Supporting Information

Self-[3+2] annulation reaction of pyridinium salts: synthesis of *N*-indolizine substituted pyridine-2(1*H*)-ones

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1. General Information

All solvents were purified according to standard methods. Melting points were recorded on a BüCHI B-540 melting pointing apparatus. NMR spectra were recorded for ^{1}H NMR at 400 MHz/ 500 MHz and for ^{13}C NMR at 100 MHz/125 MHz. For ^{1}H NMR, CDCl3 (δ = 7.26) and DMSO (δ = 2.50) were served as internal standard and data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hz and integration. For ^{13}C NMR, CDCl3 (δ = 77.23) and DMSO (δ = 39.51) were served as internal standard and spectra were obtained with complete proton decoupling. HRMS data were obtained on Agilent 1290 HPLC-6224 Time of Flight Mass Spectrometer. The X-ray diffraction measurements were carried out on a Rigaku RAXIS-RAPID single-crystal diffractometer. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. Pyridinium salts were synthesized according to literature procedure.

Reference:

(1) Visnik Kharkivs'kogo Natsional'nogo Universitetu im. V. N. Karazin, 2007, 770, 210-217.

(2) Blank, B., et al. Journal of Medicinal Chemistry, 1978, 21(5), 489-492.

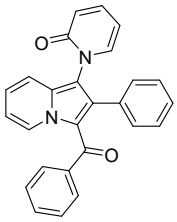
2. General procedure of 2

General procedure of **2**: A mixture of Pyridinium salt **1** (0.2 mmol, 1.0 equiv) and Cs_2CO_3 (0.4 mmol, 2.0 equiv) was stirred in 2 mL CH_3CN at 20 ^{o}C for 24 hr. After the completeness of the reaction, the solvent was removed, and the crude product was carried out by chromatography to afford **2a**-**2t** as desired products **2**.

3. General procedure of 4

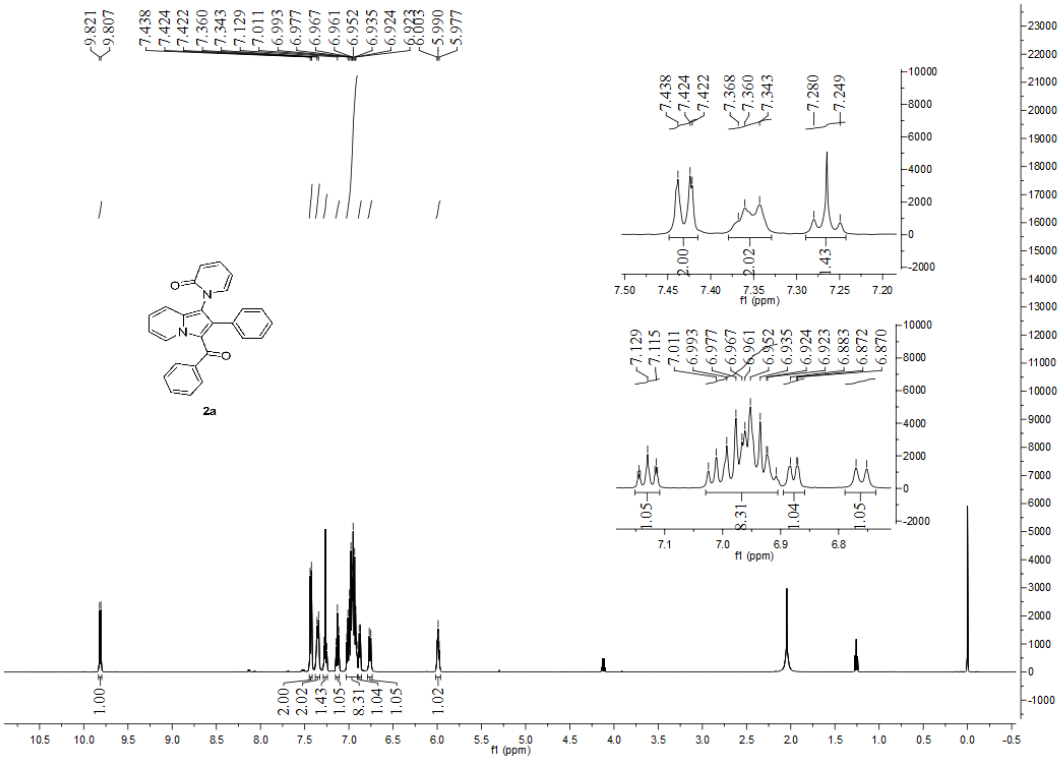
General procedure of **4**: A mixture of 2-chloro-1-(2-oxo-2-phenylethyl) -pyridin-1-ium bromide **1a** (0.2 mmol, 1.0 equiv)，aniline **3** (0.6 mmol, 3.0 equiv) and Cs_2CO_3 (0.4 mmol, 2.0 equiv) was stirred in 2 mL CH_3CN at 20 ^{o}C for 24 hr. After the completeness of the reaction, the solvent was removed, and the crude product was carried out by chromatography to afford **4a**-**4d** as desired products **4**.

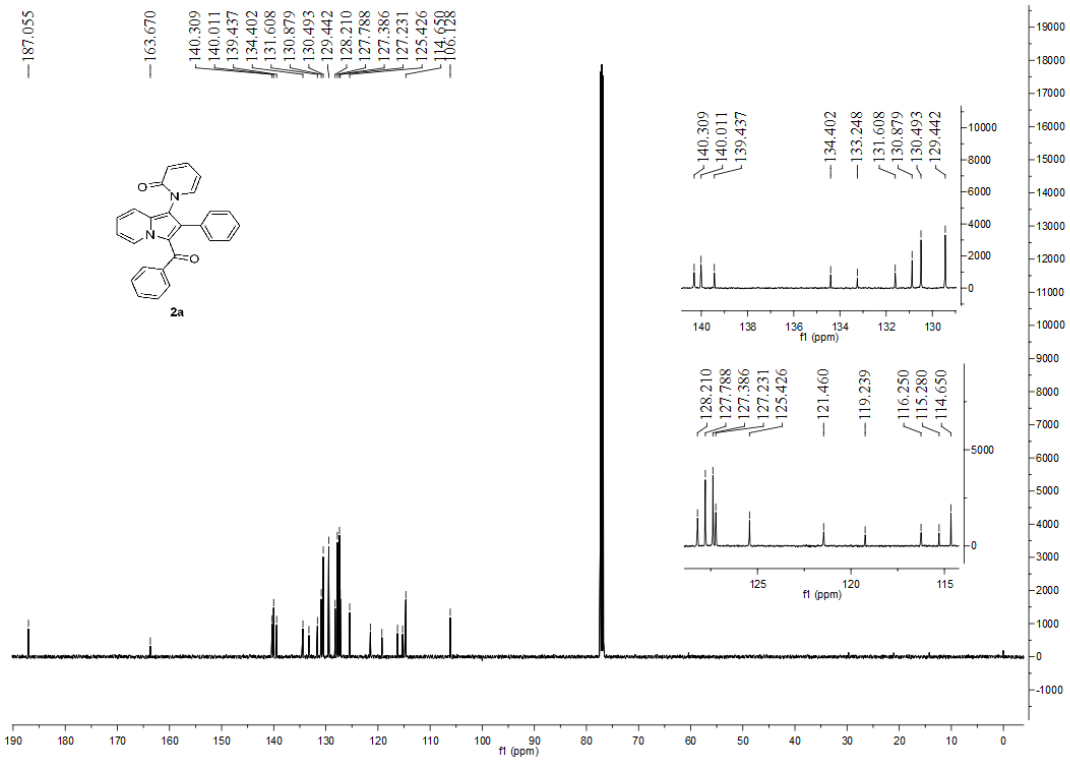
4. The NMR-spectrums of target compounds 2 and 4



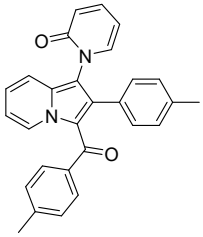
1-(3-benzoyl-2-phenylindolizin-1-yl) pyridin-2(1*H*)-one (**2a**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2a** as a yellow solid. 78% yield. m.p.:186.3-187.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (d, J = 7.0 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.38 – 7.33 (m, 2H), 7.26 (d, J = 15.5 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.03 – 6.90 (m, 8H), 6.89 – 6.86 (m, 1H), 6.76 (d, J = 9.5 Hz, 1H), 5.99 (t, J = 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.06, 163.67, 140.31, 140.01, 139.44, 134.40, 133.25, 131.61, 130.88, 130.49, 129.44, 128.21, 127.79, 127.39, 127.23, 125.43, 121.46, 119.24, 116.25, 115.28, 114.65, 106.13.HRMS (ESI): m/z calcd for $[M+H]^+$: 391.1441, found: 391.1448.



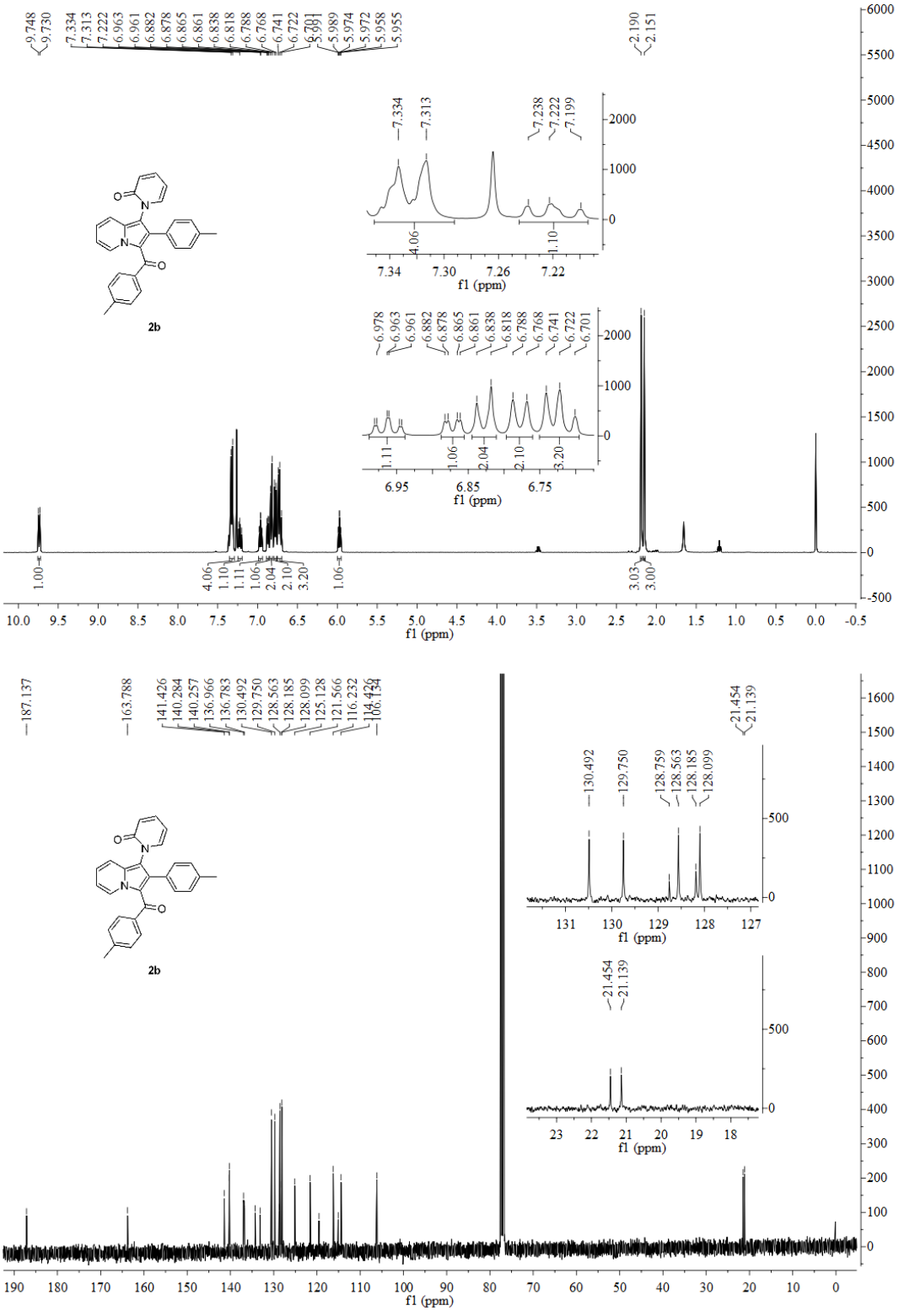


The ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2a**

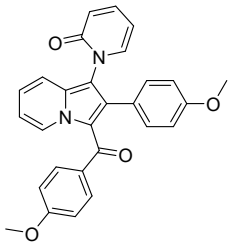


1-(3-(4-methylbenzoyl)-2-(p-tolyl) indolizin-1-yl) pyridin-2(1*H*)-one (**2b**)

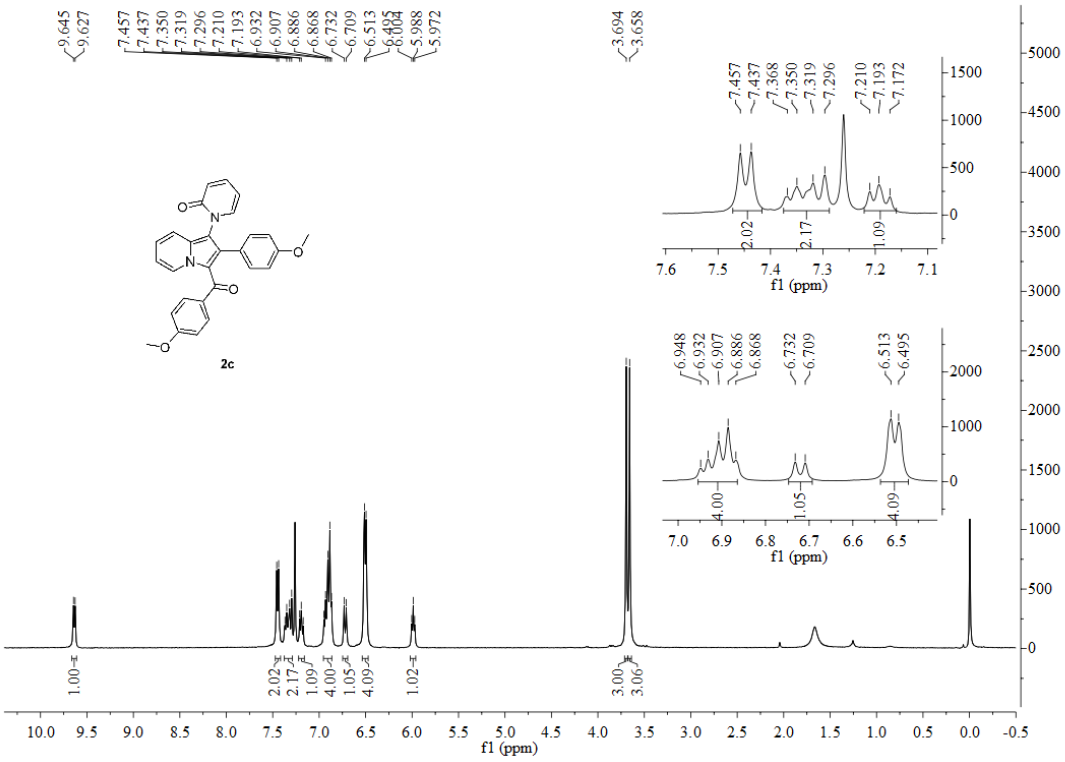
Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2b** as a yellow solid. 61% yield. m.p.:199.6-200.3 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (d, J = 7.2 Hz, 1H), 7.35 – 7.29 (m, 4H), 7.25 – 7.19 (m, 1H), 6.96 (td, J = 7.2, 1.2 Hz, 1H), 6.87 (dd, J = 6.8, 1.6 Hz, 1H), 6.83 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 7.9 Hz, 2H), 6.75 – 6.69 (m, 3H), 5.97 (td, J = 6.8, 0.8 Hz, 1H), 2.19 (s, 3H), 2.15 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 187.14, 163.79, 141.43, 140.28, 140.26, 136.97, 136.78, 134.27, 133.14, 130.49, 129.75, 128.76, 128.56, 128.18, 128.10, 125.13, 121.57, 119.52, 116.23, 115.09, 114.43, 106.13, 21.45, 21.14. HRMS (ESI): m/z calcd for $[M+H]^{+}$: 419.1754, found: 419.1751.

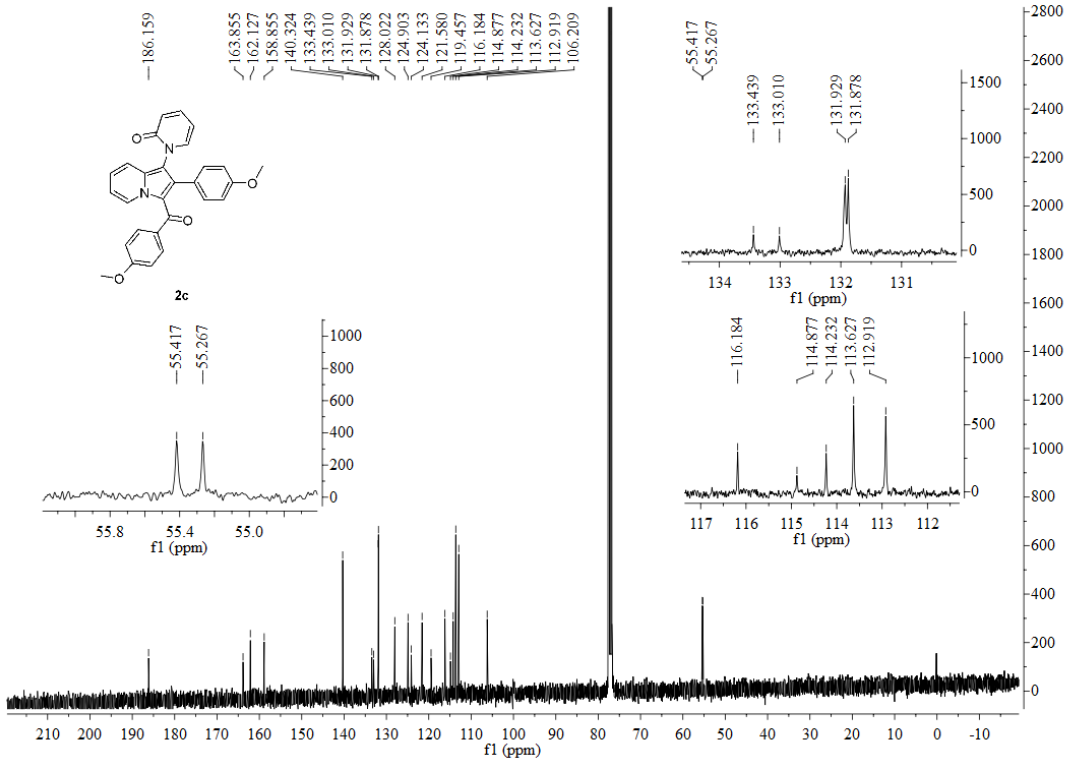


The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2b**

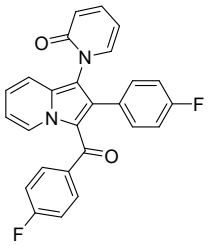


1-(3-(4-methoxybenzoyl)-2-(4-methoxyphenyl) indolizin-1-yl) pyridin-2(1*H*)-one (**2c**) Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2c** as a yellow solid. 57% yield. m.p.:185.5-186.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, J = 7.2 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.38 – 7.29 (m, 2H), 7.22 – 7.16 (m, 1H), 6.96 – 6.86 (m, 4H), 6.72 (d, J = 9.2 Hz, 1H), 6.50 (d, J = 7.2 Hz, 4H), 5.99 (t, J = 6.4 Hz, 1H), 3.69 (s, 3H), 3.66 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 186.16, 163.85, 162.13, 158.86, 140.32, 133.44, 133.01, 131.93, 131.88, 128.02, 124.90, 124.13, 121.58, 119.46, 116.18, 114.88, 114.23, 113.63, 112.92, 106.21, 55.42, 55.27. HRMS (ESI): m/z calcd for $[M+H]^+$: 451.1652, found: 471.1650.



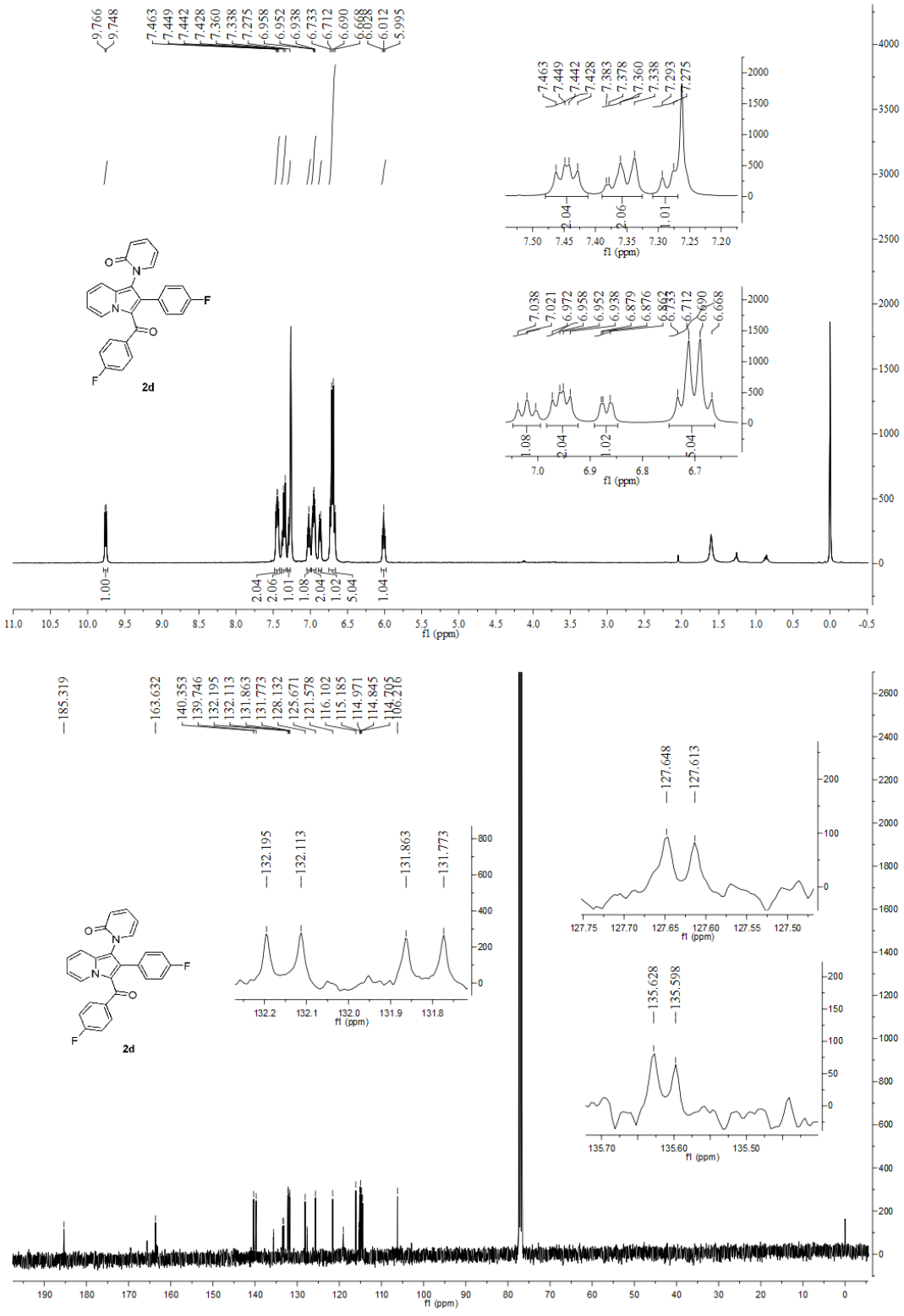


The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2c**

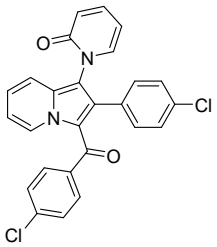


1-(3-(4-fluorobenzoyl)-2-(4-fluorophenyl) indolizin-1-yl) pyridin-2(1*H*)-one (**2d**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2d** as a yellow solid. 69% yield. m.p.:270.4-271.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (d, J = 7.2 Hz, 1H), 7.45 (dd, J = 8.4, 5.6 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.28 (d, J = 7.2 Hz, 1H), 7.02 (t, J = 6.8 Hz, 1H), 6.96 (dd, J = 8.0, 5.6 Hz, 2H), 6.89 – 6.85 (m, 1H), 6.70 (q, J = 8.8 Hz, 5H), 6.01 (t, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.32, 163.63, 140.35, 139.75, 135.61 (d, J = 3.0 Hz), 133.40, 133.22, 132.15 (d, J = 8.2 Hz), 131.82 (d, J = 9.0 Hz), 128.13, 127.63 (d, J = 3.5 Hz), 125.67, 121.58, 119.08, 116.10, 115.36, 115.19, 114.97, 114.85, 114.70, 114.49, 106.22. HRMS (ESI): m/z calcd for $[M+H]^+$: 427.1258, found: 427.1264.

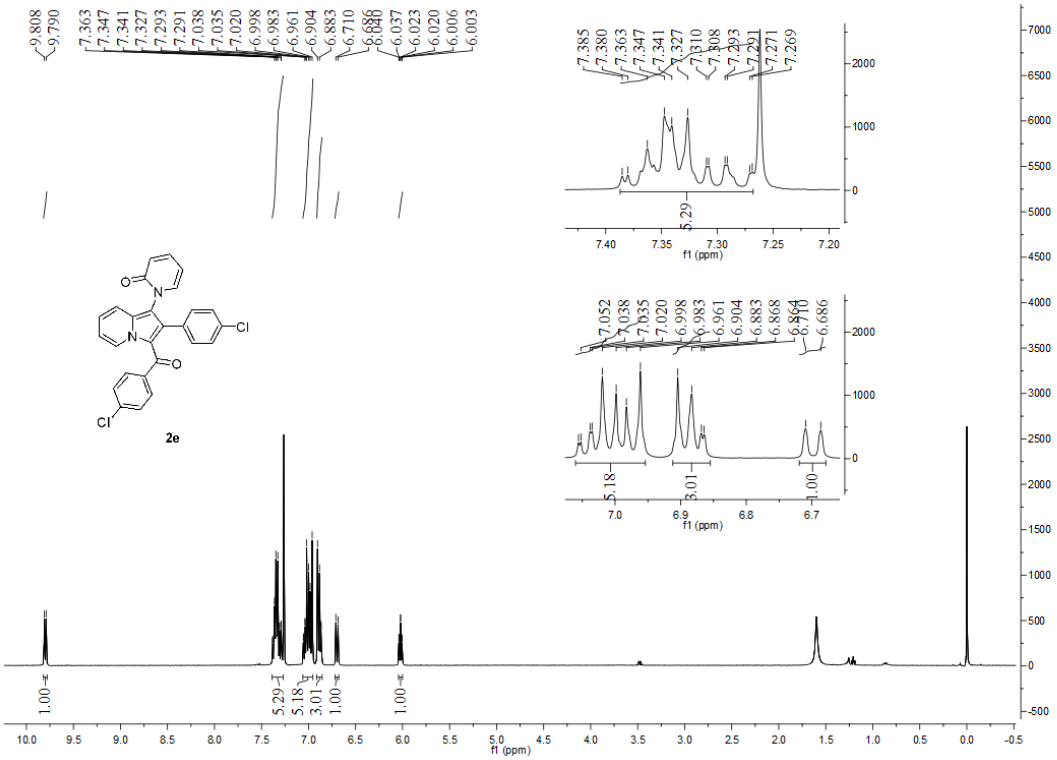


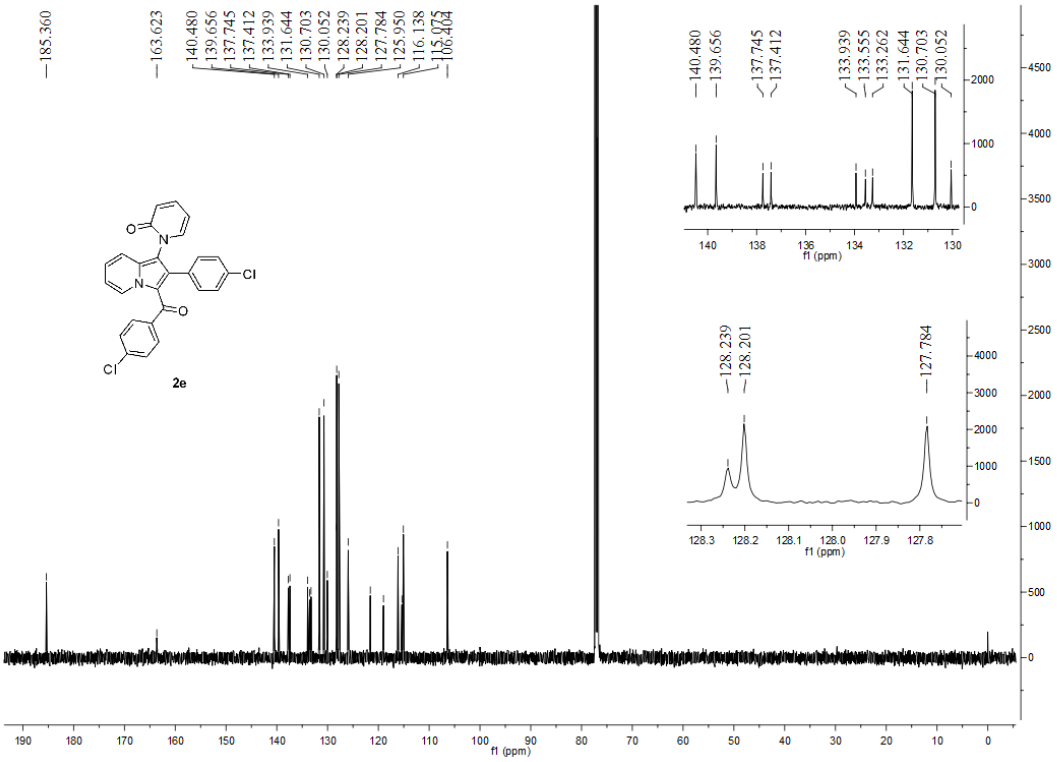
The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2d**



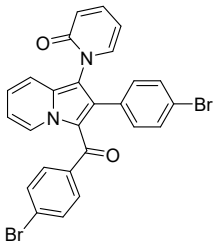
1-(3-(4-chlorobenzoyl)-2-(4-chlorophenyl) indolizin-1-yl) pyridin-2(1*H*)-one (**2e**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2e** as a yellow solid. 51% yield. m.p.:196.6-197.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (d, J = 7.2 Hz, 1H), 7.39 – 7.27 (m, 5H), 7.06 – 6.96 (m, 5H), 6.90 – 6.86 (m, 3H), 6.70 (d, J = 9.6 Hz, 1H), 6.02 (td, J = 6.8, 1.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.36, 163.62, 140.48, 139.66, 137.74, 137.41, 133.94, 133.56, 133.26, 131.64, 130.70, 130.05, 128.24, 128.20, 127.78, 125.95, 121.59, 119.00, 116.14, 115.36, 115.07, 106.40. HRMS (ESI): m/z calcd for $[M+H]^+$: 459.0662, found: 459.0658.



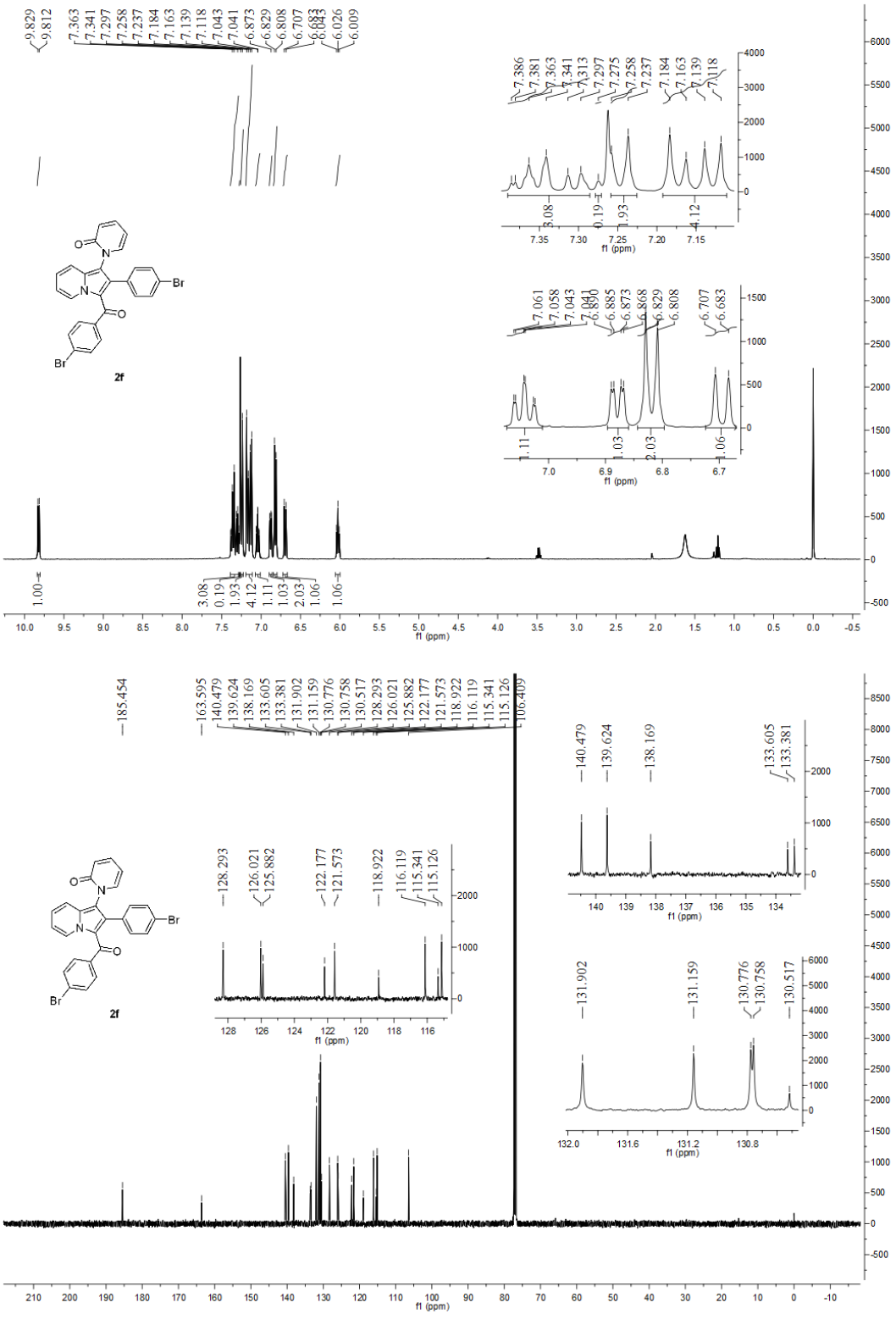


The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2e**

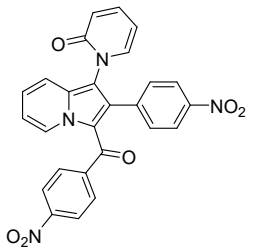


1-(3-(4-bromobenzoyl)-2-(4-bromophenyl) indolizin-1-yl) pyridin-2(1*H*)-one (**2f**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2f** as a yellow solid. 65% yield. m.p.:194.5-195.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (d, J = 7.6 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.28 – 7.23 (m, 2H), 7.15 (dd, J = 18.0, 8.4 Hz, 4H), 7.04 (td, J = 7.2, 1.2 Hz, 1H), 6.88 (dd, J = 6.8, 2.0 Hz, 1H), 6.82 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 9.6 Hz, 1H), 6.03 (t, J = 6.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.45, 163.60, 140.48, 139.62, 138.17, 133.60, 133.38, 131.90, 131.16, 130.78, 130.76, 130.52, 128.29, 126.02, 125.88, 122.18, 121.57, 118.92, 116.12, 115.34, 115.13, 106.41. HRMS (ESI): m/z calcd for $[M+H]^+$: 546.9651, found: 546.9658.

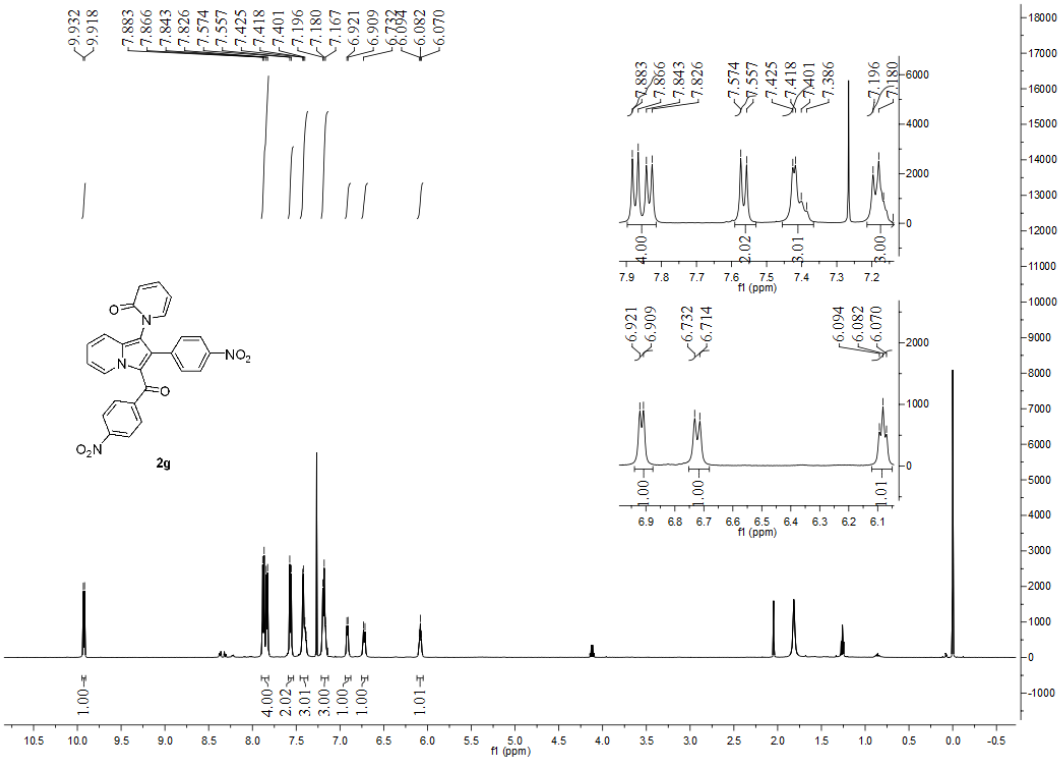


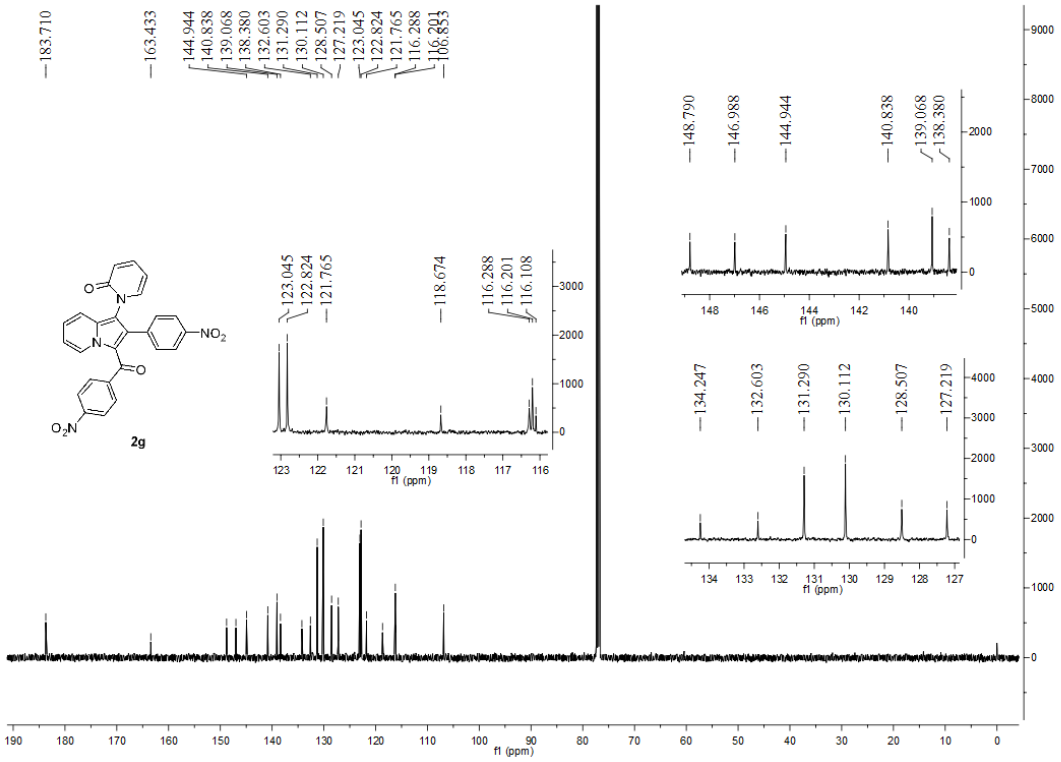
The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2f**



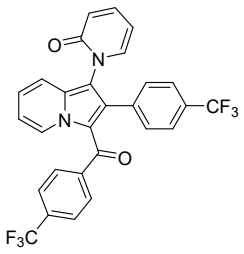
1-(3-(4-nitrobenzoyl)-2-(4-nitrophenyl) indolizin-1-yl) pyridin-2(1*H*)-one (**2g**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:3) to afford **2g** as a yellow solid. 80% yield. m.p.:218.7-219.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.92 (d, J = 7.0 Hz, 1H), 7.85 (dd, J = 20.0, 8.5 Hz, 4H), 7.57 (d, J = 8.5 Hz, 2H), 7.45 – 7.37 (m, 3H), 7.22 – 7.13 (m, 3H), 6.91 (d, J = 6.0 Hz, 1H), 6.72 (d, J = 9.0 Hz, 1H), 6.08 (t, J = 6.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.71, 163.43, 148.79, 146.99, 144.94, 140.84, 139.07, 138.38, 134.25, 132.60, 131.29, 130.11, 128.51, 127.22, 123.05, 122.82, 121.77, 118.67, 116.29, 116.20, 116.11, 106.85. HRMS (ESI): m/z calcd for $[M+H]^+$: 481.1148, found: 481.1152.



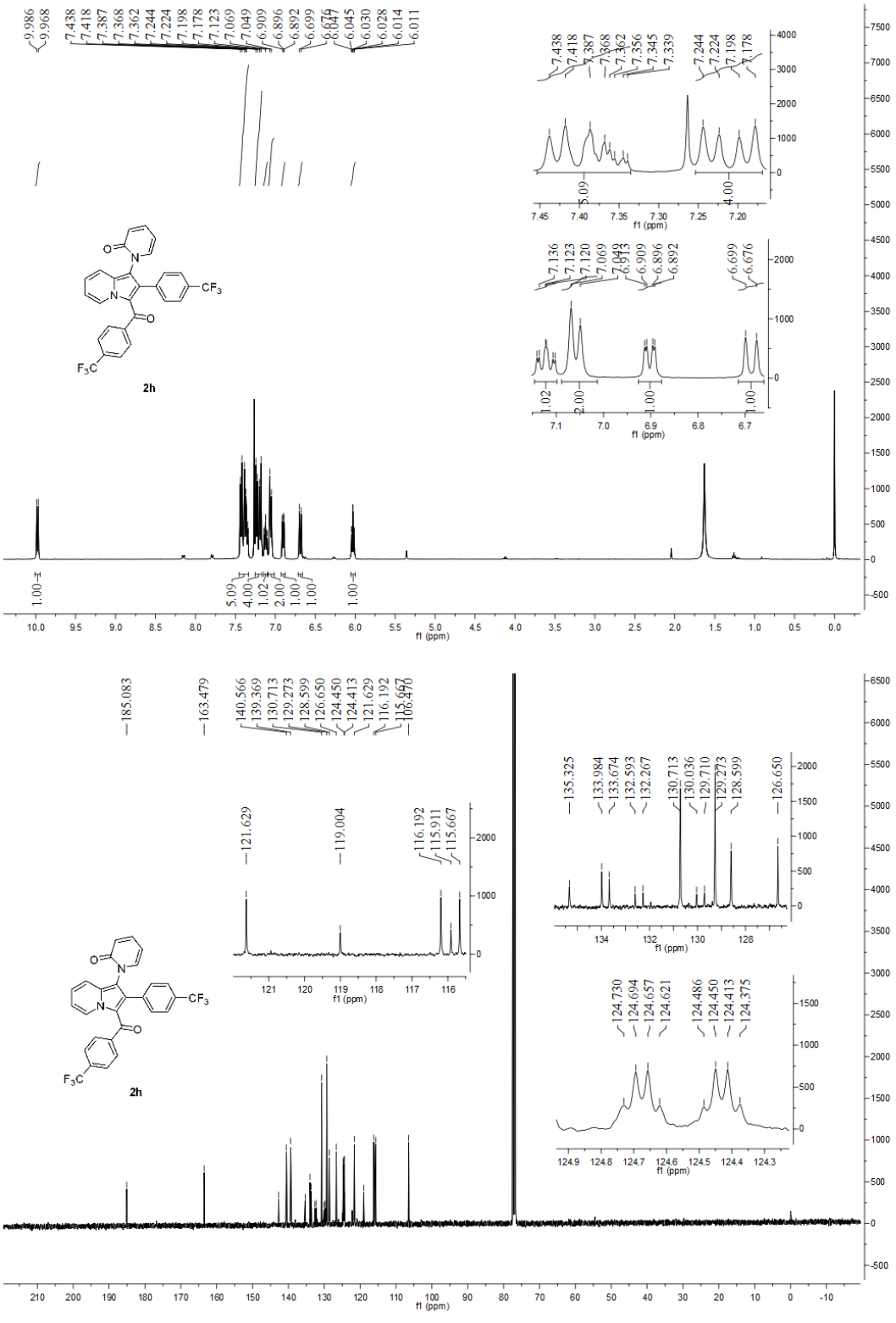


The ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2g**

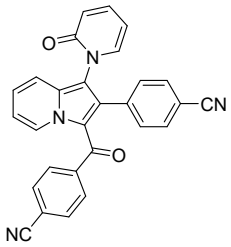


1-(3-(4-(trifluoromethyl)benzoyl)-2-(4-(trifluoromethyl)phenyl)indolizin-1-yl)pyridin-2(1*H*)-one (**2h**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2h** as a yellow solid. 75% yield. m.p.:184.4-185.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (d, J = 7.2 Hz, 1H), 7.45 – 7.34 (m, 5H), 7.21 (dd, J = 18.4, 8.0 Hz, 4H), 7.12 (td, J = 7.2, 2.0 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.90 (dd, J = 6.8, 1.6 Hz, 1H), 6.69 (d, J = 9.2 Hz, 1H), 6.03 (td, J = 6.8, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.08, 163.48, 142.73, 140.57, 139.37, 135.33, 133.98, 133.67, 132.59, 132.27, 130.71, 130.04, 129.71, 129.27, 128.60, 126.65, 124.68 (q, J = 3.6 Hz), 124.43 (q, J = 3.6 Hz), 121.63, 119.00, 116.19, 115.91, 115.67, 106.47. HRMS (ESI): m/z calcd for $[M+H]^+$: 527.1194, found: 527.1191.

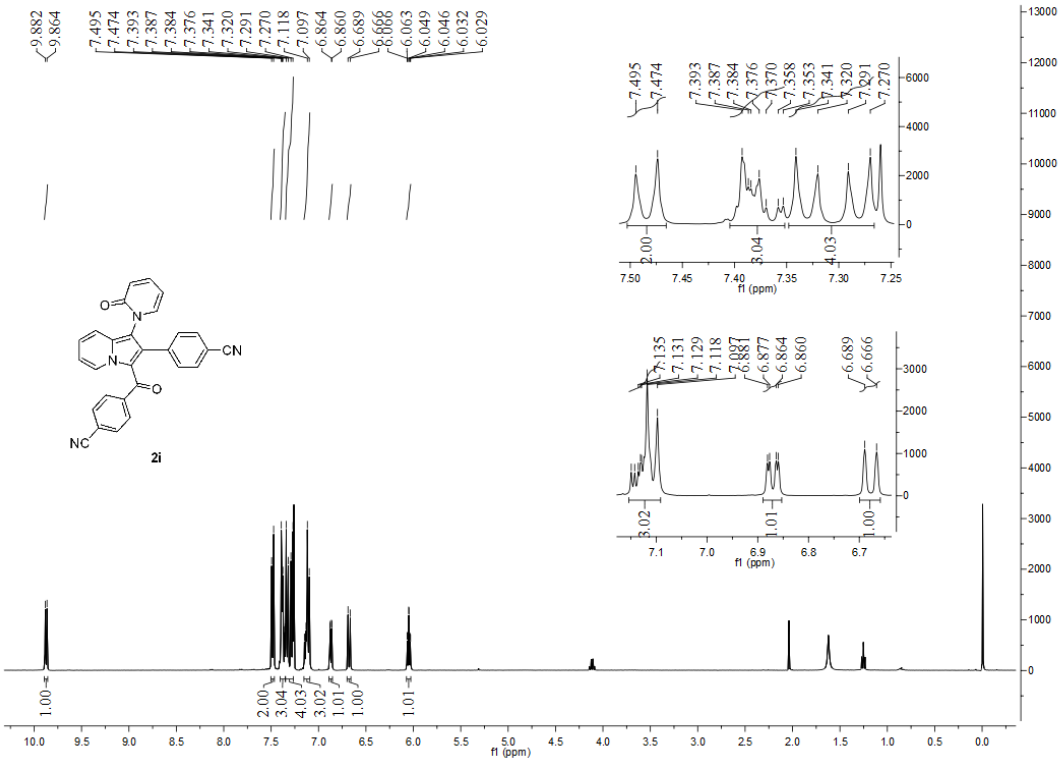


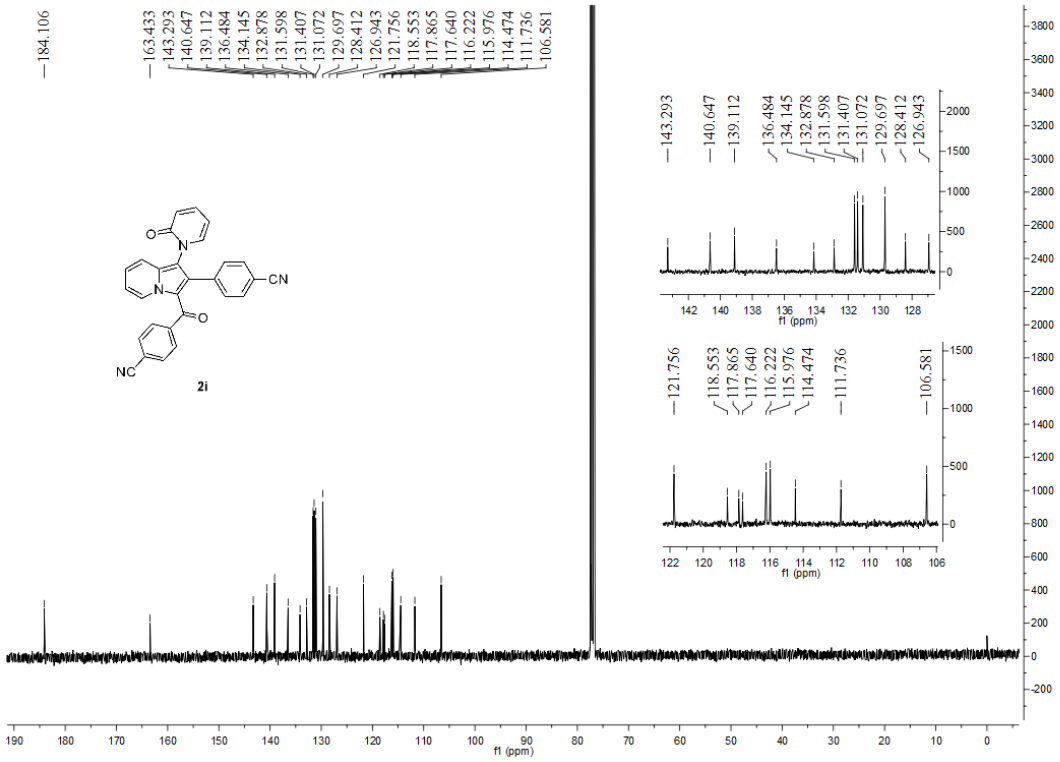
The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2h**



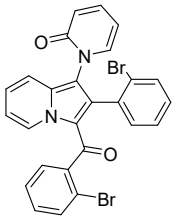
4-(3-(4-cyanobenzoyl)-1-(2-oxopyridin-1(2H)-yl) indolizin-2-yl) benzonitrile (**2i**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2i** as a yellow solid. 65% yield. m.p.:287.5-288.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (d, J = 7.2 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.31 (dd, J = 20.0, 8.4 Hz, 4H), 7.16 – 7.09 (m, 3H), 6.87 (dd, J = 6.8, 1.6 Hz, 1H), 6.68 (d, J = 9.2 Hz, 1H), 6.05 (td, J = 6.8, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.11, 163.43, 143.29, 140.65, 139.11, 136.48, 134.15, 132.88, 131.60, 131.41, 131.07, 129.70, 128.41, 126.94, 121.76, 118.55, 117.86, 117.64, 116.22, 115.98, 114.47, 111.74, 106.58. HRMS (ESI): m/z calcd for $[M+H]^+$: 441.1352, found: 441.1359.



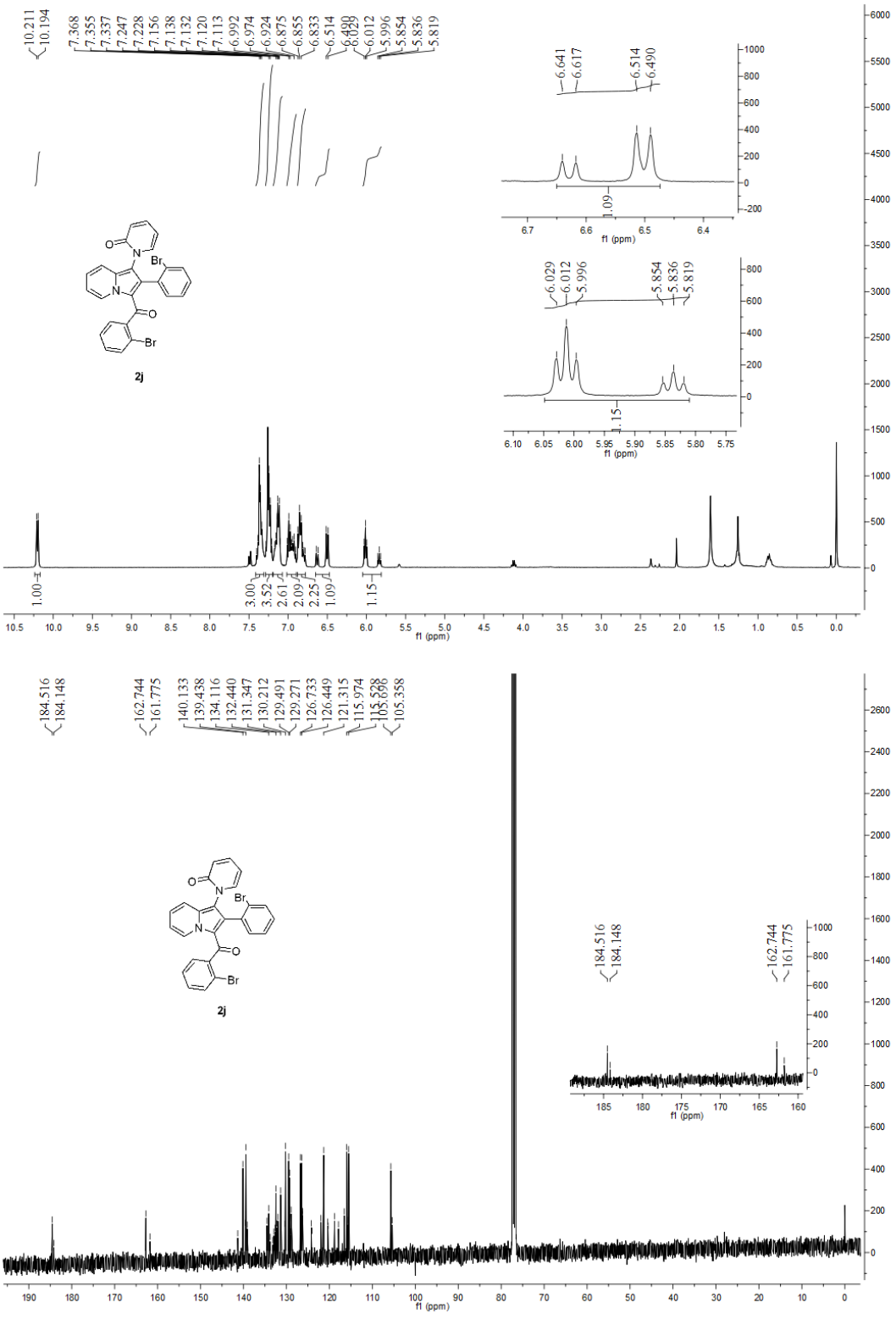


The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2i**

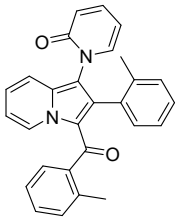


1-(3-(2-bromobenzoyl)-2-(2-bromophenyl) indolizin-1-yl) pyridin-2(1*H*)-one (**2j**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2j** as a yellow solid. 32% yield. m.p.:189.4-190.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (d, J = 6.8 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.29 – 7.20 (m, 3H), 7.19 – 7.07 (m, 3H), 7.02 – 6.90 (m, 2H), 6.89 – 6.77 (m, 2H), 6.50 (d, J = 9.6 Hz, 1H), 6.01 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.52, 184.15, 162.74, 161.78, 141.35, 140.13, 139.55, 139.44, 139.14, 134.54, 134.12, 133.77, 133.15, 132.93, 132.63, 132.44, 132.21, 131.97, 131.35, 130.31, 130.21, 129.49, 129.37, 129.27, 129.07, 128.91, 126.73, 126.52, 126.45, 126.39, 126.30, 126.23, 124.22, 124.05, 121.97, 121.31, 120.38, 120.32, 118.80, 117.89, 116.54, 115.97, 115.67, 115.53, 105.70, 105.36.HRMS (ESI): m/z calcd for $[M+H]^+$:546.9657, found: 546.9660.

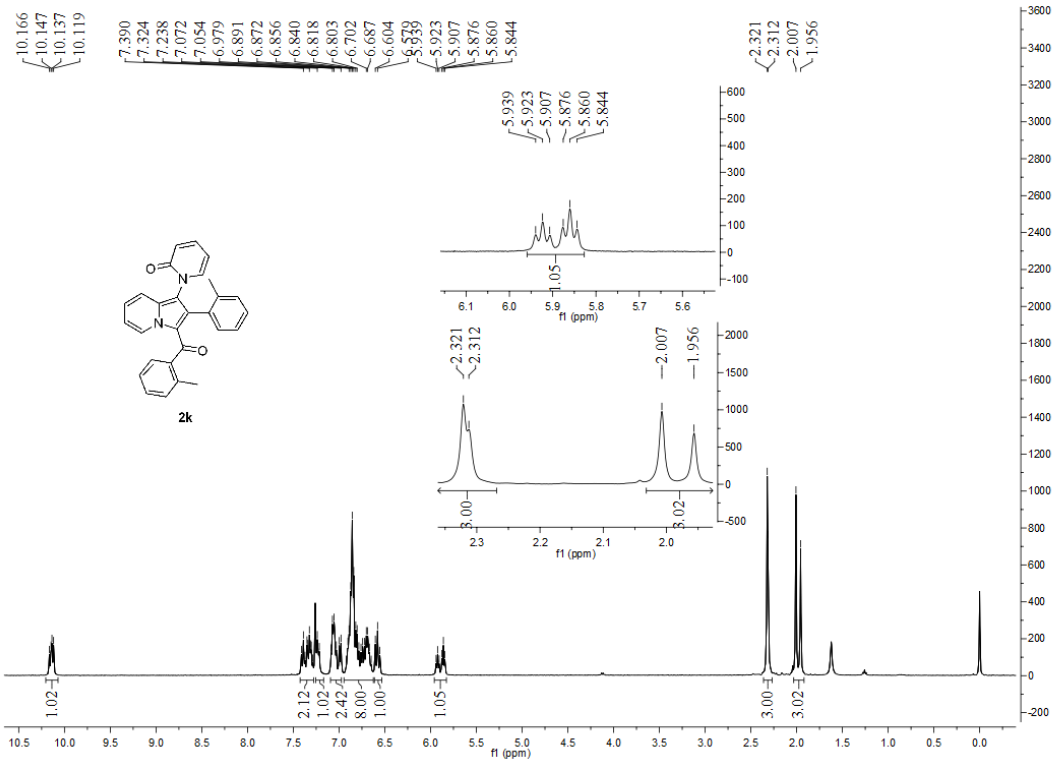


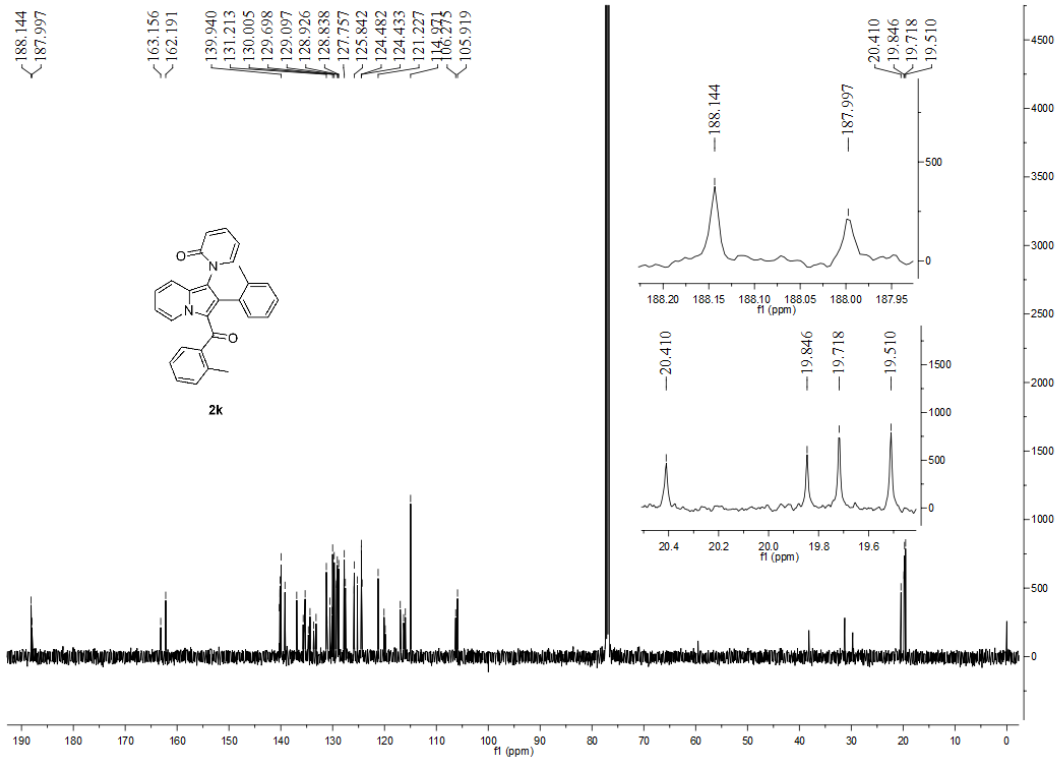
The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2j**



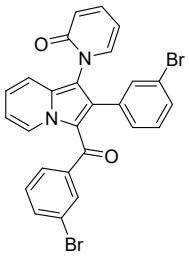
1-(3-(2-methylbenzoyl)-2-(o-tolyl) indolizin-1-yl) pyridin-2(1*H*)-one (**2k**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2k** as a yellow solid. 24% yield. m.p.:198.3-199.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (d, J = 7.2 Hz, 1H), 7.43 – 7.28 (m, 2H), 7.25 – 7.17 (m, 1H), 7.09 – 6.97 (m, 2H), 6.95 – 6.63 (m, 8H), 6.58 (t, J = 10.0 Hz, 1H), 5.86 (t, J = 6.4 Hz, 1H), 2.32 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.14, 188.00, 163.16, 162.19, 140.30, 140.17, 140.15, 139.94, 139.16, 136.93, 135.69, 135.52, 135.31, 134.69, 134.37, 133.66, 133.20, 131.21, 131.08, 130.52, 130.13, 130.00, 129.94, 129.70, 129.25, 129.10, 128.96, 128.93, 128.84, 127.82, 127.76, 127.54, 125.87, 125.84, 125.24, 124.48, 124.43, 124.31, 121.23, 120.09, 119.86, 116.96, 116.31, 116.17, 115.98, 114.97, 106.27, 105.92, 20.41, 19.85, 19.72, 19.51. HRMS (ESI): m/z calcd for $[M+H]^+$: 419.1760, found: 419.1765.



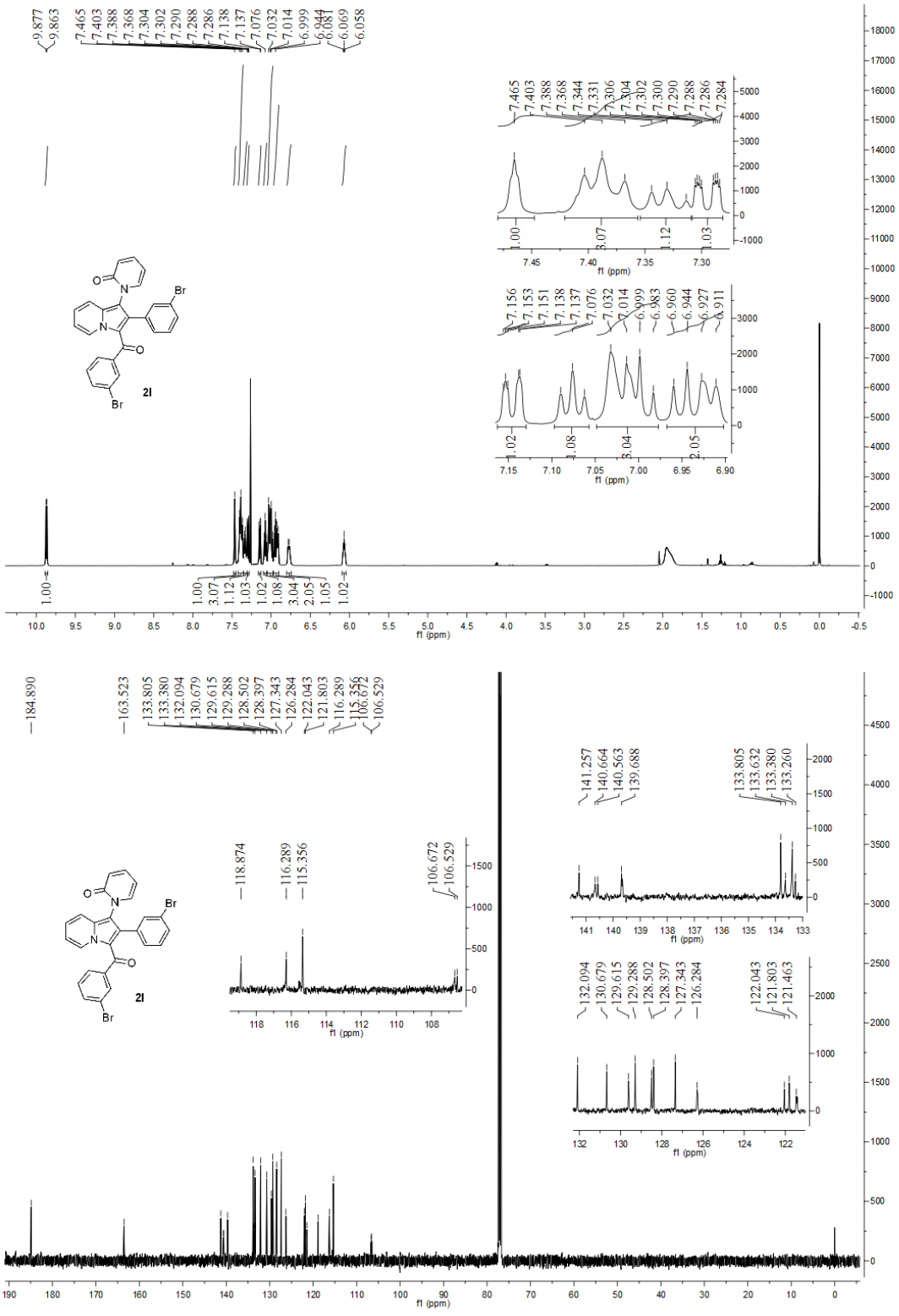


The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2k**

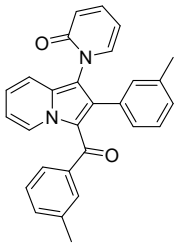


1-(3-(3-bromobenzoyl)-2-(3-bromophenyl) indolizin-1-yl) pyridin-2(1*H*)-one (**2l**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2l** as a yellow solid. 64% yield. m.p.:208.5-209.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (d, J = 7.0 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.43 – 7.36 (m, 3H), 7.35 – 7.31 (m, 1H), 7.29 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 7.16 – 7.13 (m, 1H), 7.08 (t, J = 7.0 Hz, 1H), 7.05 – 6.98 (m, 3H), 6.97 – 6.90 (m, 2H), 6.78 (d, J = 8.5 Hz, 1H), 6.07 (t, J = 5.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.89, 163.52, 141.26, 140.66, 140.56, 139.69, 133.80, 133.63, 133.38, 133.26, 132.09, 130.68, 129.62, 129.29, 128.50, 128.40, 127.34, 126.28, 122.04, 121.80, 121.46, 118.87, 116.29, 115.36, 106.67, 106.53. HRMS (ESI): m/z calcd for $[M+H]^+$:546.9657, found: 546.9650.

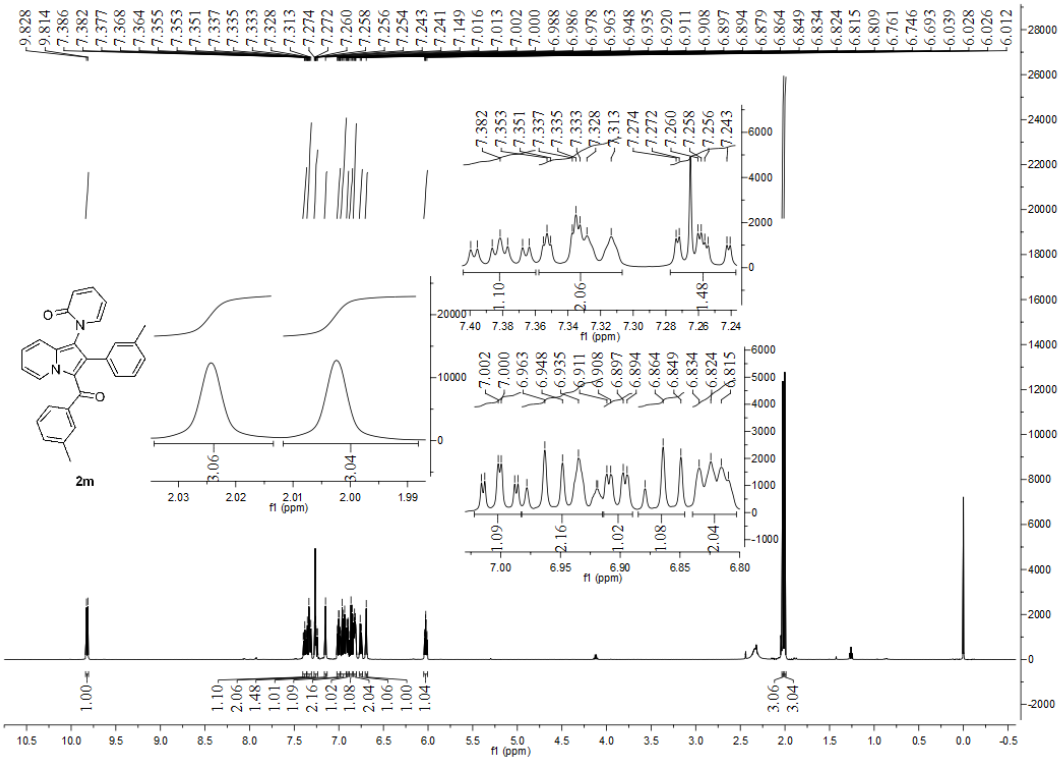


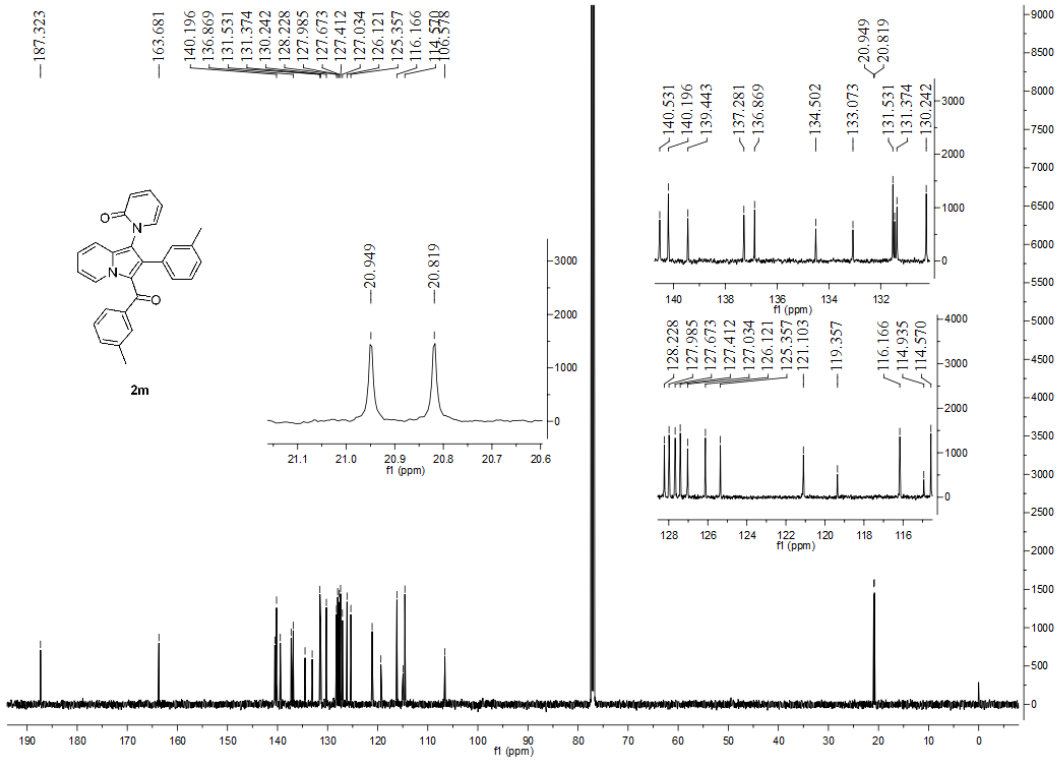
The ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2l**



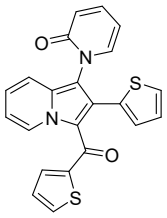
1-(3-(3-methylbenzoyl)-2-(m-tolyl) indolizin-1-yl) pyridin-2(1*H*)-one (**2m**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2m** as a yellow solid. 53% yield. m.p.:208.4-209.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (d, J = 7.0 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.36 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 7.15 (s, 1H), 7.00 (td, J = 7.0, 1.2 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.90 (dd, J = 7.0, 1.5 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 6.84 – 6.80 (m, 2H), 6.75 (d, J = 7.5 Hz, 1H), 6.69 (s, 1H), 6.03 (td, J = 7.0, 1.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.32, 163.68, 140.53, 140.20, 139.44, 137.28, 136.87, 134.50, 133.07, 131.53, 131.46, 131.37, 130.24, 128.23, 127.98, 127.67, 127.41, 127.03, 126.12, 125.36, 121.10, 119.36, 116.17, 114.93, 114.57, 106.58, 20.95, 20.82. HRMS (ESI): m/z calcd for $[M+H]^+$: 419.1760, found: 419.1758.



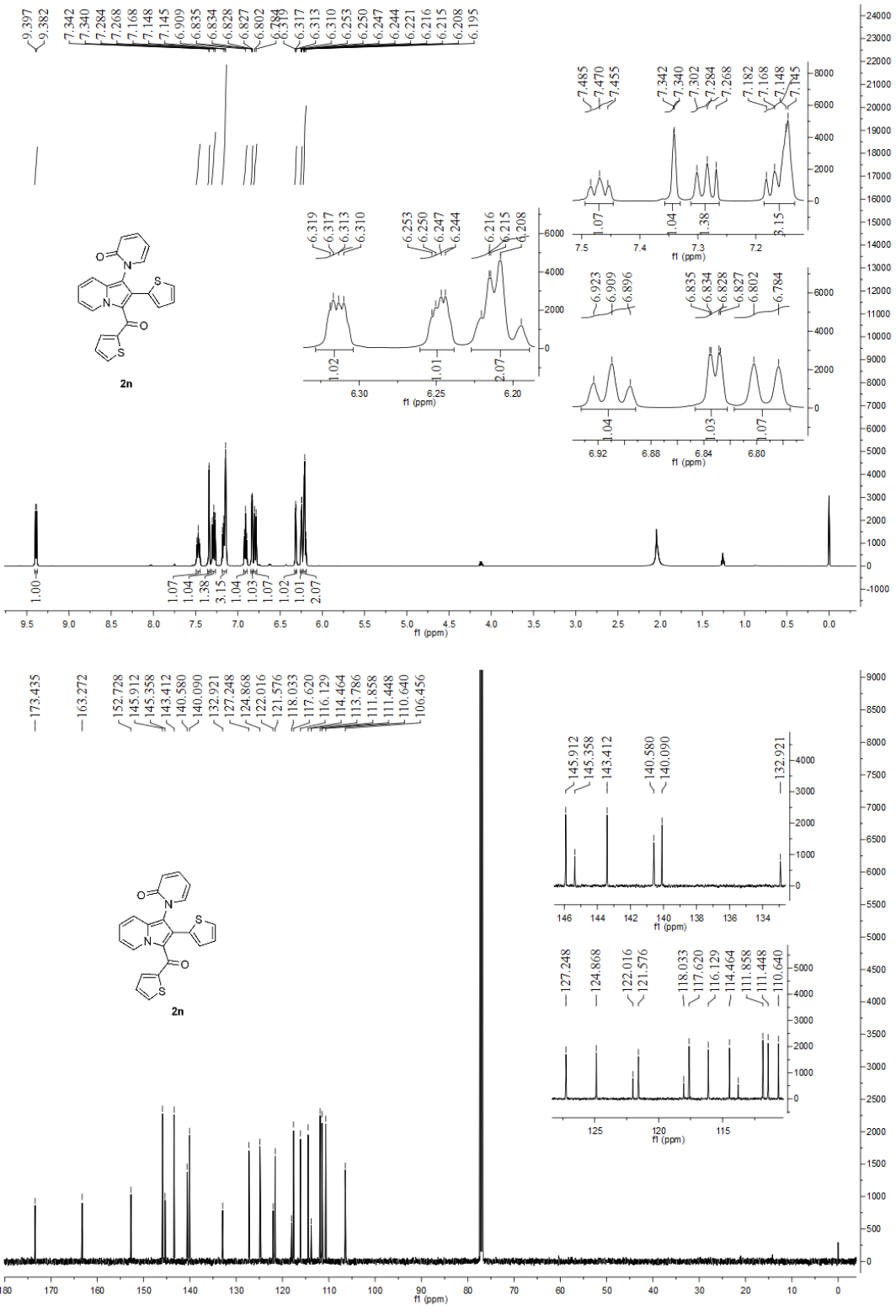


The ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2m**

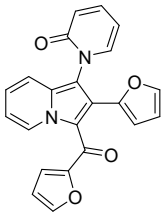


1-(2-(thiophen-2-yl)-3-(thiophene-2-carbonyl) indolizin-1-yl) pyridin-2(1*H*)-one (**2n**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2n** as a yellow solid. 48% yield. m.p.:226.7-227.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (d, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.31 – 7.26 (m, 1H), 7.19 – 7.13 (m, 3H), 6.91 (t, J = 7.0 Hz, 1H), 6.83 (dd, J = 3.5, 0.5 Hz, 1H), 6.79 (d, J = 9.0 Hz, 1H), 6.33 – 6.30 (m, 1H), 6.25 (dd, J = 3.0, 1.5 Hz, 1H), 6.23 – 6.19 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.43, 163.27, 152.73, 145.91, 145.36, 143.41, 140.58, 140.09, 132.92, 127.25, 124.87, 122.02, 121.58, 118.03, 117.62, 116.13, 114.46, 113.79, 111.86, 111.45, 110.64, 106.46. HRMS (ESI): m/z calcd for $[M+H]^+$: 403.0575, found: 403.0579.

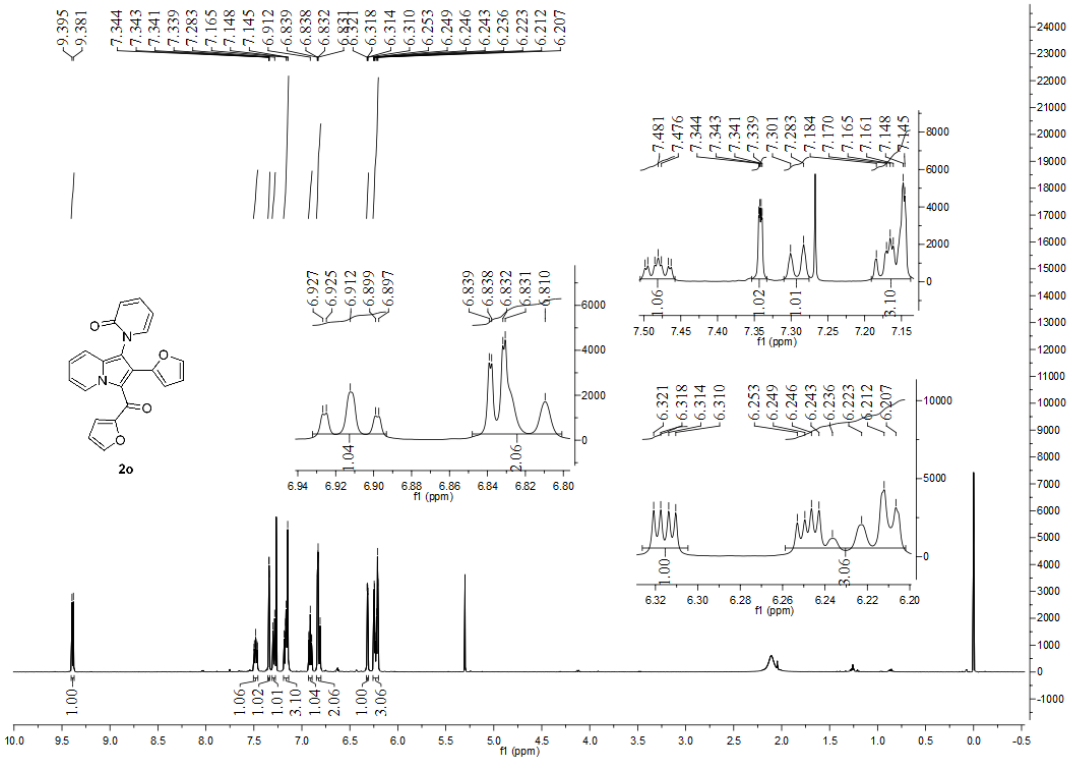


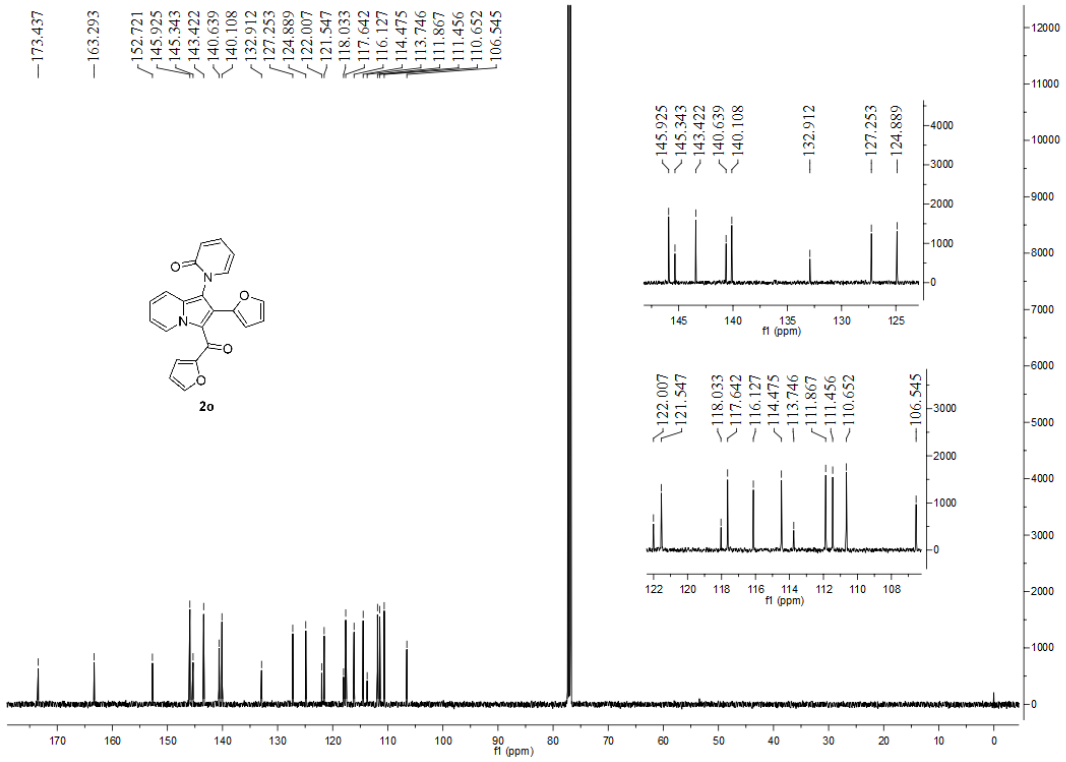
The ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2n**



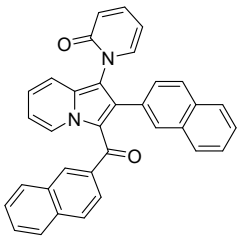
1-(3-(furan-2-carbonyl)-2-(furan-2-yl) indolizin-1-yl) pyridin-2(1*H*)-one (**2o**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2o** as a yellow solid. 35% yield. m.p.:209.3-210.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (d, J = 7.0 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.35 – 7.33 (m, 1H), 7.29 (d, J = 9.0 Hz, 1H), 7.19 – 7.14 (m, 3H), 6.93 – 6.89 (m, 1H), 6.85 – 6.80 (m, 2H), 6.32 (dd, J = 3.8, 1.8 Hz, 1H), 6.26 – 6.20 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.44, 163.29, 152.72, 145.93, 145.34, 143.42, 140.64, 140.11, 132.91, 127.25, 124.89, 122.01, 121.55, 118.03, 117.64, 116.13, 114.47, 113.75, 111.87, 111.46, 110.65, 106.55. HRMS (ESI): m/z calcd for $[M+H]^+$: 371.1032, found: 371.1029.



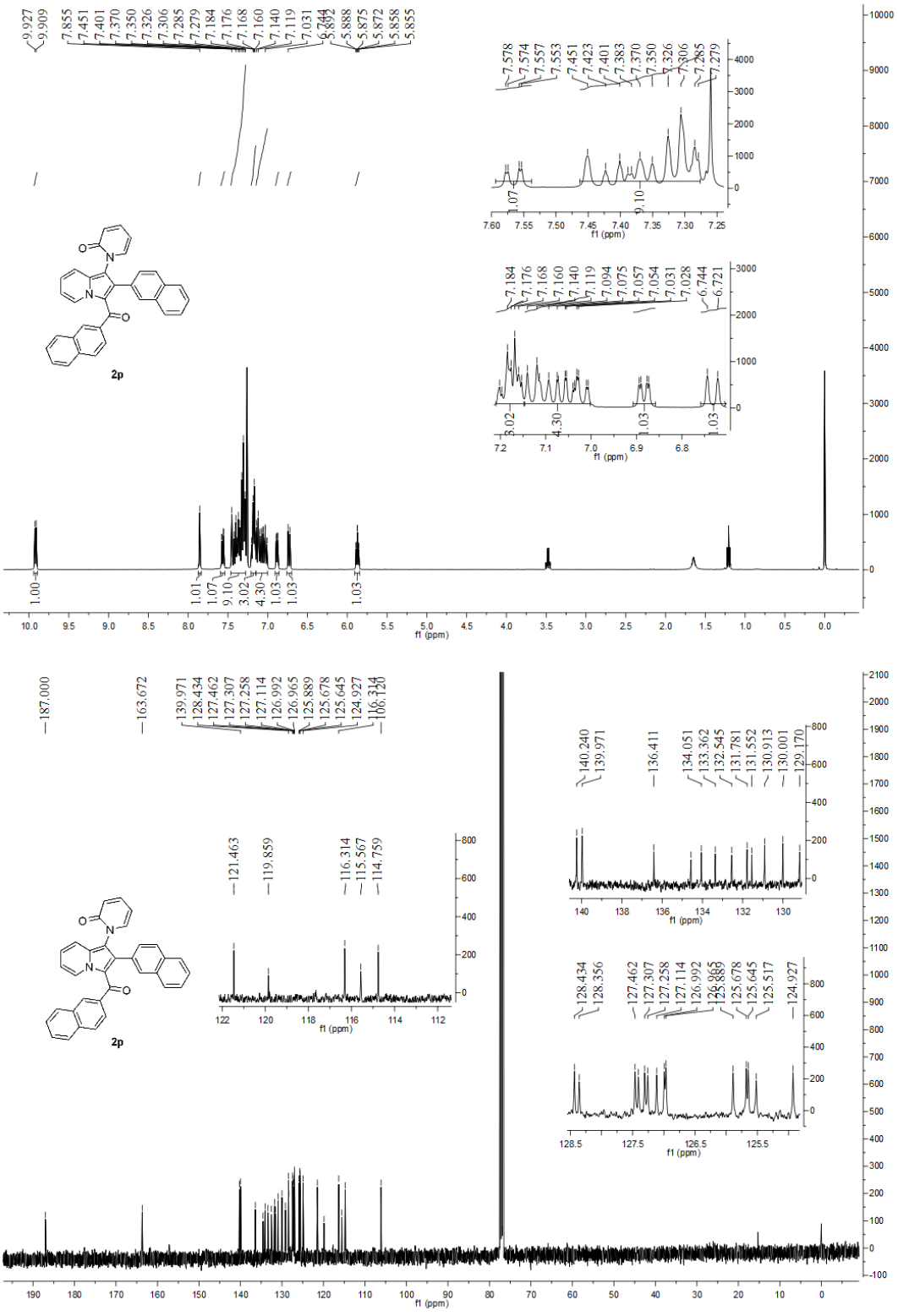


The ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2o**

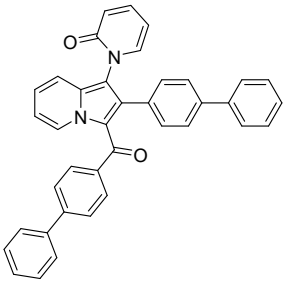


1-(3-(2-naphthoyl)-2-(naphthalen-2-yl) indolizin-1-yl) pyridin-2(1*H*)-one (**2p**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2p** as a yellow solid. 68% yield. m.p.:212.5-213.3 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (d, J = 7.2 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.57 (dd, J = 8.4, 1.6 Hz, 1H), 7.46 – 7.28 (m, 9H), 7.21 – 7.15 (m, 3H), 7.15 – 7.00 (m, 4H), 6.88 (dd, J = 6.8, 1.6 Hz, 1H), 6.73 (d, J = 9.2 Hz, 1H), 5.87 (td, J = 6.8, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.00, 163.67, 140.24, 139.97, 136.41, 134.57, 134.05, 133.36, 132.54, 131.78, 131.55, 130.91, 130.00, 129.17, 128.43, 128.36, 127.46, 127.41, 127.31, 127.26, 127.11, 126.99, 126.96, 125.89, 125.68, 125.64, 125.52, 124.93, 121.46, 119.86, 116.31, 115.57, 114.76, 106.12. HRMS (ESI): m/z calcd for $[M+H]^{+}$: 491.1760, found: 491.1768.

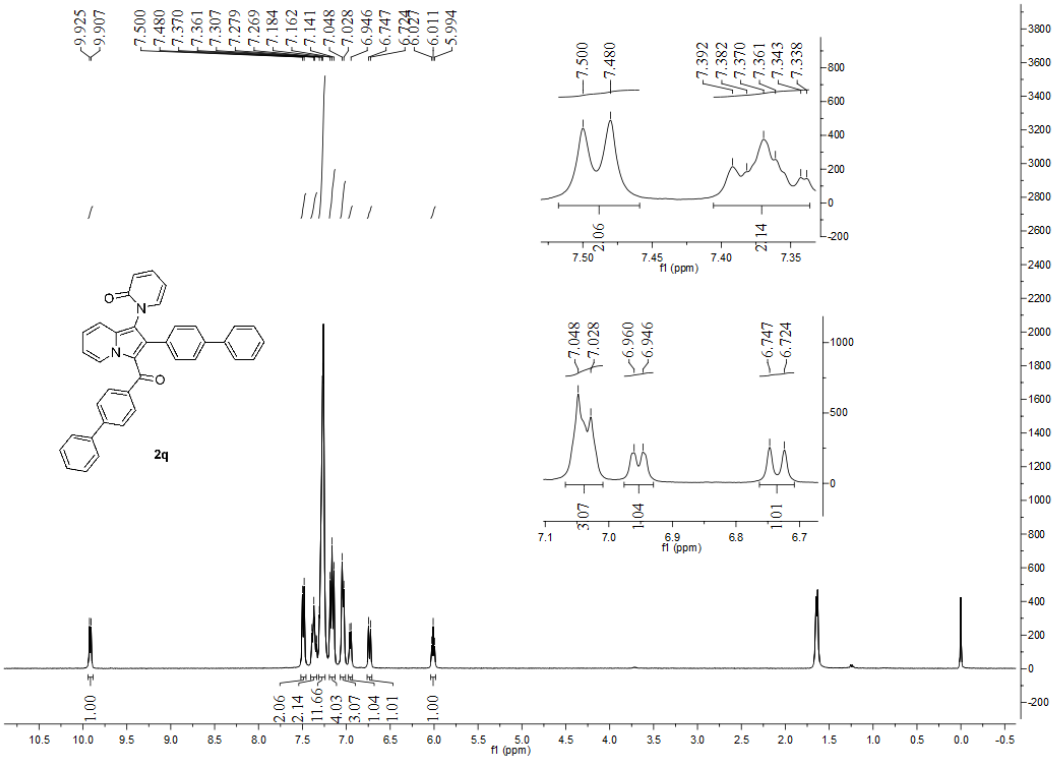


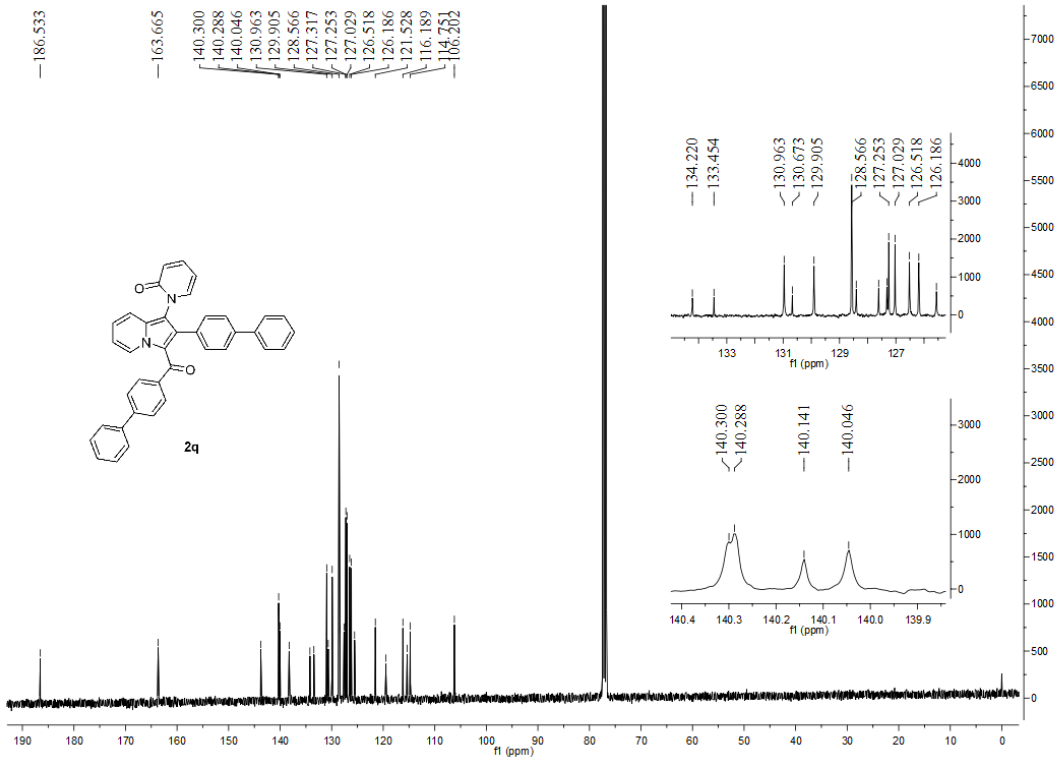
The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2p**



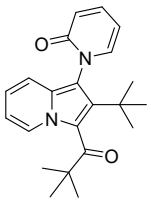
1-(3-([1,1'-biphenyl]-4-carbonyl)-2-([1,1'-biphenyl]-4-yl)indolizin-1-yl)pyridin-2(1*H*)-one (**2q**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:2) to afford **2q** as a yellow solid. 54% yield. m.p.:203.5-203.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.31 – 7.24 (m, 11H), 7.19 – 7.13 (m, 4H), 7.07 – 7.01 (m, 3H), 6.95 (d, J = 5.6 Hz, 1H), 6.74 (d, J = 9.2 Hz, 1H), 6.01 (t, J = 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.53, 163.66, 143.76, 140.30, 140.29, 140.14, 140.05, 138.26, 134.22, 133.45, 130.96, 130.67, 129.90, 128.57, 128.40, 127.61, 127.32, 127.25, 127.03, 126.52, 126.19, 125.56, 121.53, 119.47, 116.19, 115.37, 114.75, 106.20. HRMS (ESI): m/z calcd for $[M+H]^+$: 543.2073, found: 543.2076.



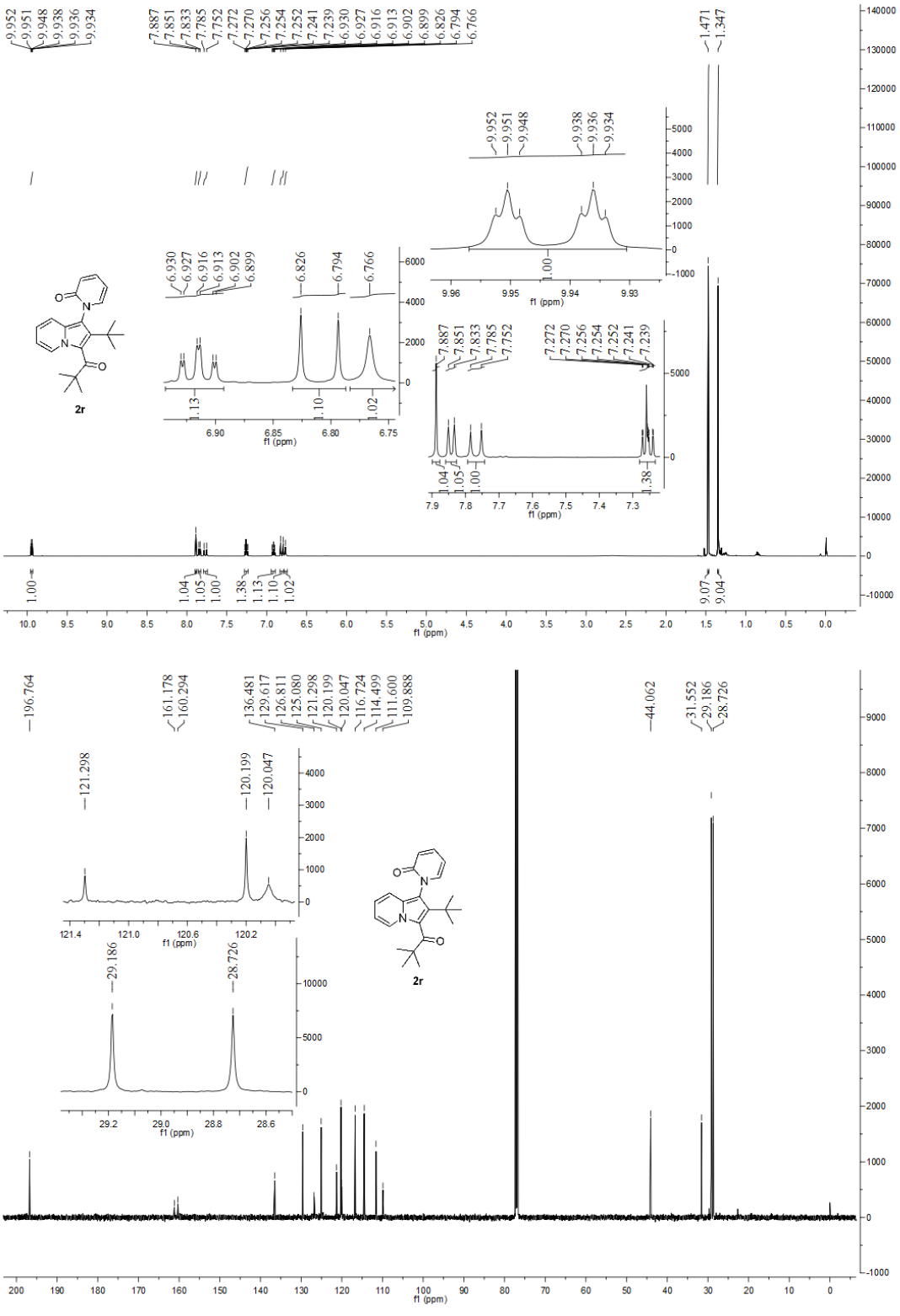


The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2q**

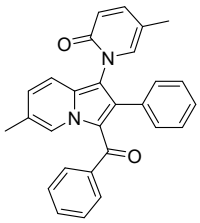


1-(2-(tert-butyl)-3-pivaloylindolizin-1-yl) pyridin-2(1*H*)-one (**2r**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 5:1) to afford **2r** as a yellow solid. 57% yield. m.p.:97.6-98.2 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (dt, J = 7.0, 1.0 Hz, 1H), 7.90 – 7.88 (m, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 16.5 Hz, 1H), 7.28 – 7.23 (m, 1H), 6.91 (td, J = 7.0, 1.5 Hz, 1H), 6.81 (d, J = 16.0 Hz, 1H), 6.78 – 6.74 (m, 1H), 1.47 (s, 9H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.76, 161.18, 160.29, 136.48, 129.62, 126.81, 125.08, 121.30, 120.20, 120.05, 116.72, 114.50, 111.60, 109.89, 44.06, 31.55, 29.19, 28.73. HRMS (ESI): m/z calcd for $[M+H]^+$: 351.2073, found: 351.2069.

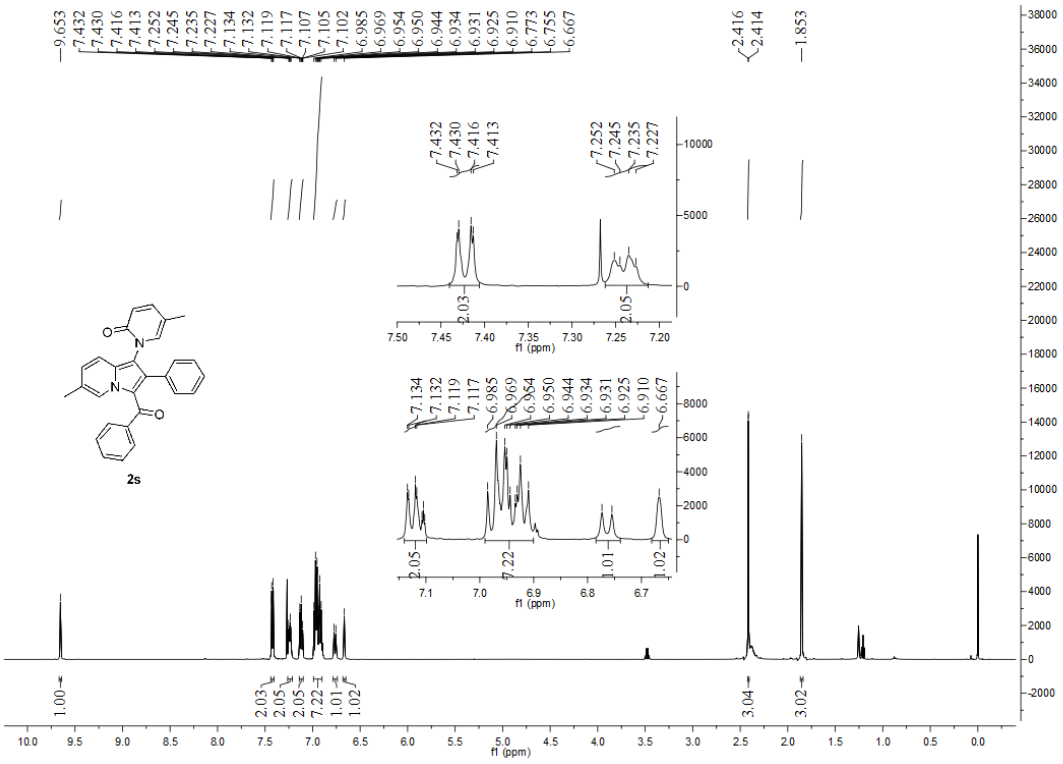


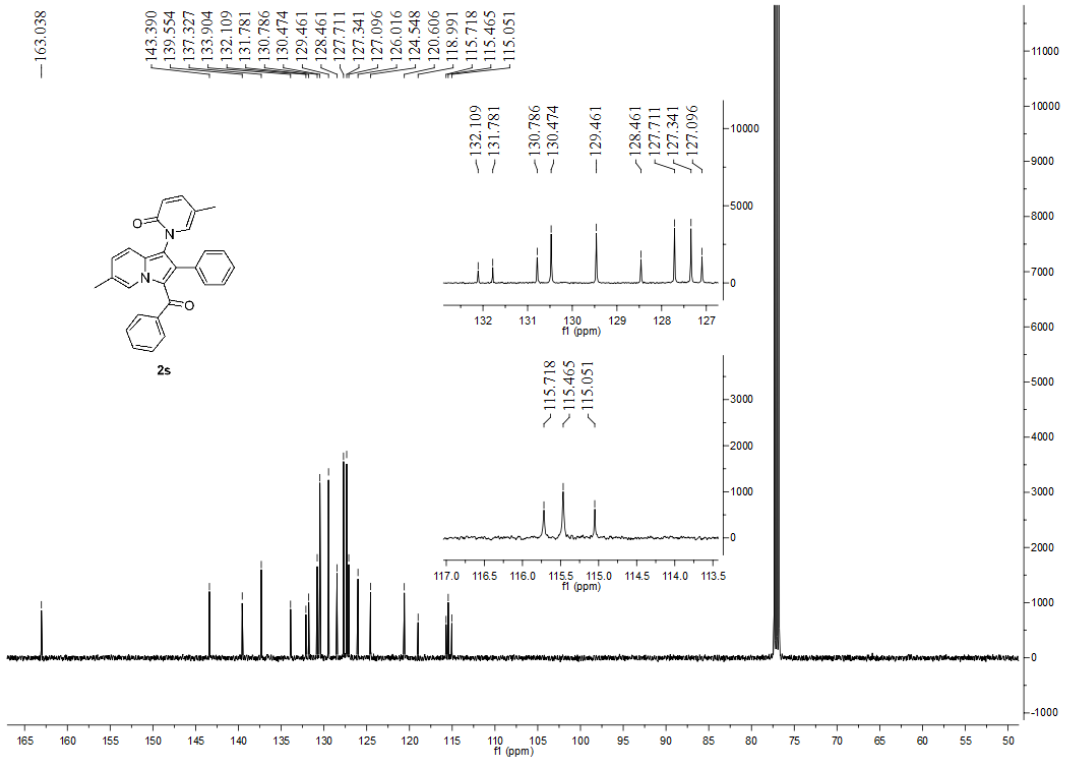
The ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2r**



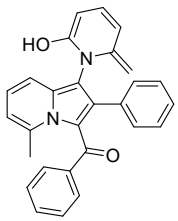
1-(3-benzoyl-6-methyl-2-phenylindolizin-1-yl)-5-methylpyridin-2(1*H*)-one (**2s**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:1) to afford **2s** as a yellow solid. 69% yield. m.p.:207.1-207.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.42 (dd, J = 8.0, 1.3 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.14 – 7.10 (m, 2H), 6.99 – 6.90 (m, 7H), 6.76 (d, J = 9.0 Hz, 1H), 6.67 (s, 1H), 2.41 (d, J = 1.0 Hz, 3H), 1.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.96, 163.04, 143.39, 139.55, 137.33, 133.90, 132.11, 131.78, 130.79, 130.47, 129.46, 128.46, 127.71, 127.34, 127.10, 126.02, 124.55, 120.61, 118.99, 115.72, 115.47, 115.05, 18.72, 16.80. HRMS (ESI): m/z calcd for $[M+H]^+$: 419.1760, found: 419.1767.



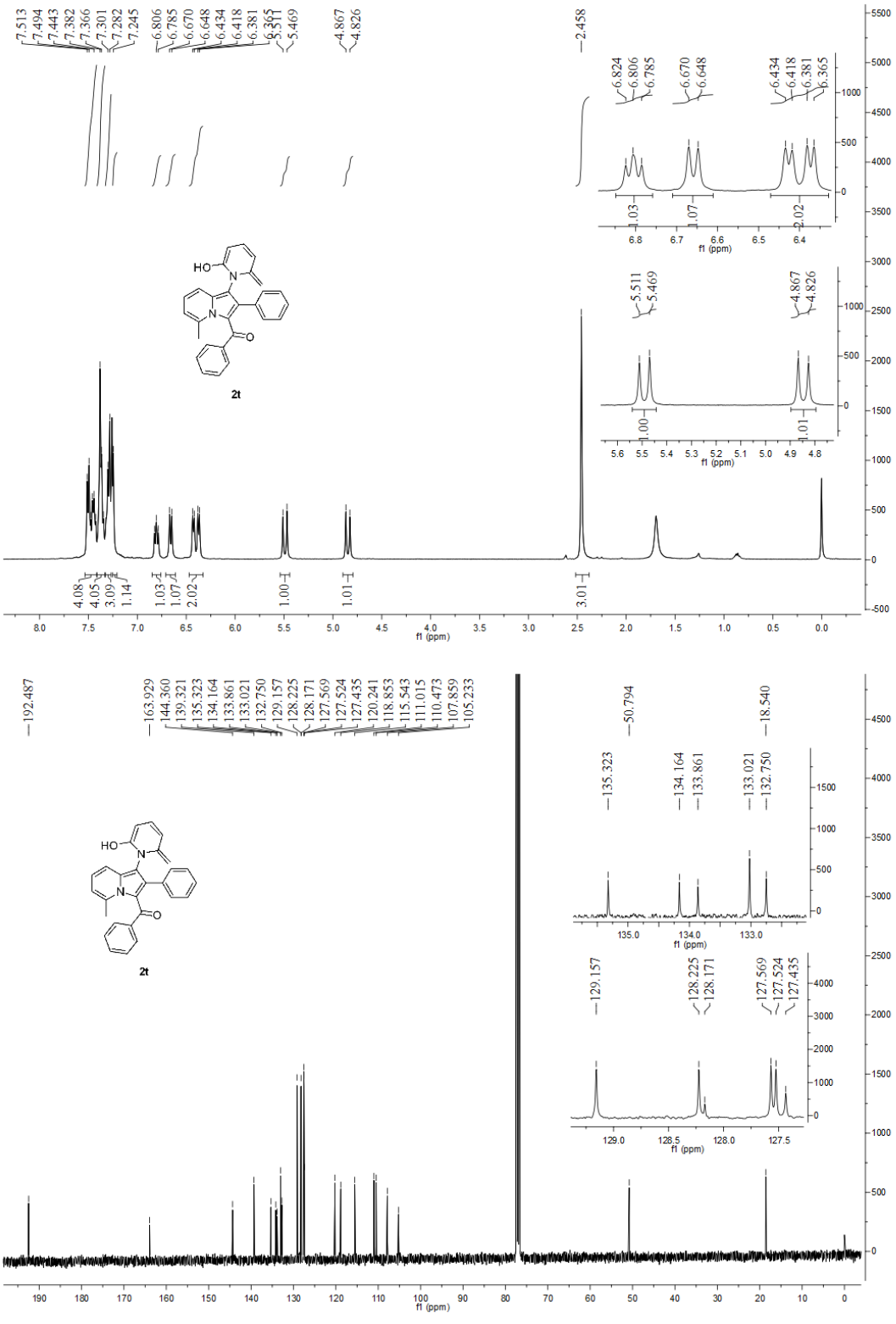


The ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **2s**

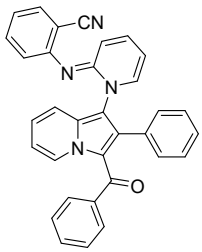


(1-(6-hydroxy-2-methylenepyridin-1(2*H*)-yl)-5-methyl-2-phenylindolizin-3-yl)(pheny-l) methanone (**2t**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 1:1) to afford **2t** as a yellow solid. 66% yield. m.p.:205.4-206.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.42 (m, 4H), 7.41 – 7.33 (m, 4H), 7.33 – 7.21 (m, 4H), 6.85 – 6.76 (m, 1H), 6.66 (d, J = 8.8 Hz, 1H), 6.40 (dd, J = 21.2, 6.4 Hz, 2H), 5.49 (d, J = 16.8 Hz, 1H), 4.85 (d, J = 16.4 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.49, 163.93, 144.36, 139.32, 135.32, 134.16, 133.86, 133.02, 132.75, 129.16, 128.22, 128.17, 127.57, 127.52, 127.43, 120.24, 118.85, 115.54, 111.02, 110.47, 107.86, 105.23, 50.79, 18.54. HRMS (ESI): m/z calcd for $[M+H]^+$: 419.1760, found: 419.1769.

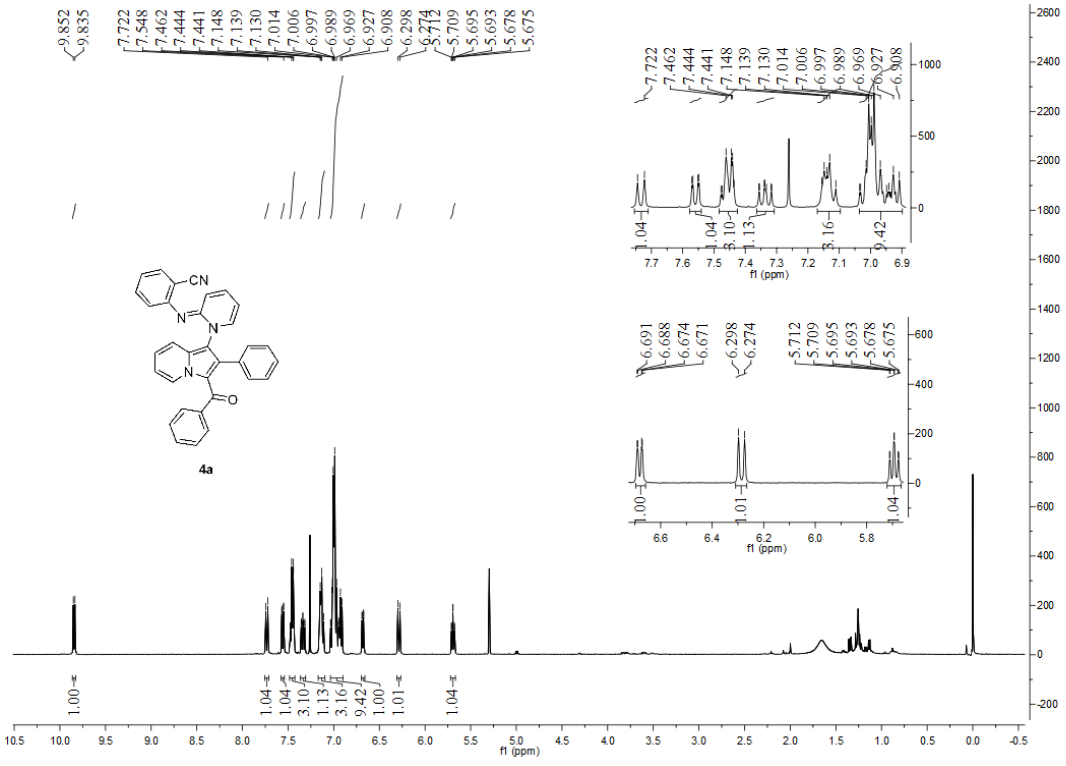


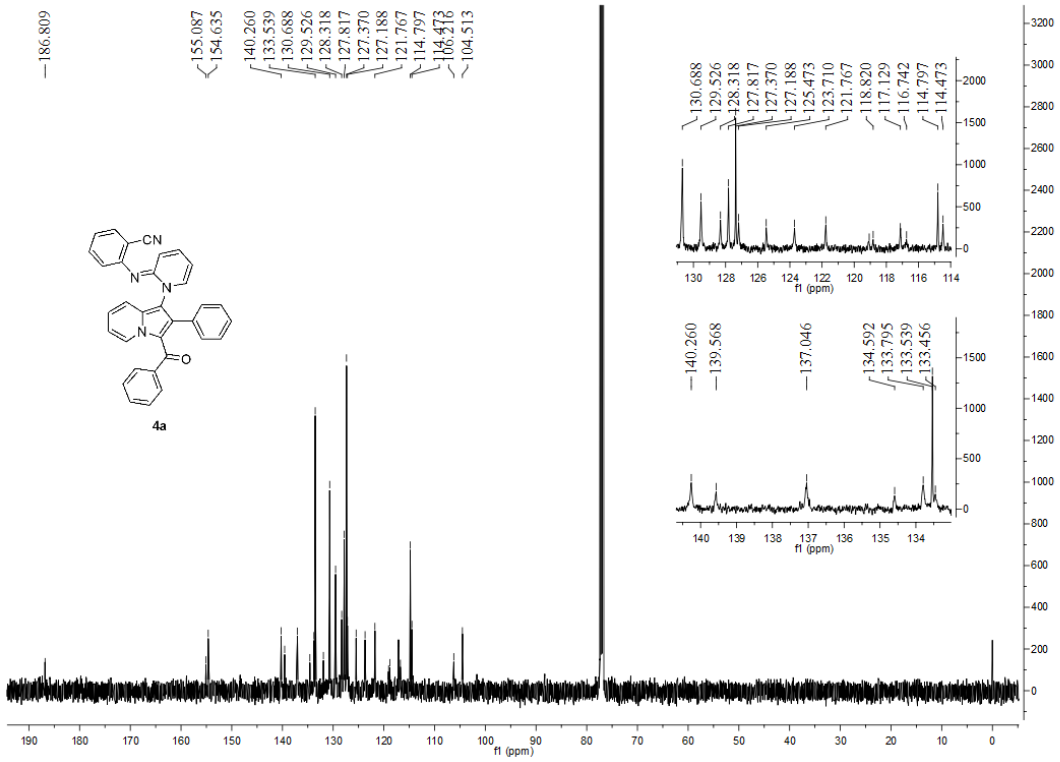
The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **2t**



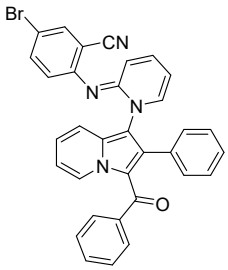
(E)-2-((1-(3-benzoyl-2-phenylindolizin-1-yl)pyridin-2(1*H*)-ylidene)amino)benzonitril-e (**4a**)

Purified by column chromatography (silica gel, petroleum: EtOAc=5:1) to afford **4a** as a yellow solid. 45% yield. m.p.:189.5-190.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (d, J = 6.8 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.56 (dd, J = 8.0, 1.6 Hz, 1H), 7.48 – 7.43(m, 3H), 7.37 – 7.30 (m, 1H), 7.17 – 7.10 (m, 3H), 7.04 – 6.90 (m, 9H), 6.68 (dd, J = 6.8, 1.2 Hz, 1H), 6.29 (d, J = 9.6 Hz, 1H), 5.69 (td, J = 6.8, 1.2 Hz, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 186.81, 155.09, 154.63, 140.26, 139.57, 137.05, 134.59, 133.80, 133.54, 133.46, 131.93, 131.88, 130.69, 129.53, 128.32, 127.82, 127.37, 127.19, 125.47, 123.71, 121.77, 119.07, 118.82, 117.13, 116.74, 114.80, 114.47, 106.22, 104.51.HRMS (ESI): m/z calcd for $[M+H]^+$: 419.1760, found: 419.1769.





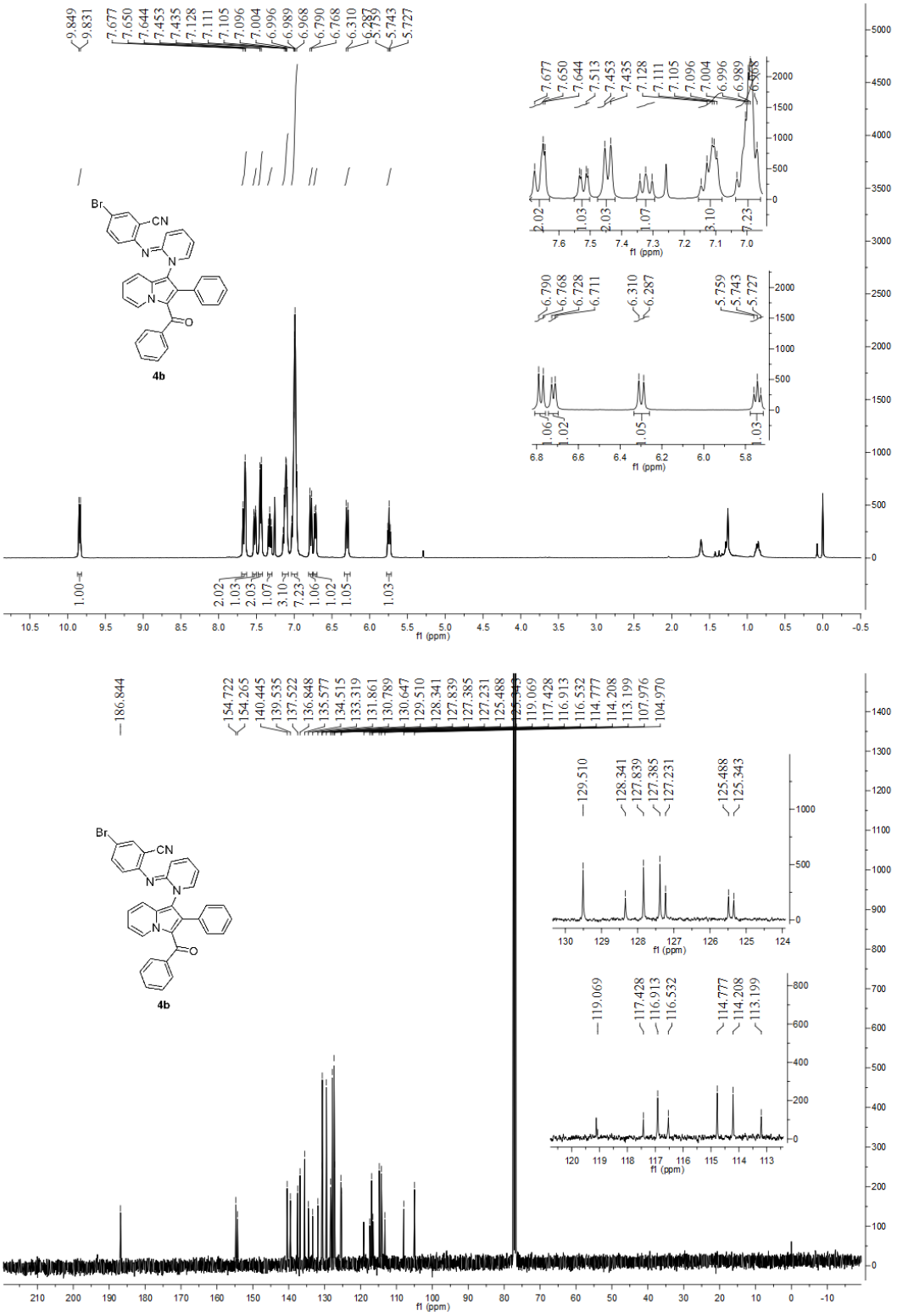
The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz) spectra of **4a**



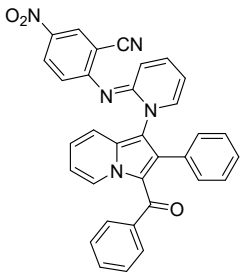
(E)-2-((1-(3-benzoyl-2-phenylindolizin-1-yl)pyridin-2(1*H*)-ylidene)amino)-5-bromobenzonitrile (**4b**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 5:1) to afford **4b** as a yellow solid. 29% yield. m.p.:208.3-208.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (d, J = 7.2 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.52 (dd, J = 8.4, 2.0 Hz, 1H), 7.44 (d, J = 7.2 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.15 – 7.08 (m, 3H), 7.04 – 6.96 (m, 7H), 6.78 (d, J = 8.6 Hz, 1H), 6.72 (d, J = 6.8 Hz, 1H), 6.30 (d, J = 9.2 Hz, 1H), 5.74 (t, J = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.84, 154.72, 154.26, 140.45, 139.53, 137.52, 136.85, 135.58, 134.51, 133.32, 131.86, 130.79, 130.65, 129.51, 128.34, 127.84, 127.39, 127.23, 125.49, 125.34, 119.07, 117.43, 116.91, 116.53, 114.78, 114.21,

113.20, 107.98, 104.97. HRMS (ESI): m/z calcd for $[M+H]^+$: 569.0977, found: 569.0982.

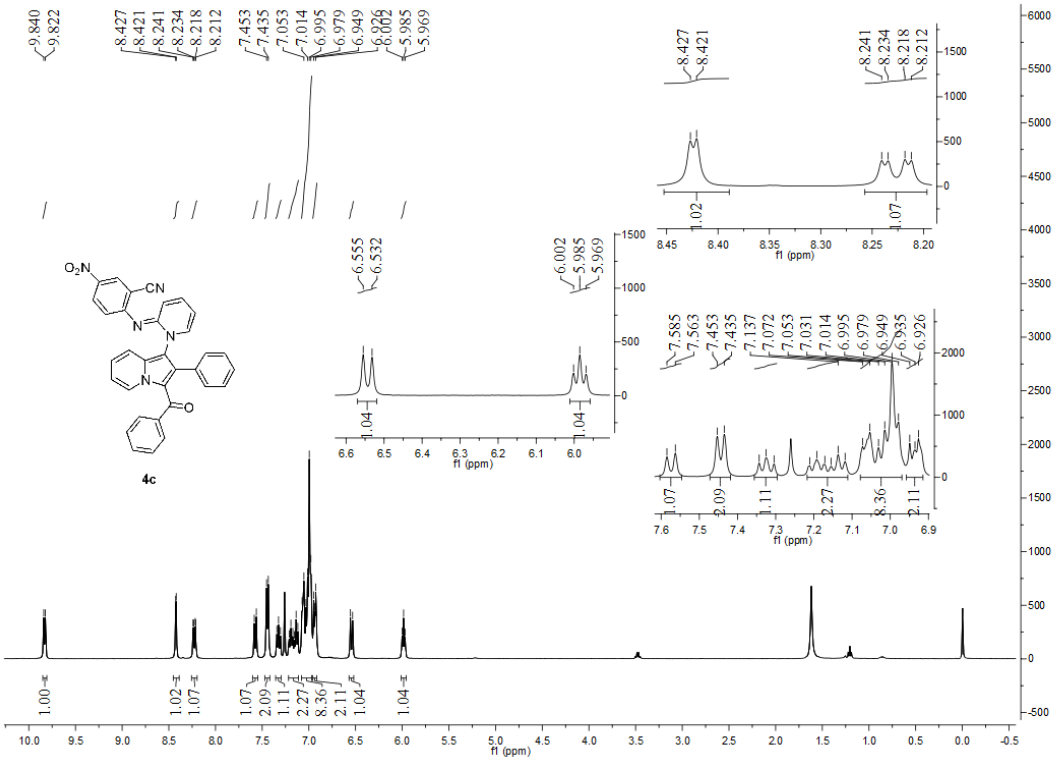


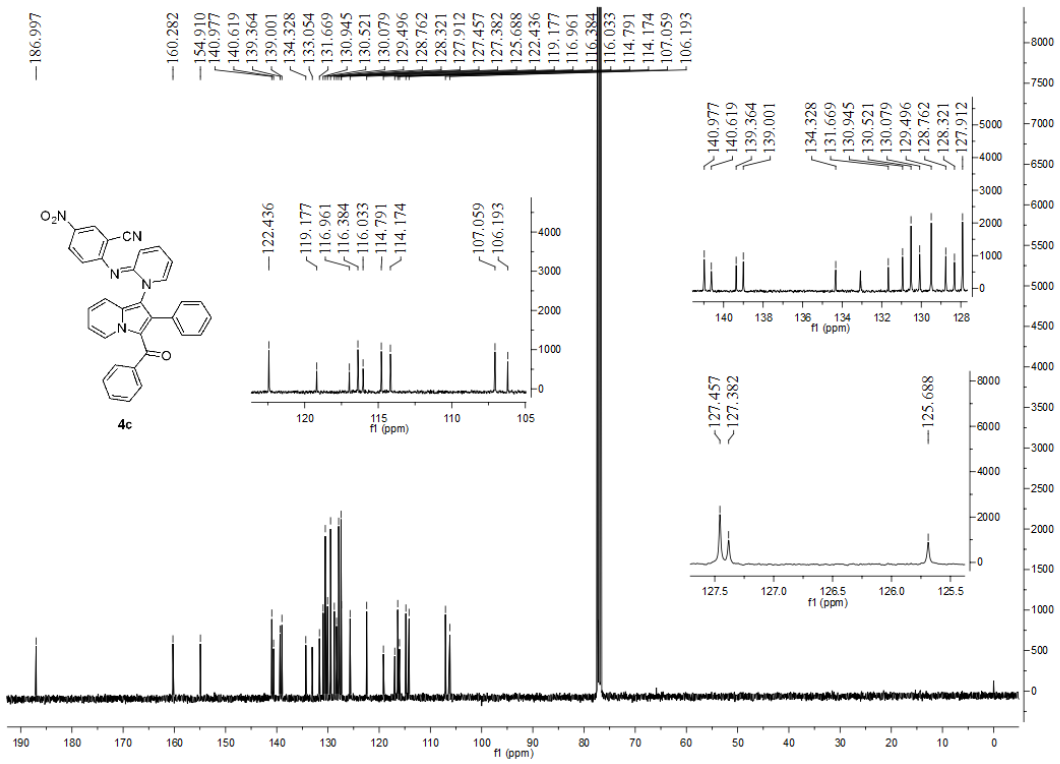
The ^1H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **4b**



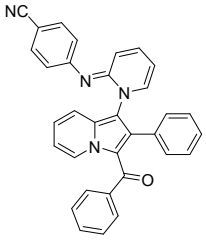
(E)-2-((1-(3-benzoyl-2-phenylindolizin-1-yl)pyridin-2(1*H*)-ylidene)amino)-5-nitrobenzonitrile (**4c**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 5:1) to afford **4c** as a yellow solid. 25% yield. m.p.:276.1-276.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (d, J = 7.2 Hz, 1H), 8.42 (d, J = 2.4 Hz, 1H), 8.23 (dd, J = 9.2, 2.8 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.44 (d, J = 7.2 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.22 – 7.11 (m, 2H), 7.09 – 6.97 (m, 8H), 6.96 – 6.92 (m, 2H), 6.54 (d, J = 9.2 Hz, 1H), 5.99 (t, J = 6.8 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 187.00, 160.28, 154.91, 140.98, 140.62, 139.36, 139.00, 134.33, 133.05, 131.67, 130.95, 130.52, 130.08, 129.50, 128.76, 128.32, 127.91, 127.46, 127.38, 125.69, 122.44, 119.18, 116.96, 116.38, 116.03, 114.79, 114.17, 107.06, 106.19. HRMS (ESI): m/z calcd for $[M+H]^+$: 536.1723, found: 536.1728.



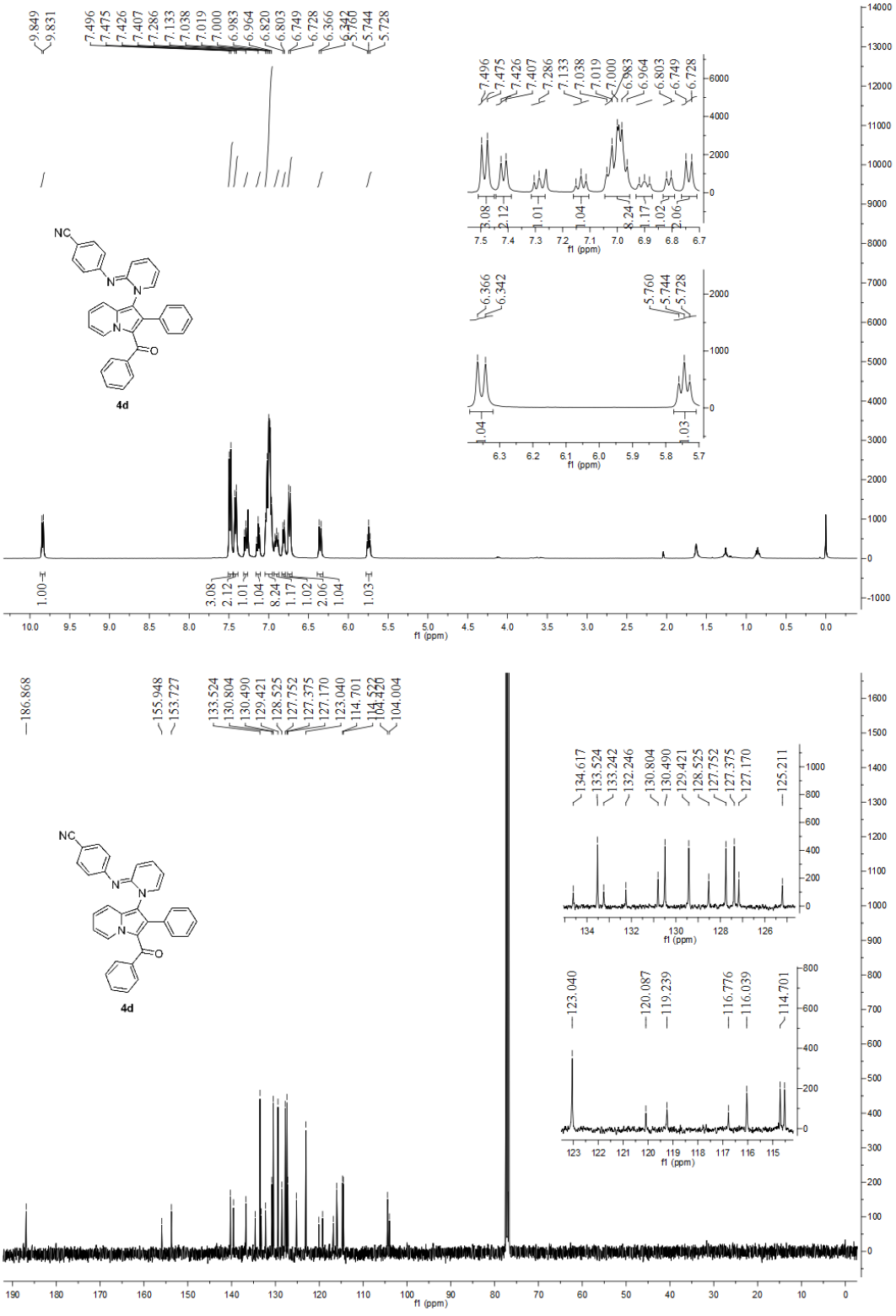


The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **4c**



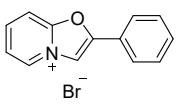
(E)-4-((1-(3-benzoyl-2-phenylindolizin-1-yl)pyridin-2(1*H*)-ylidene)amino)benzonitrie (**4d**)

Purified by column chromatography (silica gel, petroleum: EtOAc= 5:1) to afford **4d** as a yellow solid. 19% yield. m.p.:190.3-191.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 8.4 Hz, 3H), 7.42 (d, J = 7.6 Hz, 2H), 7.30 (d, J = 7.2 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.06 – 6.96 (m, 8H), 6.93 – 6.87 (m, 1H), 6.81 (d, J = 6.8 Hz, 1H), 6.74 (d, J = 8.4 Hz, 2H), 6.35 (d, J = 9.6 Hz, 1H), 5.74 (t, J = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.87, 155.95, 153.73, 140.26, 139.57, 136.72, 134.62, 133.52, 133.24, 132.25, 130.80, 130.49, 129.42, 128.53, 127.75, 127.38, 127.17, 125.21, 123.04, 120.09, 119.24, 116.78, 116.04, 114.70, 114.52, 104.42, 104.00. HRMS (ESI): m/z calcd for $[M+H]^+$: 491.1872, found: 491.1879.



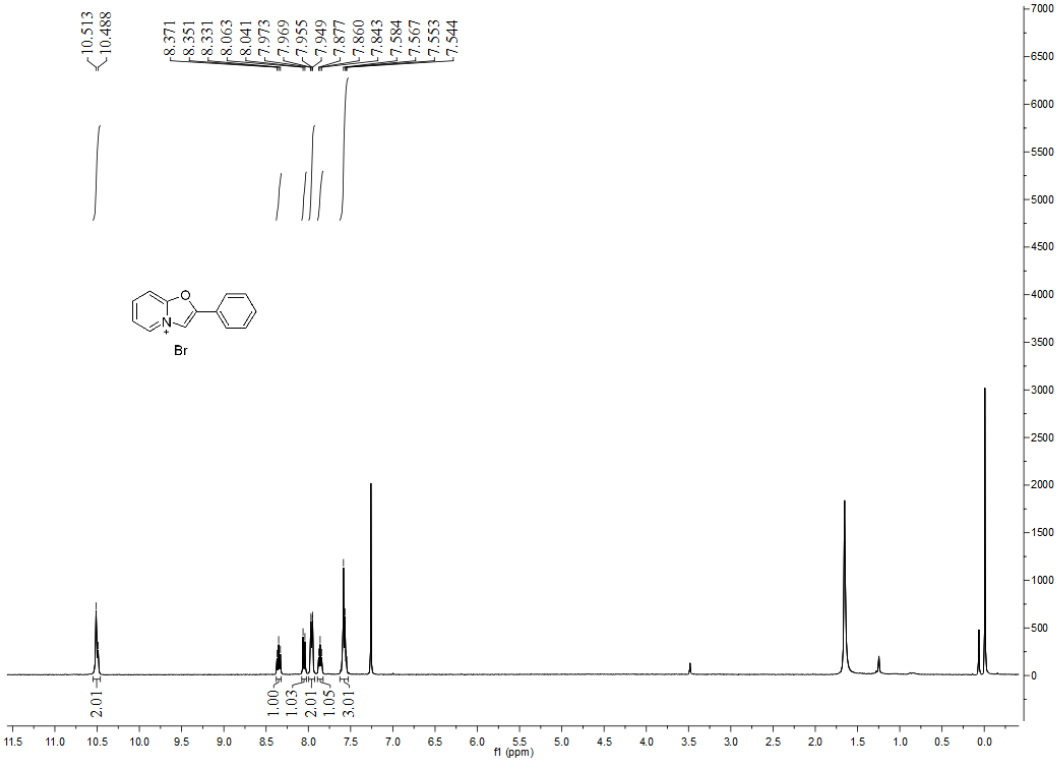
The ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of **4d**

5. Characterization Data of intermediate B



2-phenyloxazolo[3,2-a]pyridin-4-ium bromide (Intermediate **B**)

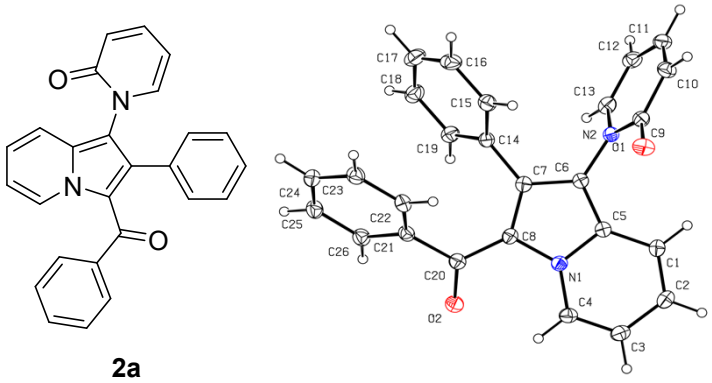
White solid. m.p.:286.2-287.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (d, J = 9.7 Hz, 2H), 8.35 (t, J = 8.1 Hz, 1H), 8.05 (d, J = 8.9 Hz, 1H), 7.96 (dd, J = 7.6, 1.7 Hz, 2H), 7.86 (t, J = 6.9 Hz, 1H), 7.63 – 7.53 (m, 3H). HRMS (ESI): m/z calcd for $[M]^+$: 196.0757, found: 196.0751.



The ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of Intermediate **B**

6. X-ray Crystallography Data of 2a and 4d

Single crystals of compound **2a** and **4d** were measured on a Rigaku PAXIS-PAPID single-crystal diffractometer. The recrystallization solvent of **2a** was MeOH. The recrystallization solvent of **4d** was MeOH and Acetone.



2a

Figure S1 X-ray crystallography of **2a**

Formula moiety	$C_{26}H_{18}N_2O_2$
Formula sum	$C_{26}H_{18}N_2O_2$
Formula weight	390.42
Temperature	170K
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a= 7.027(2) b= 17.982(5) c= 15.561(5) alpha=90 beta= 101.167(11) gamma=90
Volume	1929.1(10)
Z	4
Calculated density	1.344 g/cm^3
Absorption coefficient	0.086
F(000)	816.0
Crystal size	0.36×0.19×0.12 mm
Theta range for data collection	4.53 to 54.236 deg.
Reflections collected / unique	20840/ 4252 [R_{int} = 0.0440, R_{sigma} = 0.0326]
Data / restraints / parameters	4252/0/271

Goodness-of-fit on F2	1.029
Final R indices	R1=0.0388, wR2 = 0.0910
R indices(all data)	R1=0.0519, wR2 = 0.0990

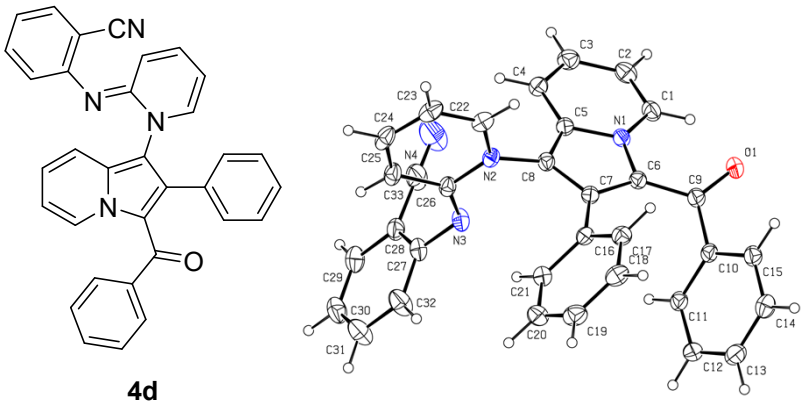


Figure S2 X-ray crystallography of **4d**

Formula moiety	$C_{33}H_{22}N_4O$
Formula sum	$C_{33}H_{22}N_4O$
Formula weight	490.54
Temperature	170K
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a= 13.710(7) b= 13.465(6) c= 14.052(6) alpha=90 beta= 104.078(12) gamma=90
Volume	2516.2(19)
Z	4
Calculated density	1.295 g/cm^3
Absorption coefficient	0.080
F(000)	1024.0
Crystal size	0.32×0.12×0.1 mm

Theta range for data collection	4.252 to 54.298 deg.
Reflections collected / unique	31446/ 5544 [R_{int} = 0.0427, R_{sigma} = 0.0296]
Data / restraints / parameters	5544/0/343
Goodness-of-fit on F2	1.046
Final R indices	R_1=0.0467, wR_2 = 0.1129
R indices(all data)	R_1=0.0621, wR_2 = 0.1227