

**One-pot assembly of functionalized (*m*-terphenyl-4'-yl)isoquinolines
from 1-methylisoquinoline and electrophilic acylacetylenes**

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The examples of the use of annulated and aryl-substituted isoquinolines

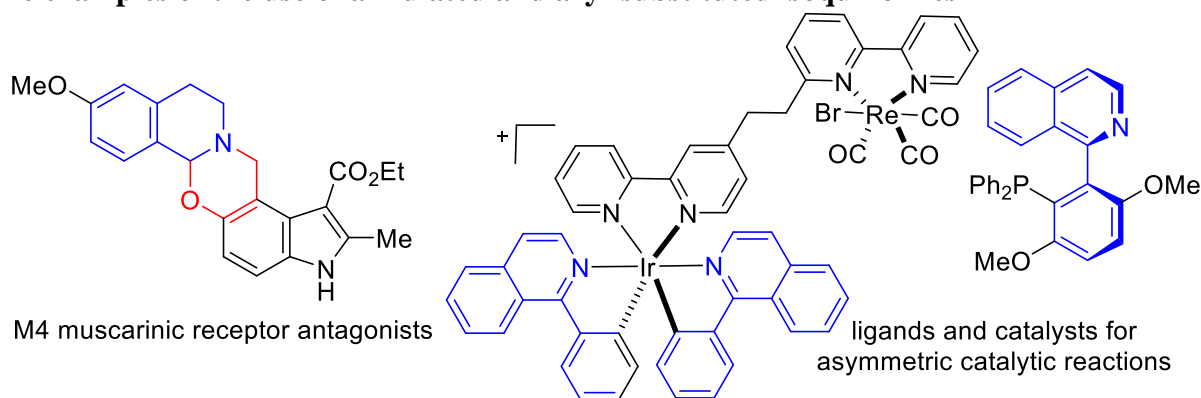
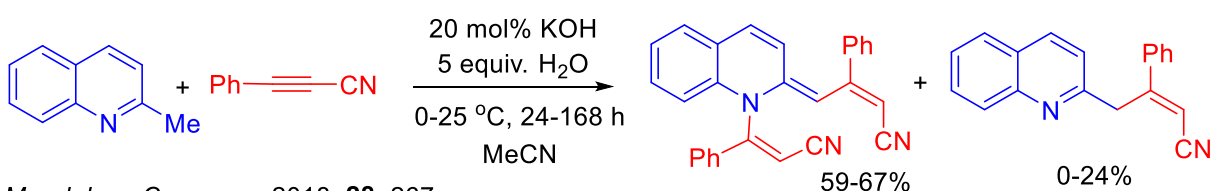


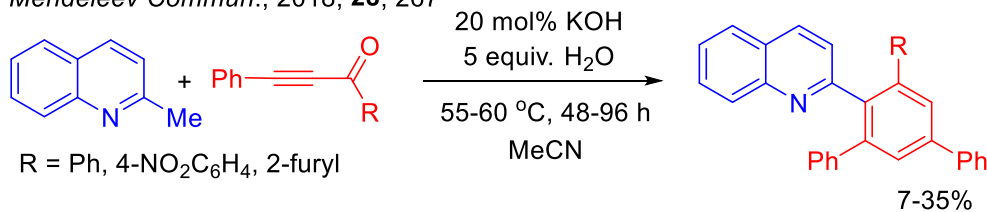
Figure S1

Examples of functionalization α -methylquinolines with electron-deficient acetylenes

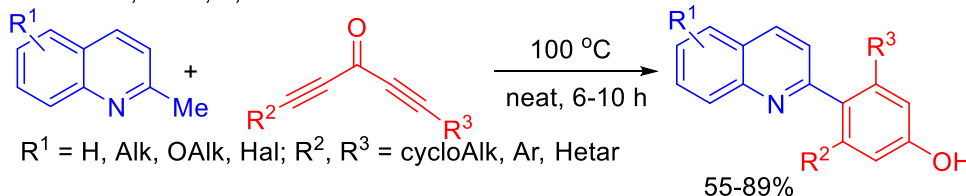
Russ. Chem. Bull., Int. Ed., 2017, **66**, 2258



Mendeleev Commun., 2018, **28**, 267



RSC Adv., 2018, **8**, 4584

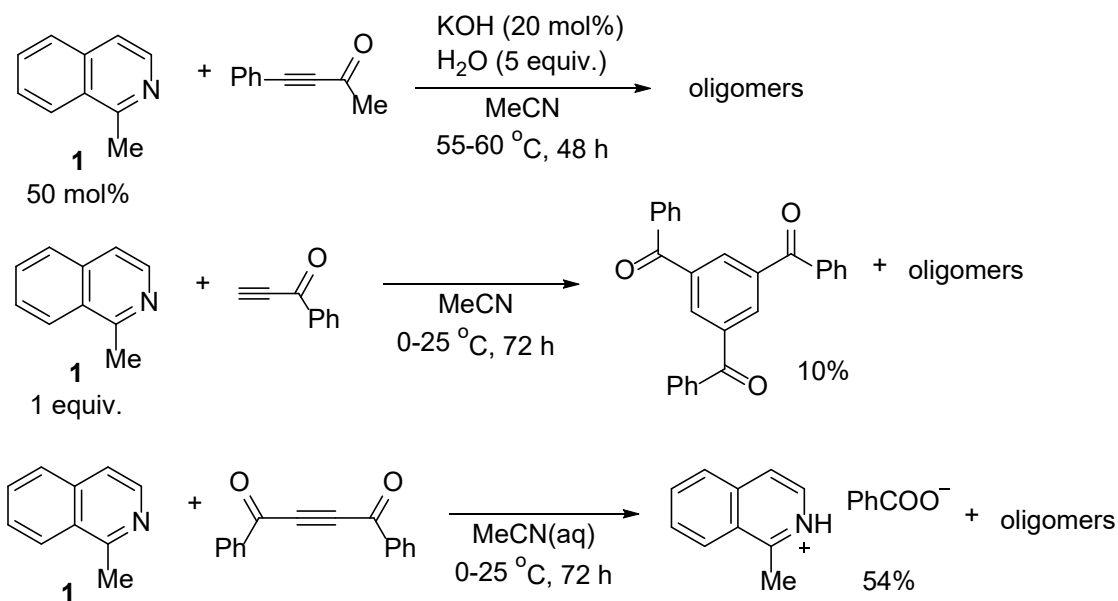


Scheme S1

Reactions 1-methylisoquinoline with other acylacetylenes

As to the question where other electrophilic acylacetylenes can tolerate the above reaction, the following experimental data were obtained. So, 1-acetyl-2-phenylacetylene did not give the expected product. Instead, it was subjected to a base-catalyzed autocondensation over the acetyl group leading to an inseparable mixture of the corresponding aldol/crotonic compounds. Terminal benzoylacetylene even without alkali (aqueous MeCN, room temperature, 72 h) in the presence of 1-methylisoquinoline underwent trimerization into tribenzoylbenzene (10% yield) along with higher open-chained oligomers. In the case of dibenzoylacetylene under the same conditions, 1-methylisoquinolin-2-ium benzoate was isolated in 54% yield. It is noteworthy that *N*-vinyl-5-phenylpyrrolylbenzoylacetylene happened to be inert (the reactants were almost completely

recovered) in the reaction with 1-methylisoquinoline **1** probably due to strong π -donating effect of the pyrrole substituent toward the triple bond, which significantly decreased its electrophilicity.



Scheme S2

General Experiment

¹H and ¹³C NMR spectra were recorded with an AV-400 Bruker BioSpin spectrometer. The internal standards were HMDS (for ¹H nuclei δ 0.05 ppm) or the residual solvent signals (for ¹³C nuclei δ 77.16 ppm). Coupling constants (*J*) are reported in hertz (Hz). The multiplicity abbreviations used are: s singlet, d doublet, dd doublet of doublets and m multiplet. Labeling of carbon and hydrogen atoms in compounds **3**, **4** and **6** used for NMR assignment are given in “Experimental Procedures”. IR spectra were recorded on a Bruker Vertex-70 instrument. HRMS spectra were recorded in ESI+ mode using Agilent 6210 mass spectrometer. Melting points (uncorrected) were measured on a digital melting point apparatus Electrothermal IA 9200. 1-Methylisoquinoline (**1**) is a commercial reagent. Acylacetylenes **2a-e**, **5** were prepared by literature method [S1, S2]. Column chromatography were carried out on silica gel 60 (0.060-0.200 mm) with chloroform/ethanol (20:1) mixture as eluent.

X-ray diffraction structural analysis data

The determination of the unit cell and the data collection for (furan-2-yl)(5'-(furan-2-yl)-6'-(isoquinolin-1-yl)-[1,1':3',1''-terphenyl]-4'-yl)methanone (**4d**) was performed on a Bruker D8 VENTURE PHOTON 100 CMOS diffractometer with CuK α radiation (λ = 1.54178) at 293.2(2) K using the ω - ϕ scan technique. A specimen of C₃₆H₂₃NO₃, 2(CHCl₃), approximate dimensions 0.38 mm x 0.28 mm x 0.13 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a triclinic unit cell with *P*-1 space group yielded a total of 65192 reflections to a maximum θ angle of 67.0°, of which 6355 were

independent (completeness = 98.8%, $R_{\text{int}} = 4.83\%$, $R_{\text{sig}} = 2.36\%$) and 4761 were greater than $2\sigma(F_2)$. The final cell constants of $a = 11.2135(3) \text{ \AA}$, $b = 12.3672(3) \text{ \AA}$, $c = 13.7438(3) \text{ \AA}$, $\alpha = 107.445(1)$, $\beta = 98.040(1)$, $\gamma = 90.728(1)$, $Z = 2$, $V = 1797.43(8) \text{ \AA}^3$. Data were corrected for absorption effects using the multi-scan method (SADABS) [S3]. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.259 and 0.541. The structure was solved using the Bruker SHELXTL Software Package [S4] and refined using Olex2 [S5] package. All H atoms were treated by mixed method.

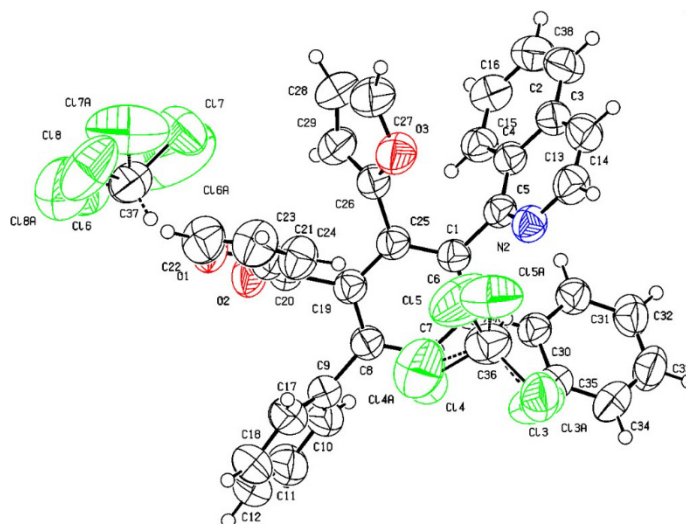
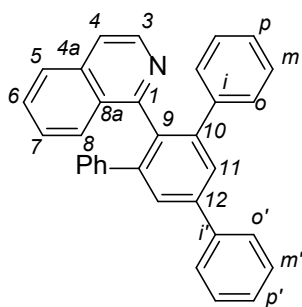


Figure S1. X-ray structure of furan-2-yl(5'-(furan-2-yl)-6'-(isoquinolin-1-yl)-[1,1':3',1''-terphenyl]-4'-yl)methanone (**4d**). Thermal ellipsoids set at 50% probability.

The final anisotropic full-matrix least-squares refinement on F_2 with 489 variables converged at $R_1 = 5.30\%$, for the observed data and $wR_2 = 15.76\%$ for all data. The goodness-of-fit was 1.05. The largest peak in the final difference electron density synthesis was 0.29 e-/\AA^3 and the largest hole was -0.42 e-/\AA^3 . On the basis of the final model, the calculated density was 1.397 g/cm^3 and $F(000)$, 772 e-.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC **2389926**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Experimental procedures, spectral and analytical data

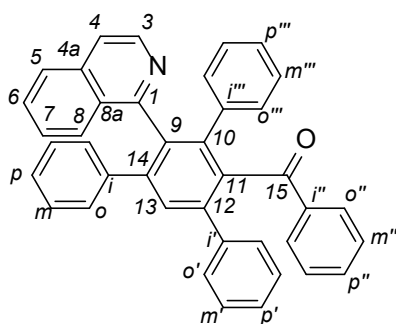


1-(5'-Phenyl-[1,1':3',1''-terphenyl]-4'-yl)isoquinoline (3a). A mixture of 1-methylisoquinoline (**1**) (72 mg, 0.5 mmol), acetylene (**2a**) (103 mg, 0.5 mmol), H₂O (45 mg, 2.5 mmol) and KOH·0.5H₂O (6 mg, 34 mol%) in 0.5 mL of MeCN was stirred for 24 h at 55-60 °C. After cooling to room temperature, solvent was removed under the reduced pressure and the reaction mixture was passed through a column to

obtain a product **3a** (36 mg, 33%) as a white powder, mp 244-245 °C (MeCN). Initial 1-methylisoquinoline (**1**) (40 mg) was recovered.

IR (microlayer): 1669, 1621, 1596, 1582 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 8.31 (d, ³J_{3,4} = 5.5 Hz, 1H, H-3), 7.74-7.75 (m, 4H, H-11, H_{o'} from Ph), 7.63 (d, ³J_{5,6} = 8.2 Hz, 1H, H-5), 7.57 (d, ³J_{7,8} = 8.1 Hz, 1H, H-8), 7.50-7.35 (m, 4H, H-6, H_{m',p'} from Ph), 7.34 (d, ³J_{3,4} = 5.5 Hz, 1H, H-4), 7.29-7.25 (m, 1H, H-7), 7.08-7.06 (m, 4H, H_o from Ph), 6.98-6.96 (m, 6H, H_{m,p} from Ph) ppm. ¹³C NMR (100.62 MHz, CDCl₃): δ 160.3 (C-1), 143.2 (C-10), 141.7 (C-3), 141.5 (C_i from Ph), 141.4 (C_{i'} from Ph), 140.7 (C-12), 135.8 (C-4a), 135.6 (C-9), 129.6 (C-6), 129.3 (C_o from Ph), 129.0 (C-11), 128.7 (C-8a), 128.2 (C_{m'} from Ph), 127.8 (C-8), 127.6 (C_m from Ph), 127.4 (C_{o'} from Ph), 127.3 (C_{p'} from Ph), 126.9 (C-7), 126.7 (C-5), 126.6 (C_p from Ph), 119.6 (C-4) ppm. HRMS (ESI): *m/z* calcd for C₃₃H₂₄N⁺ [M + H]⁺: 434.1909; found: 434.1912. MS (EI, 70 eV): *m/z* (%) = 433 (100) [M]⁺, 432 (97), 356 (19) [M – Ph]⁺, 354 (10), 330 (18) [M – PhCHCH]⁺, 216 (20), 214 (18), 208 (73), 203 (14), 201 (32) [M – 3Ph]⁺, 194 (18), 176 (46).

(2'-(Isoquinolin-1-yl)-5'-phenyl-[1,1':3',1''-terphenyl]-4'-yl)(phenyl)methanone (4a). White powder, 0.014 g (11%), mp 293-295 °C.



IR (microlayer): 1660, 1640, 1621, 1597, 1581, 1557 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 8.28 (d, ³J_{3,4} = 5.7 Hz, 1H, H-3), 7.69 (d, ³J_{7,8} = 8.2 Hz, 1H, H-8), 7.64 (s, 1H, H-13), 7.57-7.52 (m, 3H, H-5, H_{o''} from Ph), 7.47-7.39 (m, 4H, H-4, H-6, H_{o'} from Ph), 7.35-7.34 (m, 1H, H-7), 7.29-7.20 (m, 6H, H_{m',p',m'',p''} from Ph), 7.15-7.13 (m, 4H, H_{o,m} from Ph), 7.08-7.06 (m, 1H, H_p from Ph), 7.00-6.96 (m, 4H, H_{o''',m'''} from Ph), 6.67-6.63 (m, 1H, H_{p'''} from Ph) ppm. ¹³C NMR (100.62 MHz, CDCl₃): δ 198.6 (C-15), 159.5 (C-1), 143.2 (C-12), 143.2 (C-14), 141.5 (C-3), 141.3 (C-10), 140.7 (C-11), 140.7 (C_i from Ph), 140.0 (C_{i'} from Ph), 138.5 (C_{i'''} from Ph), 137.7 (C-9), 136.9 (C_{i''} from Ph), 135.5 (C-4a), 132.7 (C-13), 131.3 (C_{p''} from Ph), 129.8 (C-6), 129.6 (C_{o''} from Ph), 129.4 (C_{o'} from Ph), 129.3 (C_{m''} from Ph), 129.2 (C_o from Ph), 128.5 (C-8a), 128.3 (C_{m'} from Ph), 128.0 (C_{o'''} from Ph), 127.7 (C_m from Ph), 127.6 (C-8, C_p from Ph), 127.4 (C-7, C_{p'} from

Ph), 127.4 (C-7, C_{p'} from

Ph), 127.0 (C-5), 126.9 (C_p from Ph), 126.6 (C_m from Ph), C-7), 119.7 (C-4) ppm. HRMS (ESI): *m/z* calcd for C₄₀H₂₈NO⁺ [M + H]⁺: 538.2171; found: 538.2172. MS (EI, 70 eV): *m/z* (%) = 539 (9), 538 (36) [M]⁺, 537 (100) [M-H]⁺, 536.2 (60), 460 (28) [M-Ph]⁺, 433 (32), 432 (59) [M-PhCO]⁺, 430 (12), 354 (13), 230 (13), 229 (37), 214 (43), 207 (33), 201 (11) [M - 3Ph]⁺, 176 (17), 128 (17), 105 (38), 77 (46), .

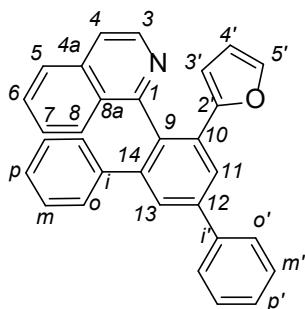
1-(3-Methoxy-5'-phenyl-[1,1':3',1''-terphenyl]-4'-yl)isoquinoline (3b). A mixture of 1-methylisoquinoline (**1**) (72 mg, 0.5 mmol), acetylene (**2b**) (118 mg, 0.5 mmol), H₂O (45 mg, 2.5 mmol) and KOH·0.5H₂O (6 mg, 34 mol%) in 0.5 mL of MeCN was stirred for 48 h at the 55-60 °C. After cooling to room temperature, the solvent was removed under the reduced pressure and the reaction mixture was passed through a column to obtain a product **3b** (29 mg, 25%) as a light-beige powder, mp 143-146 °C (MeCN). Initial 1-methylisoquinoline (**1**) (49 mg) was recovered.

IR (microlayer): 1620, 1596, 1585, 1560 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 8.31 (d, ³J_{3,4} = 5.8 Hz, 1H, H-3), 7.75-7.74 (m, 4H, H-11, H-13, H_{o'} from Ph), 7.65 (d, ³J_{5,6} = 8.4 Hz, 1H, H-5), 7.58 (d, ³J_{7,8} = 8.2 Hz, 1H, H-8), 7.48-7.41 (m, 3H, H_{m',p'} from Ph), 7.38-7.35 (m, 2H, H-4, H-6), 7.31-7.27 (m, 1H, H-7), 7.08-7.06 (m, 2H, H_o from Ph), 6.97-6.96 (m, 3H, H_{m,p} from Ph), 6.92-6.89 (m, 1H, H-5'), 6.76-6.74 (m, 1H, H-6'), 6.56 (s, 1H, H-2'), 6.52-6.50 (m, 1H, H-4'), 3.34 (s, 3H, OMe) ppm. ¹³C NMR (100.62 MHz, CDCl₃): δ 160.3 (C-1), 158.7 (C-3'), 143.2 (C-10), 143.1 (C-14), 142.7 (C-1'), 141.5 (C-3), 141.4 (C_{i,i'} from Ph), 141.0 (C-12), 135.6 (C-4a, C-9), 129.8 (C-6), 129.2 (C_o from Ph), 129.0 (C_{m'} from Ph, C-8a), 128.7 (C-5'), 128.2 (C-13), 127.8 (C-8), 127.6 (C-11), 127.5 (C_{o'} from Ph), 127.4 (C_m from Ph), 127.3 (C_{p'} from Ph), 127.0 (C-7), 126.7 (C-5), 126.6 (C_p from Ph), 121.7 (C-6'), 119.8 (C-4), 113.9 (C-2'), 113.6 (C-4'), 55.0 (OMe) ppm. HRMS (ESI): *m/z* calcd for C₃₄H₂₆NO⁺ [M + H]⁺: 464.2014; found: 464.2017. MS (EI, 70 eV): *m/z* (%) = 463 (100) [M]⁺, 448 (11) [M-Me]⁺, 224(16), 215 (20), 207 (17), 201 (28), 194 (19), 182 (10).

1-(4,4''-Dimethyl-5'-phenyl-[1,1':3',1''-terphenyl]-4'-yl)isoquinoline (3c). A mixture of 1-methylisoquinoline (**1**) (72 mg, 0.5 mmol), acetylene (**2c**) (110 mg, 0.5 mmol), H₂O (45 mg, 2.5 mmol) and KOH·0.5H₂O (6 mg, 34 mol%) in 0.5 mL of MeCN was stirred for 48 h at the 55-60 °C. After cooling to room temperature, the solvent was removed under the reduced pressure and washed with water and MeCN

to obtain a product **3c** (31 mg, 27%) as a light-beige powder, mp 94-99 °C (MeCN). Initial 1-methylisoquinoline (**1**) (53 mg) was recovered.

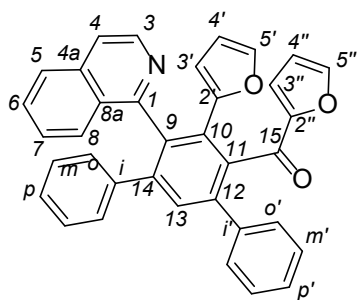
IR (microlayer): 1668, 1621, 1598, 1584, 1558 (C=C) cm^{-1} . ^1H NMR (400.13 MHz, CDCl_3): δ 8.31 (d, $^3J_{3,4} = 5.8$ Hz, 1H, H-3), 7.71-7.70 (m, 2H, H-2'',6''), 7.64-7.56 (m, 4H, H-5, H-8, H-11, H-13), 7.43-7.39 (m, 1H, H-6), 7.33 (d, $^3J_{3,4} = 5.8$ Hz, 1H, H-4), 7.27-7.22 (m, 3H, H-7, H-3'',5''), 7.05-7.04 (m, 2H, $\text{H}_{o'}$ from Ph), 6.97-6.95 (m, 5H, H-2',6', $\text{H}_{m,p}$ from Ph), 6.78-6.76 (m, 2H, H-3',5'), 2.39 (s, 3H, Me''), 2.11 (s, 3H, Me') ppm. ^{13}C NMR (100.62 MHz, CDCl_3): δ 160.5 (C-1), 143.2 (C-10), 143.1 (C-14), 141.6 (C-3, C_i from Ph), 141.3 (C-12), 138.6 (C-1''), 137.8 (C-1'), 137.6 (C-4''), 136.1 (C-4'), 135.6 (C-4a), 135.5 (C-9), 129.7 (C-2',6'), 129.6 (C-6), 129.3 (C_o from Ph), 129.1 (C-2'',6''), 128.8 (C-8a), 128.4 (C-3'',5''), 128.1 (C-8), 127.8 (C-13), 127.5 (C-3',5'), 127.4 (C-11), 127.2 (C_m from Ph), 126.8 (C-7), 126.6 (C-5), 126.5 (C_p from Ph), 119.5 (C-4) ppm. HRMS (ESI): m/z calcd for $\text{C}_{35}\text{H}_{28}\text{N}^+$ [$\text{M} + \text{H}$] $^+$: 462.2222; found: 462.2224. MS (EI, 70 eV): m/z (%) = 462 (39), 461 (100), 460 (96) [M] $^+$, 370 (11), 344 (10), 222 (15), 215 (30), 207 (14), 201 (12).



1-(5'-(Furan-2-yl)-[1,1':3',1''-terphenyl]-4'-yl)isoquinoline (3d). A mixture of 1-methylisoquinoline (**1**) (72 mg, 0.5 mmol), acetylene (**2d**) (98 mg, 0.5 mmol), H_2O (45 mg, 2.5 mmol) and $\text{KOH}\cdot 0.5\text{H}_2\text{O}$ (6 mg, 34 mol%) in 0.5 mL of MeCN was stirred for 24 h at the 55-60 °C. After cooling to room temperature, solvent was removed under the reduced pressure and washed with water and MeCN to obtain a product **3d** (34 mg, 32%) as a yellow gum. Initial 1-methylisoquinoline (**1**) (44 mg) was recovered.

IR (microlayer): 1658, 1621, 1598, 1585, 1559 (C=C) cm^{-1} . ^1H NMR (400.13 MHz, CDCl_3): δ 8.51 (d, $^3J_{3,4} = 5.7$ Hz, 1H, H-3), 8.21 (d, $^4J_{11,13} = 1.8$ Hz, 1H, H-11), 7.77-7.75 (m, 2H, $\text{H}_{o'}$ from Ph), 7.69 (d, $^3J_{5,6} = 8.2$ Hz, 1H, H-5), 7.64 (d, $^4J_{11,13} = 1.8$ Hz, 1H, H-13), 7.58 (d, $^3J_{7,8} = 8.4$ Hz, 1H, H-8), 7.54-7.46 (m, 4H, H-4, $\text{H}_{m',p'}$ from Ph), 7.40-7.36 (m, 1H, H-6), 7.31-7.28 (m, 1H, H-7), 7.18-7.17 (m, 1H, H-5'), 7.10-7.08 (m, 2H, H_o from Ph), 6.96-6.94 (m, 3H, $\text{H}_{m,p}$ from Ph), 6.00-5.98 (m, 1H, H-4'), 5.00 (d, $^3J_{3',4'} = 3.5$ Hz, 1H, H-3') ppm. ^{13}C NMR (100.62 MHz, CDCl_3): δ 160.3 (C-1), 152.3 (C-2'), 143.5 (C-14), 142.0 (C-5'), 141.8 (C-3), 141.6 (C_i from Ph), 141.1 ($\text{C}_{i'}$ from Ph), 140.6 (C-12), 136.0 (C-4a), 133.4 (C-10), 131.4 (C-9), 130.0 (C-6), 129.3 (C_o from Ph), 129.0 ($\text{C}_{m'}$ from Ph), 128.5 (C-8a), 128.2 (C-13), 127.8 ($\text{C}_{p'}$ from Ph), 127.5 ($\text{C}_{o'}$ from Ph), 127.4 (C_m from Ph), 127.2 (C-8), 126.8 (C-7), 126.7 (C-5), 126.6 (C_p from Ph), 124.7 (C-11), 120.3 (C-4), 111.5 (C-3'), 109.1 (C-4') ppm. HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{22}\text{NO}^+$ [$\text{M} + \text{H}$] $^+$: 424.1701; found: 424.1705. MS (EI, 70 eV): m/z (%) = 424 (15), 423 (35) [M] $^+$, 394 (12), 370 (32), 369 (100), 194 (11), 189 (14), 182 (23), 176 (25), 169 (12), 157 (10).

(Furan-2-yl)(5'-(furan-2-yl)-6'-(isoquinolin-1-yl)-[1,1':3',1''-terphenyl]-4'-yl)methanone (**4d**).

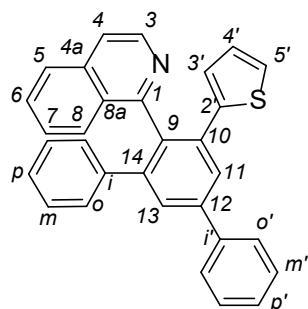


Light-beige powder, 9 mg (7%), mp 233-235 °C.

IR (microlayer): 1661 (C=O), 1622, 1585, 1563 (C=C) cm^{-1} .

^1H NMR (400.13 MHz, CDCl_3): δ 8.42 (d, $^3J_{3,4} = 5.8$ Hz, 1H, H-3), 7.70-7.67 (m, 2H, H-5, H-8), 7.61 (s, 1H, H-13), 7.54-7.40 (m, 1H, H-6), 7.47-7.46 (m, 1H, H-4), 7.46-7.40 (m, 3H, H_o from Ph, H-5''), 7.38-7.37 (m, 1H, H-7), 7.35-7.29 (m, 3H, $\text{H}_{m',p'}$ from Ph), 7.14-7.11 (m, 2H, H_o from Ph), 7.01-7.00 (m, 3H, $\text{H}_{m,p}$ from Ph), 6.85 (d, $^3J_{3'',4''} = 3.6$ Hz, 1H, H-3''), 6.82 (m, 1H, H-5'), 6.31-6.29 (dd, $^3J_{3'',4''} = 3.6$ Hz, $^3J_{4'',5''} = 1.7$ Hz, 1H, H-4''), 5.80 (m, 1H, H-4'), 5.66 (m, 1H, H-3') ppm. ^{13}C NMR (100.62 MHz, CDCl_3): δ 185.0 (C-15), 159.3 (C-1), 153.4 (C-2''), 149.4 (C-2'), 147.0 (C-5''), 144.0 (C-14), 142.3 (C-5', C-10), 141.6 (C-3), 141.3 (C-12), 140.2 (C_i from Ph), 139.6 ($\text{C}_{i'}$ from Ph), 137.2 (C-11), 136.7 (C-9), 135.7 (C-4a), 132.6 (C-13), 130.4 (C-8), 130.1 (C-6), 129.3 ($\text{C}_{o'}$ from Ph), 129.1 (C_o from Ph), 128.4 ($\text{C}_{m'}$ from Ph), 127.8 ($\text{C}_{p'}$ from Ph), 127.7 (C_m from Ph), 127.3 (C-7), 127.1 (C-8, $\text{C}_{p'}$ from Ph), 126.6 (C-5), 120.1 (C-4, C-3''), 112.1 (C-4''), 111.8 (C-3'), 110.6 (C-4') ppm. HRMS (ESI): m/z calcd for $\text{C}_{36}\text{H}_{24}\text{NO}_3^+ [\text{M} + \text{H}]^+$: 518.1756; found: 518.1758.

1-(5'-(Thiophen-2-yl)-[1,1':3',1''-terphenyl]-4'-yl)isoquinoline (**3e**). A mixture of 1-



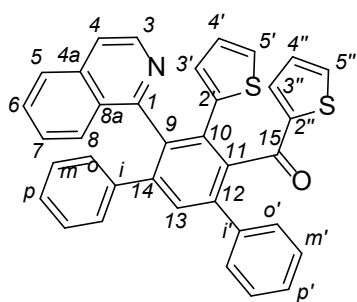
methylisoquinoline (**1**) (72 mg, 0.5 mmol), acetylene (**2e**) (106 mg, 0.5 mmol), H_2O (45 mg, 2.5 mmol) and $\text{KOH}\cdot 0.5\text{H}_2\text{O}$ (6 mg, 34 mol%) in 0.5 mL of MeCN was stirred for 24 h at the 55-60 °C. After cooling to room temperature, solvent was removed under the reduced pressure and washed with water and MeCN to obtain a product **3e** (23 mg, 21%) as a beige powder, mp 223-225 °C (MeCN). Initial 1-methylisoquinoline

(**1**) (35 mg) was recovered.

IR (microlayer): 1721, 1663, 1621, 1597, 1581, 1559 (C=C) cm^{-1} . ^1H NMR (400.13 MHz, CDCl_3): δ 8.51 (d, $^3J_{3,4} = 5.7$ Hz, 1H, H-3), 7.90 (d, $^4J_{11,13} = 1.6$ Hz, 1H, H-11), 7.75-7.73 (m, 2H, $\text{H}_{o'}$ from Ph), 7.70 (d, $^4J_{11,13} = 1.8$ Hz, 1H, H-13), 7.65 (d, $^3J_{5,6} = 8.3$ Hz, 1H, H-5), 7.62 (d, $^3J_{7,8} = 8.5$ Hz, 1H, H-8), 7.50-7.45 (m, 4H, H-4, $\text{H}_{m',p'}$ from Ph), 7.41-7.37 (m, 1H, H-6), 7.33-7.29 (m, 1H, H-7), 7.09-7.07 (m, 2H, H_o from Ph), 6.98-6.95 (m, 4H, H-5', $\text{H}_{m,p}$ from Ph), 6.64-6.62 (m, 1H, H-4'), 6.56-6.55 (m, 1H, H-3') ppm. ^{13}C NMR (100.62 MHz, CDCl_3): δ 160.0 (C-1), 143.6 (C-14), 142.7 (C-10), 141.8 (C-3), 141.7 (C_i from Ph), 141.2 ($\text{C}_{i'}$ from Ph), 140.5 (C-12), 135.8 (C-4a), 135.6 (C-9), 135.5 (C-2'), 129.9 (C-6), 129.3 (C_o from Ph), 129.1 ($\text{C}_{m'}$ from Ph), 128.9 (C-8a), 128.7 (C-13), 128.2 (C-11), 127.9 ($\text{C}_{p'}$ from Ph), 127.6 ($\text{C}_{o'}$ from Ph), 127.5 (C_m from Ph), 127.1

(C-8, C-4'), 126.8 (C-7), 126.7 (C-5, C-3', C_p from Ph), 125.8 (C-5'), 120.1 (C-4) ppm. HRMS (ESI): *m/z* calcd for C₃₁H₂₂NS⁺ [M + H]⁺: 440.1473; found: 440.1475. MS (EI, 70 eV): *m/z* (%) = 441 (20), 440 (34), 439 (100), 438 (90) [M]⁺, 406 (20), 404 (16), 212 (13), 201 (43), 195 (22), 189 (10), 179 (10).

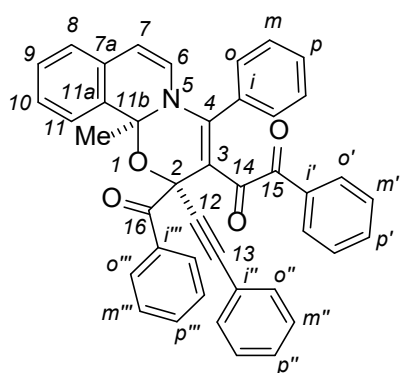
(6'-(Isoquinolin-1-yl)-5'-(thiophen-2-yl)-[1,1':3',1''-terphenyl]-4'-yl)(thiophen-2-yl)methanone



(4e). White powder, 13 mg (10%), mp 295-297 °C.

IR (microlayer): 1646 (C=O), 1581, 1562 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 8.37 (d, ³J_{3,4} = 5.8 Hz, 1H, H-3), 7.71-7.69 (m, 1H, H-8), 7.64 (s, 1H, H-13), 7.61-7.59 (m, 1H, H-5), 7.50-7.46 (m, 3H, H-6, H_{o'} from Ph), 7.44-7.42 (m, 1H, H-3''), 7.39-7.28 (m, 6H, H-4, H-7, H-5'', H_{m',p'} from Ph), 7.16-7.15 (m, 2H, H_o from Ph), 7.01-6.99 (m, 3H, H_{m,p} from Ph), 6.87-6.86 (m, 1H, H-4''), 6.75-6.74 (m, 1H, H-5'), 6.64-6.63 (m, 1H, H-3'), 6.40 (m, 1H, H-4') ppm. ¹³C NMR (100.62 MHz, CDCl₃): δ 190.3 (C-15), 159.2 (C-1), 145.6 (C-2''), 143.6 (C-(C-14)), 141.3 (C-3), 140.7 (C-12), 140.4 (C_i from Ph), 139.7 (C_{i'} from Ph), 139.5 (C-10), 138.1 (C-9), 137.9 (C-2'), 135.6 (C-4a), 135.4 (C-5''), 134.6 (C-3''), 133.3 (C-11), 132.2 (C-13), 130.4 (C-3'), 130.0 (C-6), 129.4 (C_{o'} from Ph), 129.2 (C_o from Ph), 128.9 (C-8a), 128.4 (C_{m'} from Ph), 127.8 (C-4'', C_{m,p'} from Ph), 127.4 (C-8), 127.1 (C-7, C_p from Ph), 126.8 (C-5'), 126.6 (C-5), 125.6 (C-4'), 120.1 (C-4) ppm. HRMS (ESI): *m/z* calcd for C₃₆H₂₄NOS₂⁺ [M + H]⁺: 550.1299; found: 550.1299. MS (EI, 70 eV): *m/z* (%) = 551 (12), 550 (26), 549 (63) (M⁺), 516 (16), 488 (22), 440 (13), 439 (40), 438 (100), 407 (23), 406 (71), 243 (10), 232 (13), 217 (32), 210 (25), 200 (41), 194 (17), 111 (28).

1-((2S*,11bS*)-2-Benzoyl-11b-methyl-4-phenyl-2-(phenylethynyl)-2H,11bH-[1,3]oxazino[2,3-a]-



isoquinolin-3-yl)-2-phenylethane-1,2-dione (6). A mixture of 1-methylisoquinoline (1) (18 mg, 0.125 mmol), acetylene 5 (59 mg, 0.250 mmol) in 0.5 mL of MeCN was stirred for 24 h at 0-5 °C. After warming to room temperature, the solvent was removed under the reduced pressure and then the reaction mixture was passed through column to obtain oxazinoisoquinoline 6 (42 mg, 41%) as a yellow gum. Initial 1-methylisoquinoline (1) (11 mg) was recovered.

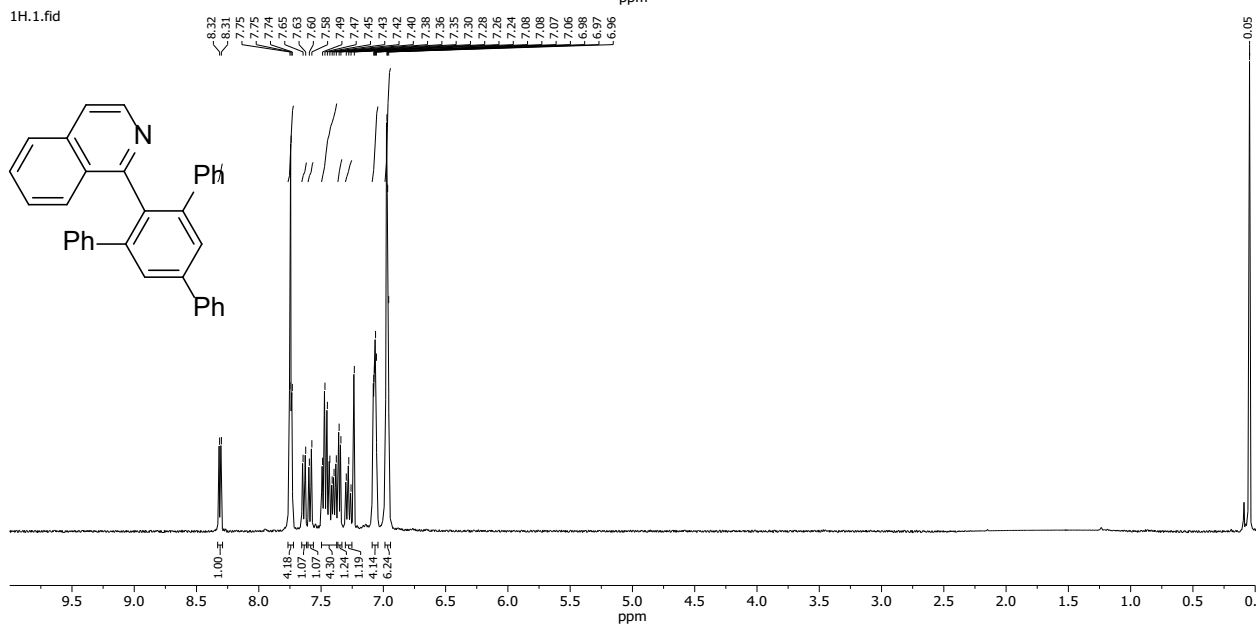
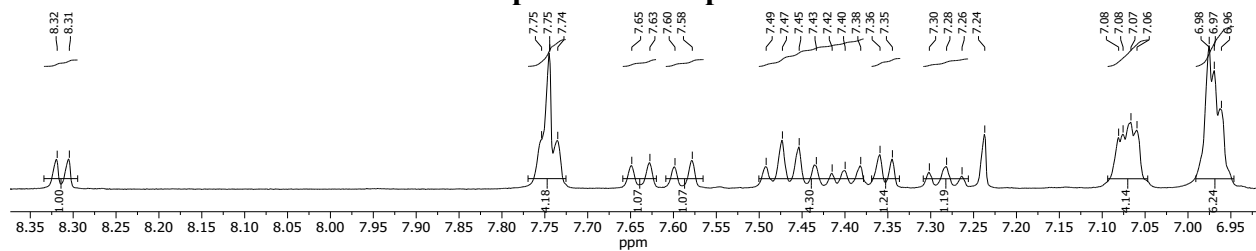
IR (microlayer): 2253 (C≡C), 1705, 1675 (C=O), 1599, 1580, 1549 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ 8.17-8.15 (m, 2H, H_{o'''} from Ph), 7.77-7.74 (m, 1H, H-11), 7.54-7.51 (m, 2H, H_{p,p'''} from Ph), 7.44-7.40 (m, 4H, H_{o',m} from Ph), 7.38-7.35 (m, 2H, H_{m'''} from Ph), 7.30-7.20 (m,

7H, H-9, H-10, H_{o,o',p'} from Ph), 7.16-7.12 (m, 2H, H_{m'} from Ph), 7.05-6.99 (m, 2H, H_{m''} from Ph), 6.75-6.73 (m, 1H, H-8), 6.59-6.55 (m, 1H, H_{p''} from Ph), 6.06 (d, ³J_{6,7} = 7.9 Hz, 1H, H-6), 5.63 (d, ³J_{6,7} = 7.9 Hz, 1H, H-7), 2.34 (s, 3H, Me) ppm. ¹³C NMR (100.62 MHz, CDCl₃): δ 191.8 (C-16), 191.1 (C-14, C-15), 152.9 (C-4), 136.3 (C_{i'''} from Ph), 133.4 (C_{p'} from Ph), 133.3 (C_i from Ph), 133.1 (C_{i'} from Ph), 132.6 (C-7a), 132.1 (C_p from Ph), 131.9 (C_{o''} from Ph), 130.9 (C_{o'''} from Ph), 130.7 (C_{p''} from Ph), 129.7 (C_{o'} from Ph), 129.6 (C_o from Ph), 129.0 (C_{p'''} from Ph), 128.6 (C-9), 128.6 (C_{m'''} from Ph), 128.4 (C_m from Ph), 128.2 (C_{m''} from Ph), 128.0 (C-11a), 127.8 (C-6), 127.7 (C_{m'} from Ph), 126.1 (C-11), 124.8 (C-10), 123.8 (C-8), 122.8 (C-3), 113.8 (C_{i''} from Ph), 106.5 (C-7), 89.7 (C-12), 89.0 (C-11b), 88.1 (C-13), 75.7 (C-2), 27.6 (Me) ppm. HRMS (ESI): *m/z* calcd for C₄₂H₃₀NO₄⁺ [M + H]⁺: 612.2175; found: 612.2177.

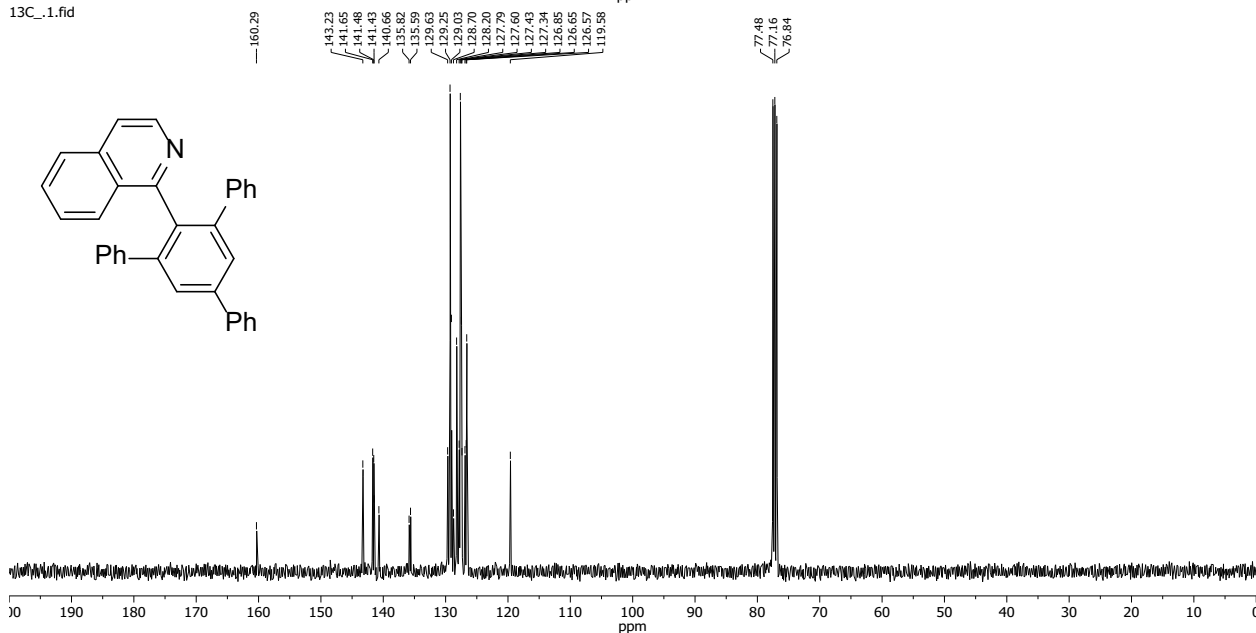
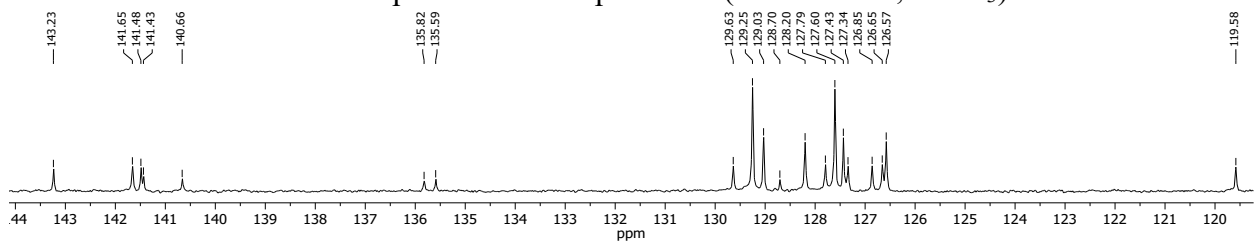
References

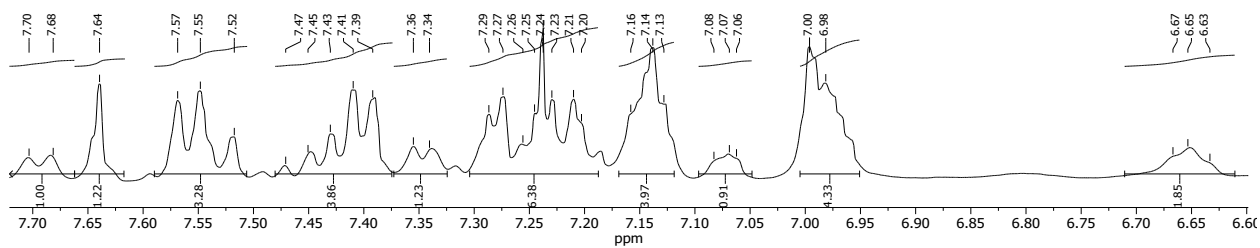
- S1 A. S. Zanina, S. I. Shergina, I. E. Sokolov and R. N. Myasnikova, *Russ. Chem. Bull.*, 1995, **44**, 689.
- S2 C. Boersch, E. Merkul, T. J. J. Müller, *Angew. Chem., Int. Ed.*, 2011, **50**, 10448; <https://doi.org/10.1002/anie.201103296>.
- S3 G. M. Sheldrick, *SADABS, Version 2008/1*, Bruker AXS, Germany, 2008.
- S4 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **D64**, 112.
- S5 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

Copies of NMR spectra

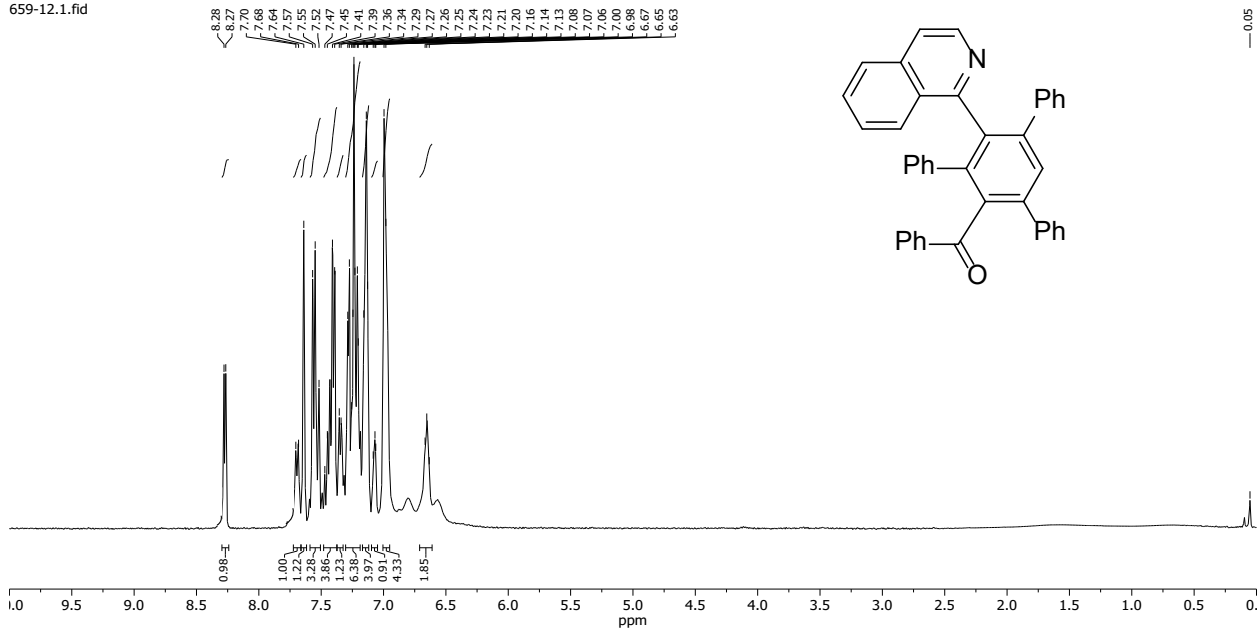


¹H NMR spectrum of compound **3a** (400.13 MHz, CDCl₃)

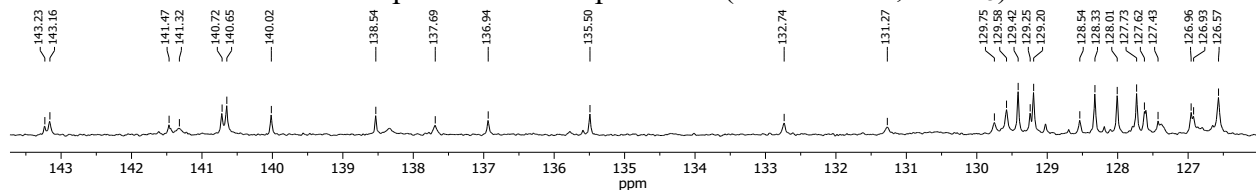




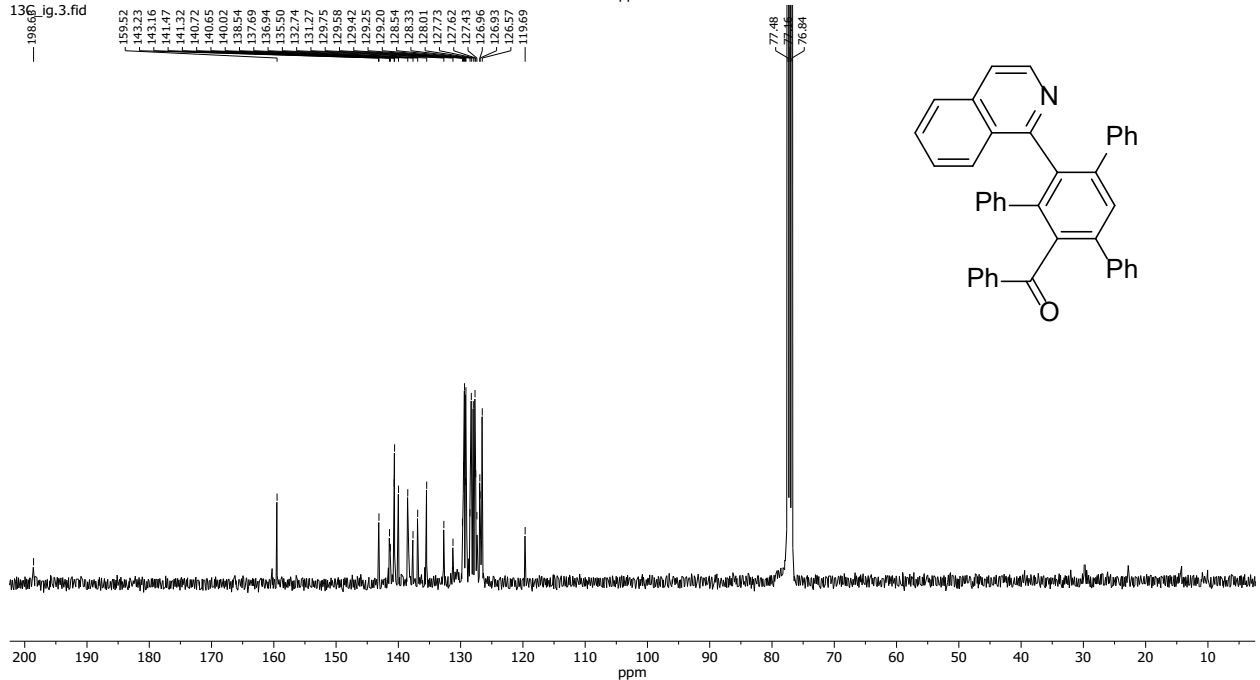
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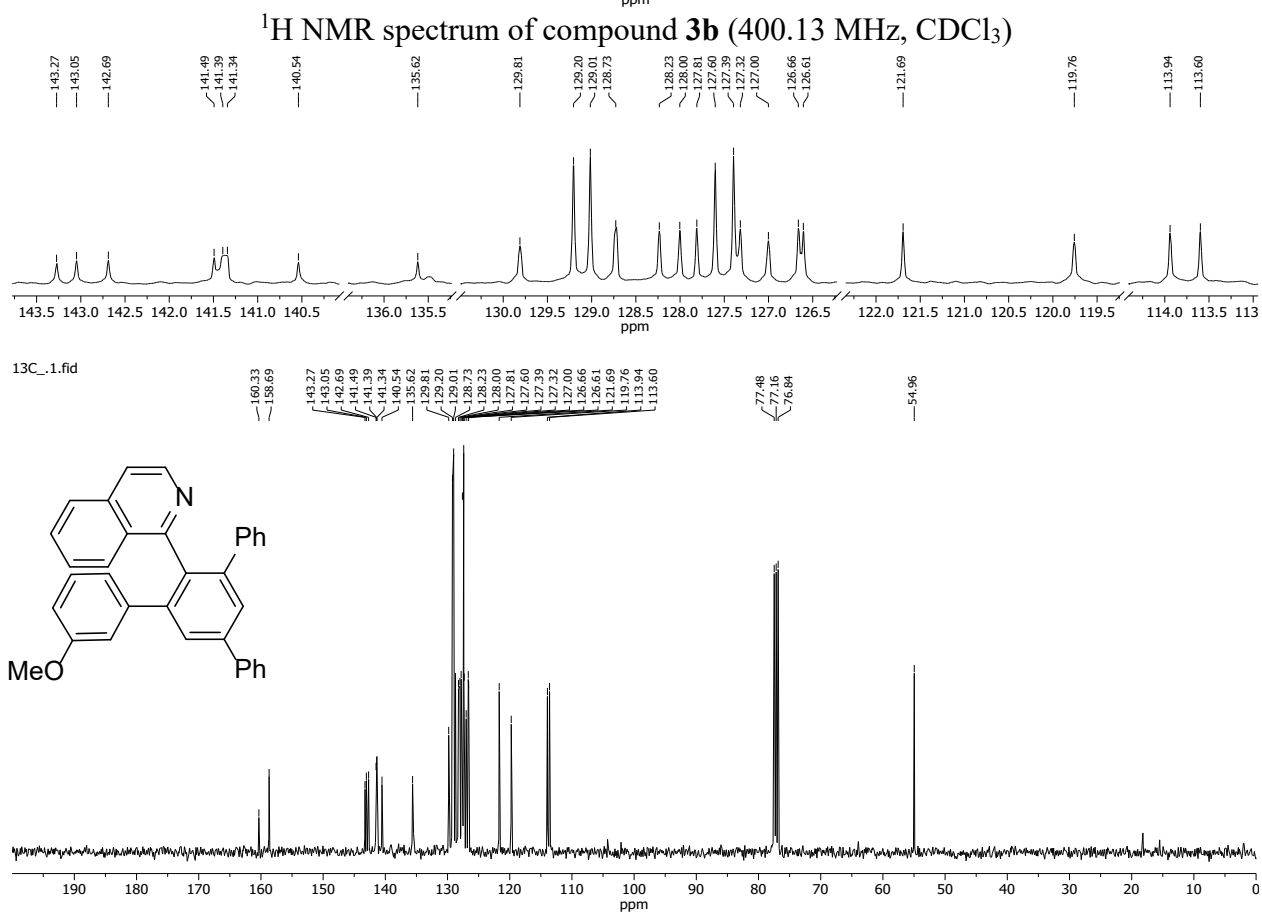
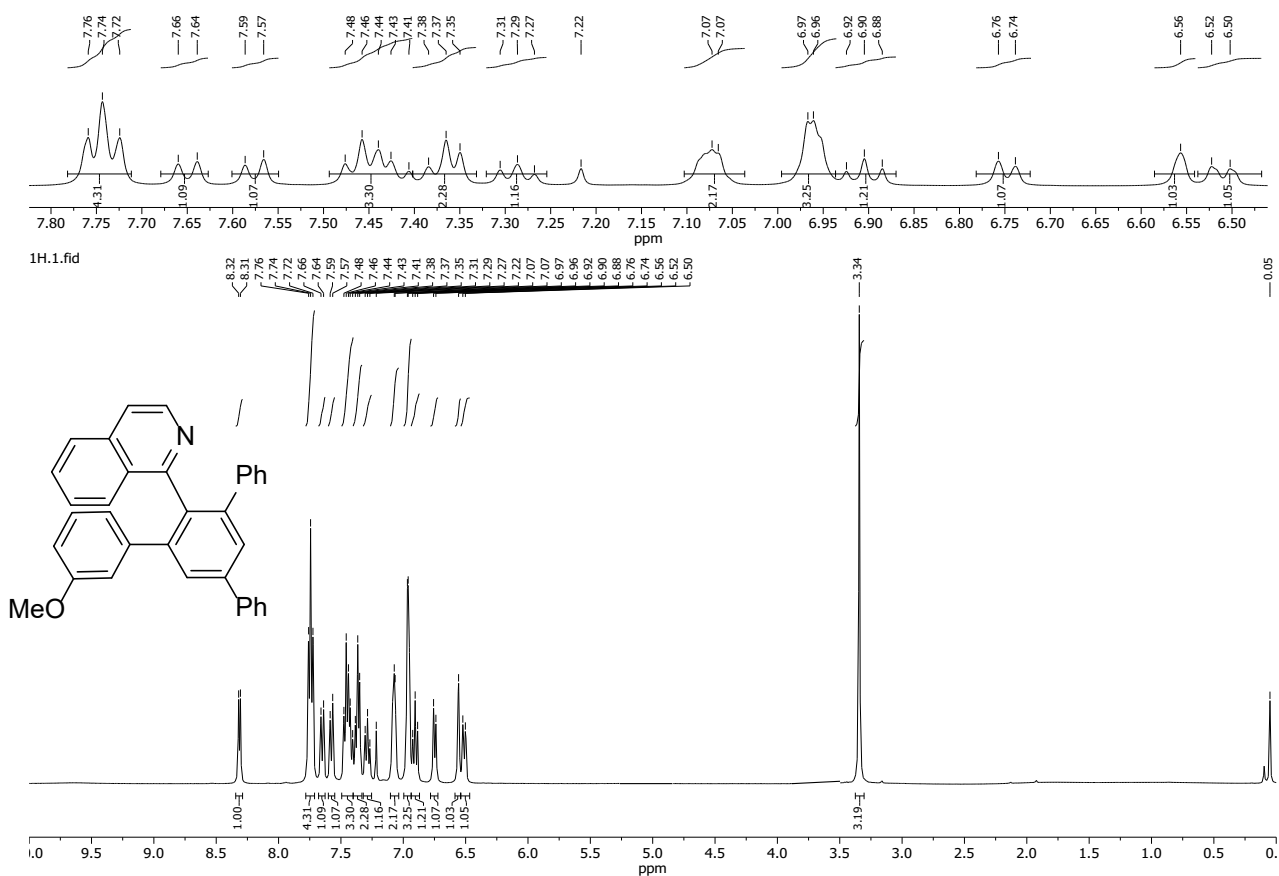
^1H NMR spectrum of compound **4a** (400.13 MHz, CDCl_3)

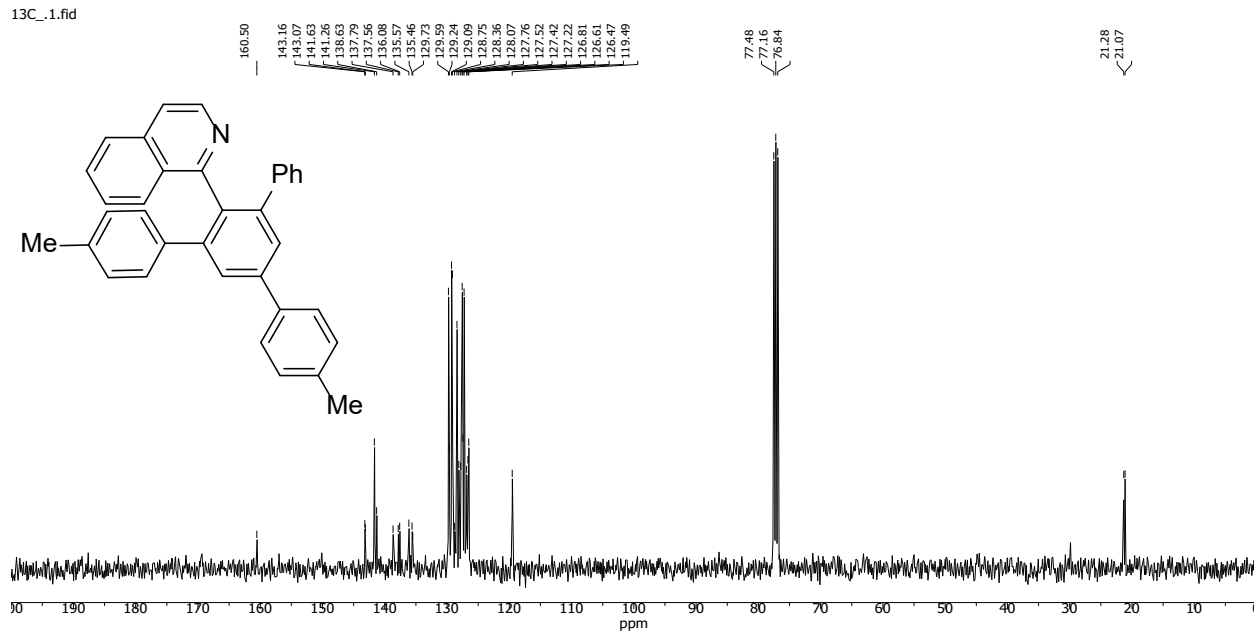
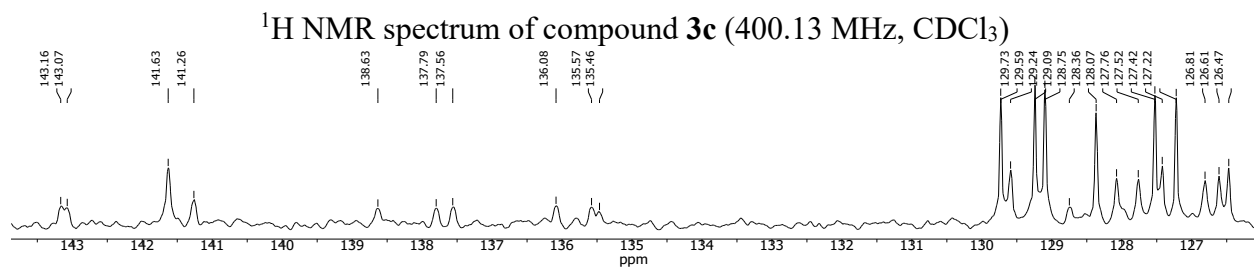
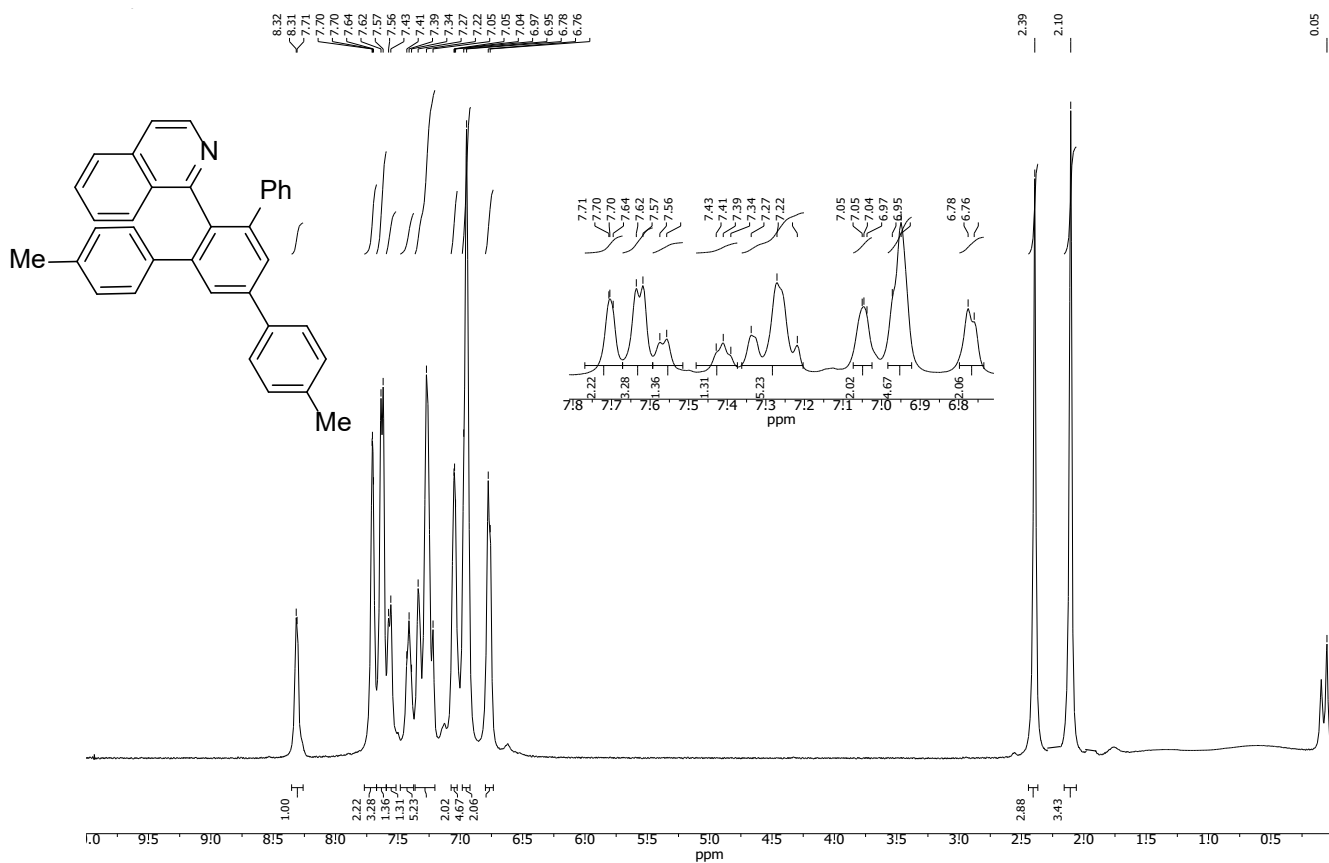


13C ig.3.fid

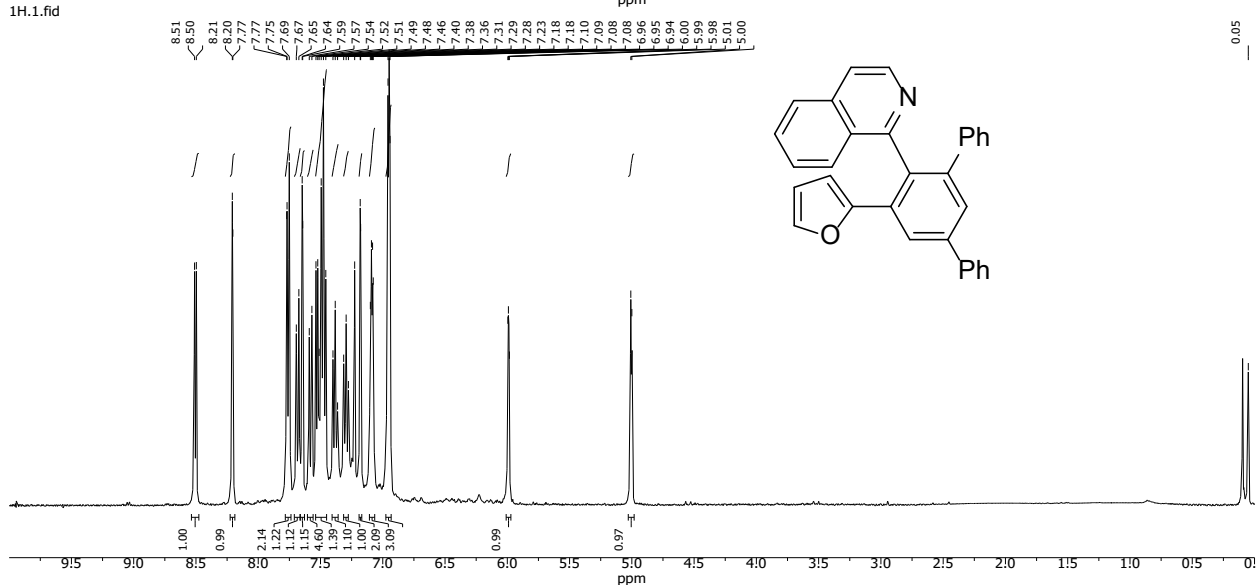
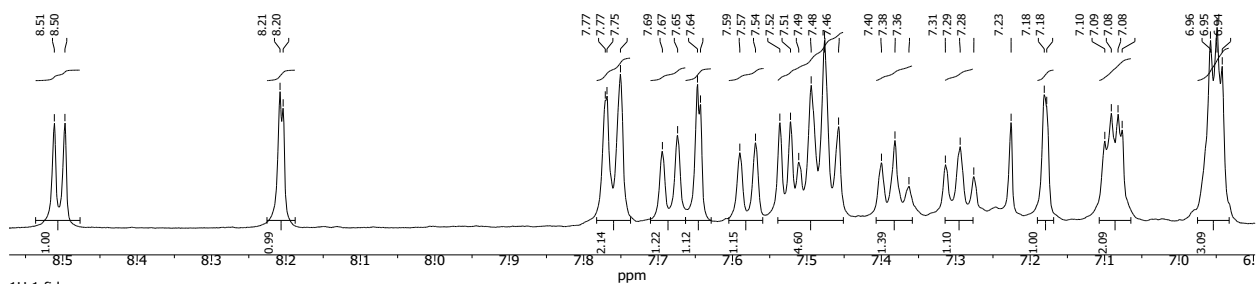


^{13}C NMR spectrum of compound **4a** (100.62 MHz, CDCl_3)

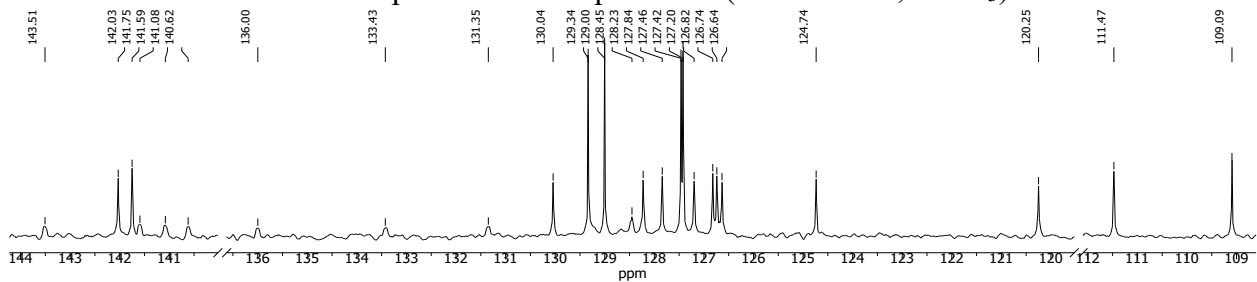




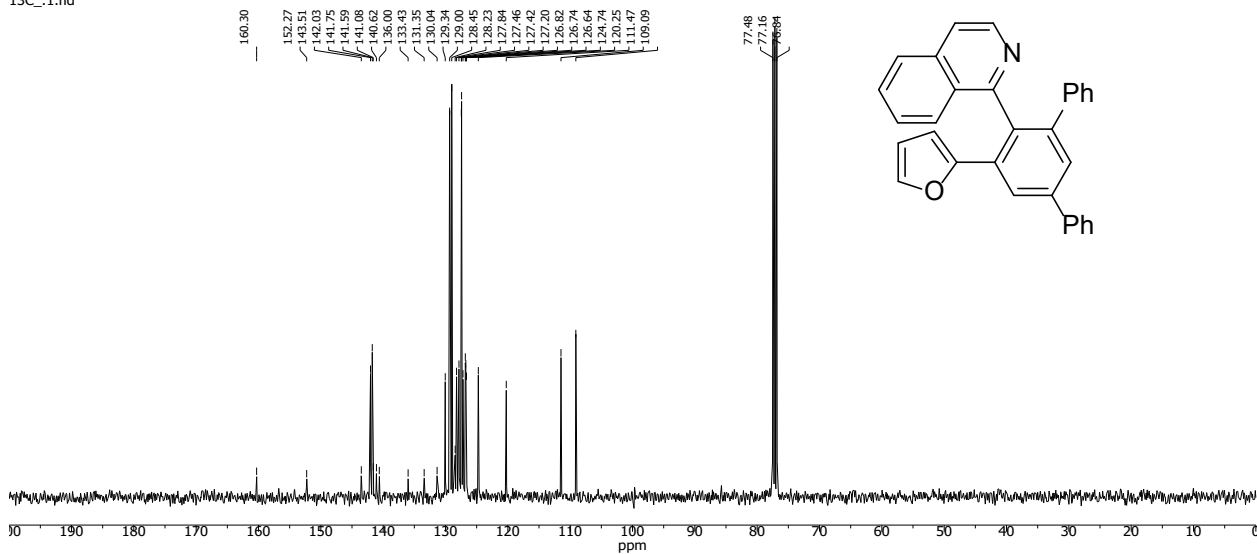
¹³C NMR spectrum of compound 3c (100.62 MHz, CDCl₃)



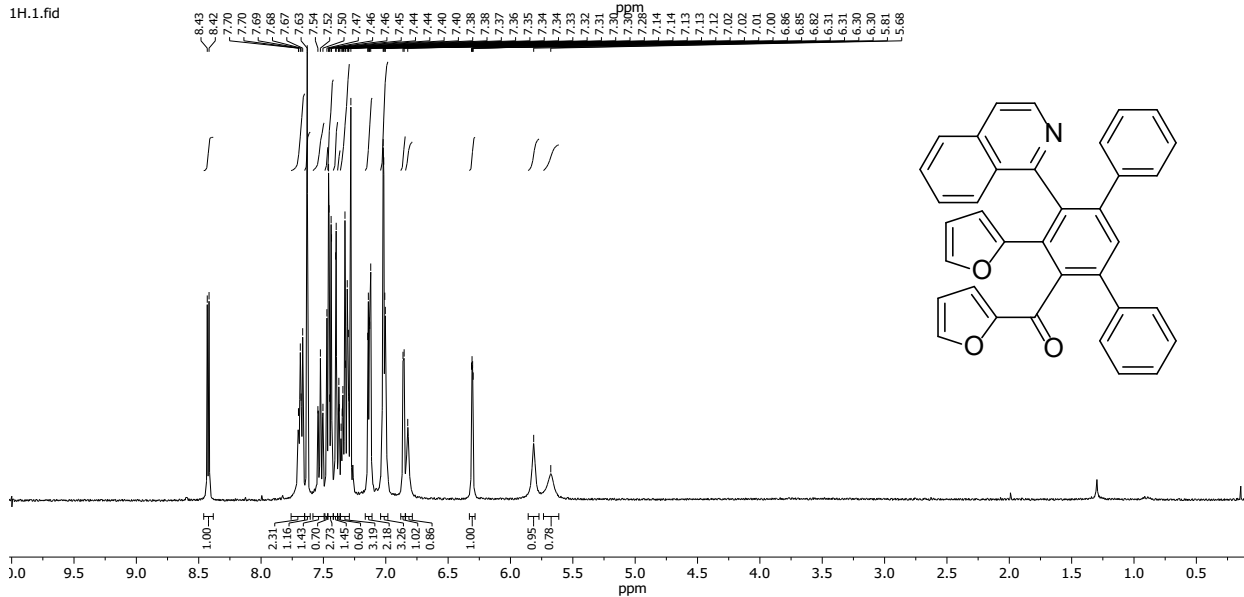
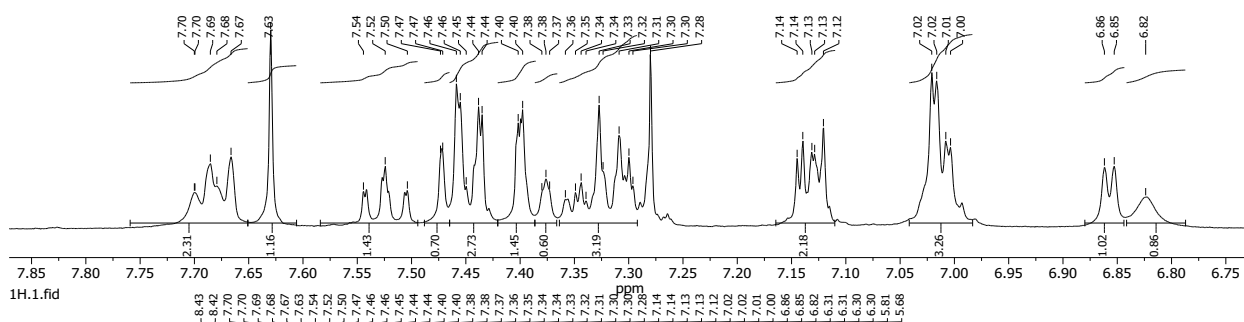
¹H NMR spectrum of compound **3d** (400.13 MHz, CDCl₃)



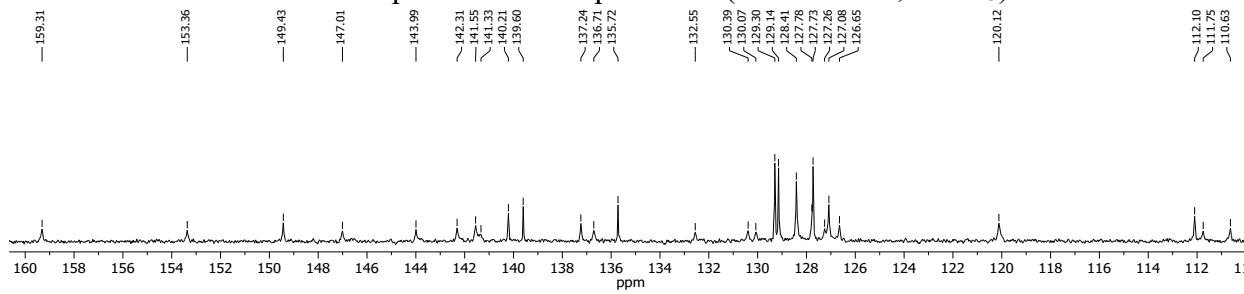
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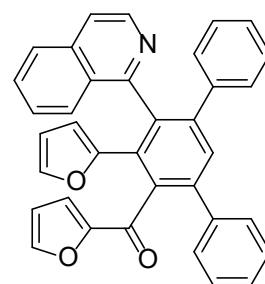
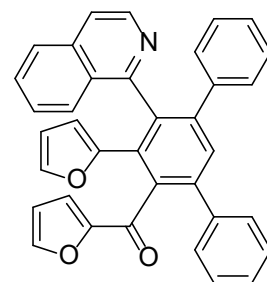
¹³C NMR spectrum of compound **3d** (100.62 MHz, CDCl₃)

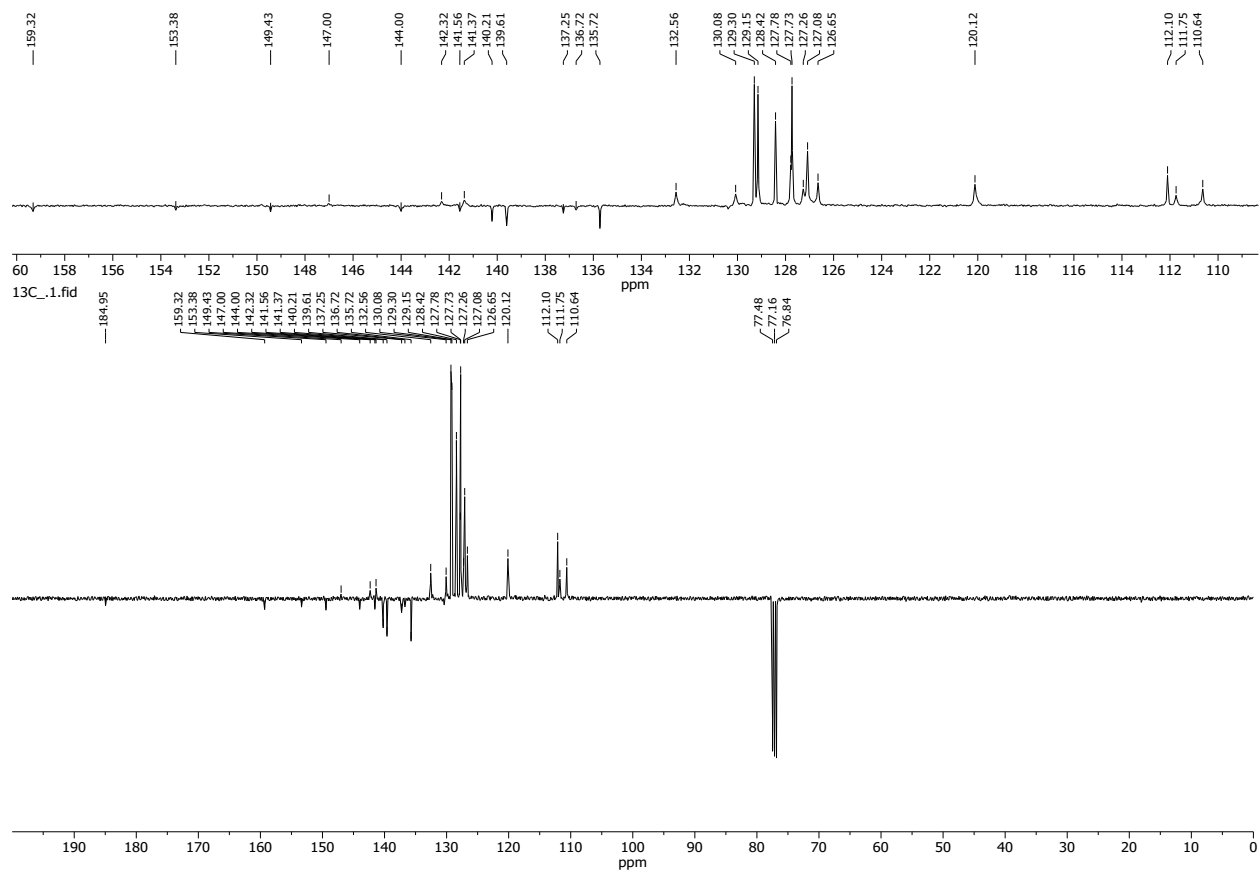


^1H NMR spectrum of compound **4d** (400.13 MHz, CDCl_3)

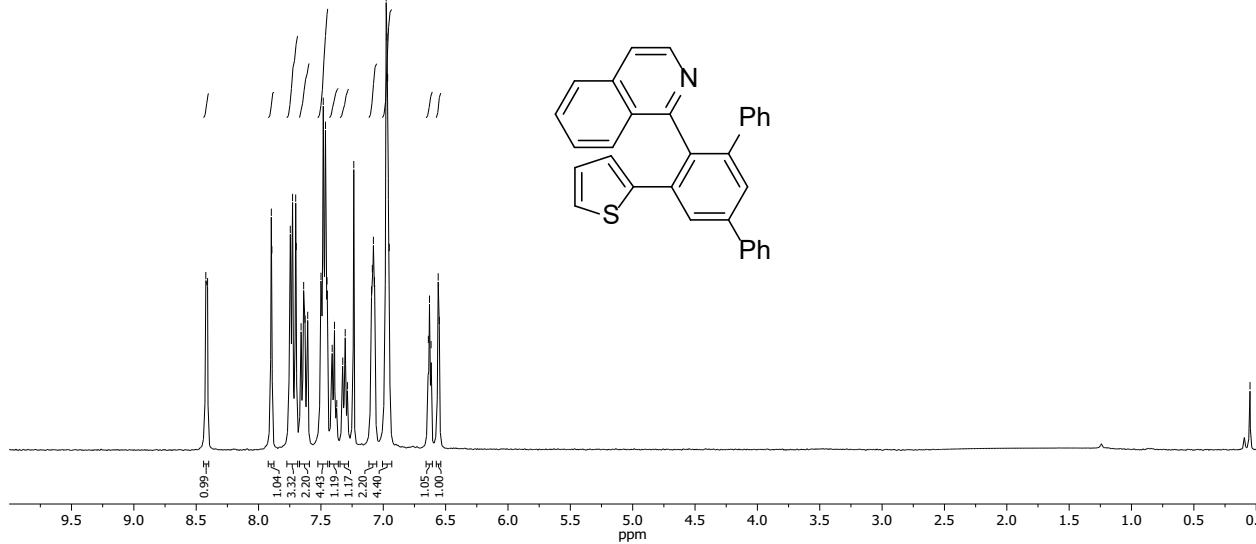
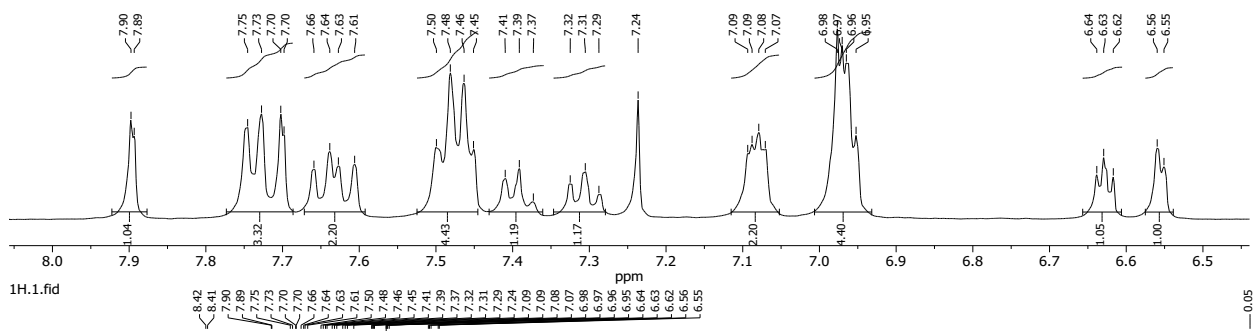


^{13}C NMR spectrum of compound **4d** (100.62 MHz, CDCl_3)

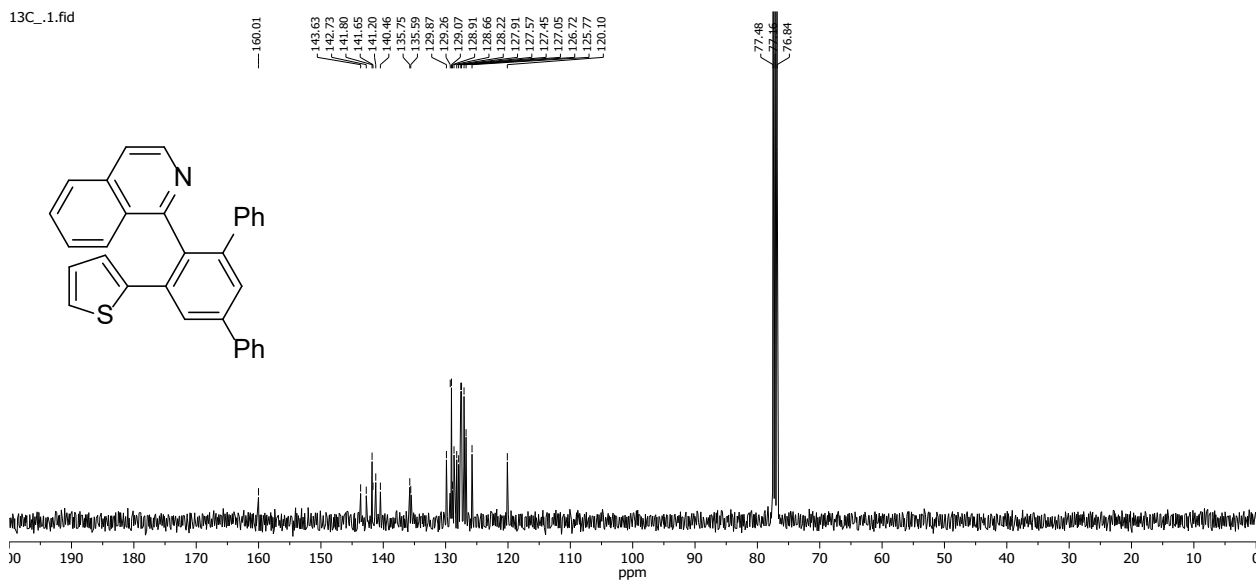
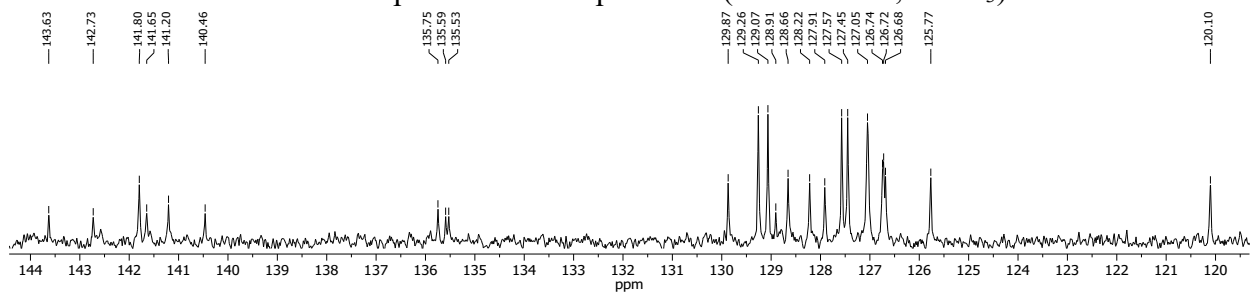




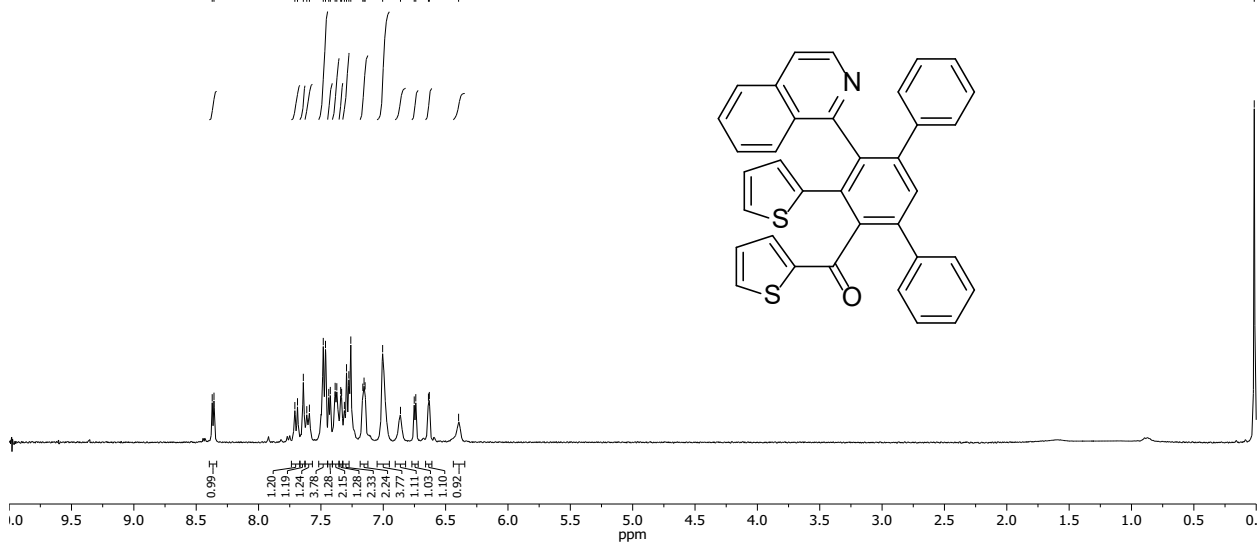
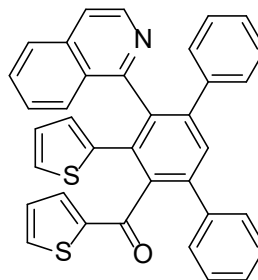
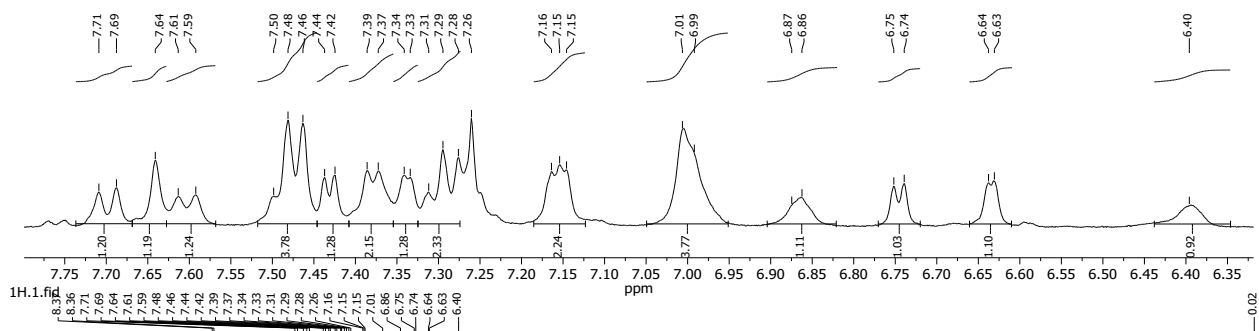
¹³C NMRjmod spectrum of compound **4d** (100.62 MHz, CDCl₃)



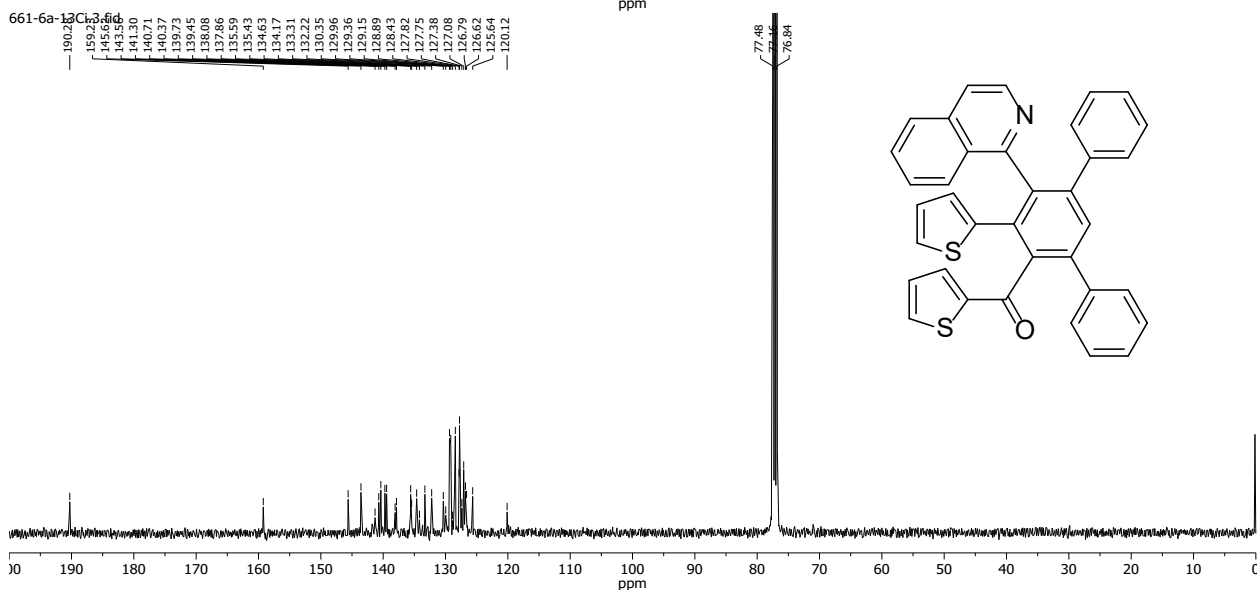
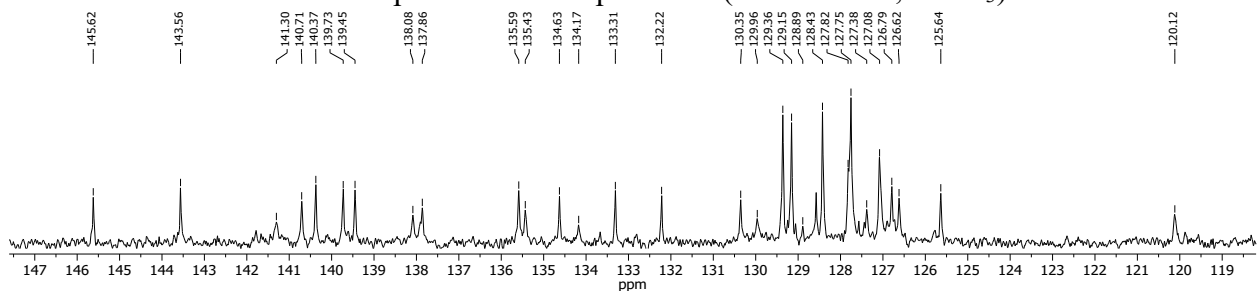
¹H NMR spectrum of compound **3e** (400.13 MHz, CDCl₃)



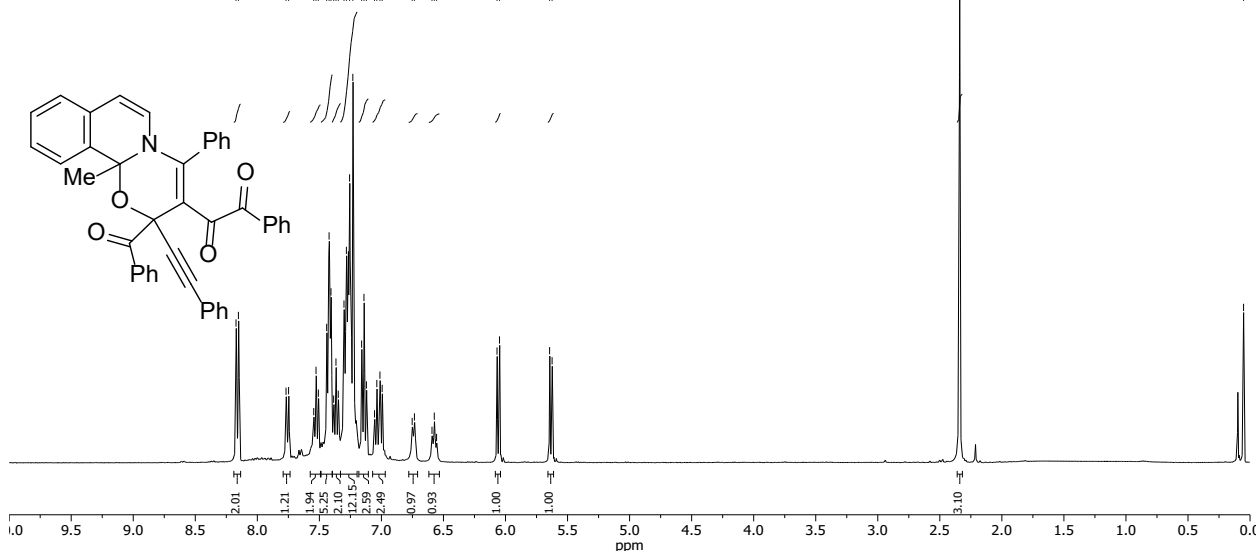
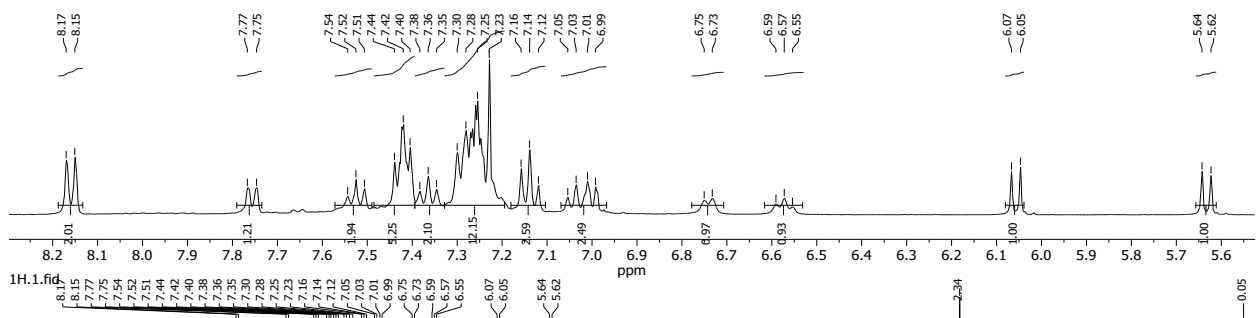
¹³C NMR spectrum of compound **3e** (100.62 MHz, CDCl₃)



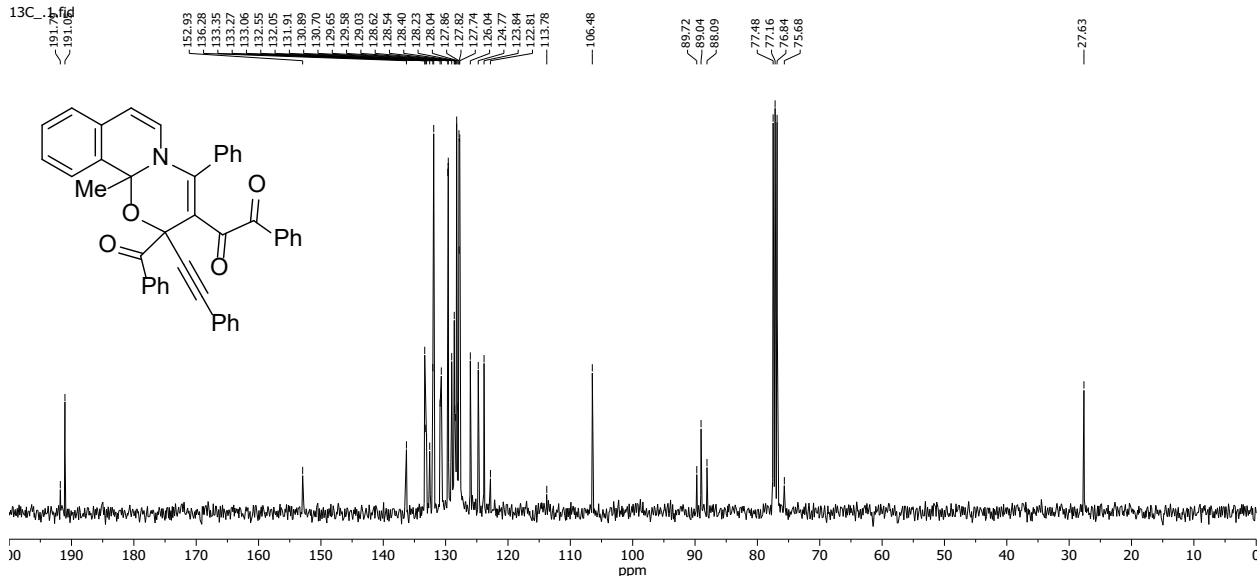
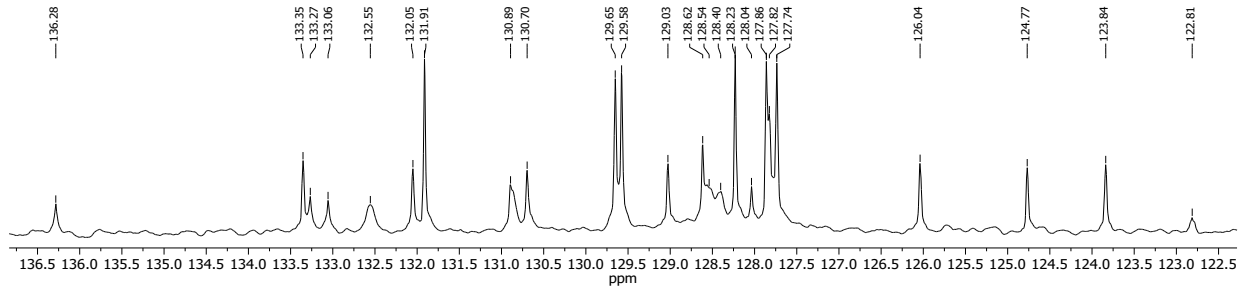
¹H NMR spectrum of compound **4e** (400.13 MHz, CDCl₃)



¹³C NMR spectrum of compound **4e** (100.62 MHz, CDCl₃)



¹H NMR spectrum of compound **6** (400.13 MHz, CDCl₃)



¹³C NMR spectrum of compound **6** (100.62 MHz, CDCl₃)