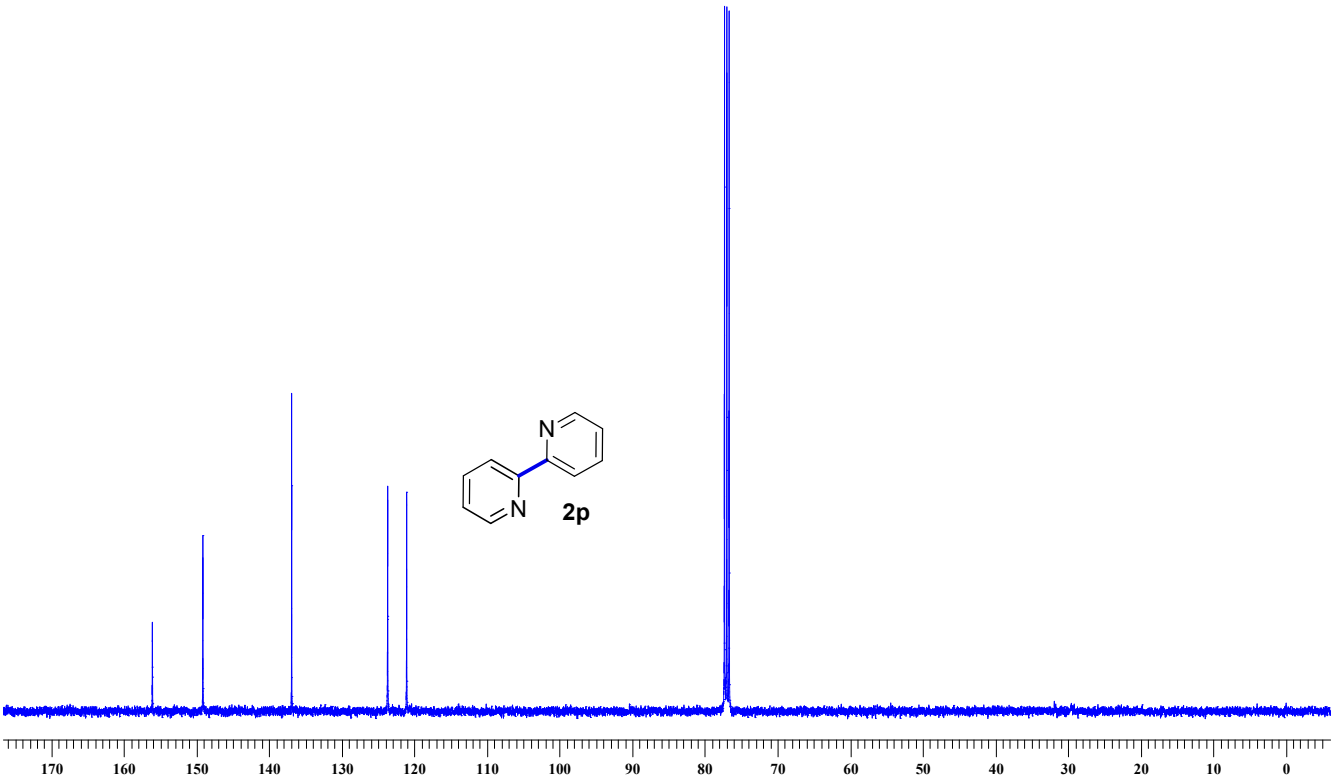
6.27. ^{13}C NMR Spectrum of **2o**



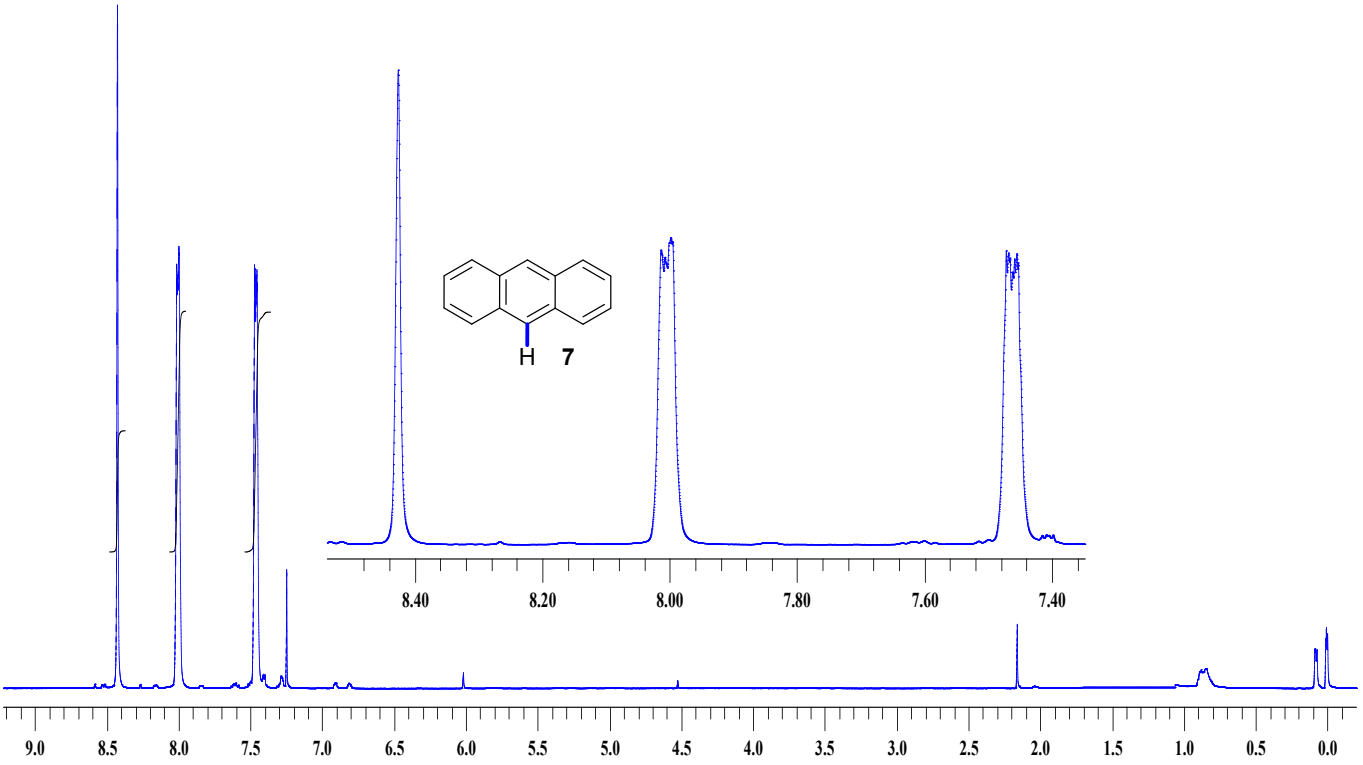
6.28. ^{1}H NMR Spectrum of **2p**



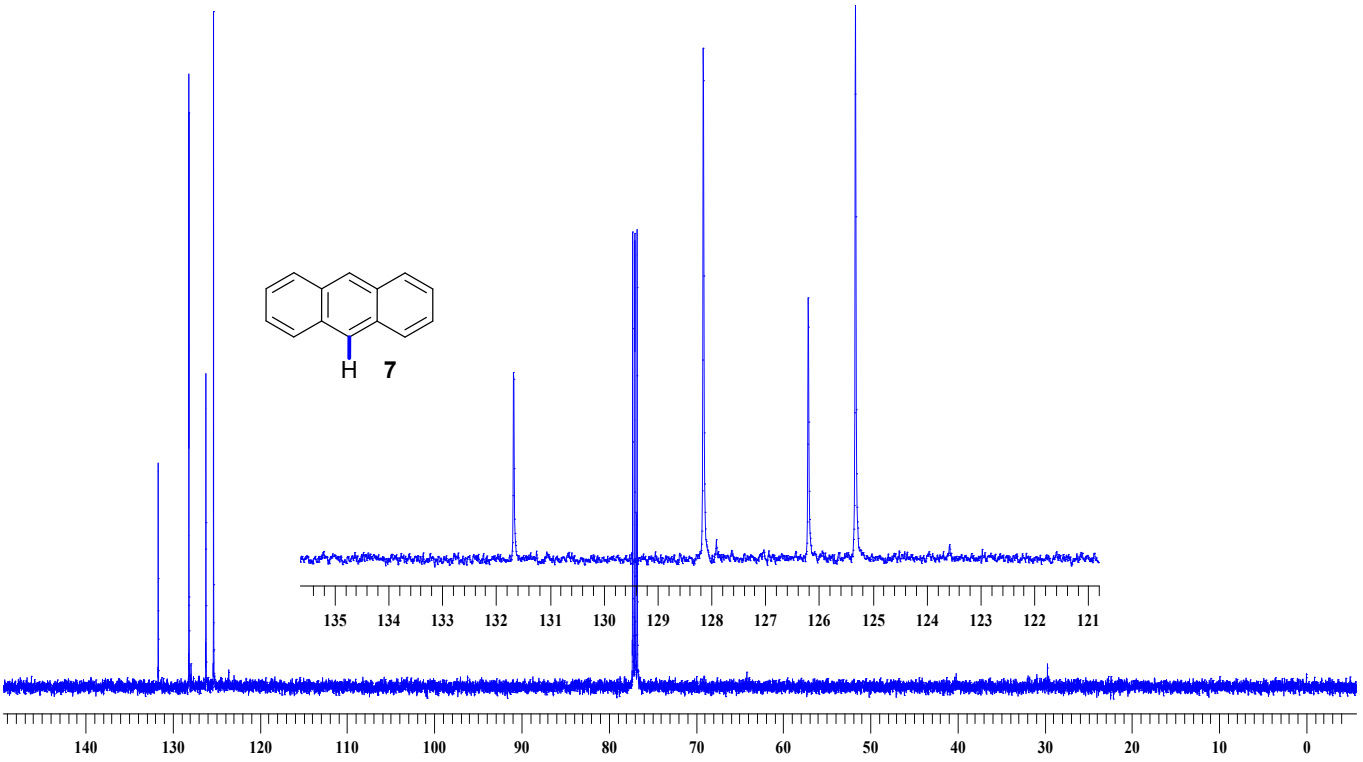
6.29. ^{13}C NMR Spectrum of **2p**



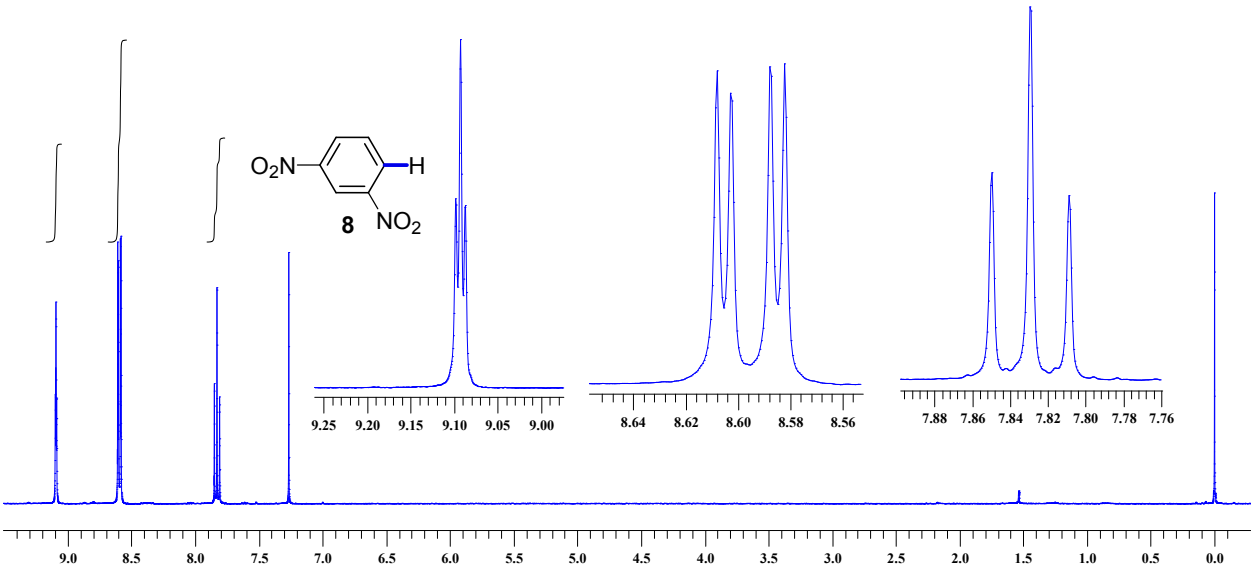
6.30. ^{1}H NMR Spectrum of **7**



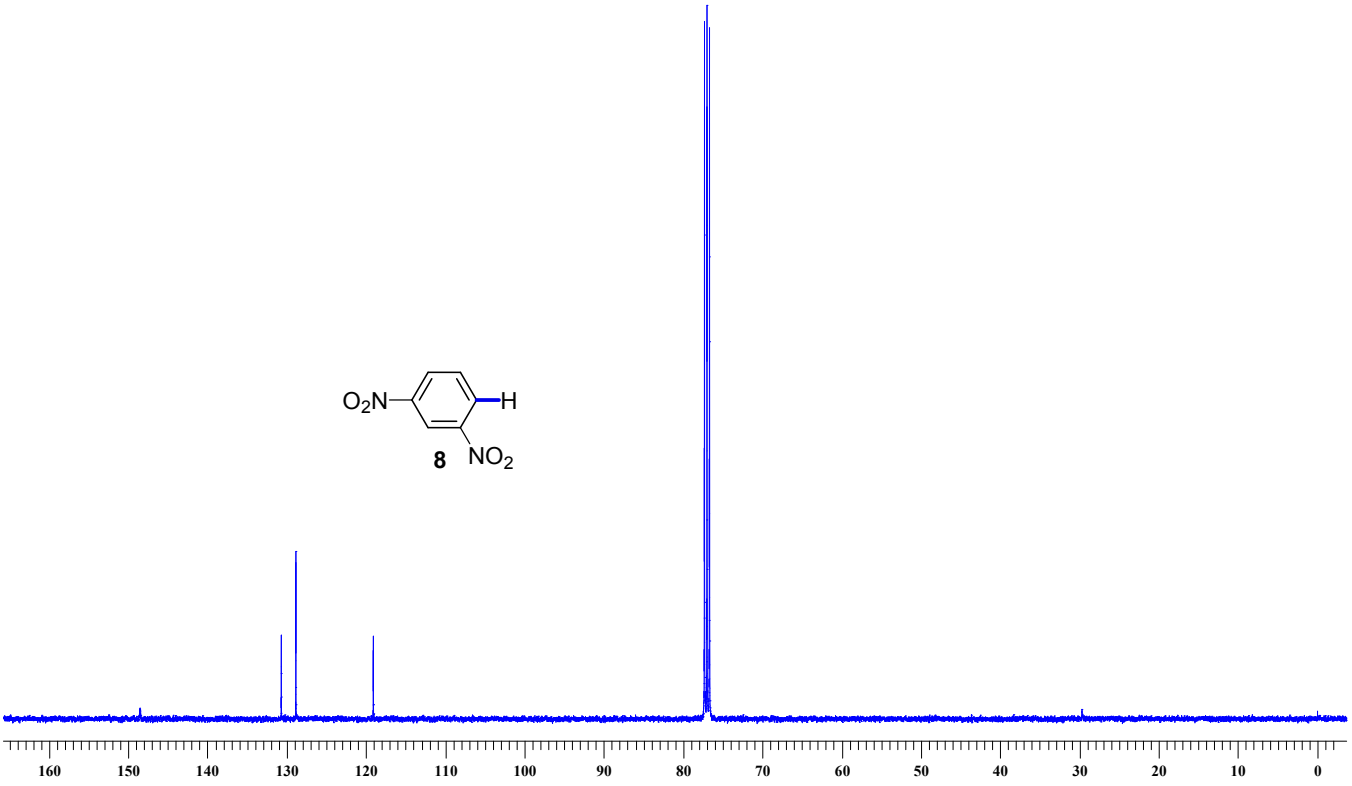
6.31. ^{13}C NMR Spectrum of **7**



6.32. ^{1}H NMR Spectrum of **8**

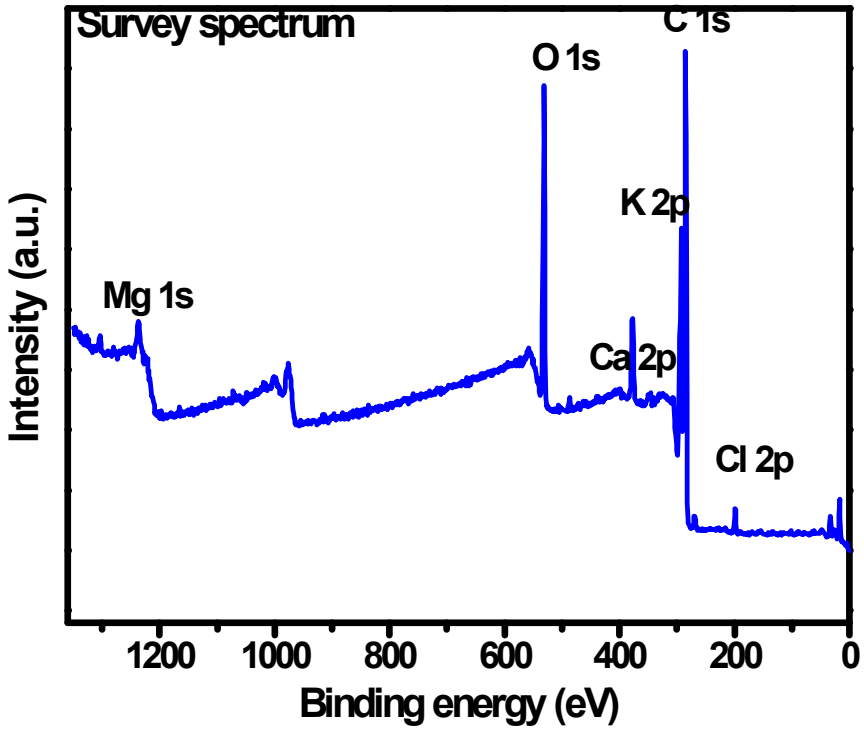


6.33. ^{13}C NMR Spectrum of **8**

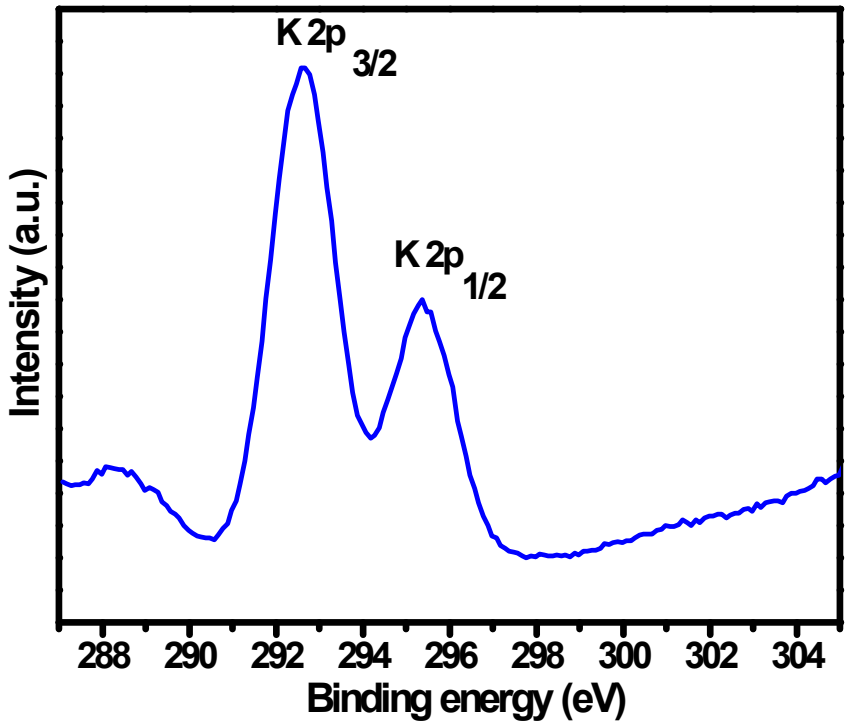


7. XPS Spectra of Pomegranate Ash:

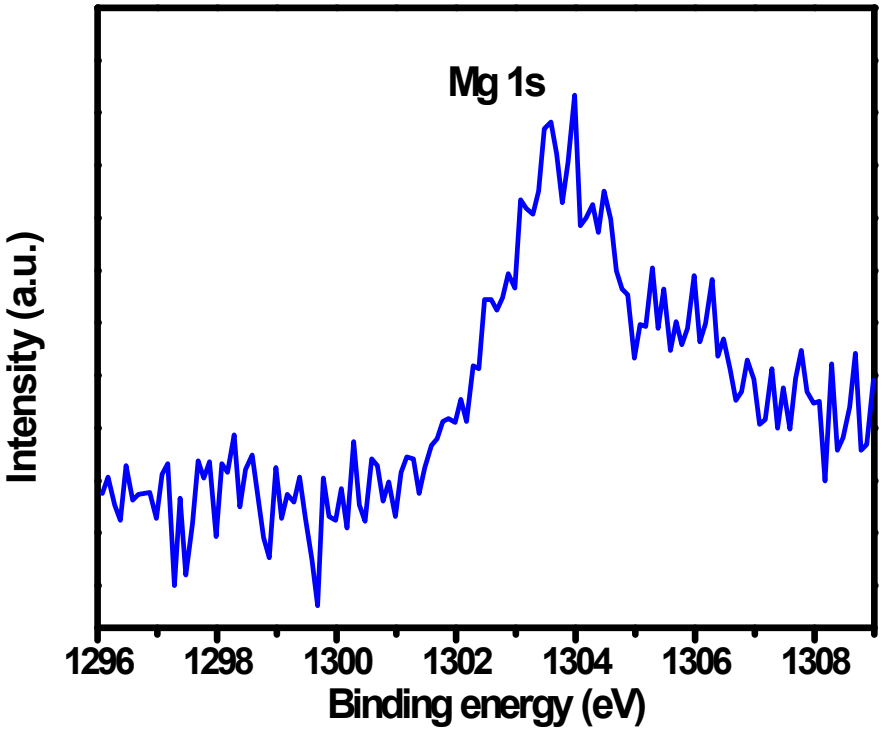
7.1. Survey XPS spectrum:



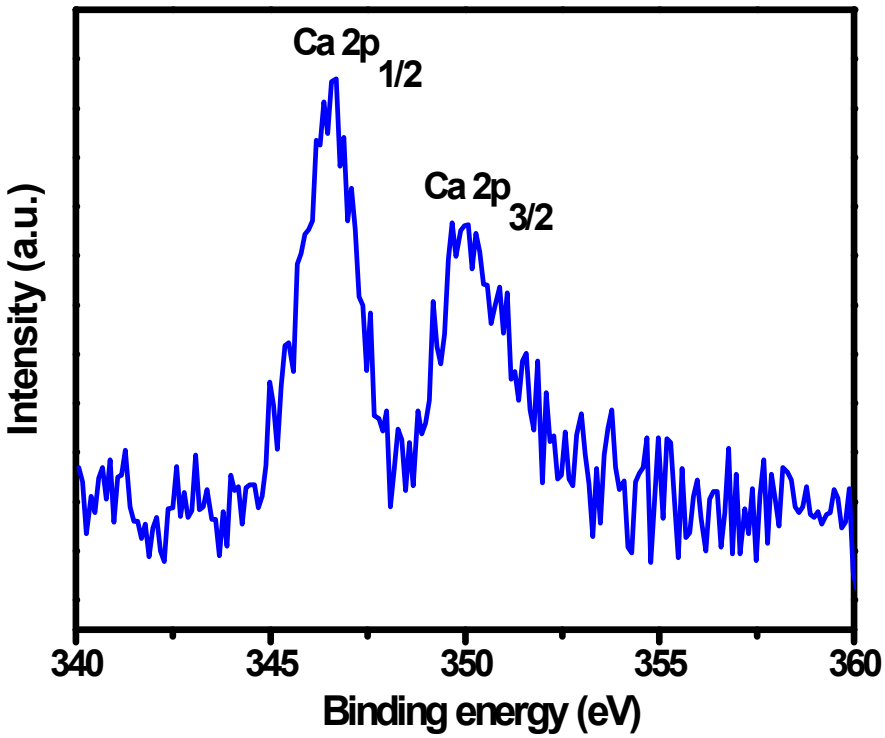
7.2. K 2p XPS Spectrum:



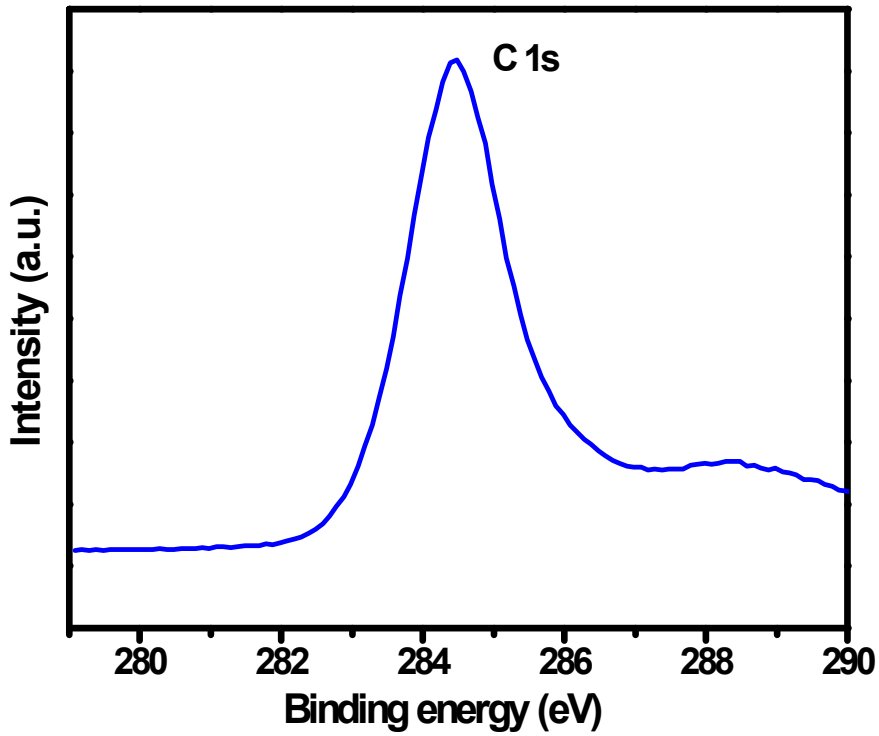
7.3. Mg 1s XPS Spectrum:



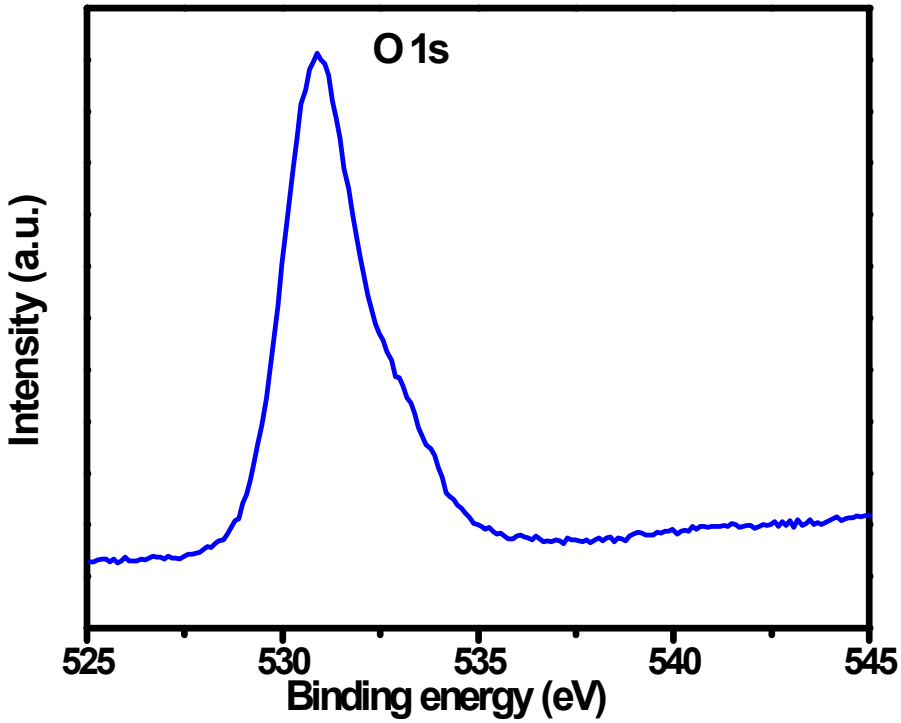
7.4. Ca 2p XPS Spectrum:



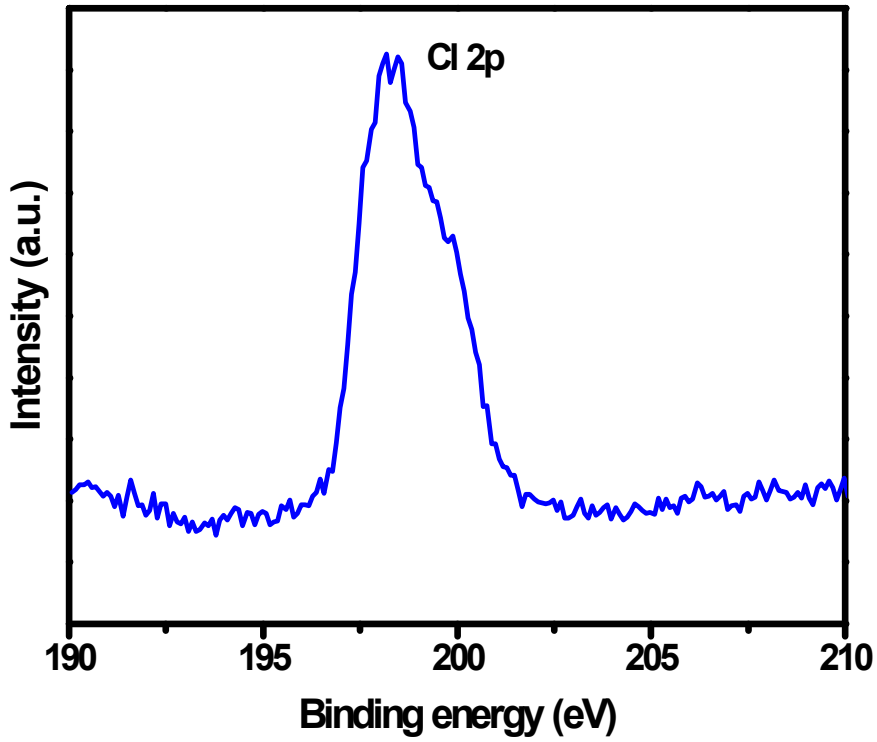
7.5. C 1s XPS Spectrum:



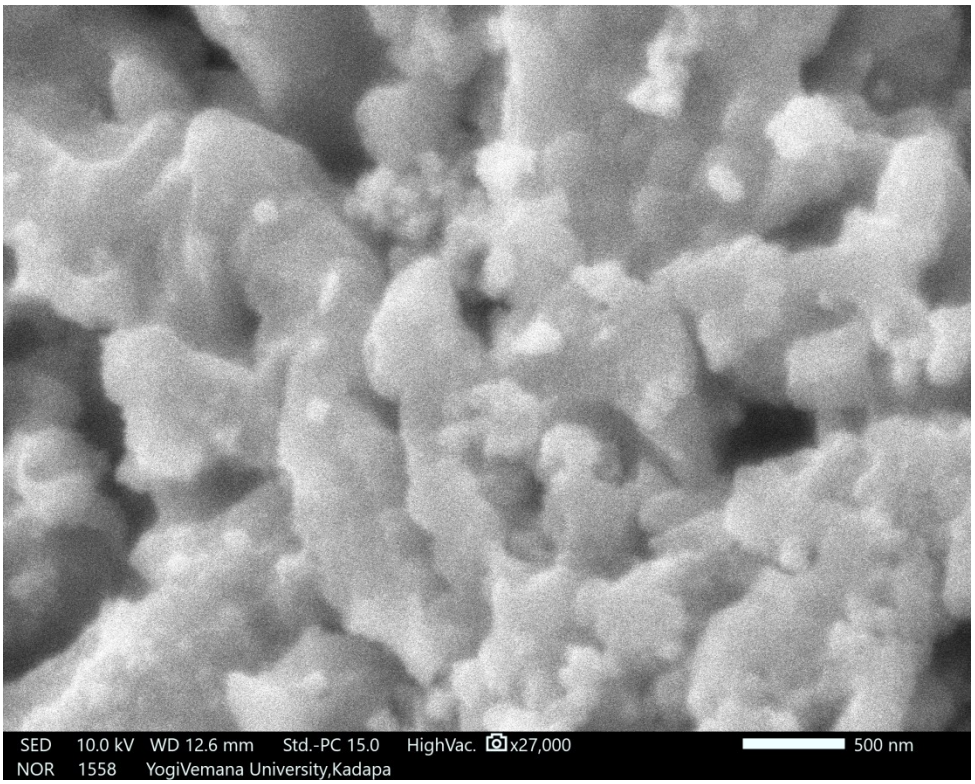
7.6. O 1s XPS Spectrum:



7.7. Cl 2p XPS Spectrum:

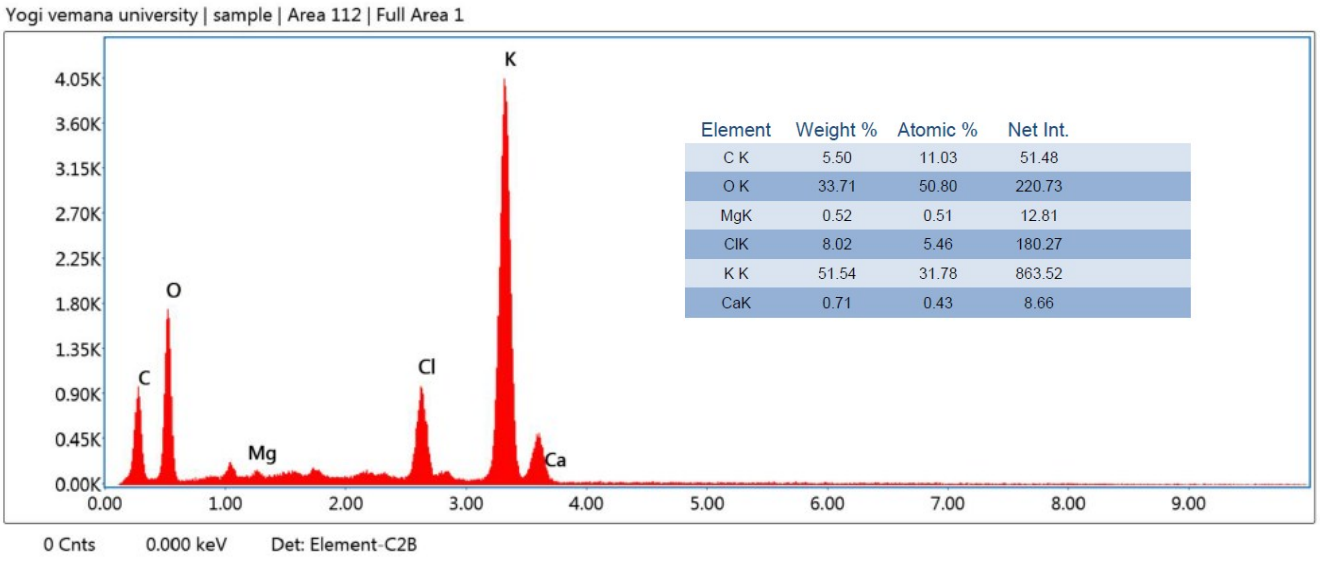


8. SEM Image of Palladium Separated after the Reaction of 1a:



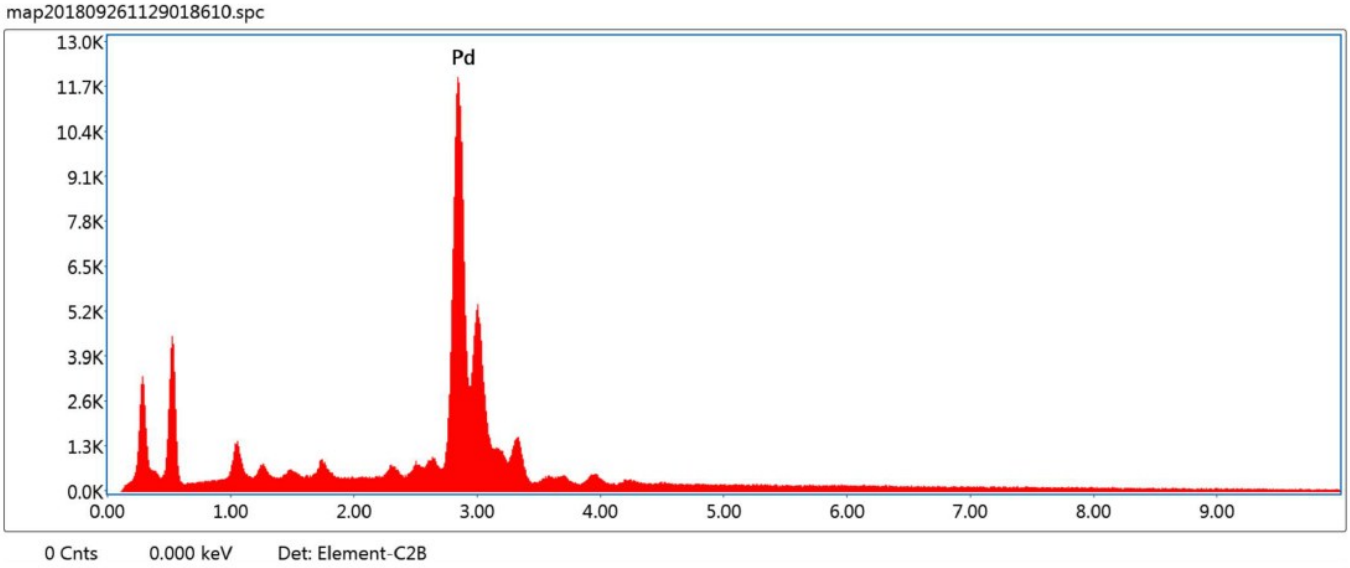
9. EDS Spectra:

9.1. EDS Spectrum of WEPA after Evaporation of Water:

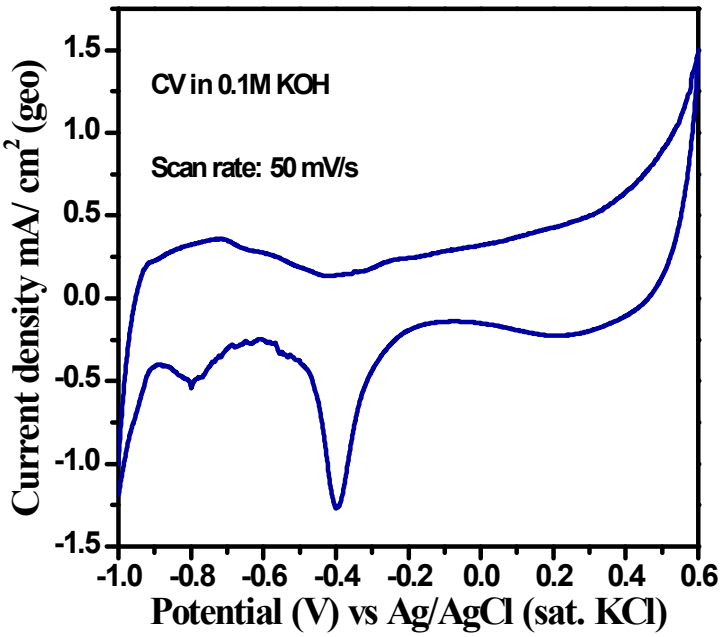


Element	Weight %	Atomic %	Net Int.
C K	5.50	11.03	51.48
O K	33.71	50.80	220.73
MgK	0.52	0.51	12.81
ClK	8.02	5.46	180.27
K K	51.54	31.78	863.52
CaK	0.71	0.43	8.66

9.2. EDS Spectrum of Palladium Separated after the Reaction of **1a**:



10. Cyclic Voltammetric Data of Palladium Separated after the Reaction of 1a:



11. Particle Size Analysis Data of Palladium Separated after the Reaction of 1a: