

Supporting Information

Palladium-Catalyzed Ligand-Regulated Divergent Synthesis of Pyrrole[2,3-*b*]indoles and Ureas from 2-Ethynylanilines and Isocyanides†

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Table of Contents

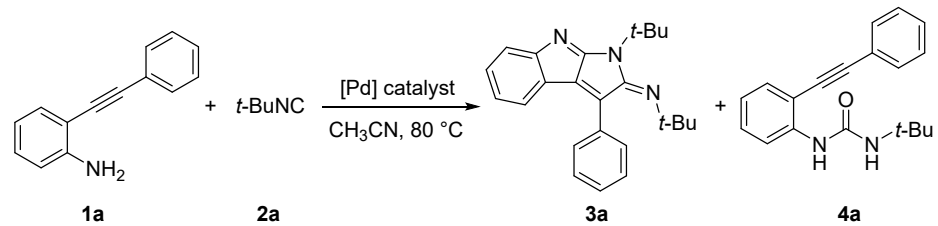
A. General Information	S2
B. Optimization of Reaction Conditions	S2
C. General Procedure for the Synthesis of Pyrrolo[2,3-<i>b</i>]Indoles	S5
D. General Procedure for the Synthesis of Ureas	S5
E. Further Synthetic Applications.....	S5
F. Characterization Data for All Products	S6
G. References	S15
H. X-ray Crystallographic Analysis	S16
I. Copies of ¹H, ¹³C, and ¹⁹F NMR Spectra	S18

A. General Information

All purchased reagents and solvents were used without further purification unless otherwise noted. Analytical thin layer chromatography was performed by using commercially prepared 100-400 mesh silica gel plates (GF₂₅₄) and visualization was effected at 254 nm. All the *o*-alkynylanilines were prepared according to known procedures. ¹H and ¹³C NMR spectra were recorded using a Bruker DRX-400 spectrometer using chloroform-*d* (CDCl₃) containing 0.03% (v/v) tetramethylsilane (TMS) as solvent. The chemical shifts are referenced to signals at 0.00 and 77.0 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument.

B. Optimization of Reaction Conditions

Table S1. Screening of palladium catalyst^a



entry ^a	[Pd] catalyst	yield of 3a (%) ^b	yield of 4a (%) ^b
1	Pd(OAc) ₂	35	10
2	-	n.d.	n.d.
3	Pd(TFA) ₂	27	3
4	PdCl ₂	11	26
5	Pd(acac) ₂	11	25
6	Pd(dba) ₂	30	15
7	Pd(PCy ₃) ₂	15	38

^a Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (2.4 equiv), [Pd] catalyst (10 mol %) in MeCN (1 mL) were added to a sealed tube at 80 °C under air for 12 h. ^bNMR yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S2. Optimization of solvent^a

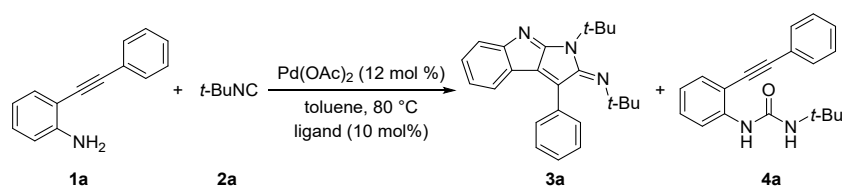
entry	solvent	yield of 3a (%) ^b	yield of 4a (%) ^b
1	EtOH	44	10
2	THF	24	7
3	DCM	40	14
4	Toluene	50	12

^a Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (2.4 equiv), Pd(OAc)₂ (10 mol %) in solvent (1 mL) were added to a sealed tube at 80 °C under air for 12 h. ^bNMR yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S3. Optimization of catalyst amounts^a

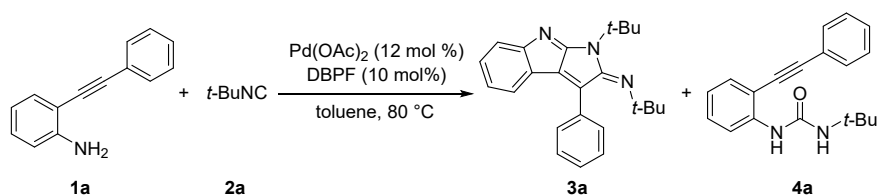
entry	Pd(OAc) ₂ (x mol %)	yield of 3a (%) ^b	yield of 4a (%) ^b
1	5	51	9
2	6	50	10
3	7	41	8
4	8	55	17
5	9	57	10
6	12	65 (62)	10
7	15	59	13

^a Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (2.4 equiv), Pd(OAc)₂ (x mol %) in toluene (1 mL) were added to a sealed tube at 80 °C under air for 12 h. ^bNMR yield was determined by ¹H NMR using CH₂Br₂ as an internal standard. Data in parentheses refer to isolated yield.

Table S4. Screening of ligands^a

entry	ligand	yield of 3a (%) ^b	yield of 4a (%) ^b
1	BPMZ	27	n.d.
2	TPTP	9	44
3	DBPF	10	65 (60)
4	<i>t</i> -Bu ₂ PCl	2	11
5	DPPF	8	24
6	DBPB	7	12
7	P(<i>t</i> -Bu) ₃	7	30

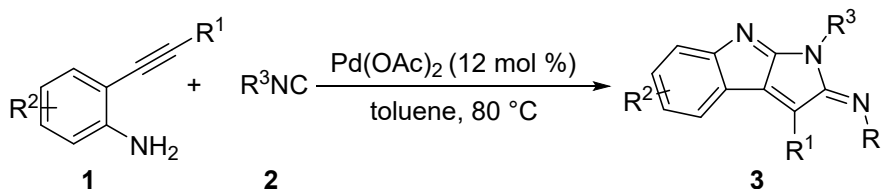
^a Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (2.4 equiv), $\text{Pd}(\text{OAc})_2$ (12 mol %), toluene (1 mL) and ligand (10 mol%) were added to a sealed tube at 80 °C under air for 12 h. ^bNMR yield was determined by ¹H NMR using CH₂Br₂ as an internal standard. BPMZ = 1,3-Bis(2,6-diisopropylphenyl)imidazolium. TPTP = tri-*p*-tolylphosphine. DBPF = 1,1-bis(di-*tert*-butylphosphino)ferrocene. DBPB = 1,4-bis(di-*tert*-butylphosphino)butane. Data in parentheses refer to isolated yield. n.d. = not detected.

Table S5. Screening of isocyanide amounts^a

entry	amount of 2a (equiv)	yield of 3a (%) ^b	yield of 4a (%) ^b
1	1.05	trace	17
2	1.25	trace	40
3	1.50	10	67
4	2.00	11	64
5	2.40	10	65

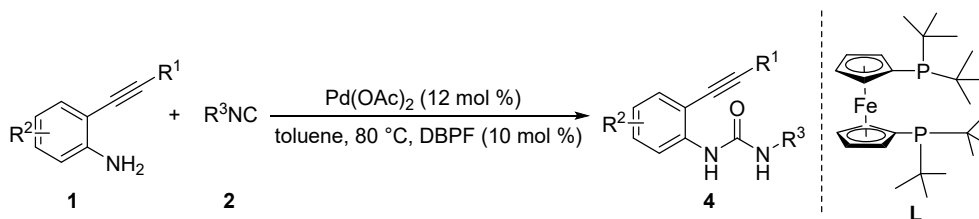
^a Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (the amount as table), Pd(OAc)₂ (12 mol %), toluene (1 mL) and DBPF (10 mol%) were added to a sealed tube at 80 °C under air for 24 h. ^bNMR yield was determined by ¹H NMR using CH₂Br₂ as an internal standard. DBPF = 1,1-bis(di-*tert*-butylphosphino)ferrocene.

C. General Procedure for the Synthesis of Pyrrole[2,3-*b*]indoles



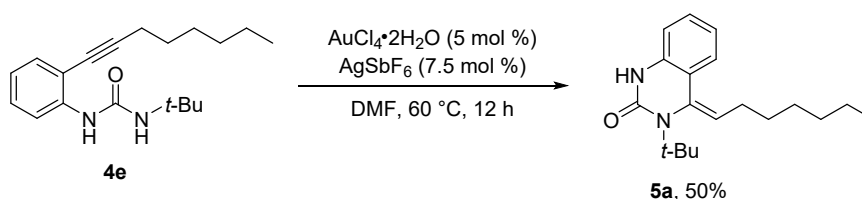
A mixture of 2-ethynylaniline **1** (0.1 mmol), isocyanide **2** (0.24 mmol), Pd(OAc)₂ (12 mol %), 1.0 mL of toluene and a stirred bar were added to a 10 mL sealed tube. The mixture was stirred at 80 °C for 12 h. Then the resulting mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄ and then evaporated under vacuum. The crude mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to deliver the desired product **3** in the corresponding yield.

D. General Procedure for the Synthesis of Ureas



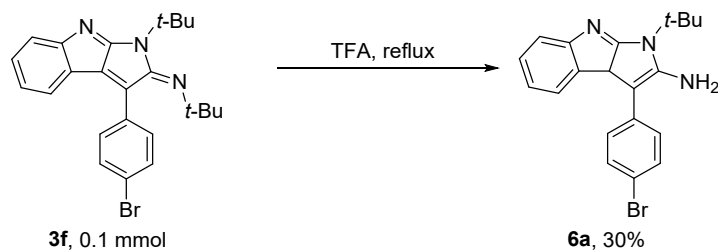
A mixture of 2-ethynylaniline **1** (0.1 mmol), isocyanide **2** (0.24 mmol), Pd(OAc)₂ (12 mol %), 1,1-bis(di-*tert*-butylphosphino)ferrocene (10 mol%), 1.0 mL of toluene and a stirred bar were added to a 10 mL sealed tube. The mixture was stirred at 80 °C for 12 h. Then the resulting mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄ and then evaporated under vacuum. The crude mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to deliver the desired product **4** in the corresponding yield.

E. Further Synthetic Applications



(a) 1-(*tert*-Butyl)-3-(2-(oct-1-yn-1-yl)phenyl)urea (**4e**, 0.1 mmol), AuCl₄·2H₂O (5 mol %), AgSbF₆ (7.5 mol %), DMF (1 mL) and a stir bar were added to a sealed tube. Then the mixture was stirred

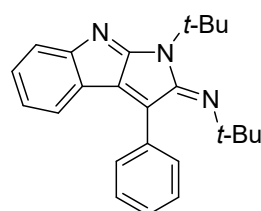
at 60 °C for 12 h. After the reaction was cooled to room temperature, the resulting mixture was extracted with ethyl acetate and the combined organic layers were evaporated under vacuum. The desired product **5a** was obtained in 50% yield after purified by column chromatography on silica gel with petroleum ether.



(b) A mixture of (*E*)-3-(4-bromophenyl)-*N*,1-di-*tert*-Butylpyrrolo[2,3-*b*]indol-2(1*H*)-imine (**3f**, 0.1 mmol), trifluoroacetic acid (1 mL), and a stir bar were added to a sealed Schlenk tube. Then the mixture was stirred at reflux for 12 h. After the reaction was cooled to room temperature, the resulting mixture was extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product **6a** was obtained in 30% yield after purification by column chromatography on silica gel with petroleum ether.

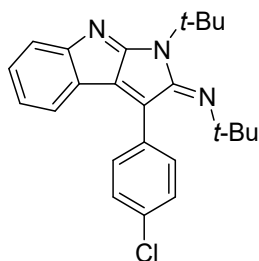
F. Characterization Data for All Products

(*E*)-*N*,1-di-*tert*-Butyl-3-phenylpyrrolo[2,3-*b*]indol-2(1*H*)-imine (**3a**)^[1]



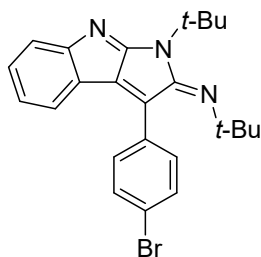
Brown solid (17.9 mg, 50%), M.p.: 140-141 °C; Isolation by column chromatography, $R_f = 0.15$, (petroleum ether/ethyl acetate: 50/1); ¹H NMR (400 MHz, CDCl₃) δ 7.44 (t, $J = 6.9$ Hz, 3H), 7.33 (d, $J = 6.4$ Hz, 2H), 7.08 (s, 2H), 6.69 – 6.53 (m, 2H), 1.75 (s, 9H), 1.11 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 147.7, 132.1, 132.0, 131.4, 129.7, 129.0, 128.6, 128.3, 128.1, 123.3, 123.2, 121.5, 118.1, 117.9, 114.3, 58.0, 56.4, 32.3, 30.1; IR: ν_{\max} (KBr) = 2965, 2924, 2853, 1657, 1615, 1557, 1493, 1432, 1389, 1361, 1298, 1212, 1079, 857, 749, 694 cm⁻¹.

(*E*)-*N*,1-di-*tert*-Butyl-3-(4-chlorophenyl)pyrrolo[2,3-*b*]indol-2(1*H*)-imine (**3b**)^[1]



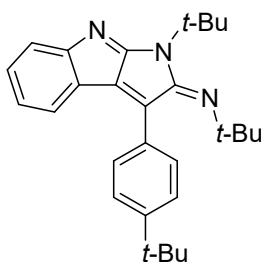
Brown solid (17.6 mg, 45%), mp: 186.8-186.9 °C; Isolation by column chromatography, $R_f = 0.15$, (petroleum ether/ethyl acetate: 50/1); ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, $J = 8.5$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.10 (d, $J = 6.2$ Hz, 2H), 6.69 – 6.57 (m, 2H), 1.74 (s, 9H), 1.12 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 150.9, 145.7, 134.7, 132.9, 132.4, 130.4, 128.7, 125.0, 123.2, 122.9, 121.7, 118.3, 58.2, 56.5, 32.4, 30.1; IR: ν_{\max} (KBr) = 3900, 3853, 3803, 3678, 3619, 2967, 2925, 1679, 1559, 1430, 1391, 1296, 1213, 1085, 1016, 846, 745, 631 cm⁻¹.

(*E*)-3-(4-Bromophenyl)-*N*,1-di-*tert*-Butylpyrrolo[2,3-*b*]indol-2(1*H*)-imine (**3c**)^[1]



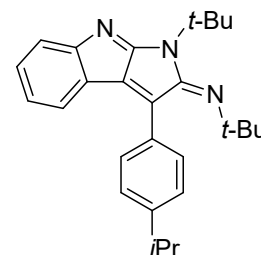
Brown solid (23.1 mg, 53%); mp: 147.2-147.3 °C; Isolation by column chromatography, $R_f = 0.15$, (petroleum ether/ethyl acetate: 50/1); ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, $J = 6.7$ Hz, 3H), 7.31 (d, $J = 7.7$ Hz, 2H), 7.21 (d, $J = 9.1$ Hz, 1H), 6.95 (d, $J = 8.3$ Hz, 1H), 6.72 (s, 1H), 1.74 (s, 9H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.3, 162.4, 150.8, 144.2, 134.3, 133.8, 129.0, 128.8, 128.5, 127.8, 125.8, 125.1, 119.3, 114.0, 58.2, 56.7, 32.3, 30.1; IR: $\nu_{\text{max}}(\text{KBr}) = 3858, 3746, 3677, 3618, 3061, 2965, 2926, 2856, 1834, 1742, 1678, 1618, 1556, 1426, 1382, 1268, 1212, 1179, 1134, 1082, 1004, 948, 822, 734, 698, 645 \text{ cm}^{-1}$.

(E)-N,1-di-tert-Butyl-3-(4-(tert-Butyl)phenyl)pyrrolo[2,3-b]indol-2(1H)-imine (3d)



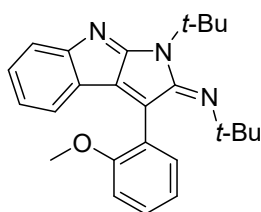
Brown solid (20.7 mg, 50%); mp: 156.2-156.5 °C; Isolation by column chromatography, $R_f = 0.20$, (petroleum ether/ethyl acetate: 50/1); ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.39 (m, 2H), 7.26 (s, 2H), 7.10 (d, $J = 4.2$ Hz, 2H), 6.79 – 6.66 (m, 1H), 6.65 – 6.58 (m, 1H), 1.75 (s, 9H), 1.37 (s, 9H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.9, 151.4, 144.8, 131.9, 131.1, 128.7, 127.0, 125.1, 123.2, 121.5, 118.0, 58.0, 56.5, 34.7, 32.2, 31.3, 30.1; IR: $\nu_{\text{max}}(\text{KBr}) = 3896, 3849, 3805, 3746, 3679, 3648, 3618, 3442, 2964, 2863, 1676, 1560, 1430, 1393, 1361, 1298, 1213, 1081, 1023, 849, 743, 632, 468 \text{ cm}^{-1}$; HRMS (ESI) m/z : calcd for $\text{C}_{28}\text{H}_{35}\text{N}_3$ $[\text{M}+\text{H}]^+$ 413.2831, found 413.2837.

(E)-N,1-di-tert-Butyl-3-(4-isopropylphenyl)pyrrolo[2,3-b]indol-2(1H)-imine (3e)



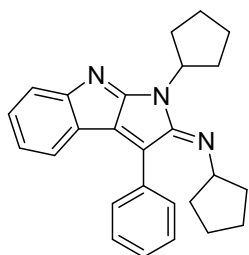
Brown solid (24.4 mg, 61%); mp: 113.4-113.6 °C; Isolation by column chromatography, $R_f = 0.17$, (petroleum ether/ethyl acetate: 50/1); ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.3$ Hz, 2H), 7.09 (d, $J = 3.8$ Hz, 2H), 6.71 (d, $J = 7.2$ Hz, 1H), 6.65 – 6.57 (m, 1H), 2.98 (p, $J = 6.9$ Hz, 1H), 1.75 (s, 9H), 1.30 (d, $J = 6.9$ Hz, 6H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 163.4, 151.5, 149.5, 144.9, 131.9, 131.6, 128.9, 127.0, 126.3, 123.3, 123.2, 121.5, 118.1, 57.9, 56.5, 33.9, 23.9; IR: $\nu_{\text{max}}(\text{KBr}) = 3897, 3859, 3745, 3678, 3618, 2963, 1742, 1682, 1647, 1558, 1428, 1393, 1295, 1213, 1082, 939, 849, 744, 626, 521, 463 \text{ cm}^{-1}$; HRMS (ESI) m/z : calcd for $\text{C}_{27}\text{H}_{33}\text{N}_3$ $[\text{M}+\text{H}]^+$: 400.2747, found 400.2739.

(E)-N,1-di-tert-Butyl-3-(2-methoxyphenyl)pyrrolo[2,3-b]indol-2(1H)-imine (3f)



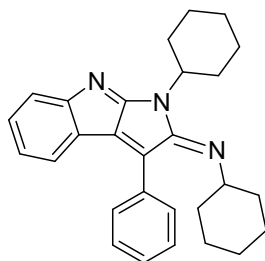
Brown liquid (16.7 mg, 43%); Isolation by column chromatography, $R_f = 0.15$, (petroleum ether/ethyl acetate: 50/1); ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.37 (m, 1H), 7.22 (d, $J = 9.1$ Hz, 1H), 7.12 – 7.00 (m, 3H), 6.94 (d, $J = 8.4$ Hz, 1H), 6.62 – 6.55 (m, 2H), 3.75 (s, 3H), 1.75 (s, 9H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.8, 151.7, 131.7, 130.5, 130.2, 123.3, 123.2, 121.4, 120.2, 117.9, 110.7, 57.9, 56.2, 55.1, 31.9, 30.1; IR: $\nu_{\text{max}}(\text{KBr}) = 3943, 3896, 3852, 3745, 3678, 3619, 3567, 3501, 3358, 3304, 3229, 3183, 3120, 3058, 2923, 2854, 2372, 1918, 1835, 1741, 1697, 1647, 1552, 1518, 1462, 1398, 1263, 1030, 961, 755, 720, 627, 519, 456 \text{ cm}^{-1}$; HRMS (ESI) m/z : calcd for $\text{C}_{25}\text{H}_{29}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 388.2383, found 388.2376.

(E)-N,1-Dicyclopentyl-3-phenylpyrrolo[2,3-b]indol-2(1H)-imine (3g)



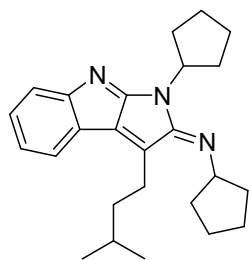
Brown solid (16.0 mg, 42%); mp: 123.9-124.3 °C; Isolation by column chromatography, $R_f = 0.15$, (petroleum ether/ethyl acetate: 50/1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (s, 5H), 7.14 (d, $J = 4.0$ Hz, 2H), 6.98 (d, $J = 7.3$ Hz, 1H), 6.67 (dt, $J = 8.2, 4.3$ Hz, 1H), 4.68 (p, $J = 8.5$ Hz, 1H), 4.20 (p, $J = 5.8$ Hz, 1H), 2.33 – 2.21 (m, 2H), 1.91 (d, $J = 10.2$ Hz, 6H), 1.79 – 1.72 (m, 2H), 1.58 (dt, $J = 18.9, 5.7$ Hz, 6H), 1.46 – 1.39 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.9, 164.1, 154.2, 142.5, 133.6, 132.1, 128.7, 128.5, 128.1, 126.6, 123.6, 123.5, 121.7, 118.4, 59.1, 53.4, 36.0, 29.2, 24.6, 24.2; IR: $\nu_{\text{max}}(\text{KBr}) = 2954, 2865, 1651, 1618, 1576, 1432, 1345, 1303, 1146, 1082, 745, 699, 641 \text{ cm}^{-1}$. HRMS (ESI) m/z : calcd for $\text{C}_{26}\text{H}_{27}\text{N}_3$ $[\text{M}+\text{H}]^+$ 382.2278, found 382.2276.

(E)-N,1-Dicyclohexyl-3-phenylpyrrolo[2,3-b]indol-2(1H)-imine (3h)^[2]



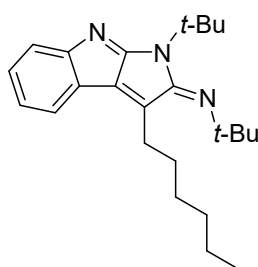
Brown solid (9.0 mg, 22%); Isolation by column chromatography, $R_f = 0.15$, (petroleum ether/ethyl acetate: 50/1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (s, 5H), 7.14 (d, $J = 6.5$ Hz, 2H), 6.92 (d, $J = 7.2$ Hz, 1H), 6.72 – 6.61 (m, 1H), 4.27 – 4.16 (m, 1H), 3.64 (tt, $J = 9.3, 3.6$ Hz, 1H), 2.23 (q, $J = 14.2, 13.1$ Hz, 2H), 1.85 (d, $J = 8.3$ Hz, 4H), 1.68 (s, 4H), 1.53 – 1.44 (m, 2H), 1.43 – 1.31 (m, 5H), 1.14 (q, $J = 12.4$ Hz, 1H), 0.89 – 0.76 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.1, 164.4, 153.9, 142.9, 133.9, 132.1, 128.8, 128.6, 127.8, 126.5, 123.7, 123.6, 121.8, 118.5, 56.7, 52.2, 35.0, 30.2, 26.0, 25.4, 25.3, 24.0; $\nu_{\text{max}}(\text{KBr}) = 3057, 2927, 2853, 1622, 1575, 1431, 1369, 1302, 1151, 1084, 882, 741, 700, 644 \text{ cm}^{-1}$.

(E)-N,1-Dicyclopentyl-3-isopentylpyrrolo[2,3-b]indol-2(1H)-imine (3i)



Brown solid (7.8 mg, 21%); mp: 102.3-102.5 °C; Isolation by column chromatography, $R_f = 0.15$, (petroleum ether/ethyl acetate: 50/1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (d, $J = 7.3$ Hz, 1H), 7.15 (d, $J = 6.8$ Hz, 2H), 6.83 (td, $J = 7.3, 2.4$ Hz, 1H), 4.59 (dt, $J = 17.3, 8.1$ Hz, 2H), 2.88 – 2.73 (m, 2H), 2.23 – 2.11 (m, 2H), 1.92 – 1.83 (m, 7H), 1.67 (dd, $J = 13.3, 6.6$ Hz, 7H), 1.61 – 1.55 (m, 3H), 0.99 (d, $J = 6.6$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 131.2, 130.2, 123.6, 121.7, 118.3, 58.6, 53.2, 38.3, 36.2, 29.1, 28.4, 26.9, 24.5, 24.2, 22.2; IR: $\nu_{\text{max}}(\text{KBr}) = 2952, 2861, 1646, 1575, 1428, 1337, 1085, 744 \text{ cm}^{-1}$. HRMS (ESI) m/z : calcd for $\text{C}_{25}\text{H}_{33}\text{N}_3$ $[\text{M}+\text{H}]^+$ 376.2747, found 376.2744.

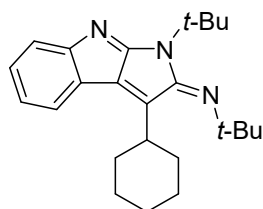
(E)-N,1-di-tert-Butyl-3-hexylpyrrolo[2,3-b]indol-2(1H)-imine (3j)



Brown solid (12.1 mg, 32%); mp: 148.2-148.5 °C; Isolation by column chromatography, $R_f = 0.15$, (petroleum ether/ethyl acetate: 50/1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.21 (d, $J = 7.2$ Hz, 1H), 7.13 (dd, $J = 13.4, 6.1$ Hz, 2H), 6.81 (t, $J = 7.2$ Hz, 1H), 2.83 – 2.68 (m, 2H), 1.69 (s, 2H), 1.67 (s, 9H), 1.48 (s, 9H), 1.47 (s, 2H), 1.36 – 1.30 (m, 4H), 0.90 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.9, 153.4, 144.2, 131.2, 128.6, 123.8, 123.6, 121.6, 118.1, 57.7, 55.0, 32.5, 31.4, 30.1, 29.6, 29.4, 28.7, 22.5, 13.9; IR: $\nu_{\text{max}}(\text{KBr}) = 3897,$

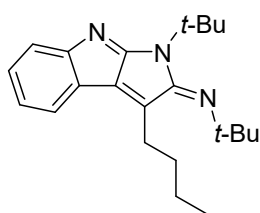
3853, 3808, 3744, 3679, 3618, 3565, 3233, 2926, 2856, 1835, 1741, 1648, 1560, 1460, 1394, 1290, 1213, 1078, 750, 630, 588, 512 cm^{-1} ; HRMS (ESI) m/z : calcd for $\text{C}_{24}\text{H}_{35}\text{N}_3$ $[\text{M}+\text{H}]^+$ 366.2904, found 366.2896.

(E)-N,1-di-tert-Butyl-3-cyclohexylpyrrolo[2,3-b]indol-2(1H)-imine (3k)



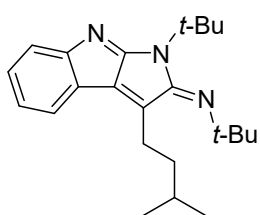
Brown solid (14.9 mg, 41%); mp: 147.3-147.5 °C; Isolation by column chromatography, R_f = 0.15, (petroleum ether/ethyl acetate: 50/1); ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, J = 7.4 Hz, 1H), 7.16 – 7.06 (m, 2H), 6.80 (t, J = 7.2 Hz, 1H), 3.26 (ddd, J = 18.5, 10.6, 7.8 Hz, 1H), 1.97 (ddt, J = 34.3, 17.4, 8.0 Hz, 6H), 1.75 (d, J = 6.0 Hz, 2H), 1.68 (s, 9H), 1.66 (s, 2H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 142.3, 134.0, 131.0, 125.6, 121.4, 118.1, 57.8, 55.1, 39.1, 32.9, 32.3, 26.0; IR: ν_{max} (KBr) = 3847, 3746, 3676, 3618, 3567, 3503, 3470, 3426, 3383, 3322, 3246, 3185, 2925, 2854, 1834, 1741, 1649, 1548, 1457, 1367, 1213, 1072, 959, 897, 747, 626, 517, 460 cm^{-1} ; HRMS (ESI) m/z : calcd for $\text{C}_{24}\text{H}_{33}\text{N}_3$ $[\text{M}+\text{H}]^+$ 364.2746, found 364.2739.

(E)-N,1-di-tert-Butyl-3-butylpyrrolo[2,3-b]indol-2(1H)-Imine (3l)



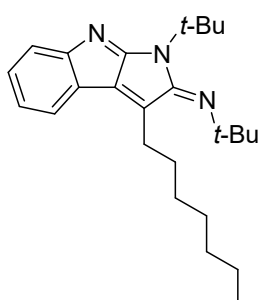
Brown liquid (8.4 mg, 25%); Isolation by column chromatography, R_f = 0.17, (petroleum ether/ethyl acetate: 50/1); ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, J = 7.2 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.81 (td, J = 7.2, 1.3 Hz, 1H), 2.85 – 2.69 (m, 2H), 1.79 (s, 2H), 1.68 (s, 9H), 1.65 – 1.56 (m, 2H), 1.48 (s, 9H), 0.98 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.4, 144.2, 131.2, 128.6, 123.7, 123.6, 121.6, 118.1, 57.7, 55.0, 32.5, 31.5, 30.1, 28.4, 23.0, 13.7; ν_{max} (KBr) = 2964, 2928, 2866, 1667, 1613, 1560, 1431, 1392, 1361, 1286, 1212, 1080, 1009, 751 cm^{-1} ; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{31}\text{N}_3$ $[\text{M}+\text{H}]^+$ 338.2591, found 338.2584.

(E)-N,1-di-tert-Butyl-3-isopentylpyrrolo[2,3-b]indol-2(1H)-imine (3m)



Brown solide (11.2 mg, 32%), M.p.: 73-74 °C; Isolation by column chromatography, R_f = 0.15, (petroleum ether/ethyl acetate: 50/1); ^1H NMR (400 MHz, CDCl_3) δ 7.21 (d, J = 7.2 Hz, 1H), 7.16 – 7.07 (m, 2H), 6.81 (t, J = 7.2 Hz, 1H), 2.92 – 2.65 (m, 2H), 1.72 (d, J = 6.7 Hz, 2H), 1.67 (s, 9H), 1.53 (dt, J = 12.1, 7.1 Hz, 1H), 1.49 (s, 9H), 1.00 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.4, 144.2, 131.2, 128.8, 123.7, 123.6, 121.6, 118.1, 57.7, 55.0, 38.0, 32.6, 30.1, 28.8, 26.7, 22.3; ν_{max} (KBr) = 2961, 2862, 1667, 1560, 1432, 1392, 1361, 1287, 1212, 1080, 1011, 749 cm^{-1} ; HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{33}\text{N}_3$ $[\text{M}+\text{H}]^+$ 352.2747, found 352.2740.

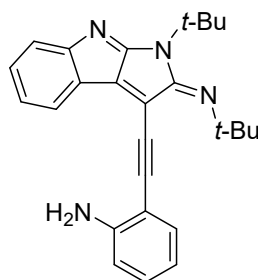
(E)-N,1-di-tert-Butyl-3-heptylpyrrolo[2,3-b]indol-2(1H)-imine (3n)



Brown liquid (10.6 mg, 28%); Isolation by column chromatography, R_f = 0.15, (petroleum ether/ethyl acetate: 50/1); ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, J = 7.3 Hz, 1H), 7.13 (q, J = 8.1 Hz, 2H), 6.82 (td, J = 7.2, 1.5 Hz, 1H), 2.92 – 2.63 (m, 2H), 1.77 (s, 2H), 1.68 (s, 9H), 1.62 (ddd, J = 12.5, 8.2, 4.9 Hz, 2H), 1.48 (s, 9H), 1.47 – 1.39 (m, 2H), 1.34 (dd, J = 9.7, 6.2 Hz, 2H),

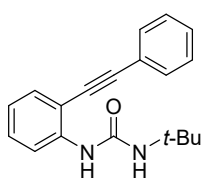
1.30 (s, 2H), 0.89 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.3, 144.2, 131.3, 128.7, 123.6, 121.7, 118.1, 57.8, 55.1, 32.5, 31.7, 30.1, 29.9, 29.4, 28.9, 28.7, 22.5, 14.0; $\nu_{\text{max}}(\text{KBr}) = 2962, 2927, 2855, 1670, 1614, 1561, 1431, 1393, 1362, 1288, 1213, 1179, 1081, 1005, 864, 741, 629\text{ cm}^{-1}$; HRMS (ESI) m/z : calcd for $\text{C}_{25}\text{H}_{37}\text{N}_3$ $[\text{M}+\text{H}]^+$ 380.3060, found 380.3053.

(E)-N,1-di-tert-Butyl-3-(phenylethynyl)pyrrolo[2,3-b]indol-2(1H)-imine (3o)



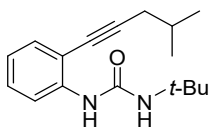
Brown solid (17.2 mg, 45%); mp: 168.2-168.5 °C; Isolation by column chromatography, $R_f = 0.20$, (petroleum ether/ethyl acetate: 30/1); ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 7.2$ Hz, 1H), 7.37 (d, $J = 7.0$ Hz, 1H), 7.19 (dtd, $J = 18.6, 7.9, 1.2$ Hz, 2H), 7.09 (d, $J = 7.7$ Hz, 1H), 6.87 – 6.70 (m, 3H), 4.36 (s, 1H), 1.72 (s, 9H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.5, 150.9, 148.7, 148.2, 132.9, 132.2, 131.2, 123.6, 123.3, 122.1, 118.5, 118.2, 114.7, 106.9, 106.4, 102.0, 90.5, 58.5, 55.8, 31.9, 29.9; IR: $\nu_{\text{max}}(\text{KBr}) = 3474, 3427, 3348, 3205, 3060, 2921, 2850, 2178, 1648, 1558, 1459, 1386, 1314, 1260, 1214, 1088, 1025, 864, 752, 634\text{ cm}^{-1}$.

1-(tert-Butyl)-3-(2-(phenylethynyl)phenyl)urea (4a)



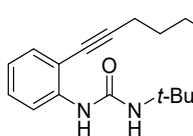
Yellow liquid (17.5 mg, 60%); Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 8.3$ Hz, 1H), 7.53 (dd, $J = 6.5, 2.9$ Hz, 2H), 7.45 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.39 – 7.33 (m, 3H), 7.31 – 7.26 (m, 1H), 7.02 – 6.89 (m, 2H), 4.84 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.9, 140.3, 132.0, 131.5, 129.6, 128.6, 128.4, 122.6, 121.8, 118.9, 111.5, 95.4, 85.0, 50.8, 29.3; IR: $\nu_{\text{max}}(\text{KBr}) = 3846, 3807, 3678, 3617, 3506, 3060, 2968, 2925, 2855, 2127, 1698, 1506, 1365, 1260, 1187, 1087, 1028, 801, 753, 693, 594, 514, 456\text{ cm}^{-1}$; HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$ $[\text{M}-\text{H}]^-$ 291.1503, found 291.1504.

1-(tert-Butyl)-3-(2-(4-methylpent-1-yn-1-yl)phenyl)urea (4b)



White solid (16.9 mg, 62%); mp: 174.2-174.5 °C; Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, CDCl_3) δ 8.05 (t, $J = 6.5$ Hz, 1H), 7.35 (d, $J = 6.9$ Hz, 1H), 7.26 (dd, $J = 12.8, 5.6$ Hz, 1H), 6.92 (dd, $J = 16.0, 8.2$ Hz, 2H), 4.55 (s, 1H), 2.40 (d, $J = 6.5$ Hz, 2H), 1.97 (dt, $J = 13.3, 6.6$ Hz, 1H), 1.42 (s, 9H), 1.10 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 153.9, 140.1, 131.7, 128.7, 121.6, 118.4, 112.3, 95.9, 50.8, 29.3, 28.7, 28.1, 22.0; IR: $\nu_{\text{max}}(\text{KBr}) = 3901, 3851, 3802, 3679, 3617, 3328, 3085, 2962, 2920, 2862, 1742, 1694, 1655, 1559, 1517, 1450, 1394, 1363, 1297, 1266, 1209, 1116, 948, 756, 653\text{ cm}^{-1}$; HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}$ $[\text{M}-\text{H}]^-$ 271.1816, found 271.1815.

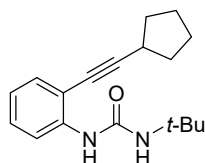
1-(tert-Butyl)-3-(2-(6-chlorohex-1-yn-1-yl)phenyl)urea (4c)



White solid (12.9 mg, 42%); mp: 201.4-201.6 °C; Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.3$ Hz, 1H), 7.32 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.25 – 7.20 (m, 1H), 6.91 (td, $J = 7.6, 0.9$ Hz, 1H), 6.80 (s, 1H), 4.64 (s, 1H),

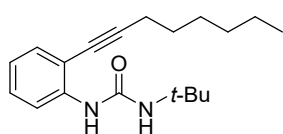
3.62 (t, $J = 6.4$ Hz, 2H), 2.54 (t, $J = 6.9$ Hz, 2H), 2.04 – 1.92 (m, 2H), 1.80 (p, $J = 7.0$ Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.9, 140.1, 131.9, 128.9, 121.7, 118.6, 112.0, 95.9, 50.9, 44.6, 31.6, 29.3, 25.8, 19.0; IR: $\nu_{\text{max}}(\text{KBr}) = 3899, 3849, 3802, 3679, 3616, 3501, 3332, 2961, 2859, 1654, 1554, 1518, 1447, 1396, 1360, 1298, 1263, 1204, 1103, 1024, 946, 803, 753, 646 \text{ cm}^{-1}$; HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{23}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 307.1572, found 307.1565.

1-(*tert*-Butyl)-3-(2-(cyclopentylethynyl)phenyl)urea (4d)



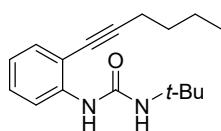
White solid (12.8 mg, 45%); mp: 184.5-184.6 °C; Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.3$ Hz, 1H), 7.31 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.25 – 7.19 (m, 1H), 6.90 (td, $J = 7.6, 0.9$ Hz, 1H), 6.81 (s, 1H), 4.51 (s, 1H), 2.90 (q, $J = 7.4$ Hz, 1H), 2.22 – 1.93 (m, 2H), 1.85 – 1.67 (m, 4H), 1.63 (s, 2H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.9, 140.0, 131.7, 128.7, 121.7, 118.5, 112.4, 101.4, 75.9, 50.8, 34.0, 30.9, 29.3, 24.9; IR: $\nu_{\text{max}}(\text{KBr}) = 3948, 3857, 3811, 3747, 3677, 3621, 3494, 3449, 3312, 3220, 3159, 3083, 2962, 2924, 2859, 2668, 2216, 1835, 1741, 1654, 1557, 1517, 1451, 1398, 1360, 1299, 1266, 1207, 1114, 1034, 946, 756, 645, 520, 418 \text{ cm}^{-1}$. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 285.1961, found 285.1954.

1-(*tert*-Butyl)-3-(2-(oct-1-yn-1-yl)phenyl)urea (4e)



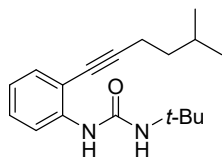
White solid (19.8 mg, 66%); mp: 142.5-142.8 °C; Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.22 (t, $J = 7.4$ Hz, 1H), 6.89 (dd, $J = 13.6, 5.7$ Hz, 2H), 4.59 (s, 1H), 2.47 (t, $J = 7.1$ Hz, 2H), 1.63 (td, $J = 15.9, 14.9, 8.6$ Hz, 3H), 1.52 – 1.43 (m, 1H), 1.40 (s, 9H), 1.32 (dt, $J = 7.2, 3.7$ Hz, 4H), 0.91 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.9, 140.1, 131.8, 128.7, 121.6, 118.4, 112.2, 97.1, 76.5, 50.8, 31.3, 29.3, 28.6, 28.6, 22.5, 19.6, 14.0; IR: $\nu_{\text{max}}(\text{KBr}) = 3745, 3330, 3085, 2959, 2928, 2860, 2225, 2133, 1653, 1560, 1518, 1448, 1392, 1362, 1297, 1265, 1207, 1111, 1031, 946, 804, 753, 658 \text{ cm}^{-1}$. HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 301.2274, found 301.2269.

1-(*tert*-Butyl)-3-(2-(hex-1-yn-1-yl)phenyl)urea (4f)



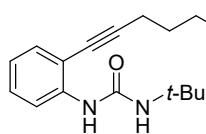
White solid (14.1 mg, 52%); mp: 146.3-146.8 °C; Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.3$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.23 (t, $J = 7.9$ Hz, 1H), 6.95 – 6.82 (m, 2H), 4.59 (s, 1H), 2.48 (t, $J = 7.0$ Hz, 2H), 1.62 (m, $J = 7.0$ Hz, 2H), 1.55 – 1.45 (m, 2H), 1.40 (s, 9H), 0.96 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.9, 140.1, 131.8, 128.7, 121.6, 118.4, 112.2, 97.0, 76.5, 50.8, 30.7, 29.3, 22.0, 19.3, 13.6; IR: $\nu_{\text{max}}(\text{KBr}) = 3327, 3089, 2961, 2929, 2865, 1649, 1563, 1513, 1445, 1389, 1362, 1297, 1265, 1209, 1114, 946, 754, 664 \text{ cm}^{-1}$; HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 273.1961, found 273.1955.

1-(*tert*-Butyl)-3-(2-(5-methylhex-1-yn-1-yl)phenyl)urea (4g)



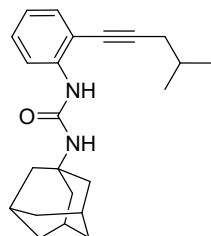
White solid (17.2 mg, 60%); mp: 133.1-133.4 °C; Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.3$ Hz, 1H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.23 (t, $J = 7.9$ Hz, 1H), 6.88 (dd, $J = 18.1, 10.6$ Hz, 2H), 4.54 (s, 1H), 2.49 (t, $J = 7.2$ Hz, 2H), 1.77 (dt, $J = 13.4, 6.7$ Hz, 1H), 1.53 (q, $J = 7.1$ Hz, 2H), 1.40 (s, 9H), 0.96 (d, $J = 6.6$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 153.9, 140.1, 131.7, 128.7, 121.6, 118.4, 112.2, 97.1, 76.4, 50.8, 37.5, 29.3, 27.3, 22.1, 17.6; IR: ν_{max} (KBr) = 3425, 3330, 3182, 3132, 3097, 2959, 2924, 2852, 2349, 1650, 1563, 1514, 1447, 1391, 1362, 1265, 1211, 1072, 950, 798, 753, 666 cm^{-1} ; HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 287.2118, found 287.2112.

1-(tert-Butyl)-3-(2-(non-1-yn-1-yl)phenyl)urea (4h)



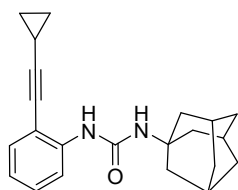
White solid (18.2 mg, 58%); mp: 100.7-100.9 °C; Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.3$ Hz, 1H), 7.32 (d, $J = 7.5$ Hz, 1H), 7.23 (t, $J = 7.8$ Hz, 1H), 6.89 (dd, $J = 14.0, 5.8$ Hz, 2H), 4.59 (s, 1H), 2.47 (t, $J = 7.0$ Hz, 2H), 1.64 (dd, $J = 17.1, 9.7$ Hz, 4H), 1.44 (d, $J = 7.7$ Hz, 2H), 1.40 (s, 9H), 1.30 (s, 4H), 0.89 (t, $J = 6.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 153.9, 140.1, 131.8, 128.7, 121.6, 118.4, 112.2, 97.1, 76.5, 50.8, 31.7, 29.3, 28.9, 28.8, 28.7, 22.6, 19.6, 14.0; IR: ν_{max} (KBr) = 3426, 3338, 2960, 2927, 1655, 1556, 1516, 1446, 1391, 1362, 1299, 1263, 1205, 1113, 940, 797, 752, 667 cm^{-1} ; HRMS (ESI) m/z : calcd for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 315.2431, found 315.2425.

1-((3s,5s,7s)-Adamantan-1-yl)-3-(2-(4-methylpent-1-yn-1-yl)phenyl)urea (4i)



White solid (21.7 mg, 62%), M.p. 88-90 °C; Isolation by column chromatography, $R_f = 0.20$, (petroleum ether/ethyl acetate: 10/1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.3$ Hz, 1H), 7.29 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.24 – 7.17 (m, 1H), 6.93 – 6.81 (m, 2H), 4.51 (s, 1H), 2.10 (s, 3H), 2.04 (s, 6H), 1.69 (s, 6H), 1.65 (s, 2H), 1.50 (ddd, $J = 13.3, 8.3, 5.1$ Hz, 1H), 0.98 – 0.78 (m, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 153.6, 140.4, 132.0, 128.7, 121.6, 118.5, 112.1, 100.0, 71.5, 51.4, 42.2, 36.3, 29.5, 9.0, 0.4. IR: ν_{max} (KBr) = 3899, 3847, 3617, 3467, 3342, 3232, 3176, 3088, 2962, 2922, 2853, 1917, 1833, 1795, 1740, 1650, 1558, 1515, 1447, 1393, 1362, 1290, 1212, 1100, 1037, 947, 755, 691, 639 cm^{-1} ; HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 351.2431, found 351.2424.

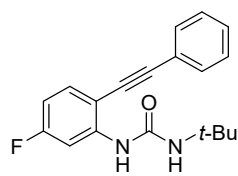
1-((3s,5s,7s)-Adamantan-1-yl)-3-(2-(cyclopropylethynyl)phenyl)urea (4j)



White solid (25.1 mg, 75%); mp: 79.1-79.5 °C; Isolation by column chromatography, $R_f = 0.22$, (petroleum ether/ethyl acetate: 10/1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.3$ Hz, 1H), 7.29 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.21 (t, $J = 7.9$ Hz, 1H), 6.87 (dd, $J = 17.0, 9.4$ Hz, 2H), 4.49 (s, 1H), 2.10 (s, 3H), 2.04 (s, 6H), 1.69 (s, 6H), 1.50 (ddd, $J = 13.2, 8.3, 5.1$ Hz, 1H), 0.92 (dt, $J = 7.9, 3.0$ Hz, 2H), 0.86 – 0.80 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 153.65, 140.47, 132.05, 128.77, 121.66, 118.57, 112.13, 100.10, 71.54, 51.44, 42.28, 36.34, 29.53, 9.00, 0.40; IR: ν_{max} (KBr) = 3745, 3677, 3618,

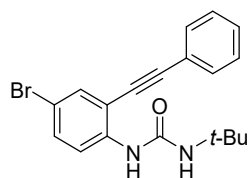
3324, 2906, 2848, 2215, 1836, 1743, 1696, 1641, 1548, 1512, 1454, 1353, 1293, 1238, 1036, 948, 812, 750, 628, 521 cm^{-1} ; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 335.2118, found 335.2108.

1-(*tert*-Butyl)-3-(5-fluoro-2-(phenylethynyl)phenyl)urea (4k)



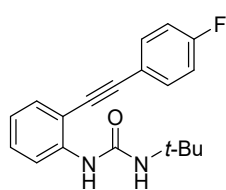
White solid (16.7 mg, 54%); mp: 138.8-138.9 °C; Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.57 (m, 3H), 7.39 – 7.30 (m, 4H), 7.17 (dd, $J = 8.8, 2.9$ Hz, 1H), 7.06 (dd, $J = 8.8, 5.2$ Hz, 1H), 6.95 (td, $J = 8.8, 8.4, 3.0$ Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.9 (d, $J = 242$ Hz), 137.7 (d, $J = 2.9$ Hz), 133.6, 131.7, 128.7, 128.3, 125.0 (d, $J = 8.7$ Hz), 122.9, 119.7 (d, $J = 9.8$ Hz), 119.2 (d, $J = 23.7$ Hz), 116.5, 116.4 (d, $J = 22.7$ Hz), 95.9, 85.4, 57.4, 31.4. IR: ν_{max} (KBr) = 3896, 3849, 3809, 3746, 3677, 3649, 3617, 3423, 3381, 3309, 3218, 3050, 2965, 2923, 2853, 2588, 2551, 2252, 2123, 1917, 1869, 1834, 1740, 1697, 1652, 1511, 1461, 1402, 1365, 1252, 1186, 1133, 1081, 1026, 954, 867, 813, 754, 691, 627, 591, 516 cm^{-1} . HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{19}\text{FN}_2\text{O}$ $[\text{M}-\text{H}]^-$ 309.1409, found 309.1410.

1-(4-Bromo-2-(phenylethynyl)phenyl)-3-(*tert*-butyl)urea (4l)



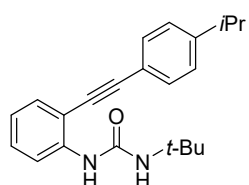
Yellow liquid (20.7 mg, 56%); Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.58 (m, 4H), 7.38 – 7.30 (m, 5H), 6.97 (d, $J = 8.6$ Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 135.4, 132.9, 132.1, 131.7, 128.7, 128.3, 125.3, 122.9, 120.4, 116.5, 96.2, 85.1, 57.6, 31.4. IR: ν_{max} (KBr) = 3953, 3897, 3847, 3708, 3447, 3388, 3292, 3230, 3058, 2969, 2926, 2854, 2360, 2208, 2123, 1870, 1833, 1797, 1771, 1740, 1698, 1647, 1553, 1499, 1366, 1259, 1235, 1185, 1098, 1024, 881, 848, 810, 752, 690, 648, 602 cm^{-1} . HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{19}\text{BrN}_2\text{O}$ $[\text{M}-\text{H}]^-$ 369.0608, found 369.0609.

1-(*tert*-Butyl)-3-(2-((4-fluorophenyl)ethynyl)phenyl)urea (4m)



White solid (19.8 mg, 64%); mp: 164.5-164.8 °C; Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.4$ Hz, 1H), 7.53 (dd, $J = 8.3, 5.5$ Hz, 2H), 7.46 (d, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 7.9$ Hz, 1H), 7.07 (t, $J = 8.5$ Hz, 2H), 6.98 (dd, $J = 16.2, 8.6$ Hz, 2H), 4.89 (s, 1H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.7 (d, $J = 249$ Hz), 154.0, 140.3, 133.5 (d, $J = 8.4$ Hz), 132.2, 129.7, 122.0, 119.1, 118.8 (d, $J = 3.4$ Hz), 115.7 (d, $J = 21.9$ Hz), 111.5, 94.4, 84.8, 50.9, 29.3. IR: ν_{max} (KBr) = 3955, 3861, 3677, 3619, 3312, 3087, 2970, 2921, 2854, 1835, 1700, 1645, 1560, 1510, 1450, 1362, 1289, 1218, 1155, 1101, 948, 834, 753, 647, 515, 549, 416 cm^{-1} . HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{19}\text{FN}_2\text{O}$ $[\text{M}-\text{H}]^-$ 309.1409, found 309.1408.

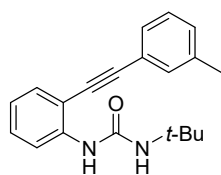
1-(*tert*-Butyl)-3-(2-((4-isopropylphenyl)ethynyl)phenyl)urea (4n)



White solid (22.7 mg, 68%); mp: 178.3-178.5 °C; Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.4$ Hz, 1H), 7.46 (dd, $J = 11.8, 8.5$ Hz, 3H),

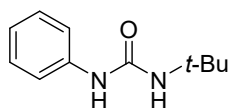
7.30 (d, $J = 8.5$ Hz, 1H), 7.27 – 7.21 (m, 2H), 6.96 (t, $J = 7.5$ Hz, 1H), 6.88 (s, 1H), 4.63 (s, 1H), 2.93 (p, $J = 7.0$ Hz, 1H), 1.40 (s, 9H), 1.27 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.8, 153.9, 150.0, 140.3, 132.0, 131.6, 129.5, 126.7, 121.8, 119.9, 118.8, 111.7, 95.8, 84.3, 51.0, 34.1, 29.4, 23.8. IR: ν_{max} (KBr) = 3900, 3851, 3802, 3679, 3617, 3328, 3085, 2962, 2920, 2861, 1741, 1694, 1654, 1559, 1517, 1450, 1393, 1363, 1297, 1266, 1208, 1115, 948, 756, 653 cm^{-1} . HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 335.2118, found 335.2109.

1-(*tert*-Butyl)-3-(2-(*m*-tolylethynyl)phenyl)urea (4o)



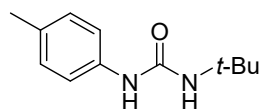
White solid (17.8 mg, 58%); mp: 156.2-156.3 $^{\circ}\text{C}$; Isolation by column chromatography, $R_f = 0.25$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.4$ Hz, 1H), 7.47 – 7.41 (m, 1H), 7.38 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 7.27 – 7.24 (m, 1H), 7.19 (d, $J = 7.6$ Hz, 1H), 6.96 (t, $J = 7.5$ Hz, 1H), 6.89 (s, 1H), 4.68 (s, 1H), 2.37 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.9, 140.3, 138.3, 132.2, 132.1, 129.6, 129.6, 128.7, 128.4, 122.5, 121.9, 118.9, 111.6, 95.8, 84.7, 50.9, 29.3, 21.2. IR: ν_{max} (KBr) = 3899, 3847, 3807, 3744, 3675, 3617, 3467, 3342, 3232, 3176, 3088, 2962, 2922, 2853, 1917, 1833, 1795, 1740, 1650, 1558, 1515, 1447, 1393, 1362, 1290, 1212, 1100, 1037, 947, 755, 691, 639, 455 cm^{-1} . HRMS (ESI) m/z : calcd for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 307.1805, found 307.1798.

1-(*tert*-Butyl)-3-phenylurea (4p)^[3]



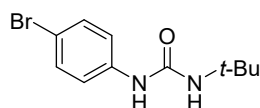
White solid (12.5 mg, 65%); mp: 168.1-169.2 $^{\circ}\text{C}$; Isolation by column chromatography, $R_f = 0.20$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, MeOD) δ 7.31 (dd, $J = 8.4, 1.6$ Hz, 2H), 7.24 (t, $J = 7.6$ Hz, 2H), 6.95 (t, $J = 7.6$ Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (101 MHz, MeOD) δ 156.0, 139.7, 128.4, 121.7, 118.5, 49.7, 28.2.

1-(*tert*-butyl)-3-(*p*-tolyl)urea (4q)^[4]



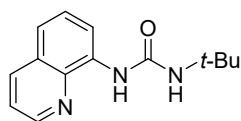
White solid (13.8 mg, 67%); mp: 189-190 $^{\circ}\text{C}$; Isolation by column chromatography, $R_f = 0.20$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, MeOD) δ 7.18 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 3.27 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (101 MHz, MeOD) δ 156.2, 137.0, 131.3, 128.8, 118.8, 49.6, 28.3, 19.4.

1-(4-Bromophenyl)-3-(*tert*-butyl)urea (4r)^[5]



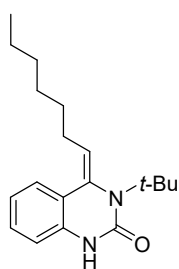
White solid (18.5 mg, 68%); mp: 198.9-200.2 $^{\circ}\text{C}$; Isolation by column chromatography, $R_f = 0.20$, (petroleum ether/ethyl acetate: 10/1); ^1H NMR (400 MHz, MeOD) δ 7.36 (d, $J = 8.8$ Hz, 2H), 7.26 (d, $J = 8.8$ Hz, 2H), 1.37 (s, 9H); ^{13}C NMR (101 MHz, MeOD) δ 155.6, 139.2, 131.3, 120.1, 120.0, 113.6, 49.8, 28.2.

1-(4-Bromophenyl)-3-(*tert*-butyl)urea (4s)^[6]



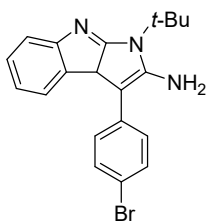
White solid (9.7 mg, 40%); mp: 171-172 °C; Isolation by column chromatography, R_f = 0.15, (petroleum ether/ethyl acetate: 10/1); $^1\text{H NMR}$ (400 MHz, MeOD) δ 8.96 (s, 1H), 8.72 (dd, J = 4.0, 1.6 Hz, 1H), 8.55 (dd, J = 7.6, 1.2 Hz, 1H), 8.11 (dd, J = 8.0, 2.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.43-7.31 (m, 2H), 5.06 (s, 1H), 1.42 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.4, 147.5, 138.2, 136.5, 136.1, 128.1, 127.6, 121.3, 119.2, 114.8, 50.8, 29.4.

(*E*)-3-(*tert*-Butyl)-4-heptylidene-3,4-dihydroquinazolin-2(1*H*)-one (5a)



White solid (12.2 mg, 50%); mp: 74.2-74.3 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 (dd, J = 20.6, 7.8 Hz, 2H), 7.16 (dt, J = 21.2, 7.2 Hz, 2H), 6.31 (s, 1H), 5.58 (s, 1H), 2.94 (t, J = 7.6 Hz, 2H), 1.75 – 1.60 (m, 4H), 1.52 (s, 9H), 1.39 (dd, J = 12.7, 6.5 Hz, 2H), 1.36 – 1.29 (m, 2H), 0.89 (t, J = 6.1 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 190.1, 189.2, 150.6, 141.8, 135.4, 128.9, 122.1, 121.3, 120.2, 111.1, 103.7, 52.0, 31.6, 29.0, 28.9, 28.8, 28.1, 22.5, 14.0; IR: ν_{max} (KBr) = 3298, 3055, 2957, 2924, 2854, 1668, 1541, 1453, 1363, 1319, 1206, 1015, 787, 741, 655 cm^{-1} ; HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 301.2274, found 301.2267.

3-(4-Bromophenyl)-1-(*tert*-Butyl)-1,3a-dihydropyrrolo[2,3-*b*]indol-2-amine (6a)

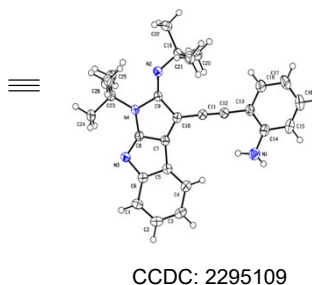
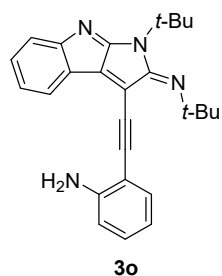


Brown solid (11.4 mg, 30%); mp: 150.1-150.2 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51 (d, J = 6.9 Hz, 2H), 7.36 (dt, J = 14.3, 6.9 Hz, 2H), 7.30 (dd, J = 11.7, 2.0 Hz, 3H), 6.55 (d, J = 8.6 Hz, 1H), 3.56 (s, 2H), 1.68 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.3, 171.2, 143.4, 136.4, 133.5, 133.4, 130.4, 129.3, 128.6, 118.1, 116.0, 110.0, 58.1, 28.9; IR: ν_{max} (KBr) = 3474, 3357, 3183, 3138, 3092, 3060, 3023, 2965, 2924, 2923, 2920, 2851, 2800, 2643, 1868, 1835, 1759, 1741, 1698, 1649, 1593, 1482, 1461, 1460, 1423, 1402, 1396, 1395, 1348, 1261, 1086, 1085, 971, 880, 740, 699, 669, 612 cm^{-1} ; HRMS (ESI) m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{BrN}_3$ $[\text{M}+\text{H}]^+$ 382.0914, found 382.0907.

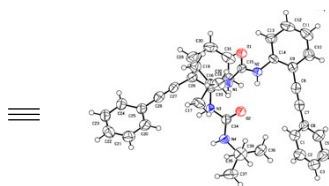
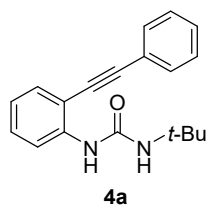
G. References

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H. X-ray Crystallographic Analysis



Empirical formula	C ₂₆ H ₂₈ N ₄
Formula weight	396.52
Temperature	170.0 K
Wavelength	0.71073
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions	a = 15.2301(4) Å alpha = 90 deg. b = 10.2357(3) Å beta = 95.8280(10) deg. c = 28.4109(8) Å gamma = 90 deg.
Volume	4406.1(2) Å ³
Z, Calculated density	8, 1.196 g/cm ³
Absorption coefficient	0.072 mm ⁻¹
F(000)	1696.0
Crystal size	0.12 × 0.07 × 0.05 mm ³
Theta range for data collection	4.802 to 52.804 deg.
Index ranges	-18 ≤ h ≤ 18, -12 ≤ k ≤ 12, -35 ≤ l ≤ 35
Reflections collected / unique	24779 / 4510 [R _{int} = 0.0420, R _{sigma} = 0.0298]
Completeness to theta = 26.402	0.995
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4510/0/285
Goodness-of-fit on F ²	0.959
Final R indices [I > 2sigma(I)]	R ₁ = 0.0410, wR ₂ = 0.0941
R indices (all data)	R ₁ = 0.0576, wR ₂ = 0.1071

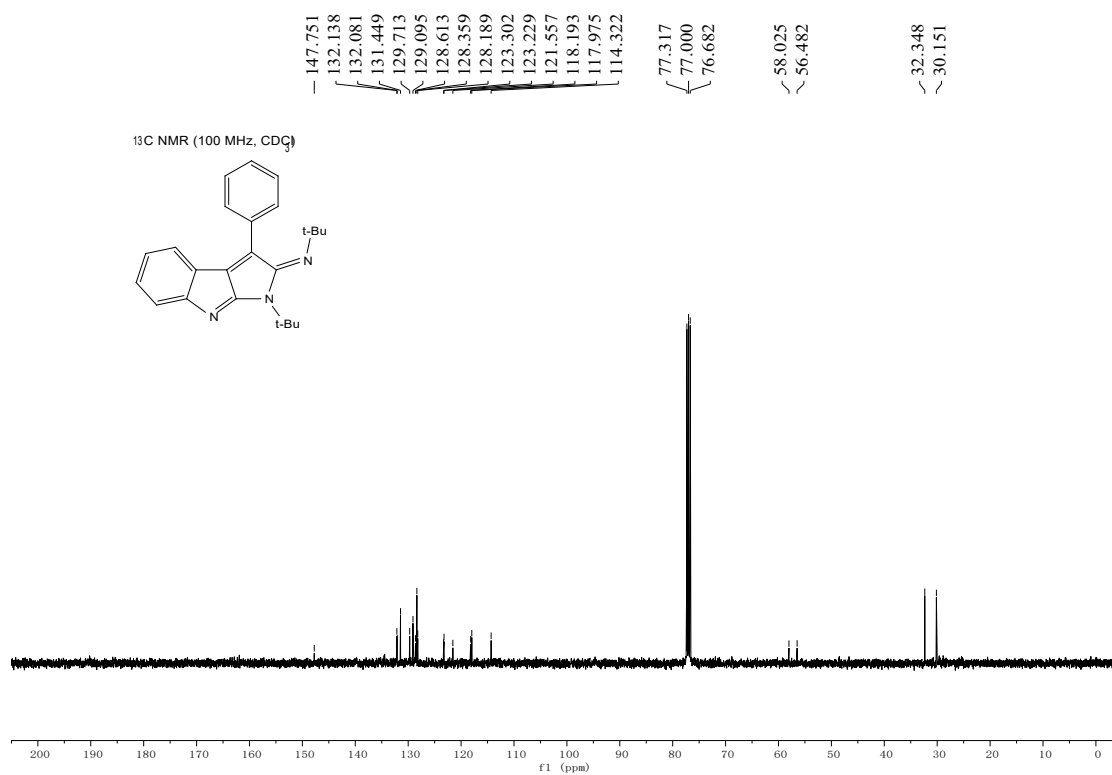
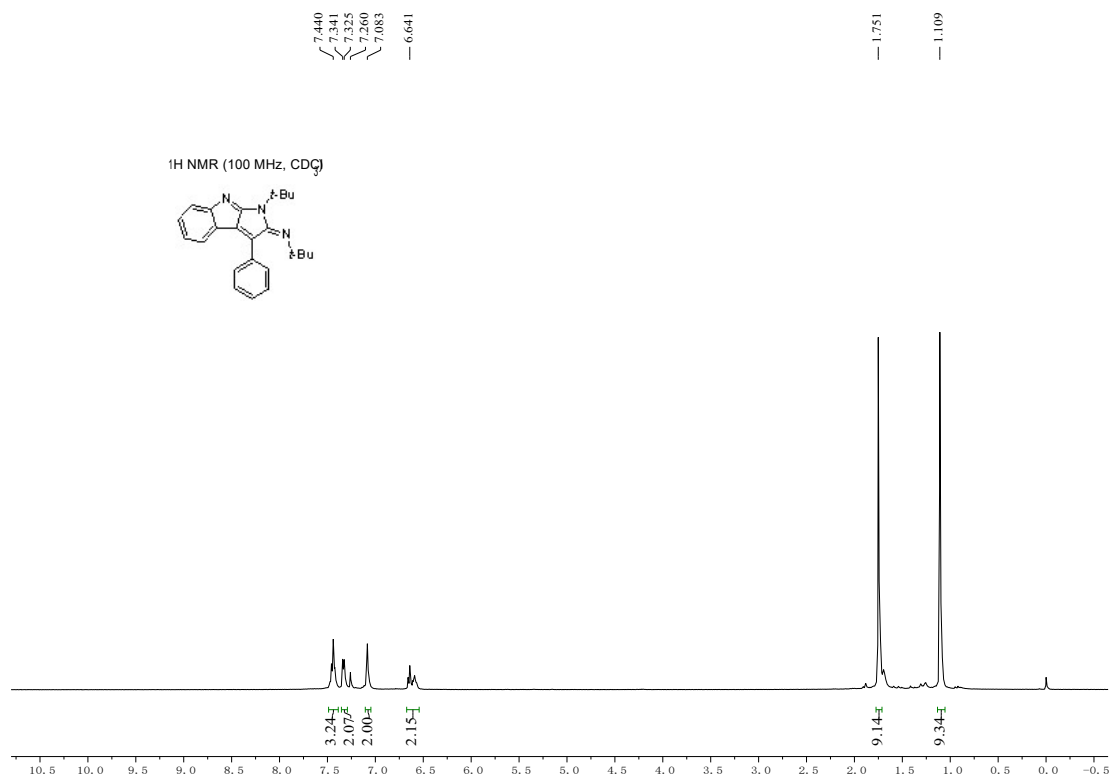


CCDC: 2295108

Empirical formula	C ₁₉ H ₂₀ N ₂ O
Formula weight	292.37
Temperature	170.0 K
Wavelength	0.71073
Crystal system, space group	monoclinic, P2 ₁ /c
Unit cell dimensions	a = 8.637(3) Å alpha = 90 deg. b = 13.293(4) Å beta = 96.679(9) deg. c = 29.631(8) Å gamma = 90 deg.
Volume	3378.8(17) Å ³
Z, Calculated density	8, 1.149 g/cm ³
Absorption coefficient	0.072 mm ⁻¹
F(000)	1248.0
Crystal size	0.11 × 0.04 × 0.02 mm ³
Theta range for data collection	4.13 to 52.862 deg.
Index ranges	-8 ≤ h ≤ 10, -13 ≤ k ≤ 16, -37 ≤ l ≤ 37
Reflections collected / unique	23319 / 6847 [R _{int} = 0.1175, R _{sigma} = 0.1246]
Completeness to theta = 0.985	26.431
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6847/0/403
Goodness-of-fit on F ²	1.018
Final R indices [I > 2sigma(I)]	R ₁ = 0.0726, wR ₂ = 0.1353
R indices (all data)	R ₁ = 0.1894, wR ₂ = 0.1840

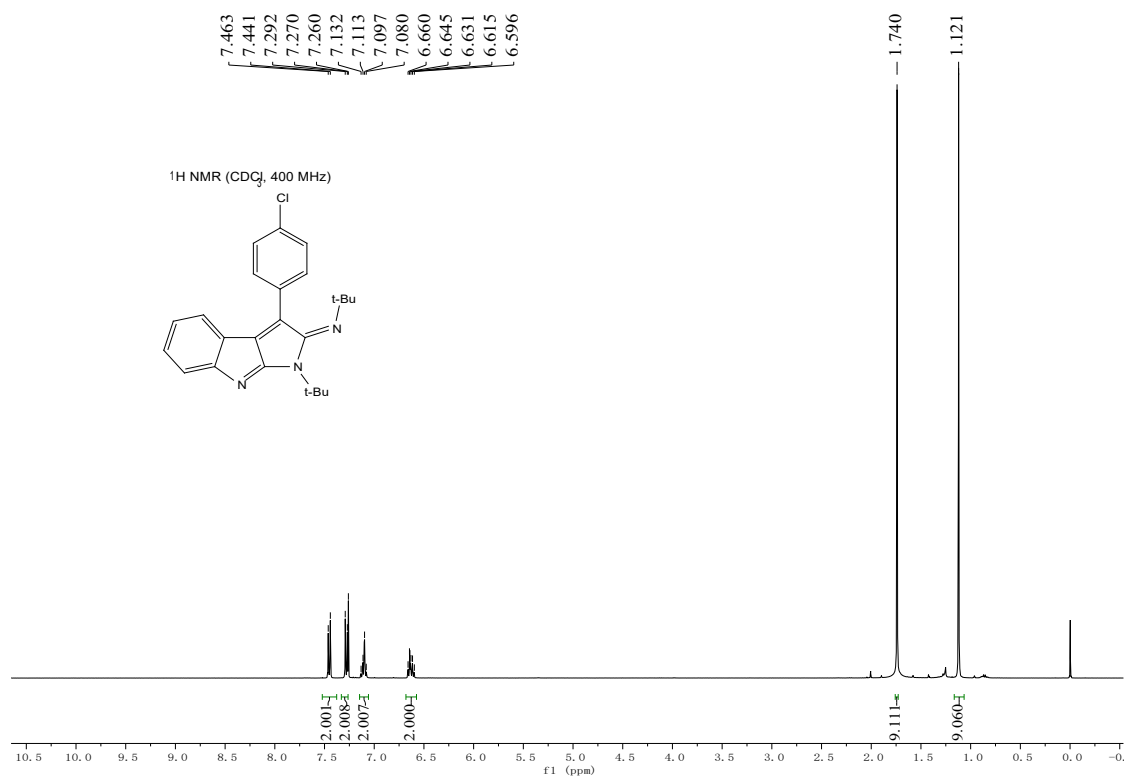
I. Copies of ^1H , ^{13}C , and ^{19}F NMR Spectra

(*E*)-*N*,1-di-*tert*-Butyl-3-phenylpyrrolo[2,3-*b*]indol-2(*1H*)-imine (3a)

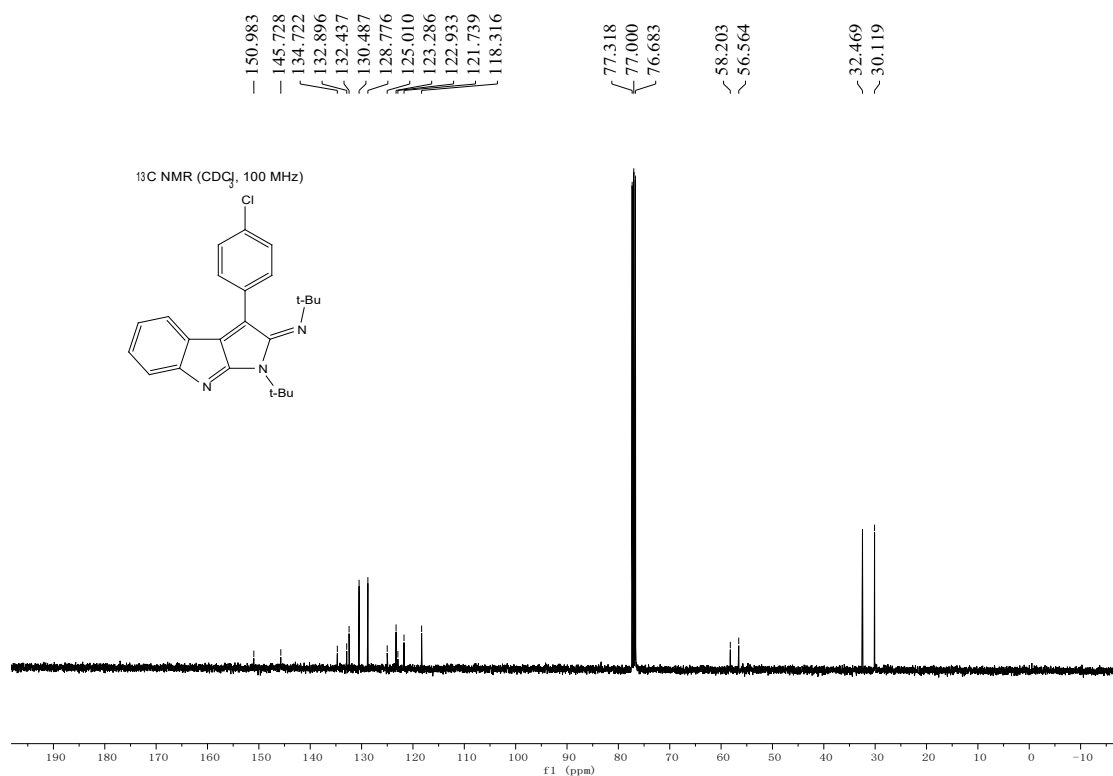


(E)-N,1-di-tert-Butyl-3-(4-chlorophenyl)pyrrolo[2,3-b]indol-2(1H)-imine (3b)

¹H NMR (400 MHz, CDCl₃) of compound **3b**

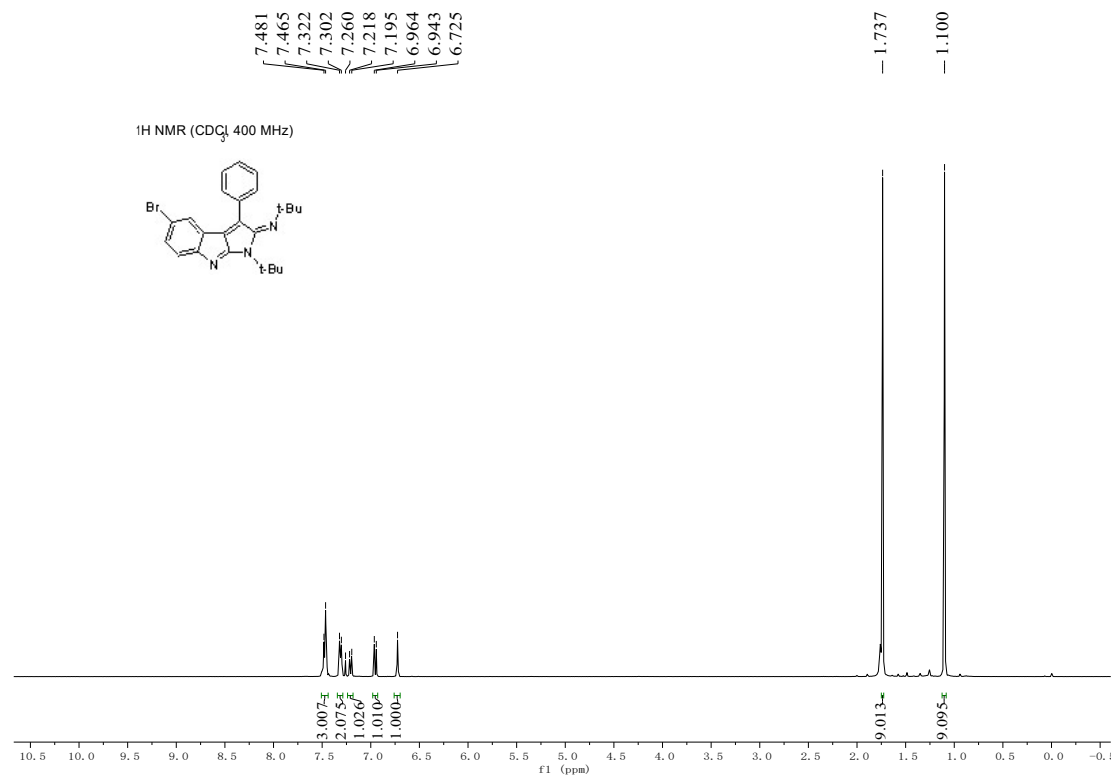


¹³C NMR (100 Mz, CDCl₃) of compound **3b**

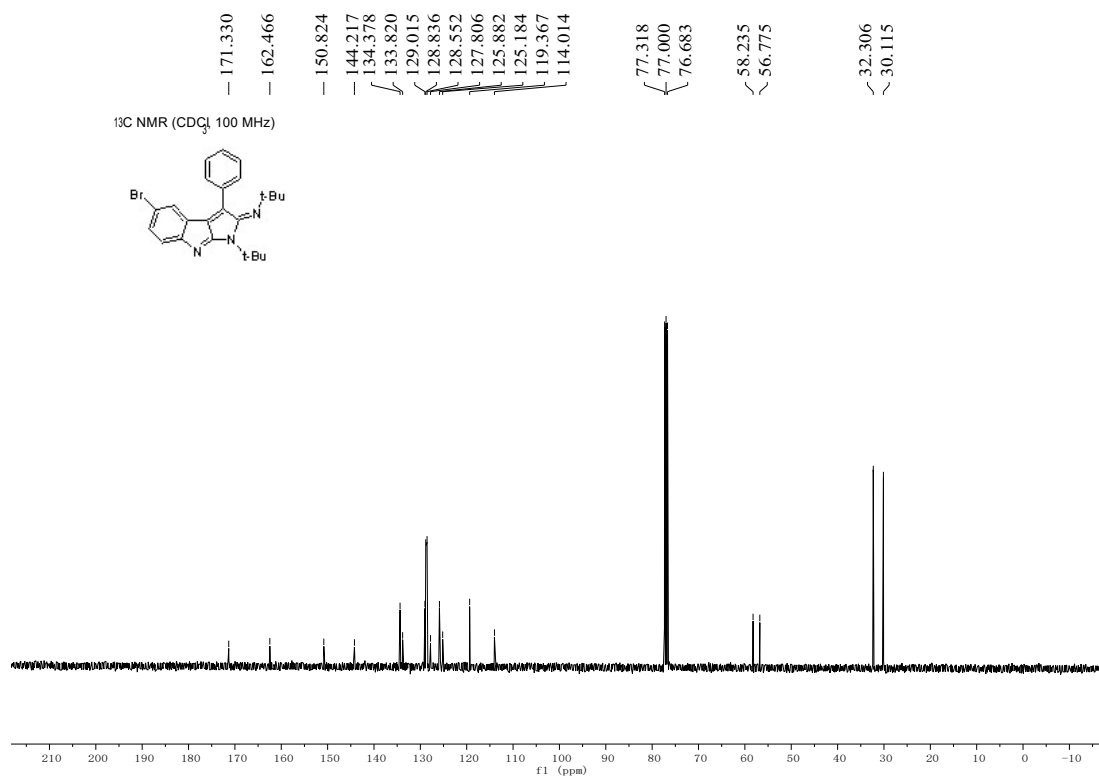


(E)-3-(4-Bromophenyl)-N,1-di-tert-butylpyrrolo[2,3-b]indol-2(1H)-imine (3c)

¹H NMR (400 MHz, CDCl₃) of compound **3c**

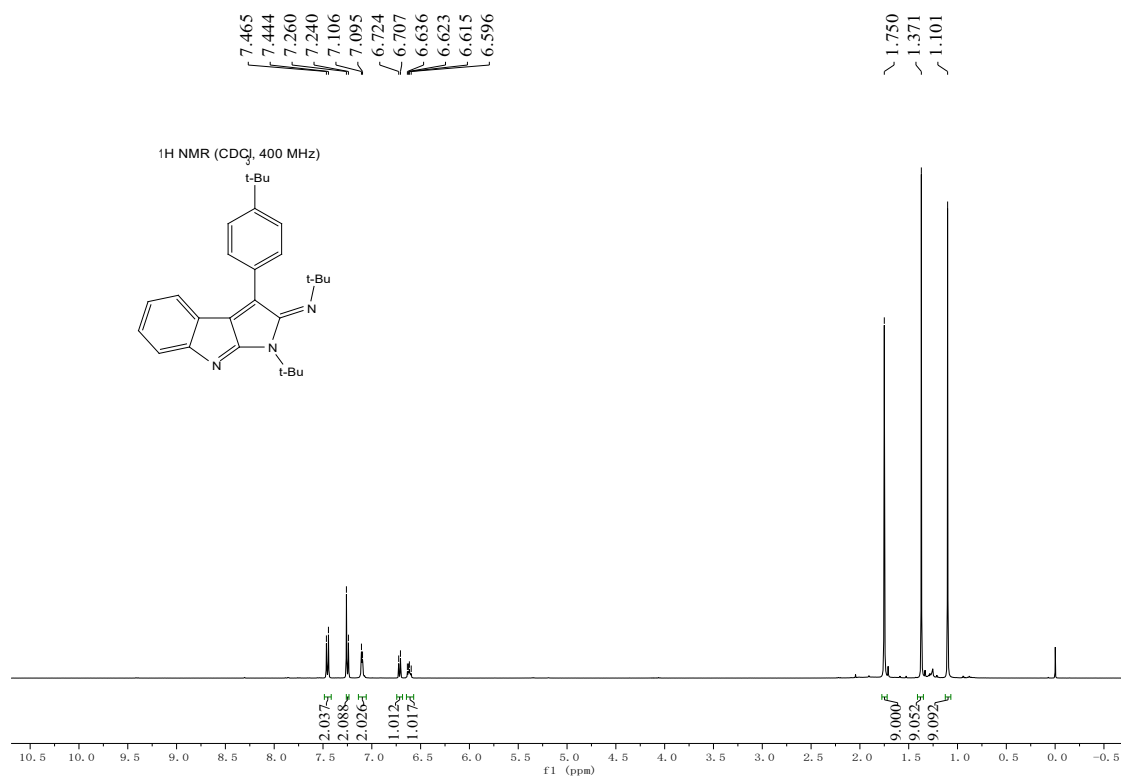


¹³C NMR (100 Mz, CDCl₃) of compound **3c**

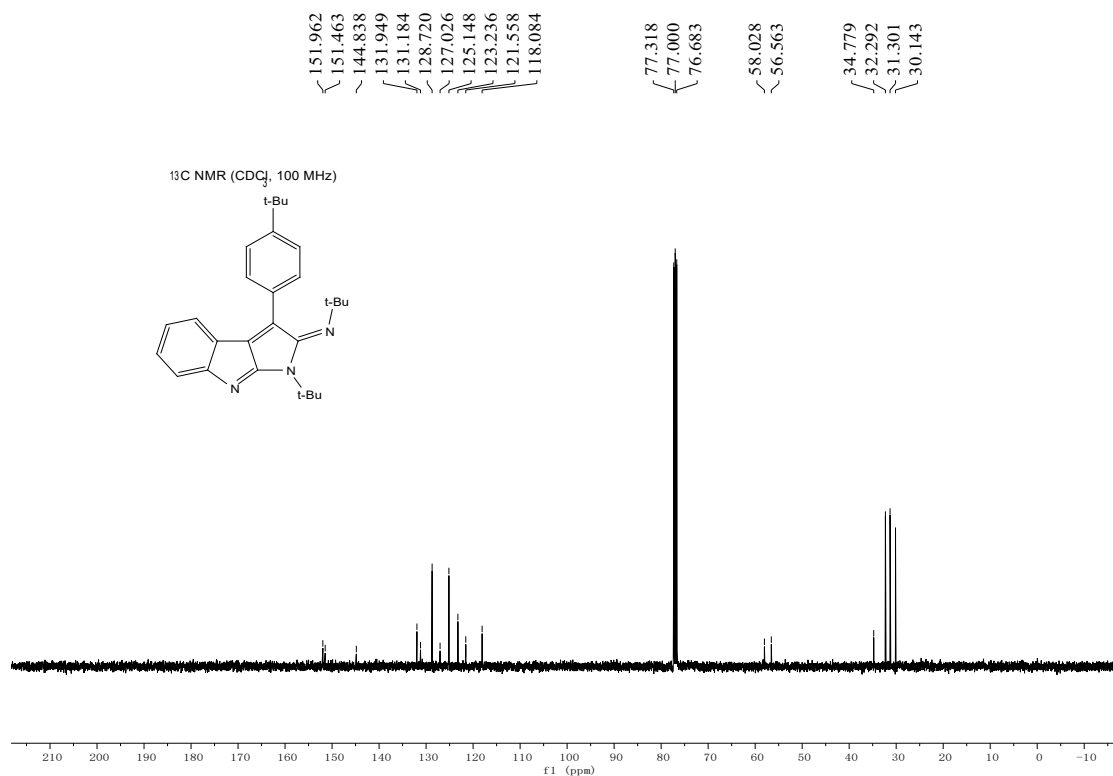


(E)-N,1-di-tert-Butyl-3-(4-(tert-butyl)phenyl)pyrrolo[2,3-b]indol-2(1H)-imine (3d)

¹H NMR (400 MHz, CDCl₃) of compound **3d**



¹³C NMR (100 Mz, CDCl₃) of compound **3d**

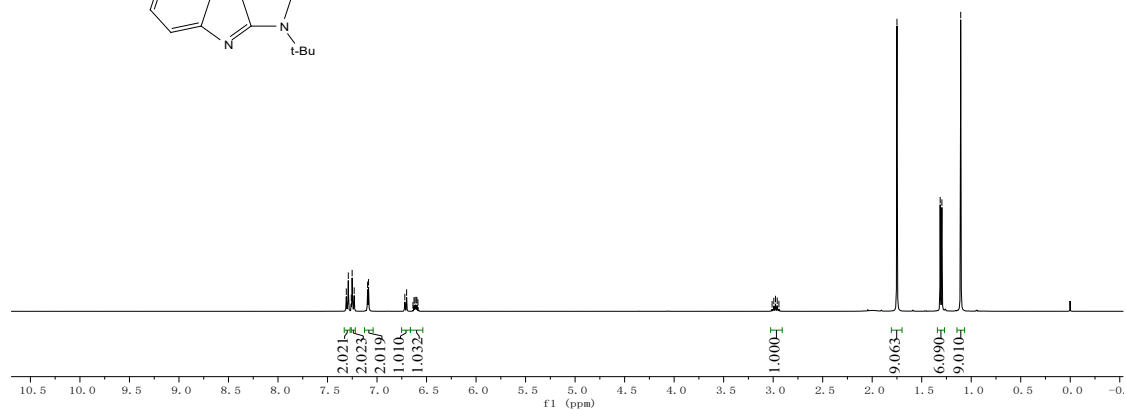
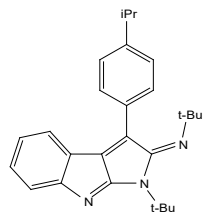


(E)-N,1-di-tert-Butyl-3-(4-isopropylphenyl)pyrrolo[2,3-b]indol-2(1H)-imine (3e)

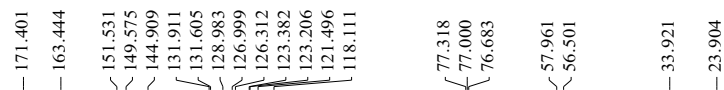
¹H NMR (400 MHz, CDCl₃) of compound 3e



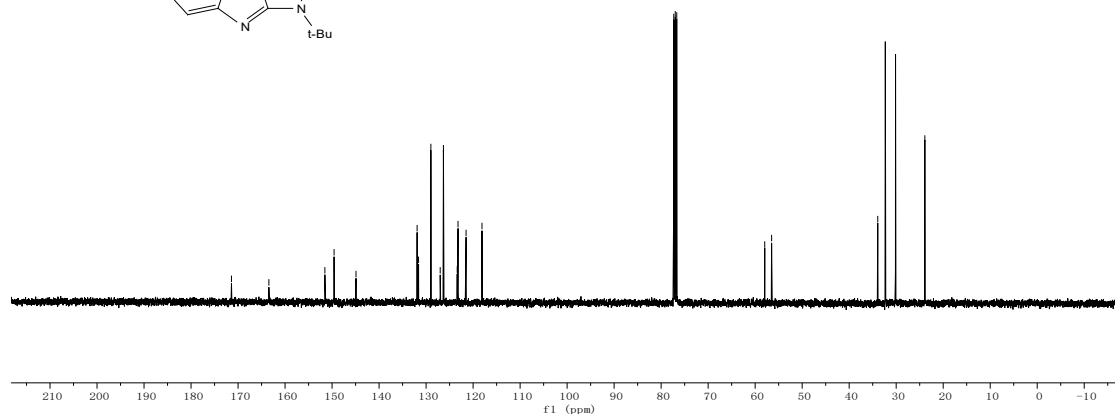
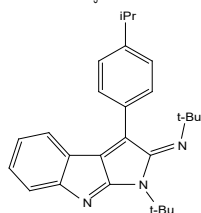
¹H NMR (CDCl₃, 400 MHz)



¹³C NMR (100 Mz, CDCl₃) of compound 3e

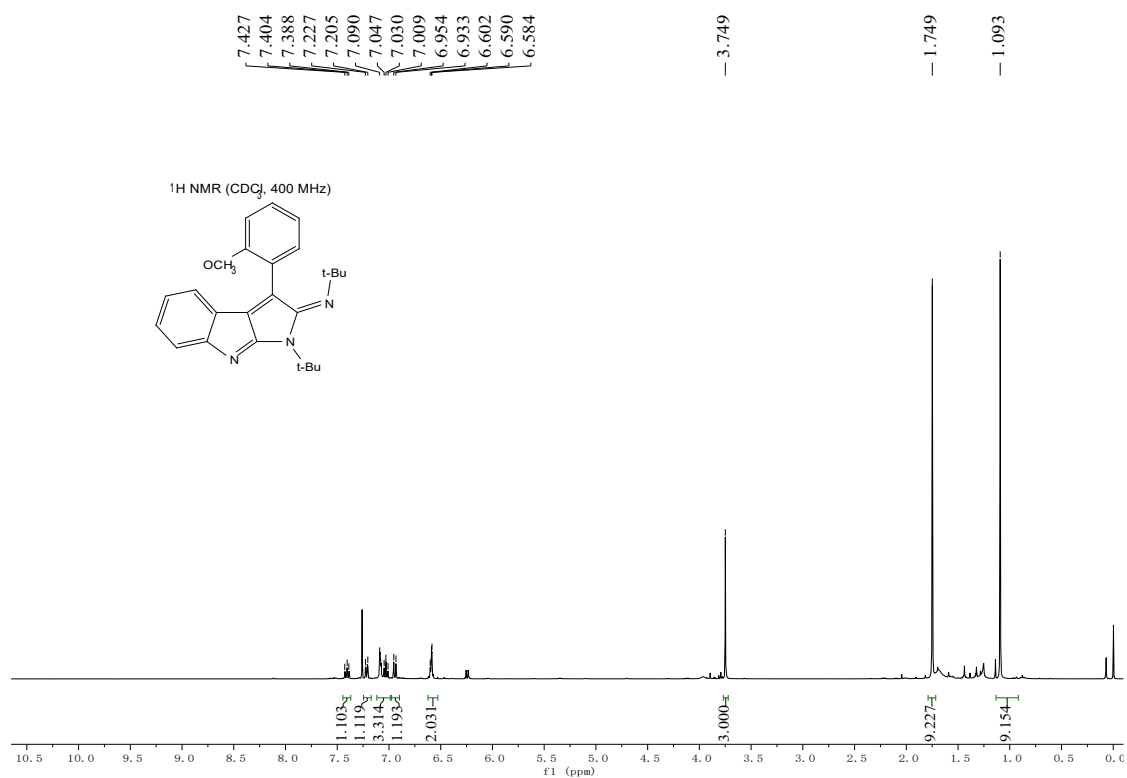


¹³C NMR (CDCl₃, 100 MHz)

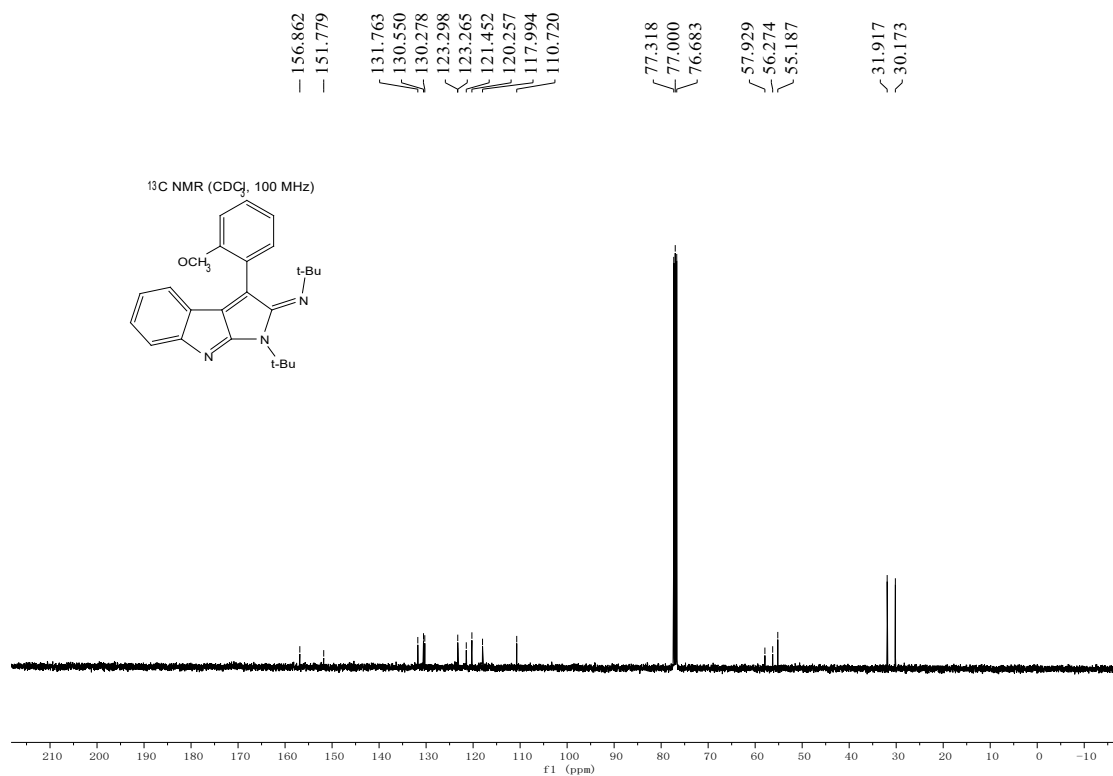


(E)-N,1-di-tert-Butyl-3-(2-methoxyphenyl)pyrrolo[2,3-b]indol-2(1H)-imine (3f)

¹H NMR (400 MHz, CDCl₃) of compound **3f**

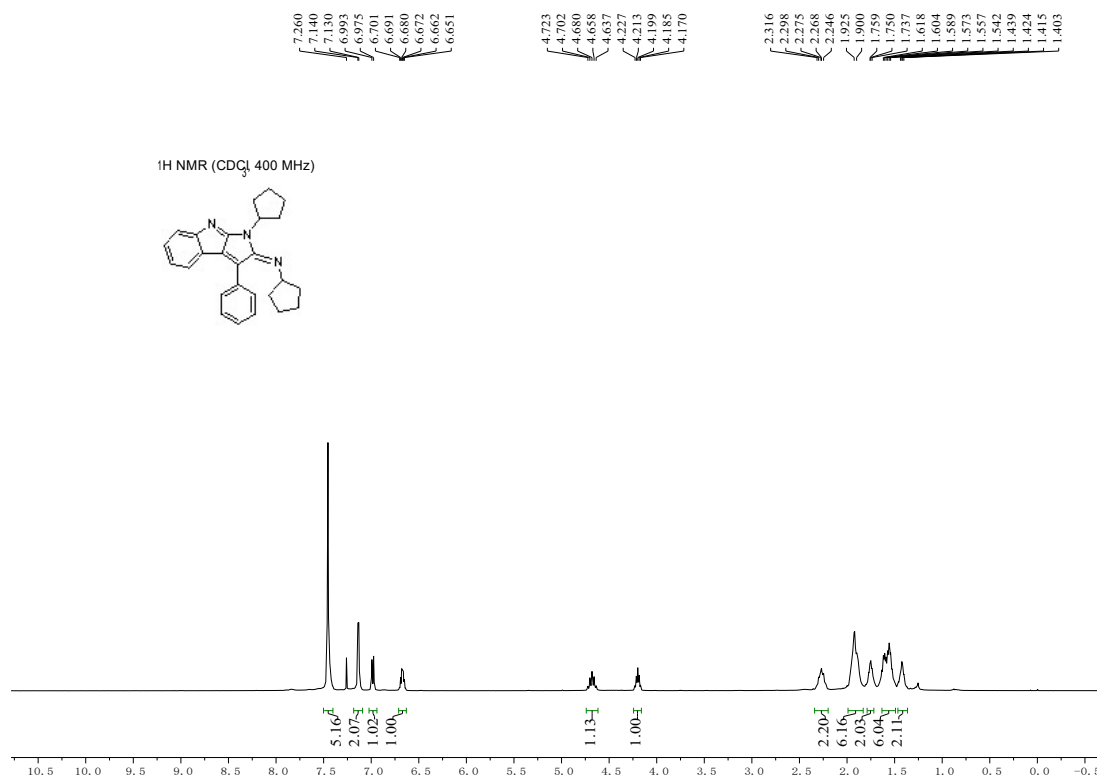


¹³C NMR (100 Mz, CDCl₃) of compound **3f**



***(E)*-*N*,1-Dicyclopentyl-3-phenylpyrrolo[2,3-*b*]indol-2(1*H*)-imine (3g)**

¹H NMR (400 MHz, CDCl₃) of compound 3g



^{13}C NMR (100 Mz, CDCl_3) of compound **3g**

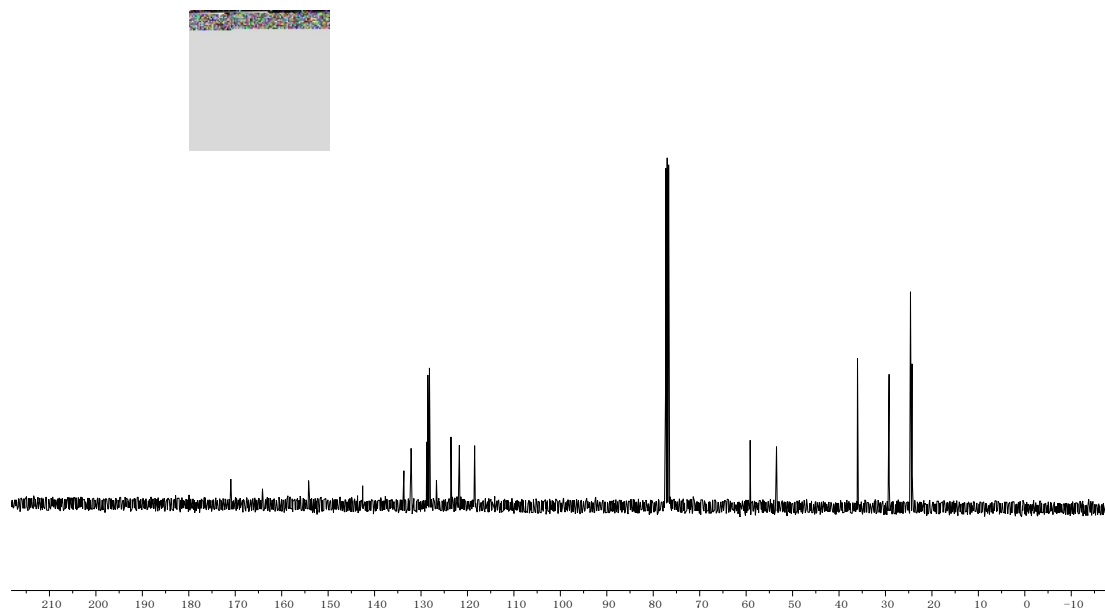
— 170.952
— 164.130
— 154.203
— 142.564
— 133.685
— 132.136
— 128.979
— 128.525
— 128.186
— 126.677
— 123.679
— 123.555
— 121.744
— 118.455

— 77.318
— 77.000
— 76.682

— 59.133
— 53.458

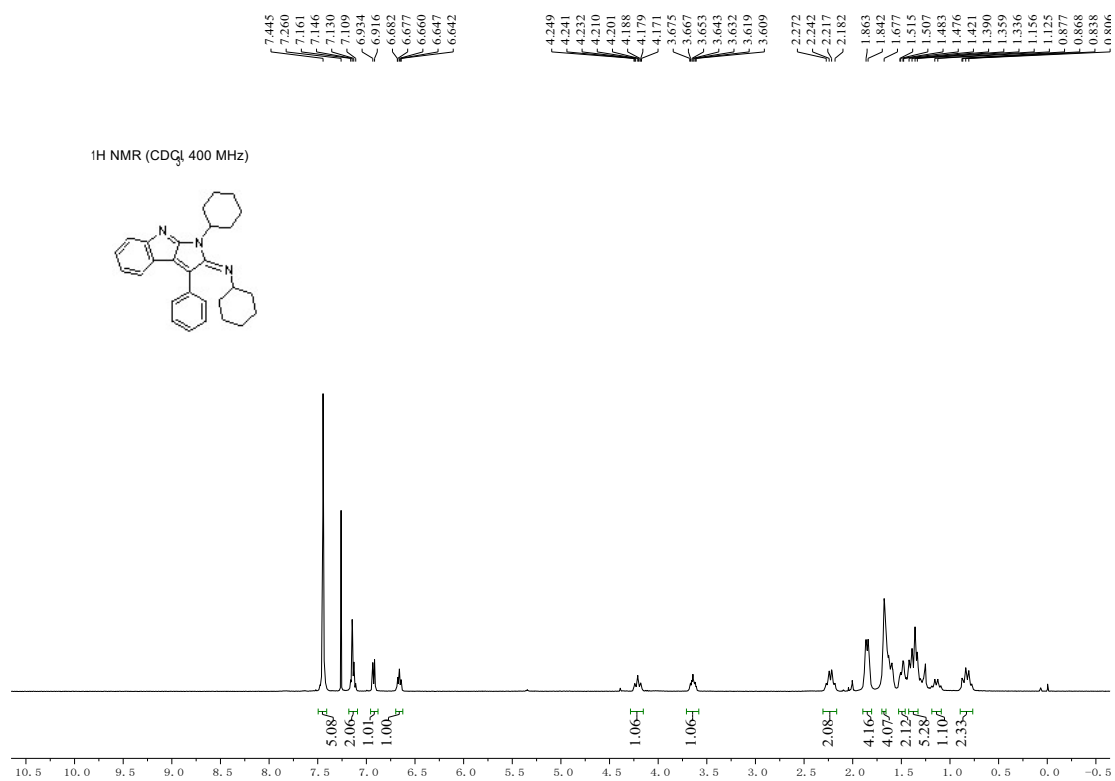
— 36.023
— 29.219
— 24.605
— 24.286

^{13}C NMR (CDCl_3 , 100 MHz)

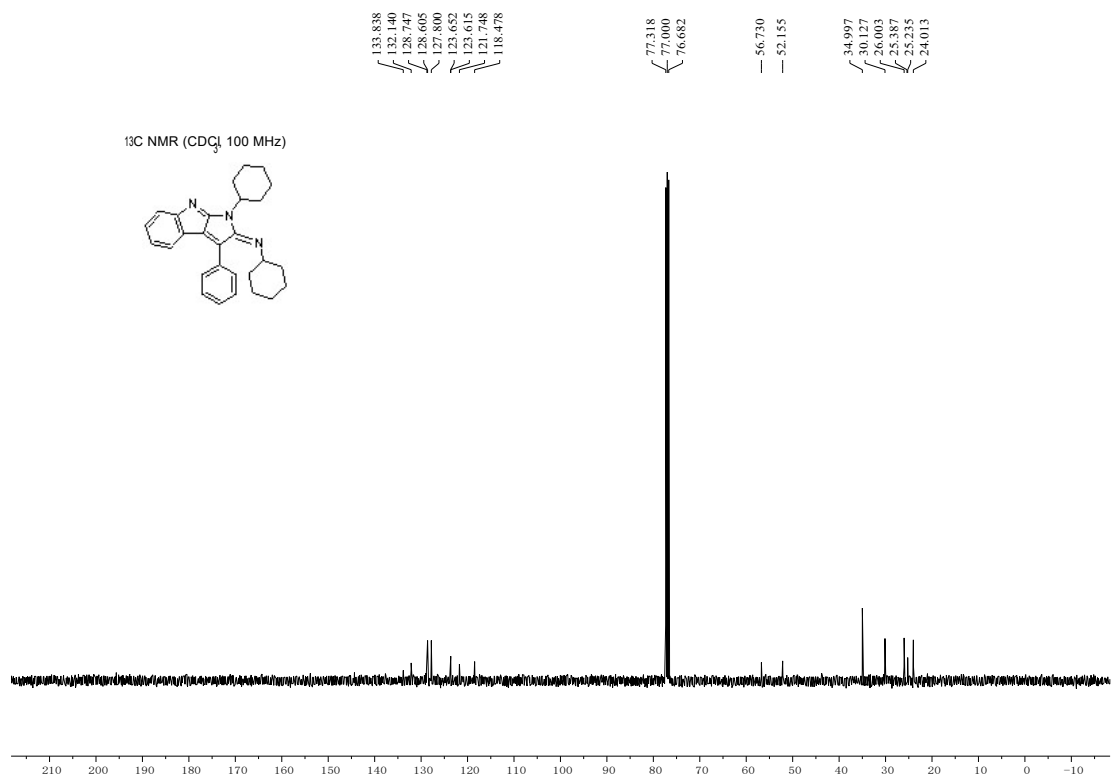


(E)-N,1-Dicyclohexyl-3-phenylpyrrolo[2,3-b]indol-2(1H)-imine (3h)

¹H NMR (400 MHz, CDCl₃) of compound **3h**

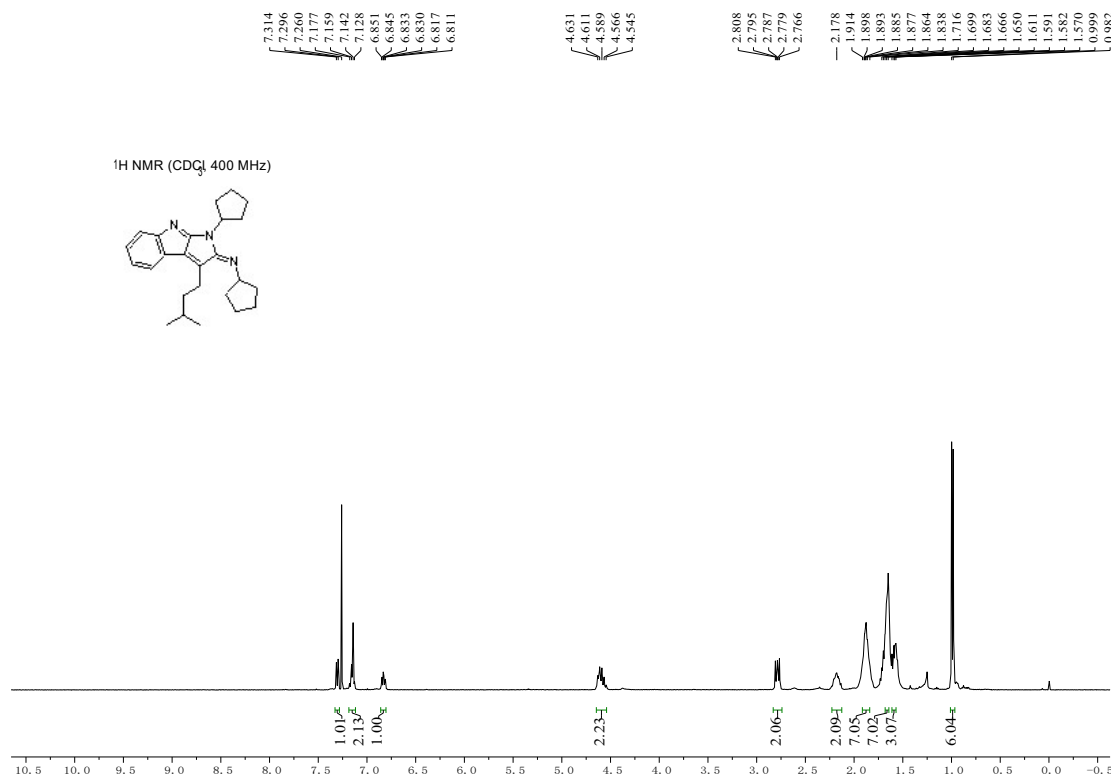


¹³C NMR (100 Mz, CDCl₃) of compound **3h**

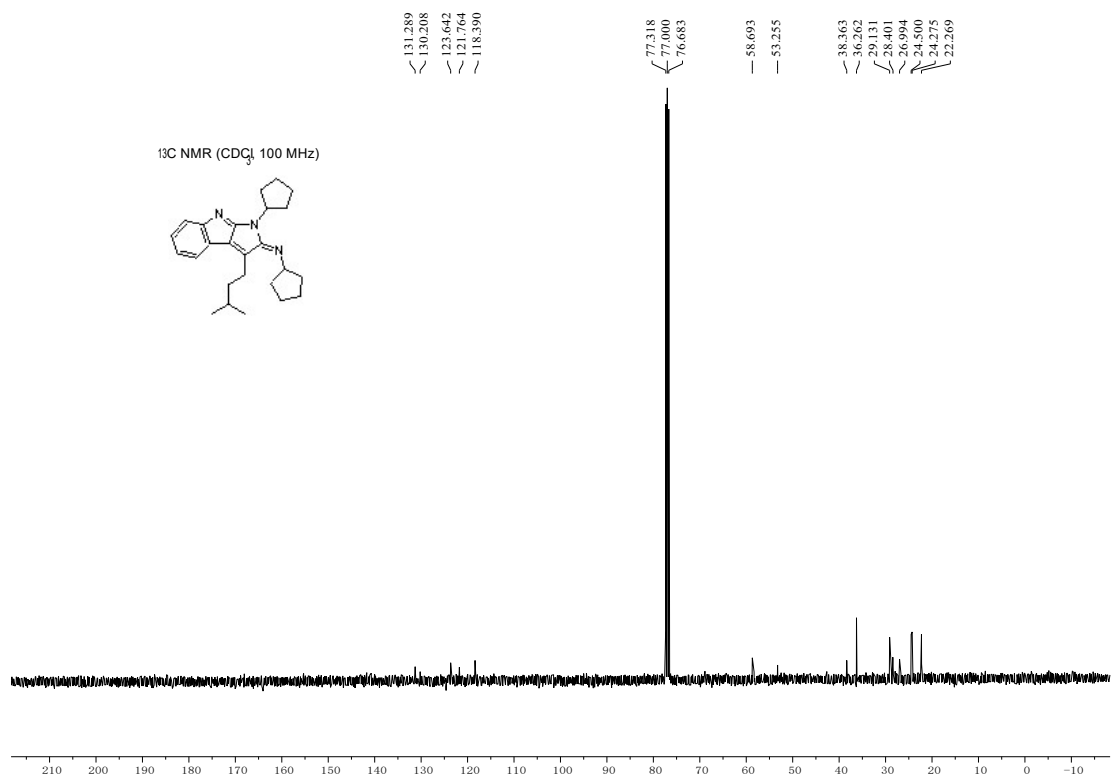


(E)-N,1-Dicyclopentyl-3-isopentylpyrrolo[2,3-b]indol-2(1H)-imine (3i)

¹H NMR (400 MHz, CDCl₃) of compound 3i

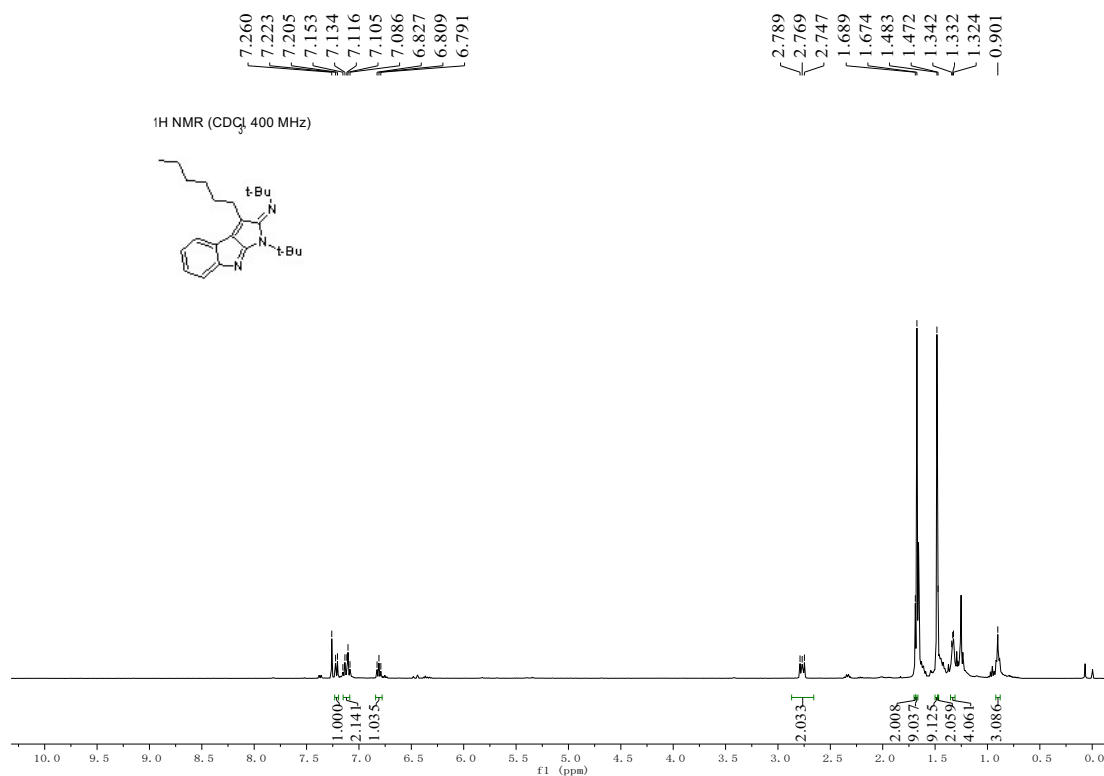


¹³C NMR (100 Mz, CDCl₃) of compound 3i

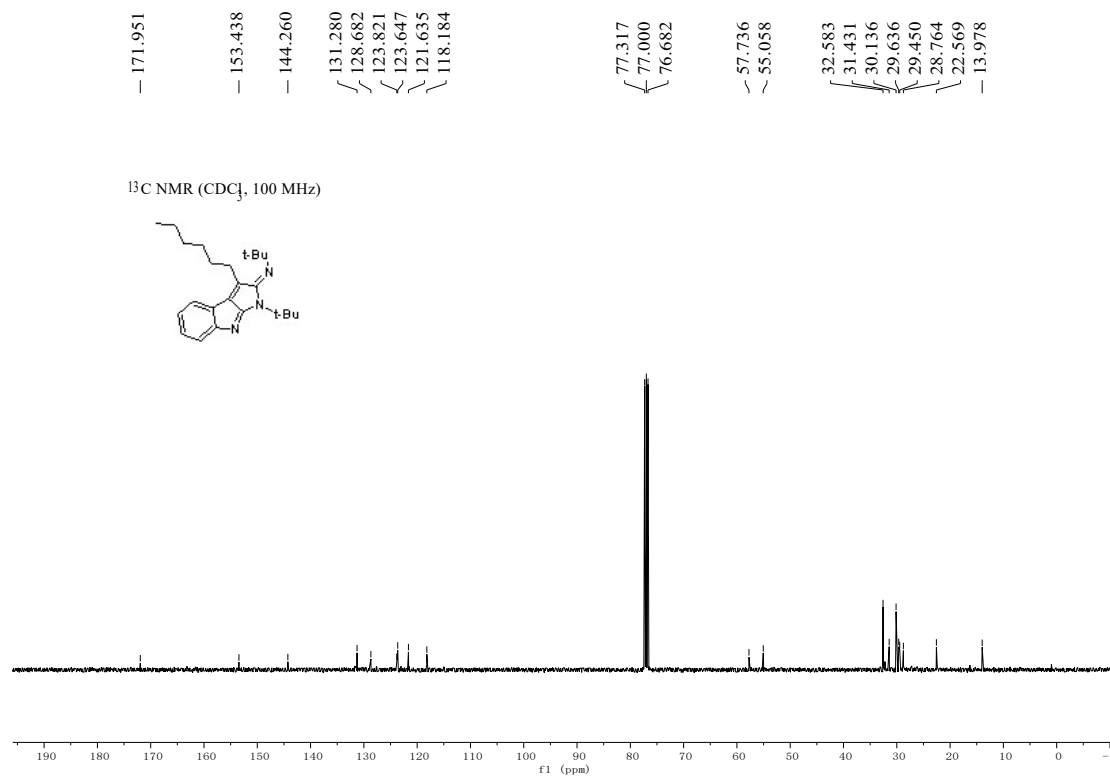


(E)-N,1-di-tert-Butyl-3-hexylpyrrolo[2,3-b]indol-2(1H)-imine (3j)

¹H NMR (400 MHz, CDCl₃) of compound **3j**

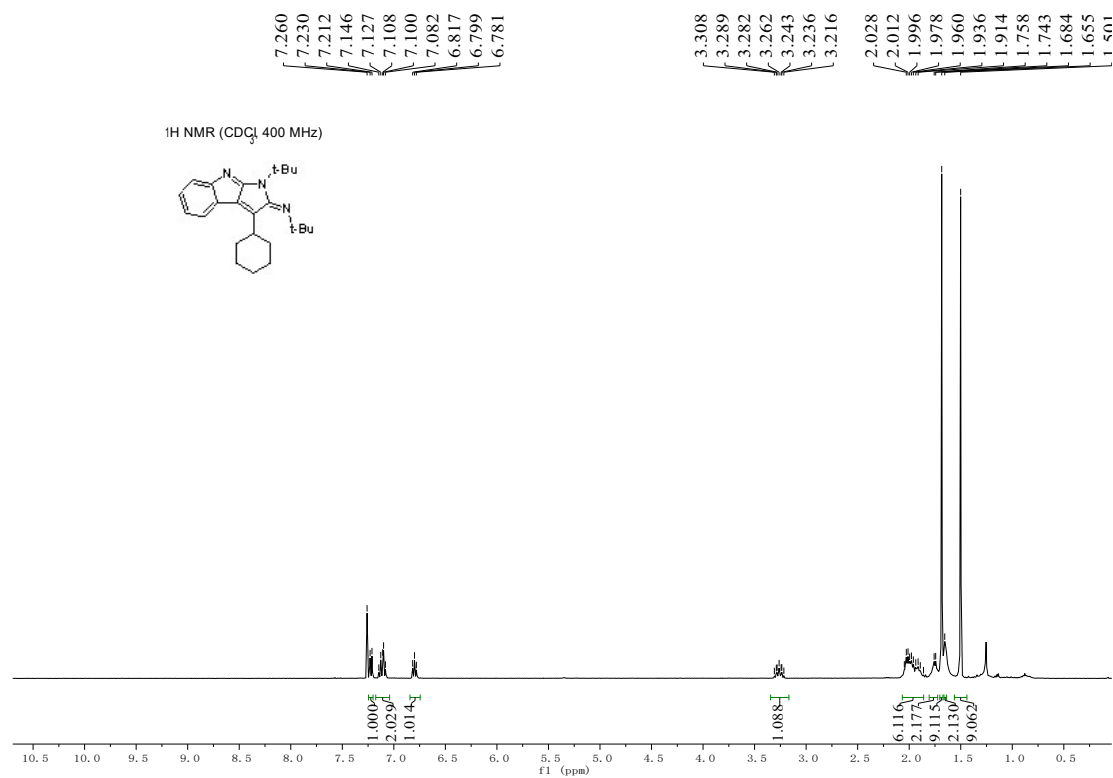


¹³C NMR (100 Mz, CDCl₃) of compound **3j**

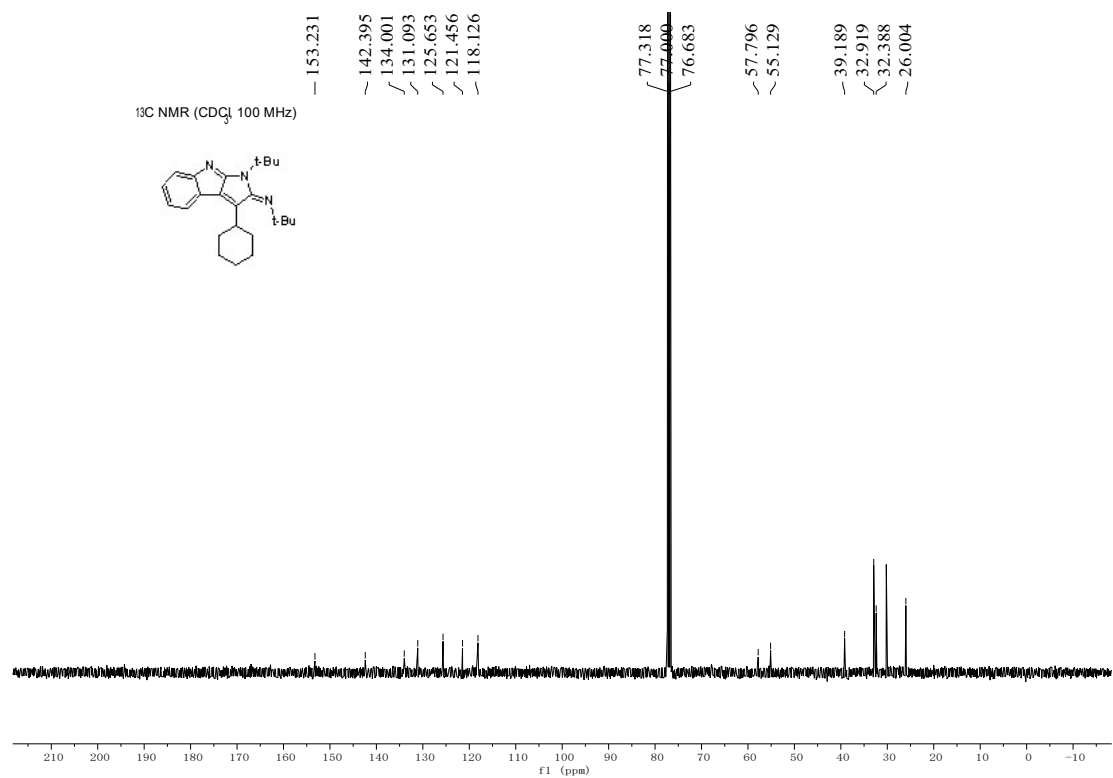


(E)-N,1-di-tert-Butyl-3-cyclohexylpyrrolo[2,3-b]indol-2(1H)-imine (3k)

¹H NMR (400 MHz, CDCl₃) of compound **3k**

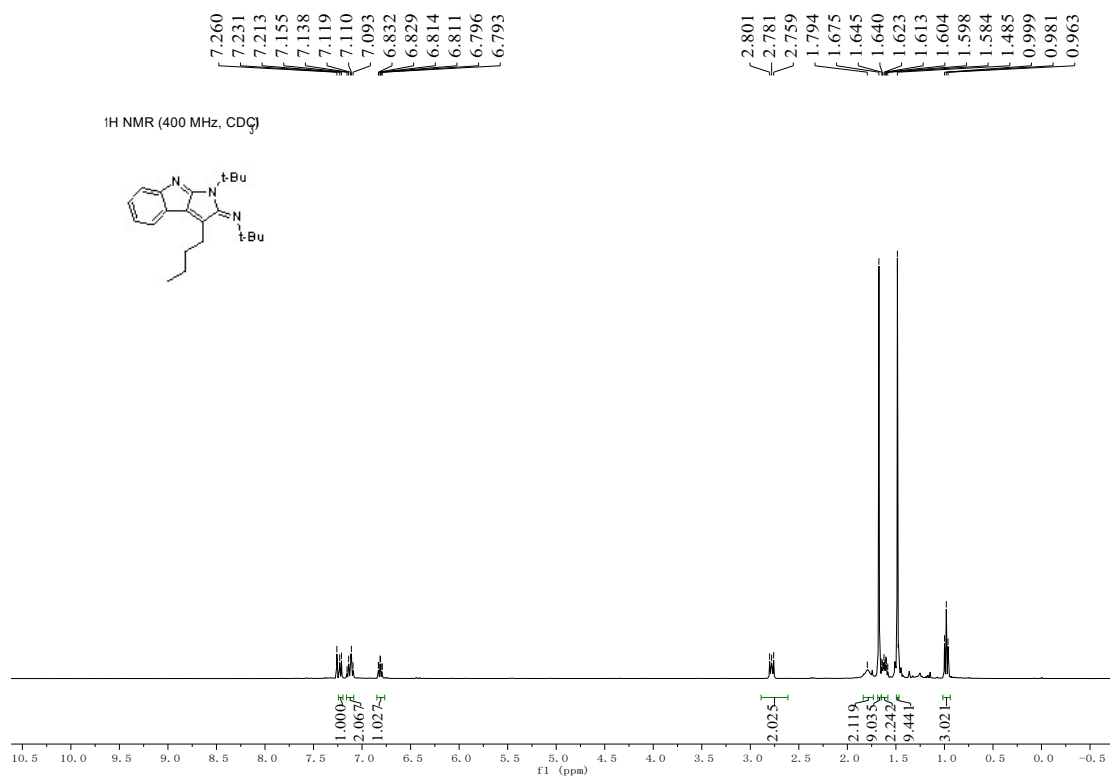


¹³C NMR (100 Mz, CDCl₃) of compound **3k**

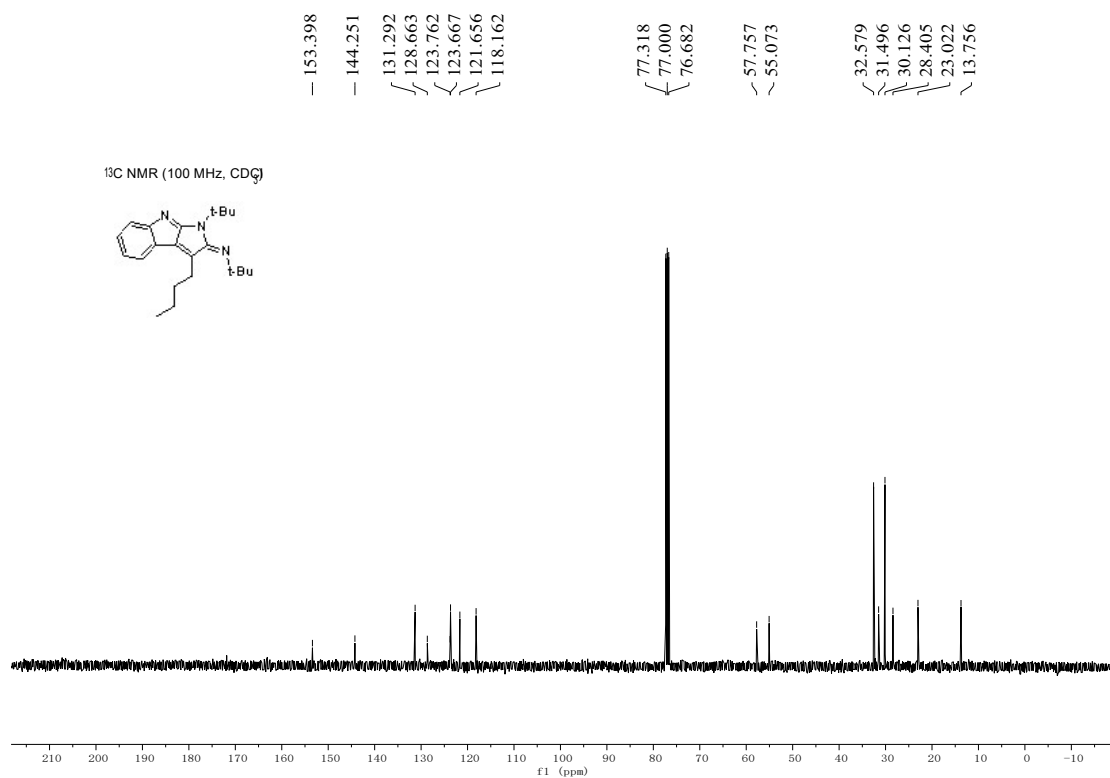


(E)-N,1-di-tert-Butyl-3-butylpyrrolo[2,3-b]indol-2(1H)-imine (31)

¹H NMR (400 MHz, CDCl₃) of compound **31**

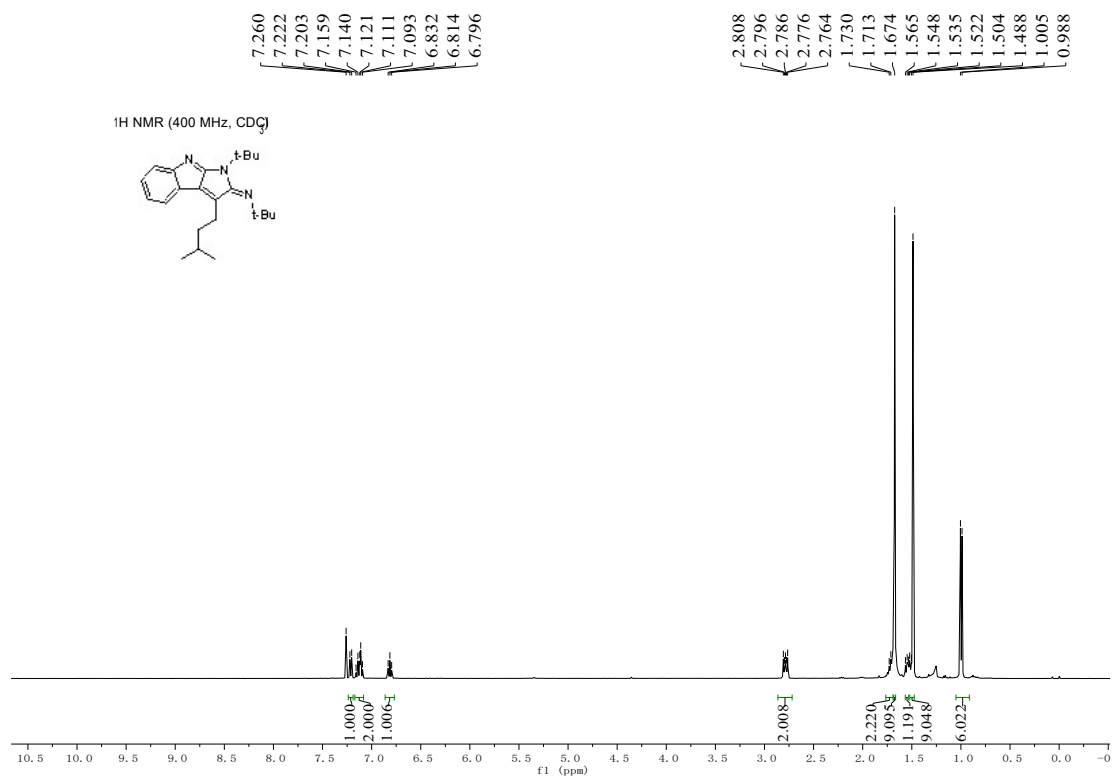


¹³C NMR (100 Mz, CDCl₃) of compound **31**

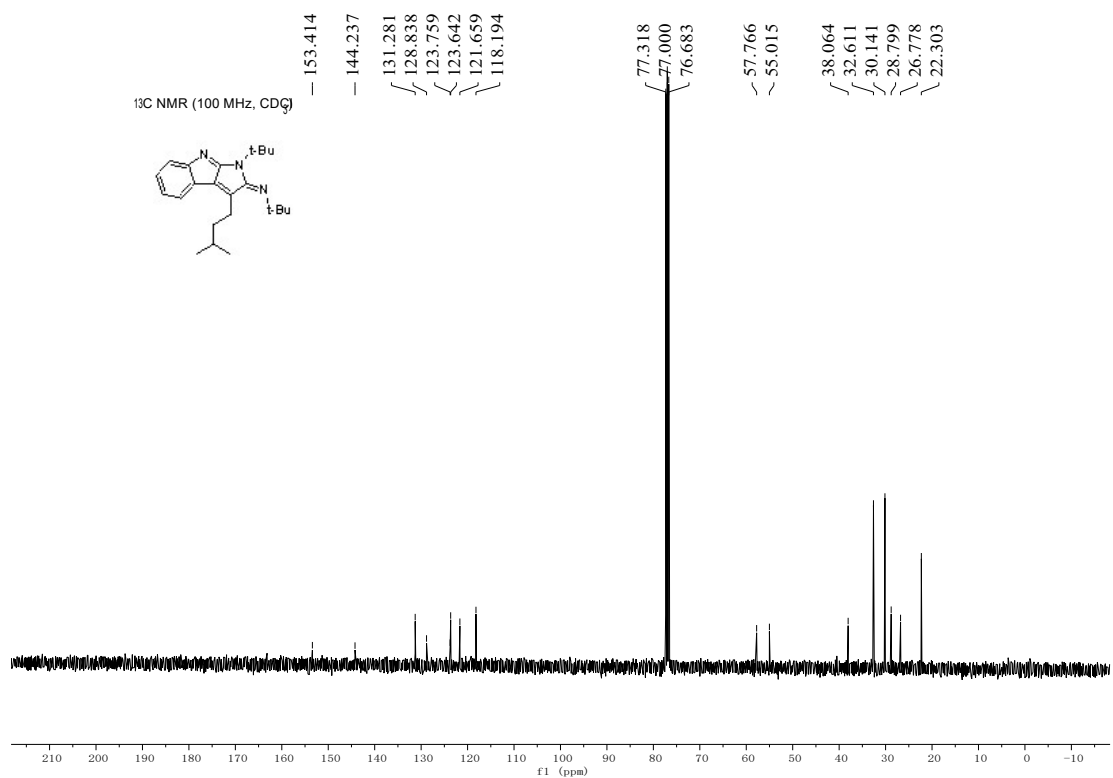


(E)-N,1-di-tert-Butyl-3-isopentylpyrrolo[2,3-b]indol-2(1H)-imine (3m)

¹H NMR (400 MHz, CDCl₃) of compound **3m**

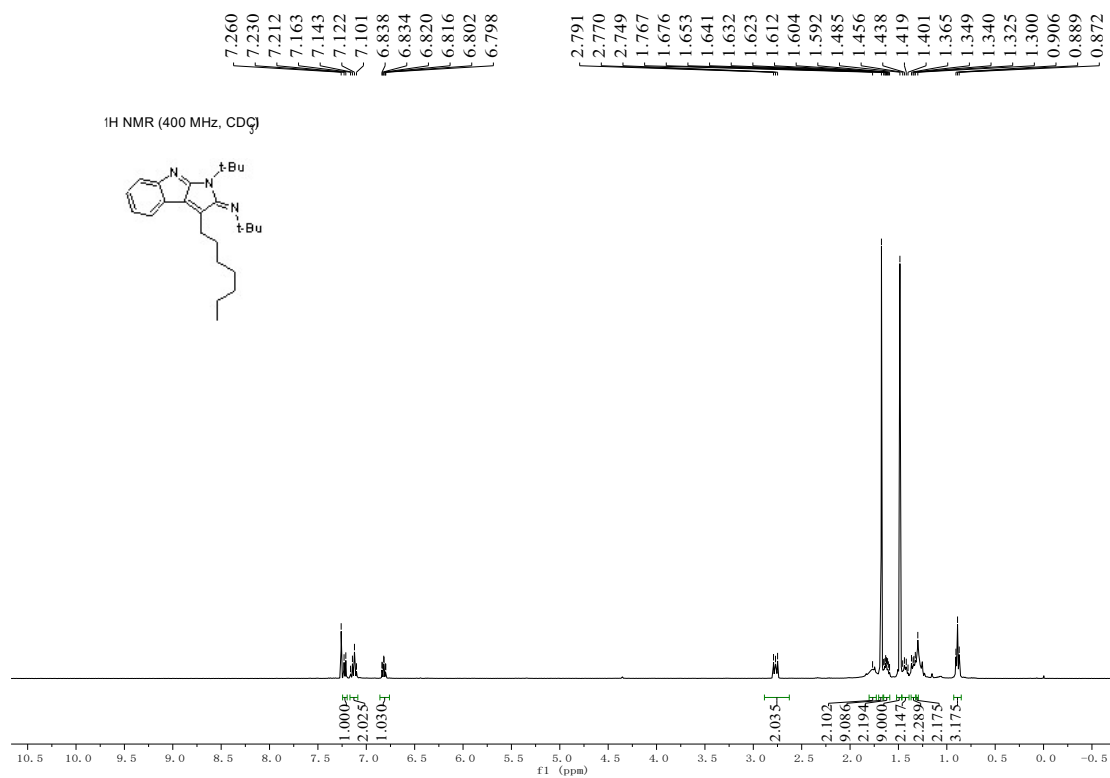


¹³C NMR (100 MHz, CDCl₃) of compound **3m**

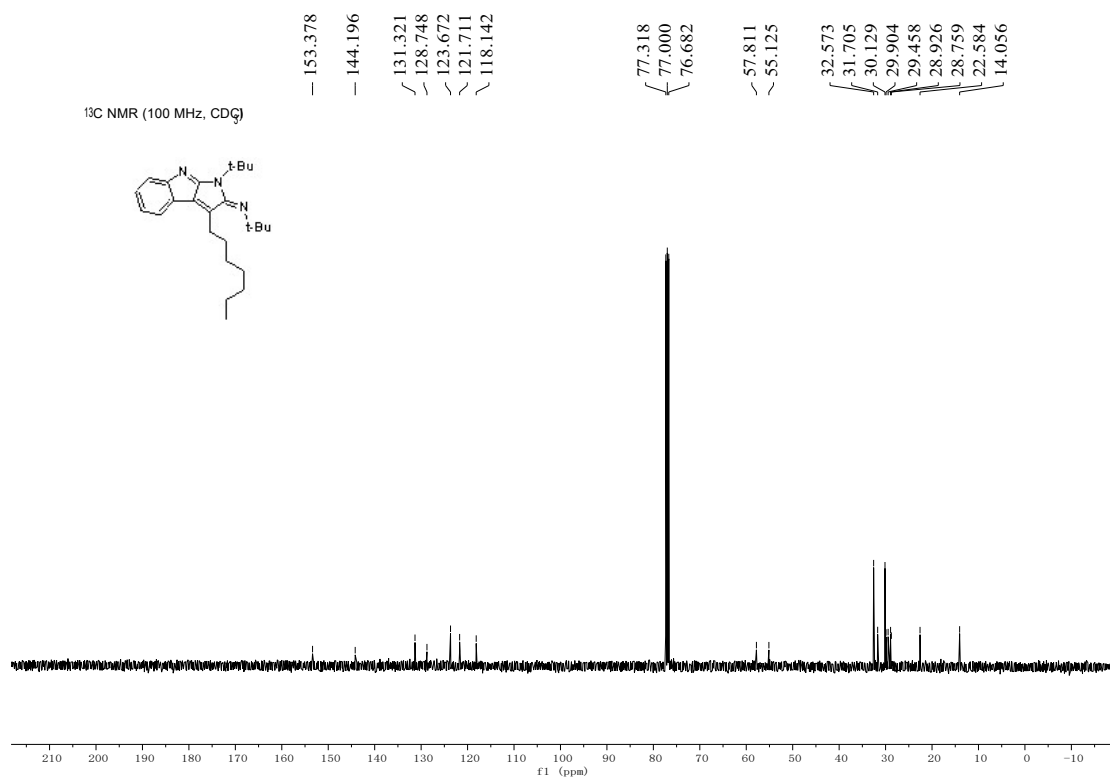


(E)-N,1-di-tert-Butyl-3-heptylpyrrolo[2,3-b]indol-2(1H)-imine (3n)

¹H NMR (400 MHz, CDCl₃) of compound **3n**

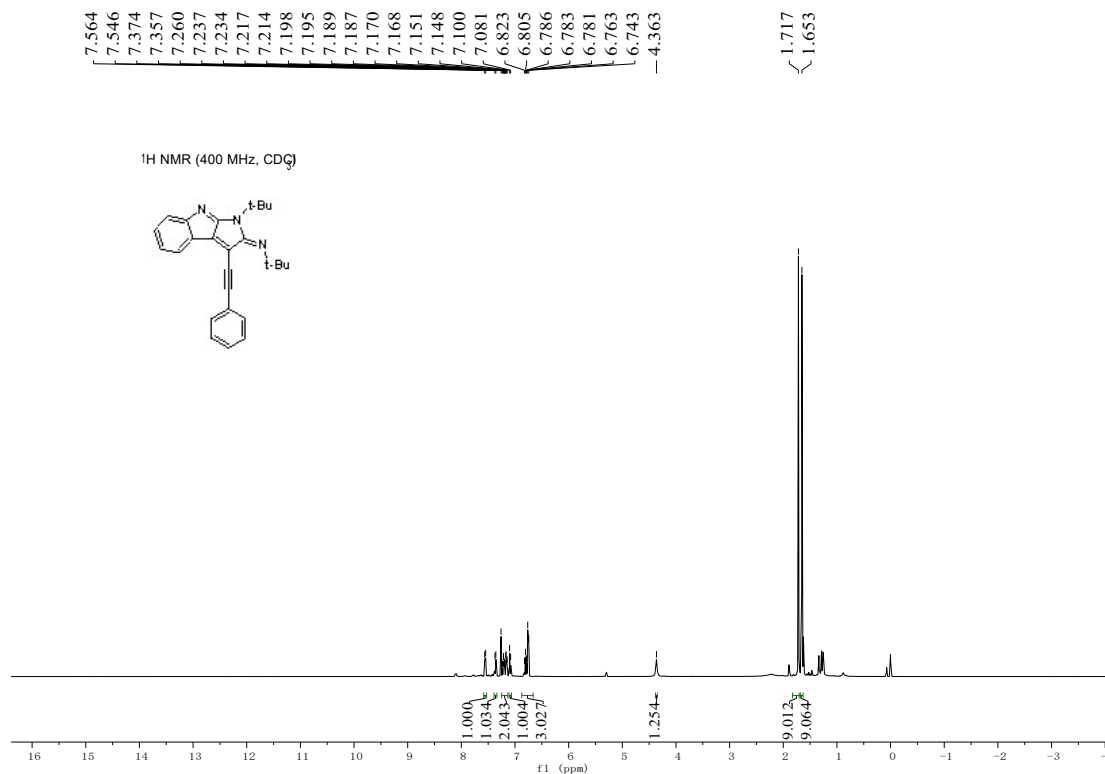


¹³C NMR (100 Mz, CDCl₃) of compound **3n**

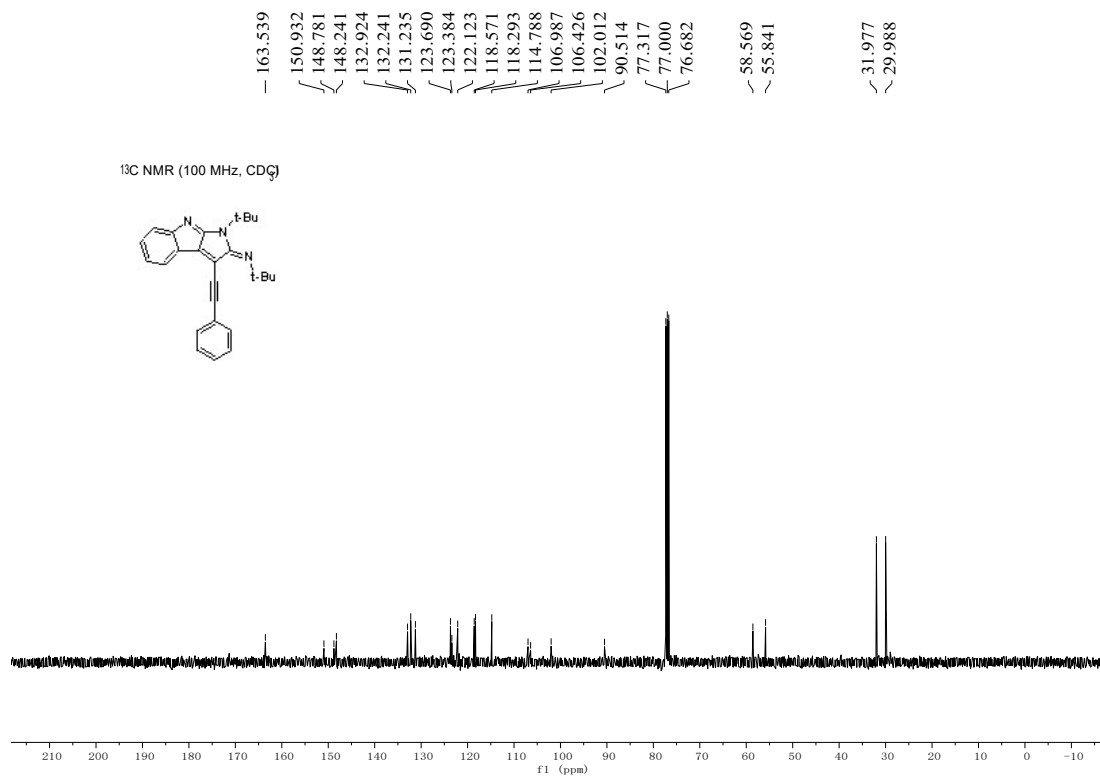


(E)-N,1-di-tert-Butyl-3-(phenylethynyl)pyrrolo[2,3-b]indol-2(1H)-imine (3o)

¹H NMR (400 MHz, CDCl₃) of compound **3o**

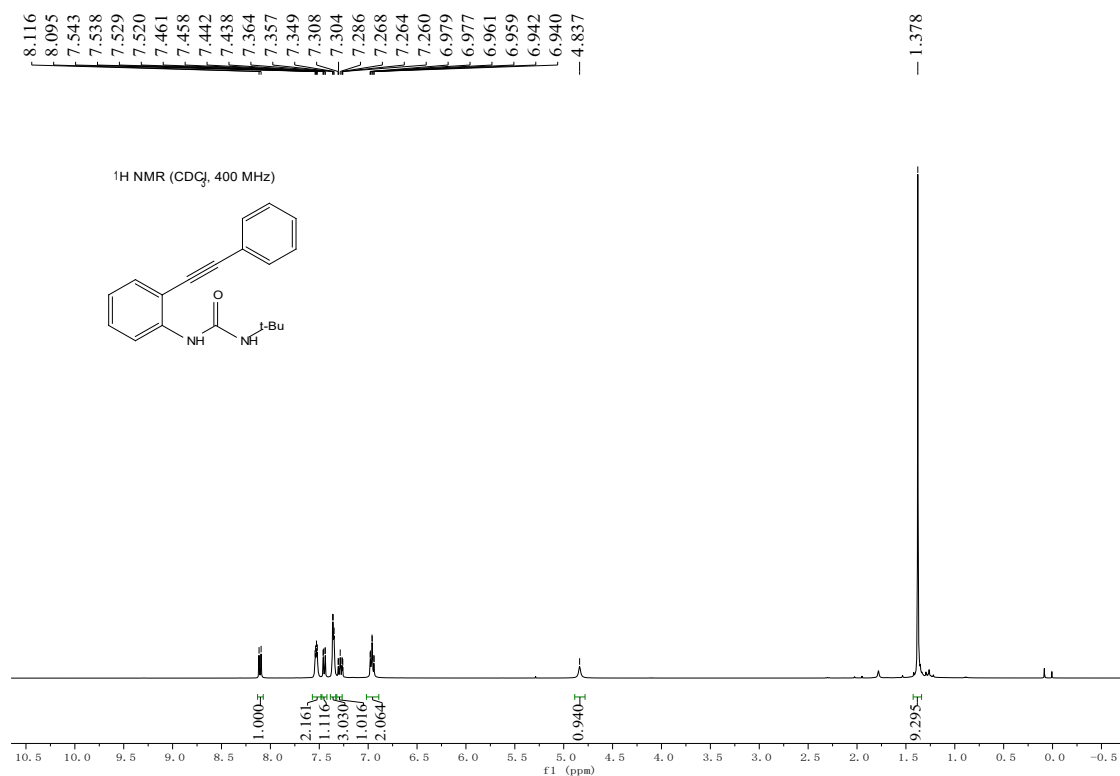


¹³C NMR (100 MHz, CDCl₃) of compound **3o**

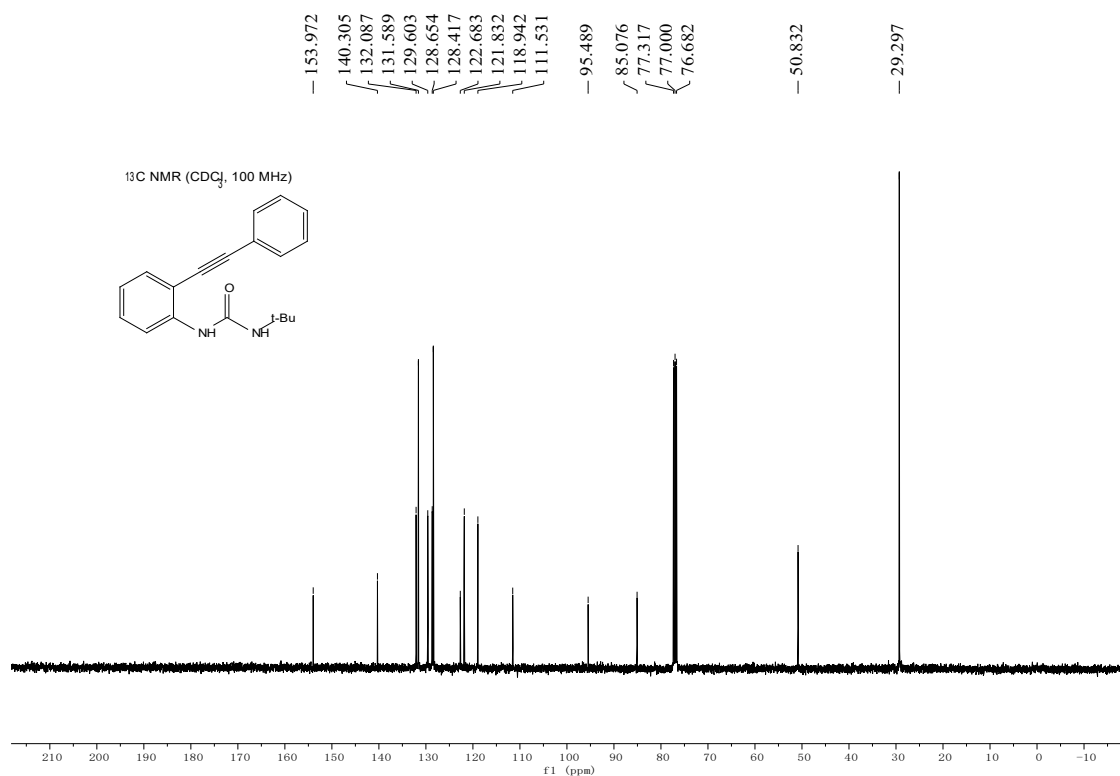


1-(*tert*-Butyl)-3-(2-(phenylethynyl)phenyl)urea (**4a**)

¹H NMR (400 MHz, CDCl₃) of compound **4a**

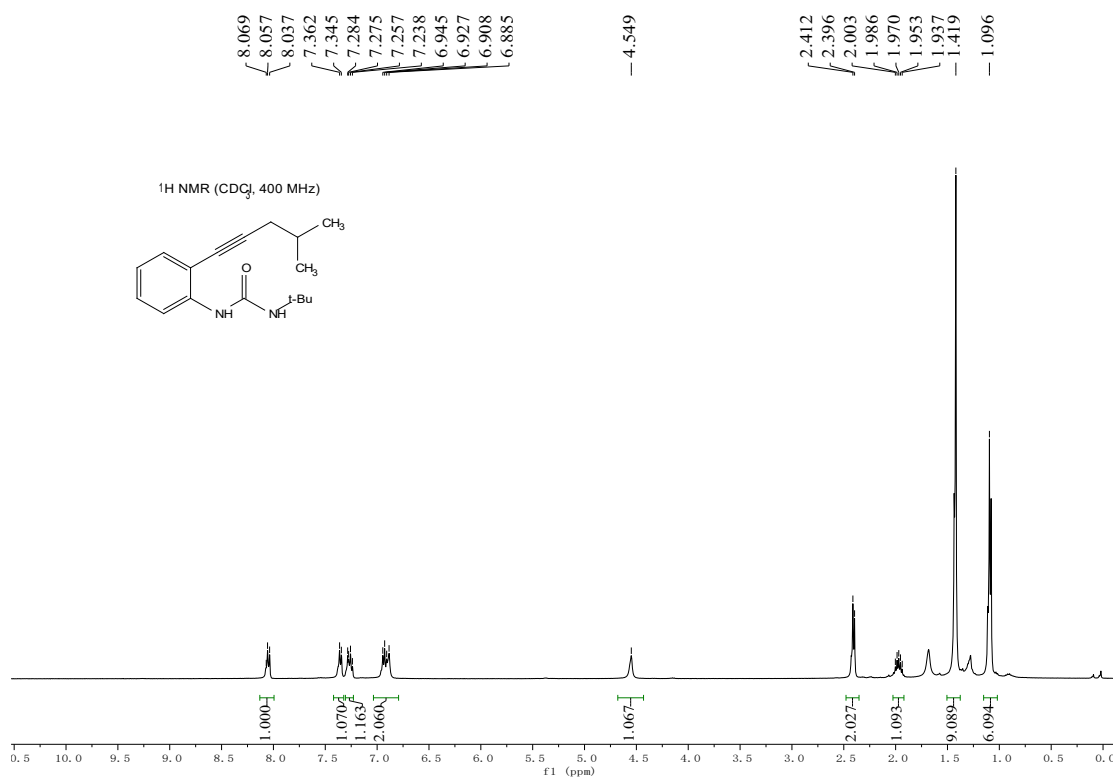


¹³C NMR (100 Mz, CDCl₃) of compound **4a**



1-(*tert*-Butyl)-3-(2-(4-methylpent-1-yn-1-yl)phenyl)urea (4b)

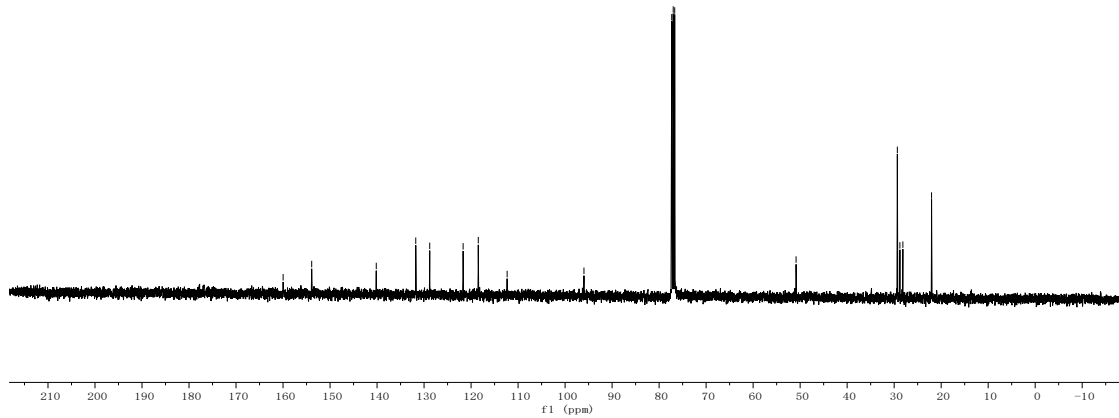
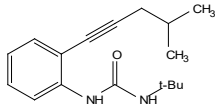
¹H NMR (400 MHz, CDCl₃) of compound **4b**



¹³C NMR (100 Mz, CDCl₃) of compound **4b**

— 159.982
 — 153.904
 — 140.169
 — 131.767
 — 128.795
 — 121.692
 — 118.466
 — 112.329
 — 95.987
 — 77.317
 — 77.000
 — 76.682
 — 50.864
 — 29.321
 — 28.780
 — 28.147
 — 22.044

¹³C NMR (CDCl₃, 100 MHz)

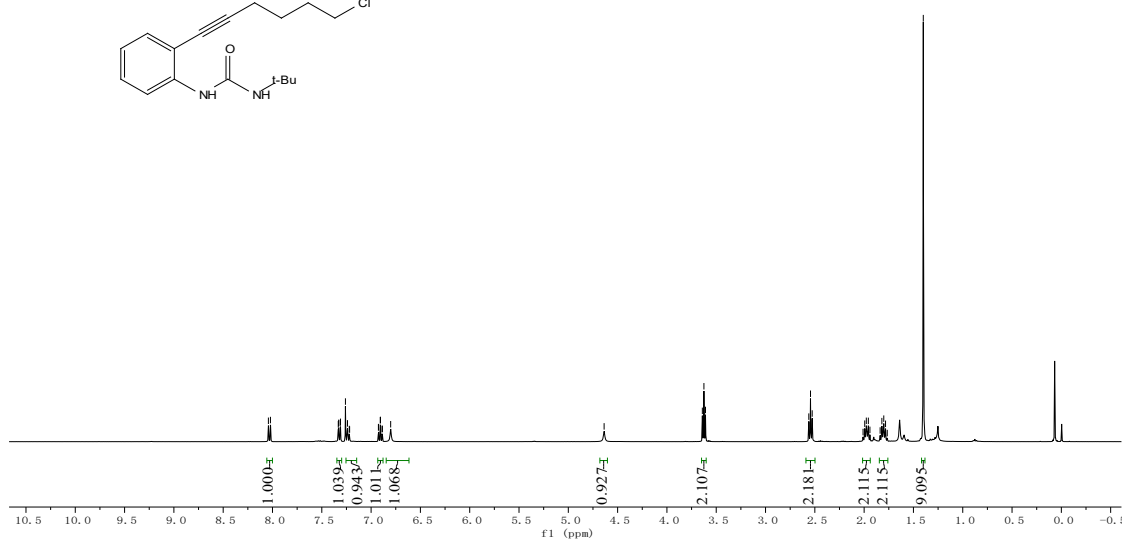
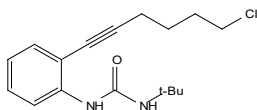


1-(*tert*-Butyl)-3-(2-(6-chlorohex-1-yn-1-yl)phenyl)urea (4c)

¹H NMR (400 MHz, CDCl₃) of compound 4c

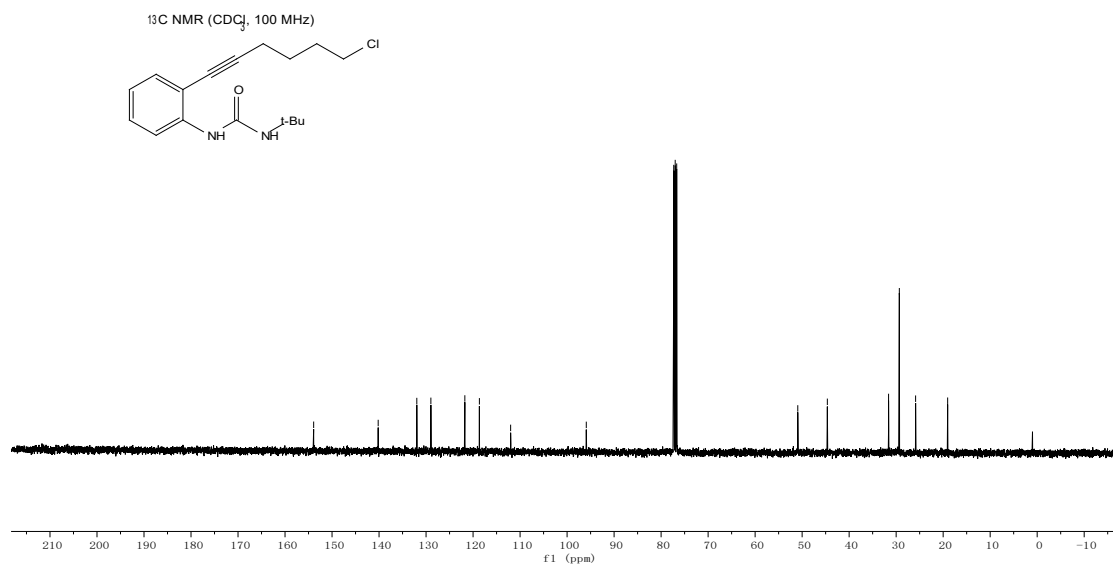
— 8.041
 — 8.021
 — 7.333
 — 7.329
 — 7.314
 — 7.310
 — 7.260
 — 7.239
 — 7.221
 — 7.218
 — 6.926
 — 6.924
 — 6.907
 — 6.905
 — 6.888
 — 6.886
 — 6.802
 — 4.637
 — 3.641
 — 3.625
 — 3.609
 — 2.561
 — 2.544
 — 2.527
 — 2.011
 — 1.994
 — 1.978
 — 1.957
 — 1.941
 — 1.838
 — 1.820
 — 1.801
 — 1.783
 — 1.766
 — 1.400

¹H NMR (CDCl₃, 400 MHz)



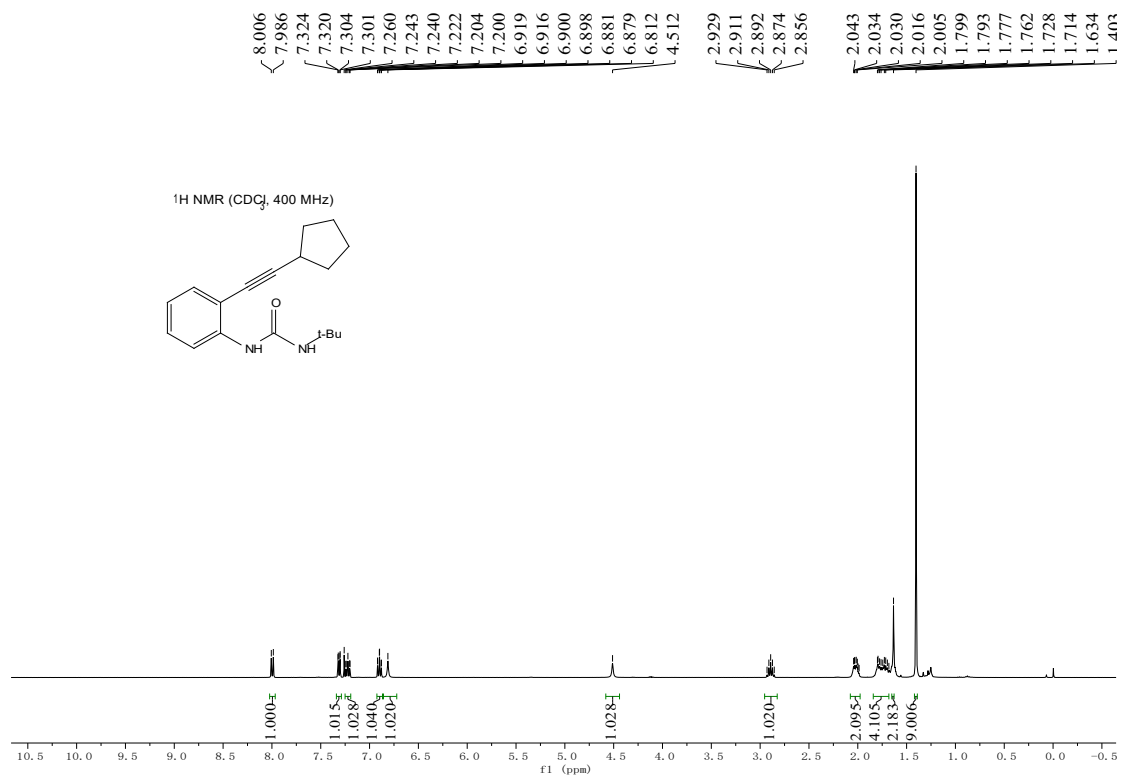
^{13}C NMR (100 MHz, CDCl_3) of compound **4c**

— 153.911
~ 140.184
~ 131.968
~ 128.976
~ 121.750
~ 118.655
~ 112.009
— 95.916
{ 77.318
77.000
76.683
— 50.925
— 44.636
~ 31.612
~ 29.323
~ 25.862
~ 19.044

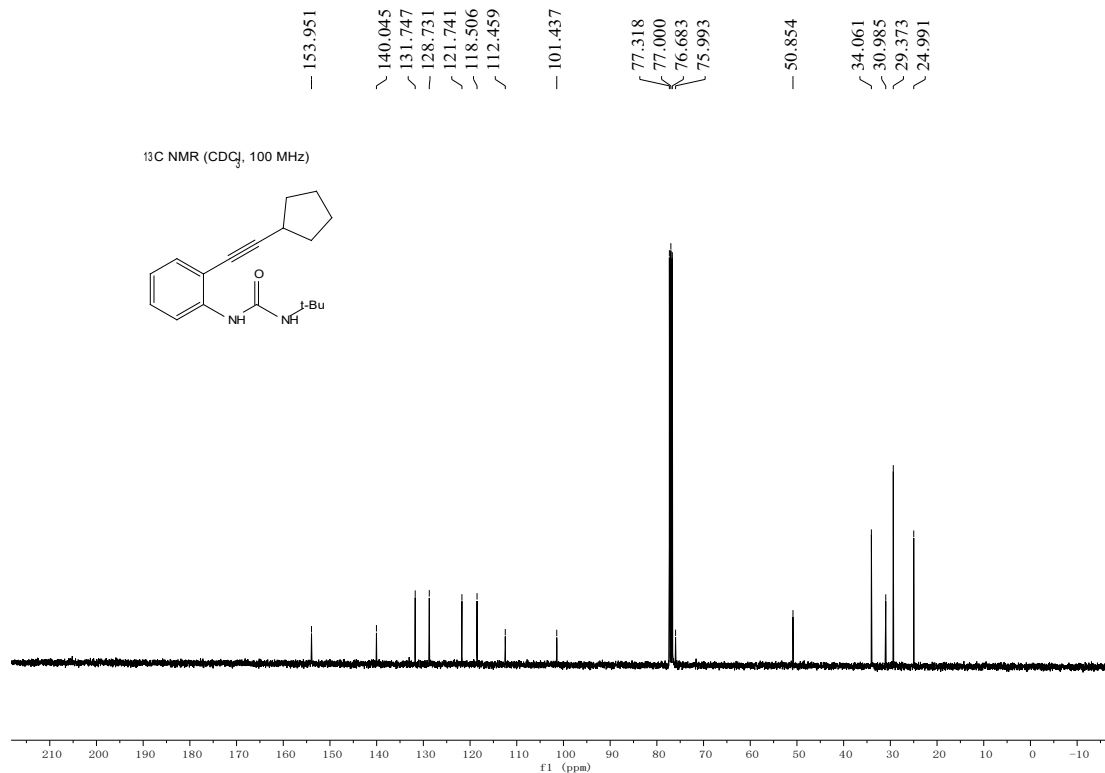


1-(*tert*-Butyl)-3-(2-(cyclopentylethynyl)phenyl)urea (4d)

^1H NMR (400 MHz, CDCl_3) of compound **4d**

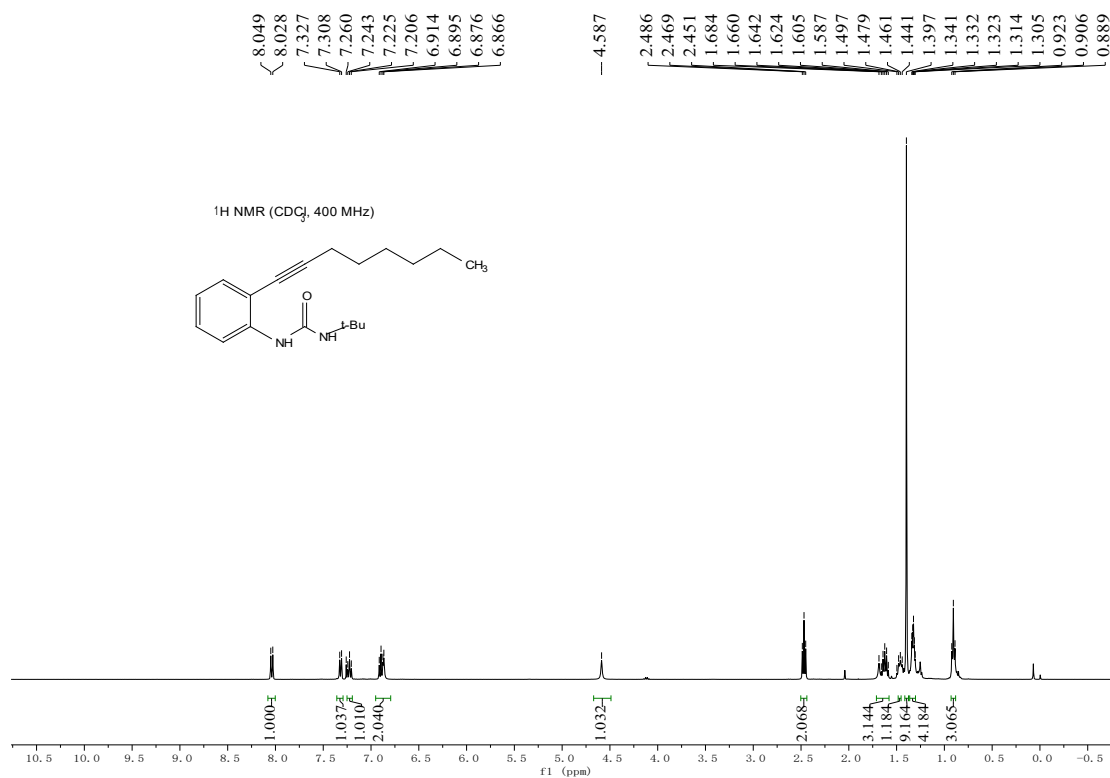


¹³C NMR (100 Mz, CDCl₃) of compound 4d

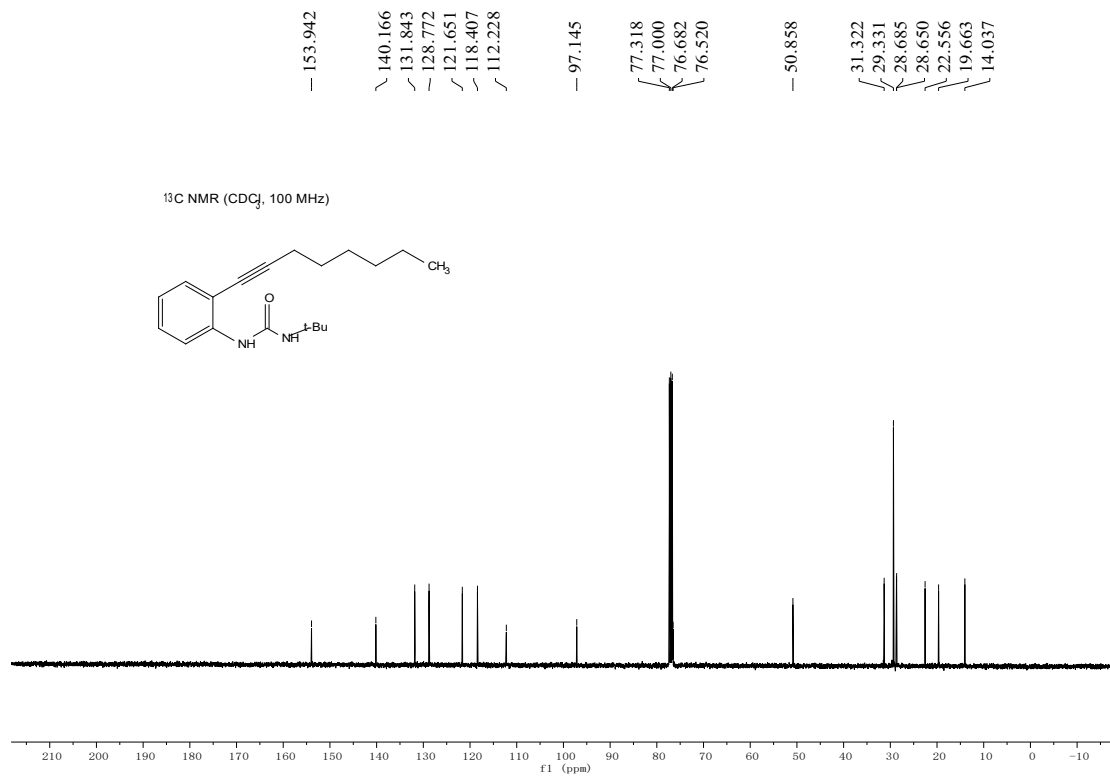


1-(*tert*-Butyl)-3-(2-(oct-1-yn-1-yl)phenyl)urea (**4e**)

¹H NMR (400 MHz, CDCl₃) of compound **4e**

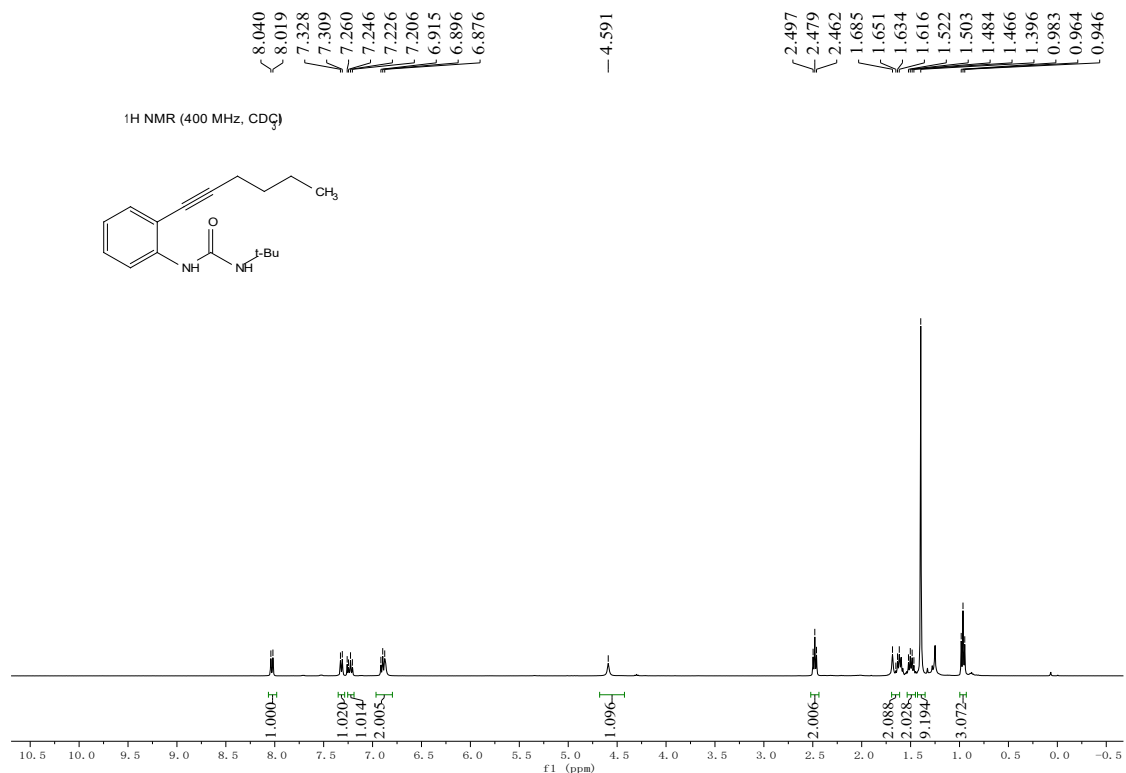


¹³C NMR (100 Mz, CDCl₃) of compound **4e**

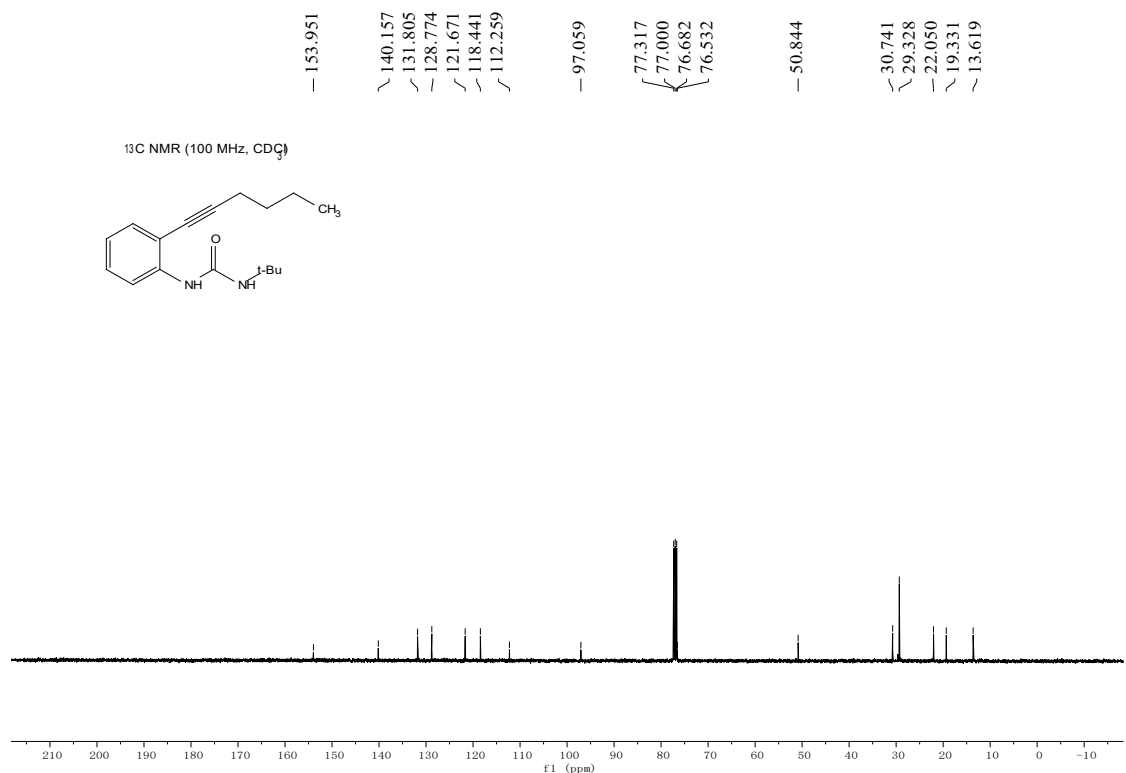


1-(*tert*-Butyl)-3-(2-(hex-1-yn-1-yl)phenyl)urea (4f)

¹H NMR (400 MHz, CDCl₃) of compound **4f**

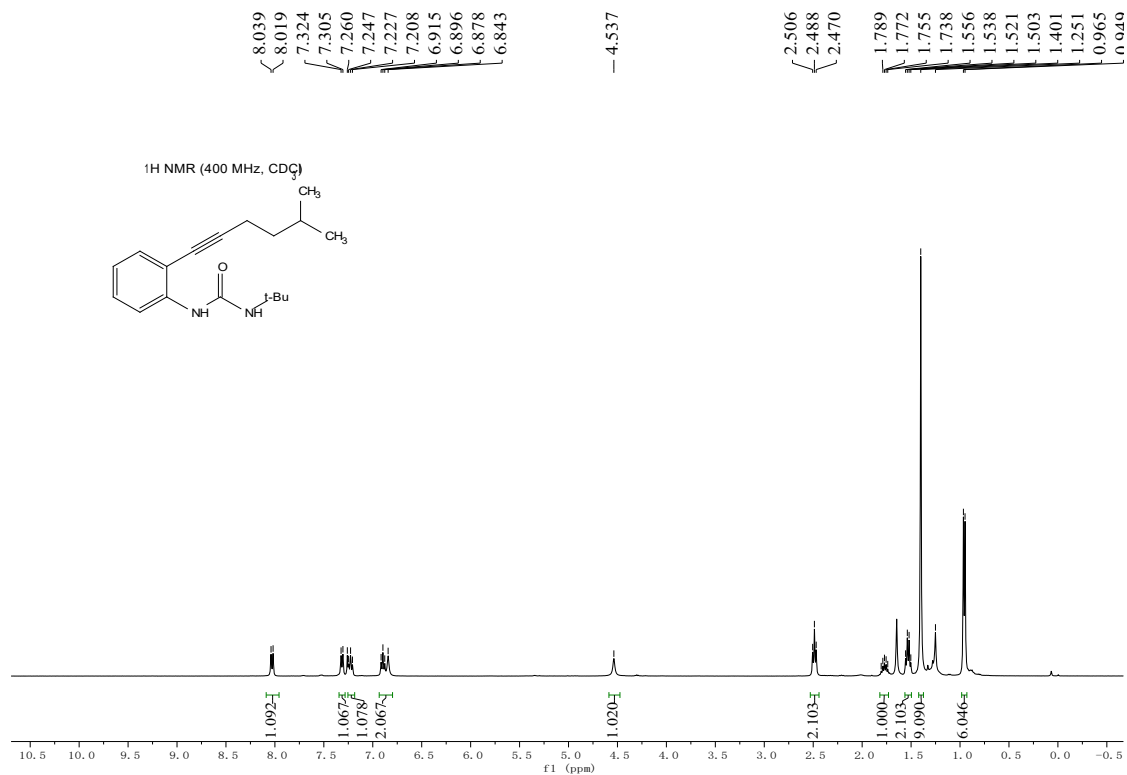


¹³C NMR (100 Mz, CDCl₃) of compound **4f**

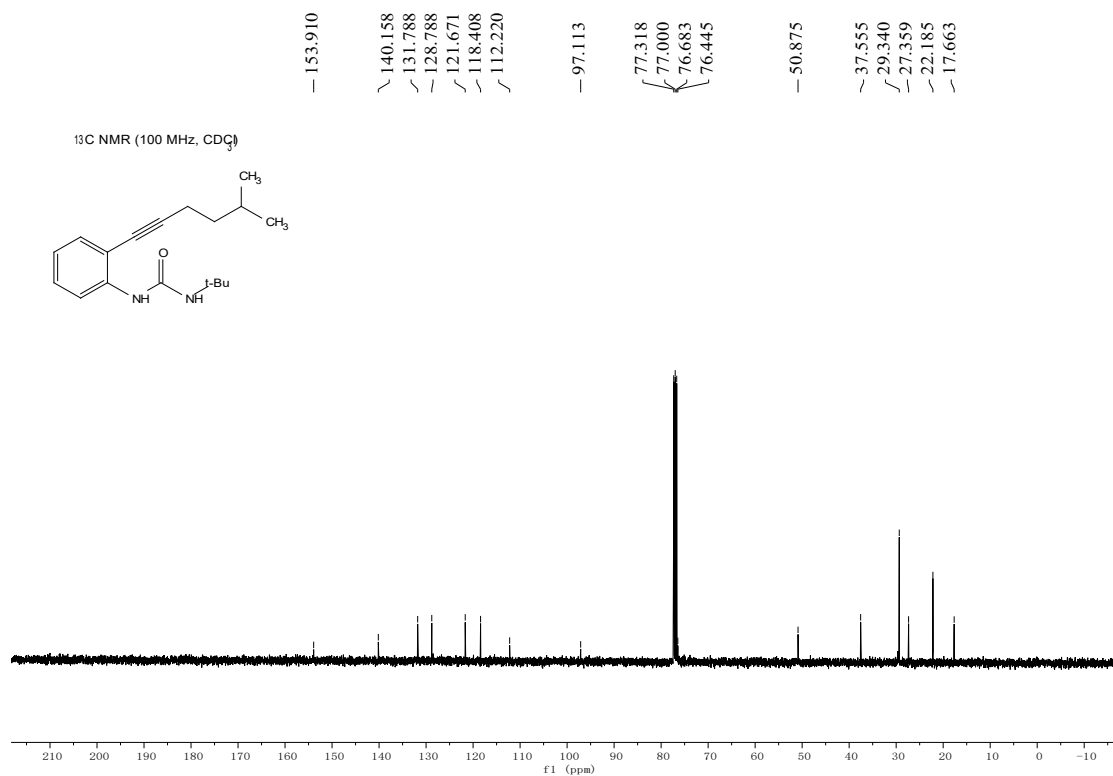


1-(*tert*-Butyl)-3-(2-(5-methylhex-1-yn-1-yl)phenyl)urea (4g)

¹H NMR (400 MHz, CDCl₃) of compound **4g**

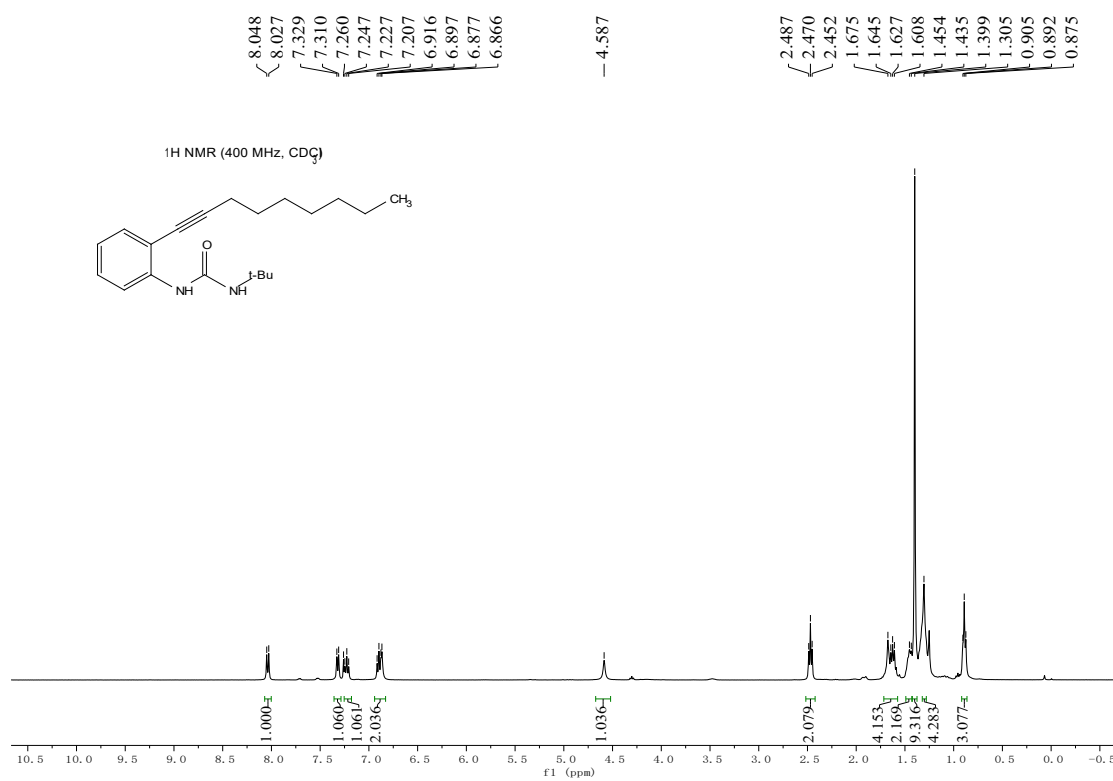


¹³C NMR (100 Mz, CDCl₃) of compound **4g**

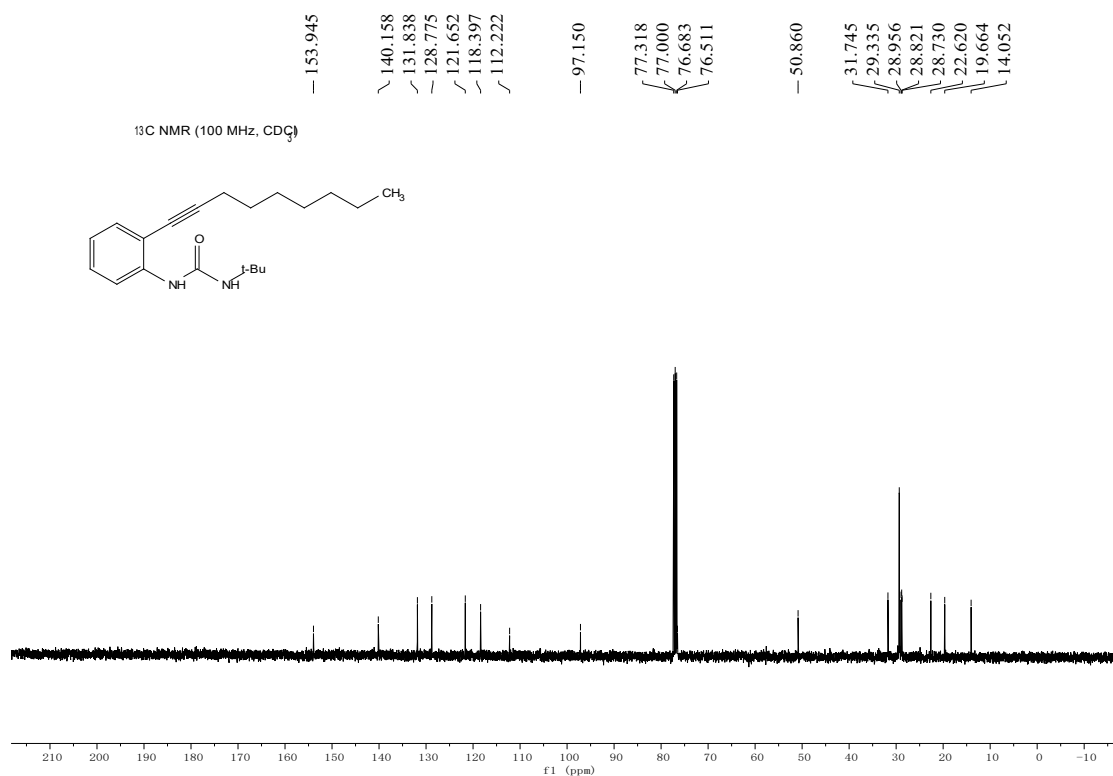


1-(*tert*-Butyl)-3-(2-(non-1-yn-1-yl)phenyl)urea (4h)

¹H NMR (400 MHz, CDCl₃) of compound 4h



^{13}C NMR (100 Mz, CDCl_3) of compound **4h**

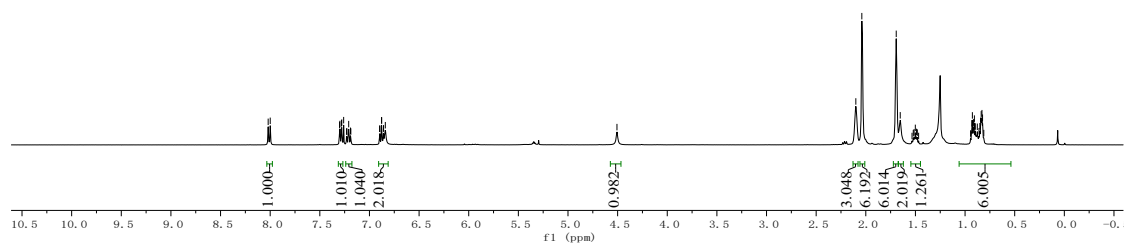
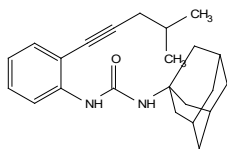


1-((1R,3S,5r,7r)-Adamantan-2-yl)-3-(2-(4-methylpent-1-yn-1-yl)phenyl)urea (4i)

^1H NMR (400 MHz, CDCl_3) of compound **4i**

8.020
8.000
7.301
7.298
7.282
7.279
7.260
7.230
7.227
7.209
7.191
7.188
6.897
6.895
6.878
6.877
6.860
6.858
6.840
4.507
2.100
2.040
1.693
1.653
1.534
1.522
1.514
1.501
1.489
1.481
1.468
0.944
0.932
0.926
0.917
0.912
0.906
0.897
0.877
0.859
0.851
0.838
0.830
0.824
0.811

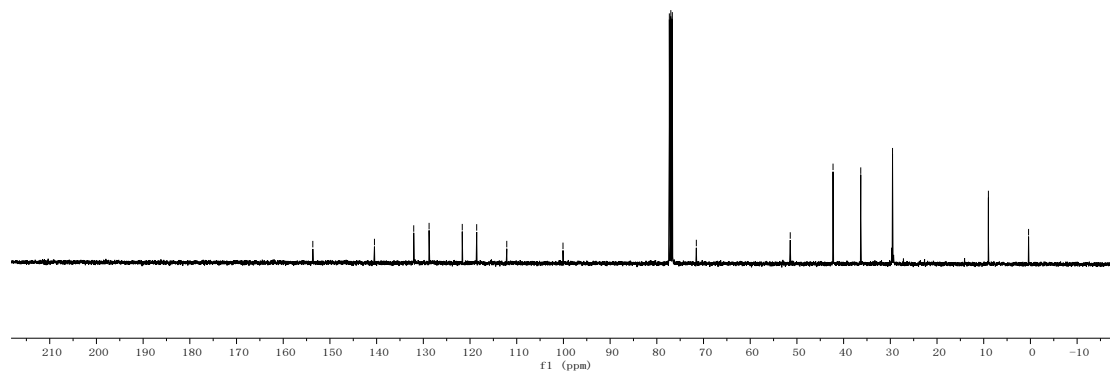
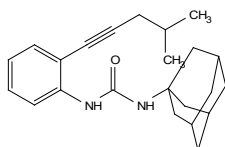
¹H NMR (CDCl₃, 400 MHz)



¹³C NMR (100 Mz, CDCl₃) of compound 4i

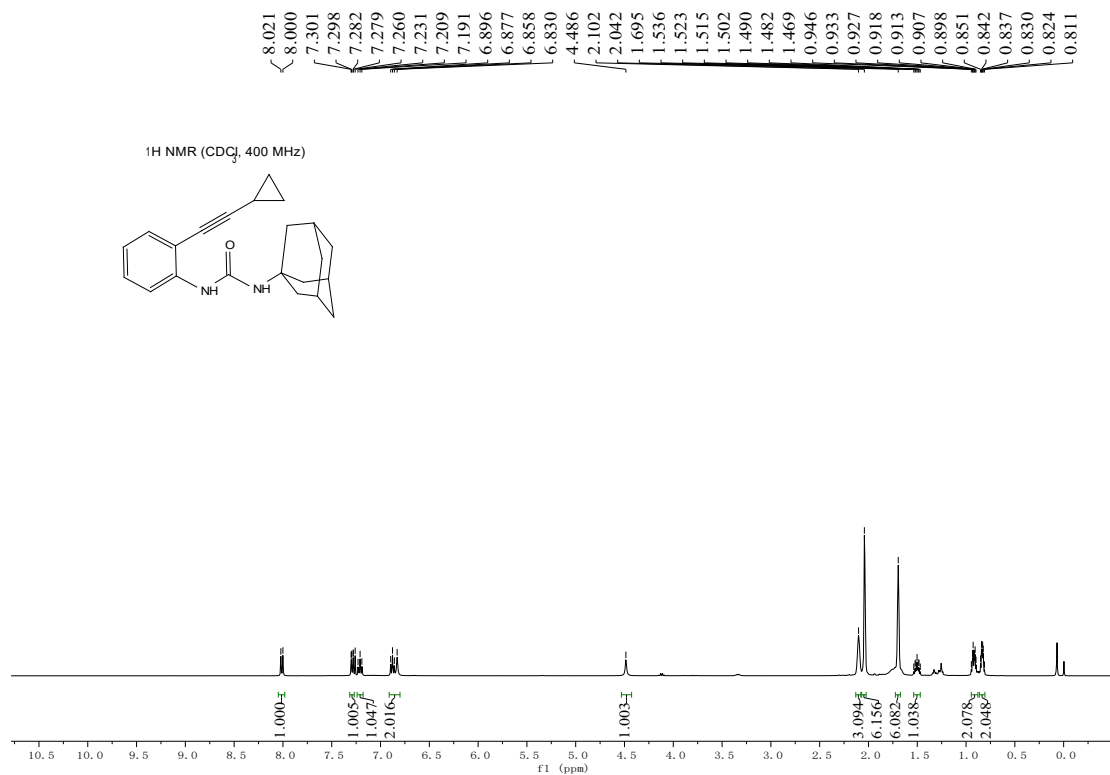
153.665
140.464
132.056
128.767
121.662
118.575
112.133
100.092
77.317
77.000
76.682
71.537
51.428
42.267
36.331
29.526
8.995
0.395

¹³C NMR (CDCl₃, 100 MHz)

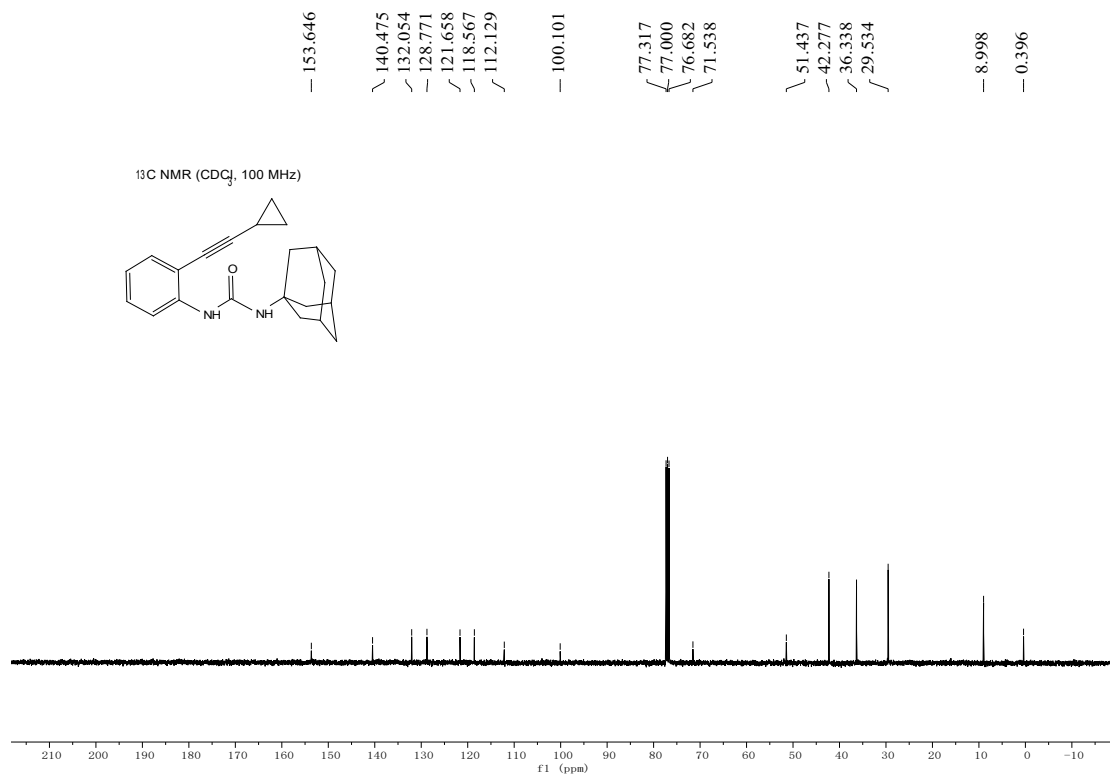


1-((1R,3S,5r,7r)-Adamantan-2-yl)-3-(2-(cyclopropylethynyl)phenyl)urea (4j**)**

¹H NMR (400 MHz, CDCl₃) of compound **4j**

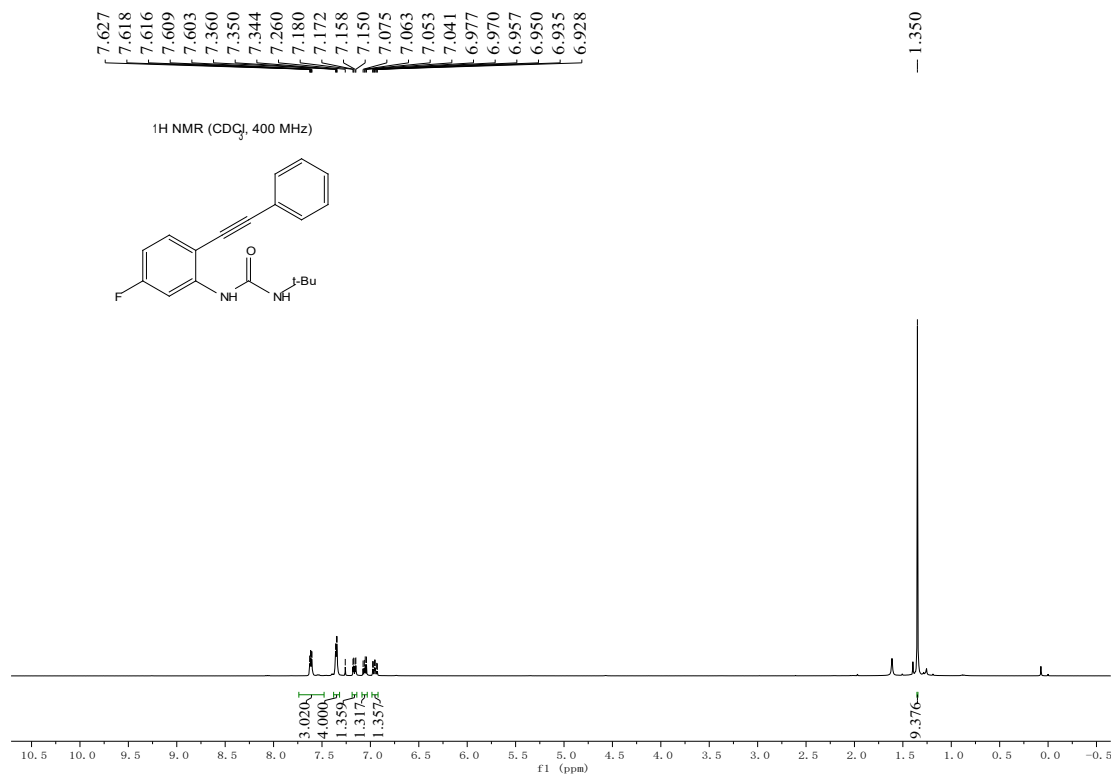


¹³C NMR (100 Mz, CDCl₃) of compound **4j**

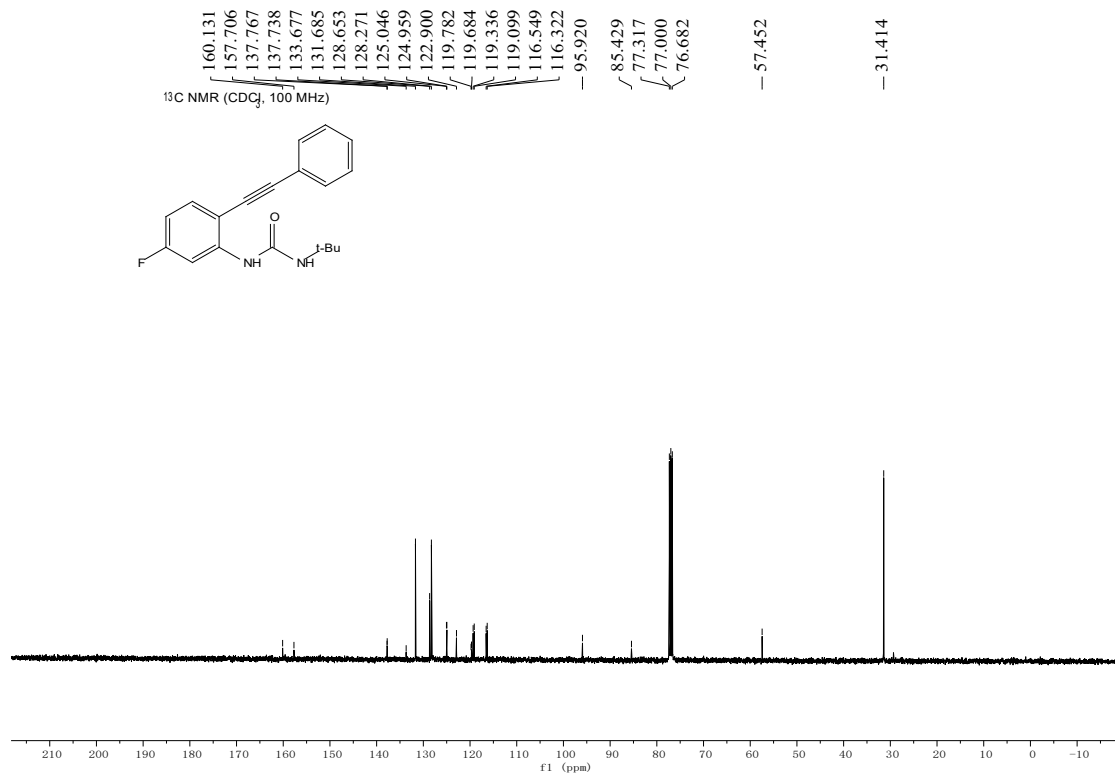


1-(*tert*-Butyl)-3-(5-fluoro-2-(phenylethynyl)phenyl)urea (4k)

¹H NMR (400 MHz, CDCl₃) of compound 4k



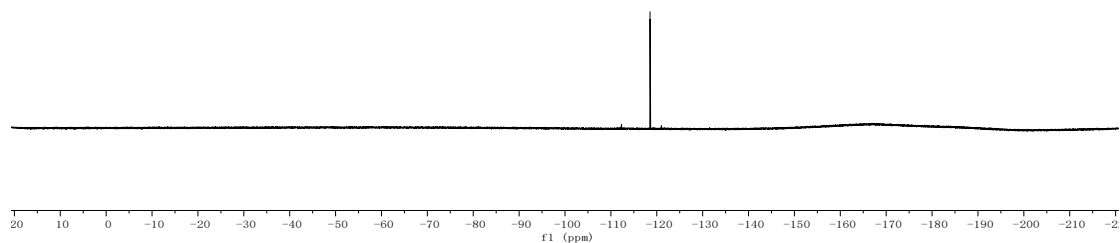
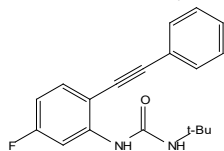
¹³C NMR (100 Mz, CDCl₃) of compound 4k



^{19}F NMR (376 MHz, CDCl_3) of compound **4k**

-118.534

^{19}F NMR (376 MHz, CDCl_3)



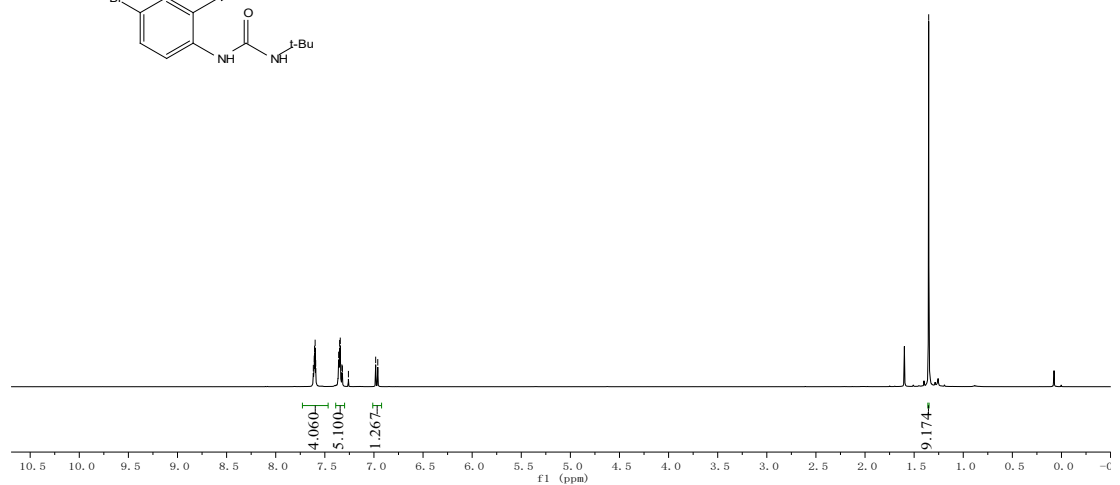
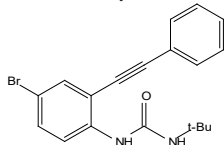
1-(4-Bromo-2-(phenylethynyl)phenyl)-3-(*tert*-Butyl)urea (**4l**)

^1H NMR (400 MHz, CDCl_3) of compound **4l**

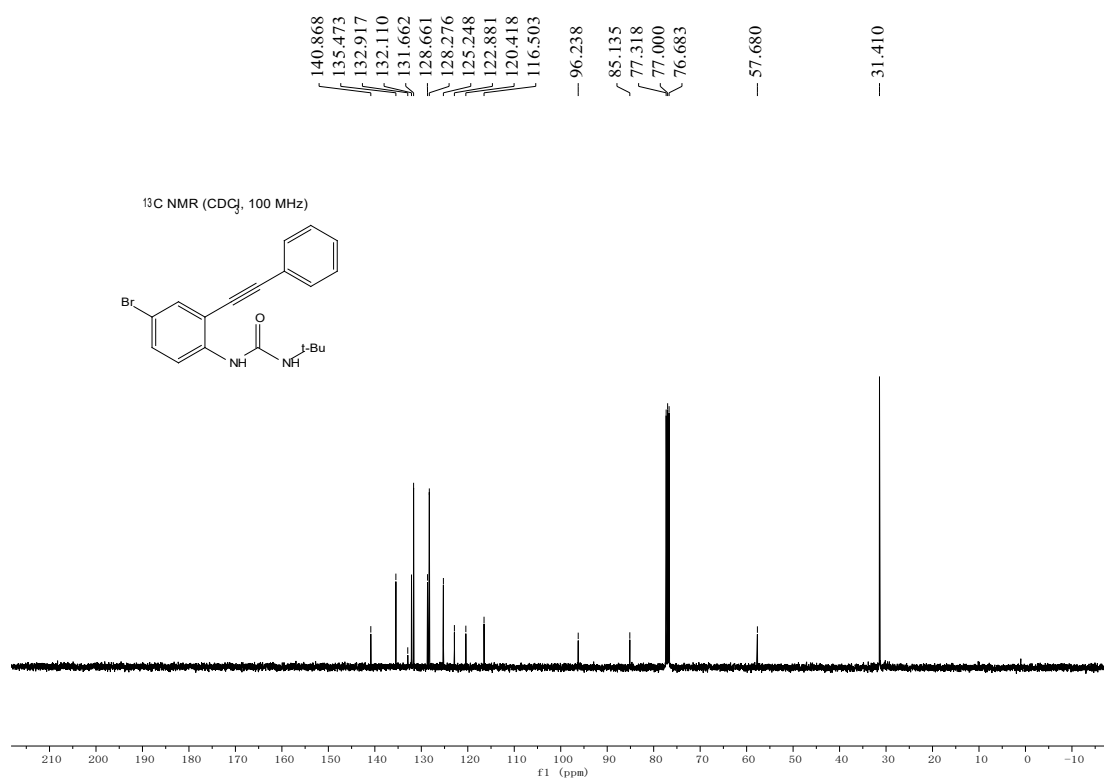
7.617
7.608
7.605
7.599
7.593
7.359
7.349
7.343
7.327
7.321
7.260
6.982
6.961

-1.352

^1H NMR (CDCl_3 , 400 MHz)

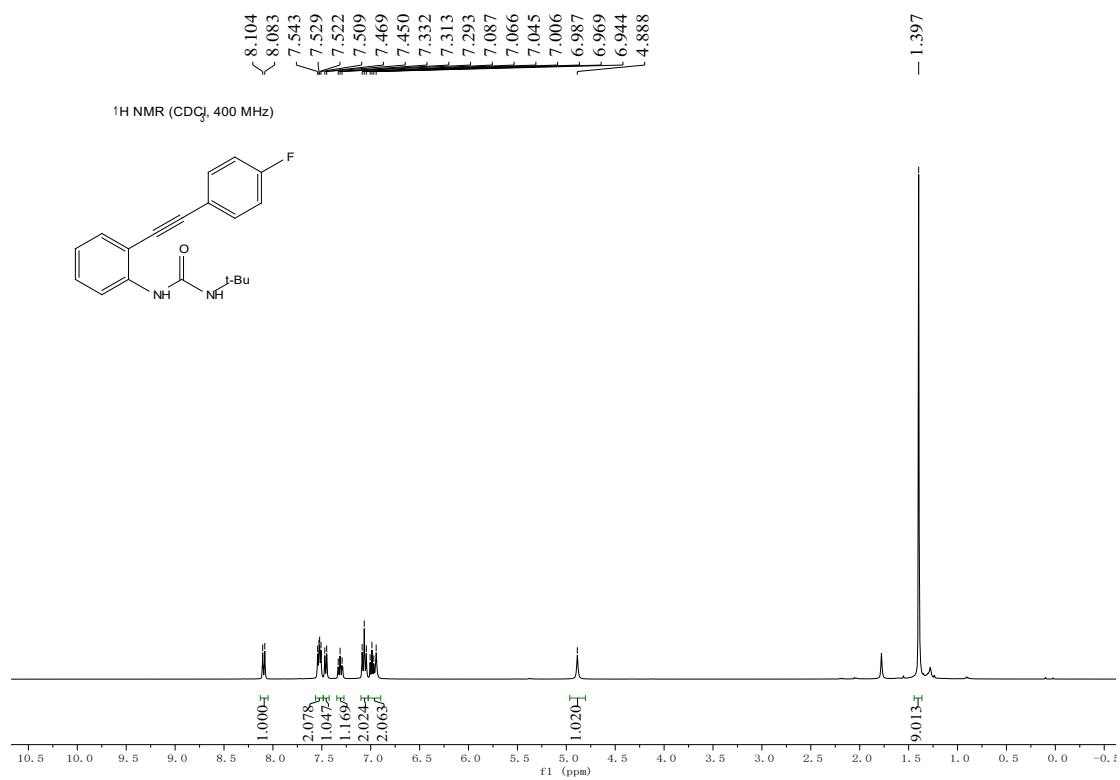


¹³C NMR (100 Mz, CDCl₃) of compound **4l**

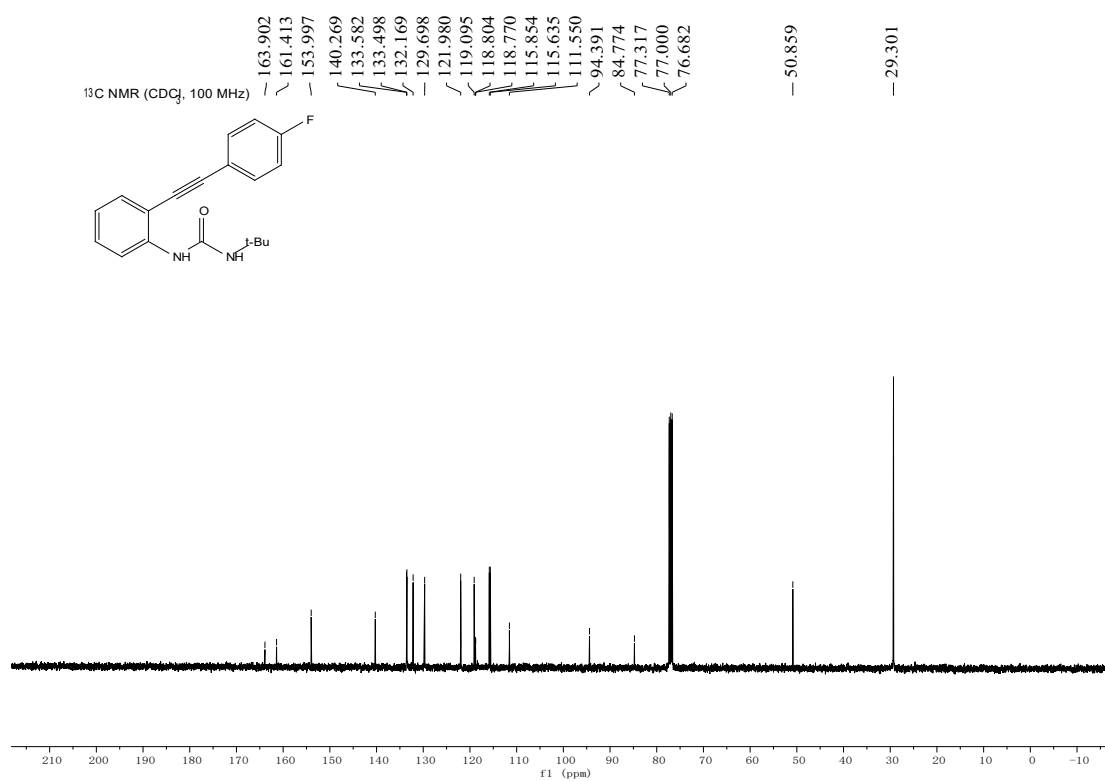


1-(*tert*-Butyl)-3-(2-((4-fluorophenyl)ethynyl)phenyl)urea (4m)

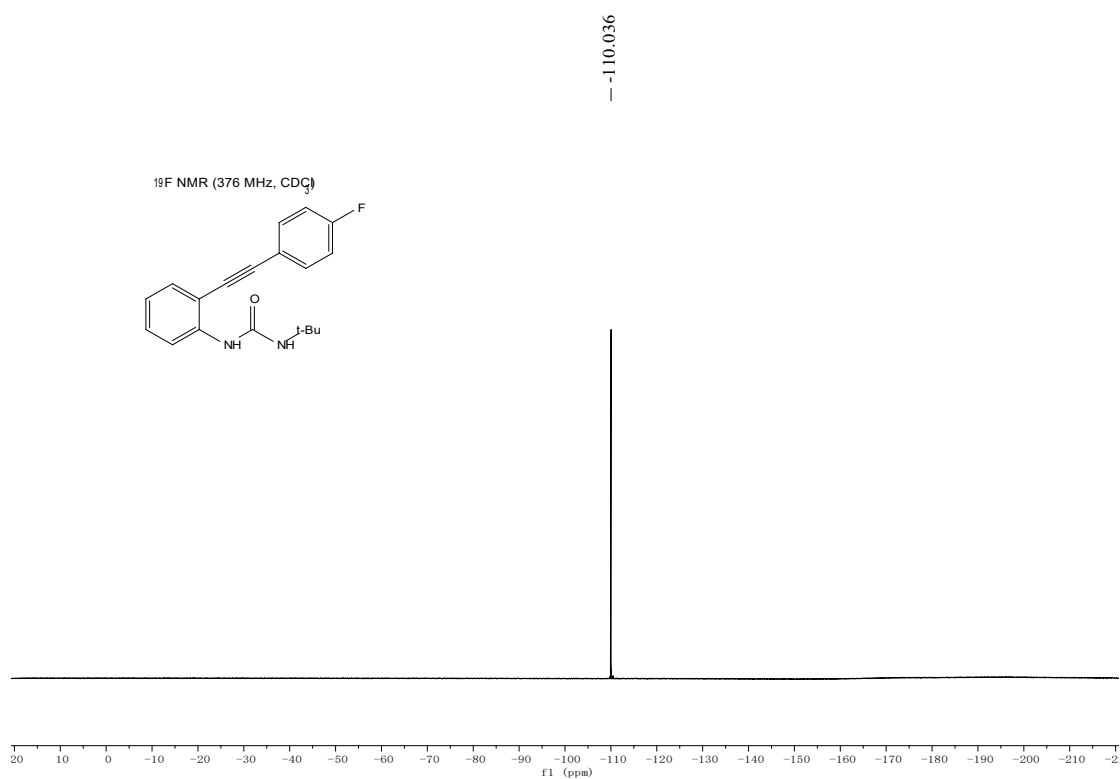
¹H NMR (400 MHz, CDCl₃) of compound **4m**



¹³C NMR (100 Mz, CDCl₃) of compound **4m**

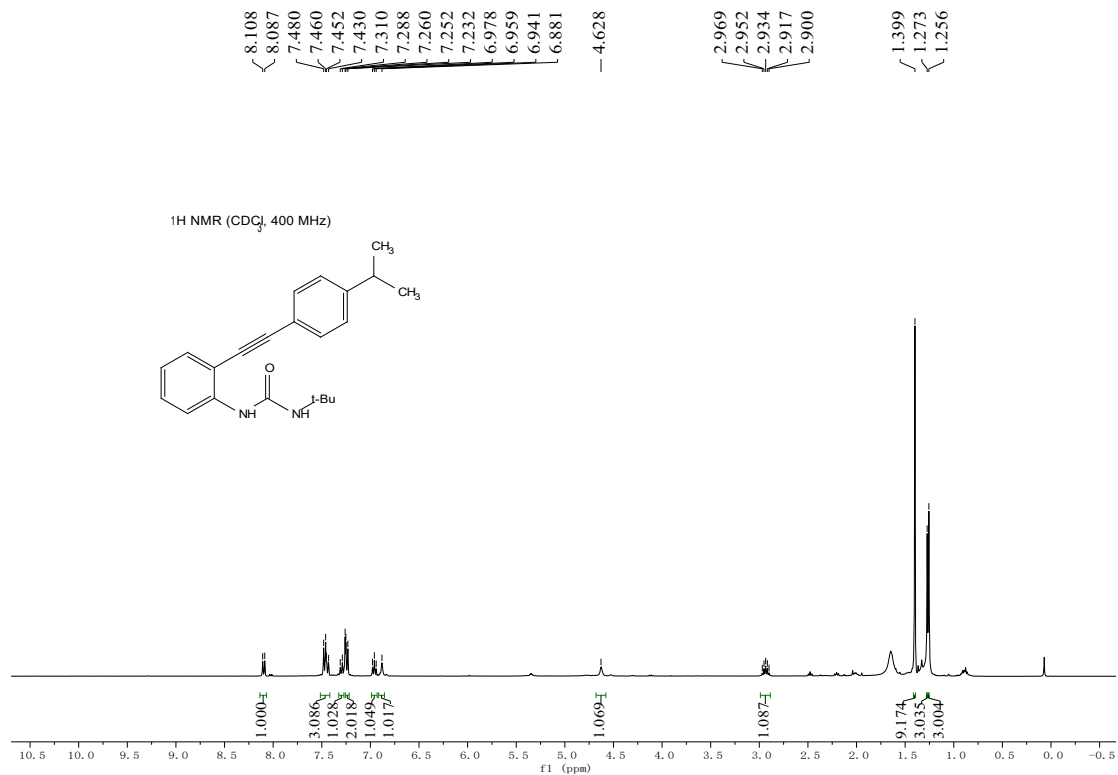


¹⁹F NMR (376 MHz, CDCl₃) of compound **4m**

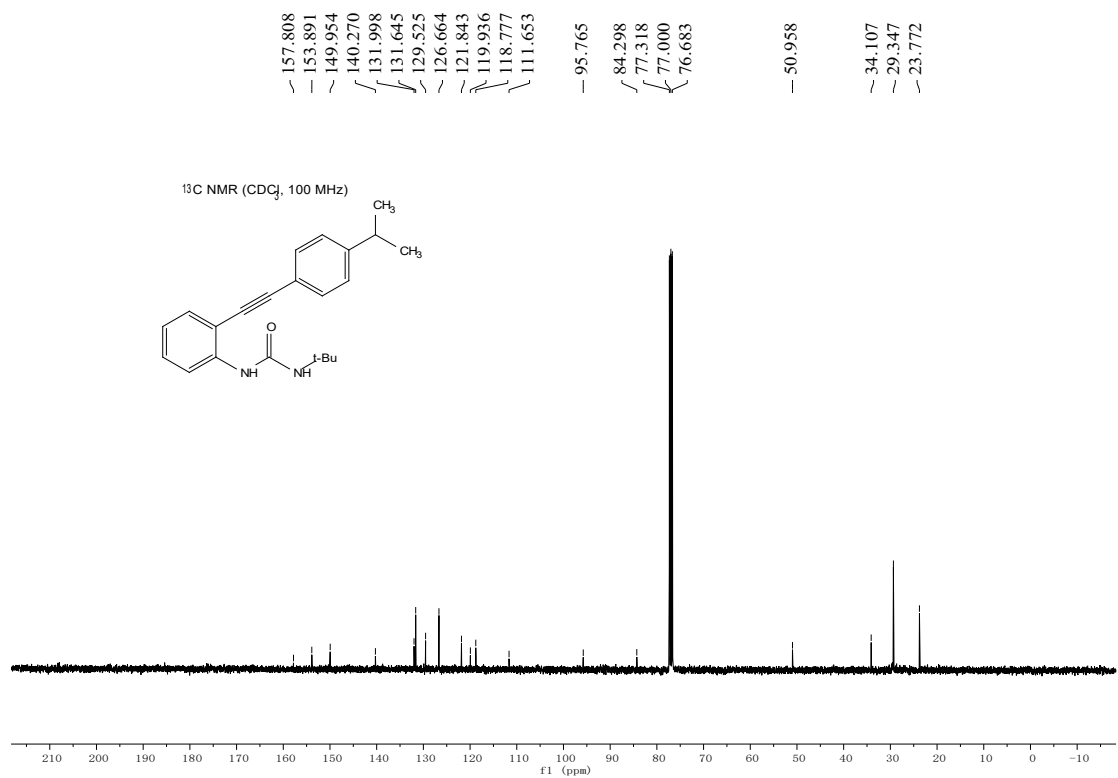


1-(*tert*-Butyl)-3-(2-((4-isopropylphenyl)ethynyl)phenyl)urea (**4n**)

¹H NMR (400 MHz, CDCl₃) of compound **4n**

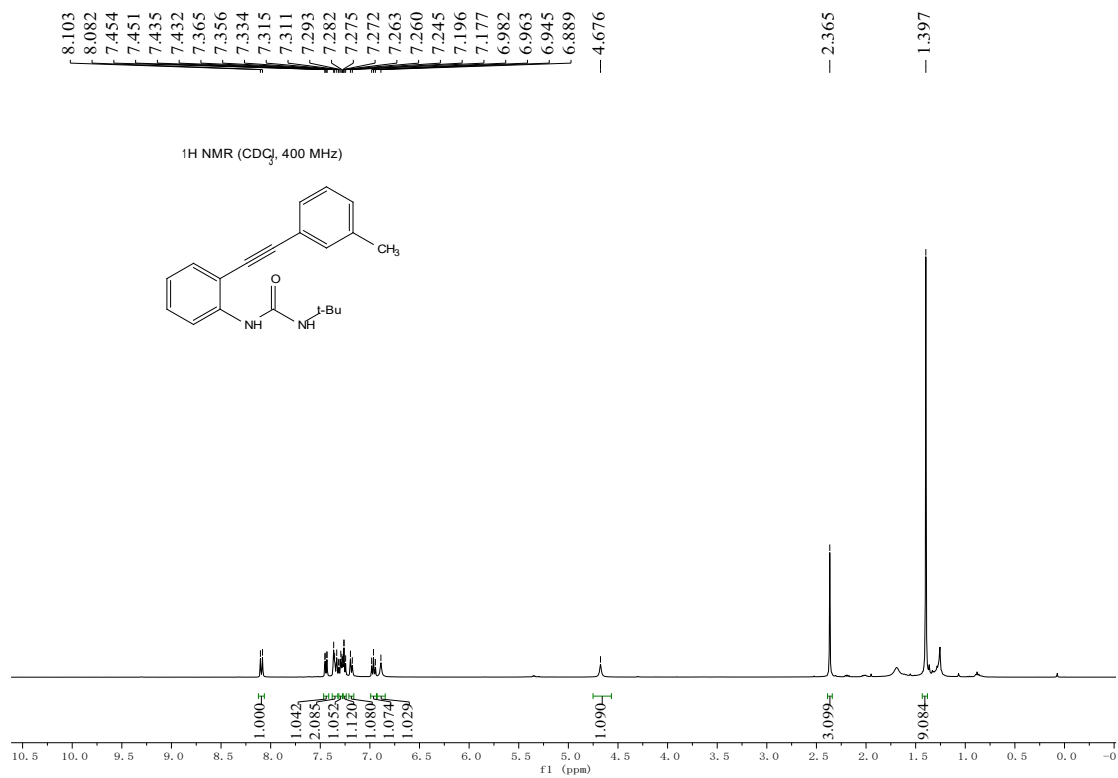


¹³C NMR (100 Mz, CDCl₃) of compound **4n**



1-(*tert*-Butyl)-3-(2-(*m*-tolylethynyl)phenyl)urea (4o)

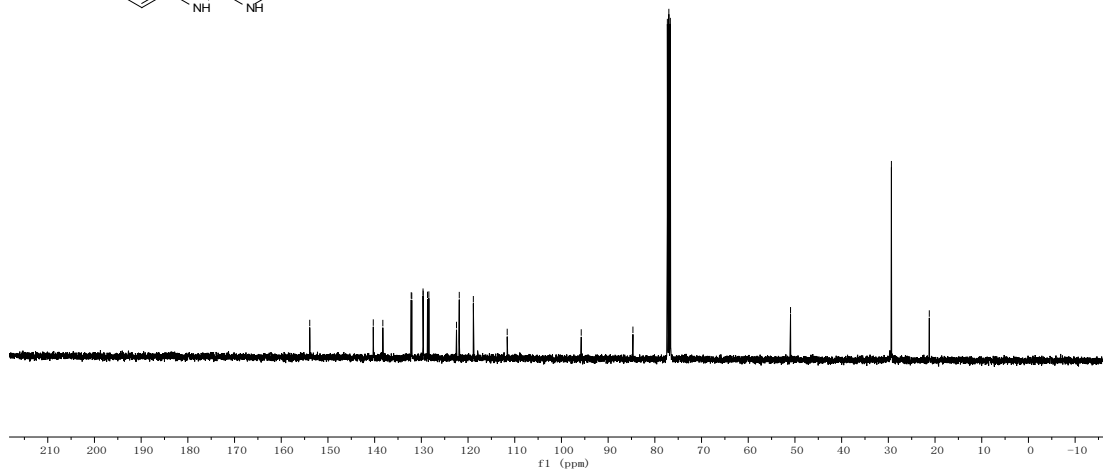
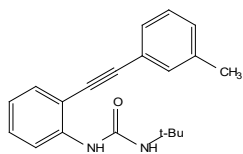
¹H NMR (400 MHz, CDCl₃) of compound **4o**



¹³C NMR (100 Mz, CDCl₃) of compound **4o**

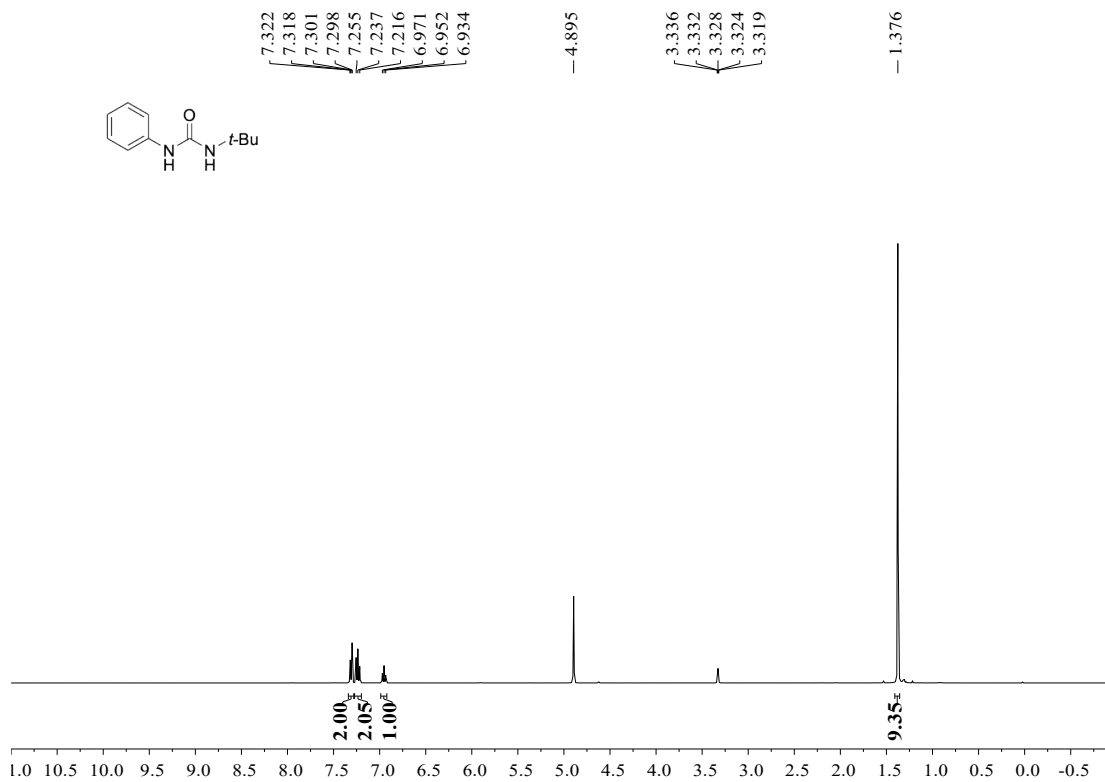
153.898
140.292
138.248
132.171
132.049
129.638
129.602
128.679
128.390
122.474
121.878
118.864
111.614
— 95.763
84.693
77.318
77.000
76.682
— 50.942
— 29.342
— 21.227

¹³C NMR (CDCl₃, 100 MHz)

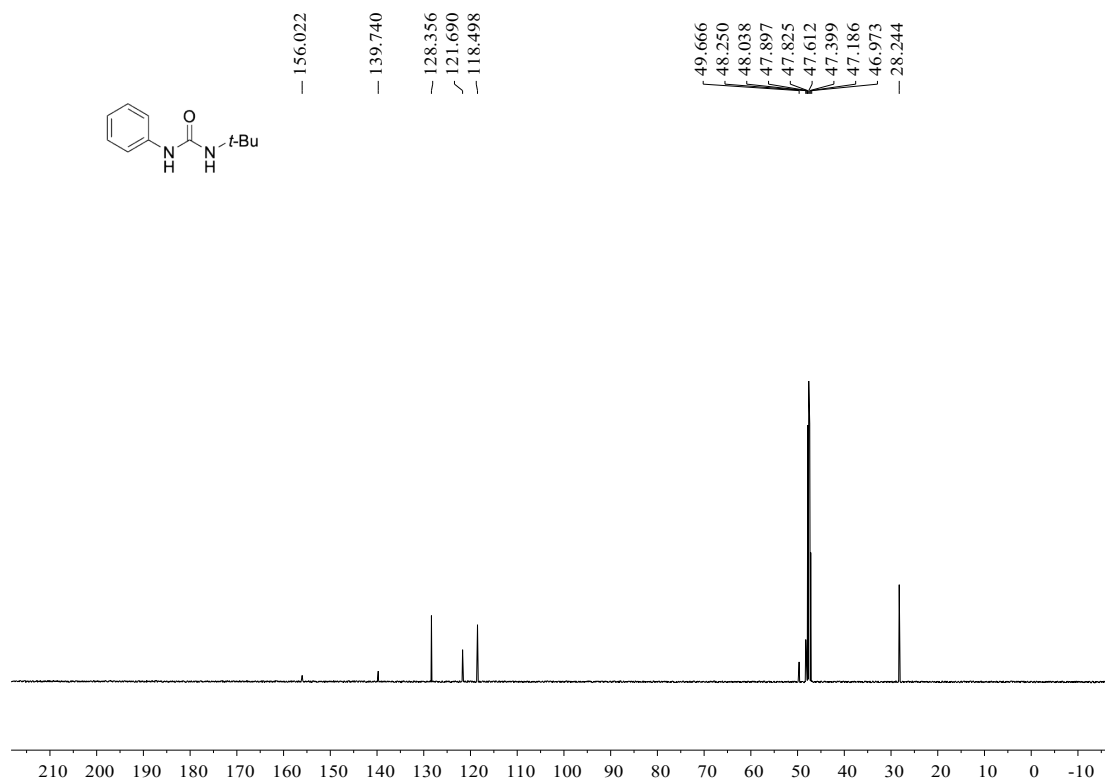


1-(*tert*-Butyl)-3-phenylurea (4p)

¹H NMR (400 MHz, MeOD) of compound 4p

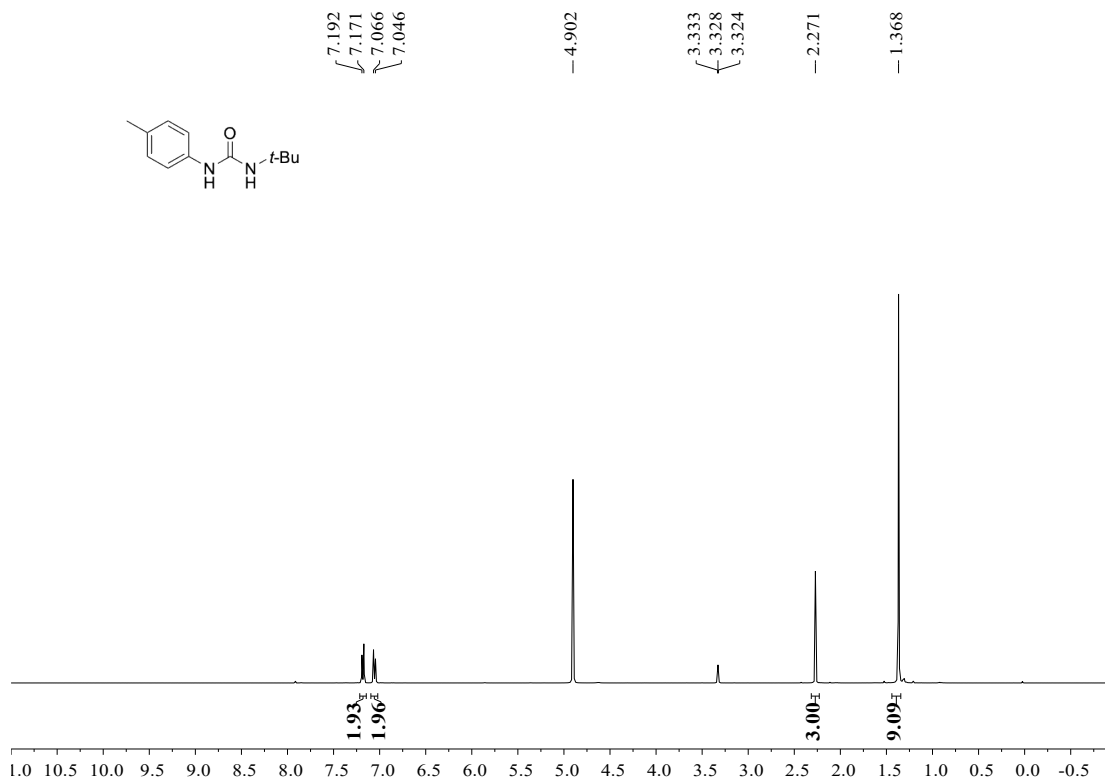


¹³C NMR (100 Mz, MeOD) of compound 4p

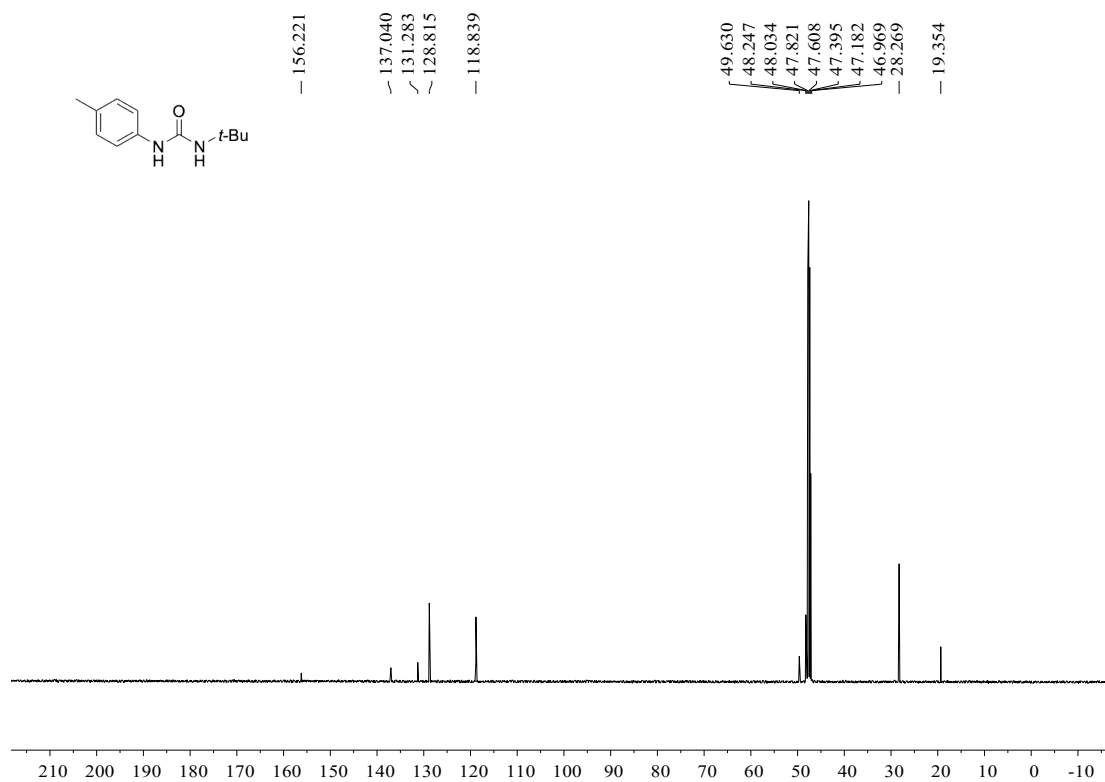


1-(*tert*-Butyl)-3-(*p*-tolyl)urea (**4q**)

¹H NMR (400 MHz, MeOD) of compound **4q**

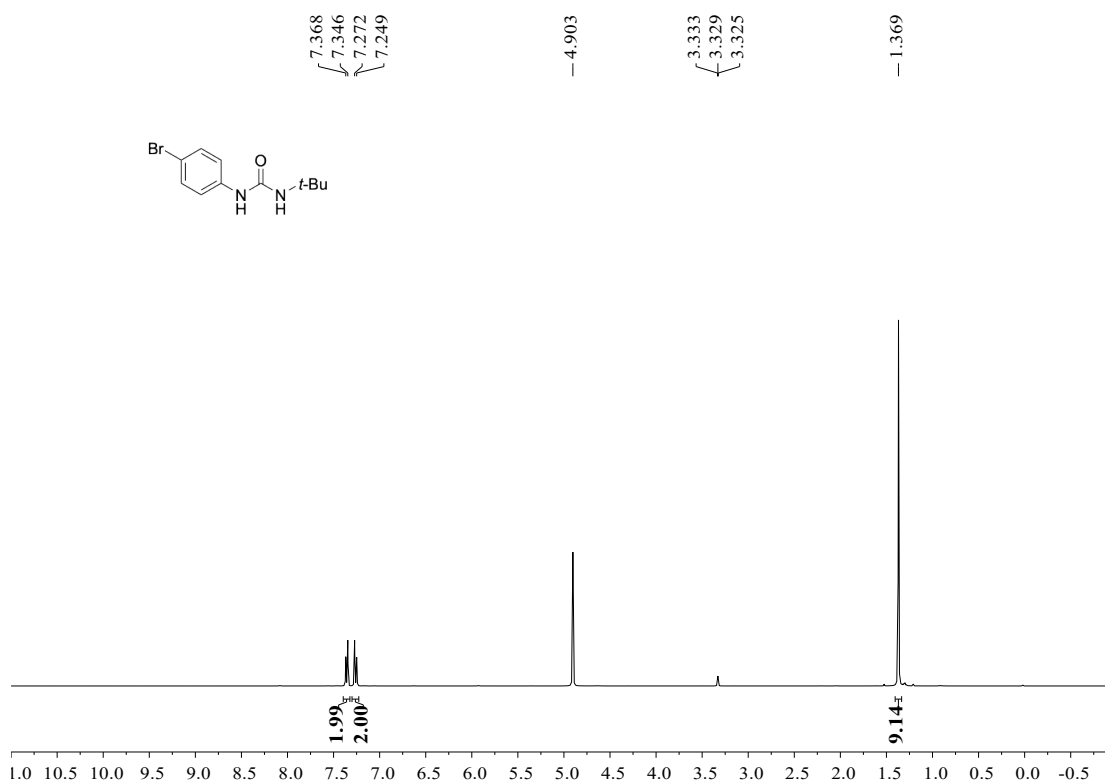


¹³C NMR (100 Mz, MeOD) of compound **4q**

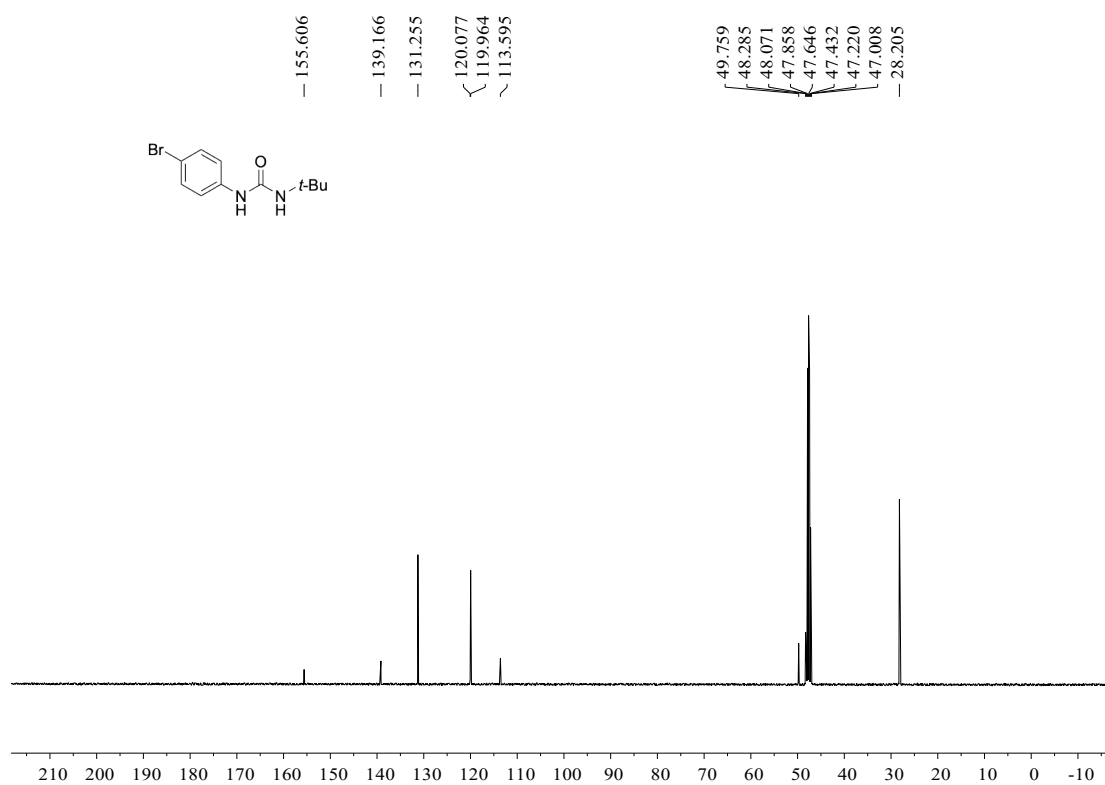


1-(4-Bromophenyl)-3-(*tert*-butyl)urea (**4r**)

¹H NMR (400 MHz, MeOD) of compound **4r**

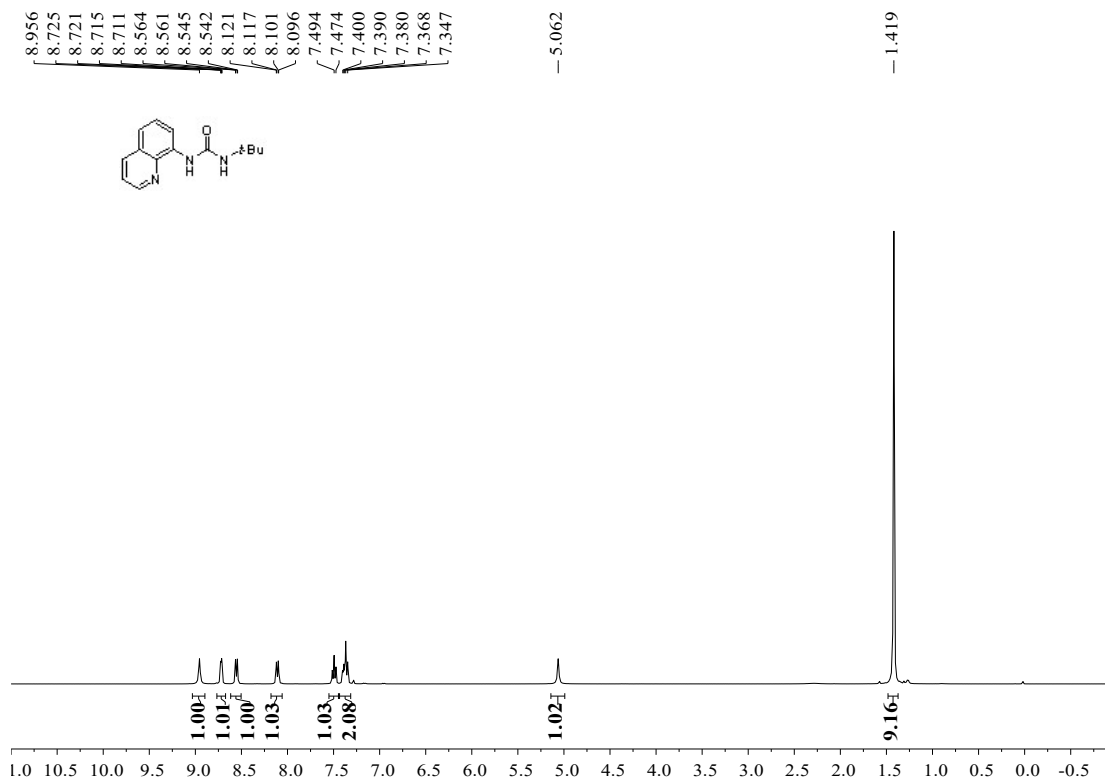


¹³C NMR (100 Mz, MeOD) of compound **4r**

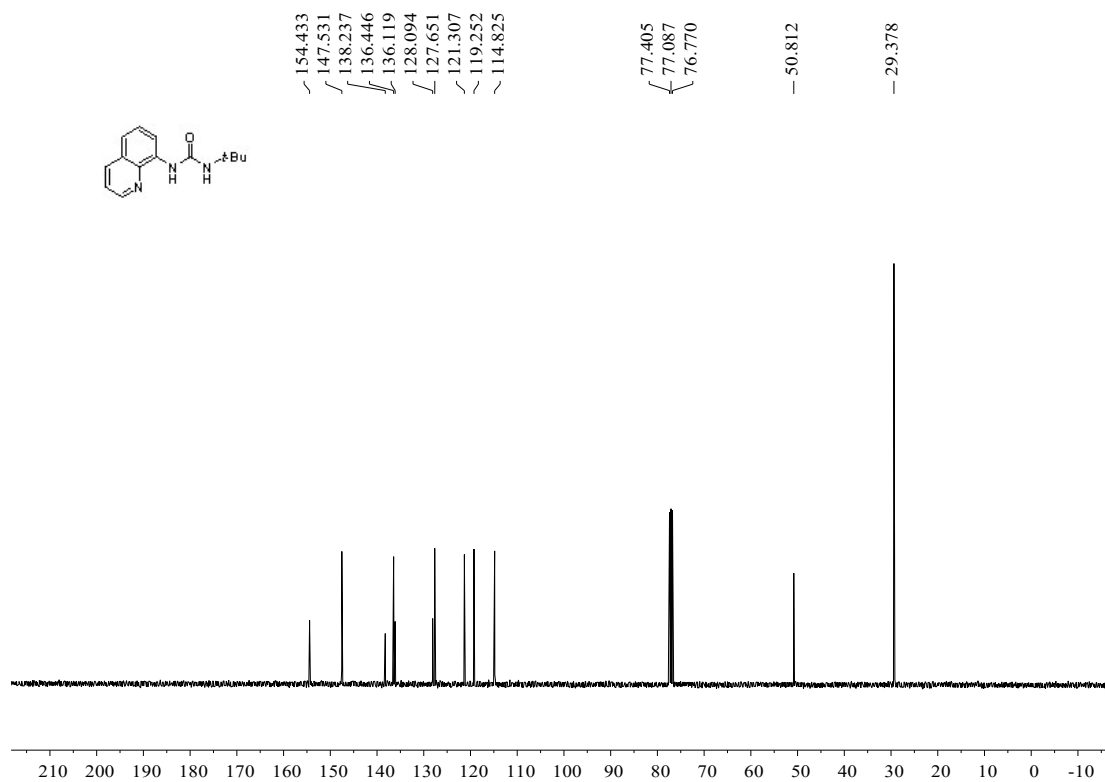


1-(4-Bromophenyl)-3-(*tert*-butyl)urea (**4s**)

^1H NMR (400 MHz, CDCl_3) of compound **4s**

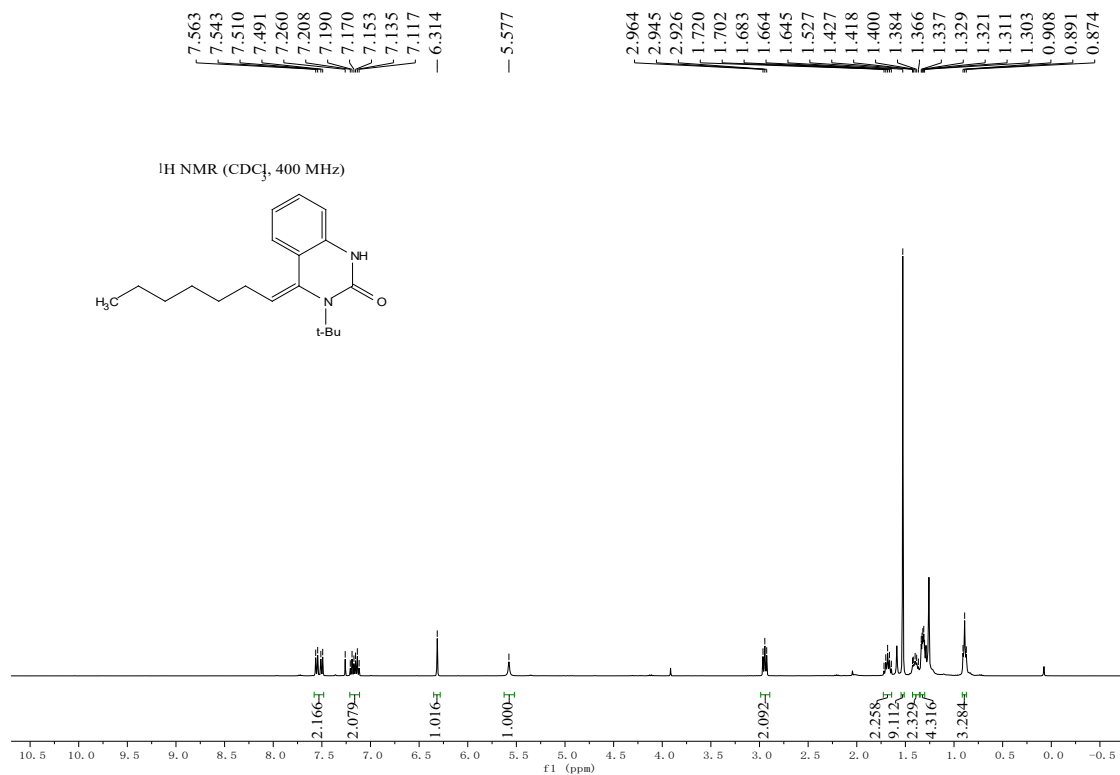


^{13}C NMR (100 Mz, CDCl_3) of compound **4s**

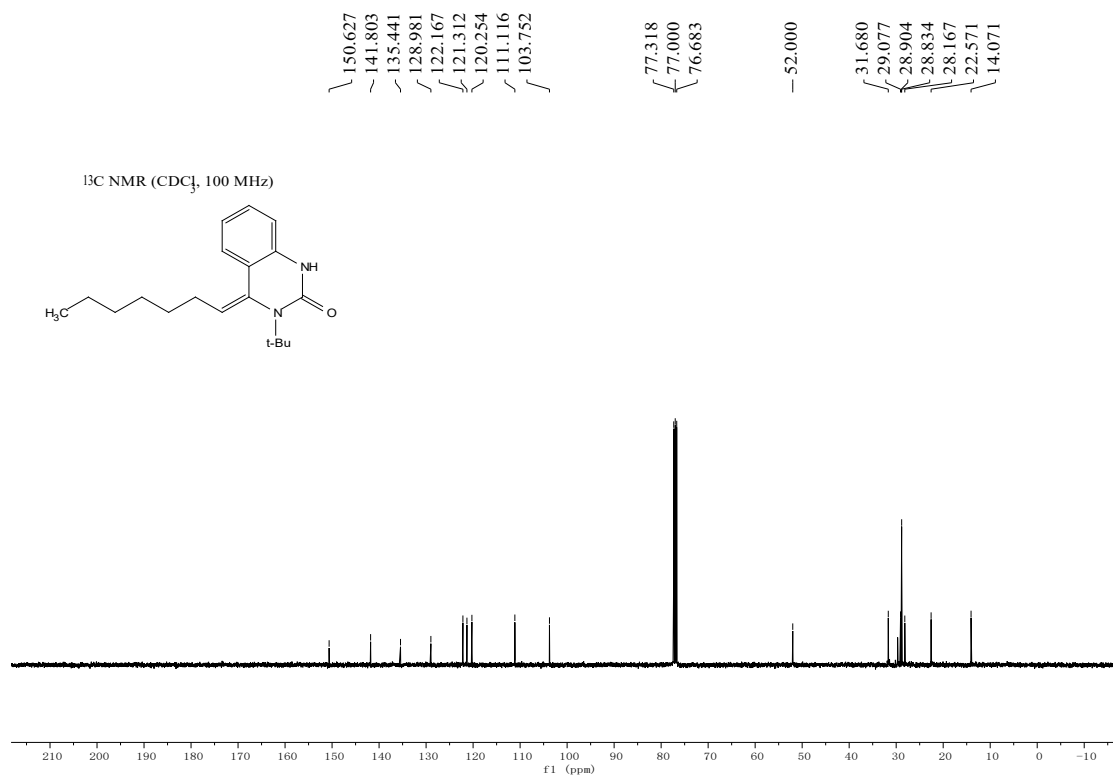


(E)-4-Heptylidene-3,4-dihydroquinazolin-2(1H)-one (5a)

¹H NMR (400 MHz, CDCl₃) of compound **5a**

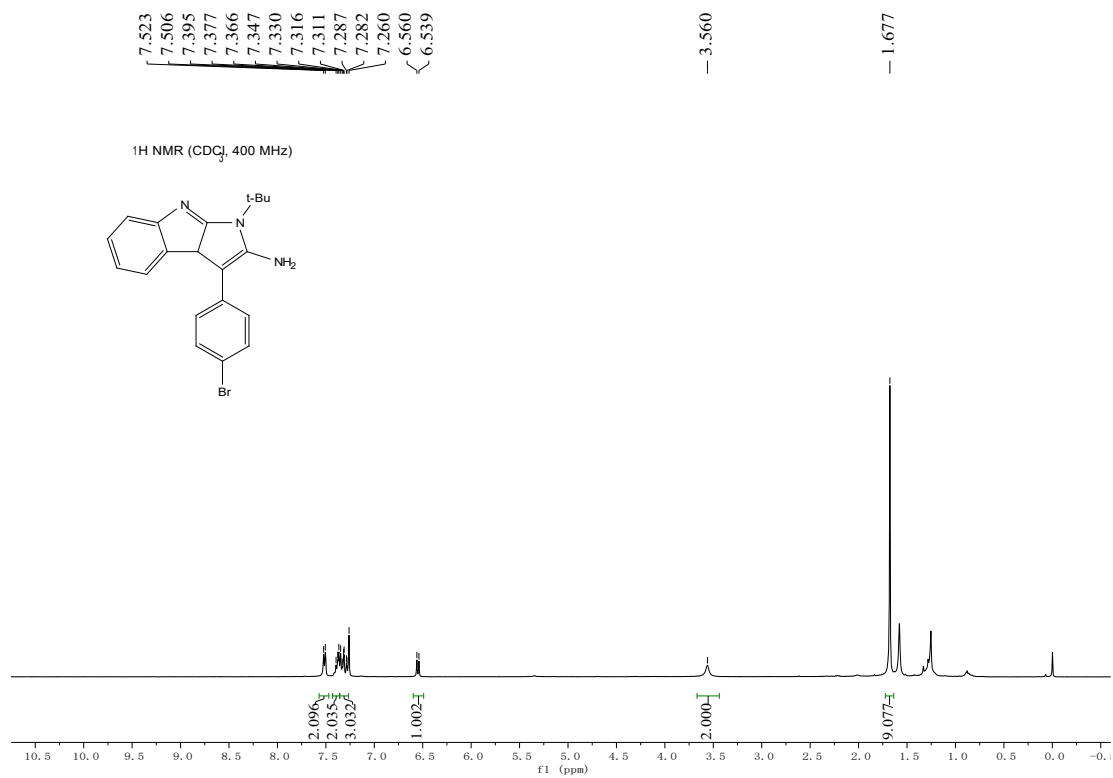


¹³C NMR (100 Mz, CDCl₃) of compound **5a**



3-(4-Bromophenyl)-1-(*tert*-butyl)-1,3a-dihydropyrrolo[2,3-*b*]indol-2-amine (6a)

¹H NMR (400 MHz, CDCl₃) of compound 6a



¹³C NMR (100 Mz, CDCl₃) of compound 6a

