Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Gram-Scale Synthesis of Aligned C_3N_4-Polypyrrole Heterojuction Aerogel with Tunable Band Structures as an Efficient Visible and Near Infrared Light -Driven Metal-Free Photocatalyst

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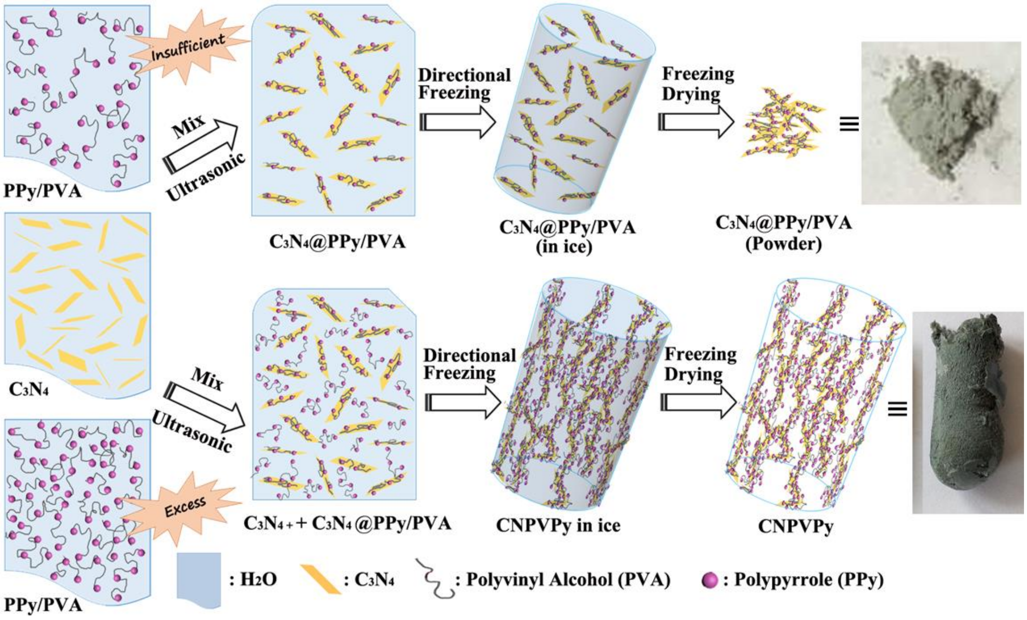


Scheme S1. Proposed formation mechanism of CNPVPy with different amount of PPy/PVA and C_3N_4 by directional freezing.

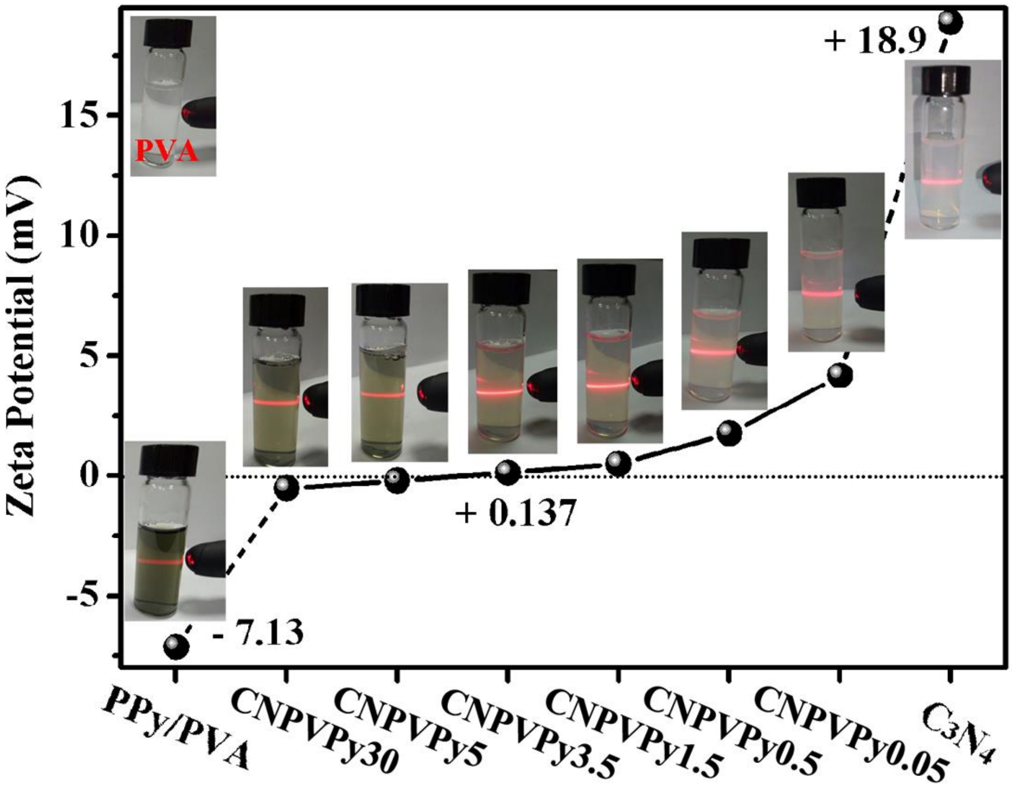


Figure S1. Zeta potential of various mixtures between PPy/PVA and C_3N_4. Insert photo images are the corresponding Tyndall effect. (We denoted CNPVPyx, x is the ratio of PPy/PVA weight to C_3N_4 weight).

As shown in Figure S1, it is observed that PPy/PVA is negative charge, while C_3N_4 is significant positive charge, which is consistent with that of Zhang's work.[1] The zeta potential gradually becomes positive with the increase of C_3N_4 doping amount, indicating the interaction between the two building blocks. Especially, the attachment of less C_3N_4 nanosheets on the surface may explain the slight negative zeta potential in CNPVPy20. This doping amount can not alter the orderly aligned self-assembly structures, which is broadly consistent with the observation by SEM. However, further increase of C_3N_4 doping will exposure more C_3N_4 nanosheets on the archictures, and even destroy the orderly aligned self-assembly property. We carefully drew the synthetic route of CNPVPy in Scheme S1.

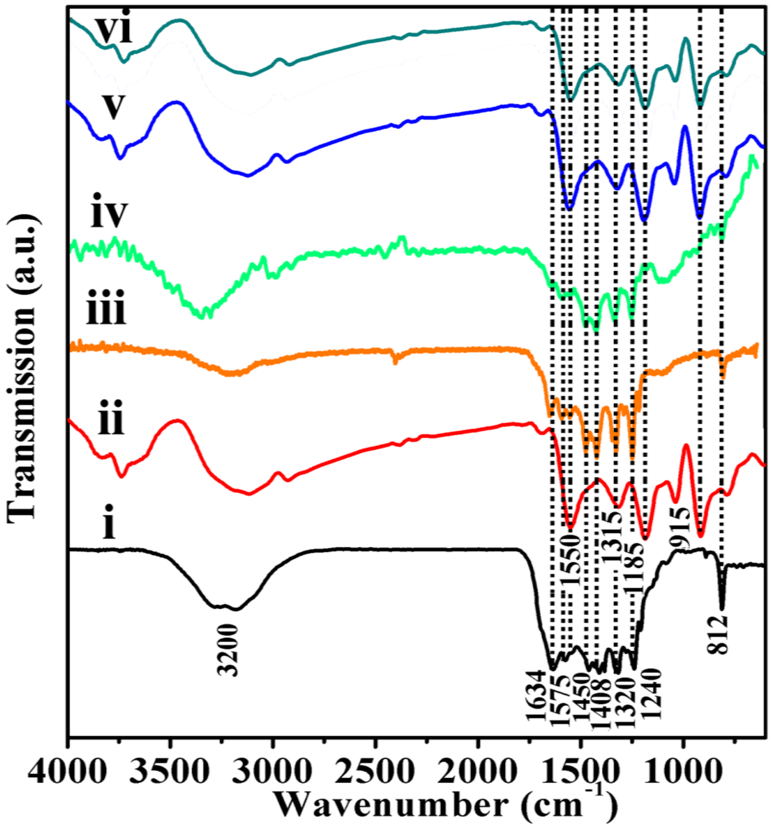


Figure S2. FT-IR spectra of various nanohybrids. (i~vi) C_3N_4, PPy/PVA, CNPVPy0.5, CNPVPy3.5, CNPVPy20, and CNPVPy30.

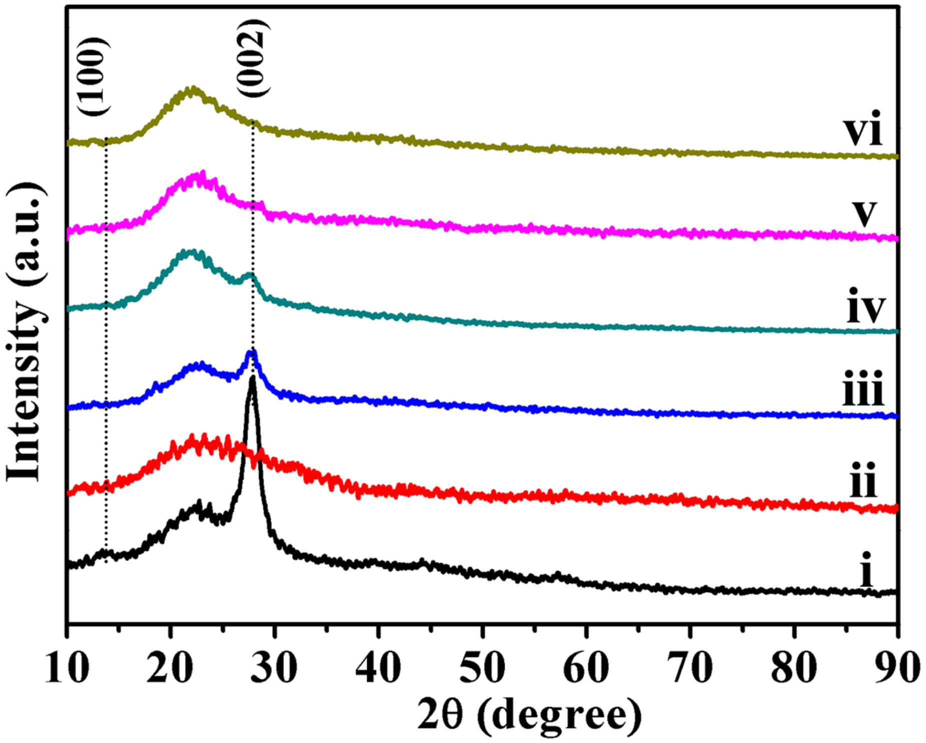


Figure S3. XRD of (i~vi) C_3N_4, PPy/PVA, CNPVPy0.5, CNPVPy3.5, CNPVPy 20, and CNPVPy30.

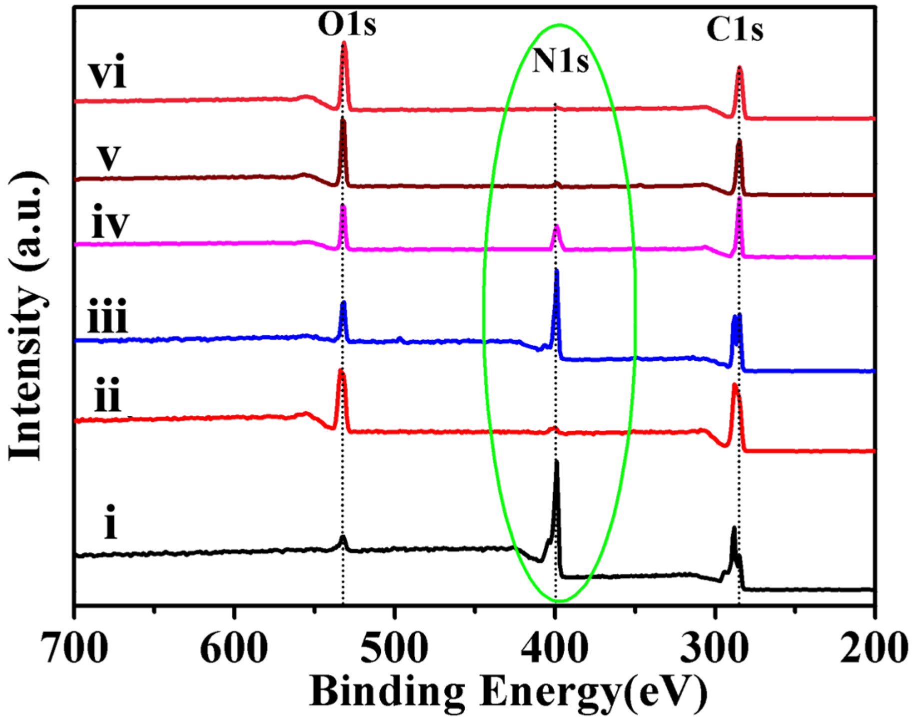


Figure S4. XPS spectra wide scan of (i~vi) C_3N_4, PPy/PVA, CNPVPy0.5, CNPVPy3.5, CNPVPy20, and CNPVPy30.

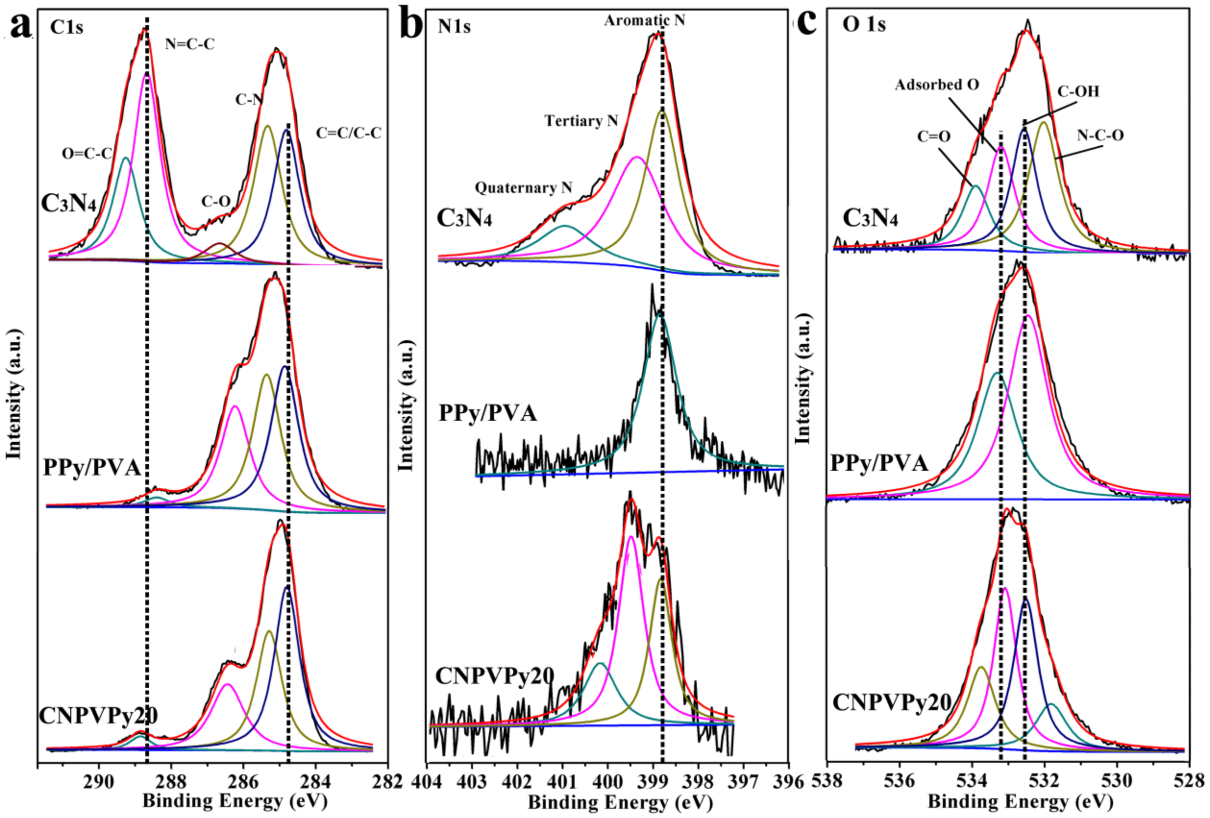


Figure S5. XPS in high-resolution (a) C1s, (b) N1s, and (c) O1s spectra of C_3N_4, PPy/PVA, and CNPVPy20.

The high-resolution XPS survey spectra of C1s, N1s, and O1s were showed in Figure S5. In the primarily C_3N_4 nanosheets, the C1s spectrum (Figure S5a) showed five deconvoluted peaks at 289.6, 288.7, 286.6, 285.8 and 284.8 eV assigning to O=C–C, N=C–C, C–O, C–N, and sp^2-hybridized C–C/C=C species.[2] However, there were only C–O, C–N, and C–C/C=C species in PPy/PVA, and O=C–C, N=C–C, C–O, C–N, and C–C/C=C species in CNPVPy20. In Figure S5b, N1s peak at 400.5, 399.5, and 398.8eV correspond to quaternary N, tertiary N in the form of N–(C)3 or H–N–(C)2, and aromatic N (C=N–C).[2] The O1s core level spectra (Figure S5c) had four distinct components at 533.8, 533.2, 532.4, and 531.6 eV assigning to O=C, adsorbed O, C–OH, and O–C–N.[2]

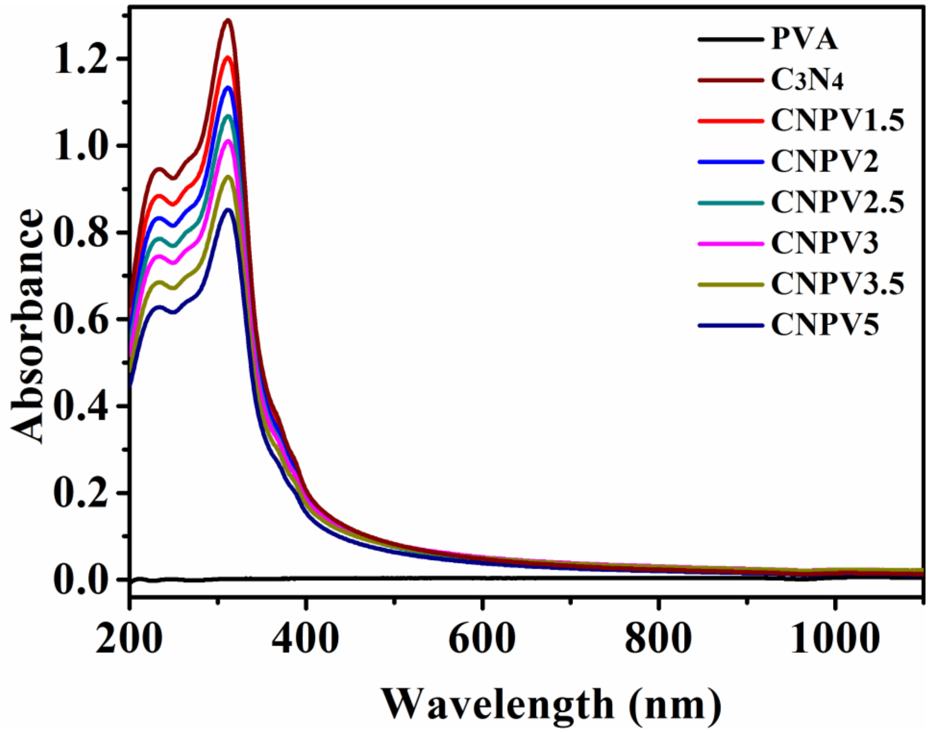


Figure S6. UV-vis-NIR spectra of PVA, C$_3$N$_4$, and CNPV in water.

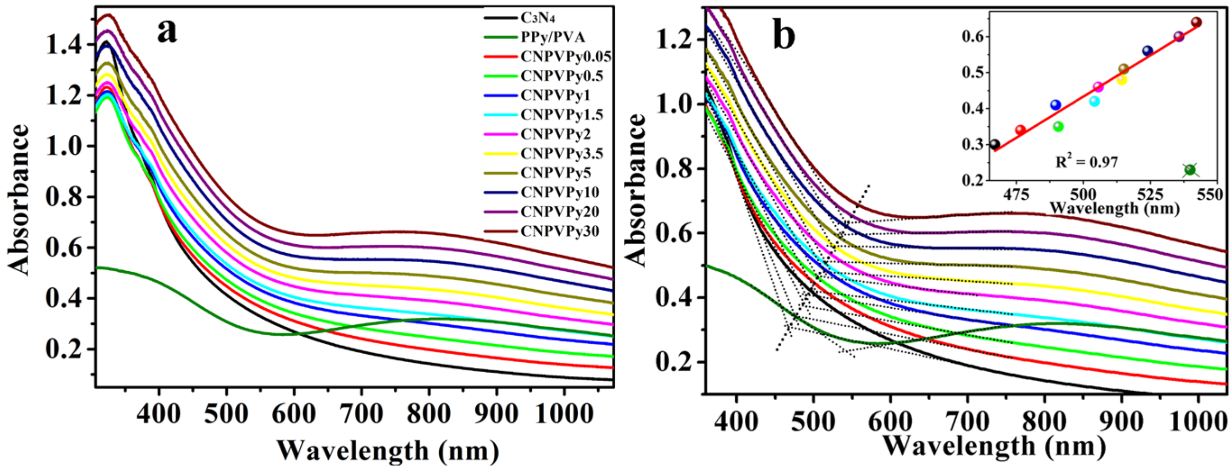


Figure S7. (a) UV-vis-NIR spectra and (b) the corresponding partial enlarged detail of C$_3$N$_4$, PPy/PVA, and CNPVPy composites in water when fixed volumes of PPy/PVA suspension and different volumes of C$_3$N$_4$ suspension were used. Insert of (b) is the linear fitting of absorption edge *vs* wavelength.

The UV-vis-NIR absorption spectra for the CNPVPy are shown in Figure S7. With the increase of PPy/PVA content to C_3N_4 suspension, the absorption intensity in the whole UV-vis-NIR range of CNPVPy heightened. In Figure S7b, the absorption edge is estimated by the intersection point of the tangent of the curves and the abscissa. For bare C_3N_4 and PPy/PVA, the absorption edge is 460 nm and 546 nm, respectively. With the increase of PPy/PVA content to C_3N_4 suspension, the absorption edge gradually red shift, indicating that the E_g of the macrosturctures gradually decrease. It is reasonable that the E_g of each component will be almost constant when the heterojunction is formed between two components.[2, 3] That is, the red-shift of the E_g for CNPVPyx demonstrated the intrinsic heterojunction in this macrostructures. Especially, the absorption edge at ~535 nm of CNPVPy20 is almost the same of PPy/PVA (546 nm), which encouraged us to use CNPVPy20 as enhanced photocatalyst.

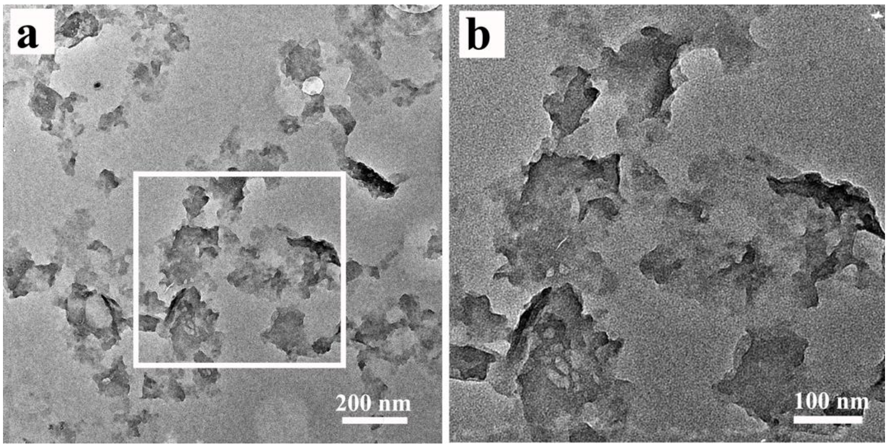


Figure S8. TEM images of C_3N_4 nanosheets.

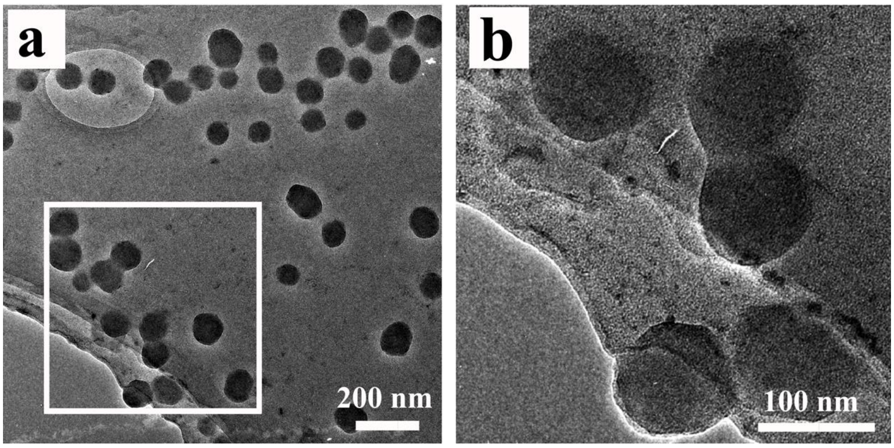


Figure S9. TEM image of PPy/PVA.

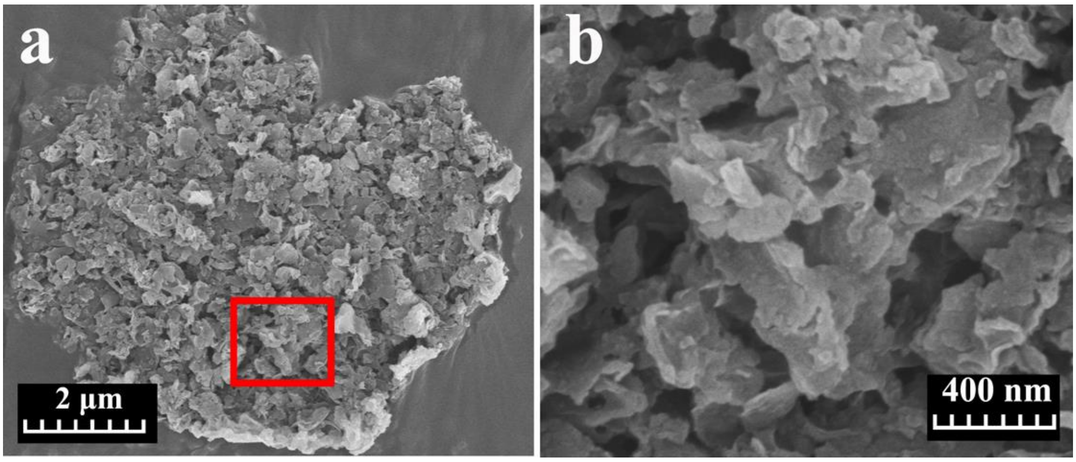


Figure S10. SEM images of C_3N_4 nanosheets.

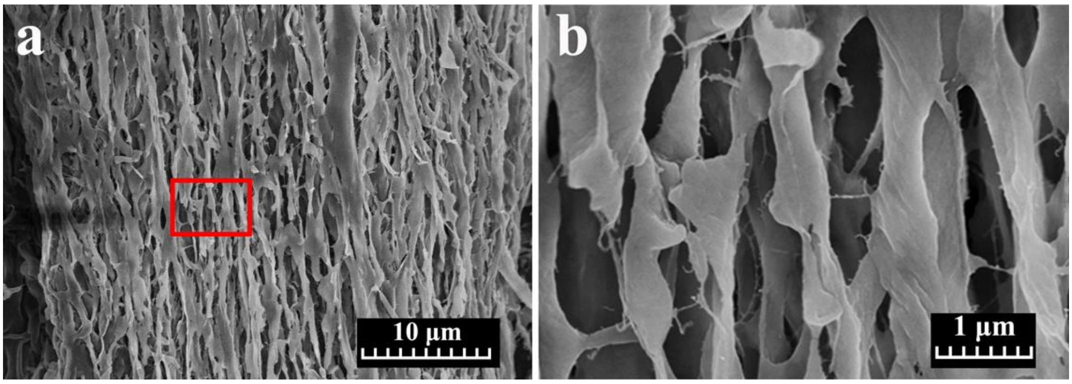


Figure S11. SEM images of orderly aligned self-assembly composites PVA.

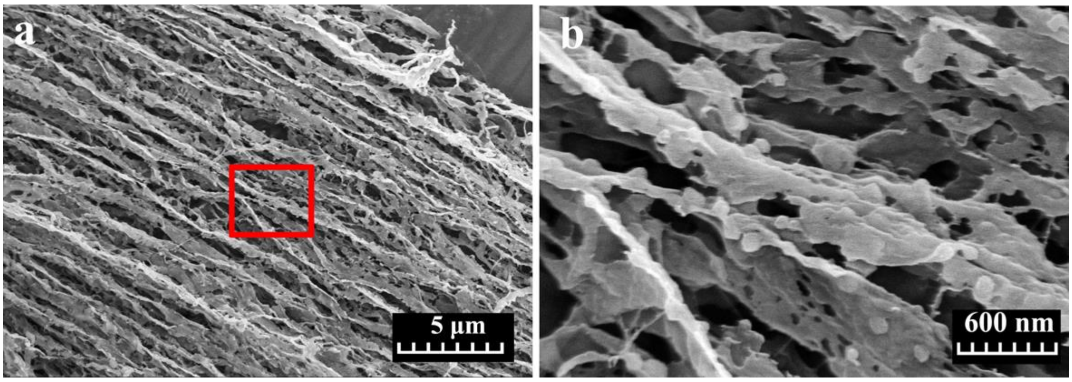


Figure S12. SEM images of orderly aligned self-assembly composites PPy/PVA.

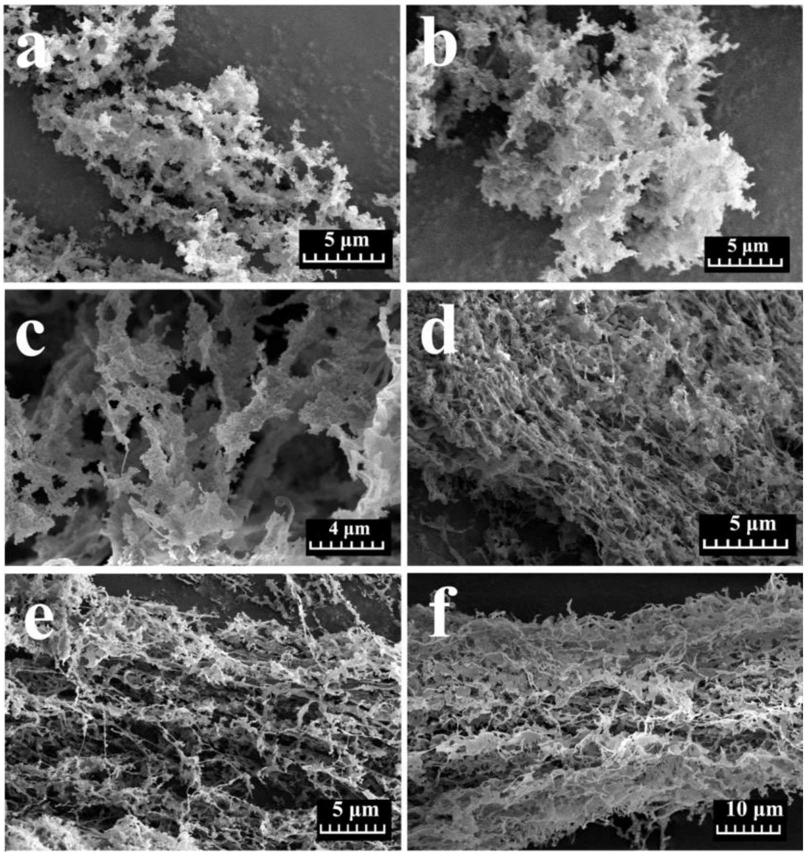


Figure S13. SEM images of self-assembly composites CNPVPy by directional freezing into liquid nitrogen at a uniform rate of 5 mm·min^{-1}. (a~ f) CNPVPy0.05, CNPVPy0.2, CNPVPy0.35, CNPVPy0.5, CNPVPy0.7, CNPVPy1.

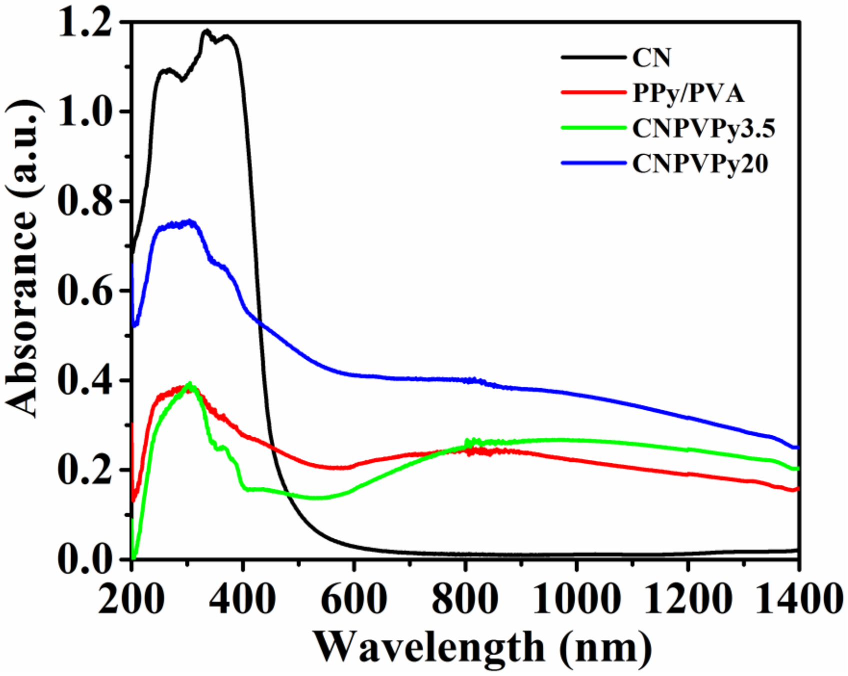


Figure S14. UV-vis-NIR diffuse reflectance spectra (UV-vis-NIR DRS) of C_3N_4 nanosheets, PPy/PVA, CNPVPy3.5, and CNPVPy20.

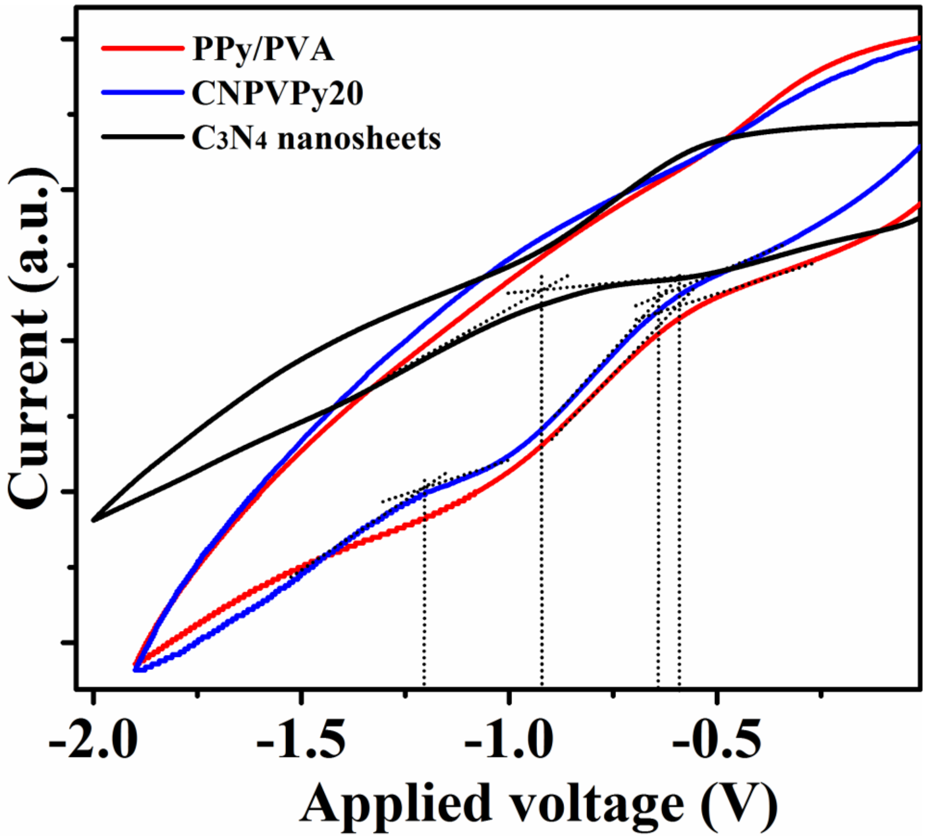
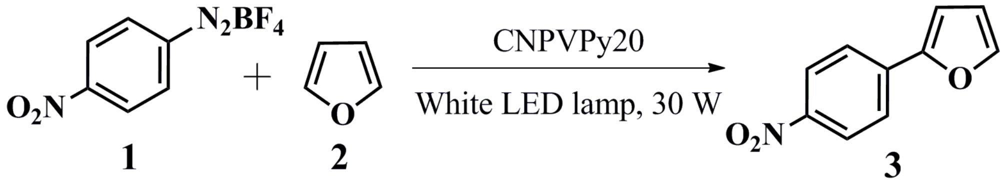


Figure S15. Reduction cyclic voltammograms (CV) of C_3N_4 nanosheets, PPy/PVA, and CNCPVPy20.

In Figure S15, using ferrocene as the reference material in CV analysis, the E_{red} of C_3N_4 nanosheets was determined to be −0.91 V.[4] The corresponding E_{LUMO} was −0.91 V. Combined the E_{red} with the optical energy band gap (E_g = 2.77 eV), we calculated the E_{HOMO} to be +1.86 V. Similarly, E_{LUMO} of PPy was determined to be −0.59 V, and the corresponding E_{HOMO} to be +1.65 V. After contacting with each other in CNPVPy20, the E_{LUMO} of C_3N_4 and PPy turned to −0.64 V and −1.20 V, respectively. Thus, the corresponding E_{HOMO} were calculated to be +2.05 V and +0.89 V.

Table S1. Optimization of Reaction Conditions.



Entry	T (h)	Solvent	Light	Yield (%)[d]
1	0.5	EtOH	+	20%
2	1.0	EtOH	+	95%
3	2.0	EtOH	+	50%
4	3.0	EtOH	+	38%
5	1.0	MeOH	+	78%
6	1.0	H_2O	+	26%
7	1.0	CH_3CN	+	32%
8	1.0	THF	+	16%
9	2.0	EtOH	-	12%
10	1.0	EtOH	-, 60 °C	56%

Reaction condition: CNPVPy20 (5 mg), **1** (0.1 mmol), **2** (1 mL), EtOH (2 mL), irradiation with white LED lamp (30 W). Yields of products were determined by GC.

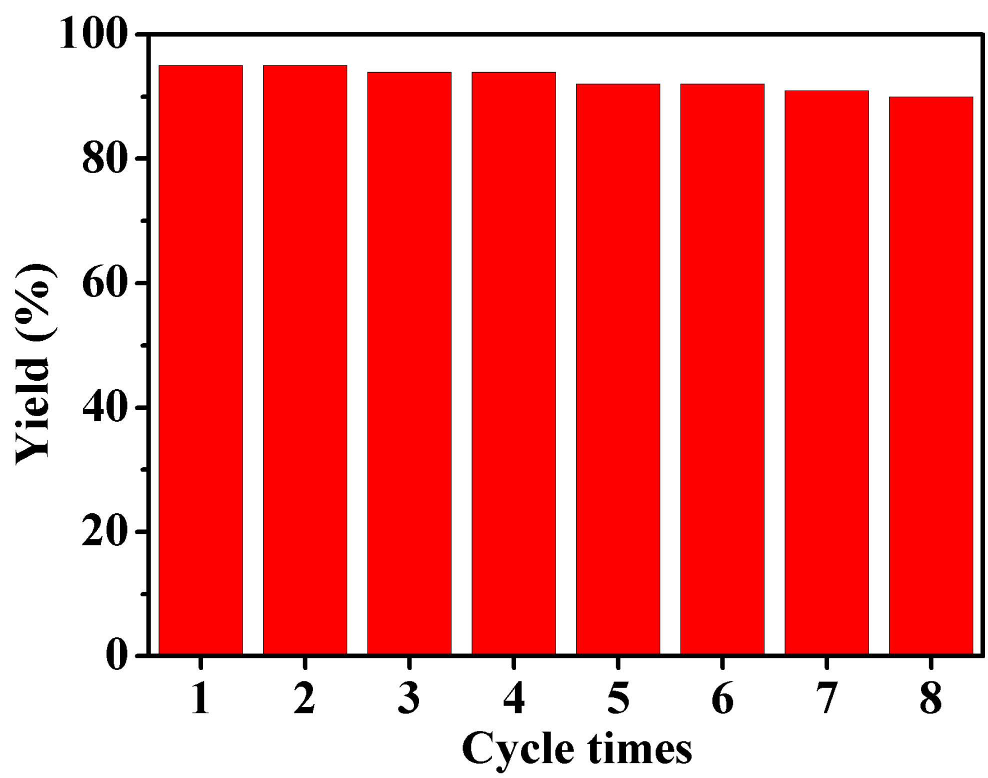


Figure S16. Recycling abilities of CNPVPy20 for the reaction under visible light irradiation.

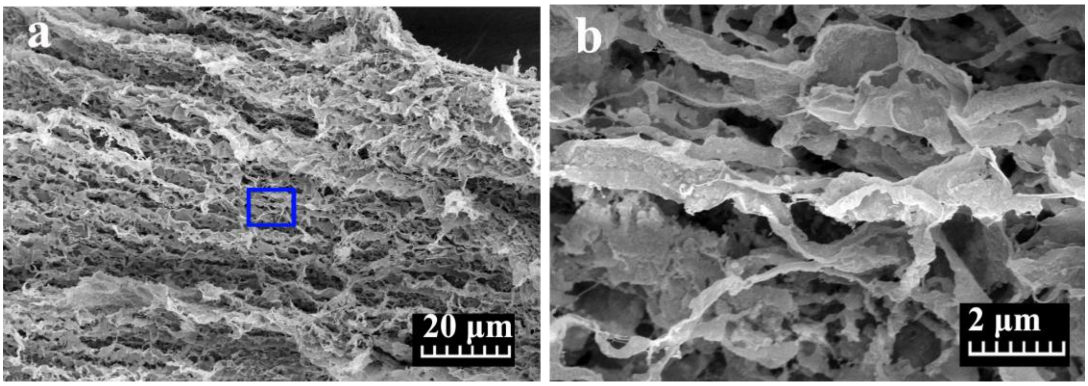


Figure S17. Typical SEM image of reused CNPVPy20 after 8th photocatalytic cycles.

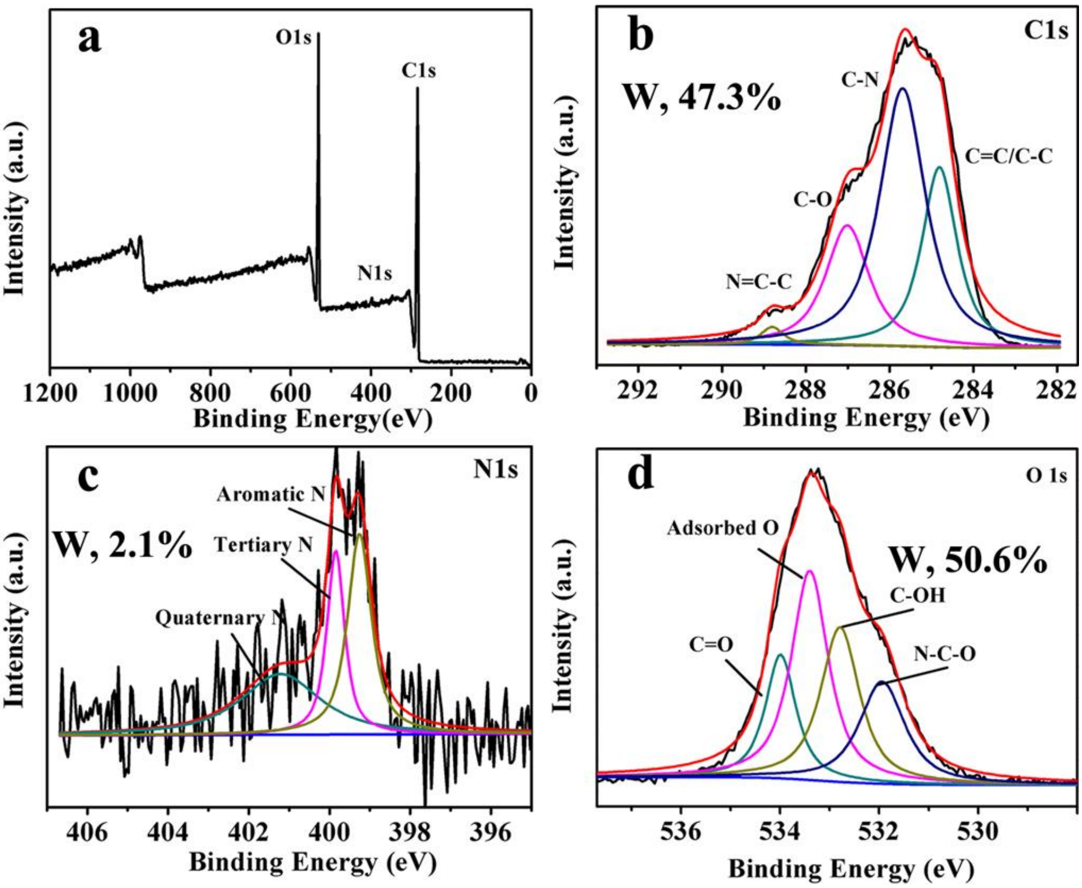


Figure S18. XPS in wide scan (a), and in high-resolution (b) C1s, (c) N1s, (d) O1s spectra of CNPVPy20 after 8th recycle.

In Figure S18, XPS depth analysis indicated that the contents of C, N and O in the CNPVPy20 after 8th recycle are 47.3%, 2.1%, and 50.6%, respectively, which is similar to that in primary CNPVPy20. (C 46.4%, N 1.2%, and O 52.4% in Figure 1c) The negligible change of elements in XPS analysis suggest the stability of CNPVPy20 in this reaction system, which is consistent with the results of SEM in Figure 8a and S17.

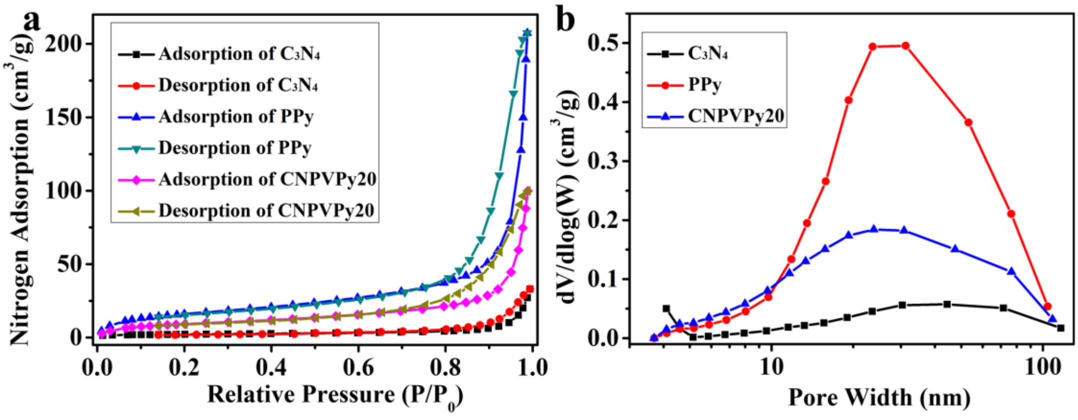


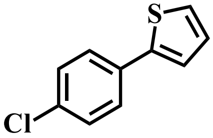
Figure S19. (a) Nitrogen adsorption and desorption isotherms and (b) pore size distribution of C_3N_4, PPy, and CNPVPy20.

Table S2. Summary of parameters from N_2 adsorption-desorption isotherms.

Sample	BET Surface Area (m^2/g)	Average Pore Size (nm)	Pore Volume (cm^3/g)
C_3N_4	9.4449	23.0648	0.054461
PPy	59.2950	22.4376	0.332609
CNPVPy20	35.3874	18.3170	0.162048

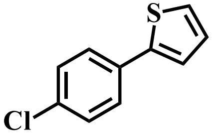
Characterization of synthesized products:

2-(4-Chlorophenyl)furan[5]



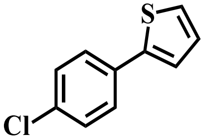
^1H-NMR (400 MHz, $CDCl_3$): δ/ppm 7.62-7.59 (m, 2H), 7.48-7.47 (m, 1H), 7.37-7.34 (m, 2H), 6.65-6.64 (m, 1H), 6.49-6.48 (m, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$): *δ*/ppm 153.0, 142.4, 133.0, 129.4, 129.0, 125.1, 111.9, 105.5.

2-(4-Bromophenyl)furan[5]



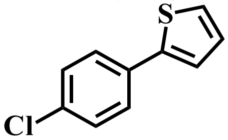
^1H-NMR (400 MHz, $CDCl_3$): δ/ppm 7.54-7.48 (m, 4H), 7.47-7.46 (m, 1H), 6.65-6.64 (m, 1H), 6.48-6.46 (m, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$): *δ*/ppm 153.0, 142.5, 131.9, 129.9, 125.4, 121.2, 111.9, 105.7.

2-(4-Fluorophenyl)furan[6]



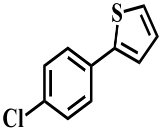
^1H-NMR (400 MHz, $CDCl_3$): δ/ppm 7.67-7.64 (m, 2H), 7.48-7.47 (m, 1H), 7.13-7.07 (m, 2H), 6.60 (m, 1H), 6.49-6.48 (m, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm 163.4, 161.0, 153.2, 142.0, 127.3, 125.6, 115.7, 111.8, 104.7.

2-(4-Nitrophenyl)furan[5]



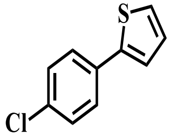
^1H-NMR (400 MHz, $CDCl_3$): *δ*/ppm 8.24-8.22 (d, *J* = 8 Hz, 2H), 7.78-7.76 (d, *J* = 8 Hz, 2H), 7.56 (m, 1H), 6.88-6.87 (*J* = 4 Hz, 1H), 6.55-6.54 (m, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$): *δ*/ppm 151.7, 146.4, 144.2, 136.5, 124.4, 124.0, 112.5, 109.1.

2-Phenylfuran[5]



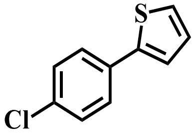
^1H-NMR (400 MHz, $CDCl_3$): δ/ppm 7.68-7.66 (m, 2H), 7.4-7.44 (m, *J* = 8 Hz 1H), 7.39-7.35 (m, 2H), 7.26-7.24 (m, 1H), 6.64-6.63 (m, *J* = 4 Hz, 1H), 6.46-6.45 (m, *J* = 4 Hz, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$): *δ*/ppm 154.1, 142.2, 131.0, 128.8, 127.4, 123.9, 111.8, 105.1.

2-(2-Methylphenyl) furan[7]



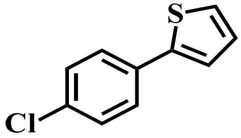
^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm 7.70-7.68 (m, 1H), 7.50-7.49 (m, 1H), 7.25-7.20 (m, 3H), 6.54-6.53 (m, 1H), 6.50-649 (m,1H), 2.491 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$): *δ*/ppm 153.6, 141.8, 134.7, 131.3, 130.3, 127.6, 127.1, 126.1, 111.4, 108.6, 22.0.

2-(4-Methylphenyl) furan[5]



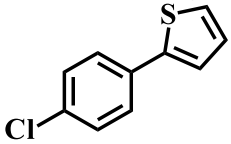
^{1}H-NMR (400 MHz, $CDCl_3$): *δ*/ppm 7.56 (d, *J* = 8 Hz, 2H), 7.42-7.41 (m, 1H), 7.17 (d, *J* = 8 Hz, 2H), 6.57-6.56 (m, 1H), 6.44-6.42 (m, 1H), 2.332(s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$): *δ*/ppm 154.3, 141.8, 137.2, 129.5, 128.3, 123.8, 111.7, 104.3, 21.4.

2-(4-Methoxyphenyl)furan[5]



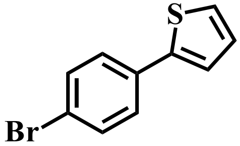
^{1}H-NMR (400 MHz, $CDCl_3$): *δ*/ppm 7.64 (d, *J* = 8 Hz, 2H), 7.46 (m, 1H), 6.95 (d, *J* = 8 Hz, 2H), 6.55-6.54 (m, 1H), 6.48-6.47 (m, 1H), 3.84 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$): *δ*/ppm 159.1, 154.1, 141.5, 125.3, 124.1, 114.2, 111.7, 103.5, 55.4.

2-(4-Chlorophenyl)thiophene[8]



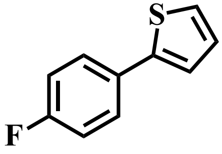
^{1}H-NMR (400 MHz, $CDCl_3$): *δ*/ppm 7.50-7.52 (m, 2H), 7.31-7.38 (m, 2H), 7.24-7.27 (m, 2H), 7.04-7.07 (m, 1H);
^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm 143.2, 133.7, 133.0, 129.1, 128.3, 127.2, 125.3, 123.6.

2-(4-Bromophenyl)thiophene[9]



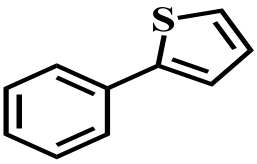
^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm 7.51-7.48 (m, 4H), 7.31-7.30 (d, *J* = 4 Hz, 2H), 7.09-7.07 (m, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm 143.2, 133.4, 132.1, 128.4, 127.5, 125.4, 123.6, 121.4.

2-(4-Fluorophenyl) thiophene[8]



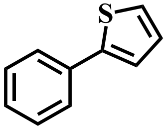
^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm 7.59-7.42 (m, 3H), 7.27-7.23 (m, 1H), 7.09-7.05 (m, 2H), 7.03-6.99 (m, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm 163.9, 161.5, 153.2, 142.0, 132.2, 128.1, 127.6, 116.5.

2-(4-Nitrophenyl)thiophene[10]



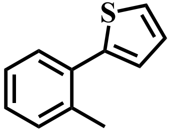
^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm 8.25-8.22 (m, 2H), 7.76-7.72 (m, 2H), 7.49-7.47 (m, 1H), 7.45-7.44 (m, 1H), 7.17-7.14 (m, 1H).
^{13}C-NMR (100 MHz, CDCl$_3$): δ/ppm 146.6, 141.7, 140.7, 128.8, 127.8, 126.1, 125.8, 124.5.

2-Phenylthiophene[9]



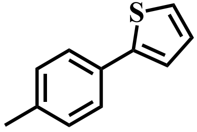
^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm 7.64-7.60 (m, 2H), 7.46-7.37 (m, 3H), 7.33-7.26 (m, 3H).
^{13}C-NMR (100 MHz, CDCl$_3$): δ/ppm 144.5, 134.5, 129.0, 128.1, 127.6, 127.2, 126.6, 126.0.

2-(2-Methylphenyl)thiophene



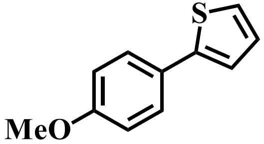
^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm 7.42-7.39 (m, 1H), 7.37-7.30 (m, 2H), 7.22-7.19 (m, 1H), 7.16-7.12 (m, 1H), 7.10-7.06 (m, 2H), 2.43 (s, 3H).
^{13}C-NMR (100 MHz, CDCl$_3$): δ/ppm 143.2, 136.2, 134.3, 130.8, 130.6, 127.9, 127.2, 126.5, 126.0, 125.2, 21.3.

2-(4-Methylphenyl) thiophene



^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm 7.52 -7.49 (m, 3H), 7.37 (d, J = 4 Hz, 1H), 7.22-7.20 (m, 2H), 7.08-7.06 (m, 1H), 2.37(s, 3H).
^{13}C-NMR (100 MHz, CDCl$_3$): δ/ppm 144.7, 137.4, 131.7, 130.0, 129.7, 126.4, 126.0, 114.4, 21.3.

2-(4-Methoxyphenyl) thiophene[11]



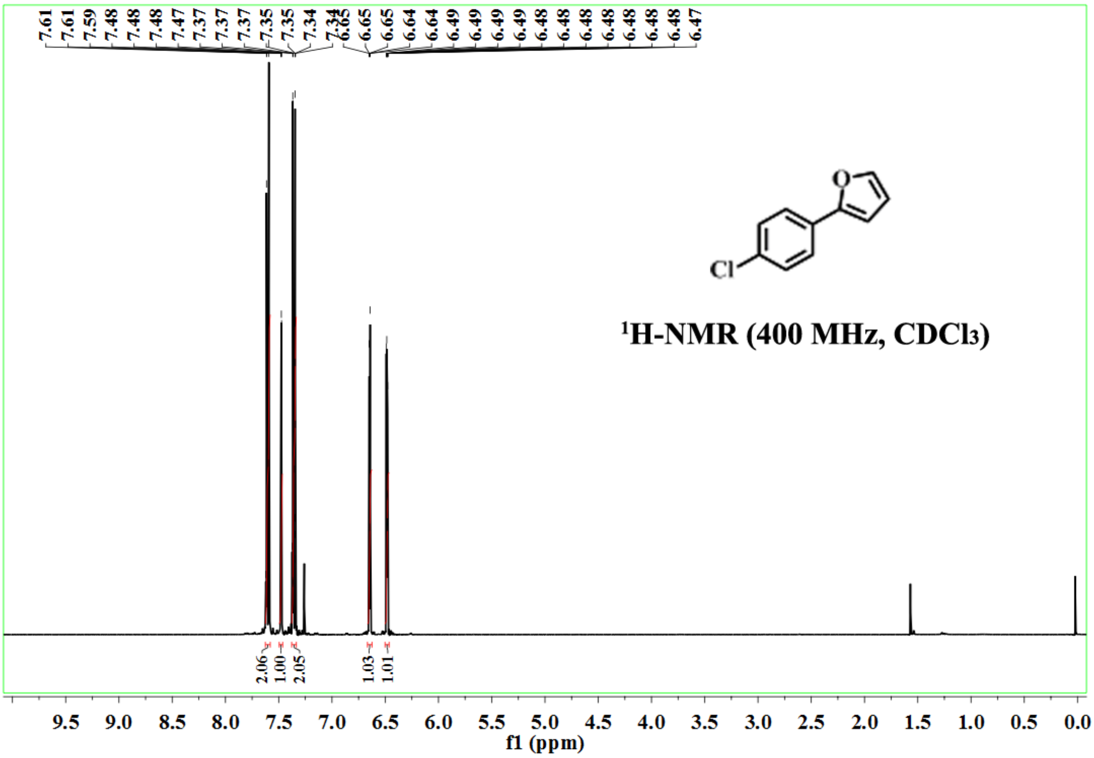
^{1}H-NMR (400 MHz, CDCl$_3$): δ/ppm 7.55-7.53 (m, 2H), 7.46 (m, 1H), 7.23-7.20 (m, 2H), 7.07-7.04 (m, 1H), 6.93-6.91 (m, 2H), 3.84 (s, 3H).
^{13}C-NMR (100 MHz, CDCl$_3$): δ/ppm 155.1, 150.4, 128.0, 127.3, 123.9, 122.2, 114.3, 55.5.

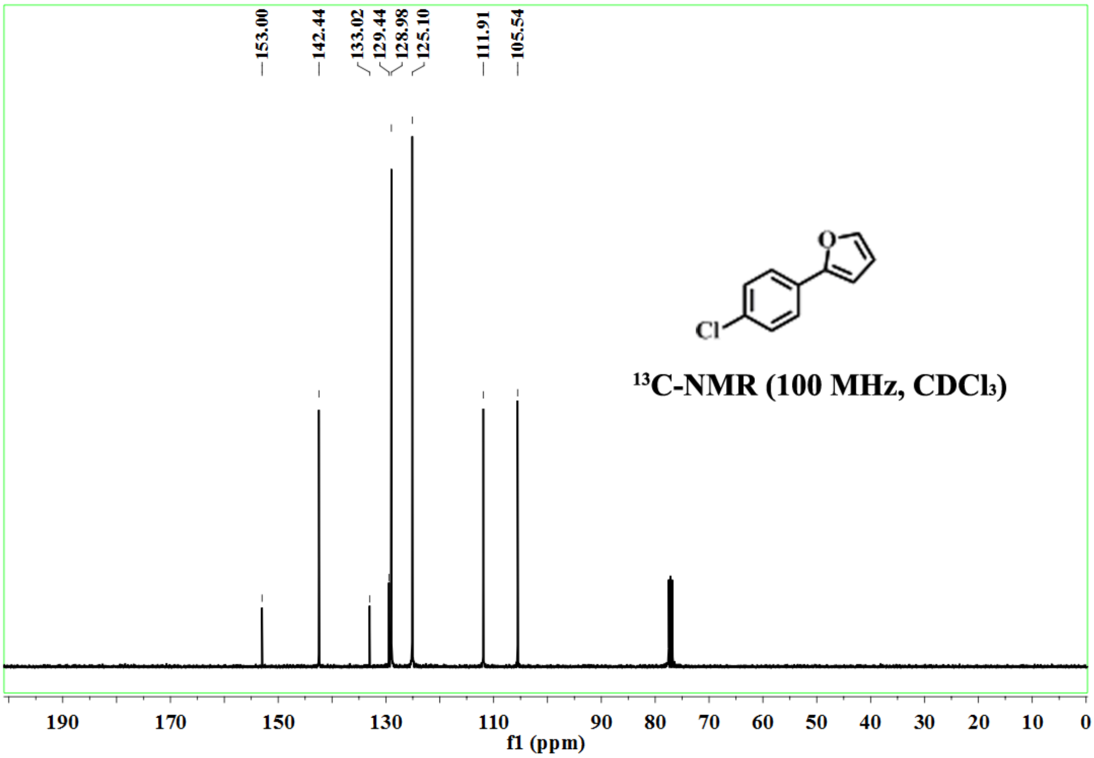
Reference

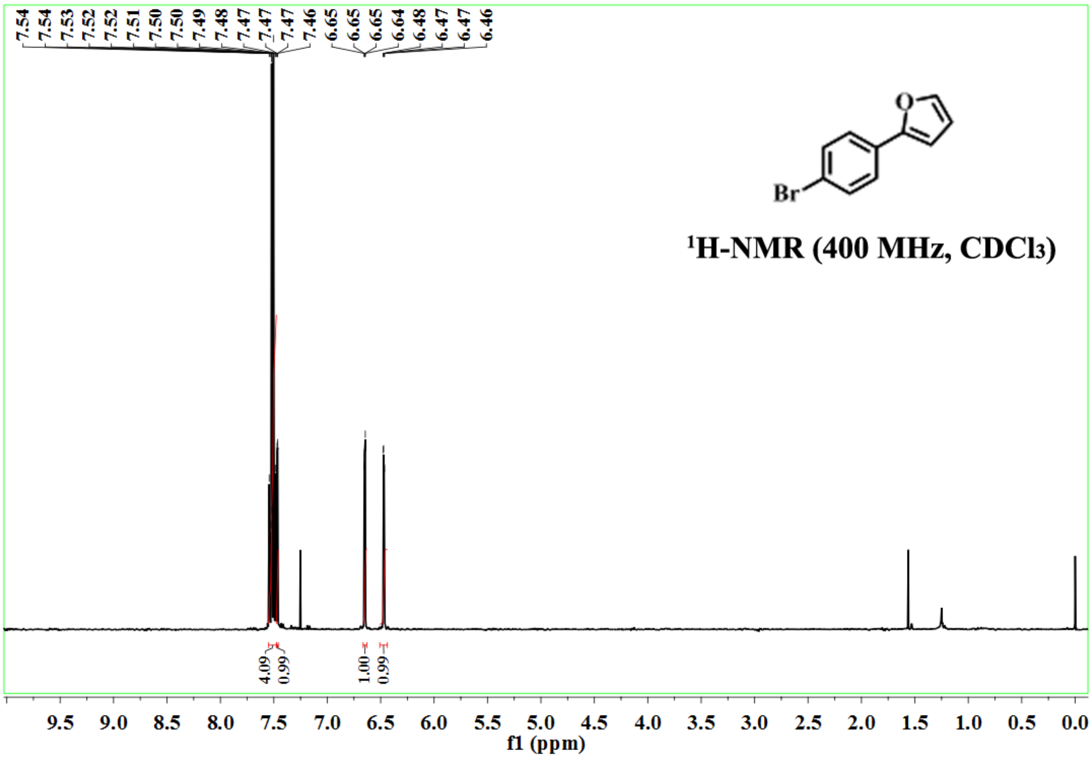
1. G. Li, C. A. Morales-Rivera, Y. Wang, F. Gao, G. He, P. Liu, G. Chen, *Chem. Sci.*, 2016, **7**, 6407.
2. Y. Zhang, A. Thomas, M. Antonietti, X. Wang, *J. Am. Chem. Soc.*, 2009, *131*, 50-51.
3. J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S. Lee, Z. Kang, *Science* 2015, **347**, 970-974.
4. L. Ye, D. Wang, S. Chen, L. Ye, D. Wang, S. Chen, *ACS Appl. Mater. Inter.*, 2016, **8**, 5280-5289
5. Z. Li, A. L. Lui, K. H. Lam, L. Xi, Y. M. Lam, Z. Li, A. L. Lui, K. H. Lam, L. Xi, Y. M. Lam, *Inorg.*

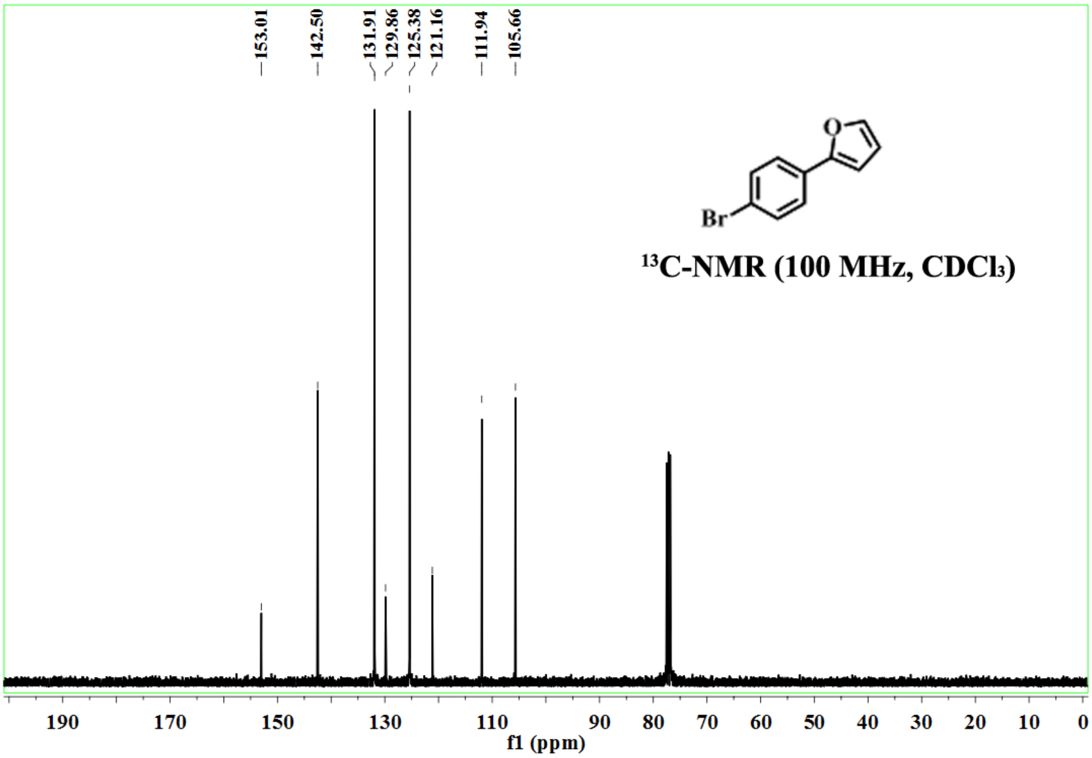
Chem., 2014, **53**, 10874-10880.

6. C. Zhou, P. Chan, C. Che, *Org. Lett.*, 2006, **8**,325-328.
7. S. Guchhait, M. Kashyap, S. Saraf, S. Guchhait, M. Kashyap, S. Saraf, *Synthesis* 2010, **7**, 166-1170.
8. S. Denmark, J. Baird, C. Regens, *J. Org. Chem.*, 2008, **73**, 1440-1455.
9. N. Kuhl, M. N. Hopkinson, F. Glorius, N. Kuhl, M. N. Hopkinson, F. Glorius, *Angew. Chem. Int. Ed.*, 2012, **51**, 8230-8234.
10. N. Uchiyama, E. Shirakawa, R. Nishikawa, T. Hayashi, N. Uchiyama, E. Shirakawa, R. Nishikawa, T. Hayashi, *Chem. Commun.*, 2011, **47**, 11671-11673.
11. J. Li, Y. Liang, D. Wang, W. Liu, Y. Xie, D. Yin, *J. Org. Chem.*, 2005, **70**, 2832-2834.




153.00
142.44
133.02
129.44
128.98
125.10
111.91
105.54
Cl
O
13C-NMR (100 MHz, CDCl3)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.47
7.47
7.47
7.46
6.65
6.65
6.65
6.64
6.48
6.47
6.47
6.46
Br
O
1H-NMR (400 MHz, CDCl3)
4.09
0.99
1.00
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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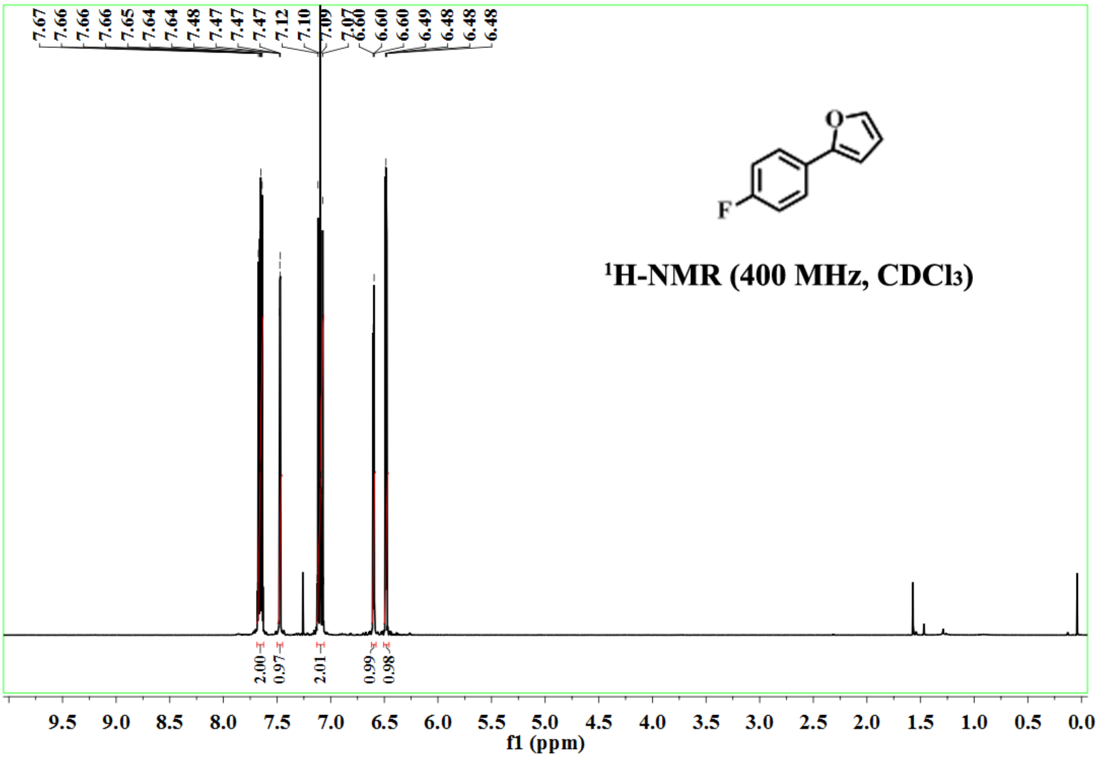
142.50
131.91
129.86
125.38
121.16
111.94
105.66
O
Br
13C-NMR (100 MHz, CDCl3)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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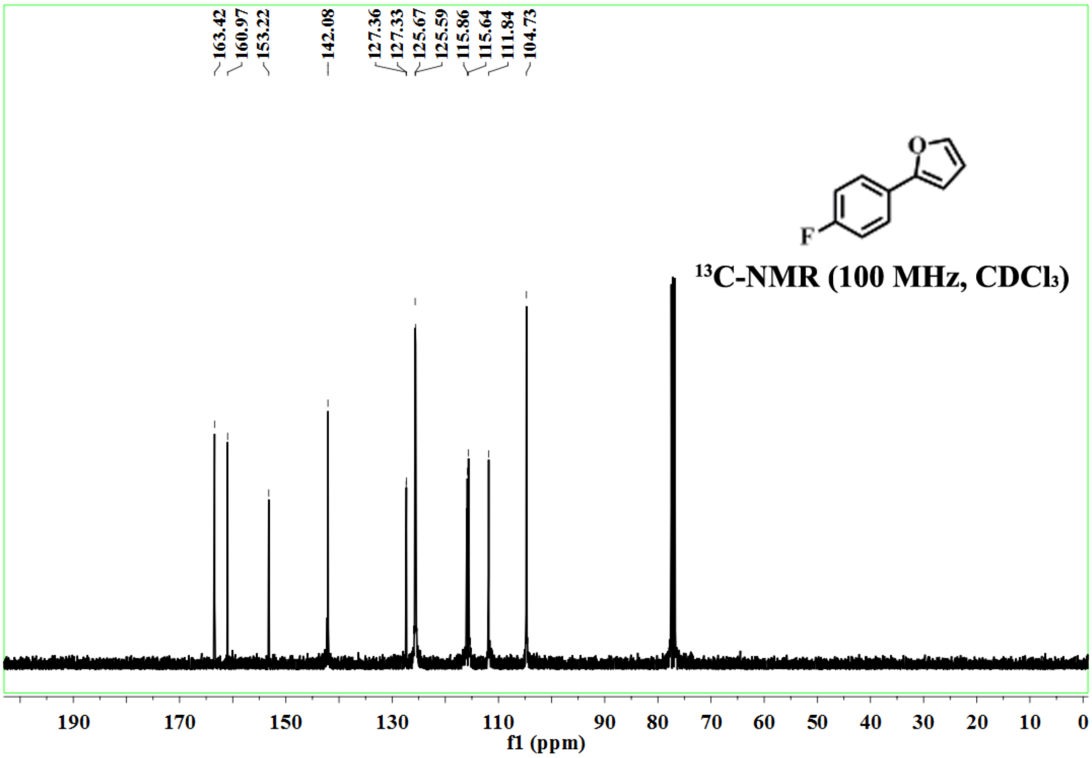
7.66
7.66
7.66
7.65
7.64
7.64
7.48
7.47
7.47
7.47
7.12
7.10
7.09
7.07
6.60
6.60
6.60
6.60
6.49
6.48
6.48
6.48
O
F
1H-NMR (400 MHz, CDCl3)
2.00
0.97
2.01
0.99
0.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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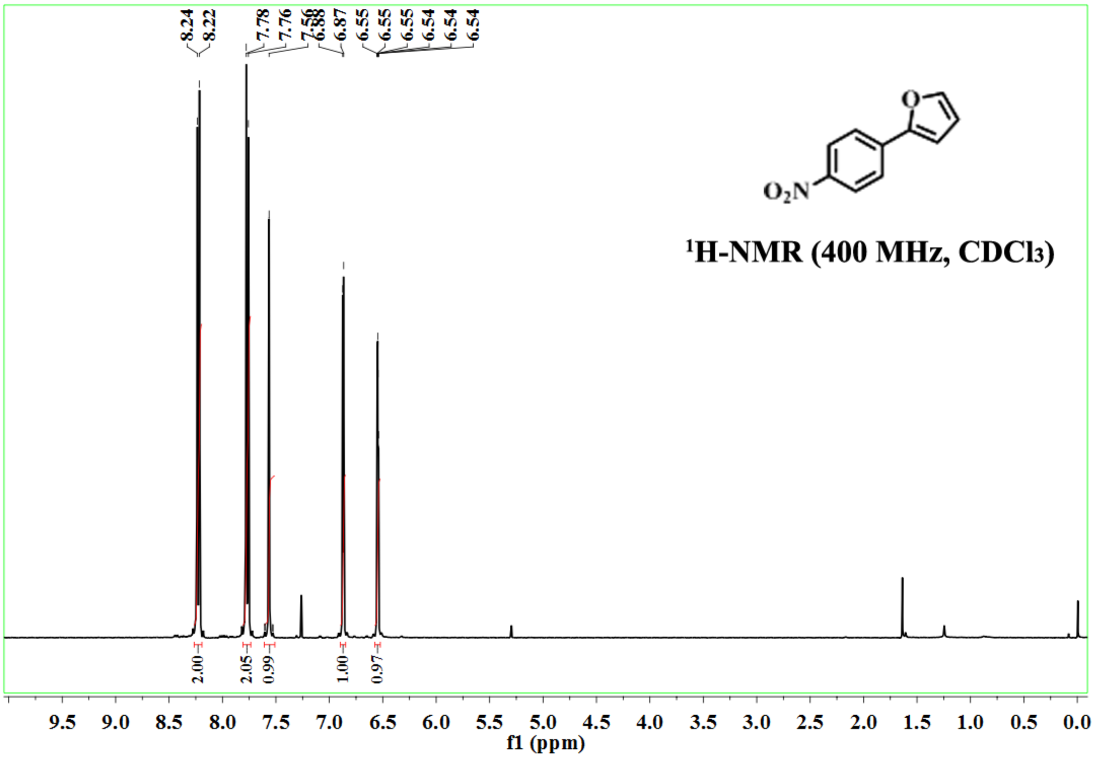
160.97
153.22
142.08
127.36
127.33
125.67
125.59
115.86
115.64
111.84
104.73
F
O
^{13}C-NMR (100 MHz, CDCl$_3$)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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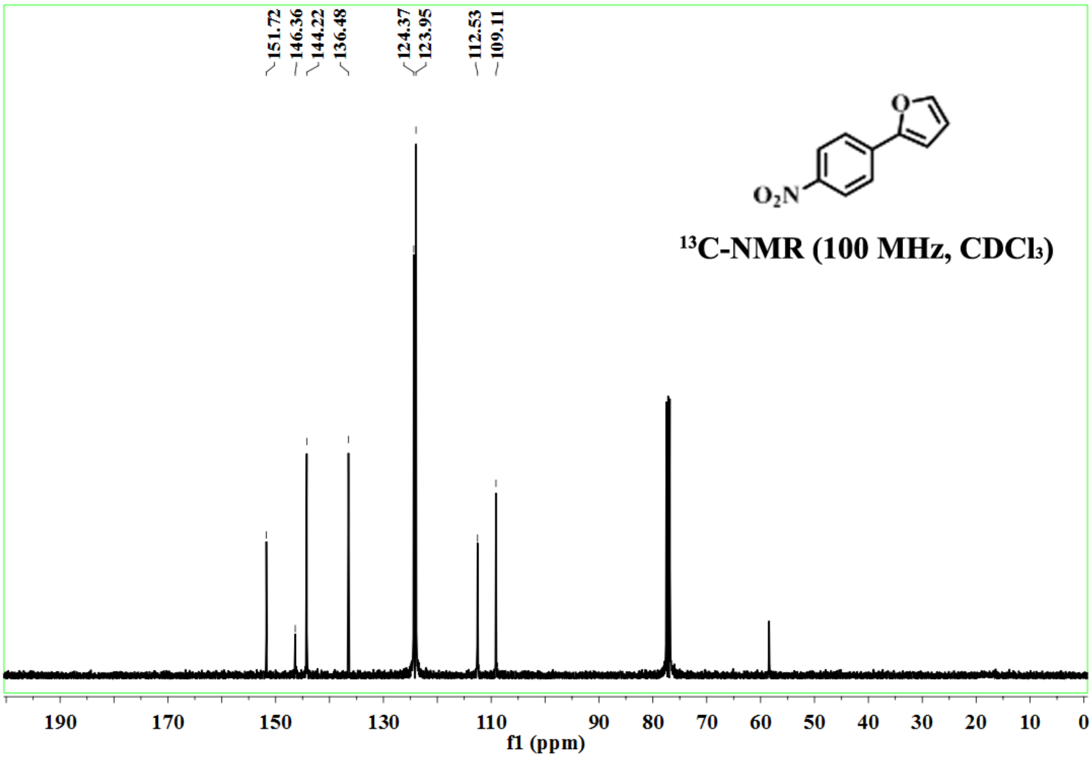
7.76
7.56
6.88
6.87
6.55
6.55
6.55
6.54
6.54
6.54
O
O_2N
^{1}H-NMR (400 MHz, CDCl$_3$)
2.00
2.05
0.99
1.00
0.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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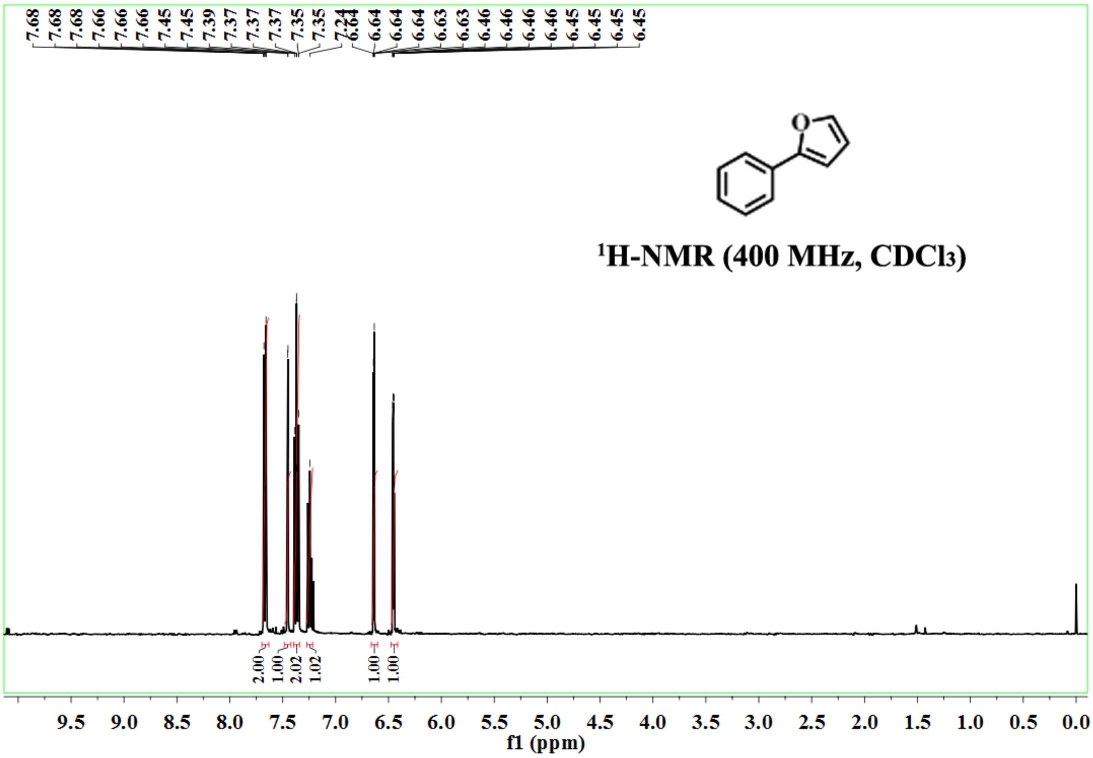
146.36
144.22
136.48
124.37
123.95
112.53
109.11
O
O2N
13C-NMR (100 MHz, CDCl3)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.68
7.68
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7.37
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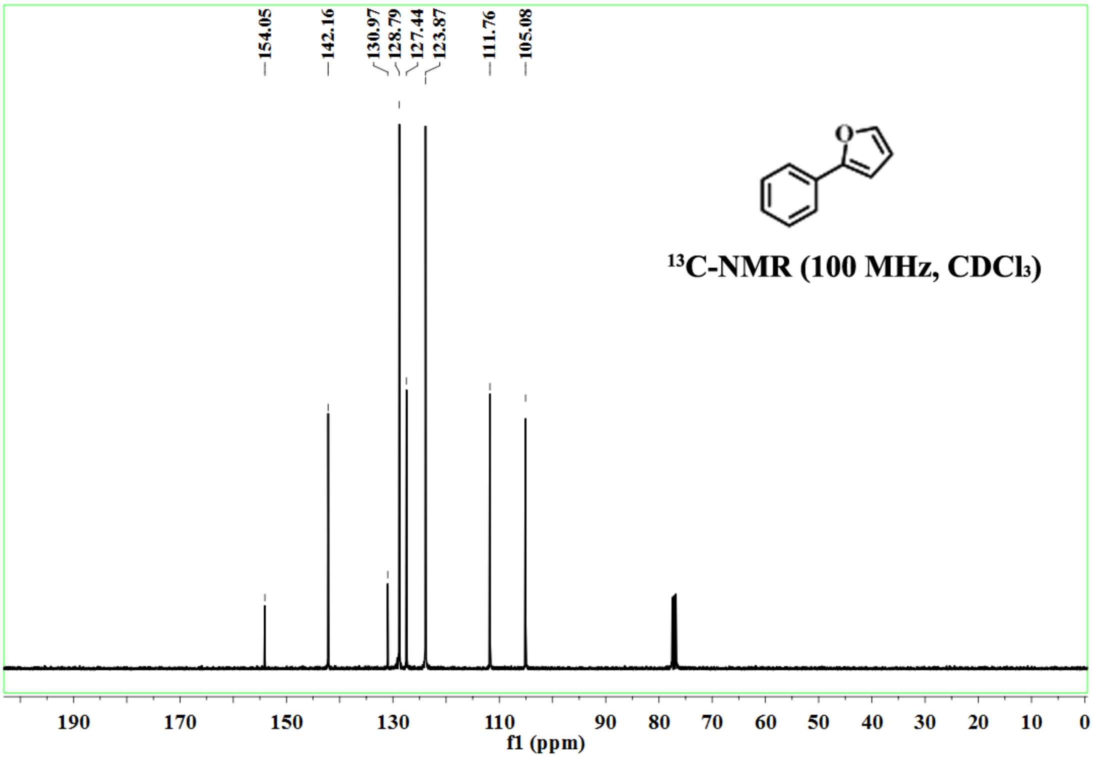
7.35
7.24
6.64
6.64
6.64
6.64
6.63
6.63
6.46
6.46
6.46
6.46
6.45
6.45
6.45
6.45
O
1H-NMR (400 MHz, CDCl3)
2.00
1.00
2.02
1.02
1.00
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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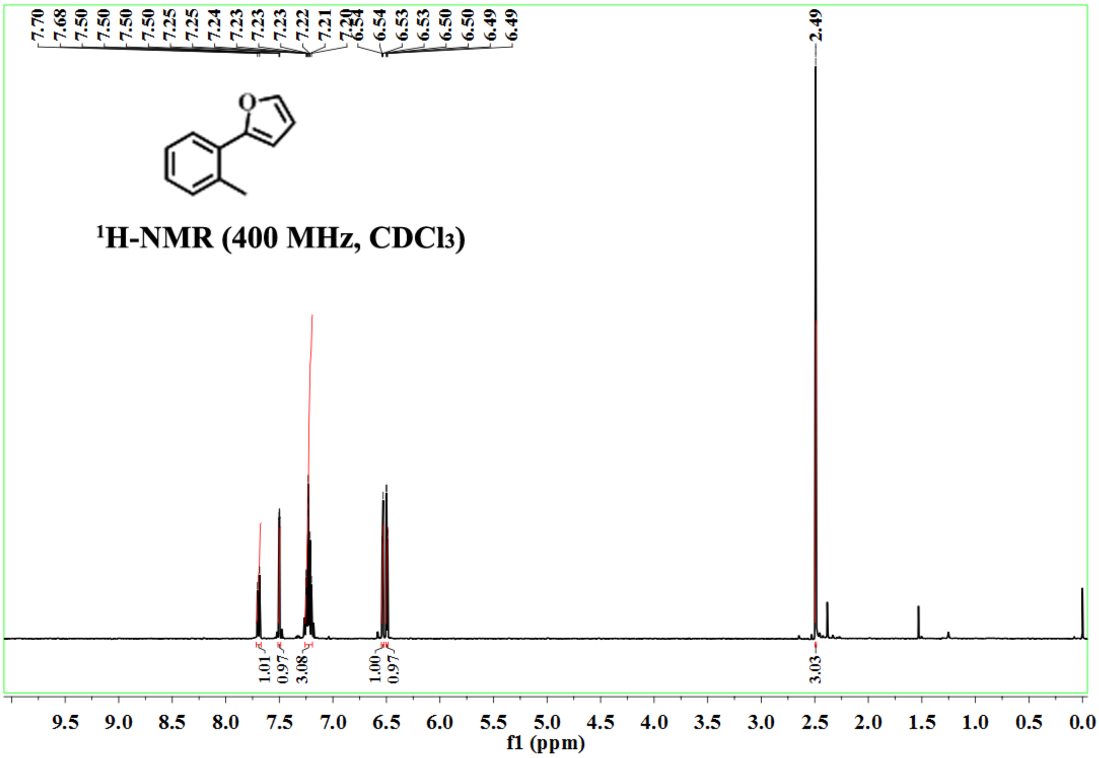
142.16
130.97
128.79
127.44
123.87
111.76
105.08
^{13}C-NMR (100 MHz, CDCl$_3$)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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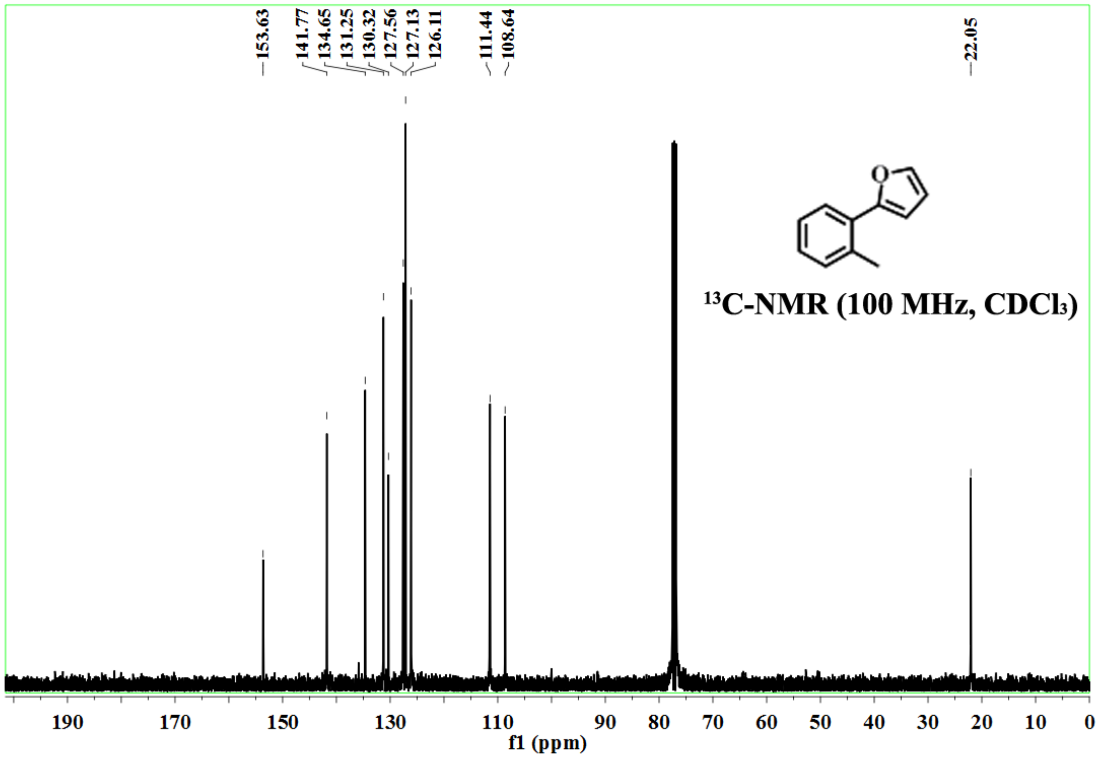
7.23
7.23
7.23
7.22
7.21
7.20
6.54
6.54
6.53
6.53
6.50
6.50
6.49
6.49
2.49
^{1}H-NMR (400 MHz, CDCl$_3$)
1.01
0.97
3.08
1.00
0.97
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.65
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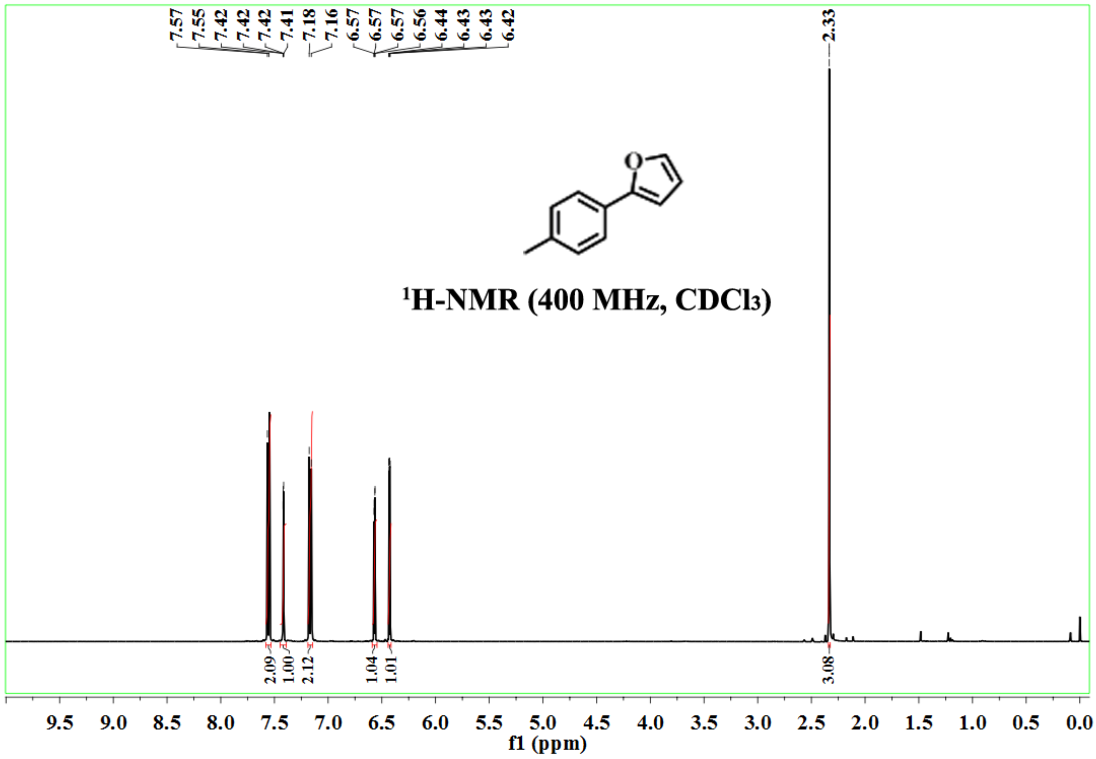
130.32
127.56
127.13
126.11
111.44
108.64
22.05
O
13C-NMR (100 MHz, CDCl3)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.16
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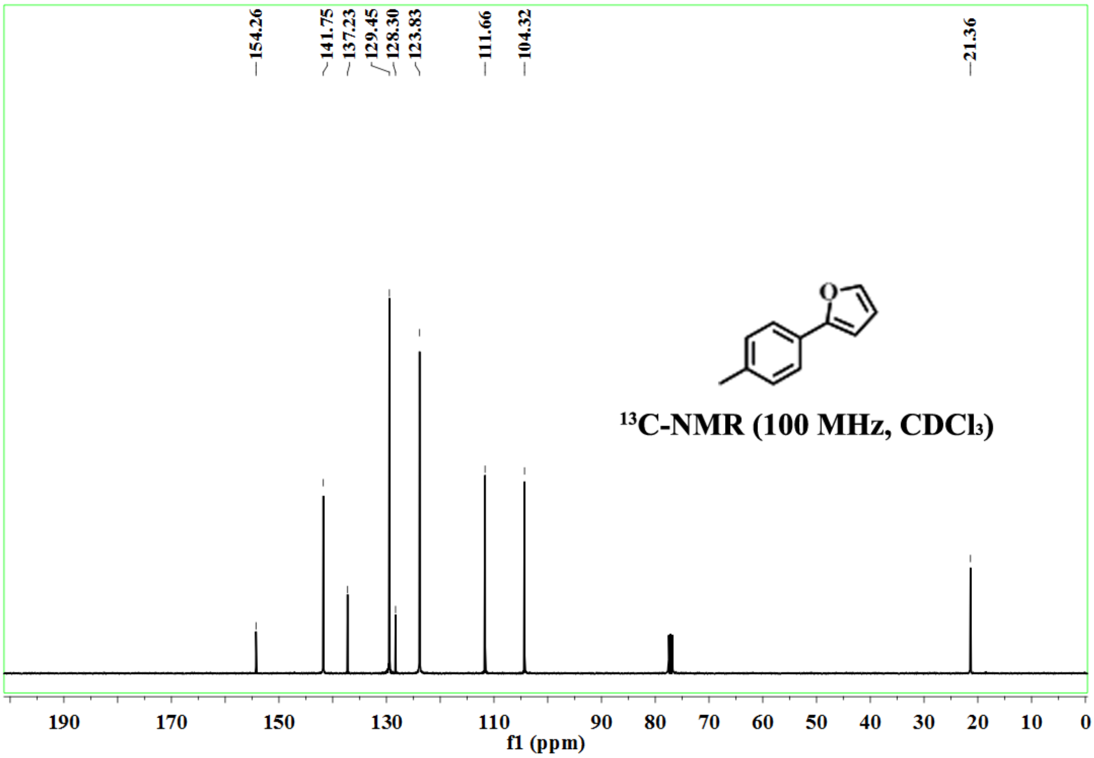
6.57
6.57
6.56
6.44
6.43
6.43
6.42
2.33
O
1H-NMR (400 MHz, CDCl3)
2.09
1.00
2.12
1.04
1.01
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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141.75
137.23
129.45
128.30
123.83
111.66
104.32
21.36
O
^{13}C-NMR (100 MHz, CDCl$_3$)
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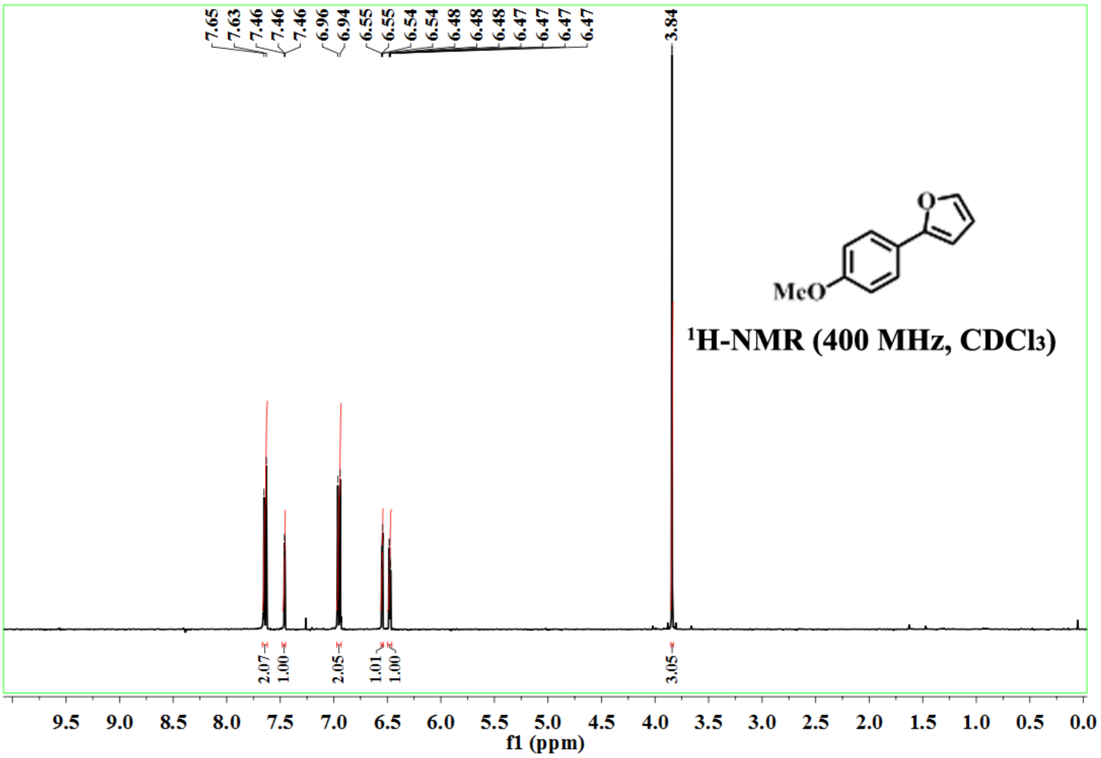
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.54
6.54
6.48
6.48
6.48
6.47
6.47
6.47
6.47
3.84
O
MeO
^{1}H-NMR (400 MHz, CDCl$_3$)
2.07
1.00
2.05
1.01
1.00
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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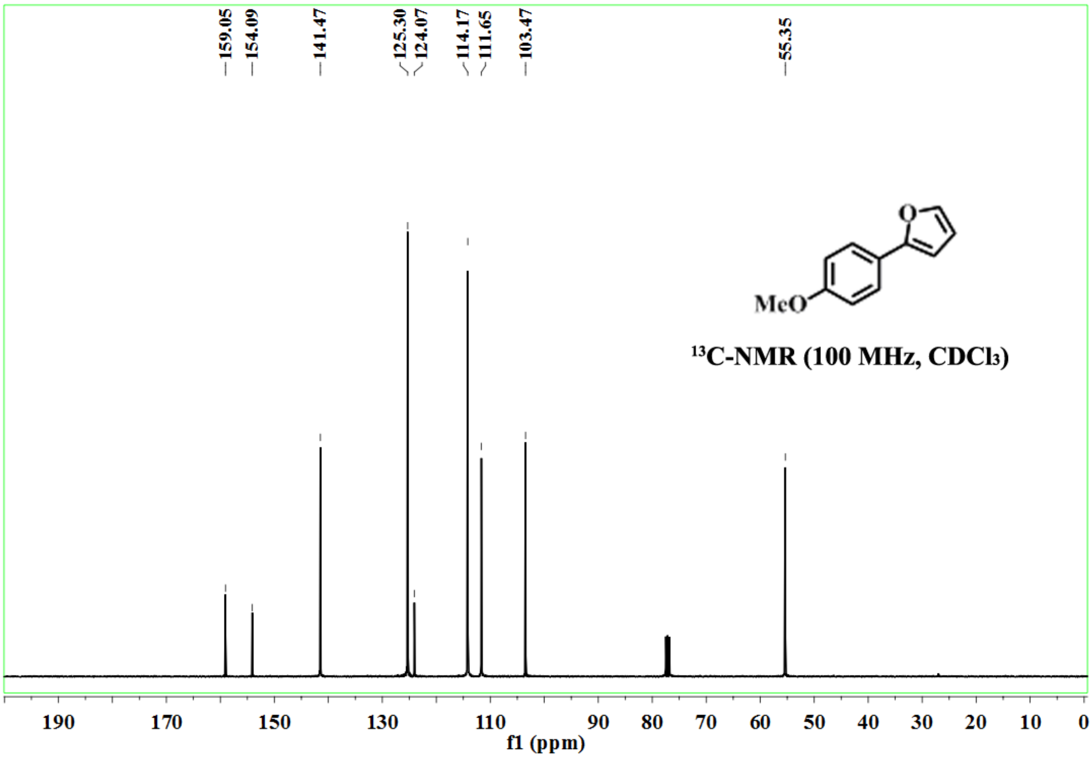
0.0
f1 (ppm)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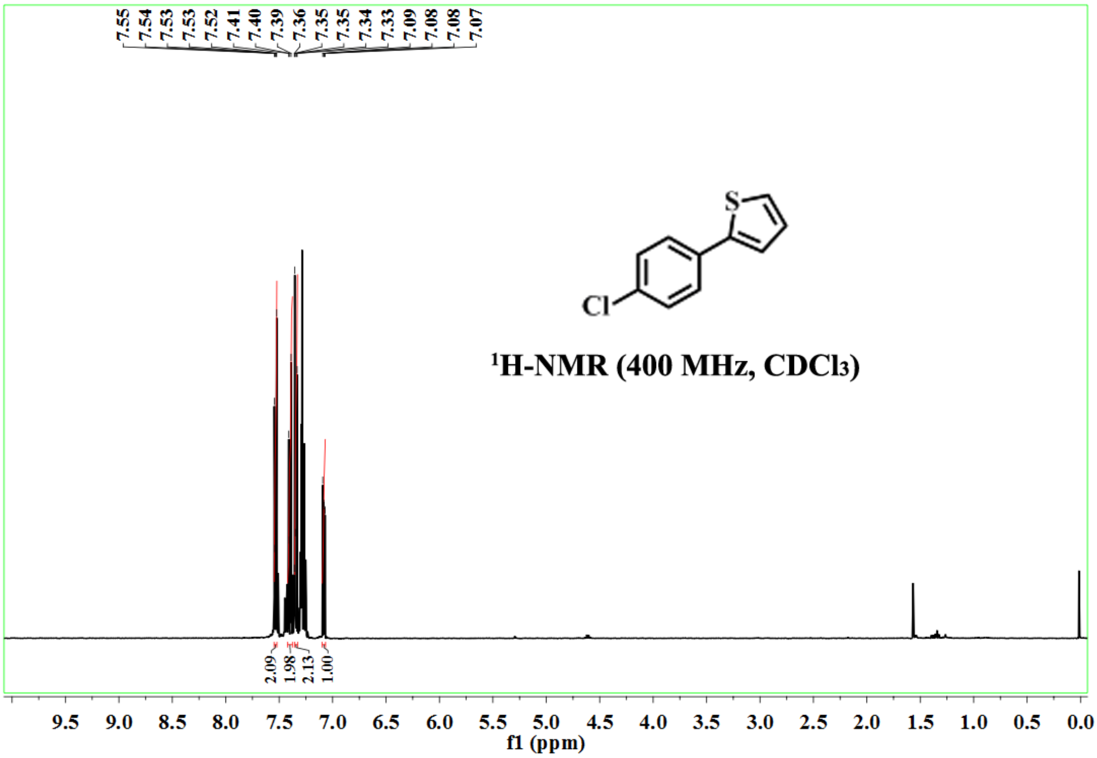
125.30
124.07
114.17
111.65
103.47
55.35
O
MeO
^{13}C-NMR (100 MHz, CDCl$_3$)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.41
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7.36
7.35
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7.34
7.33
7.09
7.08
7.08
7.07
S
Cl
^{1}H-NMR (400 MHz, CDCl$_3$)
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1.98
2.13
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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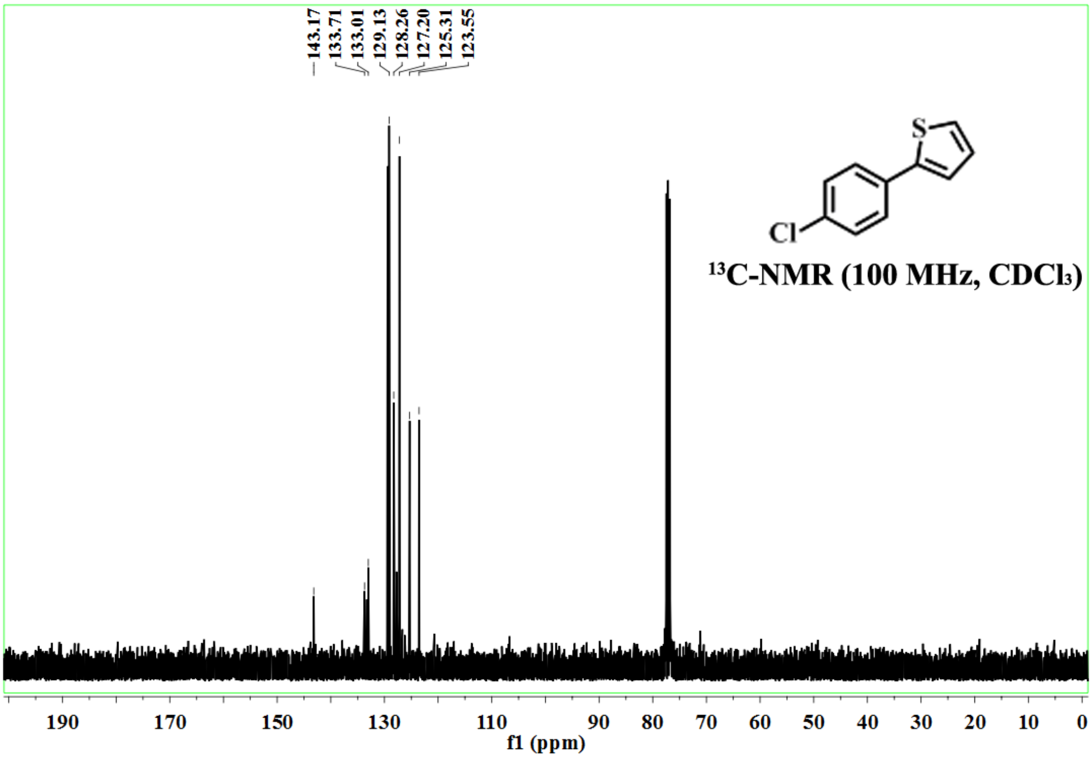
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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123.55
S
Cl
13C-NMR (100 MHz, CDCl3)
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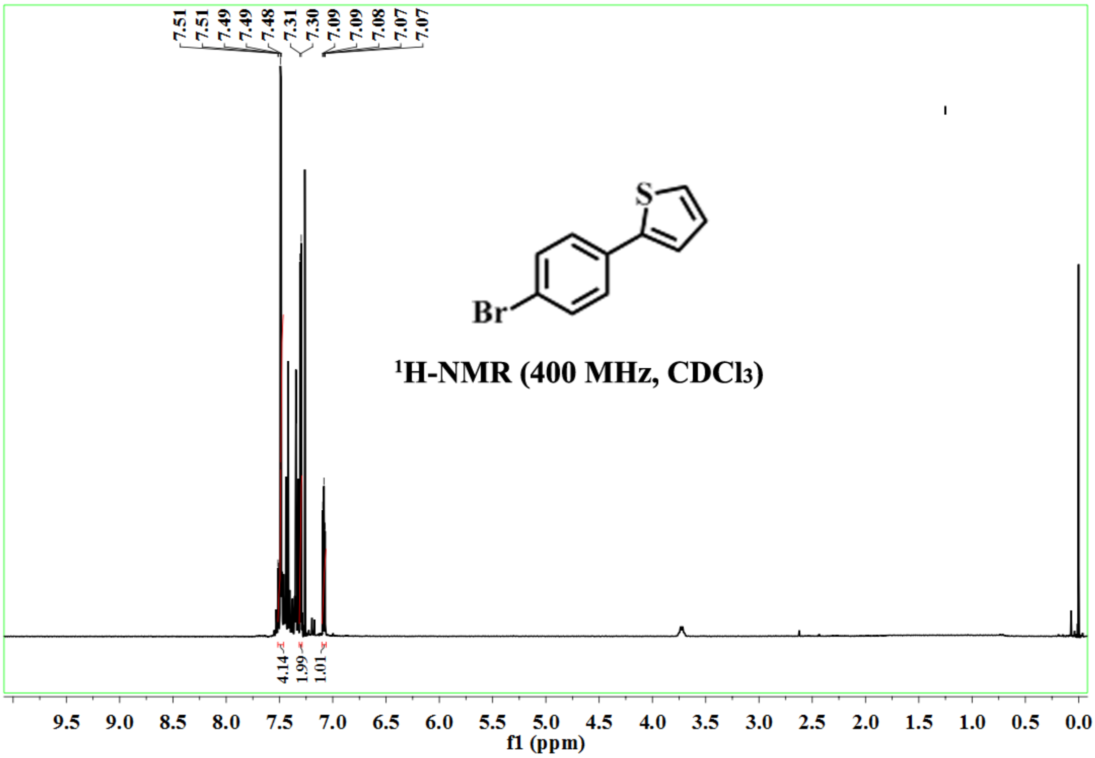
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.49
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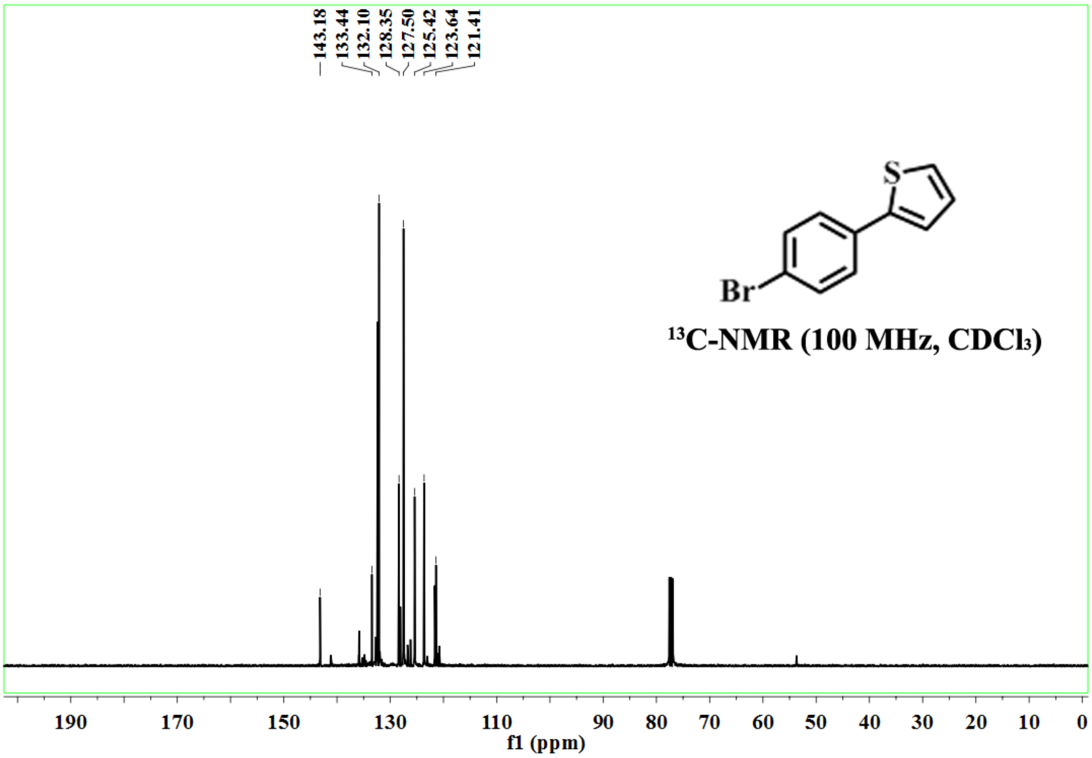
7.30
7.09
7.09
7.08
7.07
7.07
S
Br
1H-NMR (400 MHz, CDCl3)
4.14
1.99
1.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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121.41
S
Br
13C-NMR (100 MHz, CDCl3)
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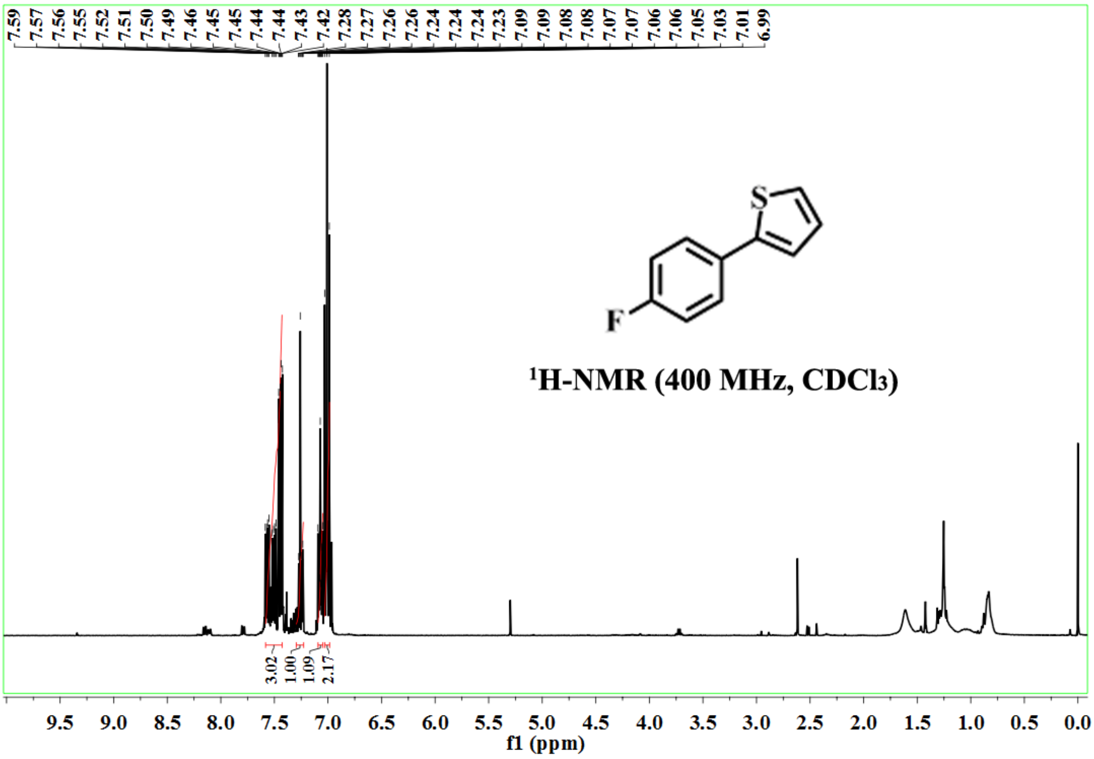
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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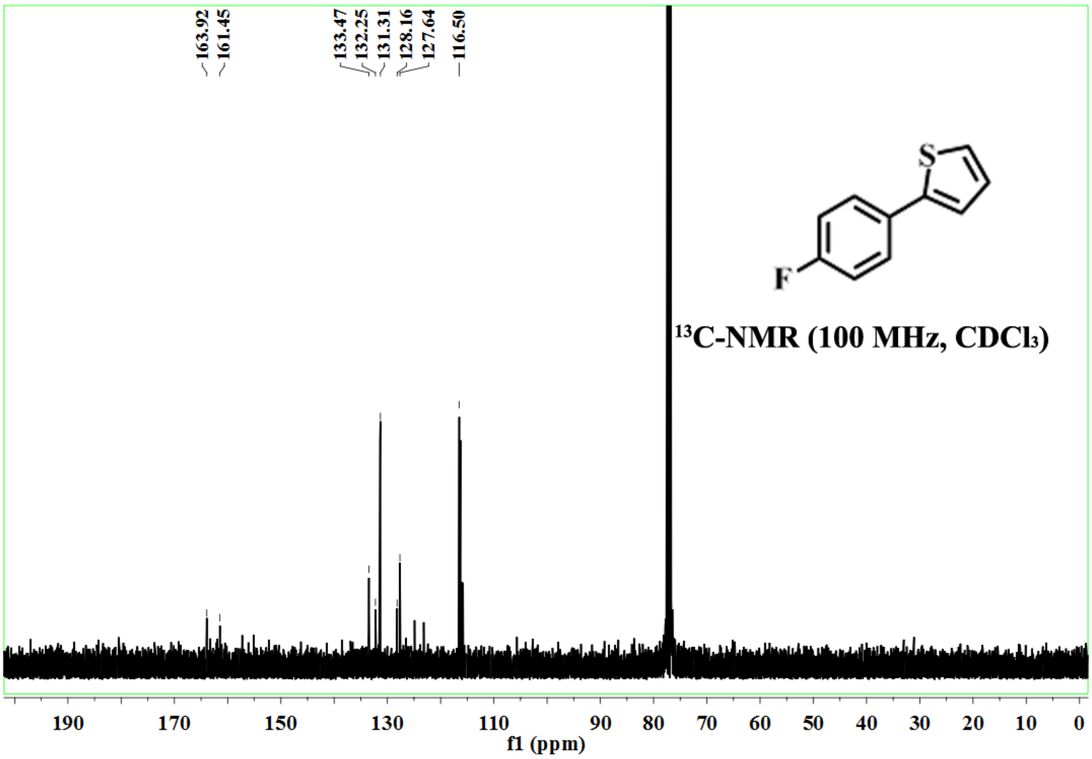
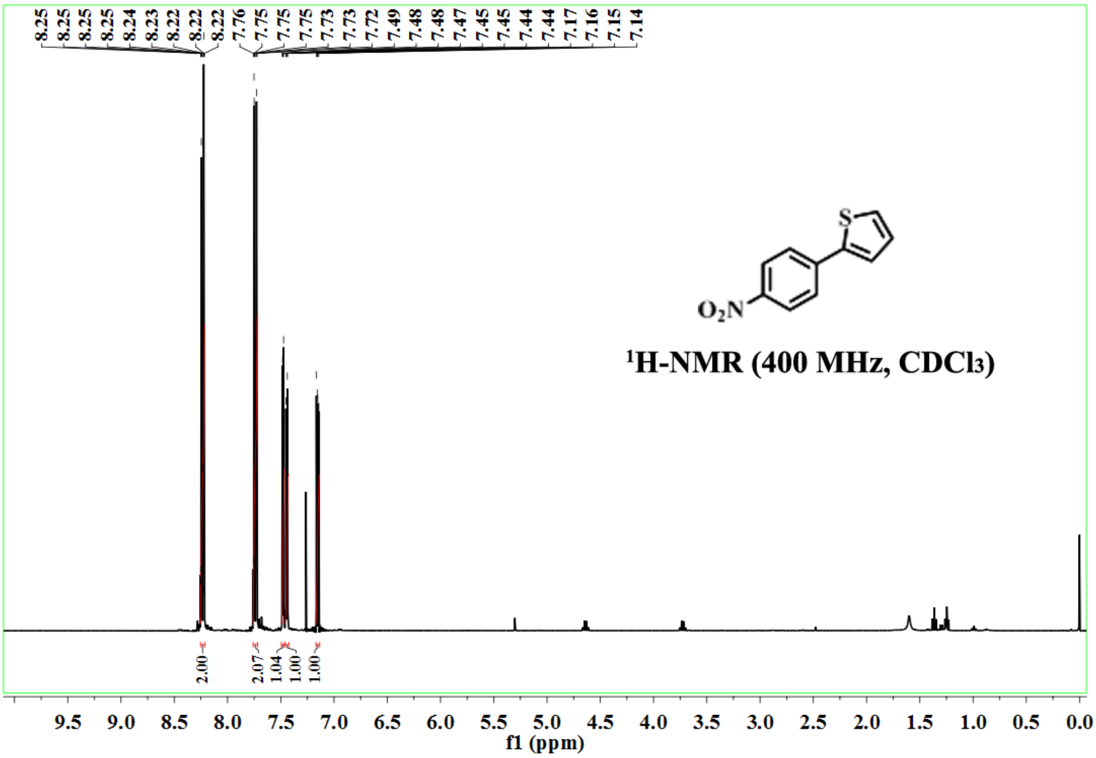
7.44
7.43
7.42
7.28
7.27
7.26
7.26
7.24
7.24
7.24
7.23
7.09
7.09
7.08
7.08
7.07
7.07
7.06
7.06
7.05
7.03
7.01
6.99
S
F
1H-NMR (400 MHz, CDCl3)
3.02
1.00
1.09
2.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.92
161.45
133.47
132.25
131.31
128.16
127.64
116.50
S
F
13C-NMR (100 MHz, CDCl3)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.75
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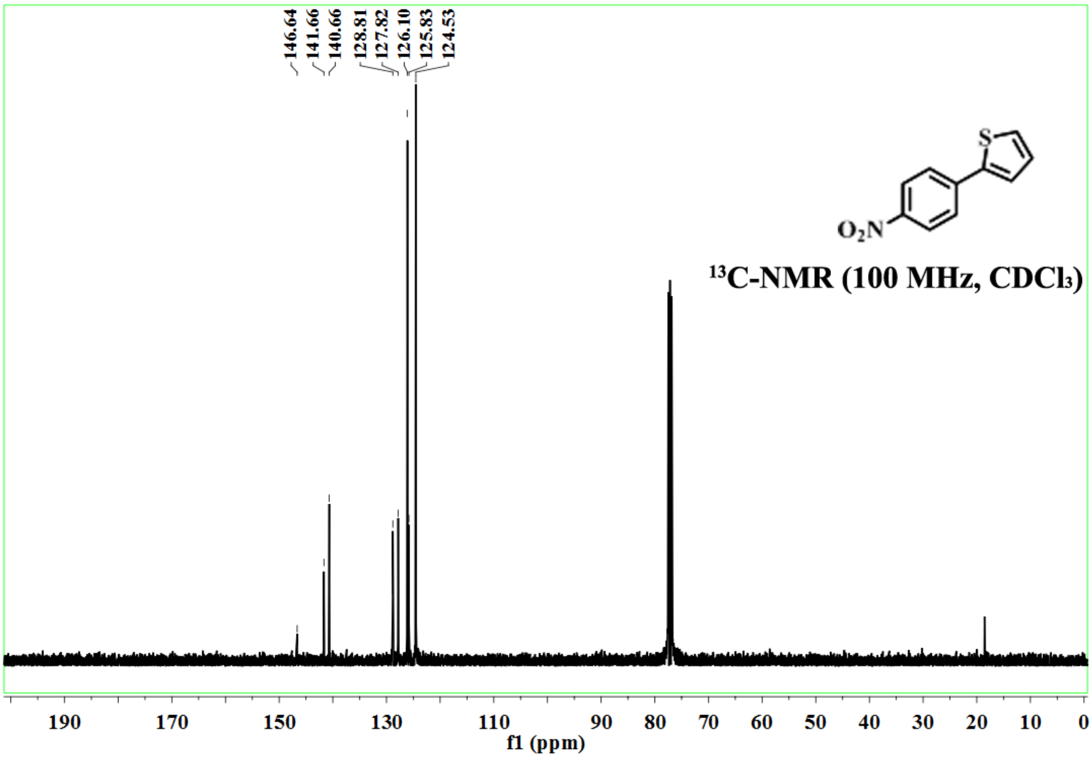
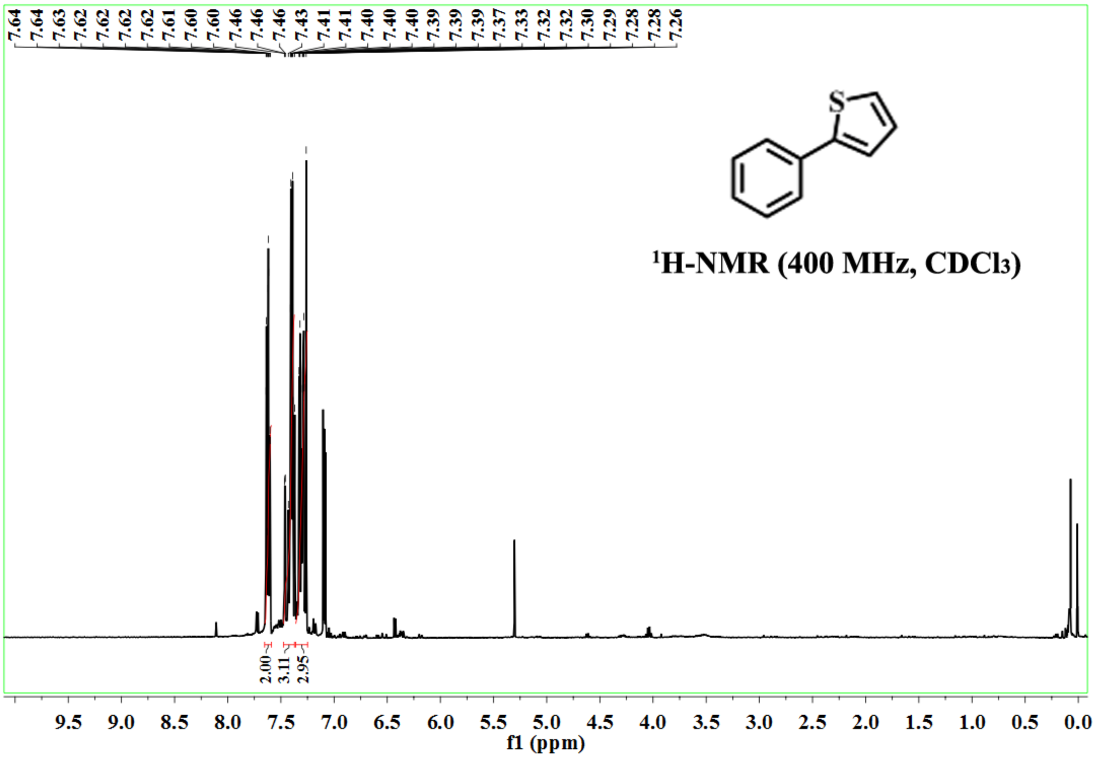
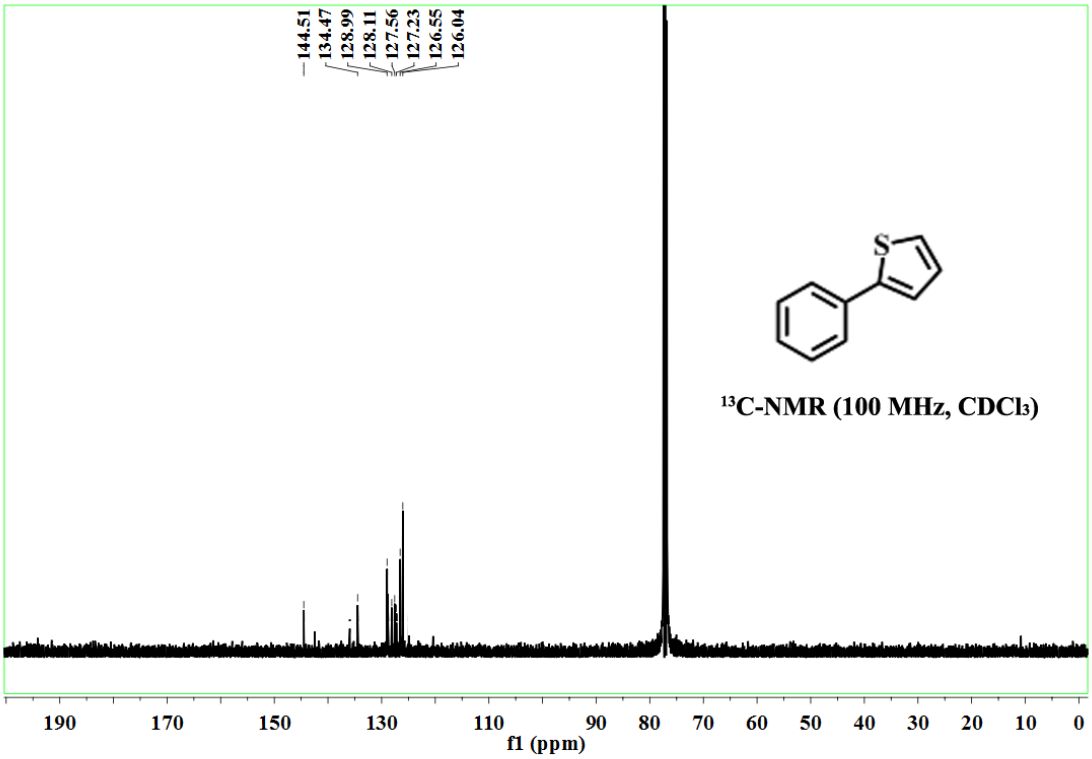
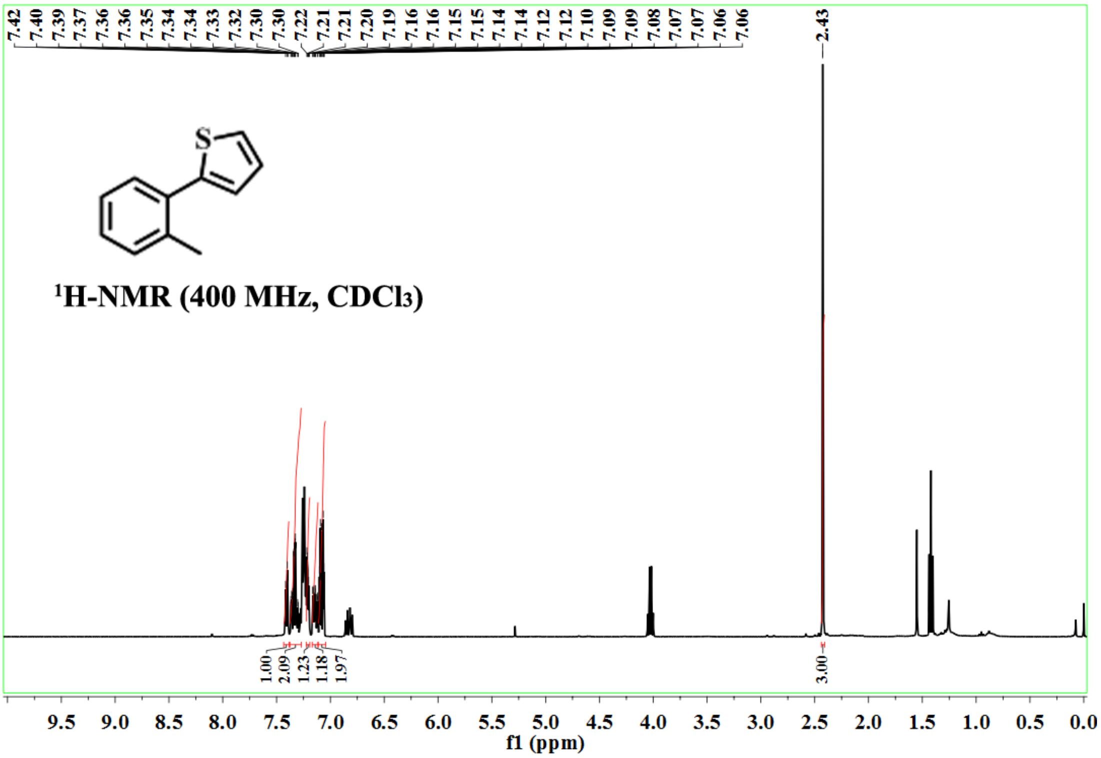
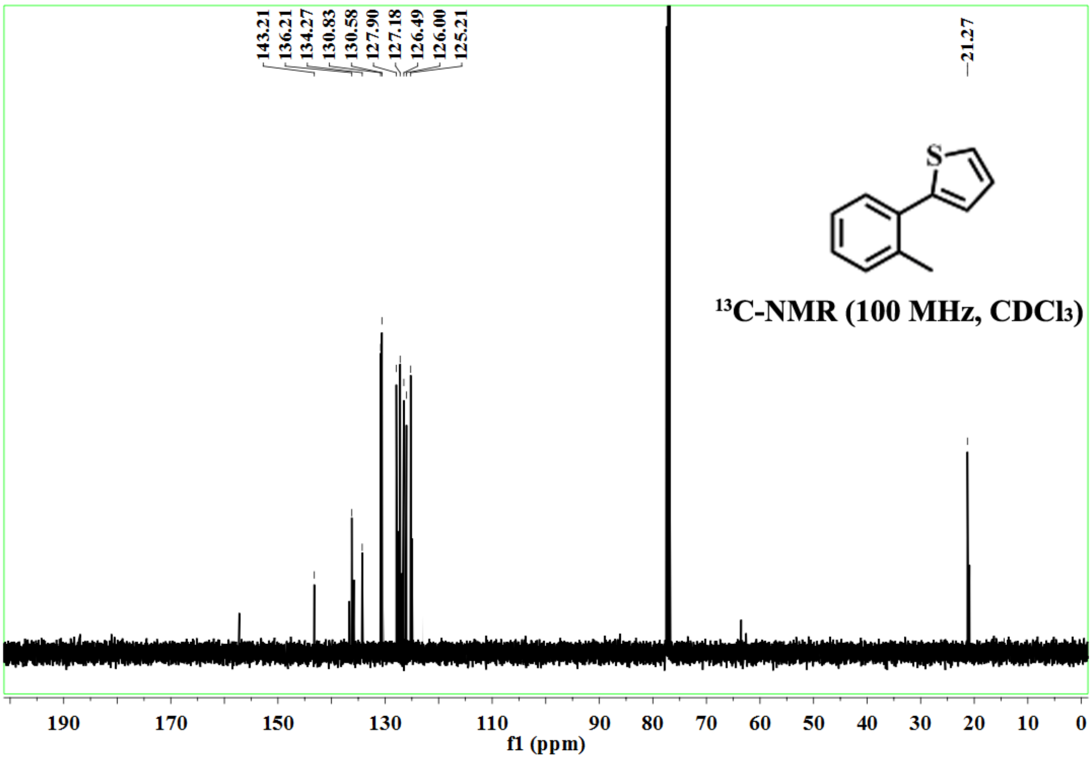
7.73
7.73
7.72
7.49
7.48
7.48
7.47
7.45
7.45
7.44
7.44
7.17
7.16
7.15
7.14
S
O2N
1H-NMR (400 MHz, CDCl3)
2.00
2.07
1.04
1.00
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

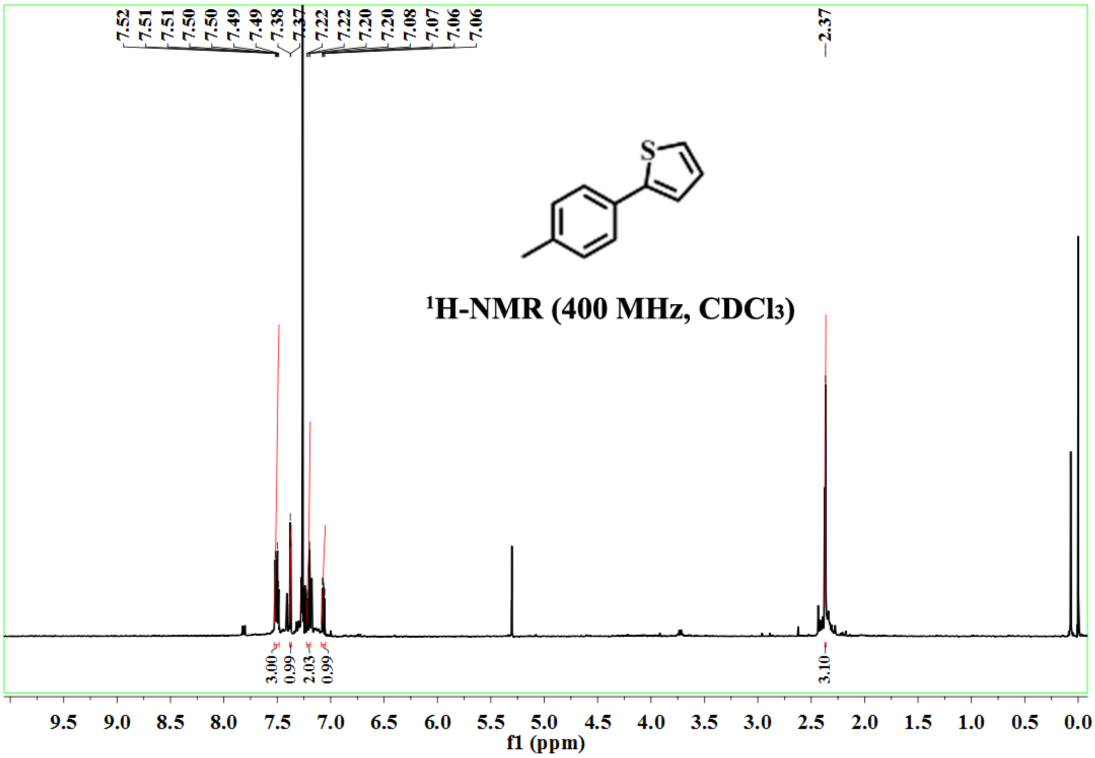

146.64
141.66
140.66
128.81
127.82
126.10
125.83
124.53
O2N
S
13C-NMR (100 MHz, CDCl3)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

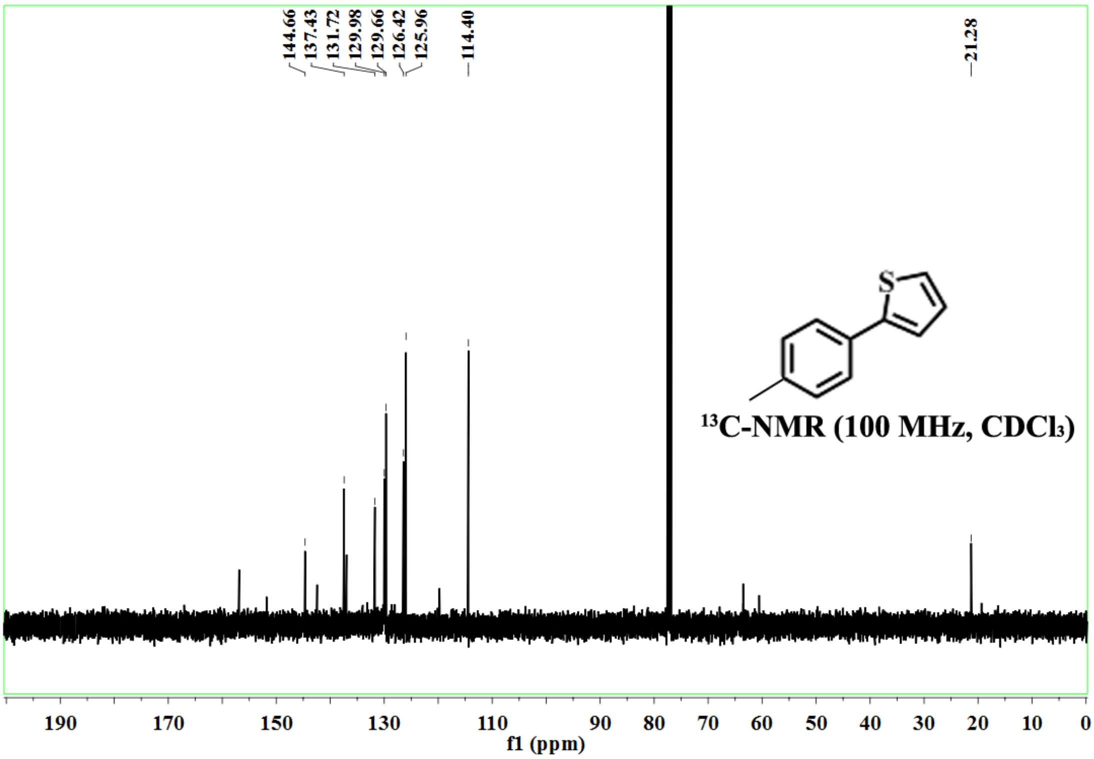

7.64
7.64
7.63
7.62
7.62
7.62
7.62
7.61
7.60
7.60
7.46
7.46
7.46
7.43
7.41
7.40
7.40
7.40
7.39
7.39
7.37
7.33
7.32
7.32
7.30
7.29
7.28
7.28
7.26
S
1H-NMR (400 MHz, CDCl3)
2.00
3.11
2.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

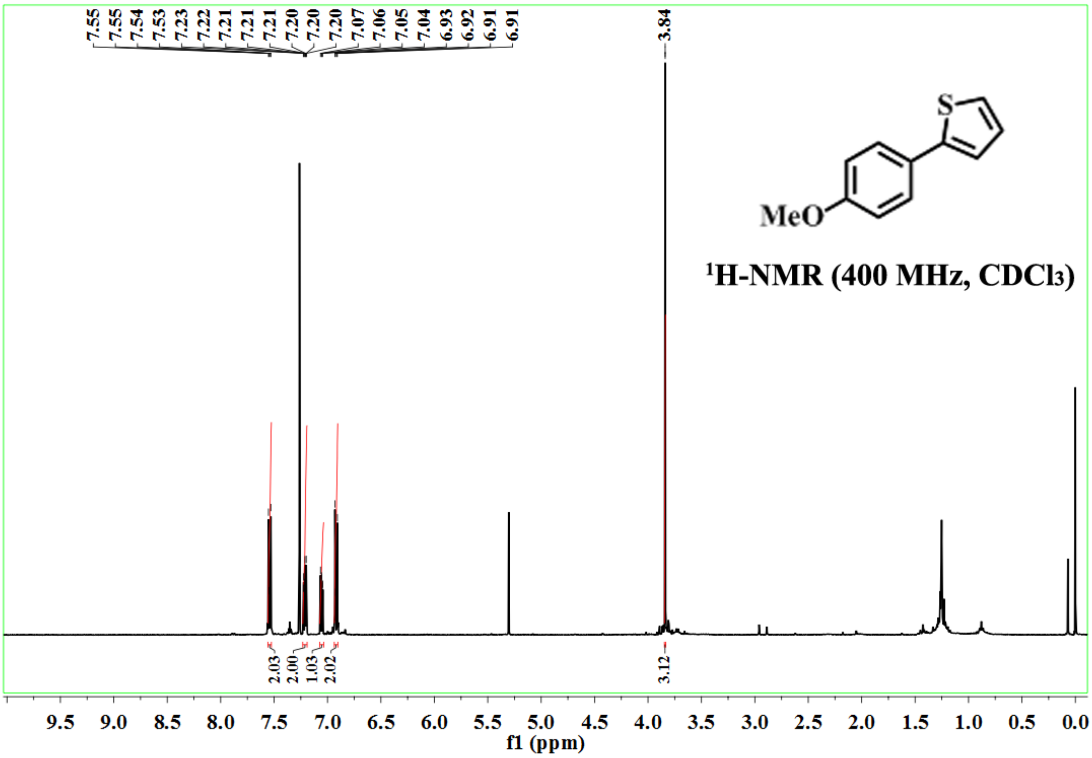

144.51
134.47
128.99
128.11
127.56
127.23
126.55
126.04
^{13}C-NMR (100 MHz, CDCl$_3$)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

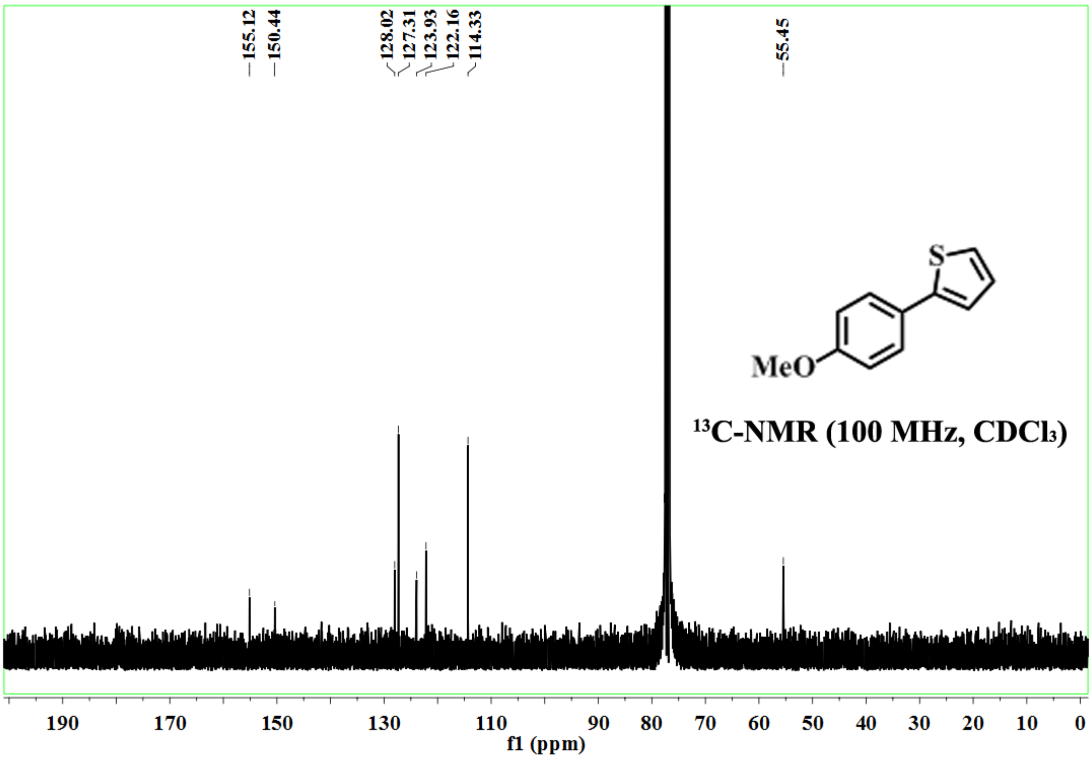

7.42
7.40
7.39
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.30
7.30
7.22
7.21
7.21
7.20
7.19
7.16
7.16
7.15
7.15
7.14
7.14
7.12
7.10
7.09
7.09
7.08
7.07
7.07
7.06
7.06
2.43
^{1}H-NMR (400 MHz, CDCl$_3$)
1.00
2.09
1.23
1.18
1.97
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.21
136.21
134.27
130.83
130.58
127.90
127.18
126.49
126.00
125.21
21.27
S
13C-NMR (100 MHz, CDCl3)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.38
7.37
7.22
7.22
7.20
7.20
7.08
7.07
7.06
7.06
2.37
S
1H-NMR (400 MHz, CDCl3)
3.00
0.99
2.03
0.99
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.66
137.43
131.72
129.98
129.66
126.42
125.96
114.40
21.28
S
^{13}C-NMR (100 MHz, CDCl$_3$)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.55
7.55
7.54
7.53
7.23
7.22
7.21
7.21
7.21
7.20
7.20
7.20
7.07
7.06
7.05
7.04
6.93
6.92
6.91
6.91
3.84
S
MeO
^{1}H-NMR (400 MHz, CDCl$_3$)
2.03
2.00
1.03
2.02
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.12
150.44
128.02
127.31
123.93
122.16
114.33
55.45
S
MeO
^{13}C-NMR (100 MHz, $CDCl_3$)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)