

Electronic supplementary materials *Mendeleev Commun.*, 2024, **34**, 401–403

**Copper(II)-catalyzed three-component coupling sequence
for the efficient synthesis of 2-arylquinolines: 1,4-dioxane serving
as the C₂ building block**

Yong Zhang, Junxue Bai and Song Sun

Contents

1 General experimental details.....	S2
2 Characterization data for the products	S2
3 Copies of ¹ H NMR and ¹³ C NMR spectra of 3a-3u	S11

1 General experimental details

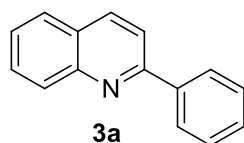
All chemicals were used as received without special purification. 1,4-Dioxane used in this reaction was purchased from Adamas (Grade: AR, > 99.5%). ^1H and ^{13}C NMR were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ^{13}C NMR). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl_3 (δ 7.26 or 77.0 ppm) as the internal standard.

General procedure:

Aldehyde **1** (0.1 mmol), aniline **2** (0.2 mmol), trifluoromethanesulfonic acid (4.9 μL , 0.05 mmol), CuCl_2 (0.02 mmol, 2.69 mg) and 1,4-dioxane (4 mL) was added into a 20 mL Schlenk tube equipped with a stir bar under air. The sealed Schlenk tube was stirred at 90 $^\circ\text{C}$ for about 12 h. After the reaction mixture was cooled to room temperature, the reaction mixture was diluted with EtOAc and washed with water. The organic layer was dried over anhydrous MgSO_4 , filtered and the filtrate was concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether (b.p 60-90 $^\circ\text{C}$) ethyl acetate as eluent to give the desired product. Characteristics of known products are referenced in [S1]-[S4].

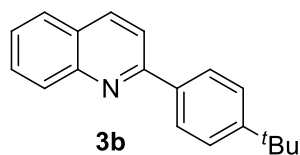
2 Characterization data for the products

2-Phenylquinoline (3a)



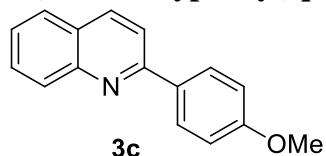
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3a** (12.7 mg, 62% yield) as a colorless solid.. The compound is known.^{S1} ^1H NMR (CDCl_3 400 MHz): δ 8.16-8.24 (m, 4H), 7.82-7.89 (m, 2H), 7.72-7.76 (m, 1H), 7.52-7.55 (m, 3H), 7.46-7.49 (m, 1H). ^{13}C NMR (CDCl_3 100 MHz): δ 157.4, 148.2, 139.6, 136.8, 129.7, 129.6, 129.3, 128.8, 127.6, 127.4, 127.1, 126.2, 119.0.

2-(4-*tert*-Butylphenyl)quinoline (3b)



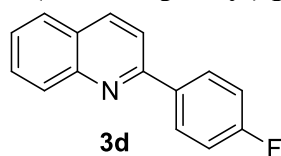
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3b** (13.3 mg, 51% yield) as a white solid. The compound is known.^{S4} ¹H NMR (CDCl₃ 400 MHz): δ 8.09-8.22 (m, 2H), 8.09-8.11 (d, J = 8.4 Hz, 2H), 7.81-7.88 (m, 2H), 7.70-7.74 (m, 1H), 7.50-7.57 (m, 3H), 1.39 (s, 9H). ¹³C NMR (CDCl₃ 100 MHz): δ 157.4, 152.5, 148.3, 137.0, 136.6, 129.7, 129.6, 127.4, 127.3, 127.1, 126.1, 125.8, 119.0, 34.8, 31.3.

2-(4-Methoxyphenyl)quinoline (3c)



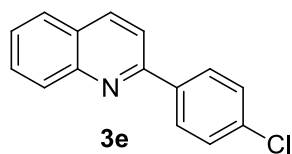
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 20) gave **3c** (9.9 mg, 42% yield) as a white solid. The compound is known.^{S1} ¹H NMR (CDCl₃ 400 MHz): δ 8.13-8.19 (m, 4H), 7.79-7.85 (m, 2H), 7.69-7.73 (m, 1H), 7.48-7.52 (m, 1H), 7.04-7.06 (d, J = 8.3 Hz, 2H), 3.89 (s, 3H). ¹³C NMR (CDCl₃ 100 MHz): δ 160.8, 156.9, 148.3, 136.6, 132.3, 129.6, 129.5, 128.9, 127.4, 126.9, 125.9, 118.6, 114.2, 100.0, 55.4.

2-(4-Fluorophenyl)quinoline (3d)



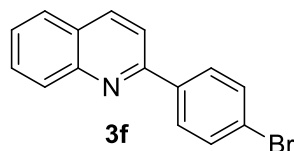
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 20) gave **3d** (12.9 mg, 58% yield) as a white solid. The compound is known.^{S1} ¹H NMR (CDCl₃ 400 MHz): δ 8.14-8.22 (m, 4H), 7.81-7.84 (d, J = 8.5 Hz, 2H), 7.72-7.76 (m, 1H), 7.51-7.55 (m, 1H), 7.19-7.23 (m, 2H). ¹³C NMR (CDCl₃ 100 MHz): δ 163.8 (d, J = 247.5 Hz), 156.2, 148.2, 136.9, 135.8, 129.7 (d, J = 17.6 Hz), 129.4, 129.3, 127.4, 127.0, 126.3, 118.6, 115.7 (d, J = 21.5 Hz).

2-(4-Chlorophenyl)quinoline (3e)



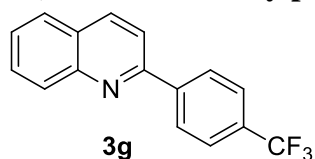
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3e** (15.5 mg, 65% yield) as a white solid. The compound is known.^{S1} The compound is known.¹ ¹H NMR (CDCl₃ 400 MHz): δ 8.21-8.23 (d, J = 8.6 Hz, 1H), 8.11-8.17 (m, 3H), 7.82-7.85 (m, 2H), 7.72-7.76 (m, 1H), 7.49-7.56 (m, 3H). ¹³C NMR (CDCl₃ 100 MHz): δ 156.0, 148.2, 138.0, 136.9, 135.5, 129.8, 129.7, 129.0, 128.8, 127.5, 127.2, 126.5, 118.5.

2-(4-Bromophenyl)quinoline (3f)



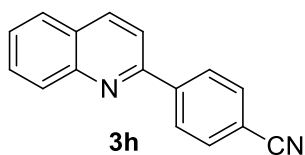
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3f** (19.2 mg, 68% yield) as a white solid..The compound is known.^{S1} ¹H NMR (CDCl₃ 400 MHz): δ 8.15-8.22 (dd, J = 8.6 Hz, 2H), 8.04-8.06 (d, J = 8.3 Hz, 2H), 7.81-7.83 (d, J = 8.4 Hz, 2H), 7.72-7.75 (t, J = 7.1 Hz, 1H), 7.64-7.66 (d, J = 8.3 Hz, 2H), 7.52-7.56 (t, J = 7.4 Hz, 1H). ¹³C NMR (CDCl₃ 100 MHz): δ 156.0, 148.2, 138.4, 136.9, 131.9, 129.8, 129.6, 129.0, 127.4, 127.2, 126.5, 123.9, 118.4.

2-(4-Trifluoromethylphenyl)quinoline (3g)



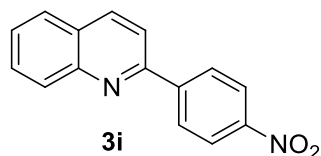
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3g** (17.1 mg, 63% yield) as a white solid. The compound is known.^{S1} ¹H NMR (CDCl₃ 400 MHz): δ 8.26-8.30 (m, 3H), 8.18-8.20 (d, J = 8.5 Hz, 1H), 7.85-7.90 (m, 2H), 7.75-7.79 (m, 3H), 7.55-7.59 (t, J = 7.7 Hz, 1H). ¹³C NMR (CDCl₃ 100 MHz): δ 155.6, 148.2, 142.9, 137.1, 131.0 (d, J = 32.3Hz), 129.8 (d, J = 14.1Hz), 127.8 (2C), 127.5, 127.4, 126.8, 125.5 (q, J = 274.7 Hz), 125.7(q, J = 3.0 Hz), 118.8.

4-(Quinolin-2-yl)benzonitrile (3h)



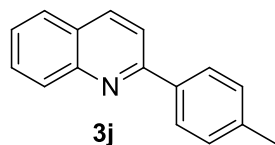
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 10) gave **3h** (13.1 mg, 57% yield) as a white solid. The compound is known.^{S2} ¹H NMR (CDCl₃ 400 MHz): δ 8.26-8.30 (m, 3H), 8.16-8.18 (d, J = 8.4 Hz, 1H), 7.84-7.89 (m, 2H), 7.75-7.77 (m, 3H), 7.56-7.60 (m, 1H). ¹³C NMR (CDCl₃ 100 MHz): δ 154.9, 148.2, 143.6, 137.2, 132.5, 130.1, 129.8, 128.0, 127.5, 127.4, 127.1, 127.0, 118.6, 112.7.

2-(4-Nitrophenyl)quinoline (3i)



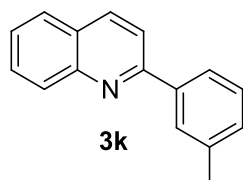
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **2i** (10.7 mg, 43% yield) as a white solid. The compound is known.^{S4} ¹H NMR (CDCl₃ 400 MHz): δ 8.33-8.38 (m, 4H), 8.29 (d, J = 8.6 Hz, 1H), 8.18 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.6 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.76-7.80 (m, 1H), 7.59 (t, J = 7.3 Hz, 1H). ¹³C NMR (CDCl₃ 100 MHz): δ 154.5, 148.3, 148.2, 145.5, 137.3, 130.2, 130.0, 128.3 (2C), 127.6, 127.3, 124.0, 118.8.

2-(*p*-Tolyl)quinoline (3j)



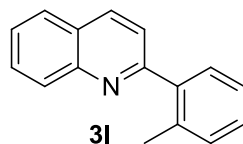
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3b** (13.4 mg, 61% yield) as a white solid. The compound is known.^{S1} ¹H NMR (CDCl₃ 400 MHz): δ 8.15-8.21 (m, 2H), 8.05-8.06 (d, J = 8.08 Hz, 2H), 7.81-7.88 (m, 2H), 7.70-7.74 (m, 1H), 7.50-7.53 (m, 1H), 7.33-7.35 (d, J = 8.00 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (CDCl₃ 100 MHz): δ 157.3, 148.3, 139.4, 136.9, 136.6, 129.6, 129.5, 127.5, 127.4, 127.1, 126.1, 118.8, 21.3.

2-(*m*-Tolyl)quinoline (3k)



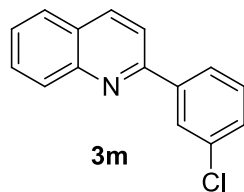
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3k** (11.6 mg, 53% yield) as a white solid. The compound is known.^{S2} ¹H NMR (CDCl₃ 400 MHz): δ 8.19-8.21 (d, J = 8.5 Hz, 2H), 8.03 (s, 1H), 7.93-7.95 (d, J = 7.7 Hz, 1H), 7.81-7.88 (m, 2H), 7.72-7.76 (m, 1H), 7.51-7.56 (m, 1H), 7.41-7.45 (m, 1H), 7.26-7.30 (m, 1H), 2.50 (s, 3H). ¹³C NMR (CDCl₃ 100 MHz): δ 157.5, 148.2, 139.6, 138.4, 136.6, 130.0, 129.6, 129.5, 128.7, 128.2, 127.4, 127.1, 126.2, 124.6, 119.1, 21.6.

2-(*o*-Tolyl)quinoline (3l)



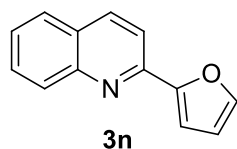
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3l** (8.1 mg, 37% yield) as a white solid. The compound is known.^{S4} ¹H NMR (CDCl₃ 400 MHz): δ 8.21-8.23 (d, J = 8.4 Hz, 1H), 8.16-8.18 (d, J = 8.5 Hz, 1H), 7.86-7.88 (d, J = 8.1 Hz, 1H), 7.73-7.76 (t, J = 7.3 Hz, 1H), 7.49-7.59 (m, 3H), 7.34-7.35 (m, 3H), 2.42 (s, 3H). ¹³C NMR (CDCl₃ 100 MHz): δ 160.2, 147.8, 140.7, 136.0, 135.9, 130.8, 129.7, 129.6, 129.5, 128.5, 127.5, 126.7, 126.4, 126.0, 122.3, 20.3.

2-(3-Chlorophenyl)quinoline (3m)



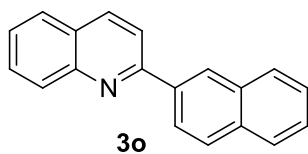
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3m** (15.0 mg, 63% yield) as a white solid. The compound is known.^{S4} ¹H NMR (CDCl₃ 400 MHz): δ 8.19-8.22 (m, 2H), 7.84-7.87 (m, 1H), 7.69-7.77 (m, 3H), 7.50-7.60 (m, 2H), 7.34-7.44 (m, 2H). ¹³C NMR (CDCl₃ 100 MHz): δ 157.3, 148.0, 139.5, 135.6, 132.2, 131.6, 130.0, 129.8, 129.6, 129.5, 127.5, 127.1, 127.0, 126.7, 122.7.

2-(Furan-2-yl)quinoline (3n)



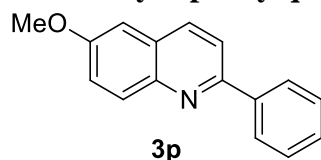
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 20) gave **3n** (12.6 mg, 65% yield) as a white solid. The compound is known.^{S1} ¹H NMR (CDCl₃ 400 MHz): δ 8.12-8.16 (t, J = 8.2 Hz, 2H), 7.76-7.82 (m, 2H), 7.68-7.72 (t, J = 8.0 Hz, 1H), 7.62 (s, 1H), 7.47-7.51 (t, J = 7.3 Hz, 1H), 7.21-7.22 (d, J = 3.3 Hz, 1H), 6.58-6.59 (d, J = 1.4 Hz, 1H). ¹³C NMR (CDCl₃ 100 MHz): δ 153.6, 149.0, 148.0, 144.1, 136.6, 129.8, 129.3, 127.5, 127.1, 126.1, 117.4, 112.1, 110.1.

2-(Naphthalen-2-yl)quinoline (3o)



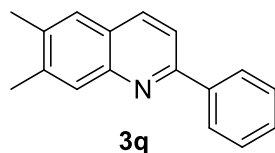
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 20) gave **3o** (15.3 mg, 60% yield) as a white solid. The compound is known.^{S4} ¹H NMR (CDCl₃ 400 MHz): δ 8.63 (s, 1H), 8.37-8.40 (m, 1H), 8.25 (t, J = 9.0 Hz, 2H), 8.00-8.04 (m, 3H), 7.90-7.92 (m, 1H), 7.84-7.86 (m, 1H), 7.74-7.78 (m, 1H), 7.52-7.57 (m, 3H). ¹³C NMR (CDCl₃ 100 MHz): δ 157.1, 148.4, 136.9, 136.8, 133.8, 133.5, 129.7, 129.6, 128.8, 128.5, 127.7, 127.5, 127.2, 127.1, 126.7, 126.4, 126.3, 125.0, 119.1.

6-Methoxy-2-phenylquinoline (3p)



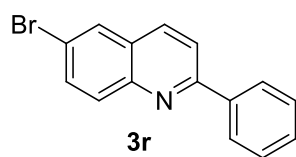
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 10) gave **3p** (10.6 mg, 45% yield) as a white solid. The compound is known.^{S3} ¹H NMR (CDCl₃ 400 MHz): δ 8.06-8.14 (m, 4H), 7.82-7.84 (m, 1H), 7.50-7.54 (m, 2H), 7.37-7.46 (m, 2H), 7.09-7.10 (m, 1H), 3.95 (s, 3H). ¹³C NMR (CDCl₃ 100 MHz): δ 157.6, 155.0, 144.3, 139.8, 135.5, 131.1, 128.9, 128.8, 128.1, 127.3, 122.3, 119.2, 105.0, 55.5.

6,7-Dimethyl-2-phenylquinoline (3q)



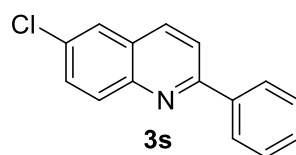
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3q** (12.8 mg, 55% yield) as a white solid. The compound is known.^{S4} ¹H NMR (CDCl₃ 300 MHz): δ 8.05-8.16 (m, 3H), 7.94 (s, 1H), 7.77-7.80 (m, 1H), 7.44-7.56 (m, 4H), 2.49 (s, 3H), 2.45 (s, 3H). ¹³C NMR (CDCl₃ 75 MHz): δ 156.4, 147.3, 139.9, 139.8, 136.1, 135.6, 129.0, 128.9, 128.7, 127.4, 126.6, 125.7, 118.2, 20.4, 20.0.

6-Bromo-2-phenylquinoline (3r)



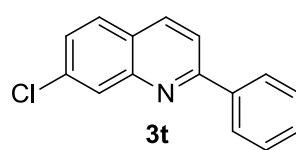
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3s** (17.5 mg, 62% yield) as a white solid. The compound is known.^{S4} ¹H NMR (CDCl₃ 400 MHz): δ 8.11-8.16 (m, 3H), 8.04 (d, J = 8.9 Hz, 1H), 7.98 (d, J = 1.9 Hz, 1H), 7.89 (d, J = 8.6 Hz, 1H), 7.77-7.80 (m, 1H), 7.46-7.55 (m, 3H). ¹³C NMR (CDCl₃ 100 MHz): δ 157.6, 146.8, 139.2, 135.7, 133.1, 131.4, 129.6, 129.5, 128.9, 128.2, 127.5, 120.0, 119.7.

6-Chloro-2-phenylquinoline (3s)



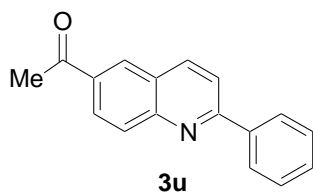
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3s** (13.8 mg, 58% yield) as a white solid. The compound is known.^{S1} ¹H NMR (CDCl₃ 400 MHz): δ 8.09-8.16 (m, 4H), 7.87-7.90 (m, 1H), 7.79-7.80 (m, 1H), 7.64-7.68 (m, 1H), 7.45-7.56 (m, 3H). ¹³C NMR (CDCl₃ 100 MHz): δ 157.5, 146.6, 139.1, 135.8, 131.8, 131.2, 130.5, 129.5, 128.9, 127.7, 127.5, 126.0, 119.8.

7-Chloro-2-phenylquinoline (3t)



The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 30) gave **3t** (13.3 mg, 56% yield) as a white solid. The compound is known.^{S1} ¹H NMR (CDCl₃ 300 MHz): δ 8.14-8.19 (m, 4H), 7.85-7.88 (m, 1H), 7.73-7.76 (m, 1H), 7.45-7.57 (m, 4H). ¹³C NMR (CDCl₃ 75 MHz): δ 158.2, 148.6, 139.1, 136.6, 135.4, 129.6, 128.9, 128.6, 127.5, 127.2, 125.5, 119.1.

1-(2-Phenylquinolin-6-yl)ethanone (**3u**)

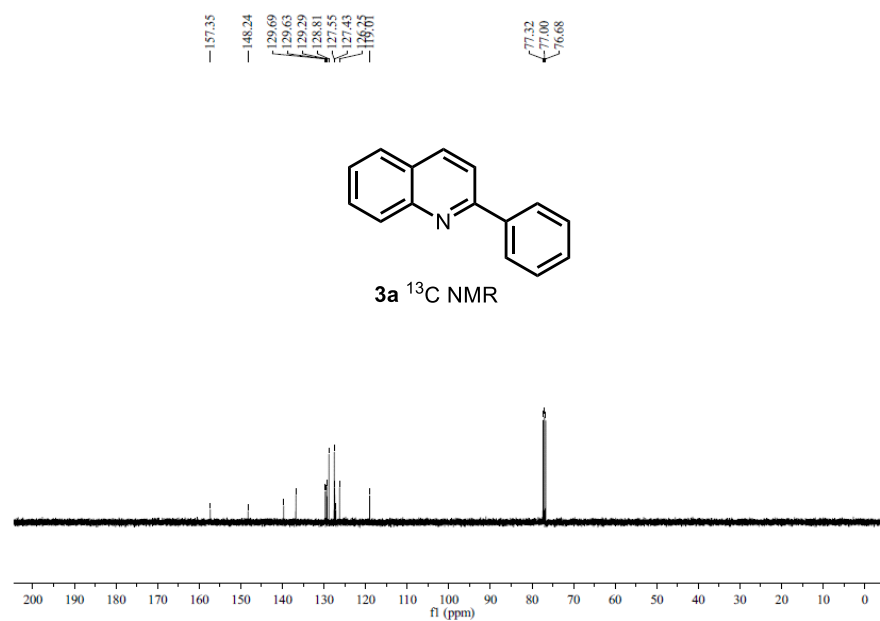
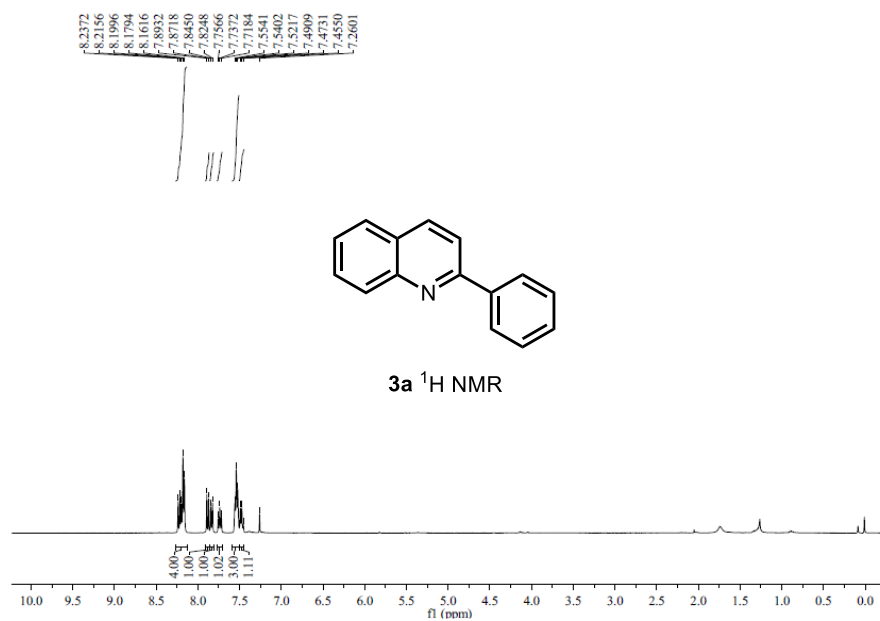


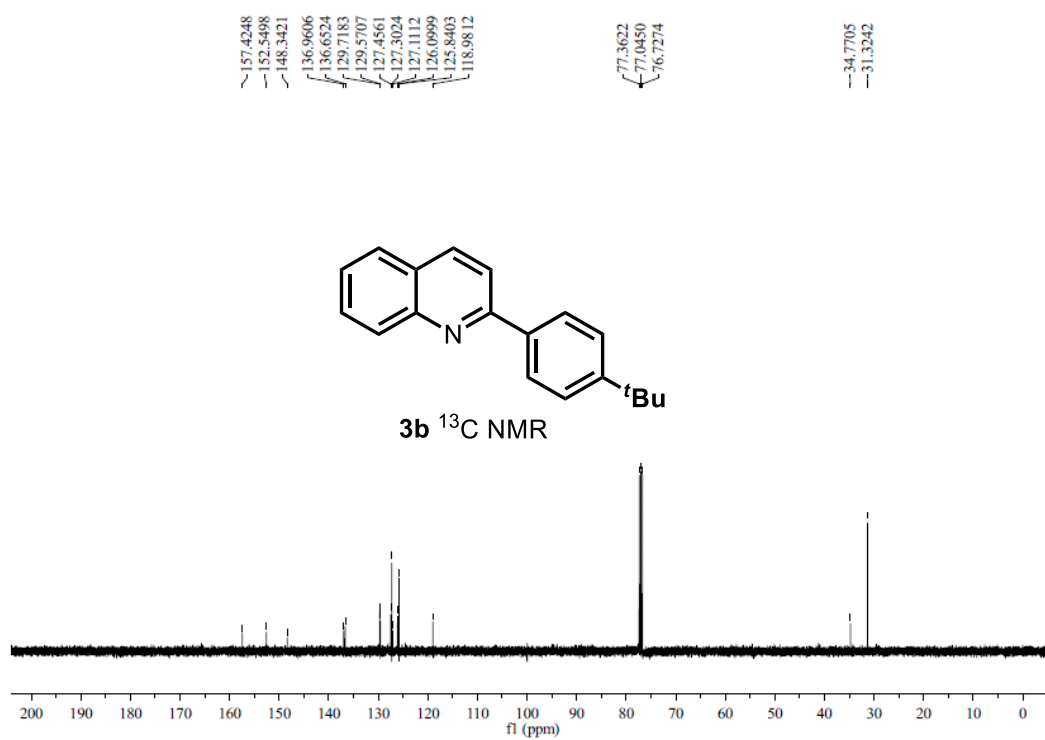
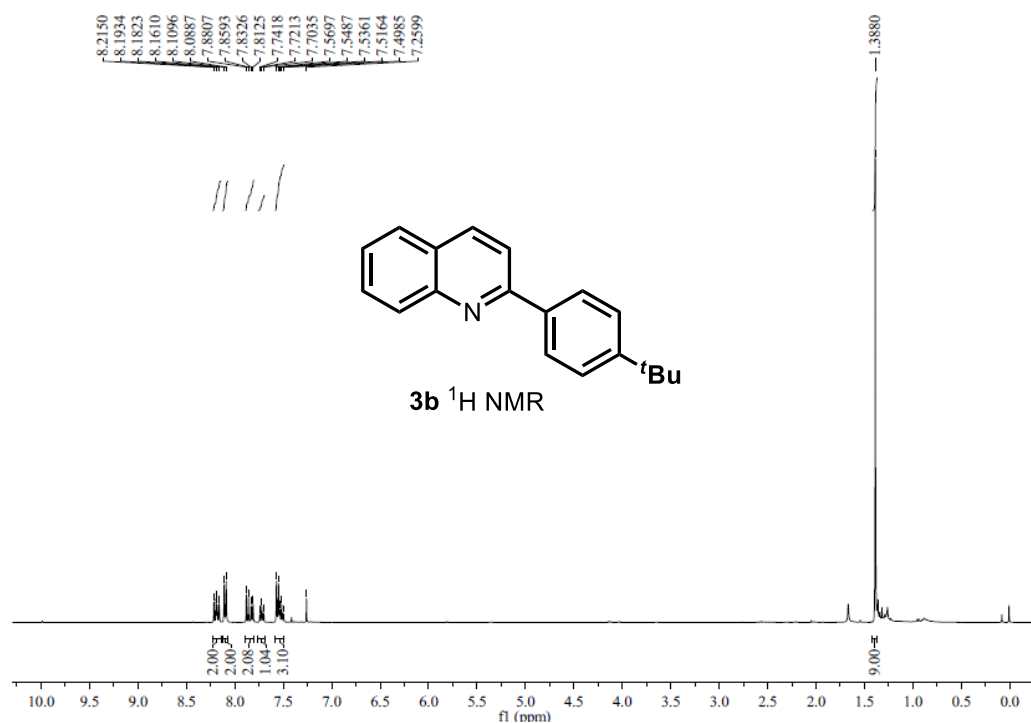
The product was purified by preparative TLC on GF254 (ethyl acetate: petroleum ether, 1: 5) gave **3u** (16.0 mg, 65% yield) as a white solid. The compound is known.^{S4} ¹H NMR (CDCl₃ 400 MHz): δ 8.44 (d, J = 1.6 Hz, 1H), 8.31 (d, J = 8.6 Hz, 1H), 8.26-8.28 (m, 1H), 8.18-8.21 (m, 3H), 7.94 (d, J = 8.6 Hz, 1H), 7.48-7.57 (m, 3H), 2.74 (s, 3H). ¹³C NMR (CDCl₃ 100 MHz): δ 197.1, 159.4, 150.2, 139.0, 138.1, 134.5, 130.2, 130.0, 128.5, 128.9, 127.9, 127.7, 126.3, 119.7, 26.7.

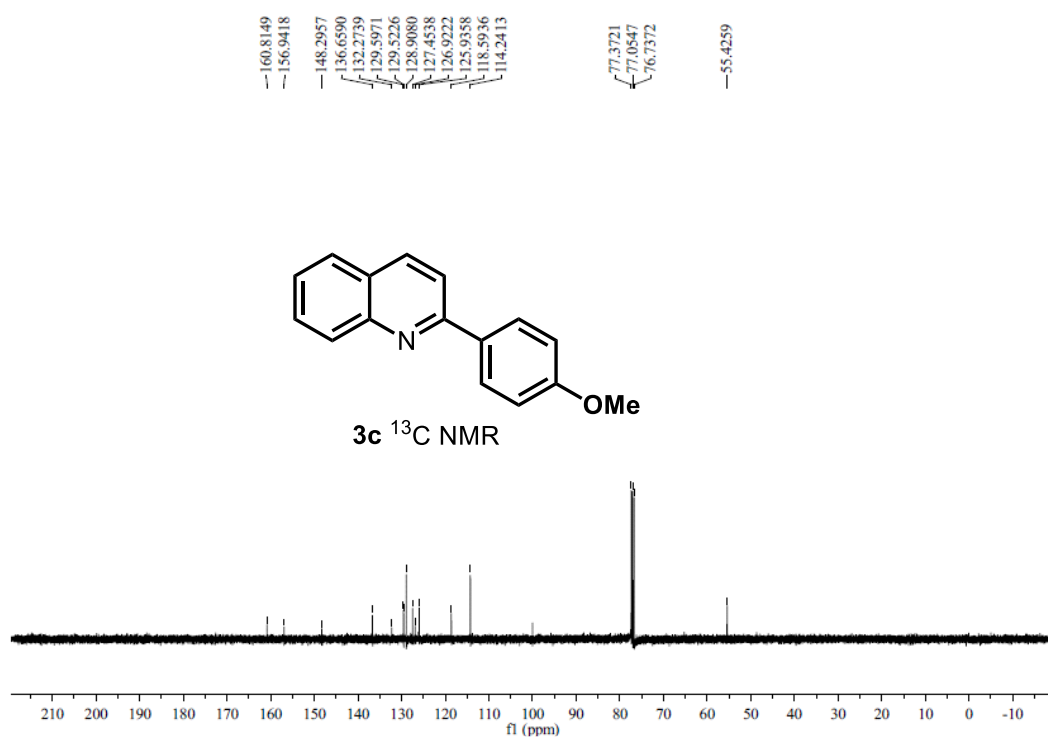
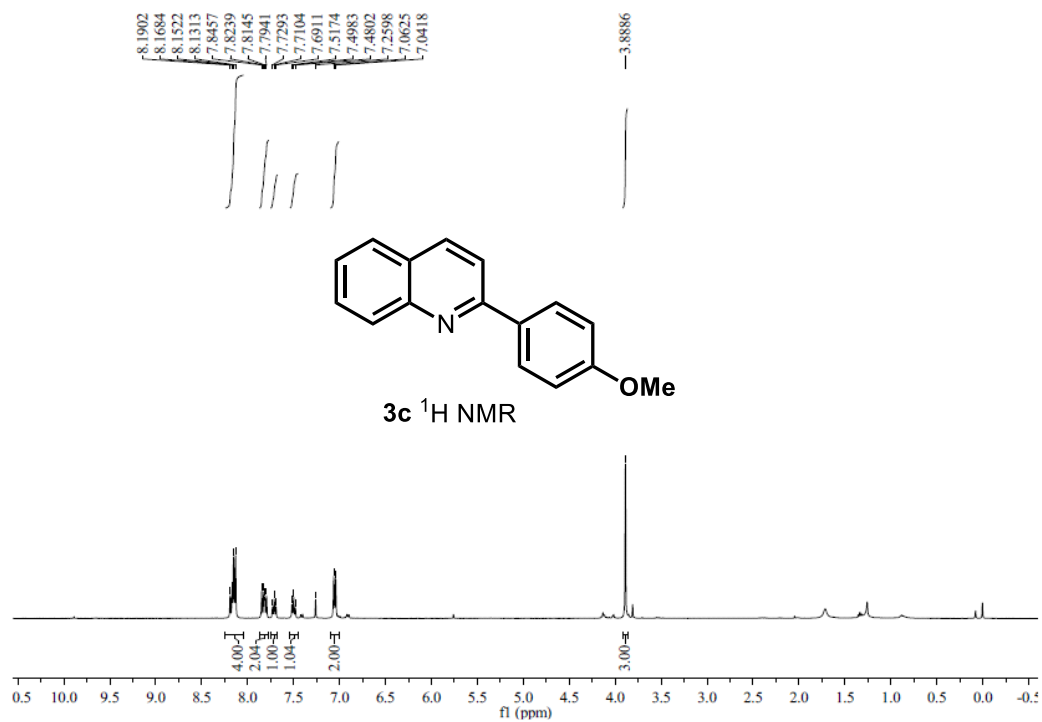
References

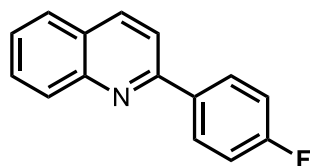
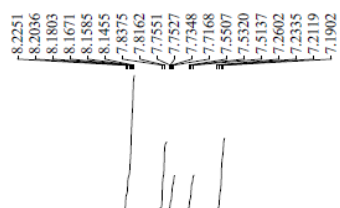
- S1. K. Patra, A. Bhattacherya, C. Li, J. K. Bera and H. S. Soo, *ACS Catal.*, 2022, **12**, 15168.
- S2. D. Pathak, B. K. Kalita, A. Sarmah, H. Sharma, B. Bora, T. K. Goswami and B. Sarma, *Green Chem.*, 2023, **25**, 7642.
- S3. Y. Ding, T. Guo, Z. Li, B. Zhang, F. E. Kühn, C. Liu, J. Zhang, D. Xu, M. Lei, T. Zhang and C. Li, *Angew. Chem., Int. Ed.*, 2022, **61**, e202206284.
- S4. X. Ji, H. Huang, Y. Li, H. Chen and H. Jiang, *Angew. Chem., Int. Ed.*, 2012, **51**, 7292.

3 Copies of ^1H NMR and ^{13}C NMR spectra of 3a-3u

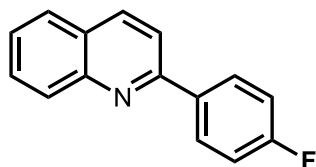
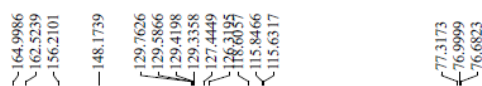
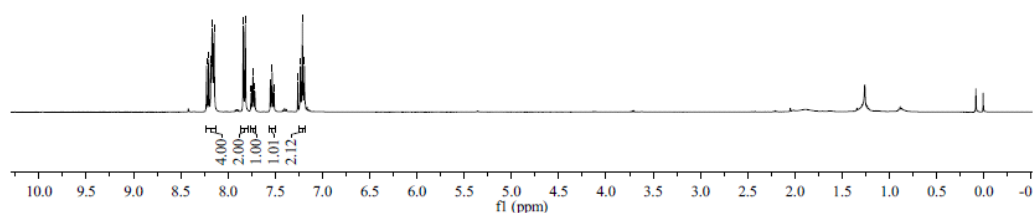




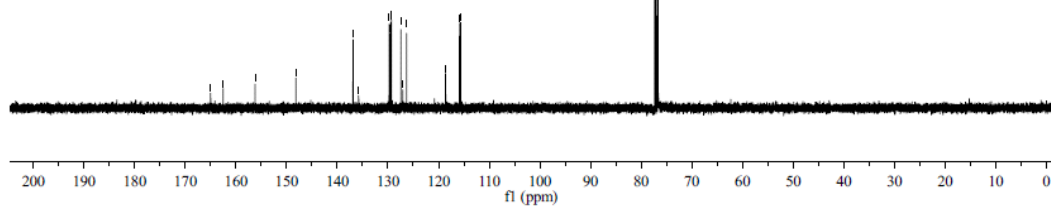


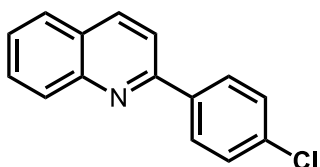
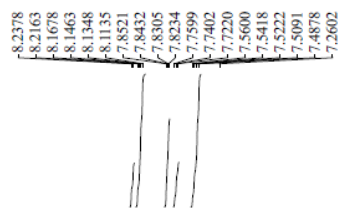


3d ^1H NMR

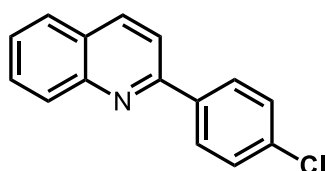
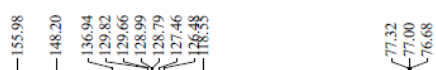
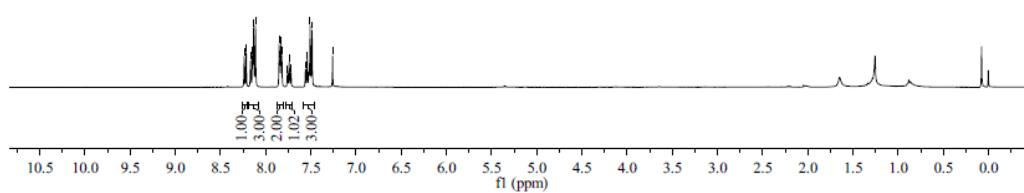


3d ^{13}C NMR

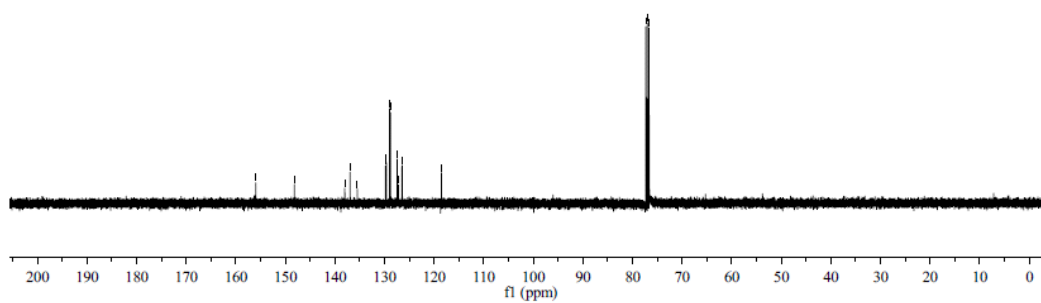


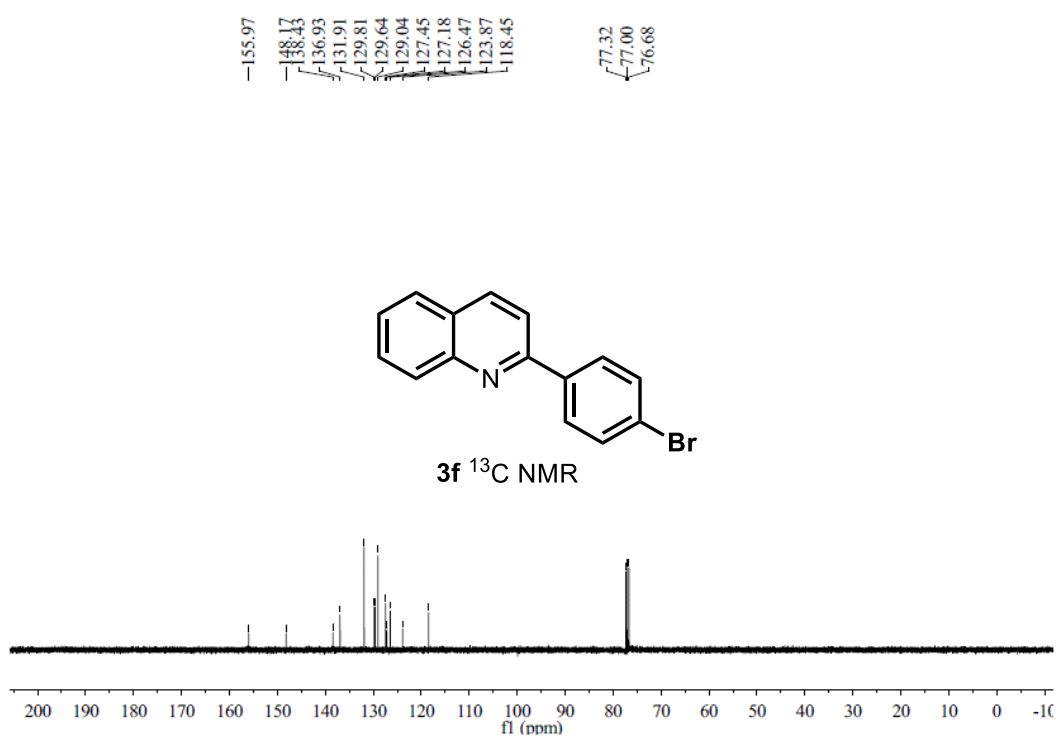
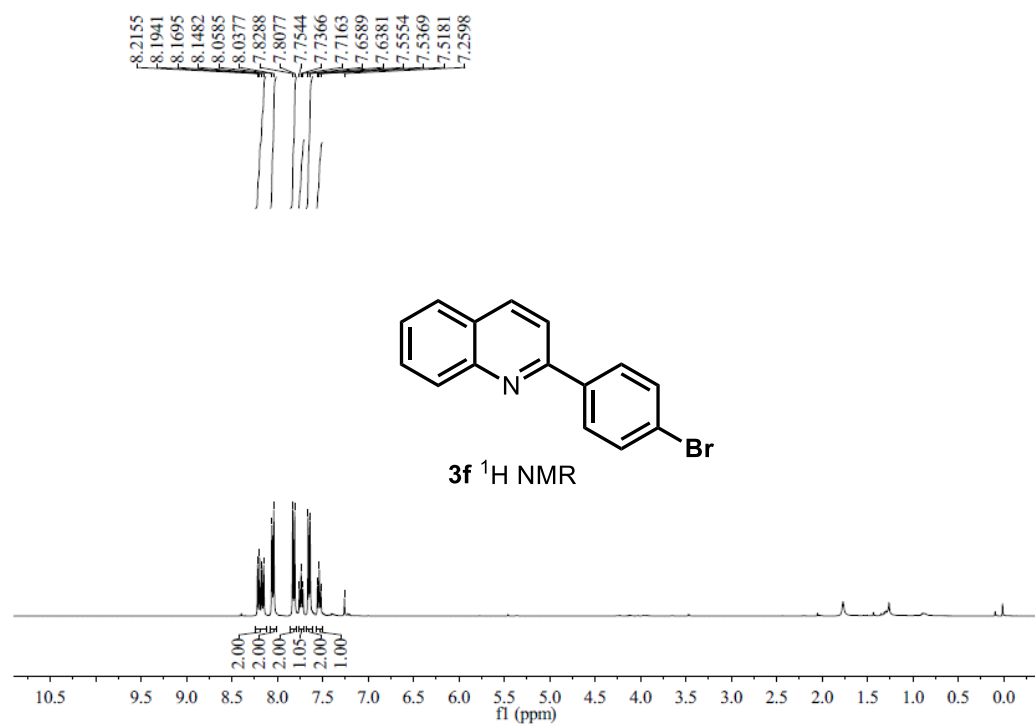


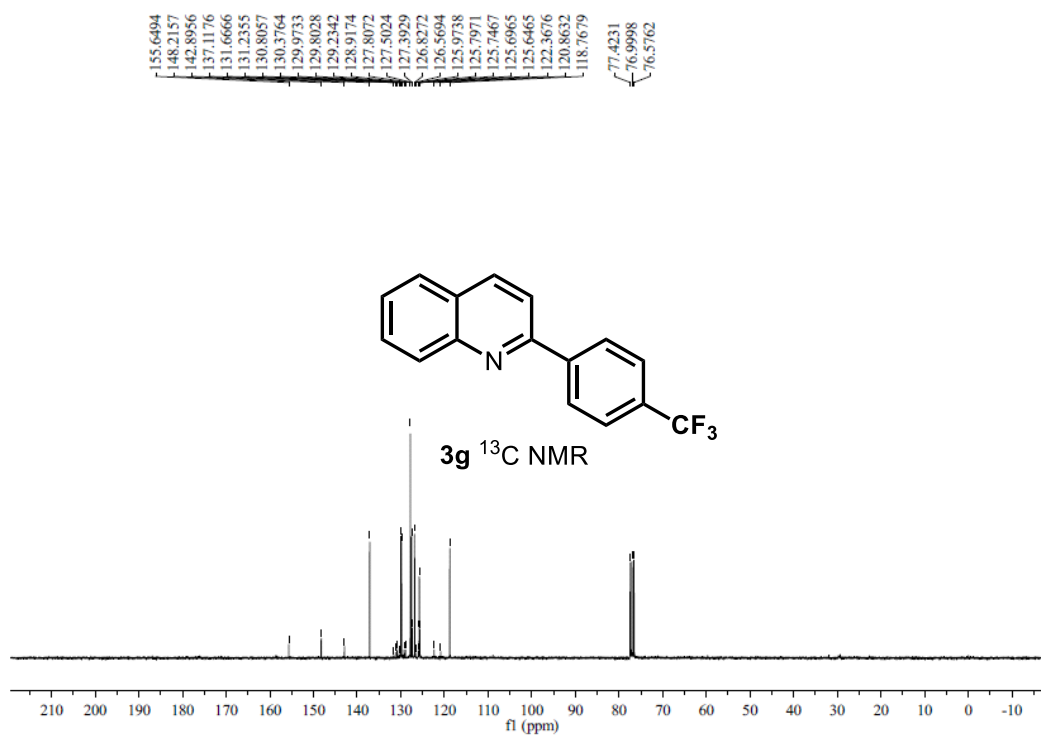
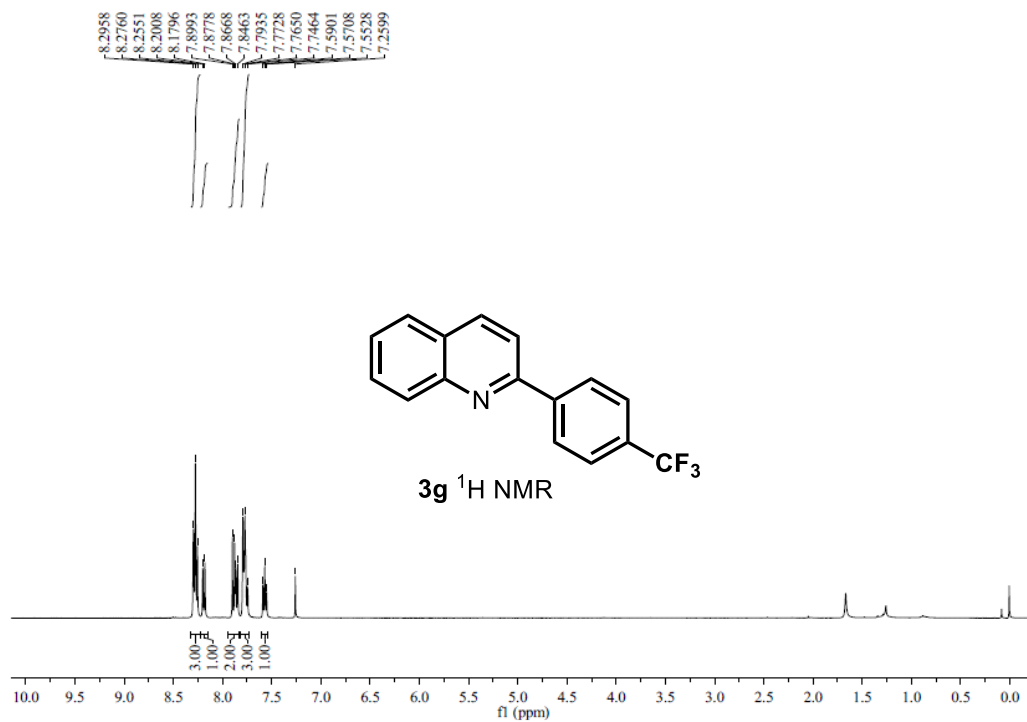
3e ^1H NMR

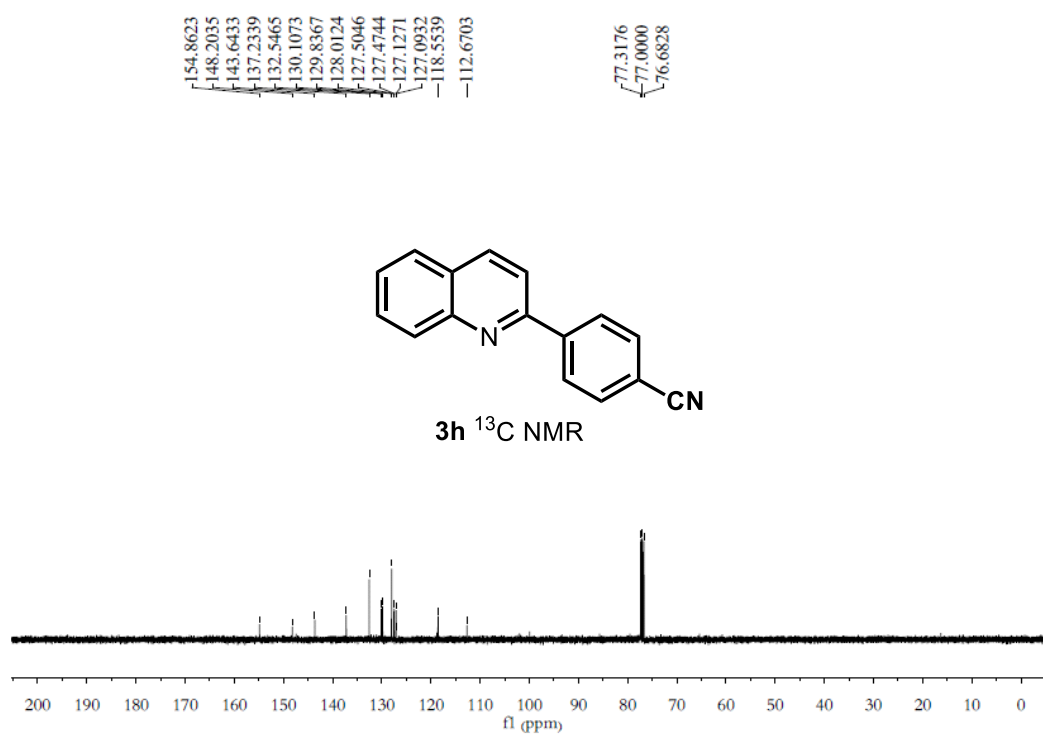
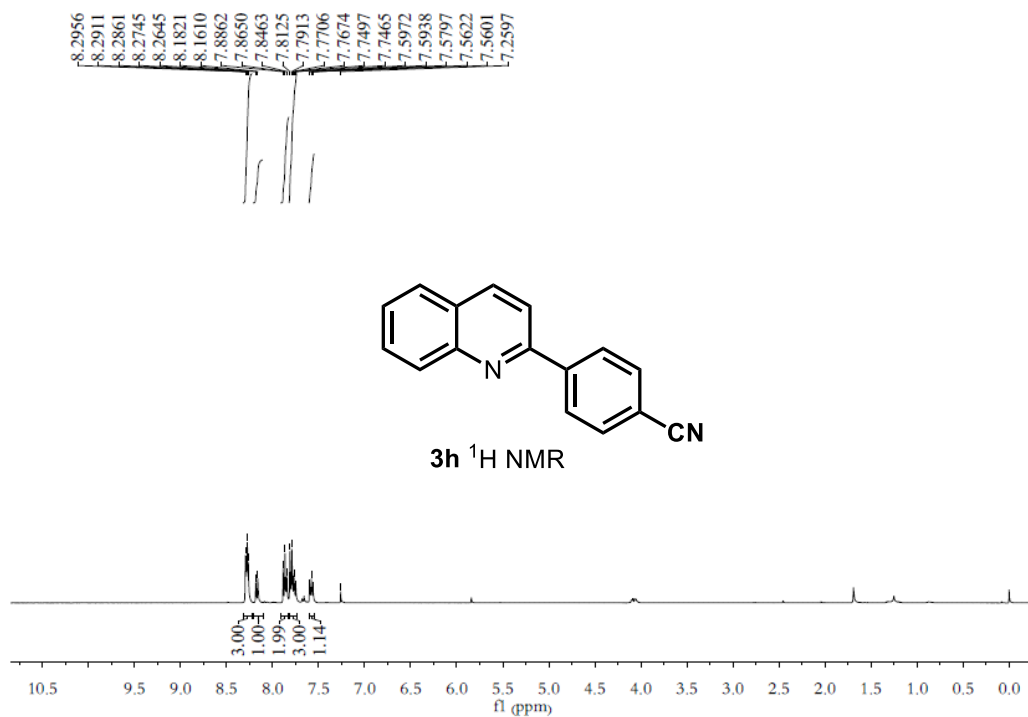


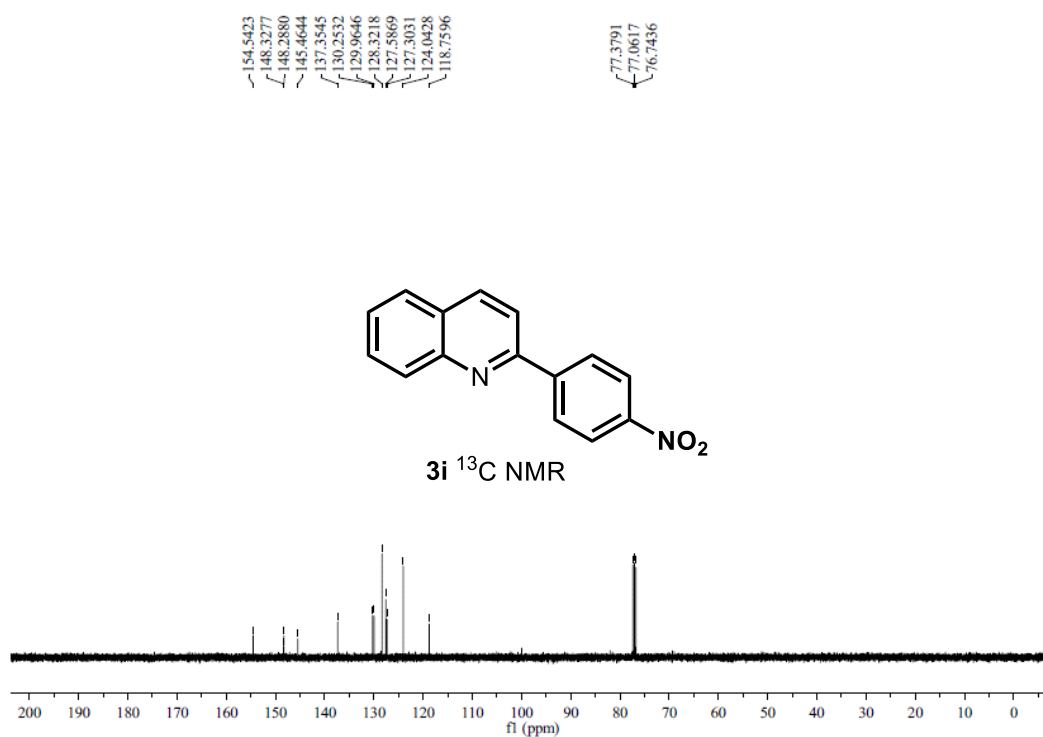
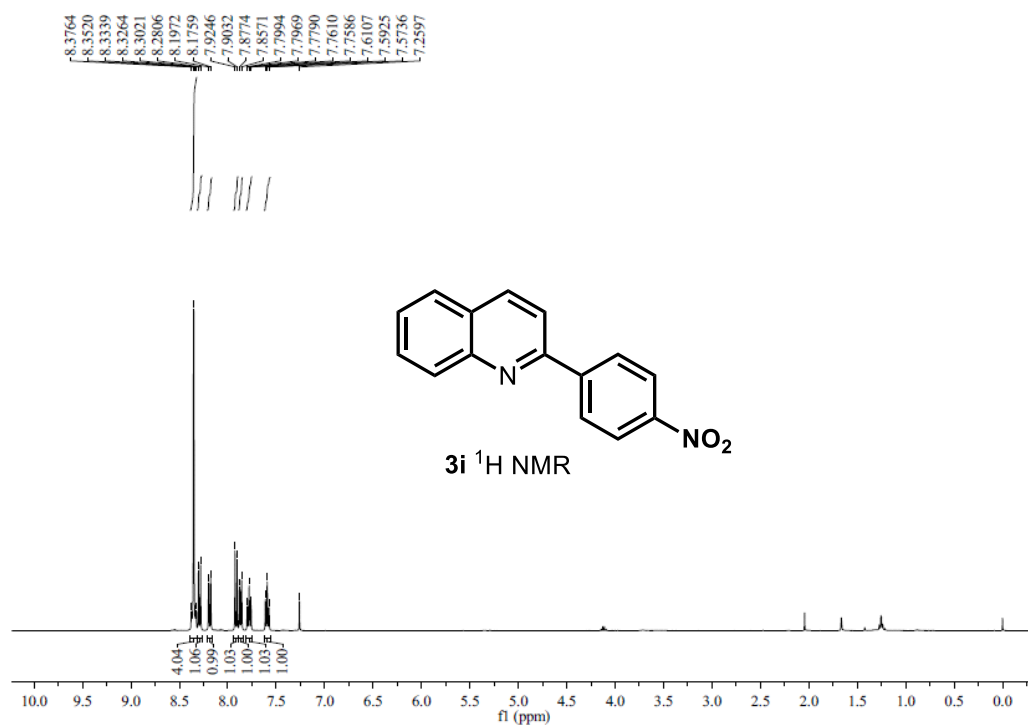
3e ^{13}C NMR

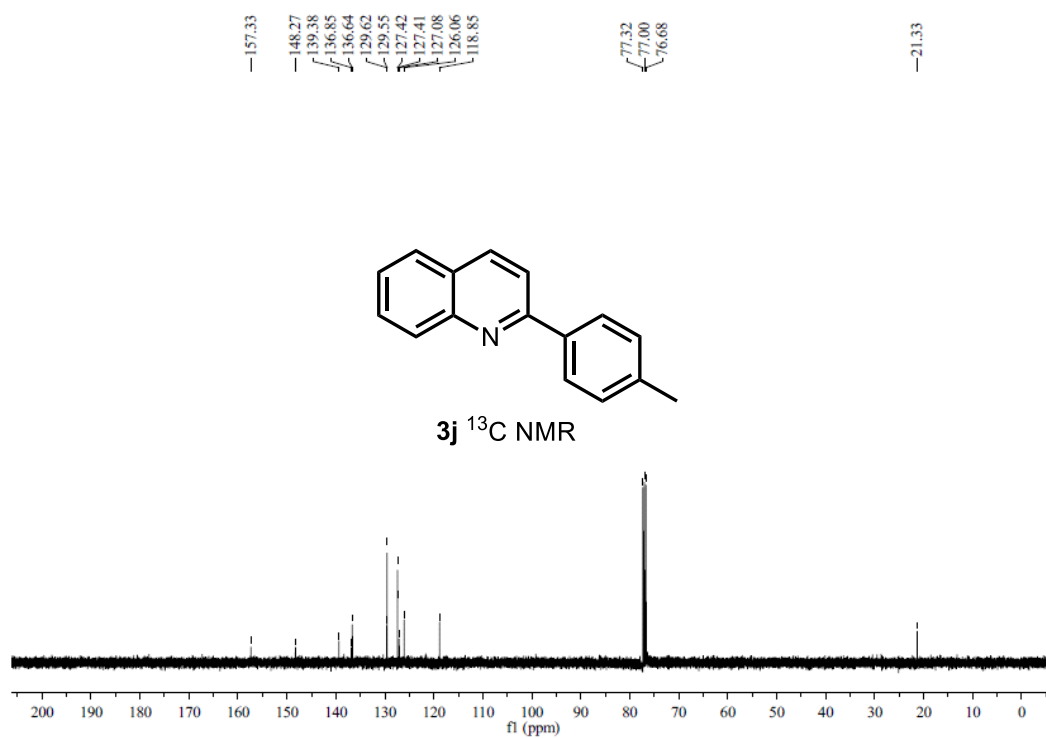
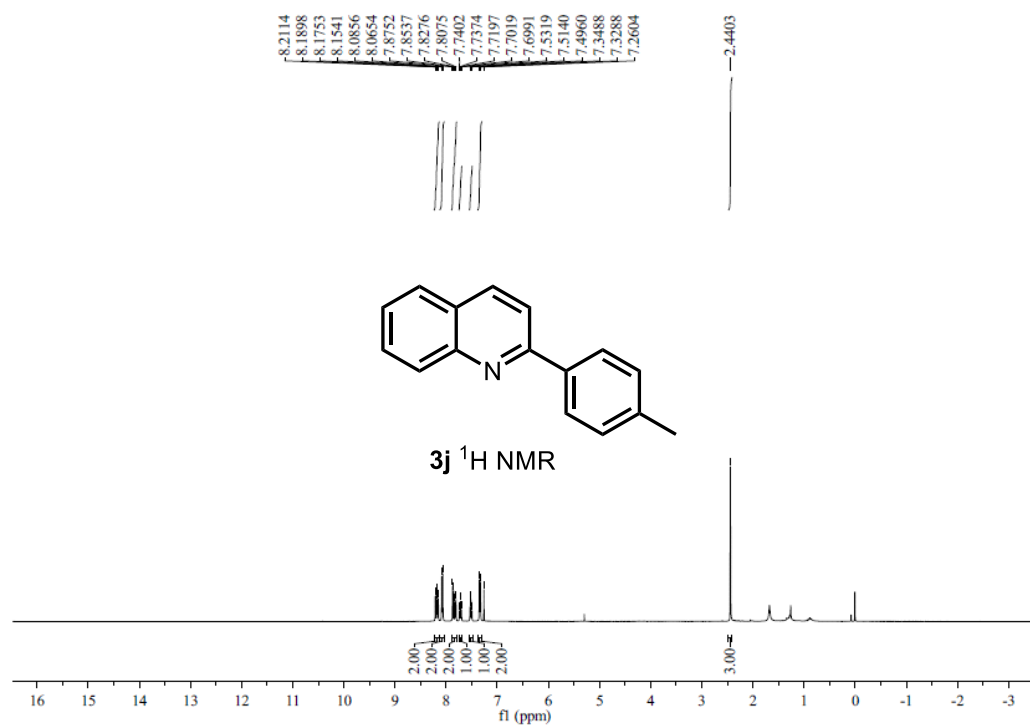


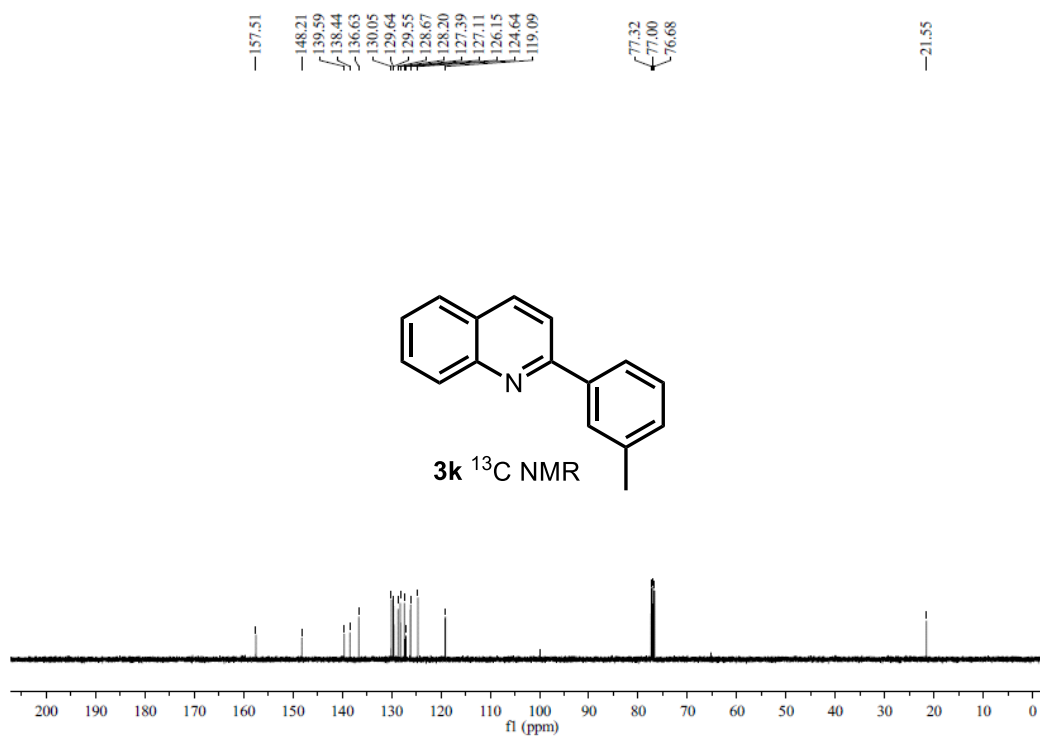
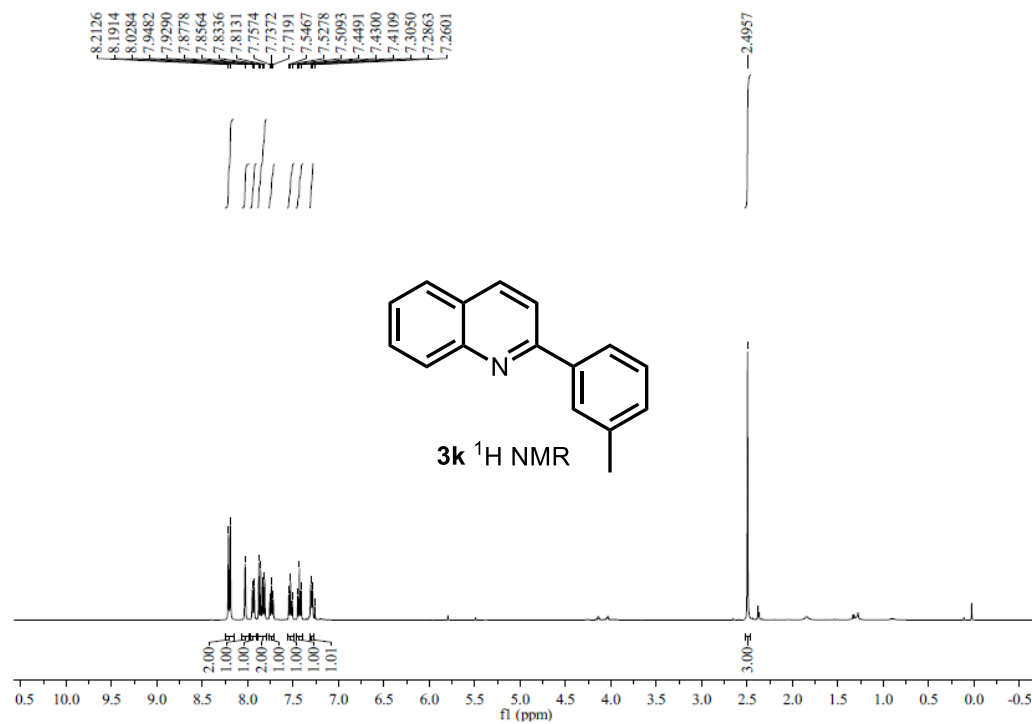


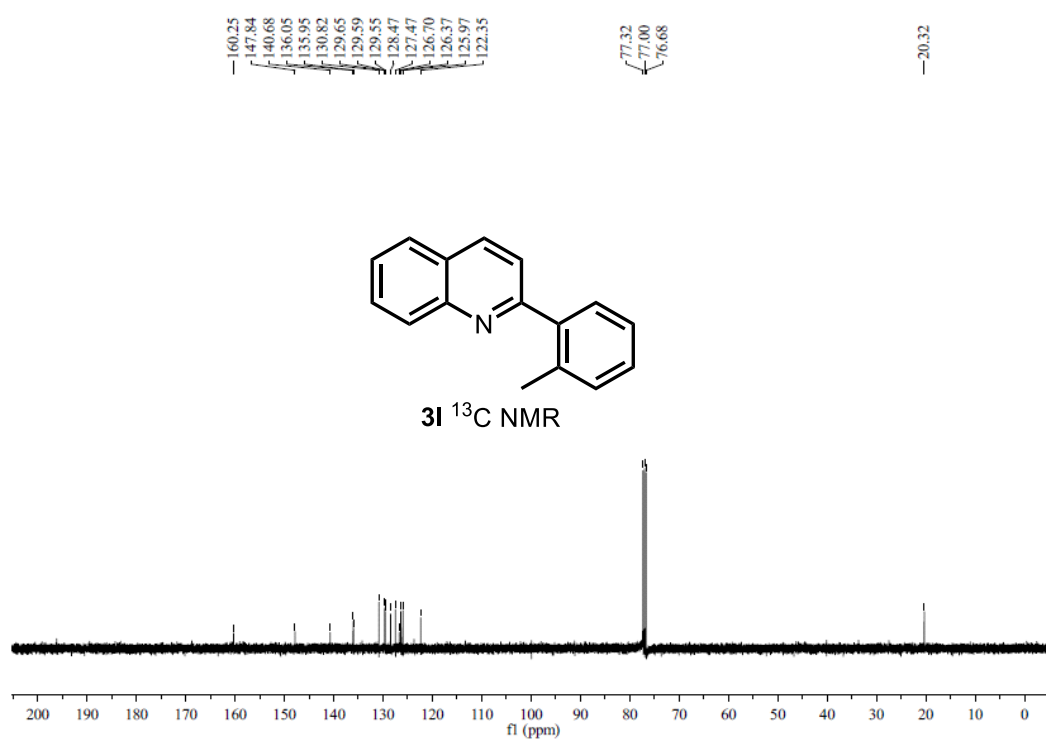
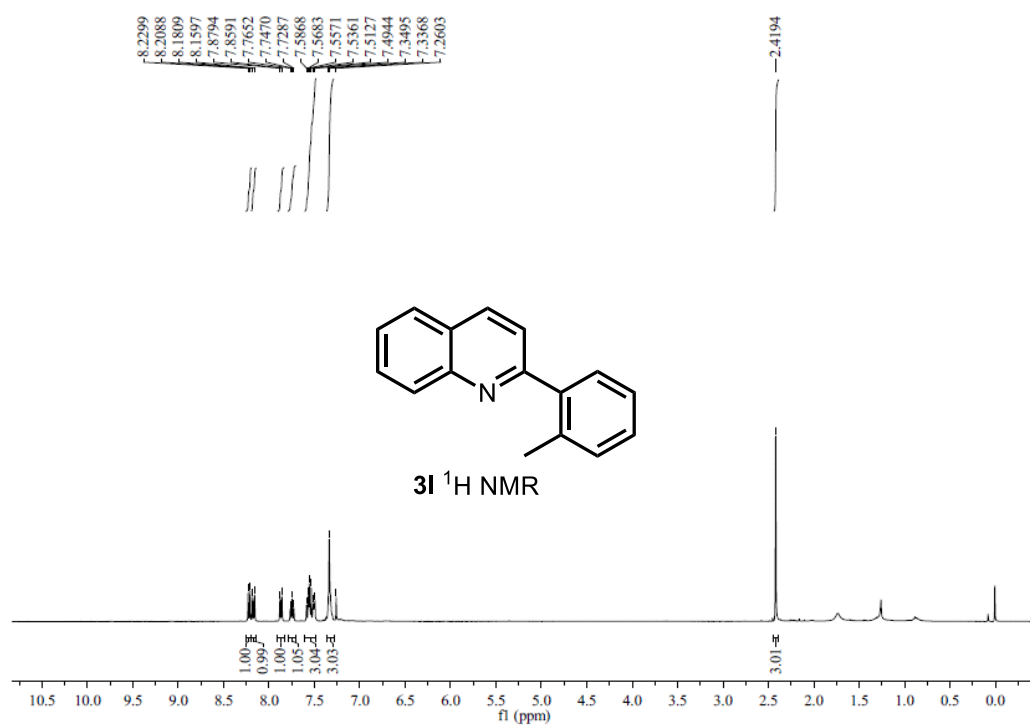


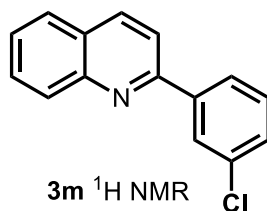
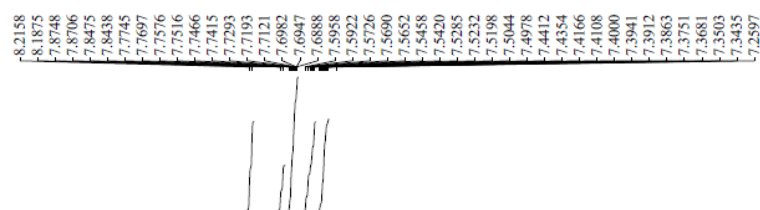




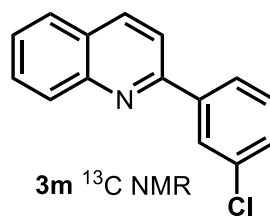
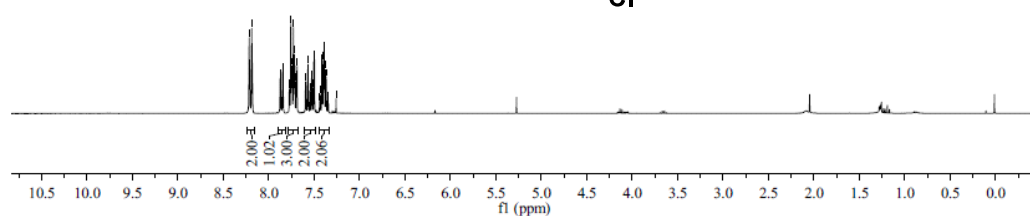




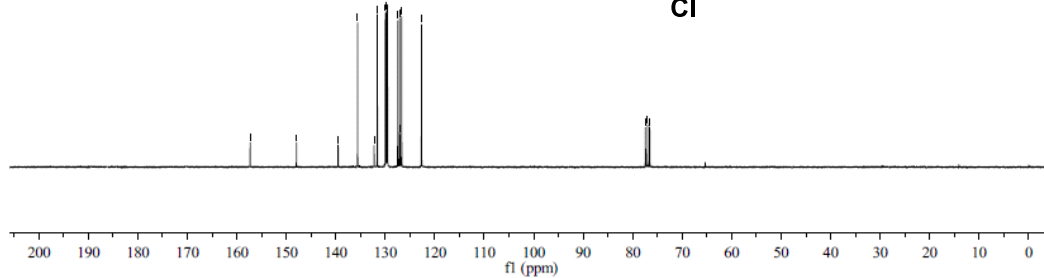


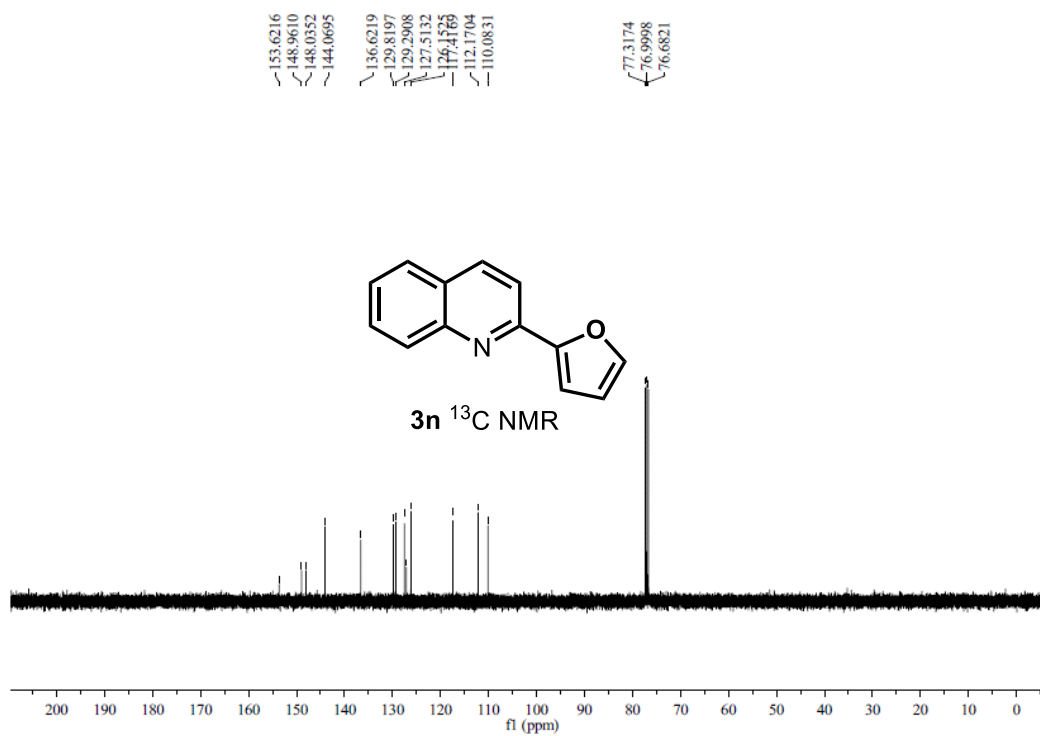
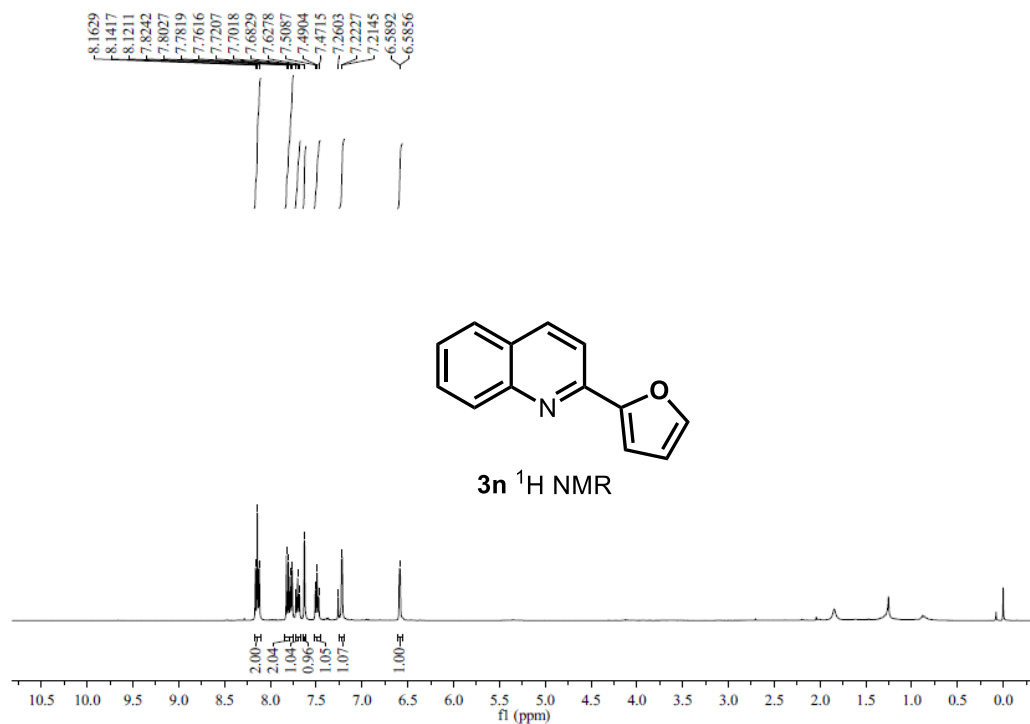


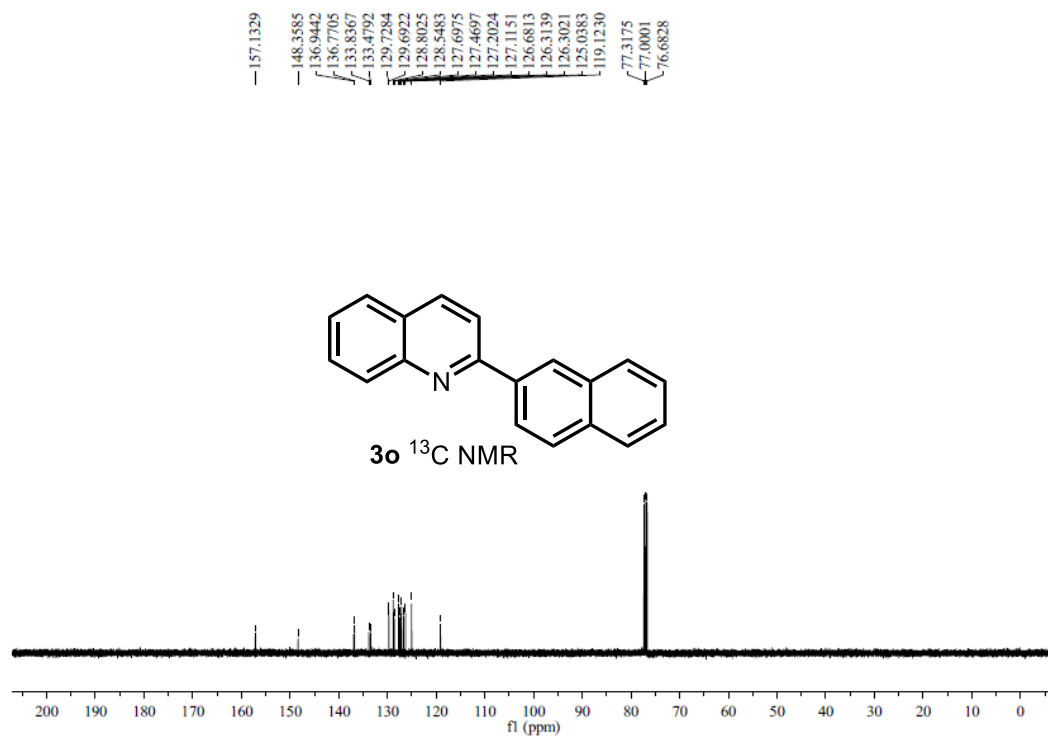
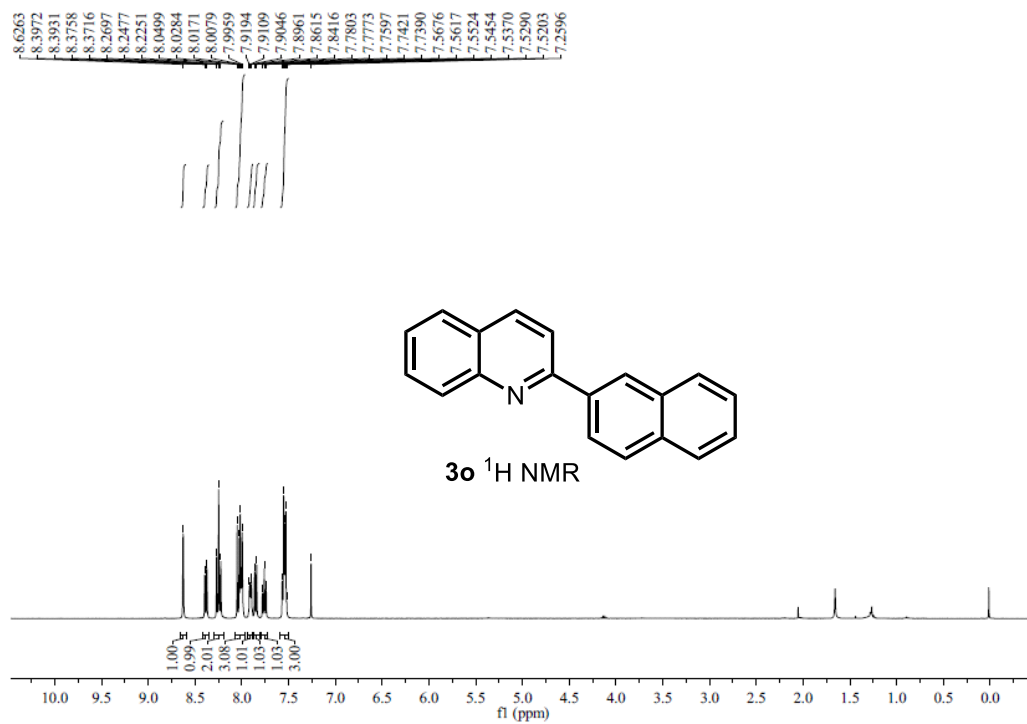
3m ^1H NMR

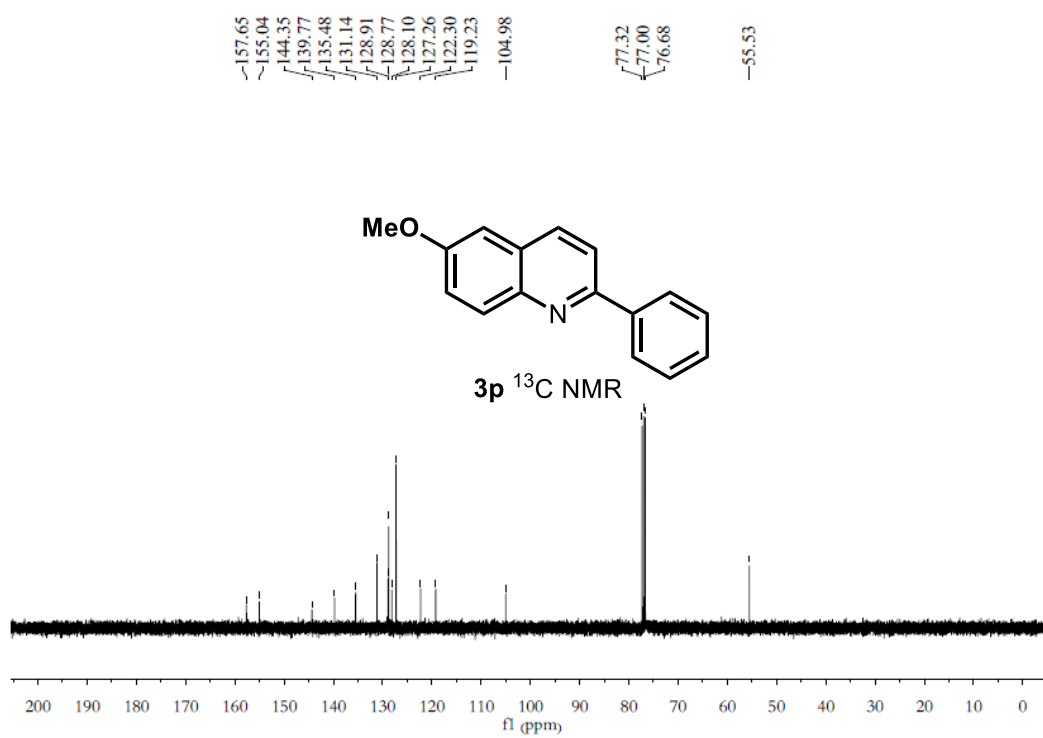
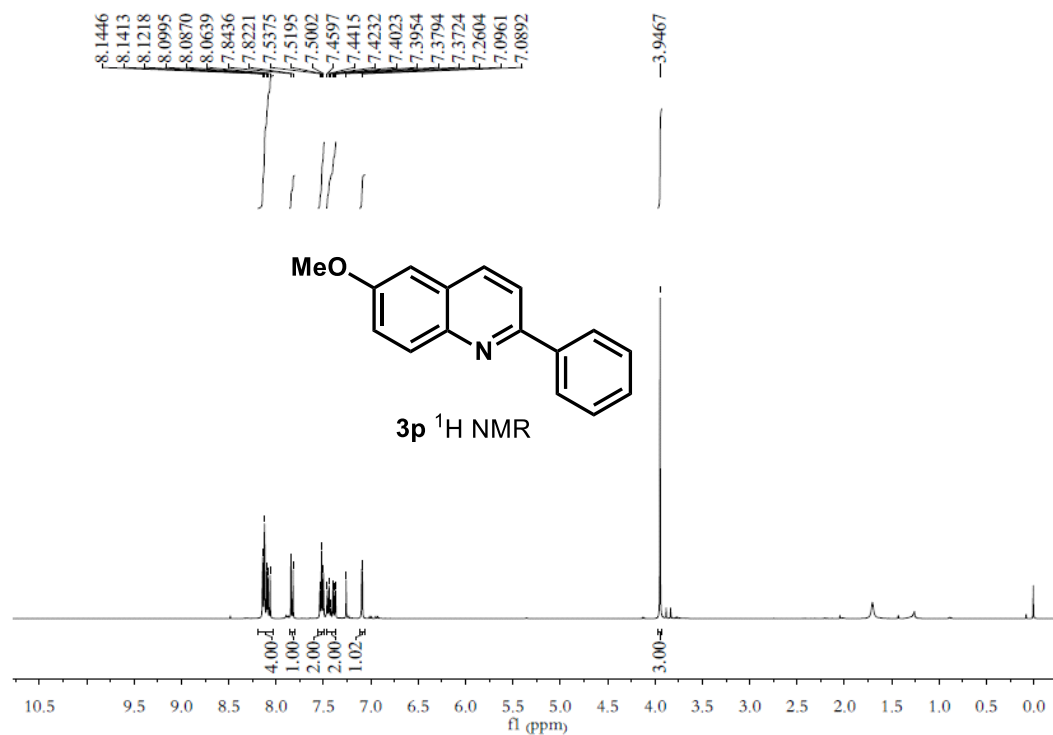


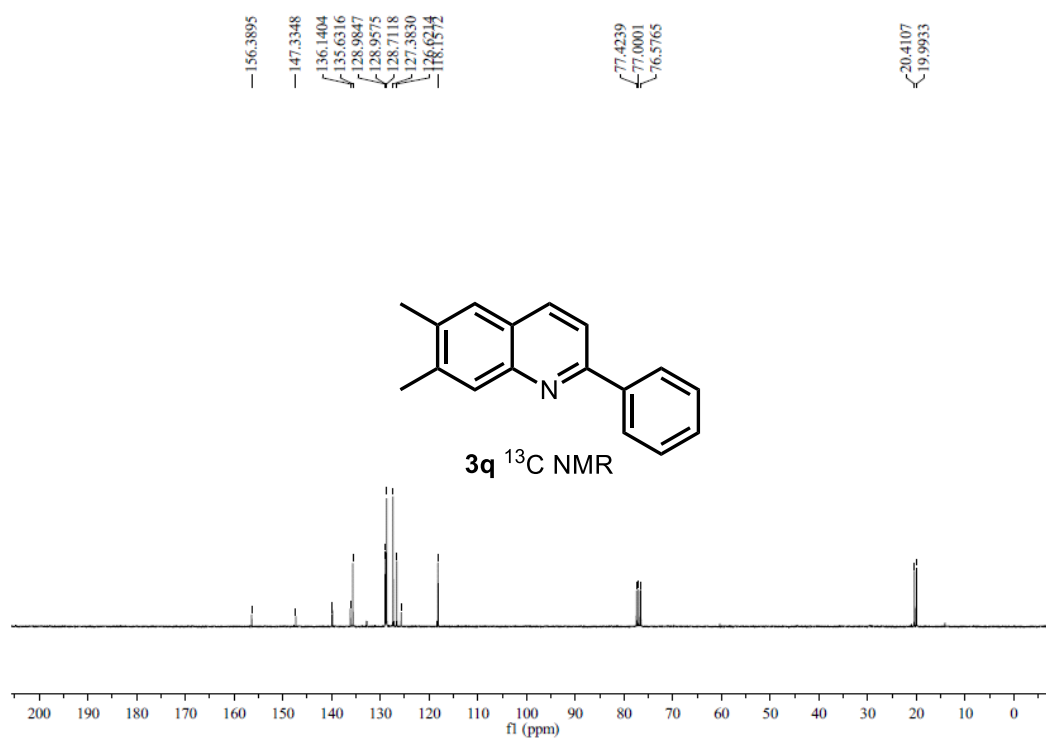
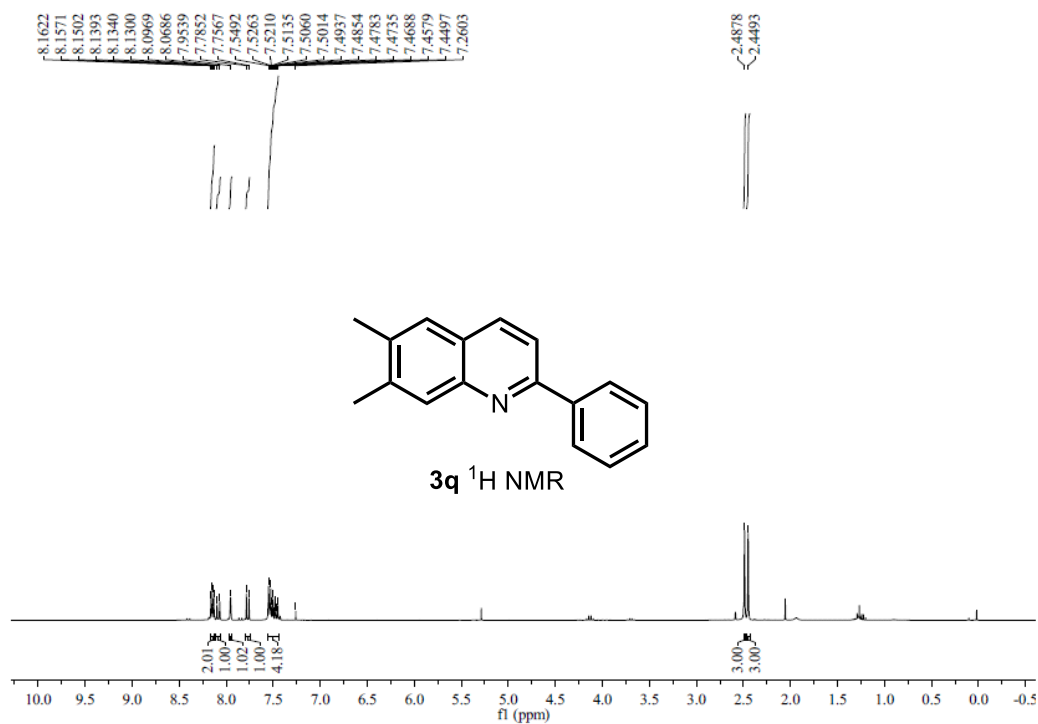
3m ^{13}C NMR

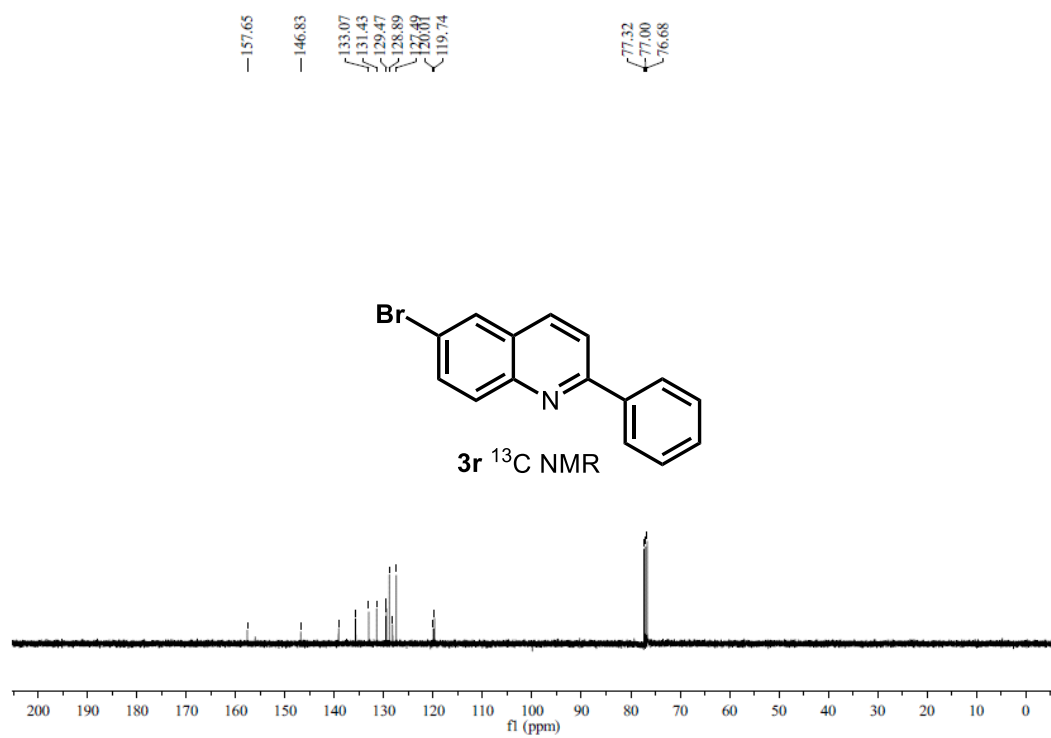
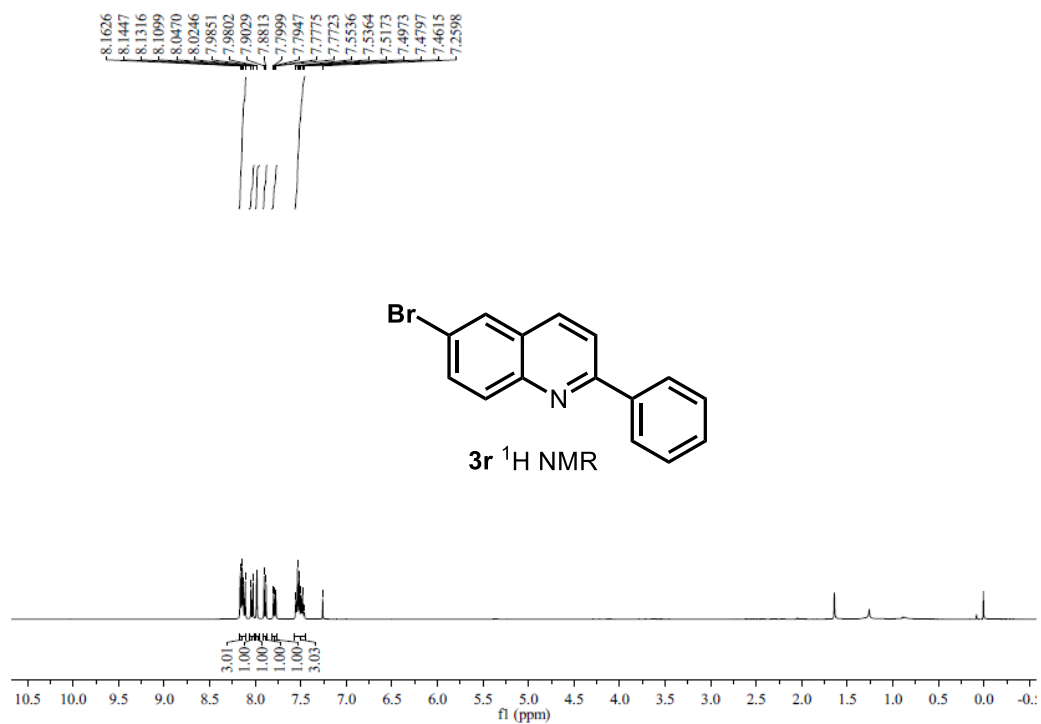


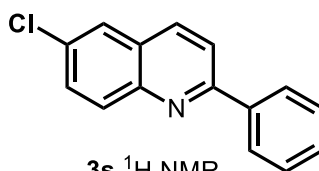
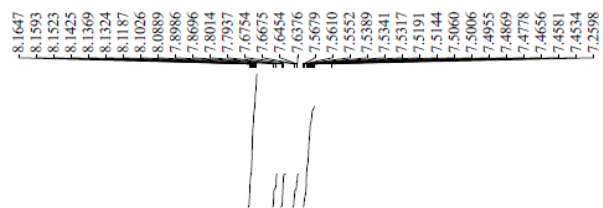




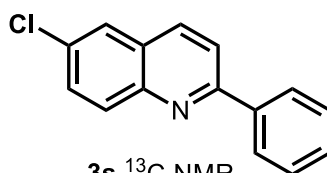
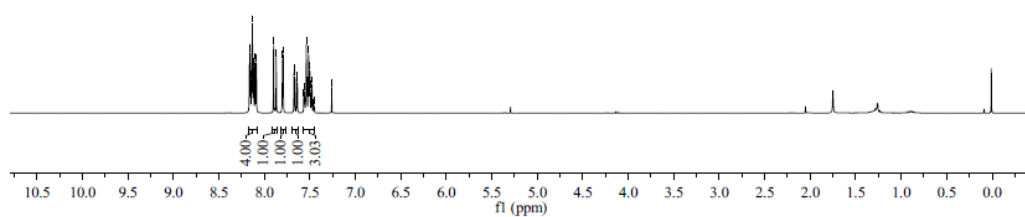








3s ^1H NMR



3s ^{13}C NMR

