Supporting information

Copper-catalyzed selective 1,2-difunctionalization of *N*-heteroaromatics through cascade C–N/C=C/C=O bond formation

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1. General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR and ^{13}C-NMR. Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-500 and referenced to 7.26 ppm and 77.16 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources (Energy chemical, J&K Chemic, TCI, Fluka, Acros, SCRC), used without further purification. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument.

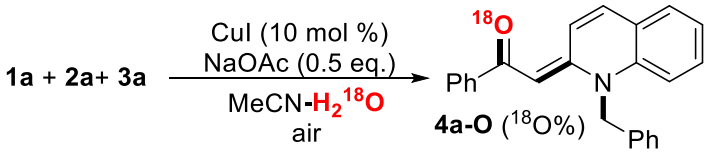
2. Typical procedure for the synthesis of the corresponding products.

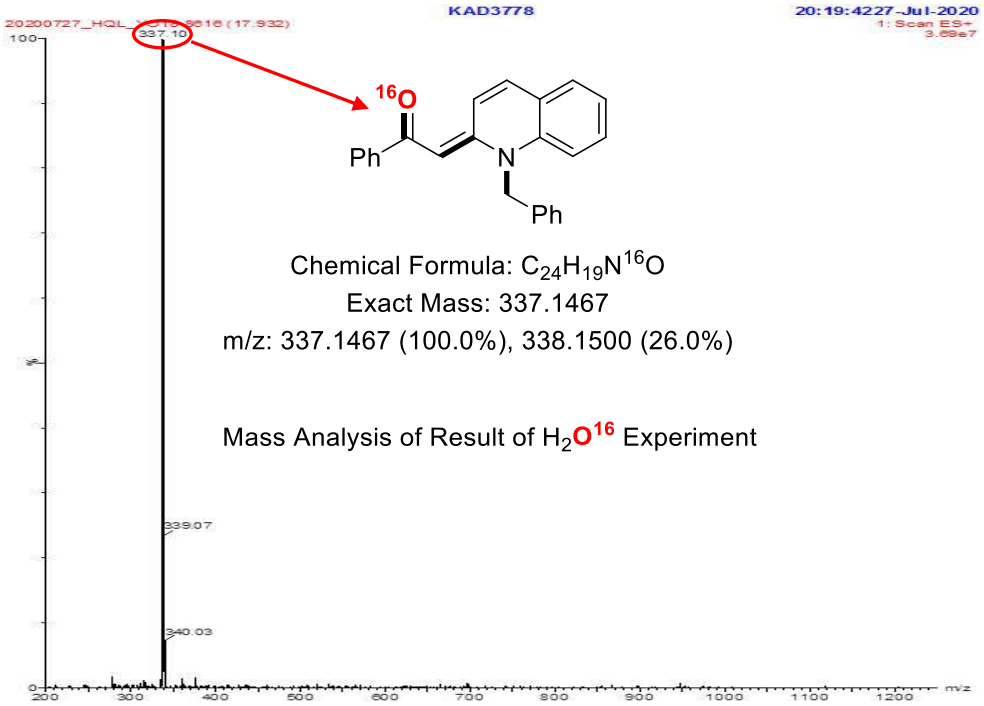
In a 25 mL Schlenk tube was combined Quinolines **1** (0.3 mmol), halides **2a** (1.0 equiv), terminal alkynes **3** (1.2 equiv), CuI (10 mol %), NaOAc (1.0 equiv), and 1.0 mL of mixed solvent (MeCN-H_2O = 6/1). The mixture was then stirred at 60 ℃ under oil-bath heating for 8 h under air atmosphere. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether (60-90 ℃): ethyl acetate (5:1) to give the corresponding products.

Synthesis of *(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-phenylethan-1-one(4a)*: In a 25 mL Schlenk tube was combined quinoline **1** (1 mmol), benzyl bromide **2a** (1.0 equiv), phenylacetylene **3a** (1.2 equiv), CuI (10 mol %), NaOAc (1.0 equiv), and 3.0 mL of mixed solvent (MeCN-H_2O = 6/1). The mixture was then stirred at 60 ℃ under oil-bath heating for 8 h under air atmosphere. Then the mixture was subjected to column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) to give the desired product **4a** as a yellow solid (821.8 mg, 81% yield).

3. The control experiments

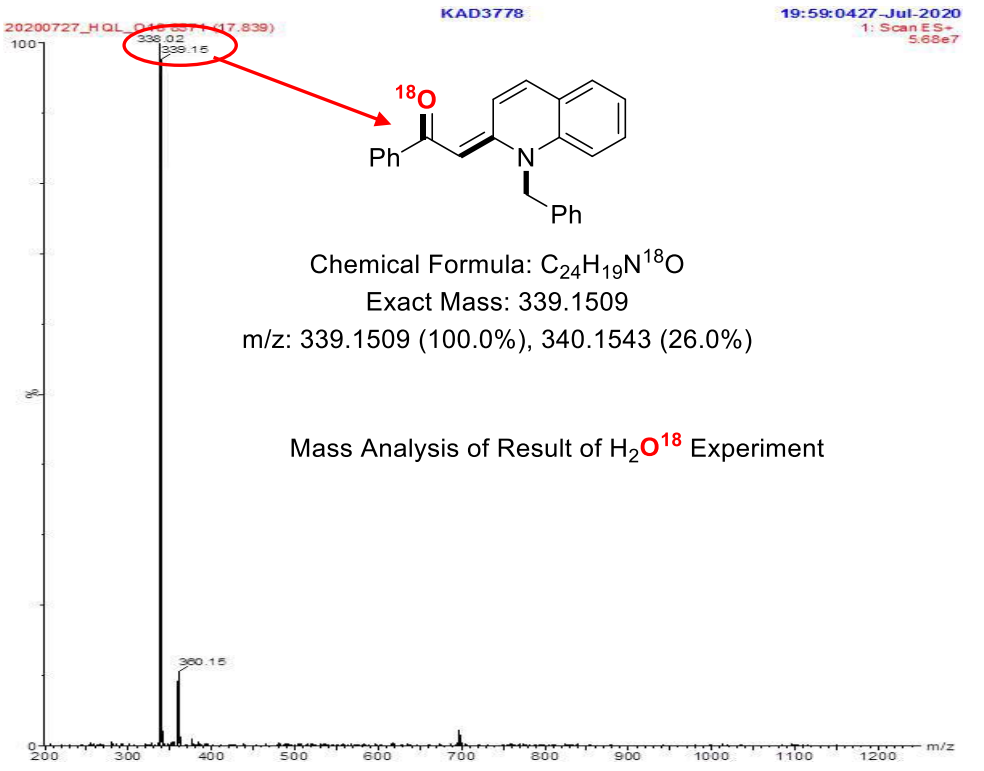
Mass Analysis about Results of H_2O^{18} Experiment:





Chemical Formula: $C_{24}H_{19}N^{16}O$
Exact Mass: 337.1467
m/z: 337.1467 (100.0%), 338.1500 (26.0%)

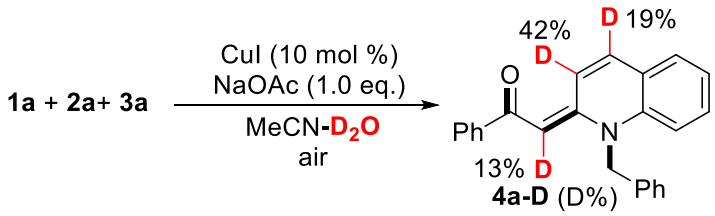
Mass Analysis of Result of H_2O^{16} Experiment

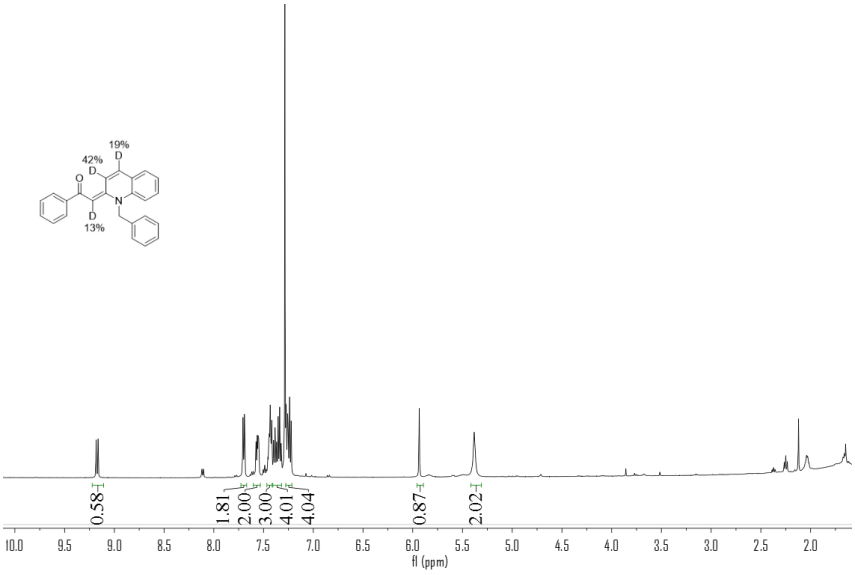


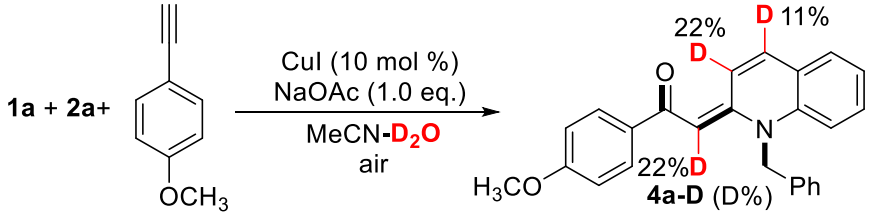
Chemical Formula: $C_{24}H_{19}N^{18}O$
Exact Mass: 339.1509
m/z: 339.1509 (100.0%), 340.1543 (26.0%)

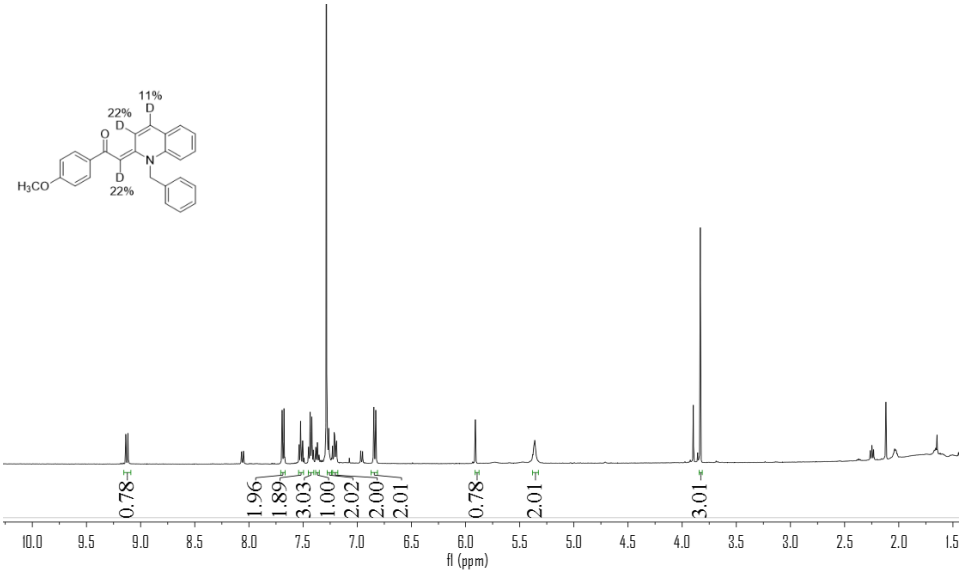
Mass Analysis of Result of H_2O^{18} Experiment

H NMR analysis about results of D_2O experiment:



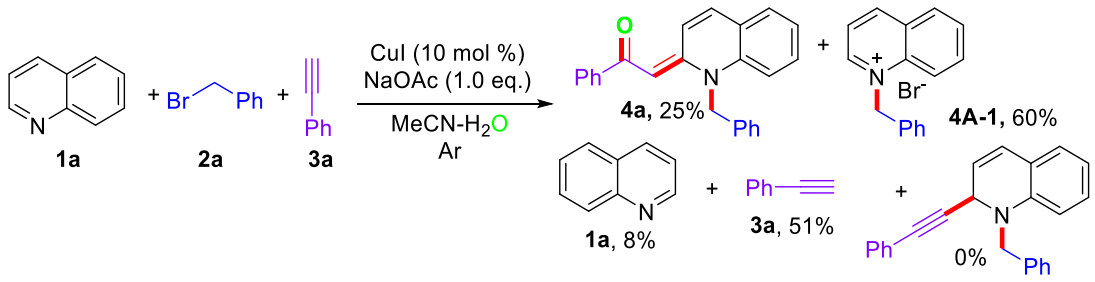






The control experiments

The reaction was carried out under a strict argon atmosphere, and the result is as shown in the figure below, and it was not detected the simple alkyne addition product.



4. Single crystal X-ray diffraction of 5a

Experimental. Single yellow block-shaped crystals of (**5a**) were obtained by recrystallisation from dichlormethane. A suitable crystal (0.22×0.20×0.18) mm^3 was selected and collected on a Bruker APEX-II CCD diffractometer. The data were refined by full-matrix least-squares techniques on F^2 with SHELXTL-2014. And the structures were solved by direct methods SHELXS-2014. All the non-hydrogen atoms were refined anisotropically. The ellipsoid contour 50% probability levels in the caption for the image of the structure. An ORTEP representation of the structure is shown below.

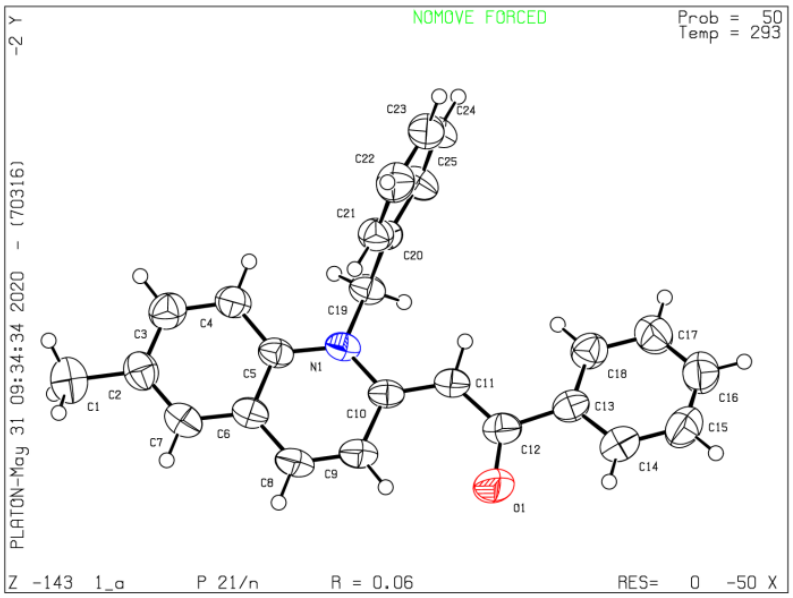


Figure 1. ORTEP drawing of **5a** with the numbering scheme.

Crystal data and structure refinement for **5a** (CCDC: 2024307)

Identification code	5a	
Empirical formula	C25 H21 N O	
Formula weight	351.43	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.197(2) Å	α= 90 °.
	b = 10.1129(18) Å	β= 96.198(17) °.

	c = 16.499(3) Å γ = 90 °.
Volume	1857.4(6) $Å^3$
Z	4
Density (calculated)	1.257 Mg/m^3
Absorption coefficient	0.076 mm^{-1}
F(000)	744
Crystal size	0.220 x 0.200 x 0.180 mm^3
Theta range for data collection	2.908 to 29.355 °.
Index ranges	-12<=h<=14, -12<=k<=13, -22<=l<=14
Reflections collected	8757
Independent reflections	4292 [R(int) = 0.0232]
Completeness to theta = 25.242 °	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4292 / 0 / 245
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0573, wR2 = 0.1293
R indices (all data)	R1 = 0.1129, wR2 = 0.1587
Extinction coefficient	n/a
Largest diff. peak and hole	0.235 and -0.194 $e.Å^{-3}$

5. Single crystal X-ray diffraction of 5l

Experimental. Yellow and transparent block-like single crystals of **5l** were grown by layering a dichlormethane solution with n-hexane at ambient temperature. A suitable crystal (0.22×0.20×0.18) mm^3 was selected and collected on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 296(2) K during data collection. The data were refined by full-matrix least-squares techniques on F^2 with SHELXTL-2014. And the structures were solved by direct methods SHELXS-2014. All the non-hydrogen atoms were refined anisotropically. The ellipsoid contour 50% probability levels in the caption for the image of the structure. An ORTEP representation of the structure is shown below.

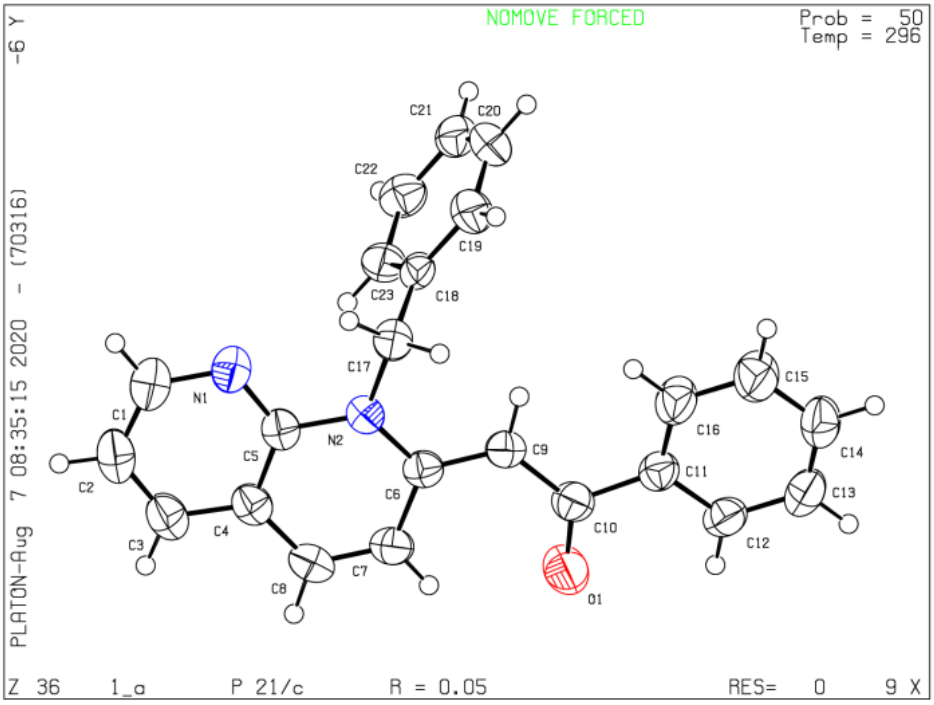


Figure 1. ORTEP drawing of **5l** with the numbering scheme.

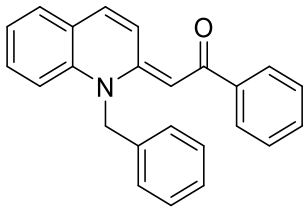
Crystal data and structure refinement for **5l**. (CCDC: 2024309)

Identification code	5l
Empirical formula	C23 H18 N2 O
Formula weight	338.39
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$

Unit cell dimensions	a = 10.951(2) Å	α= 90 °.
	b = 16.186(3) Å	β= 114.346(3) °.
	c = 10.841(2) Å	γ = 90 °.
Volume	1750.7(6) $Å^3$	
Z	4	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	712	
Crystal size	0.220 x 0.200 x 0.180 mm^3	
Theta range for data collection	2.041 to 27.609 °.	
Index ranges	-14<=h<=14, -20<=k<=21, -14<=l<=10	
Reflections collected	10682	
Independent reflections	4051 [R(int) = 0.0281]	
Completeness to theta = 25.242 °	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4051 / 0 / 235	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1161	
R indices (all data)	R1 = 0.0681, wR2 = 0.1307	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.147 and -0.210 $e.Å^{-3}$	

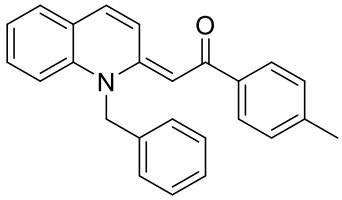
6. Analytical data of the obtained compounds

(1)



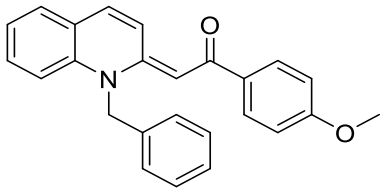
(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-phenylethan-1-one(4a). Yellow solid (86.0 mg, 85% yield), m.p: 180-182 ℃; R_f = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (d, J = 9.8 Hz, 1H), 7.70 (d, J = 7.1 Hz, 2H), 7.57 – 7.53 (m, 2H), 7.41 (dt, J = 16.0, 7.2 Hz, 4H), 7.35 (q, J = 7.0 Hz, 3H), 7.26 (d, J = 7.4 Hz, 2H), 7.23 (t, J = 7.6 Hz, 2H), 5.94 (s, 1H), 5.38 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.4, 153.3, 142.7, 140.3, 134.4, 134.2, 130.9, 130.4, 129.3, 128.3, 128.1, 127.8, 127.3, 126.1, 123.7, 122.9, 122.8, 114.9, 91.8, 52.3. IR (KBr): 3422, 3052, 2922, 1631, 1483, 1438, 1341, 1217, 1150, 875, 749, 700 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{20}NO[M+H]^+$: 338.1539; found 338.1535.

(2)



(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(p-tolyl)ethan-1-one(4b). Yellow solid (92.7 mg, 88% yield); m.p: 182-184 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, J = 9.8 Hz, 1H), 7.61 (d, J = 8.1 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.43 (t, J = 7.5 Hz, 3H), 7.36 (t, J = 7.3 Hz, 1H), 7.26 (d, J = 7.5 Hz, 2H), 7.22 (t, J = 7.9 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 5.92 (s, 1H), 5.36 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.3, 153.2, 140.8, 140.4, 140.0, 134.5, 133.9, 130.8, 129.3, 128.8, 128.3, 127.8, 127.4, 126.1, 123.6, 122.9, 122.7, 114.8, 91.9, 52.3, 21.4. IR (KBr): 3421，2920，2865，2358，1633，1481，1346，1220，1150，1062，832 cm^{-1}. HRMS (ESI) m/z calcd for $C_{25}H_{22}NO$ $[M+H]^+$: 352.1696; found 352.1689.

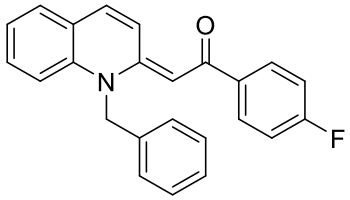
(3)



(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(4-methoxyphenyl)ethan-1-one(4c).
Yellow solid (91.4mg, 83% yield); m.p: 188-190 ℃; R_f = 0.4 (petroleum ether/ethyl

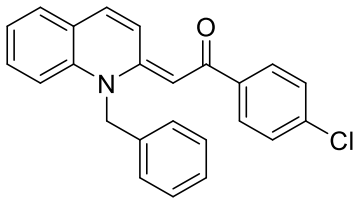
acetate =5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (d, J = 9.8 Hz, 1H), 7.69 (d, J = 8.7 Hz, 2H), 7.52 (t, J = 8.9 Hz, 2H), 7.43 (q, J = 7.3 Hz, 3H), 7.37 (t, J = 7.2 Hz, 1H), 7.26 (s, 2H), 7.23 – 7.18 (m, 2H), 6.84 (d, J = 8.7 Hz, 2H), 5.91 (s, 1H), 5.36 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.4, 161.6, 153.0, 140.4, 135.3, 134.6, 133.7, 130.7, 129.3, 129.2, 128.2, 127.8, 126.1, 123.6, 122.9, 122.7, 114.8, 113.3, 91.7, 55.3, 52.3. IR (KBr): 3454, 2923, 1596, 1490, 1442, 1345, 1211, 1161, 1023, 738 cm^{-1}. HRMS (ESI) m/z calcd for $C_{25}H_{22}NO_2$ $[M+H]^+$: 368.1645; found 368.1635.

(4)



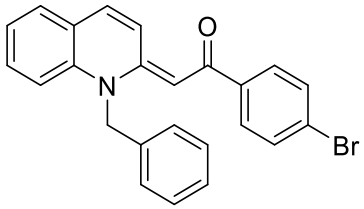
(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(4-fluorophenyl)ethan-1-one(4d). Yellow solid (85.2 mg, 80% yield); m.p: 162-164 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (d, J = 9.8 Hz, 1H), 7.69 (dd, J = 8.7, 5.6 Hz, 2H), 7.61 – 7.52 (m, 2H), 7.49 – 7.41 (m, 3H), 7.37 (t, J = 7.3 Hz, 1H), 7.28 – 7.24 (m, 3H), 7.23 (s, 1H), 7.00 (t, J = 8.7 Hz, 2H), 5.86 (s, 1H), 5.38 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.9, 164.2 (d, J = 250.5 Hz), 153.5, 140.3, 138.9 (d, J = 3.0 Hz), 134.4 (d, J = 10.5 Hz), 131.0, 129.5, 129.4, 129.4, 128.4, 127.9, 126.1, 123.7, 123.0, 122.6, 115.0 (d, J = 9.4 Hz), 114.9, 91.4, 52.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.3. IR (KBr): 3424, 3255, 3057, 2921, 1634, 1481, 1346, 1220, 1151, 838, 736 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{19}FNO$ $[M+H]^+$: 356.1445; found 356.1440.

(5)



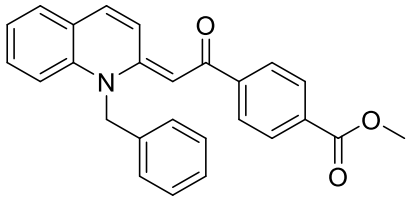
(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(4-chlorophenyl)ethan-1-one(4e). Yellow solid (90.2 mg, 81% yield); m.p: 203-205 ℃;R_f = 0.4 (petroleum ether/ethyl acetate =5/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, J = 9.8 Hz, 1H), 7.61 (d, J = 8.6 Hz, 2H), 7.57 (t, J = 8.6 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.37 (t, J = 7.3 Hz, 1H), 7.30 (s, 2H), 7.28 – 7.22 (m, 4H), 5.85 (s, 1H), 5.38 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.8, 153.6, 141.1, 140.3, 136.4, 134.5, 134.3, 131.0, 129.4, 128.7, 128.4, 128.3, 127.9, 126.1, 123.7, 123.0, 122.6, 115.0, 91.4, 52.3. IR (KBr): 3422, 2917, 1956, 1633, 1592, 1499, 1369, 1216, 1148, 1080, 831, 734 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{19}ClNO$ $[M+H]^+$: 372.1150; found 372.1146.

(6)



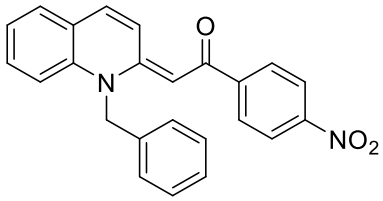
(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(4-bromophenyl)ethan-1-one(4f). Yellow solid (97.1 mg, 78% yield); m.p: 216-218 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, *J* = 9.8 Hz, 1H), 7.58 (t, *J* = 9.3 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 3H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.26 (t, *J* = 7.1 Hz, 4H), 5.84 (s, 1H), 5.38 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.9, 153.6, 141.5, 140.2, 134.5, 134.3, 131.2, 131.0, 129.4, 128.9, 128.4, 127.9, 126.1, 125.0, 123.7, 123.1, 122.6, 115.0, 91.3, 52.4. IR (KBr): 3361, 2919, 2850, 1632, 1498, 1369, 1212, 1148, 1065, 879, 735 cm^{-1}.
HRMS (ESI) m/z calcd for $C_{24}H_{19}BrNO$ $[M+H]^+$: 416.0645; found416.0638.

(7)



methyl (E)-4-(2-(1-benzylquinolin-2(1H)-ylidene)acetyl)benzoate(4g). Yellow solid (88.9 mg, 75% yield); m.p:214-216 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (d, *J* = 9.7 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.60 (dd, *J* = 16.4, 8.7 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.29 (s, 1H), 7.25 (d, *J* = 7.3 Hz, 3H), 5.90 (s, 1H), 5.40 (s, 2H), 3.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.2, 166.8, 153.7, 146.7, 140.2, 134.8, 134.2, 131.4, 131.1, 129.5, 129.4, 128.5, 128.0, 127.2, 126.1, 123.8, 123.2, 122.6, 115.1, 91.8, 52.4, 52.2. IR (KBr): 3437, 2923, 2851, 1954, 1719, 1631, 1507, 1443, 1277, 1107, 741 cm^{-1}. HRMS (ESI) m/z calcd for $C_{26}H_{22}NO_3$ $[M+H]^+$:396.1594; found 396.1584.

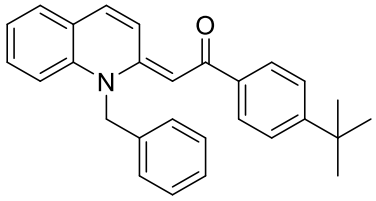
(8)



(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(4-nitrophenyl)ethan-1-one(4h). Yellow solid (78.0 mg, 68% yield); m.p:196-198 ℃;R_f = 0.3 (petroleum ether/ethyl acetate = 5/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (d, *J* = 9.7 Hz, 1H), 8.17 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 9.7 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 4.0

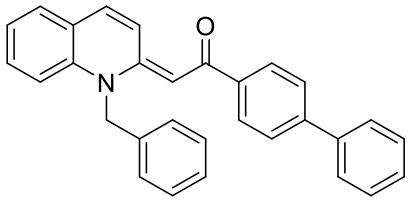
Hz, 1H), 7.32 (d, *J* = 2.7 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 2H), 5.86 (s, 1H), 5.44 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.5, 154.2, 148.6, 148.4, 140.1, 135.4, 134.0, 131.4, 129.5, 128.6, 128.1, 128.1, 126.0, 123.9, 123.5, 123.4, 122.4, 115.3, 91.4, 52.46. IR(KBr): 2922, 2862, 1630, 1511, 1340, 1211, 1152, 1095, 842, 739 cm^{-1}.
HRMS (ESI) m/z calcd for $C_{24}H_{19}N_2O_3$ $[M+H]^+$: 383.1390; found383.1384.

(9)



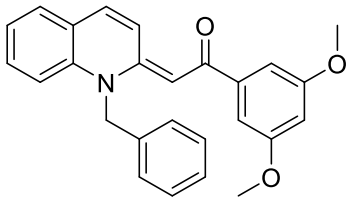
(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(4-(tert-butyl)phenyl)ethan-1-one(4i).
Yellow solid (95.5 mg, 81% yield); m.p:214-216 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (d, *J* = 9.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.43 (q, *J* = 7.3 Hz, 3H), 7.37 (t, *J* = 8.4 Hz, 3H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.24 – 7.19 (m, 2H), 5.95 (s, 1H), 5.36 (s, 2H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 140.4, 139.9, 133.9, 130.8, 129.3, 128.3, 127.8, 127.2, 126.1, 125.1, 123.6, 122.9, 122.7, 114.9, 91.9, 52.3, 34.8, 31.2. IR (KBr): 3442, 2956, 2861, 1630, 1501, 1446, 1351, 1217, 1153, 882, 741 cm^{-1}.
HRMS (ESI) m/z calcd for $C_{28}H_{28}NO$ $[M+H]^+$: 394.2165; found 394.2156.

(10)



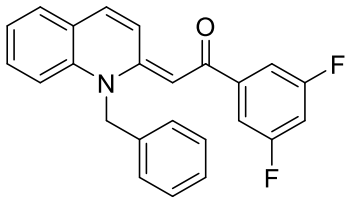
(E)-1-([1,1'-biphenyl]-4-yl)-2-(1-benzylquinolin-2(1H)-ylidene)ethan-1-one(4j).
Yellow solid (80.6 mg, 65% yield); m.p:224-226 ℃; R_f = 0.4 (petroleum ether/ethyl acetate =5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.19 (d, *J* = 9.7 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.59 – 7.55 (m, 4H), 7.48 – 7.43 (m, 5H), 7.40 – 7.35 (m, 2H), 7.29 (s, 1H), 7.28 (s, 1H), 7.24 (dd, *J* = 7.9, 4.1 Hz, 2H), 5.98 (s, 1H), 5.40 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.9, 153.3, 143.1, 141.5, 140.5, 140.3, 134.5, 134.2, 130.9, 129.4, 128.8, 128.3, 127.9, 127.8, 127.7, 127.2, 126.8, 126.1, 123.7, 122.9, 122.8, 114.9, 91.9, 52.4. IR (KBr): 3040, 2921, 2853, 1630, 1500, 1445, 1347, 1213, 1153, 880, 745 cm^{-1}. HRMS (ESI) m/z calcd for $C_{30}H_{24}NO$ $[M+H]^+$: 414.1852; found 414.1848.

(11)



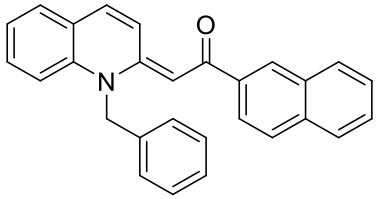
(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(3,5-dimethoxyphenyl)ethan-1-one(4k).
Yellow solid (98.9 mg, 83% yield); m.p:160-162 ℃;R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (d, *J* = 9.7 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 9.1 Hz, 4H), 6.84 (d, *J* = 2.3 Hz, 2H), 6.50 (t, *J* = 2.3 Hz, 1H), 5.86 (s, 1H), 5.37 (s, 2H), 3.72 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.9, 160.4, 153.3, 145.0, 140.3, 134.4, 134.3, 131.0, 129.3, 128.4, 127.8, 126.1, 123.7, 122.9, 122.7, 114.9, 104.8, 103.6, 92.1, 55.4, 52.3. IR (KBr): 3364, 2922, 2861, 1631, 1581, 1508, 1444, 1342, 1151, 1054, 739 cm^{-1}. HRMS (ESI) m/z calcd for $C_{26}H_{24}NO_3$ $[M+H]^+$: 398.1750; found 398.1746.

(12)



(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(3,5-difluorophenyl)ethan-1-one(4l).
Yellow solid (86.2 mg, 77% yield); m.p:180-182 ℃; R_f = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, *J* = 9.7 Hz, 1H), 7.62 (dd, *J* = 18.7, 8.7 Hz, 2H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.26 (t, *J* = 6.5 Hz, 2H), 7.17 (dd, *J* = 8.4, 2.2 Hz, 2H), 6.82 (tt, *J* = 8.6, 2.2 Hz, 1H), 5.78 (s, 1H), 5.41 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.9, 162.7 (d, *J* = 236.9 Hz), 154.0, 146.3, 140.1, 135.0, 134.1, 131.2, 129.4, 128.5, 128.0, 126.0, 123.8, 123.3, 122.5, 115.1, 110.1 (d, *J* = 25.8 Hz), 105.5(d, *J* = 25.3 Hz), 90.8, 52.4.^{19}F NMR (471 MHz, $CDCl_3$) δ -109.8. IR (KBr): 3077, 2923, 2853, 1630, 1510, 1444, 1307, 1155, 983, 858, 739 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{18}F_2NO$ $[M+H]^+$: 374.1351; found 374.1347.

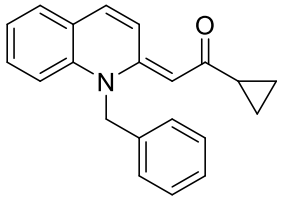
(13)



(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(naphthalen-2-yl)ethan-1-one(4m).
Yellow solid (95.2 mg, 82% yield); m.p:205-207 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (d, *J* = 9.7 Hz, 1H), 8.08 (s, 1H), 7.88 – 7.75 (m, 4H), 7.60 – 7.55 (m, 2H), 7.49 (dq, *J* = 15.1, 7.1 Hz, 5H), 7.42 (t,

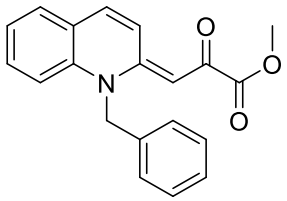
J = 7.3 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.28 – 7.23 (m, 2H), 6.08 (s, 1H), 5.42 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.2, 153.2, 140.4, 140.0, 134.5, 134.2, 132.8, 130.9, 129.4, 129.2, 128.4, 127.9, 127.8, 127.6, 127.6, 127.1, 126.2, 126.1, 124.6, 123.7, 122.9, 122.8, 114.9, 92.4, 52.3. IR (KBr): 3364, 3051, 2920, 2852, 1955, 1630, 1501, 1443, 1148, 822, 745 cm^{-1}. HRMS (ESI) m/z calcd for $C_{28}H_{22}NO$ $[M+H]^+$: 388.1696; found 388.1689.

(14)



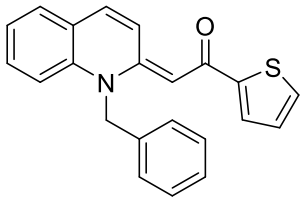
(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-cyclopropylethan-1-one(4n). Yellow solid (51.5 mg, 57% yield); m.p:161-163 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 9.8 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 4H), 7.38 – 7.32 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 5.43 (s, 1H), 5.29 (s, 2H), 1.75 – 1.67 (m, 1H), 1.04 – 0.96 (m, 2H), 0.70 (dq, *J* = 6.8, 3.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.0, 151.4, 140.2, 134.6, 133.3, 130.6, 129.3, 128.1, 127.7, 126.1, 123.4, 122.8, 122.5, 114.8, 94.3, 52.0, 22.6, 9.6. IR (KBr): 3007, 2923, 1634, 1511, 1445, 1360, 1129, 941, 742 cm^{-1}. HRMS (ESI) m/z calcd for $C_{21}H_{20}NO$ $[M+H]^+$:302.1539; found 302.1529.

(15)



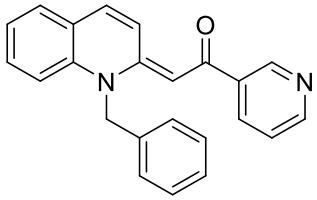
methyl (E)-3-(1-benzylquinolin-2(1H)-ylidene)-2-oxopropanoate(4o). Yellow solid (67.0 mg, 70% yield); m.p:191-193 ℃;R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.19 (dd, *J* = 9.6, 0.8 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.65 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.52 (tt, *J* = 7.1, 1.4 Hz, 1H), 7.44 – 7.31 (m, 5H), 7.23 – 7.17 (m, 2H), 6.21 (t, *J* = 1.0 Hz, 1H), 5.49 (s, 2H), 3.81 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 155.4, 139.6, 136.3, 133.8, 131.6, 129.4, 128.7, 128.0, 126.1, 124.2, 124.0, 122.7, 115.8, 89.8, 77.3, 52.6, 52.2. IR (KBr): 3362, 2921, 2852, 1957, 1725, 1600, 1508, 1244, 1147, 750 cm^{-1}. HRMS (ESI) m/z calcd for $C_{20}H_{18}NO_3$ $[M+H]^+$: 320.1281; found 320.1274.

(16)



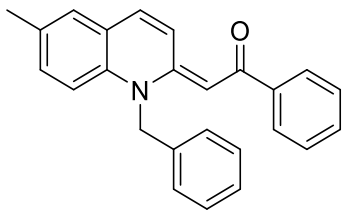
(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(thiophen-2-yl)ethan-1-one(4p). Yellow solid (80.3 mg, 78% yield); m.p:217-219 ℃;R_f = 0.3 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.11 (d, *J* = 9.8 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.46 – 7.40 (m, 3H), 7.40 (d, *J* = 4.9 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.29 (s, 1H), 7.25 (d, *J* = 9.8 Hz, 3H), 7.25 – 7.20 (m, 1H), 7.01 – 6.96 (m, 1H), 5.87 (s, 1H), 5.38 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.6, 153.1, 149.9, 140.3, 134.5, 134.0, 130.9, 130.0, 129.4, 128.4, 127.9, 127.6, 127.5, 126.1, 123.6, 122.9, 122.8, 114.9, 91.2, 52.4. IR (KBr): 3075, 2921, 2862, 1628, 1502, 1347, 1219, 1152, 831, 726 cm^{-1}. HRMS (ESI) m/z calcd for $C_{22}H_{18}NOS$ $[M+H]^+$: 344.1104; found 344.1095.

(17)



(E)-2-(1-benzylquinolin-2(1H)-ylidene)-1-(pyridin-3-yl)ethan-1-one(4q). Yellow solid (67.0 mg, 66% yield); m.p:190-192 ℃; R_f = 0.3 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (d, *J* = 9.7 Hz, 1H), 8.83 (d, *J* = 1.8 Hz, 1H), 8.60 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.07 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.64 (d, *J* = 9.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.32 – 7.29 (m, 1H), 7.27 (d, *J* = 7.1 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 2H), 5.88 (s, 1H), 5.42 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.7, 153.9, 150.9, 148.6, 140.1, 137.9, 135.0, 134.0, 131.2, 129.5, 128.5, 128.1, 126.0, 123.8, 123.3, 122.6, 115.2, 91.1, 52.4. IR (KBr): 3366, 3038, 2921, 2852, 1504, 1447, 1347, 1222, 1153, 881, 744 cm^{-1}. HRMS (ESI) m/z calcd for $C_{23}H_{19}N_2O$ $[M+H]^+$: 339.1492; found 339.1478.

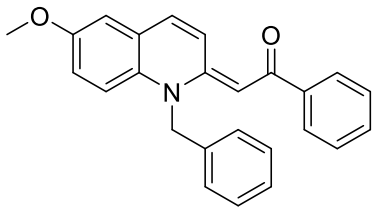
(18)



(E)-2-(1-benzyl-6-methylquinolin-2(1H)-ylidene)-1-phenylethan-1-one(5a). Yellow solid (91.7 mg, 87% yield); m.p:196-198 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (d, *J* = 9.7 Hz, 1H), 7.70 (d, *J* = 7.1 Hz,

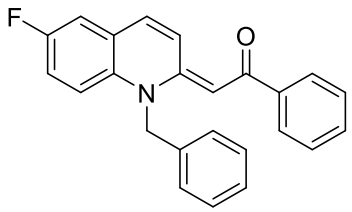
2H), 7.52 (d, *J* = 9.8 Hz, 1H), 7.41 (q, *J* = 7.2 Hz, 3H), 7.38 – 7.31 (m, 4H), 7.25 (t, *J* = 6.1 Hz, 3H), 7.14 (d, *J* = 8.6 Hz, 1H), 5.90 (s, 1H), 5.37 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.2, 153.3, 142.9, 138.3, 134.5, 134.2, 132.6, 132.1, 130.3, 129.3, 128.3, 128.1, 127.8, 127.3, 126.1, 123.6, 122.8, 114.9, 91.3, 52.2, 20.6. IR (KBr): 3042, 2921, 2855, 1628, 1504, 1345, 1216, 1154, 874, 701 cm^{-1}. HRMS (ESI) m/z calcd for $C_{25}H_{22}NO$ $[M+H]^+$: 352.1696; found 352.1687.

(19)



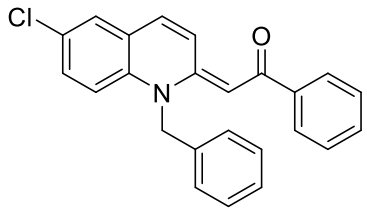
(E)-2-(1-benzyl-6-methoxyquinolin-2(1H)-ylidene)-1-phenylethan-1-one(5b).
Yellow solid (94.7 mg, 86% yield); m.p:208-210 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 9.23 (d, *J* = 9.7 Hz, 1H), 7.71 (d, *J* = 7.1 Hz, 2H), 7.54 (d, *J* = 9.8 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.1 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.17 (d, *J* = 9.2 Hz, 1H), 7.09 – 6.99 (m, 2H), 5.88 (s, 1H), 5.37 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.0, 155.3, 153.0, 143.0, 134.7, 134.5, 133.9, 130.3, 129.3, 128.1, 127.8, 127.3, 126.1, 124.6, 123.5, 119.3, 116.4, 110.1, 90.8, 55.7, 52.3. IR (KBr): 3364, 2920, 2850, 1624, 1505, 1457, 1345, 1218, 1150, 1031, 701 cm^{-1}. HRMS (ESI) m/z calcd for $C_{25}H_{22}NO_2$ $[M+H]^+$: 368.1645; found 368.1636.

(20)



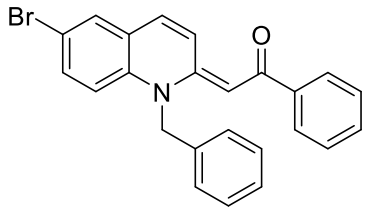
(E)-2-(1-benzyl-6-fluoroquinolin-2(1H)-ylidene)-1-phenylethan-1-one(5c). Yellow solid (83.1 mg, 78% yield); m.p:205-207 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 9.21 (d, *J* = 9.8 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.45 (dd, *J* = 18.1, 9.0 Hz, 3H), 7.41 – 7.37 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 8.3 Hz, 3H), 7.15 (d, *J* = 6.2 Hz, 2H), 5.92 (s, 1H), 5.34 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.5, 158.3 (d, *J* = 244.3 Hz), 152.9, 142.6, 136.8, 134.2, 133.1 (d, *J* = 3.0 Hz), 130.6, 129.4, 128.1, 128.0, 127.3, 126.1, 124.7 (d, *J* = 9.1 Hz), 124.2, 118.3 (d, *J* = 23.8 Hz), 116.5 (d, *J* = 8.2 Hz), 113.4 (d, *J* = 22.1 Hz), 92.0, 52.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -120.2. IR (KBr): 3852, 3033, 2921, 1631, 1514, 1446, 1214, 1148, 873, 704 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{19}FNO$ $[M+H]^+$: 356.1445; found 356.1436.

(21)



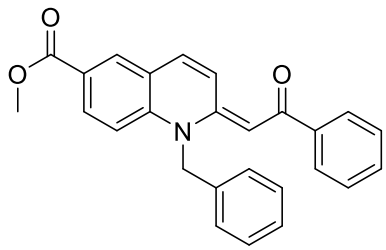
(E)-2-(1-benzyl-6-chloroquinolin-2(1H)-ylidene)-1-phenylethan-1-one(5d). Yellow solid (92.4 mg, 83% yield); m.p:215-217 ℃; R_f = 0.4 (petroleum ether/ethyl acetate =5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (d, *J* = 9.8 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.42 (s, 1H), 7.40 – 7.39 (m, 2H), 7.37 – 7.35 (m, 1H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 9.0 Hz, 1H), 5.94 (s, 1H), 5.33 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.7, 152.7, 142.4, 138.9, 134.0, 132.7, 130.7, 129.4, 128.2, 128.2, 128.0, 127.3, 126.0, 124.7, 124.1, 116.3, 92.5, 52.4. IR (KBr): 3035, 2918, 2861, 1629, 1500, 1439, 1208, 1151, 1094, 703 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{19}ClNO$ $[M+H]^+$: 372.1150; found 372.1142.

(22)



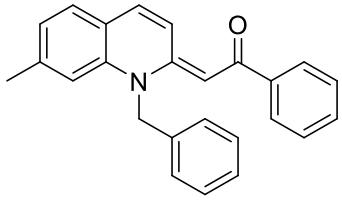
(E)-2-(1-benzyl-6-bromoquinolin-2(1H)-ylidene)-1-phenylethan-1-one(5e). Yellow solid (105.8 mg,85% yield); m.p:215-217 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, *J* = 9.8 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.48 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.45 (s, 1H), 7.44 – 7.40 (m, 3H), 7.38 (d, *J* = 9.2 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 1H), 5.94 (s, 1H), 5.31 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.7, 152.7, 142.4, 139.3, 134.0, 133.4, 132.6, 130.7, 130.3, 129.4, 128.2, 128.0, 127.3, 126.0, 125.1, 124.1, 116.5, 115.6, 92.6, 52.3. IR (KBr): 3362, 2919, 2861, 1632, 1493, 1342, 1209, 1151, 703 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{19}BrNO$ $[M+H]^+$: 416.0645; found 416.0638.

(23)



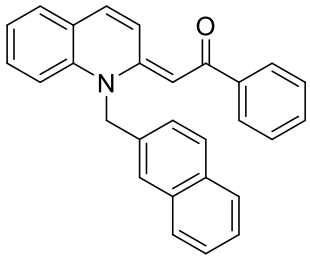
Methyl
(E)-1-benzyl-2-(2-oxo-2-phenylethylidene)-1,2-dihydroquinoline-6-carboxylate(5f).
Yellow solid (88.9 mg, 75% yield); m.p:216-218 ℃; R_f = 0.3petroleum ether/ethyl acetate =5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.11 (d, *J* = 9.8 Hz, 1H), 8.19 (d, *J* = 1.9 Hz, 1H), 8.05 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.68 (d, *J* = 7.1 Hz, 2H), 7.53 (d, *J* = 9.8 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 8.9 Hz, 1H), 6.00 (s, 1H), 5.36 (s, 2H), 3.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.0, 166.2, 152.7, 143.4, 142.2, 133.9, 133.6, 131.7, 130.8, 129.9, 129.4, 128.2, 128.0, 127.4, 126.0, 124.2, 123.5, 123.1, 114.7, 93.6, 52.5, 52.3. IR (KBr): 3061, 2921, 2860, 1716, 1633, 1506, 1439, 1269, 1205, 1153, 706 cm^{-1}. HRMS (ESI) m/z calcd for $C_{26}H_{22}NO_3$ $[M+H]^+$: 396.1594; found 396.1585.

(24)



(E)-2-(1-benzyl-7-methylquinolin-2(1H)-ylidene)-1-phenylethan-1-one(5g). Yellow solid (74.8mg, 71% yield); m.p:184-186 ℃;R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (d, *J* = 9.7 Hz, 1H), 7.68 (d, *J* = 7.0 Hz, 2H), 7.54 (d, *J* = 9.7 Hz, 1H), 7.44 (t, *J* = 8.1 Hz, 3H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 2H), 7.09 – 7.03 (m, 2H), 5.89 (s, 1H), 5.37 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.2, 142.9, 141.6, 140.4, 134.6, 134.2, 130.3, 129.3, 128.2, 128.1, 127.8, 127.3, 126.1, 124.3, 121.7, 121.5, 115.0, 91.6, 52.2, 22.3. IR (KBr): 3363, 2920, 2852, 1957, 1628, 1489, 1350, 1214, 1146, 852, 702 cm^{-1}. HRMS (ESI) m/z calcd for $C_{25}H_{22}NO$ $[M+H]^+$: 352.1696; found 352.1687.

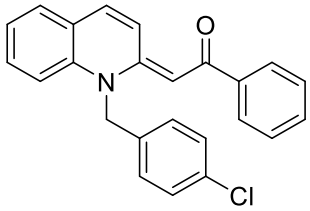
(25)



(E)-2-(1-(naphthalen-2-ylmethyl)quinolin-2(1H)-ylidene)-1-phenylethan-1-one(5h).
Yellow solid (91.8 mg, 79% yield); m.p:182-184 ℃; R_f = 0.4 (petroleum ether/ethyl acetate =3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.23 (d, *J* = 9.8 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 9.1 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 2H), 7.62 – 7.56 (m, 3H), 7.55 – 7.49 (m, 2H), 7.46 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.27 – 7.22 (m, 2H),

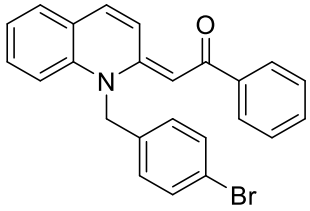
6.02 (s, 1H), 5.53 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.6, 153.5, 142.7, 140.3, 134.3, 133.6, 132.9, 131.8, 130.9, 130.4, 129.4, 128.4, 128.1, 127.9, 127.9, 127.3, 126.7, 126.3, 124.9, 124.0, 123.7, 122.9, 122.8, 115.1, 91.8, 52.6. IR (KBr): 3054, 2922, 1956, 1630, 1506, 1441, 1346, 1213, 1153, 892, 747 cm^{-1}. HRMS (ESI) m/z calcd for $C_{28}H_{22}NO$ $[M+H]^+$: 388.1696; found 388.1687.

(26)



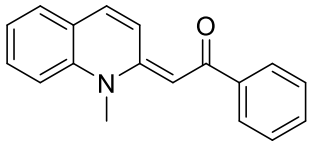
(E)-2-(1-(4-chlorobenzyl)quinolin-2(1H)-ylidene)-1-phenylethan-1-one(5i). Yellow solid (92.4mg, 83% yield); m.p:224-226 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (d, *J* = 9.8 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 9.8 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 1H), 5.88 (s, 1H), 5.33 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.5, 153.2, 142.6, 140.1, 134.2, 133.7, 133.0, 130.9, 130.6, 129.5, 128.4, 128.2, 127.6, 127.3, 123.7, 123.0, 122.7, 114.7, 91.7, 51.7. IR (KBr): 3056, 2922, 1631, 1498, 1441, 1346, 1213, 1151, 886, 746 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{19}ClNO$ $[M+H]^+$: 372.1150; found 372.1145.

(27)



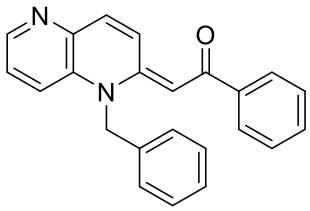
(E)-2-(1-(4-bromobenzyl)quinolin-2(1H)-ylidene)-1-phenylethan-1-one(5j). Yellow solid (100.9 mg, 81% yield); m.p:242-244 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, *J* = 9.8 Hz, 1H), 7.71 (d, *J* = 7.1 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 4H), 7.43 (q, *J* = 7.9, 7.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 3H), 5.88 (s, 1H), 5.31 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.6, 153.2, 142.6, 140.1, 134.2, 133.5, 132.5, 130.9, 130.6, 128.4, 128.2, 127.9, 127.3, 123.7, 123.0, 122.7, 121.7, 114.7, 91.7, 51.7. IR (KBr): 3361, 2920, 2862, 1956, 1633, 1488, 1439, 1348, 1216, 1150, 887, 747 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{19}BrNO$ $[M+H]^+$: 416.0645; found 416.0636.

(28)



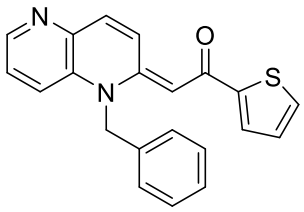
(E)-2-(1-methylquinolin-2(1H)-ylidene)-1-phenylethan-1-one(5k). Yellow solid (53.3 mg, 68% yield); m.p:113-115 ℃;R_f = 0.4 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (d, J = 9.7 Hz, 1H), 7.96 (d, J = 7.8 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.51 (d, J = 3.9 Hz, 1H), 7.47 (t, J = 7.9 Hz, 3H), 7.41 (d, J = 8.5 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 6.00 (s, 1H), 3.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.4, 153.8, 143.2, 140.2, 134.0, 130.7, 130.4, 128.5, 128.2, 127.3, 123.7, 122.6, 122.6, 114.4, 91.3, 35.2. IR (KBr): 3390, 2921, 2852, 1957, 1632, 1504, 1439, 1354, 1214, 748 cm^{-1}. HRMS (ESI) m/z calcd for $C_{18}H_{16}NO$ $[M+H]^+$: 262.1226; found 262.1218.

(29)



(E)-2-(1-benzyl-1,5-naphthyridin-2(1H)-ylidene)-1-phenylethan-1-one(5l). Yellow solid (67.0 mg, 66% yield); m.p:182-184 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 2/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (d, J = 10.1 Hz, 1H), 8.49 (d, J = 4.5 Hz, 1H), 7.74 – 7.67 (m, 3H), 7.45 (t, J = 7.3 Hz, 3H), 7.42 – 7.38 (m, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.31 (dd, J = 8.6, 4.5 Hz, 1H), 7.24 (d, J = 7.3 Hz, 2H), 5.97 (s, 1H), 5.30 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.0, 151.9, 144.6, 142.2, 141.3, 137.2, 135.0, 133.7, 130.9, 129.5, 128.2, 128.1, 127.4, 127.1, 126.1, 124.6, 121.7, 93.2, 51.7. IR (KBr): 3063, 2922, 1957, 1629, 1515, 1467, 1209, 1146, 706 cm^{-1}. HRMS (ESI) m/z calcd for $C_{23}H_{19}N_2O$ $[M+H]^+$: 339.1492; found 339.1489.

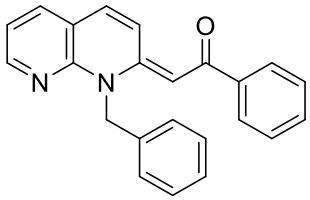
(30)



(E)-2-(1-benzyl-1,5-naphthyridin-2(1H)-ylidene)-1-(thiophen-2-yl)ethan-1-one(5m). Yellow solid (64.0 mg, 62% yield); m.p:202-204 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 2/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.11 (d, J = 9.8 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.46 – 7.40 (m, 3H), 7.40 (d, J = 4.9 Hz, 1H), 7.37 (t, J = 7.3 Hz, 1H), 7.29 (s, 1H), 7.25 (d, J = 9.8 Hz, 3H), 7.25 – 7.20 (m, 1H), 7.01 – 6.96 (m, 1H), 5.87

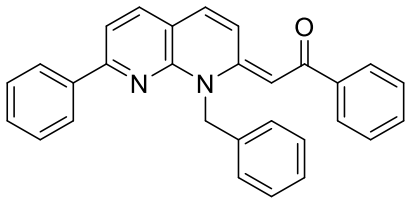
(s, 1H), 5.38 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.6, 153.1, 149.9, 140.3, 134.5, 134.0, 130.9, 130.0, 129.4, 128.4, 127.9, 127.6, 127.5, 126.1, 123.6, 122.9, 122.8, 114.9, 91.2, 52.4. IR (KBr): 3363, 3074, 2920, 2852, 1957, 1628, 1518, 1211, 1146, 836, 714 cm^{-1}. HRMS (ESI) m/z calcd for $C_{21}H_{16}N_2OSNa$ $[M+Na]^+$: 367.0876; found 367.0867.

(31)



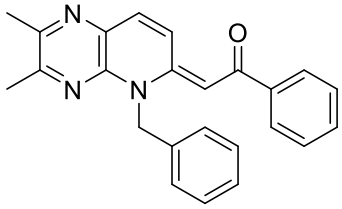
(E)-2-(1-benzyl-1,8-naphthyridin-2(1H)-ylidene)-1-phenylethan-1-one(5n). Yellow solid (79.1mg, 78% yield); m.p:224-226 ℃; R_f = 0.4 (petroleum ether/ethyl acetate =3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (d, *J* = 9.8 Hz, 1H), 8.49 (dd, *J* = 4.7, 1.8 Hz, 1H), 7.79 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 2H), 7.42 (d, *J* = 3.8 Hz, 1H), 7.41 (s, 1H), 7.39 (s, 1H), 7.37 (d, *J* = 5.9 Hz, 1H), 7.35 (s, 1H), 7.33 (d, *J* = 6.2 Hz, 1H), 7.31 (s, 1H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.16 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.05 (s, 1H), 5.77 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.1, 152.1, 150.3, 149.8, 142.4, 135.8, 135.5, 132.2, 130.8, 129.0, 128.1, 127.4, 127.4, 126.6, 124.0, 118.7, 118.3, 94.5, 48.1. IR (KBr): 3047, 2925, 1957, 1633, 1511, 1408, 1211, 1151, 887, 762 cm^{-1}. HRMS (ESI) m/z calcd for $C_{23}H_{19}N_2O$ $[M+H]^+$: 339.1492; found 339.1489.

(32)



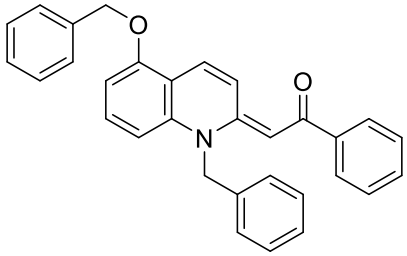
(E)-2-(1-benzyl-7-phenyl-1,8-naphthyridin-2(1H)-ylidene)-1-phenylethan-1-one(5o). Yellow solid (100.6 mg, 81% yield); m.p:205-207 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (d, *J* = 9.7 Hz, 1H), 8.05 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.67 (dd, *J* = 7.5, 5.3 Hz, 3H), 7.48 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 3H), 7.43 (d, *J* = 5.1 Hz, 2H), 7.41 (s, 1H), 7.39 (d, *J* = 5.3 Hz, 1H), 7.37 (d, *J* = 5.3 Hz, 2H), 7.34 (d, *J* = 3.9 Hz, 2H), 6.12 (s, 1H), 5.96 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.0, 156.9, 152.5, 149.9, 142.5, 138.2, 136.3, 136.3, 132.1, 130.7, 129.8, 129.0, 128.9, 128.2, 127.4, 127.4, 127.1, 126.9, 123.6, 117.2, 115.4, 94.3, 48.2. IR (KBr): 3058, 2924, 2853, 1632, 1506, 1390, 1215, 1149, 758, 695 cm^{-1}. HRMS (ESI) m/z calcd for $C_{29}H_{23}N_2O[M+H]^+$: 415.1805; found 415.1796.

(33)



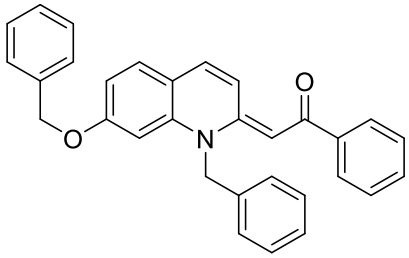
(E)-2-(5-benzyl-2,3-dimethylpyrido[2,3-b]pyrazin-6(5H)-ylidene)-1-phenylethan-1-one(5p). Yellow solid (63.9 mg, 58% yield); m.p:221-223 ℃; R_f = 0.3 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (d, J = 10.0 Hz, 1H), 7.63 – 7.56 (m, 3H), 7.41 (dd, J = 12.4, 7.4 Hz, 3H), 7.35 (t, J = 7.5 Hz, 3H), 7.24 (d, J = 7.4 Hz, 2H), 6.04 (s, 1H), 5.73 (s, 2H), 2.61 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.1, 152.2, 151.0, 147.3, 144.9, 142.2, 135.6, 133.5, 133.3, 130.8, 129.0, 128.1, 127.5, 127.4, 127.0, 126.7, 94.8, 47.5, 22.5, 21.4. IR (KBr): 3430, 3057, 2921, 2953, 1958, 1627, 1514, 1445, 1212, 1143, 696 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{22}N_3O$ $[M+H]^+$: 368.1757; found 368.1752.

(34)



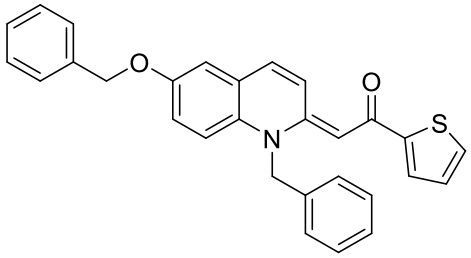
(E)-2-(1-benzyl-5-(benzyloxy)quinolin-2(1H)-ylidene)-1-phenylethan-1-one(5q). Yellow solid (94.4mg, 71% yield); m.p:217-219 ℃; R_f = 0.5 (petroleum ether/ethyl acetate =3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (d, J = 10.0 Hz, 1H), 8.09 (d, J = 10.0 Hz, 1H), 7.69 (d, J = 7.3 Hz, 2H), 7.51 (d, J = 7.1 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.43 – 7.39 (m, 3H), 7.39 – 7.35 (m, 2H), 7.33 (t, J = 7.9 Hz, 3H), 7.26 (d, J = 7.5 Hz, 2H), 6.85 (d, J = 8.7 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 5.91 (s, 1H), 5.37 (s, 2H), 5.24 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.3, 154.9, 153.6, 142.9, 141.3, 136.4, 134.6, 131.1, 130.3, 129.3, 128.8, 128.6, 128.3, 128.1, 127.8, 127.4, 127.3, 126.1, 121.4, 114.6, 107.8, 105.0, 91.5, 70.7, 52.7. IR (KBr): 3042, 2921, 2855, 1957, 1627, 1456, 1264, 1213, 1149, 1026, 700 cm^{-1}. HRMS (ESI) m/z calcd for $C_{31}H_{26}NO_2$ $[M+H]^+$: 444.1958; found 444.1949.

(35)



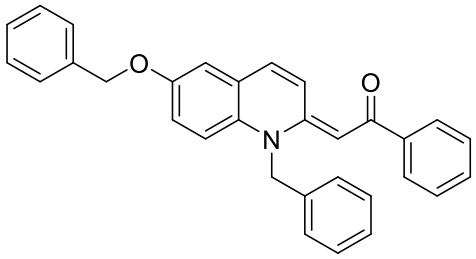
(E)-2-(1-benzyl-7-(benzyloxy)quinolin-2(1H)-ylidene)-1-phenylethan-1-one(5r).
Yellow solid (91.7 mg, 69% yield); m.p:218-220 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (d, *J* = 9.7 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.49 (dd, *J* = 17.1, 9.2 Hz, 3H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.39 (s, 1H), 7.36 (d, *J* = 2.3 Hz, 4H), 7.35 – 7.31 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.77 (s, 1H), 5.92 (s, 1H), 5.30 (s, 2H), 5.05 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.2, 161.1, 153.8, 142.9, 141.8, 136.1, 134.3, 134.1, 130.3, 129.6, 129.3, 128.7, 128.3, 128.1, 127.8, 127.6, 127.3, 126.1, 120.0, 118.1, 110.7, 101.0, 91.6, 70.4, 52.6. IR (KBr): 3360, 3191, 3033, 2920, 2862, 1625, 1490, 1434, 1227, 1148, 1033, 840, 703 cm^{-1}. HRMS (ESI) m/z calcd for $C_{31}H_{26}NO_2$ $[M+H]^+$: 444.1958; found 444.1949.

(36)



(E)-2-(1-benzyl-6-(benzyloxy)quinolin-2(1H)-ylidene)-1-(thiophen-2-yl)ethan-1-one (5s). Yellow solid (87.6 mg, 65% yield); m.p: 217-219 ℃;R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (d, *J* = 9.7 Hz, 1H), 7.50 – 7.45 (m, 4H), 7.43 (t, *J* = 6.8 Hz, 5H), 7.39 (d, *J* = 4.9 Hz, 2H), 7.25 (d, *J* = 7.3 Hz, 2H), 7.18 (d, *J* = 9.2 Hz, 1H), 7.13 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.09 (d, *J* = 2.8 Hz, 1H), 7.00 – 6.97 (m, 1H), 5.83 (s, 1H), 5.36 (s, 2H), 5.13 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.2, 154.5, 152.7, 150.1, 136.5, 134.9, 134.5, 133.7, 130.6, 129.8, 129.4, 128.8, 128.3, 127.9, 127.5, 127.2, 126.1, 124.5, 123.5, 120.0, 116.3, 111.4, 90.2, 70.5, 52.4. IR (KBr): 3451, 3067, 2921, 2865, 1967, 1723, 1507, 1151, 1024, 710 cm^{-1}. HRMS (ESI) m/z calcd for $C_{29}H_{24}NO_2S[M+H]^+$: 450.1522; found 450.1514.

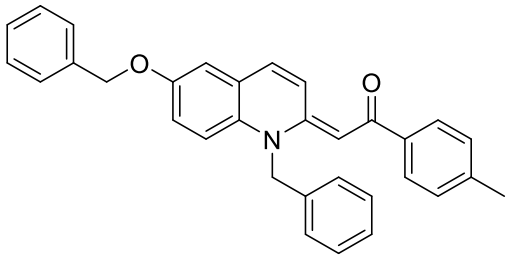
(37)



(E)-2-(1-benzyl-6-(benzyloxy)quinolin-2(1H)-ylidene)-1-phenylethan-1-one(5t).
Yellow solid (95.7mg, 72% yield); m.p: 218-220 ℃;R_f = 0.3 (petroleum ether/ethyl acetate =3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (d, *J* = 9.8 Hz, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.51 (d, *J* = 9.8 Hz, 1H), 7.47 (d, *J* = 6.9 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 4H), 7.40 – 7.36 (m, 3H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.17 (d, *J*

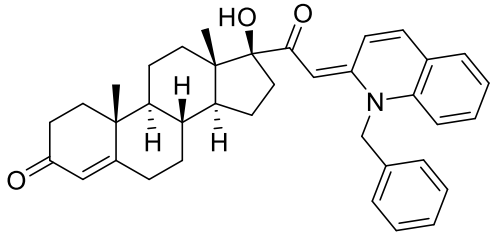
= 9.1 Hz, 1H), 7.13 – 7.11 (m, 1H), 7.10 (d, *J* = 2.7 Hz, 1H), 5.88 (s, 1H), 5.36 (s, 2H), 5.13 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.0, 154.5, 153.0, 142.9, 136.5, 134.9, 134.5, 133.9, 130.3, 129.3, 128.7, 128.3, 128.1, 127.8, 127.5, 127.3, 126.1, 124.6, 123.5, 119.9, 116.4, 111.4, 90.9, 70.5, 52.3. IR (KBr): 3045, 2920, 1957, 1725, 1564, 1503, 1449, 1343, 1219, 1149, 1023, 699 cm^{-1}. HRMS (ESI) m/z calcd for $C_{31}H_{26}NO_2$ $[M+H]^+$:444.1958; found 444.1943.

(38)



(E)-2-(1-benzyl-6-(benzyloxy)quinolin-2(1H)-ylidene)-1-(p-tolyl)ethan-1-one(5u). Yellow solid (102.9 mg, 75% yield); m.p: 221-223 ℃; R_f = 0.3(petroleum ether/ethyl acetate =3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (d, *J* = 9.7 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.45 (m, 3H), 7.42 (td, J = 7.4, 3.5 Hz, 4H), 7.36 (q, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.15 (t, J = 8.2 Hz, 3H), 7.12 (d, *J* = 2.8 Hz, 1H), 7.09 (t, J = 3.3 Hz, 1H), 5.87 (s, 1H), 5.35 (s, 2H), 5.13 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.9, 154.4, 152.8, 140.6, 140.2, 136.6, 135.0, 134.6, 133.7, 129.3, 128.8, 128.7, 128.2, 127.8, 127.5, 127.3, 126.1, 124.5, 123.6, 119.8, 116.3, 111.4, 91.0, 70.5, 52.3, 21.4. IR (KBr): 3441, 3035, 2921, 1957, 1612, 1565, 1509, 1450, 1345, 1221, 1151, 872 cm^{-1}. HRMS (ESI) m/z calcd for $C_{32}H_{28}NO_2$ $[M+H]^+$:459.2115; found 459.2123.

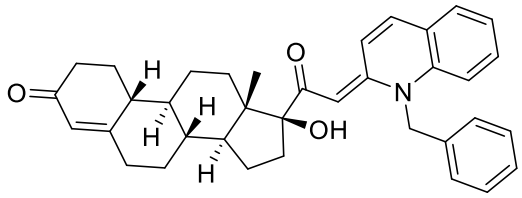
(39)



(8R,9S,10R,13S,14S,17S)-17-(2-((E)-1-benzylquinolin-2(1H)-ylidene)acetyl)-17-hydroxy-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one(6a). Yellow solid (108.5 mg, 66% yield); m.p: 177-179 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 3/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, *J* = 9.8 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.17 (dd, *J* = 7.4, 4.3 Hz, 3H), 7.11 (d, *J* = 8.5 Hz, 1H), 5.72 (s, 1H), 5.28 (s, 1H), 5.14 (s, 2H), 3.06 – 2.93 (m, 1H), 2.39 (ddd, *J* = 22.9, 17.4, 8.8 Hz, 3H), 2.27 (t, *J* = 12.3 Hz, 1H), 1.97 (d, *J* = 13.2 Hz, 1H), 1.82 (d, *J* = 12.8 Hz, 1H), 1.75 (s, 2H), 1.68 – 1.55 (m, 4H), 1.48 (dd, *J* = 20.6, 13.1 Hz, 2H), 1.37 – 1.25 (m, 3H), 1.17 (s, 3H), 1.03

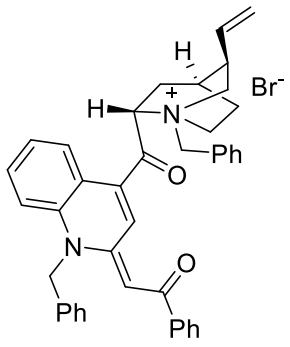
(d, *J* = 10.5 Hz, 1H), 0.94 (s, 3H), 0.89 (d, *J* = 10.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 199.6, 194.0, 171.4, 170.2, 140.3, 134.7, 133.6, 130.7, 129.3, 128.2, 127.7, 126.0, 123.8, 123.4, 122.6, 114.6, 95.9, 91.5, 52.9, 52.2, 47.0, 46.7, 38.5, 35.9, 35.6, 33.9, 32.9, 32.6, 31.5, 24.8, 20.8, 17.4, 15.2. IR (KBr): 3470, 2938, 2861, 1736, 1668, 1517, 1446, 1245, 1149, 1029, 866, 741 cm^{-1}. HRMS (ESI) m/z calcd for $C_{37}H_{42}NO_3$ $[M+H]^+$: 548.3159; found 548.3153.

(40)



(8R,9S,10R,13S,14S,17S)-17-(2-((E)-1-benzylquinolin-2(1H)-ylidene)acetyl)-17-hydroxy-13-methyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one(6b).Yellow solid (108.8 mg, 68% yield); m.p: 182-184 ℃; R_f = 0.4 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.87 (d, *J* = 9.8 Hz, 1H), 7.48 (d, *J* = 9.0 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 5.2 Hz, 3H), 7.11 (d, *J* = 8.5 Hz, 1H), 5.81 (s, 1H), 5.28 (s, 1H), 5.15 (s, 2H), 2.98 (dt, *J* = 14.7, 8.1 Hz, 1H), 2.46 (d, *J* = 13.6 Hz, 1H), 2.38 (d, *J* = 16.1 Hz, 1H), 2.23 (t, *J* = 12.8 Hz, 3H), 2.05 (s, 1H), 1.87 – 1.72 (m, 4H), 1.67 – 1.58 (m, 2H), 1.56 – 1.41 (m, 3H), 1.41 – 1.22 (m, 3H), 1.07 (d, *J* = 12.4 Hz, 1H), 0.96 (s, 3H), 0.83 – 0.76 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 200.0, 194.0, 170.2, 166.9, 140.3, 134.7, 133.7, 130.7, 129.3, 128.2, 127.7, 126.0, 124.5, 123.4, 122.6, 114.6, 95.9, 91.5, 52.2, 48.7, 46.9, 46.3, 42.5, 40.8, 36.5, 35.6, 32.6, 30.7, 26.5, 26.3, 24.6, 15.2. IR (KBr): 3485, 2934, 2864, 1735, 1667, 1516, 1446, 1366, 1250, 1149, 1031, 740 cm^{-1}. HRMS (ESI) m/z calcd for $C_{36}H_{40}NO_3$ $[M+H]^+$: 534.3003; found 534.2996.

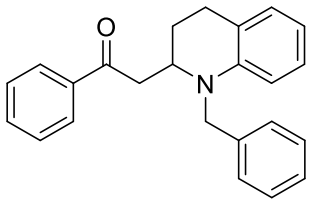
(41)



(2S,4S,5R)-1-benzyl-2-((E)-1-benzyl-2-(2-oxo-2-phenylethylidene)-1,2-dihydroquinoline-4-carbonyl)-5-vinylquinuclidin-1-ium bromide (6c). Red oil (150.8 mg, 75% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.09 – 8.02 (m, 1H), 7.75 – 7.65 (m, 2H), 7.48 – 7.41 (m, 4H), 7.39 (d, *J* = 7.3 Hz, 1H), 7.38 – 7.31 (m, 6H), 7.28 – 7.22 (m, 5H), 6.25 (dt, *J* = 17.4, 9.8 Hz, 1H), 6.02 (s, 1H), 5.36 (s, 2H), 5.13 (dd, *J* = 10.0, 8.0 Hz, 2H), 3.52 (d, *J* =

13.4 Hz, 1H), 3.45 (d, *J* = 13.4 Hz, 1H), 3.17 – 3.09 (m, 2H), 2.84 (dd, *J* = 37.9, 9.8 Hz, 2H), 2.41 (d, *J* = 6.1 Hz, 1H), 2.25 (d, *J* = 9.1 Hz, 1H), 2.08 (d, *J* = 5.1 Hz, 1H), 1.76 (d, *J* = 7.0 Hz, 1H), 1.64 – 1.61 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.7, 187.9, 151.7, 142.2, 141.0, 140.7, 139.0, 138.3, 133.9, 131.2, 130.9, 129.4, 128.8, 128.3, 128.1, 127.9, 127.3, 126.8, 126.7, 126.0, 123.8, 123.2, 119.8, 116.0, 115.3, 93.7, 63.2, 52.8, 43.4, 39.4, 38.0, 28.4. IR(KBr): 3364, 2921, 2853, 1957, 1634, 1507, 1133, 1075, 801, 628 cm^{-1}. HRMS (ESI) m/z calcd for $C_{41}H_{40}BrN_2O_2$ $[M+H]^+$: 671.2268; found 671.2267.

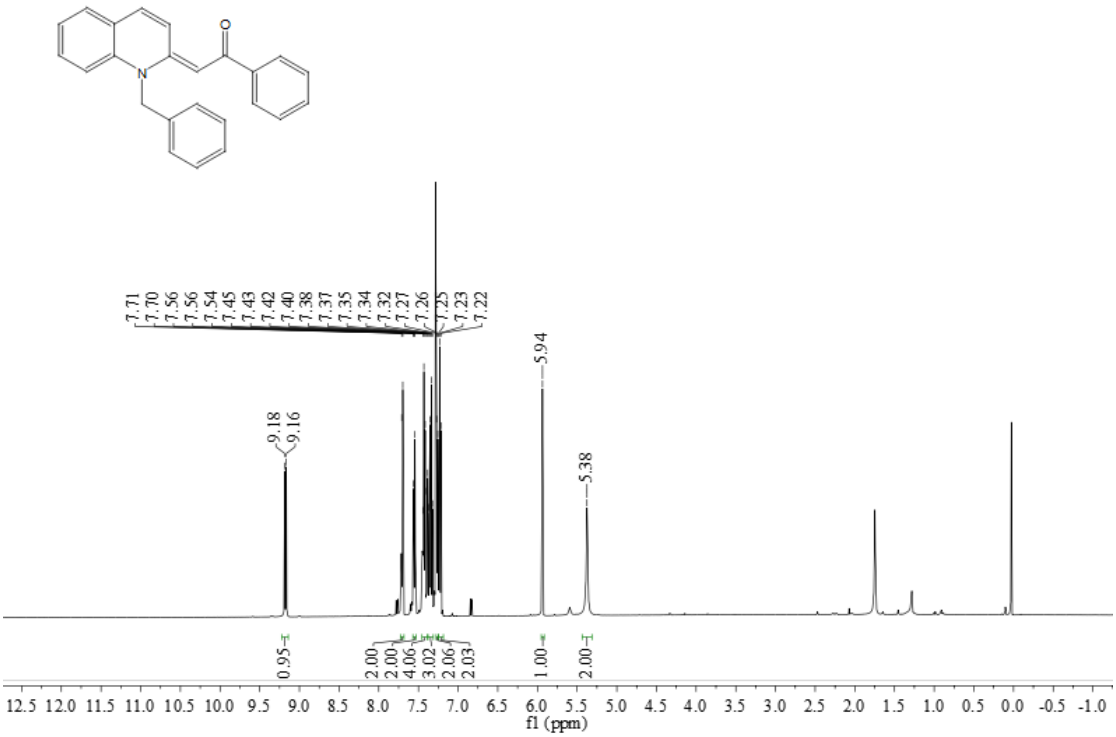
(42)



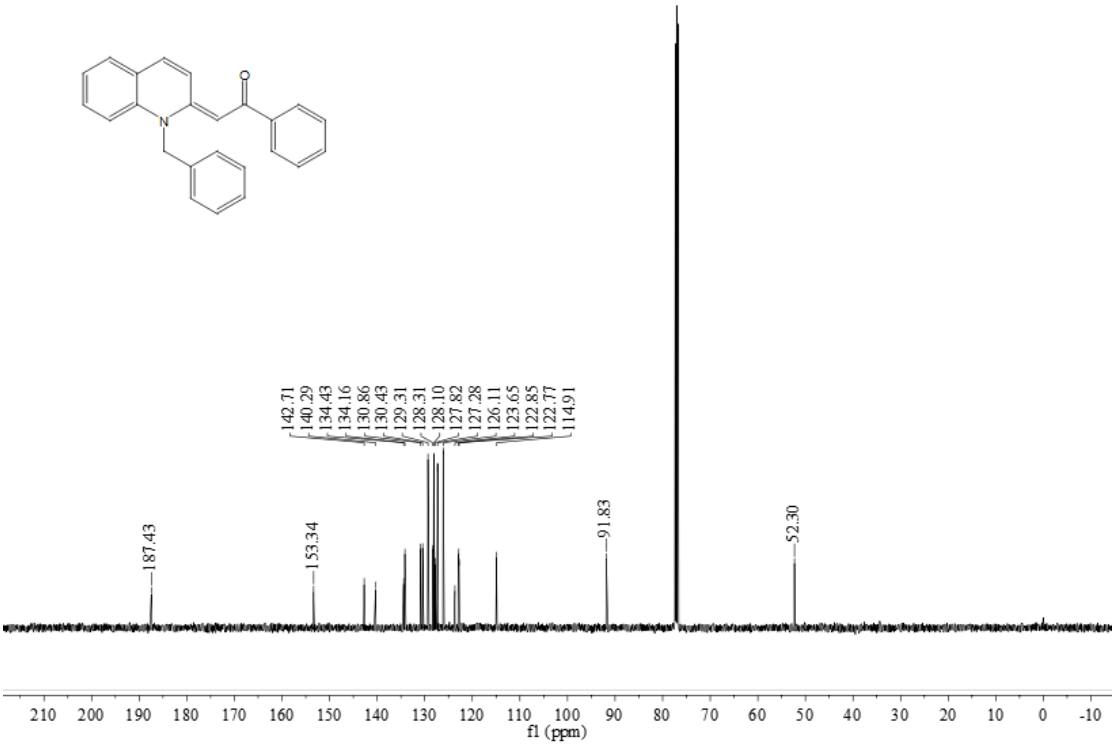
2-(1-benzyl-1,2,3,4-tetrahydroquinolin-2-yl)-1-phenylethan-1-one (4a'). Yellow oil (53.2 mg, 78% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.58 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.29 (m, 4H), 7.25 (t, *J* = 7.0 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.66 (dd, *J* = 10.6, 4.0 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 1H), 4.56 (q, *J* = 17.0 Hz, 2H), 4.24 (dd, *J* = 7.7, 3.1 Hz, 1H), 3.26 (dd, *J* = 6.5, 4.8 Hz, 2H), 3.02 – 2.94 (m, 1H), 2.85 – 2.78 (m, 1H), 2.14 (ddd, *J* = 13.1, 8.3, 4.8 Hz, 1H), 2.04 – 1.99 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 144.1, 138.9, 137.1, 133.3, 129.3, 128.7, 128.6, 128.1, 127.3, 126.9, 126.5, 121.2, 116.2, 112.1, 54.6, 54.2, 41.2, 25.4, 23.5. IR (KBr): 3456, 3061, 3026, 2922, 2864, 1675, 1594, 1495, 1450, 1347, 1206, 741, 690 cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{24}NO$ $[M+H]^+$: 342.1852; found 342.1856.

7. NMR spectra of products

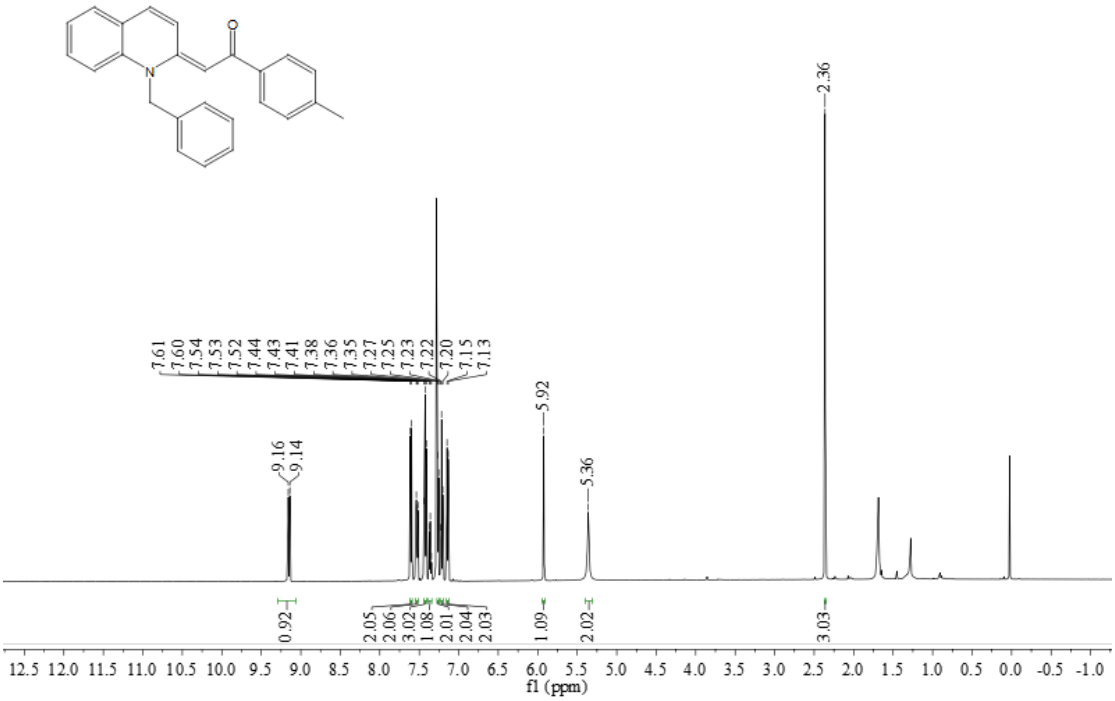
^{1}H NMR spectra of 4a (500 MHz, $CDCl_3$)



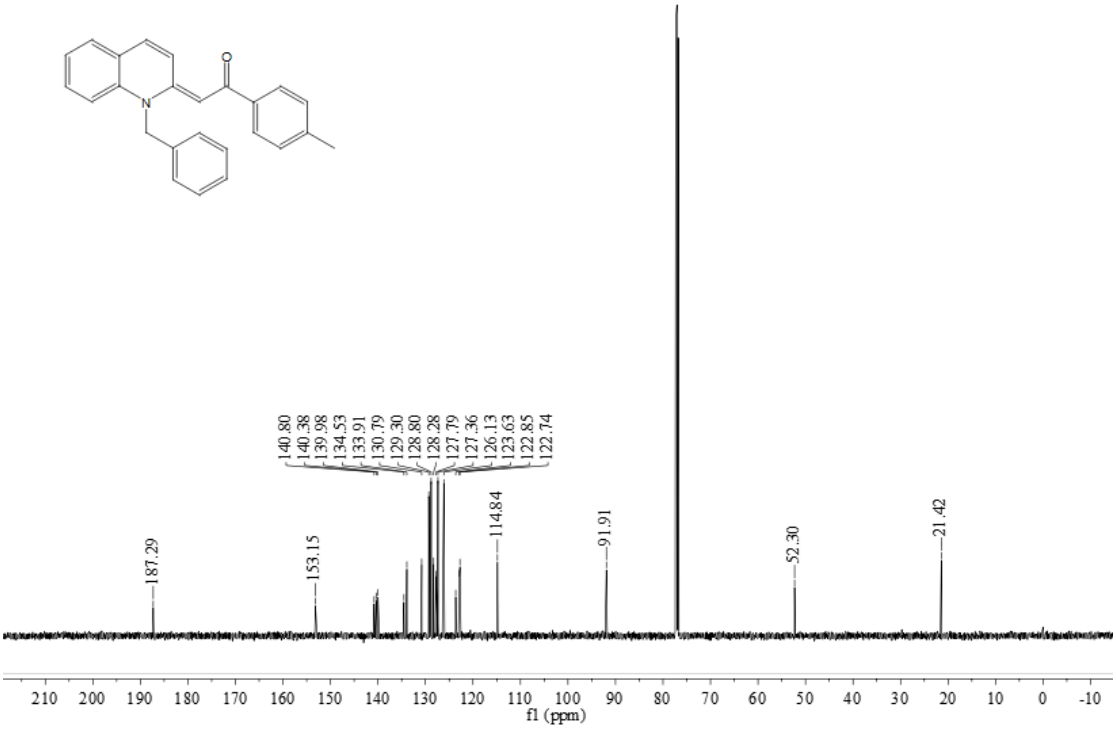
^{13}C NMR spectra of 4a (126 MHz, $CDCl_3$)



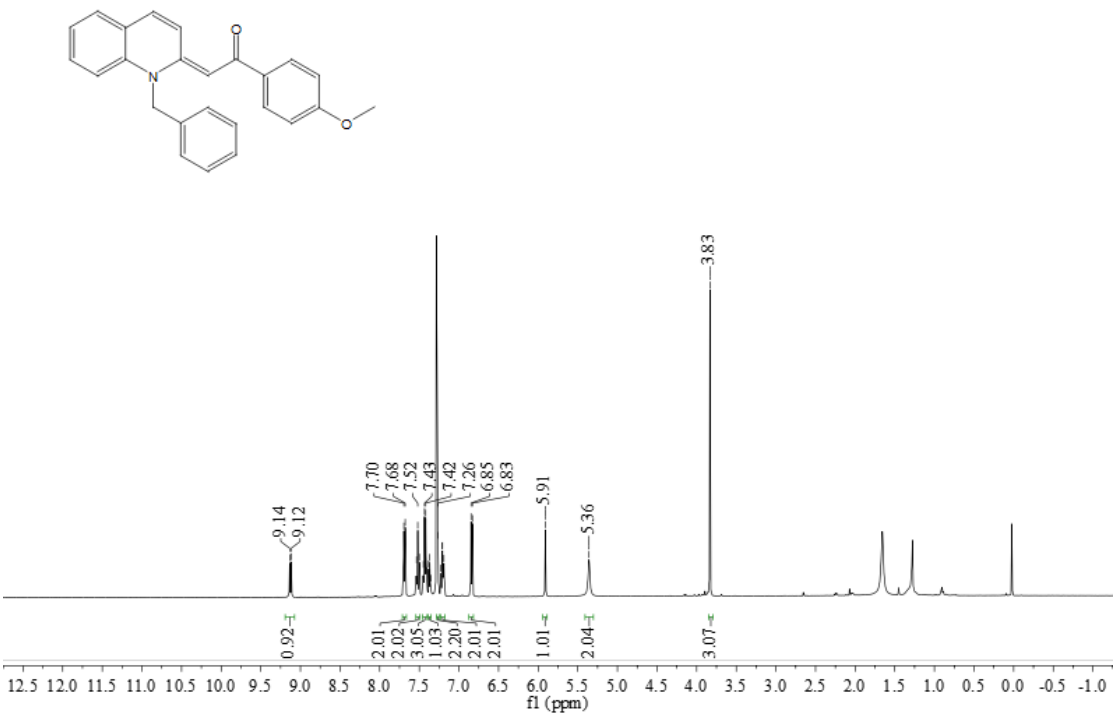
^{1}H NMR spectra of 4b (500 MHz, $CDCl_3$)



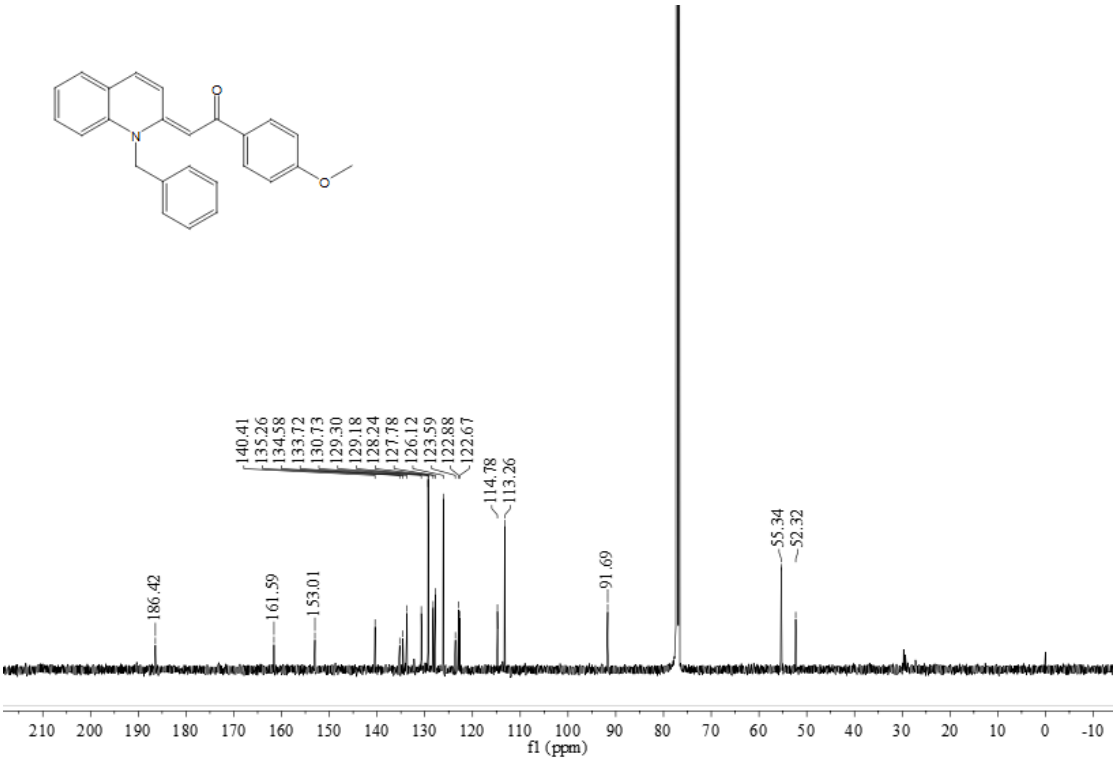
^{13}C NMR spectra of 4b (126 MHz, $CDCl_3$)



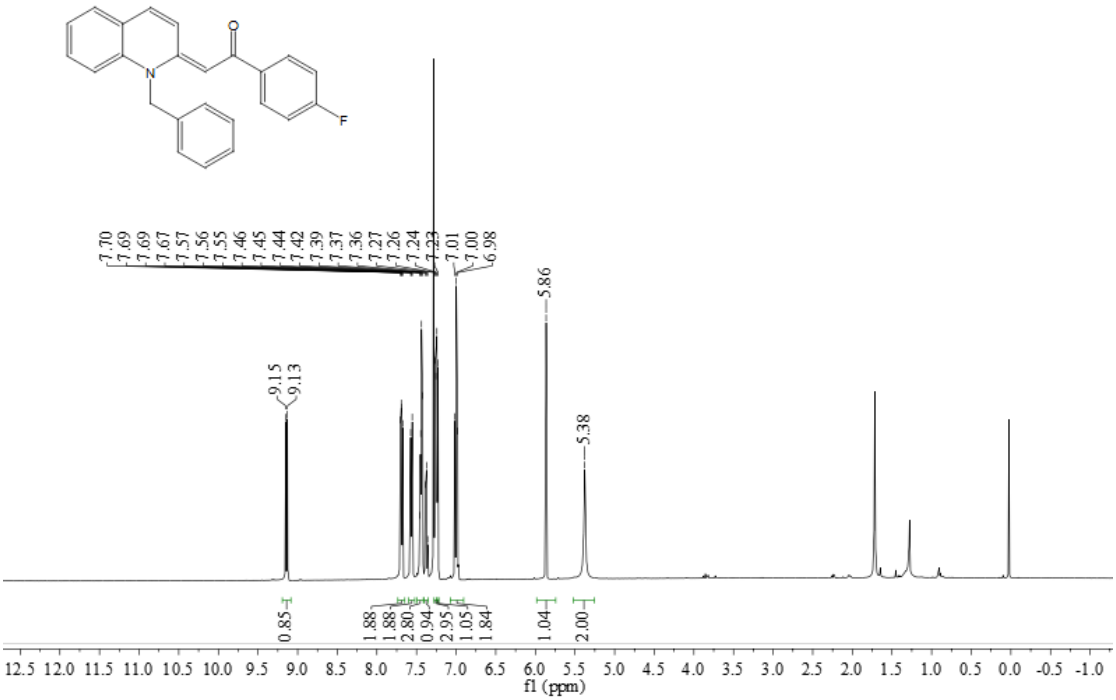
^{1}H NMR spectra of 4c (500 MHz, $CDCl_3$)



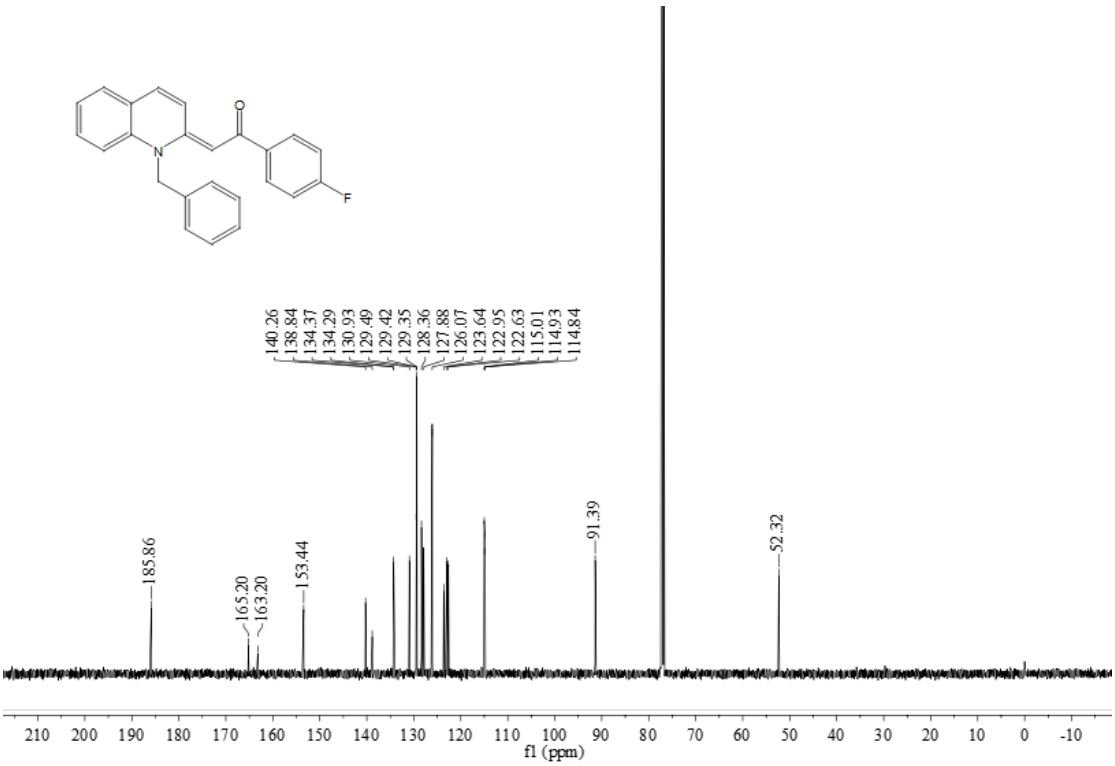
^{13}C NMR spectra of 4c (126 MHz, $CDCl_3$)



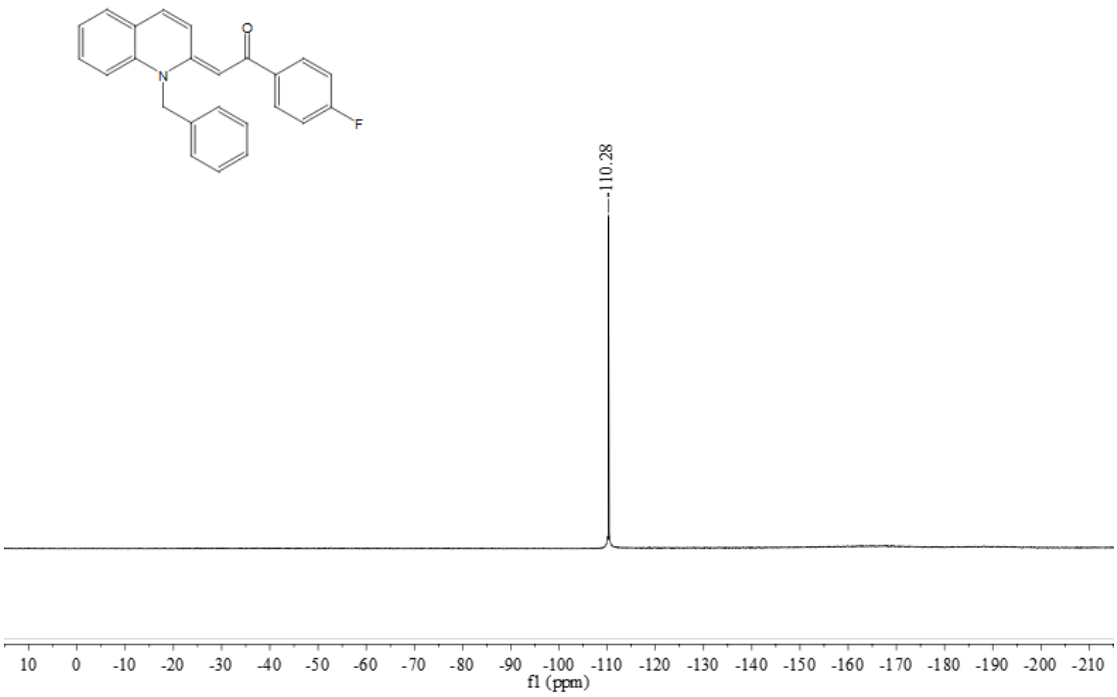
^{1}H NMR spectra of 4d (500 MHz, $CDCl_3$)



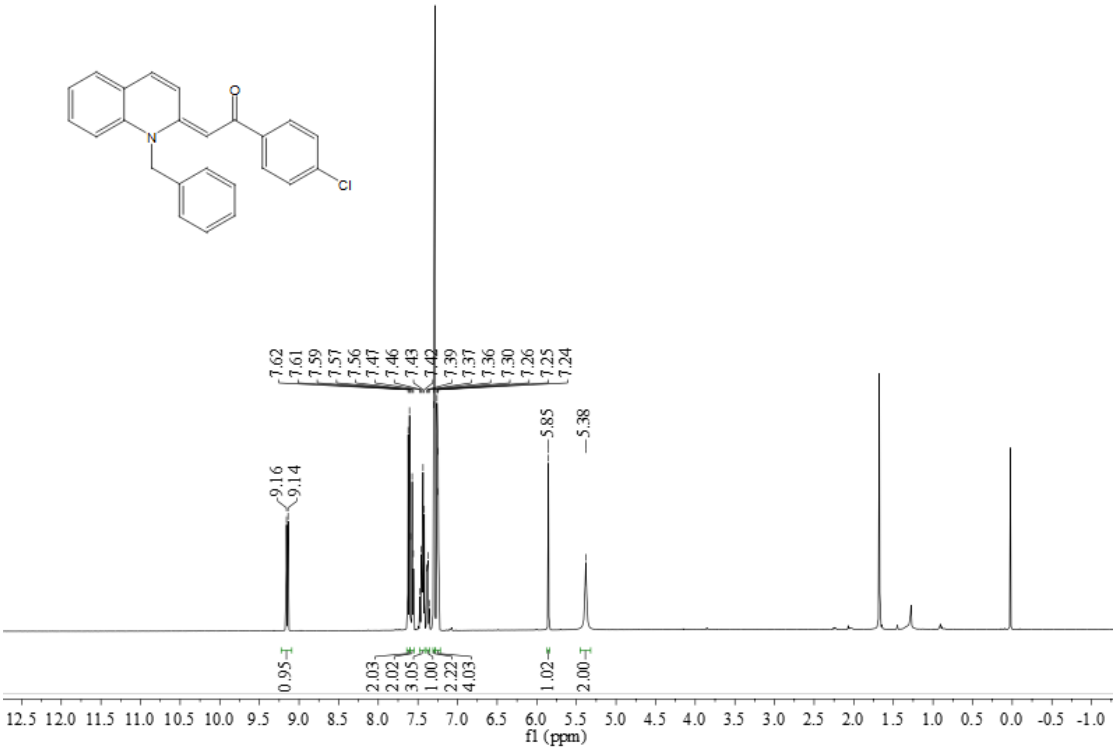
^{13}C NMR spectra of 4d (126 MHz, $CDCl_3$)



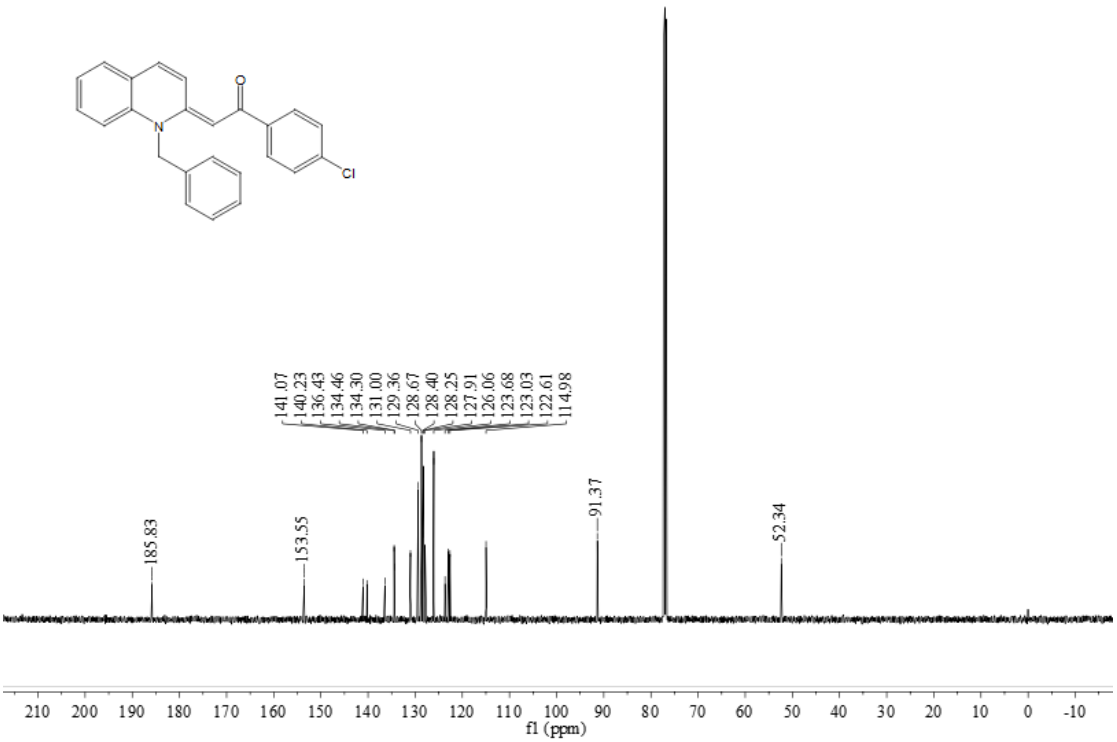
^{19}F NMR spectra of 4d (471 MHz, CDCl3)



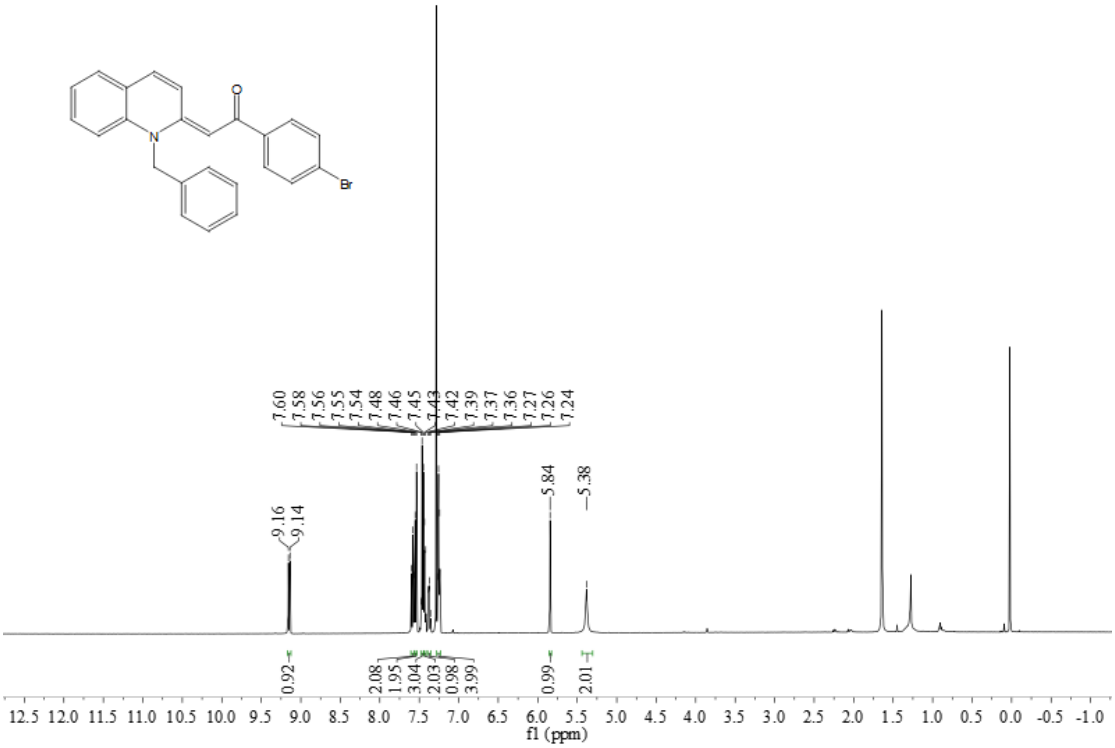
^{1}H NMR spectra of 4e (500 MHz, $CDCl_3$)



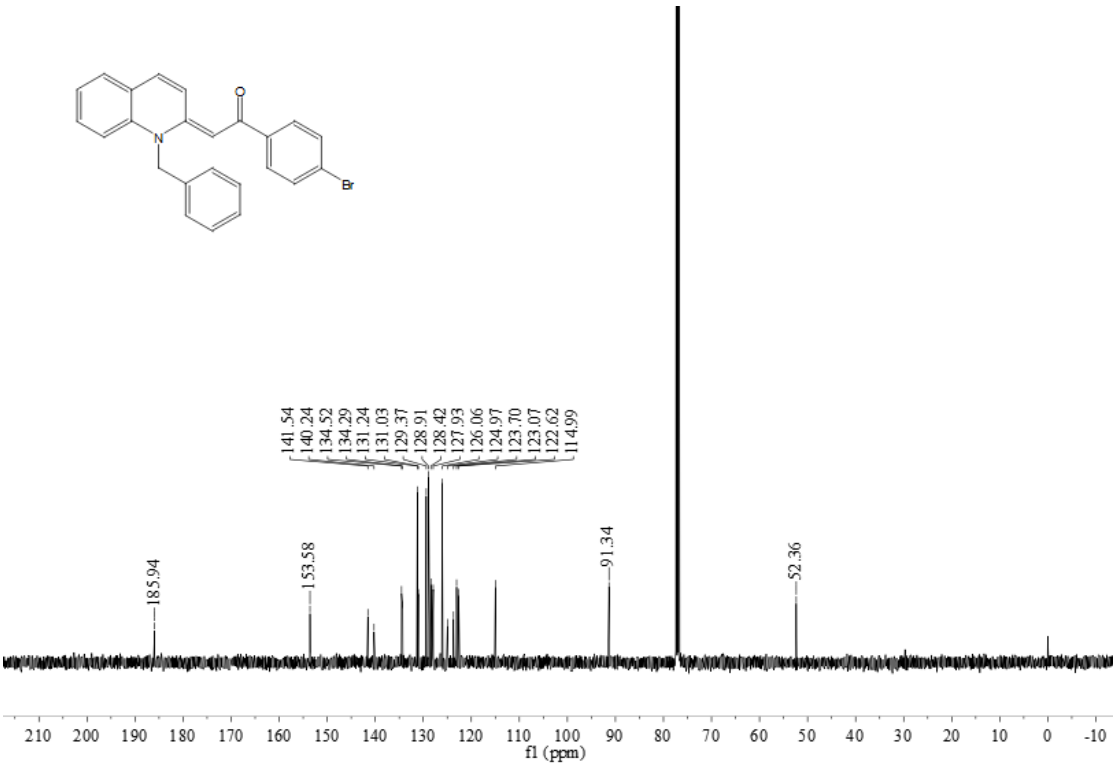
^{13}C NMR spectra of 4e (126 MHz, $CDCl_3$)



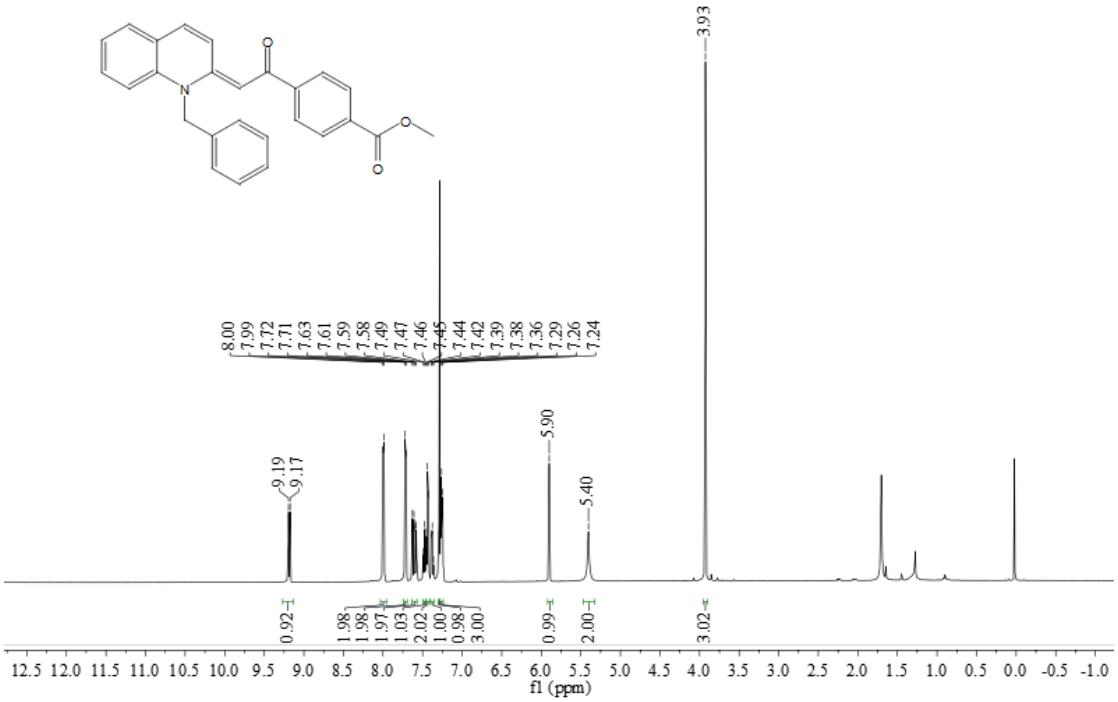
^{1}H NMR spectra of 4f (500 MHz, $CDCl_3$)



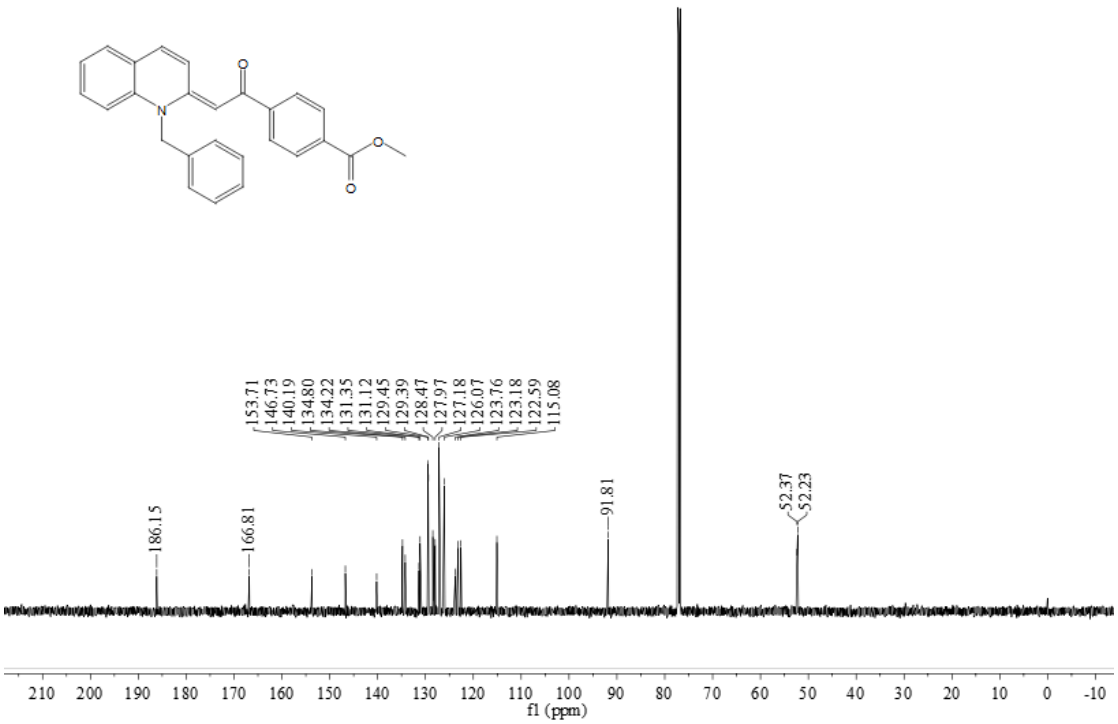
^{13}C NMR spectra of 4f (126 MHz, $CDCl_3$)



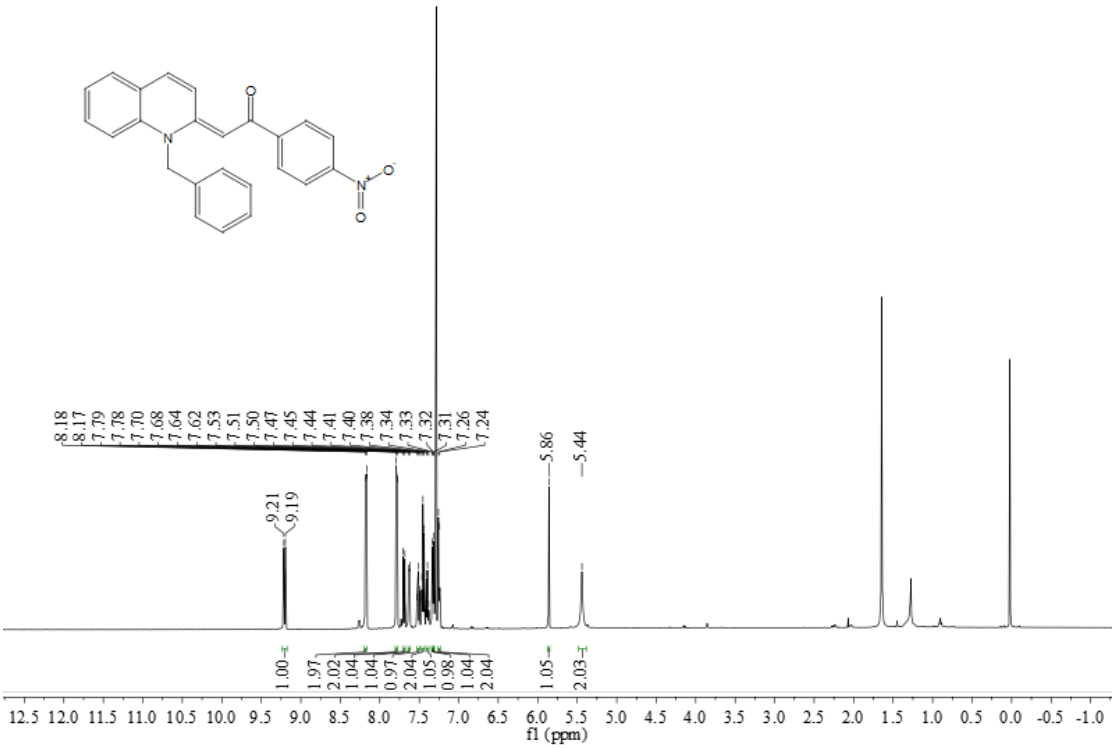
^{1}H NMR spectra of 4g (500 MHz, $CDCl_3$)



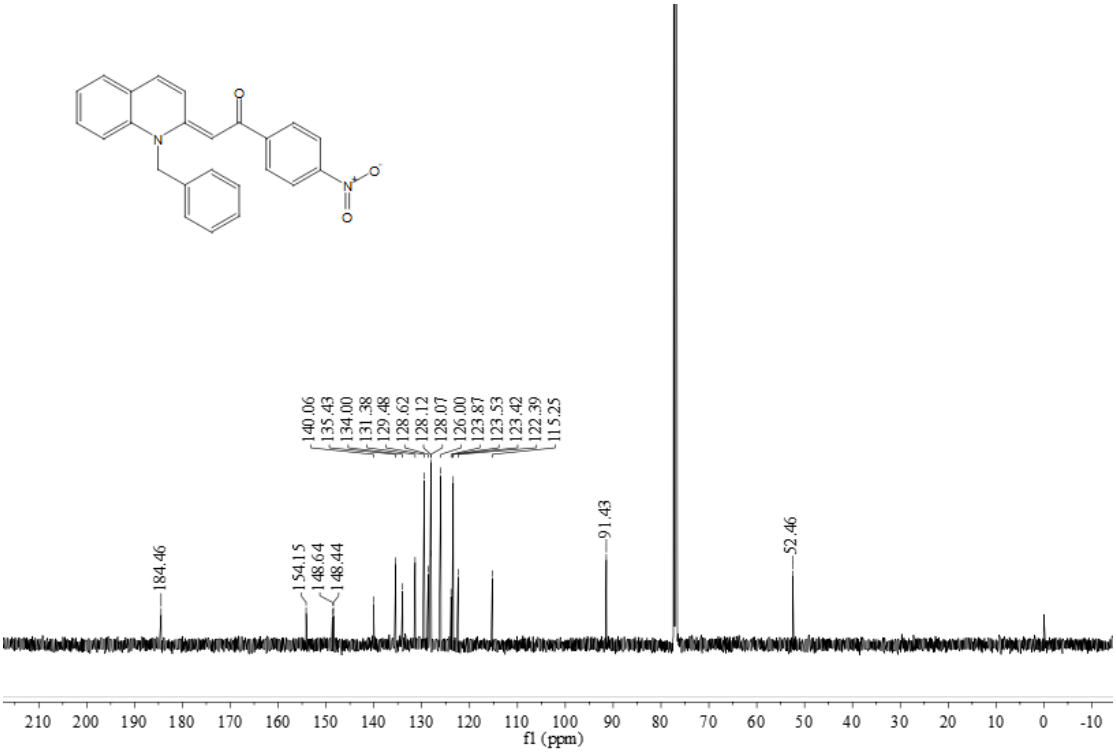
^{13}C NMR spectra of 4g (126 MHz, $CDCl_3$)



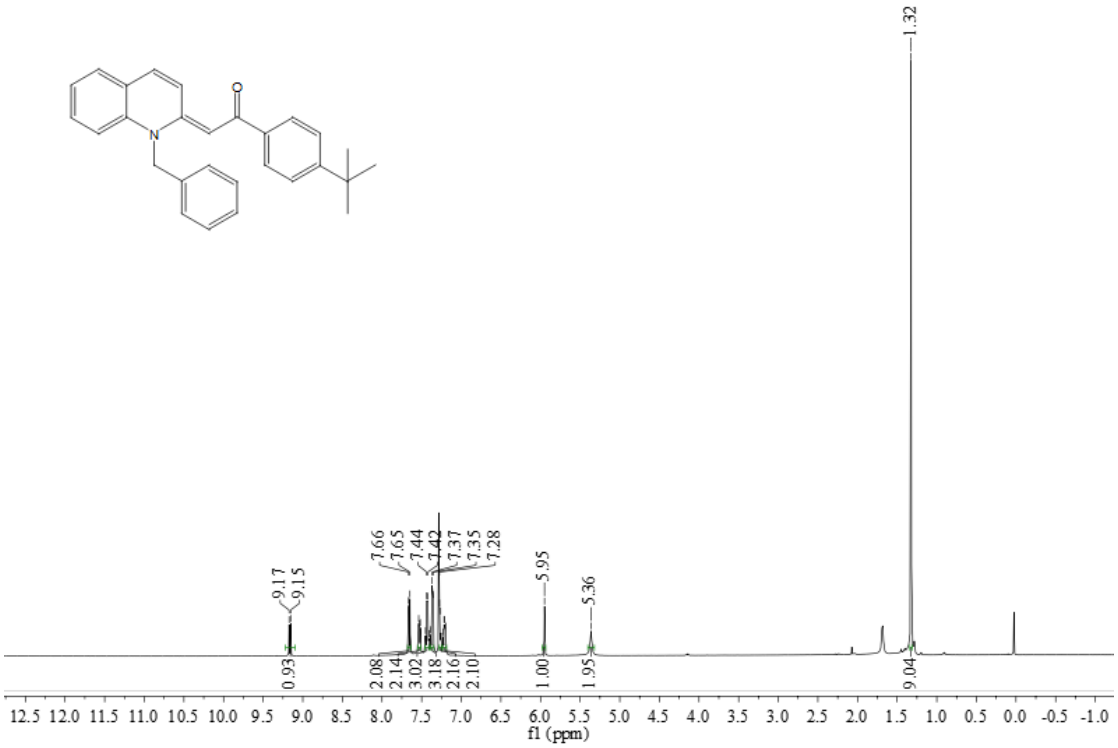
^{1}H NMR spectra of 4h (500 MHz, $CDCl_3$)



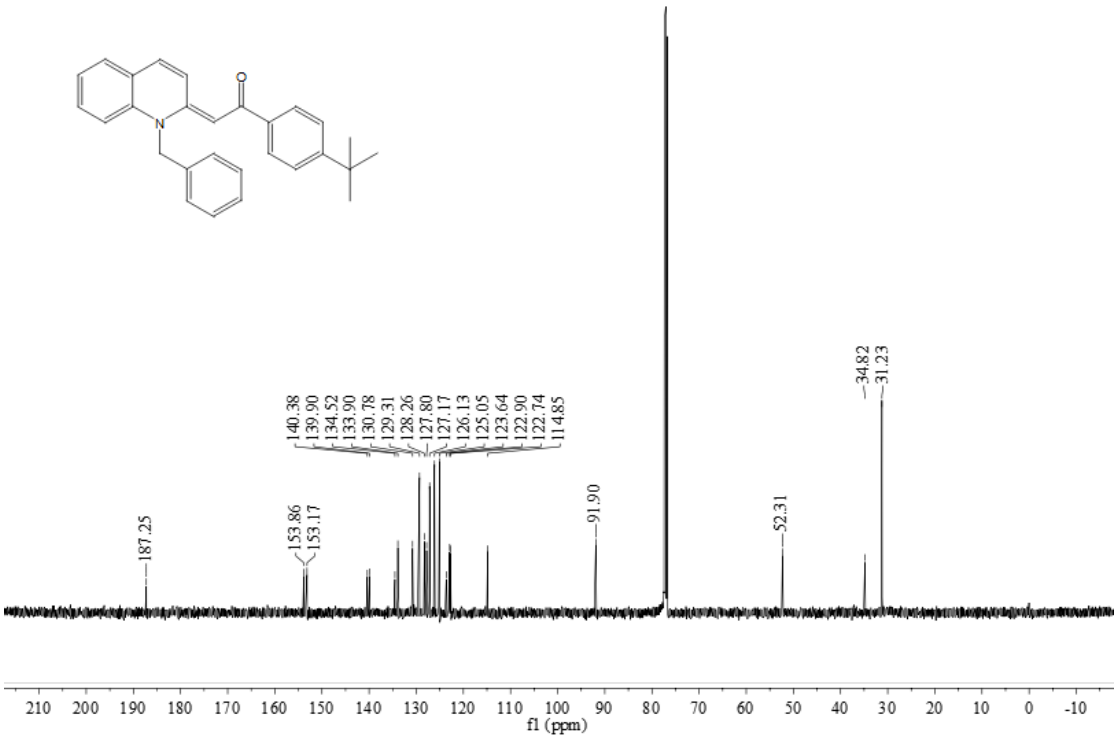
^{13}C NMR spectra of 4h (126 MHz, $CDCl_3$)



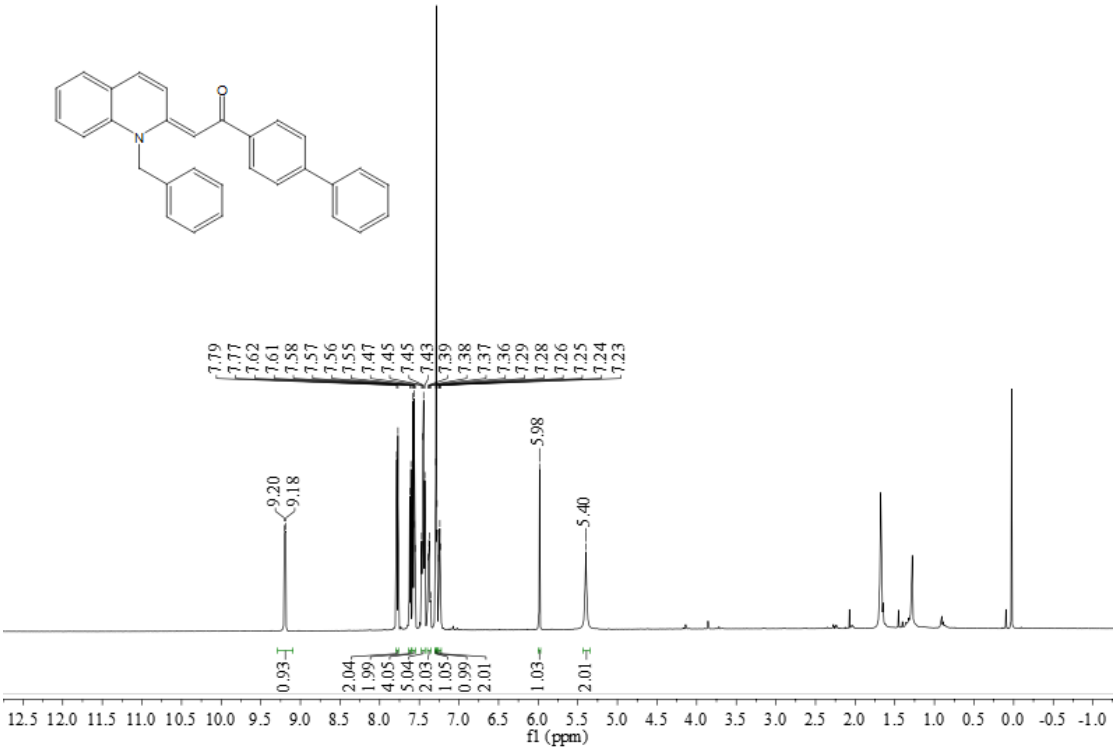
^{1}H NMR spectra of 4i (500 MHz, $CDCl_3$)



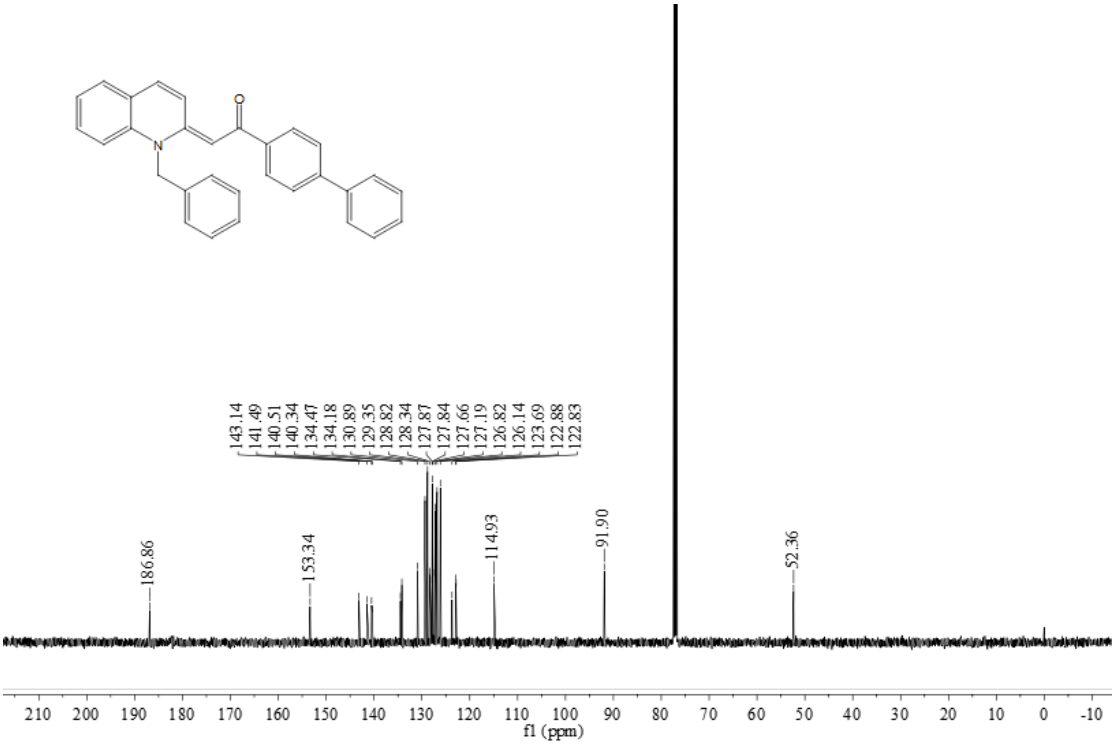
^{13}C NMR spectra of 4i (126 MHz, $CDCl_3$)



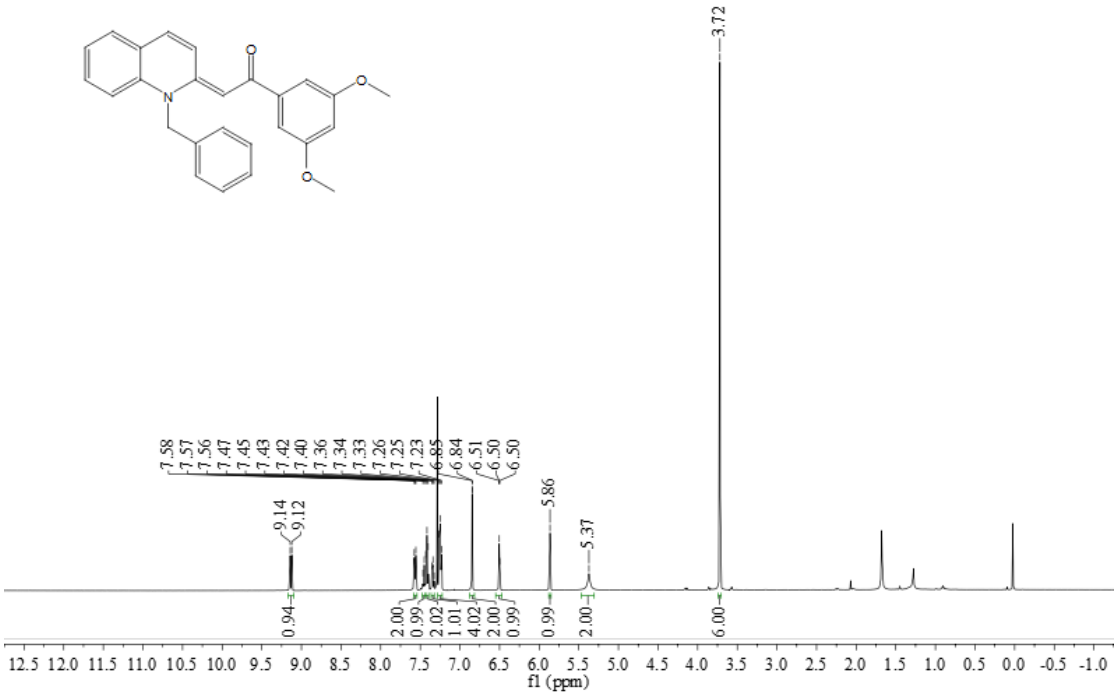
^{1}H NMR spectra of 4j (500 MHz, $CDCl_3$)



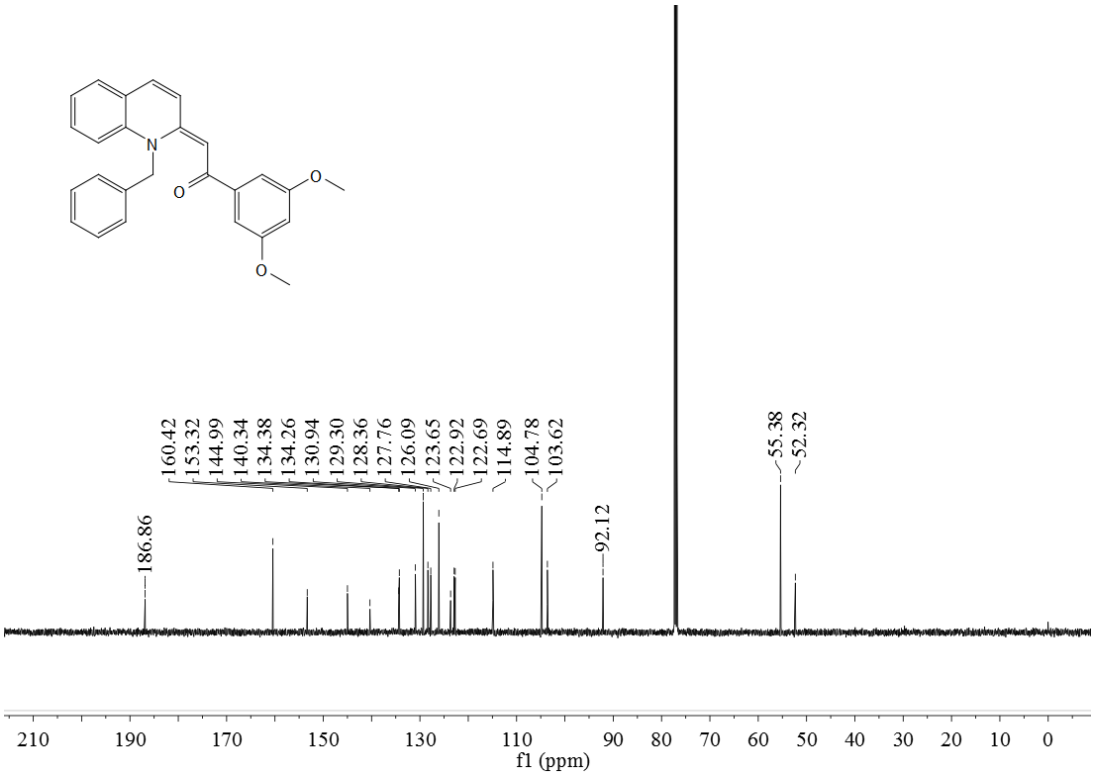
^{13}C NMR spectra of 4j (126 MHz, $CDCl_3$)



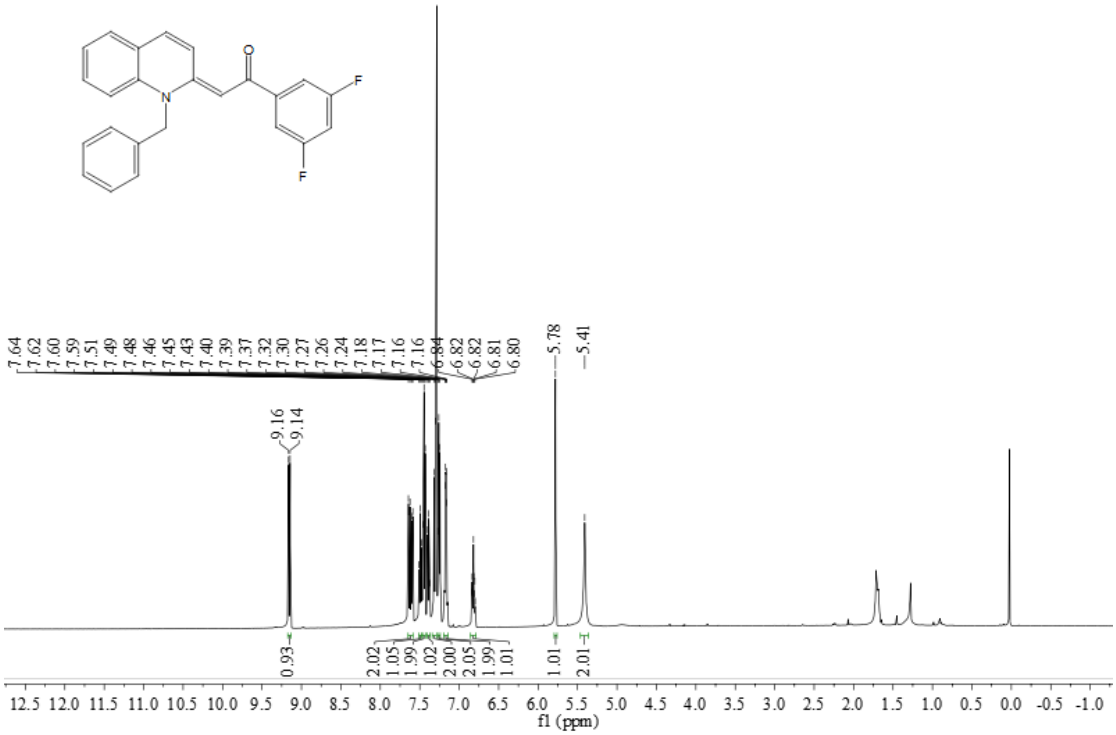
^{1}H NMR spectra of 4k (500 MHz, $CDCl_3$)



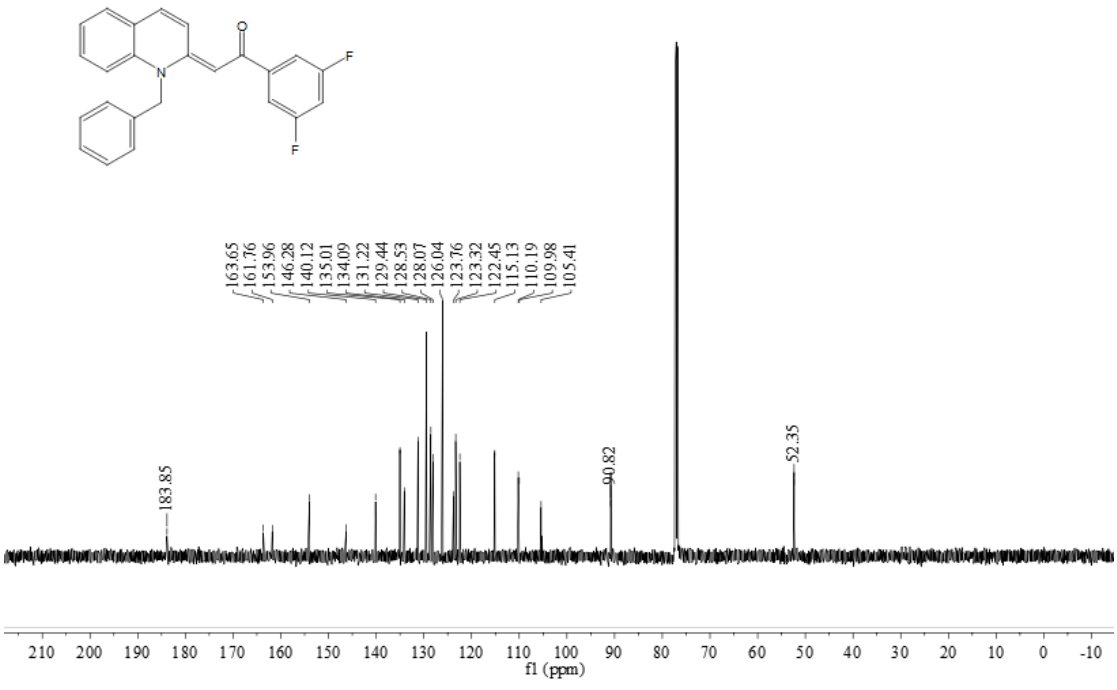
^{13}C NMR spectra of 4k (126 MHz, $CDCl_3$)



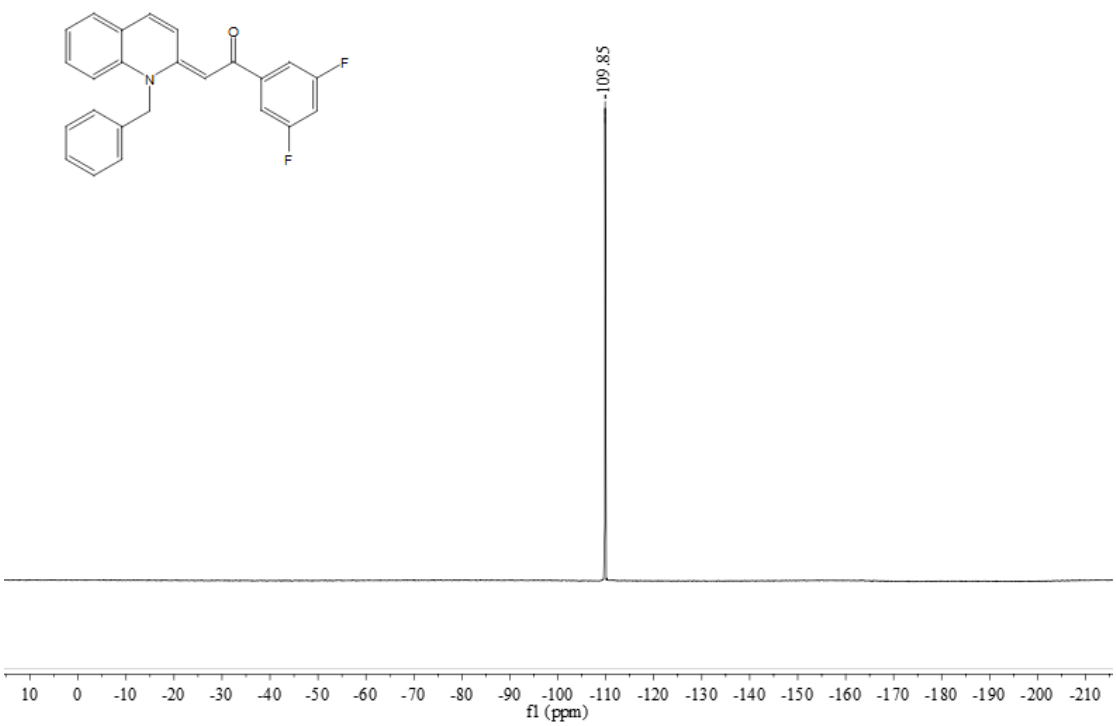
^{1}H NMR spectra of 4l (500 MHz, $CDCl_3$)



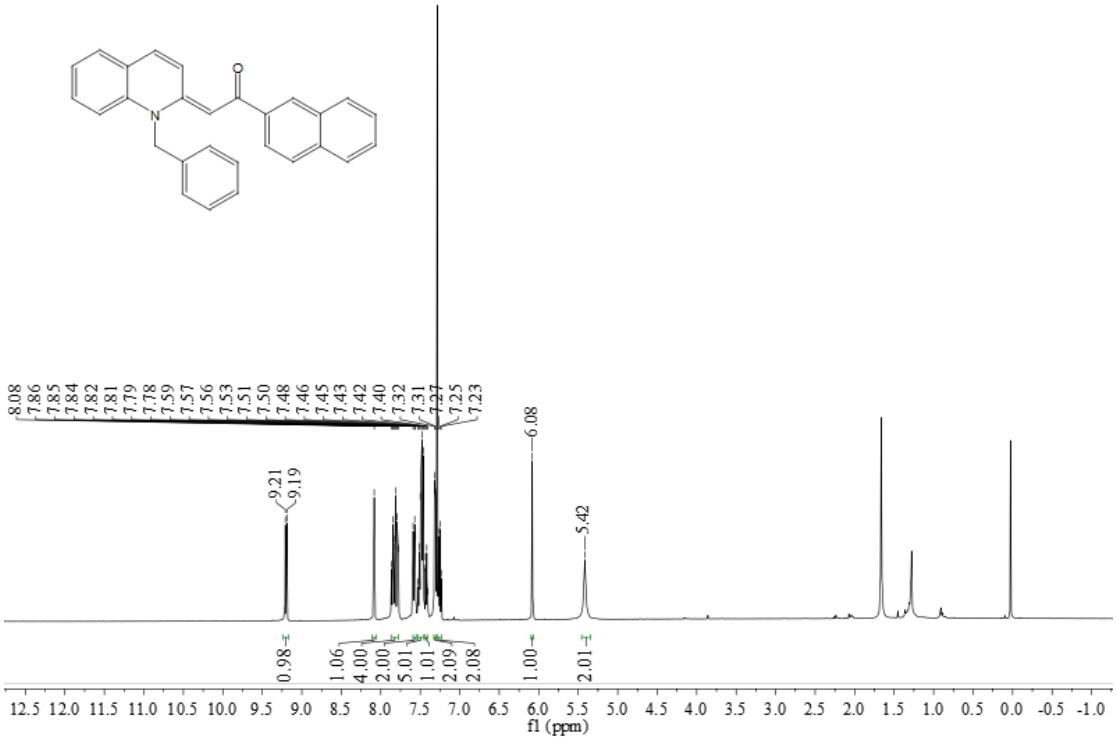
^{13}C NMR spectra of 4l (126 MHz, $CDCl_3$)



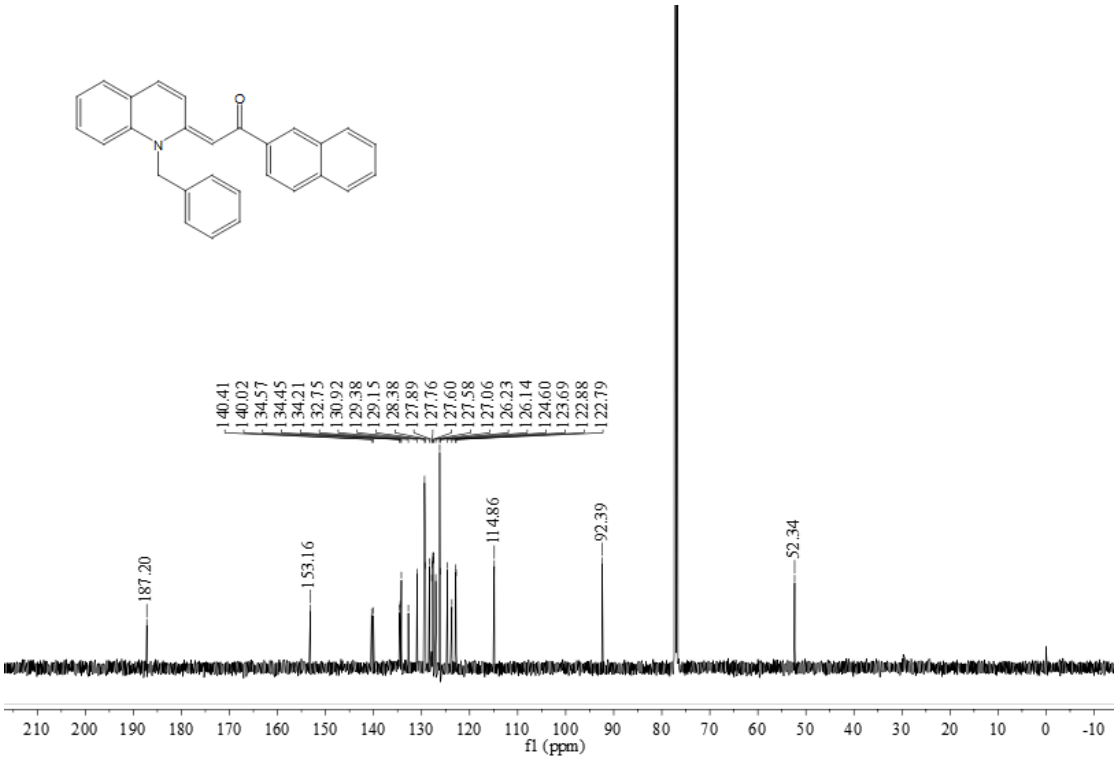
^{19}F NMR spectra of 4l (471 MHz, $CDCl_3$)



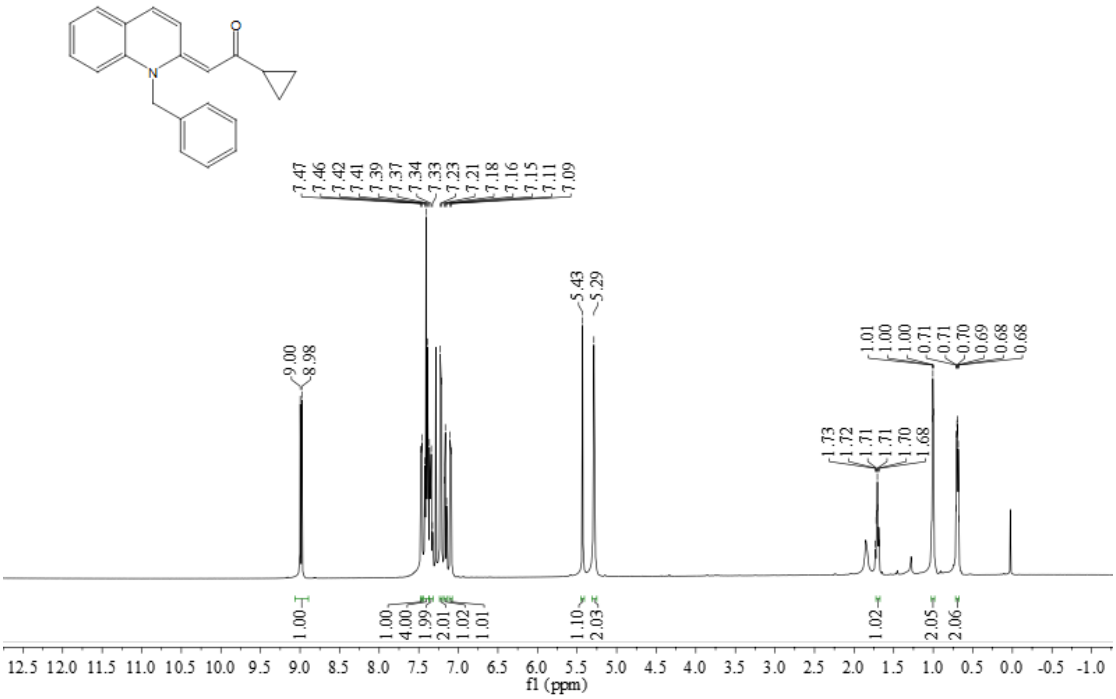
^{1}H NMR spectra of 4m (500 MHz, $CDCl_3$)



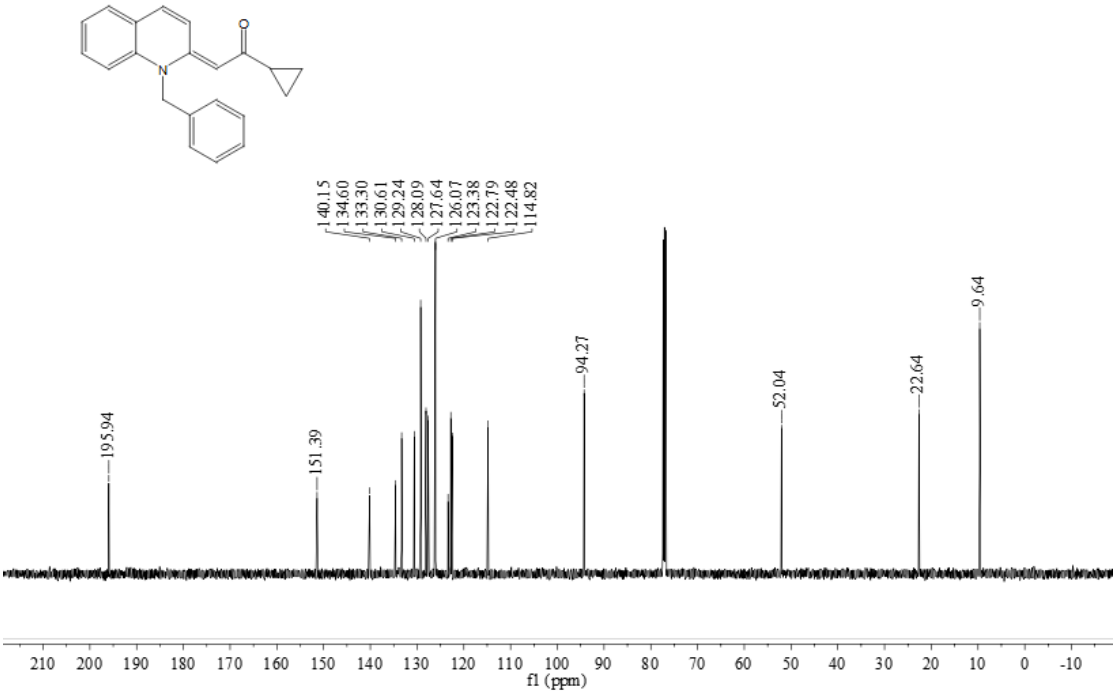
^{13}C NMR spectra of 4m (126 MHz, $CDCl_3$)



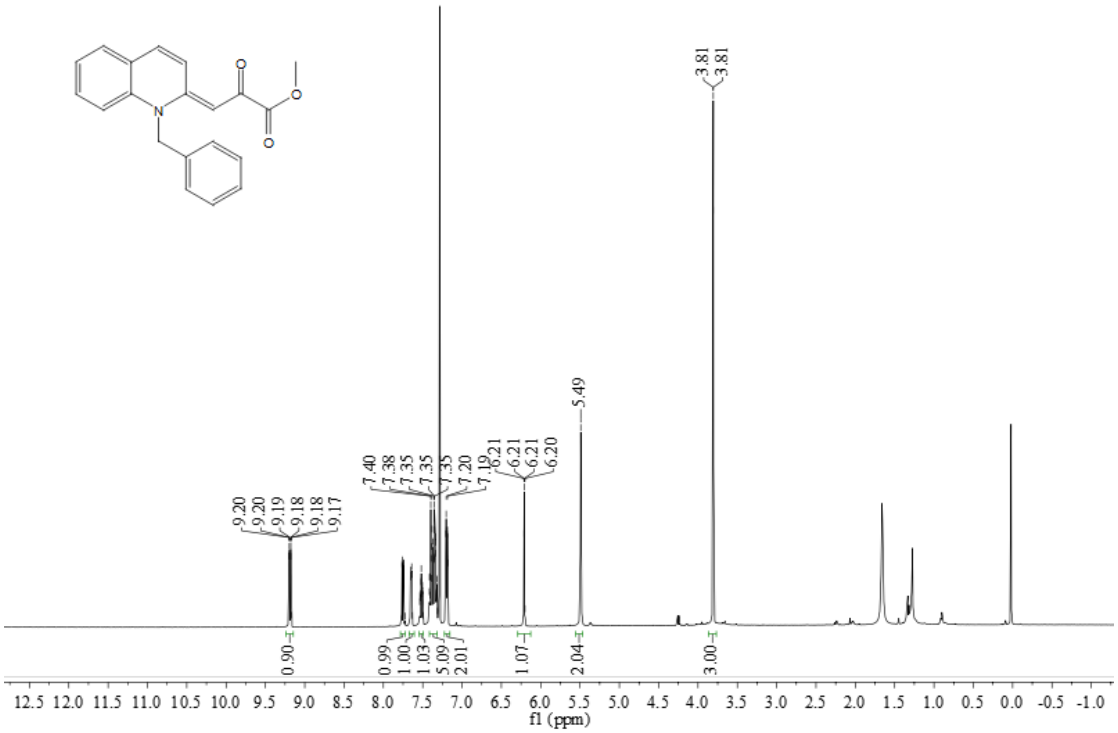
^{1}H NMR spectra of 4n (500 MHz, $CDCl_3$)



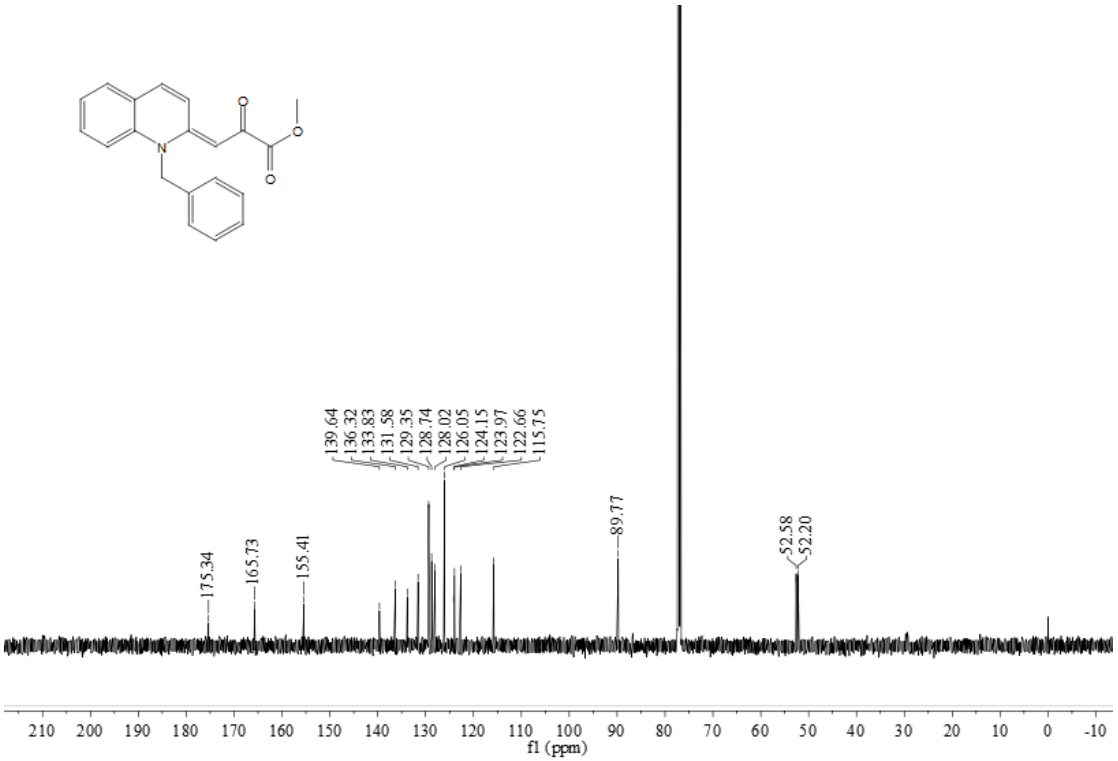
^{13}C NMR spectra of 4n (126 MHz, $CDCl_3$)



^{1}H NMR spectra of 4o (500 MHz, $CDCl_3$)

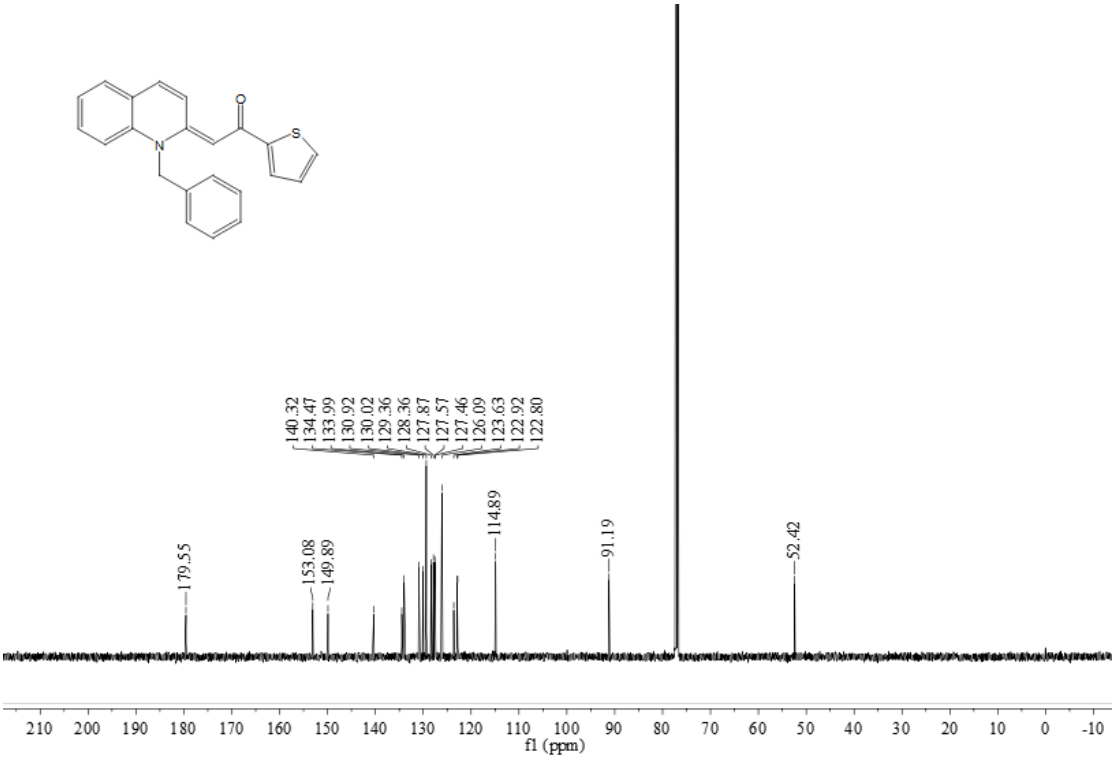


^{13}C NMR spectra of 4o (126 MHz, $CDCl_3$)

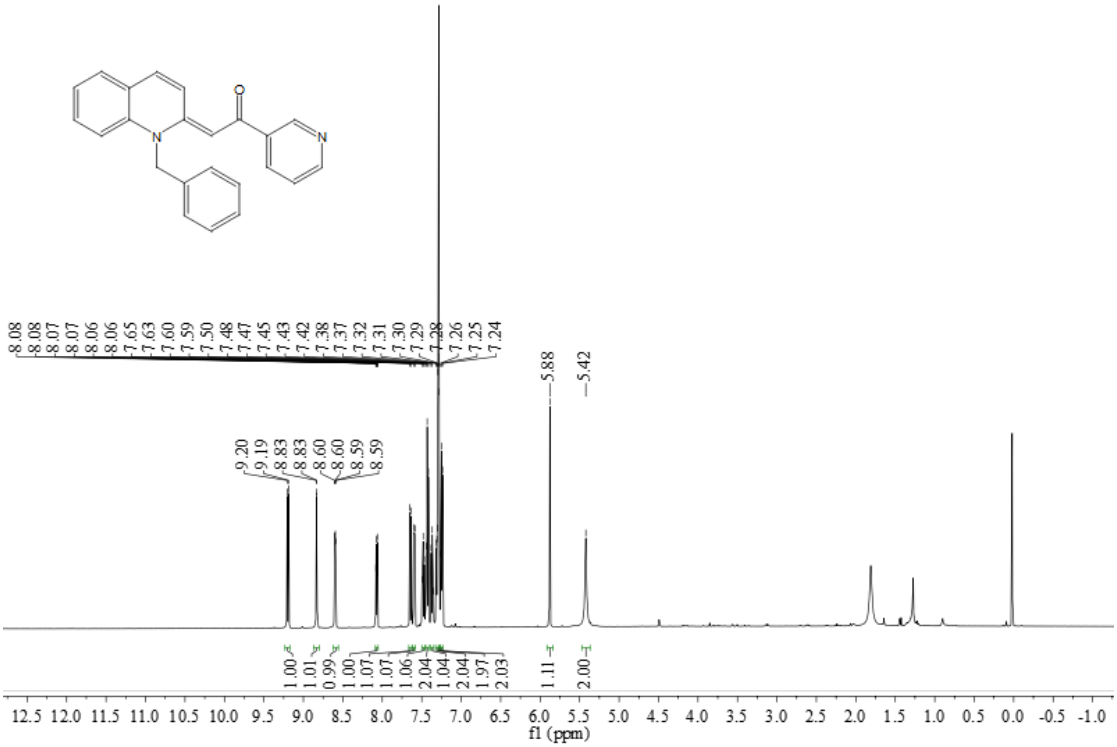


^{1}H NMR spectra of 4p (500 MHz, $CDCl_3$)

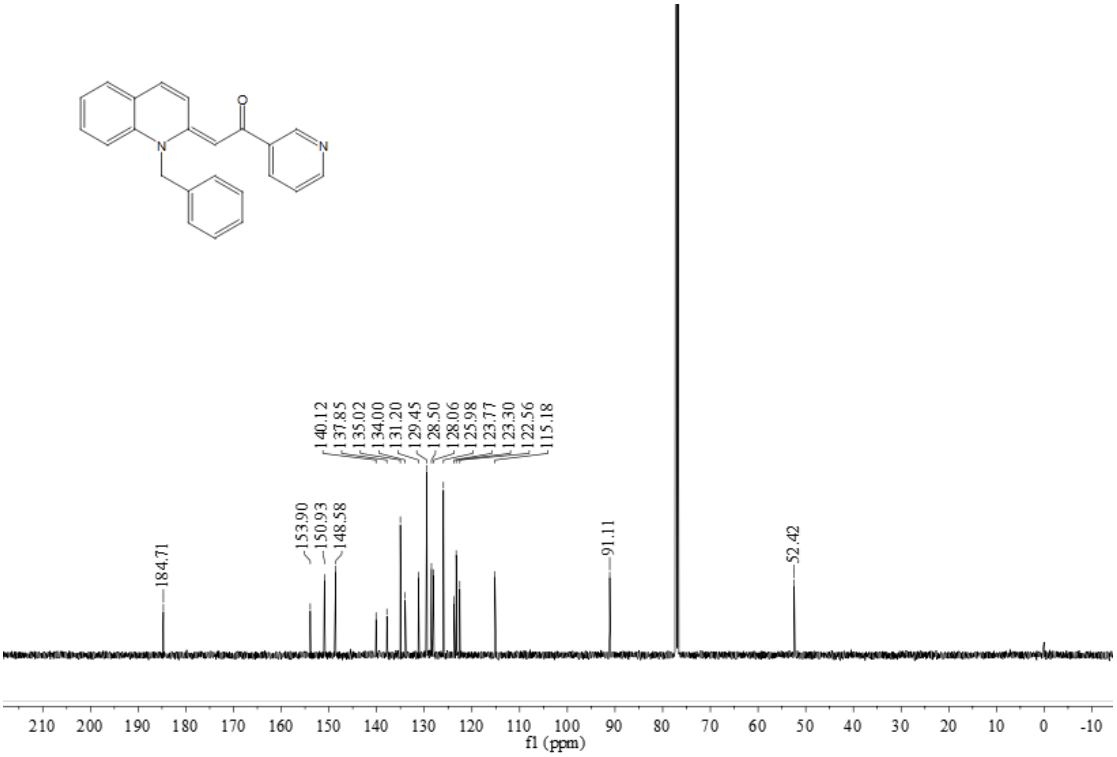
^{13}C NMR spectra of 4p (126 MHz, $CDCl_3$)



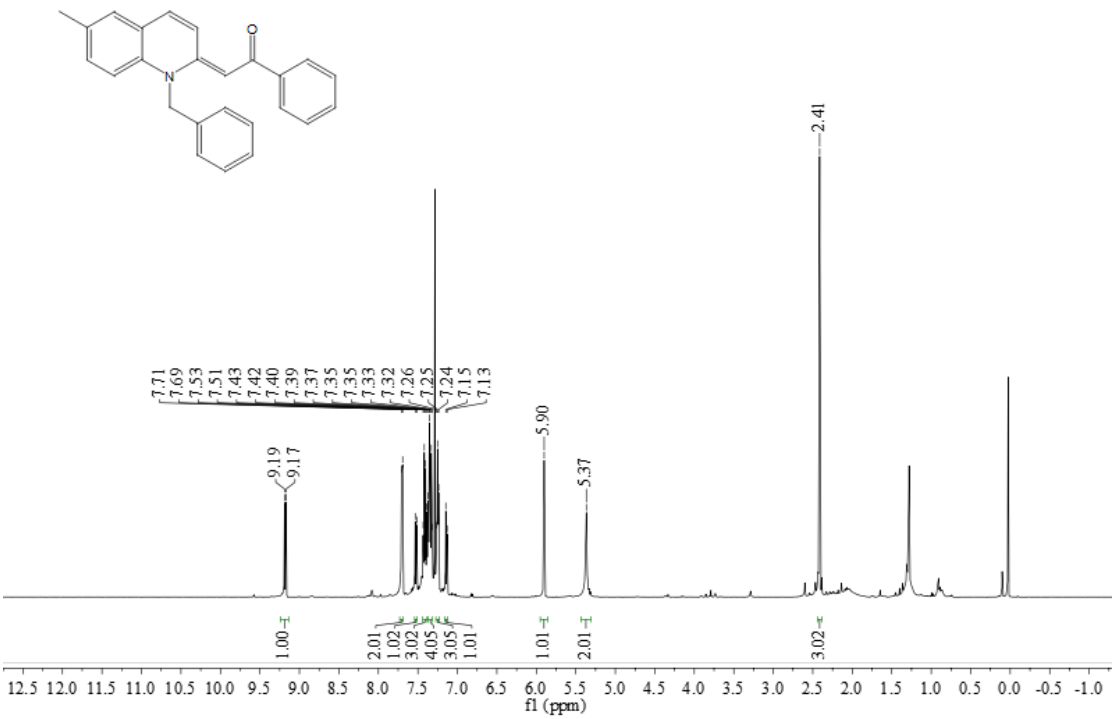
^{1}H NMR spectra of 4q (500 MHz, $CDCl_3$)



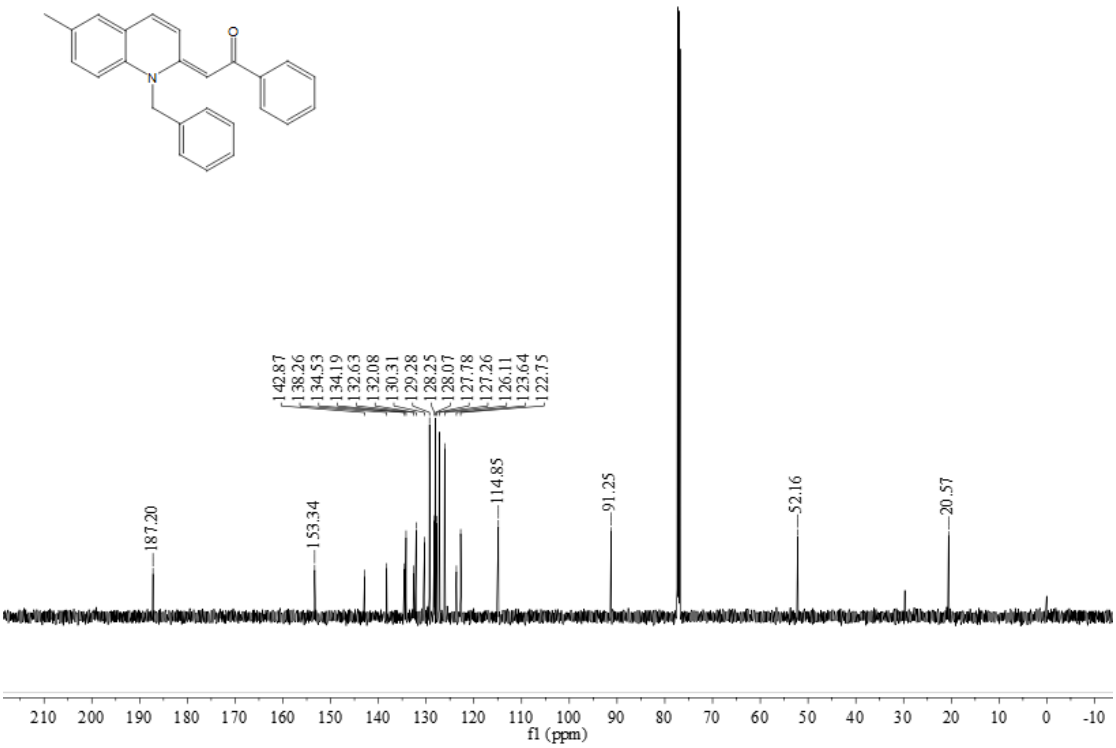
^{13}C NMR spectra of 4q (126 MHz, $CDCl_3$)



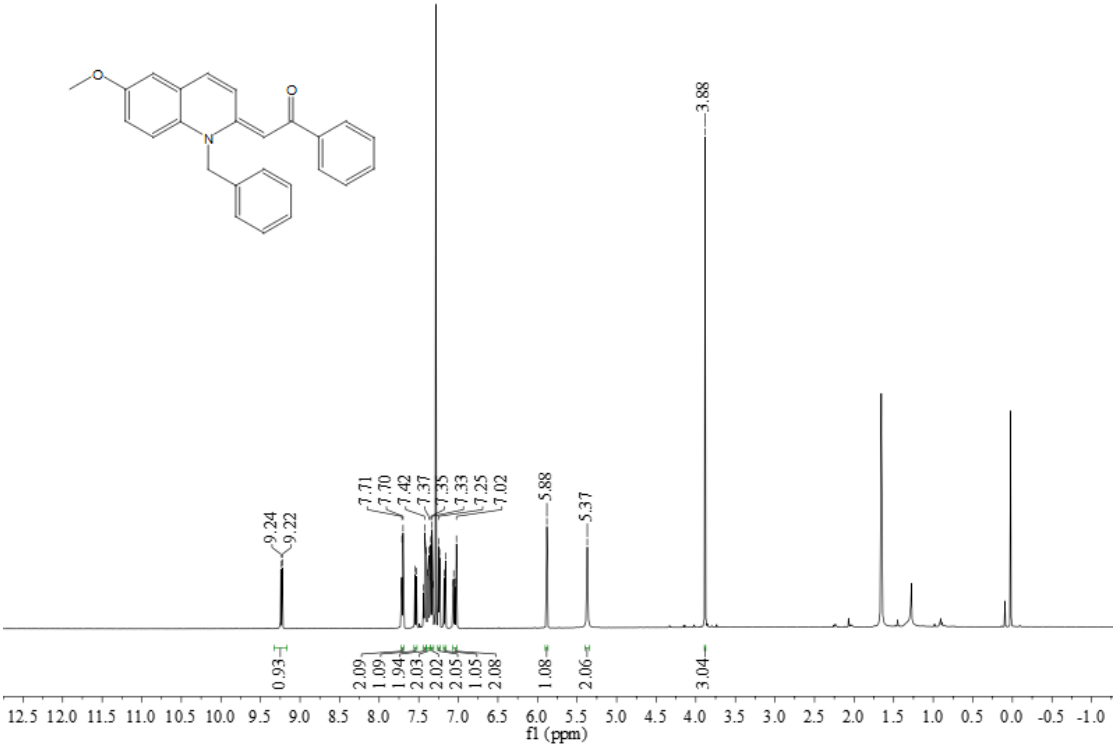
^{1}H NMR spectra of 5a (500 MHz, $CDCl_3$)



^{13}C NMR spectra of 5a (126 MHz, $CDCl_3$)



^{1}H NMR spectra of 5b (500 MHz, $CDCl_3$)



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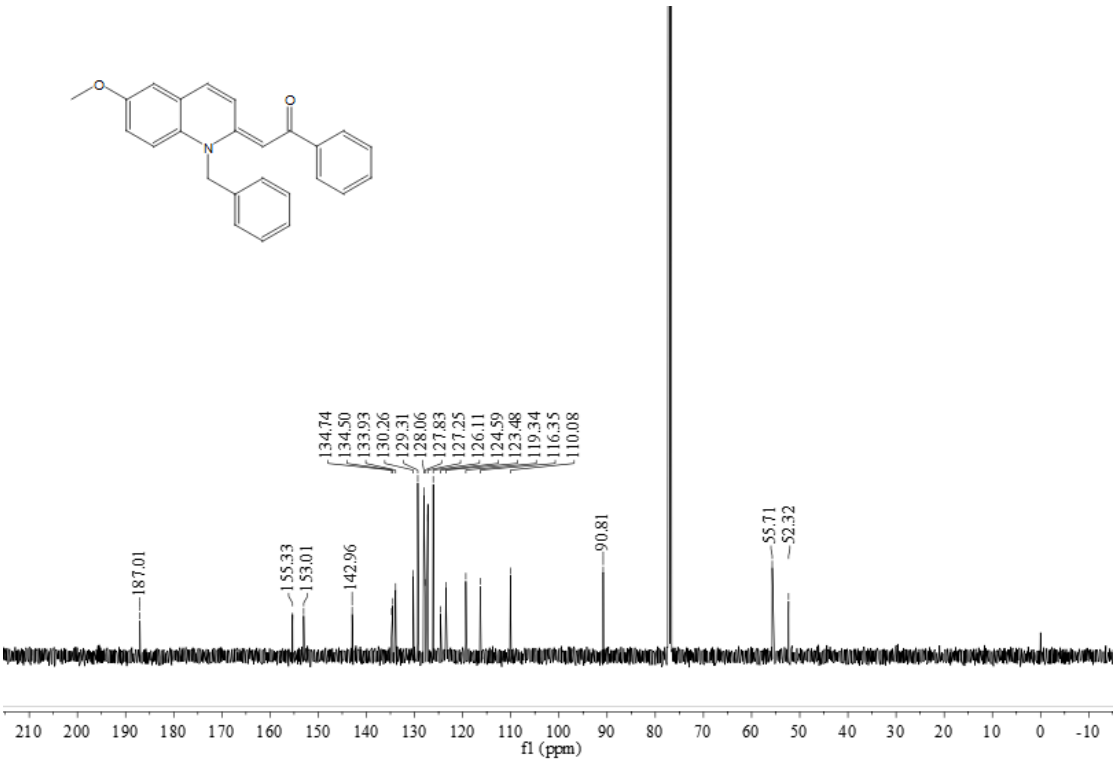
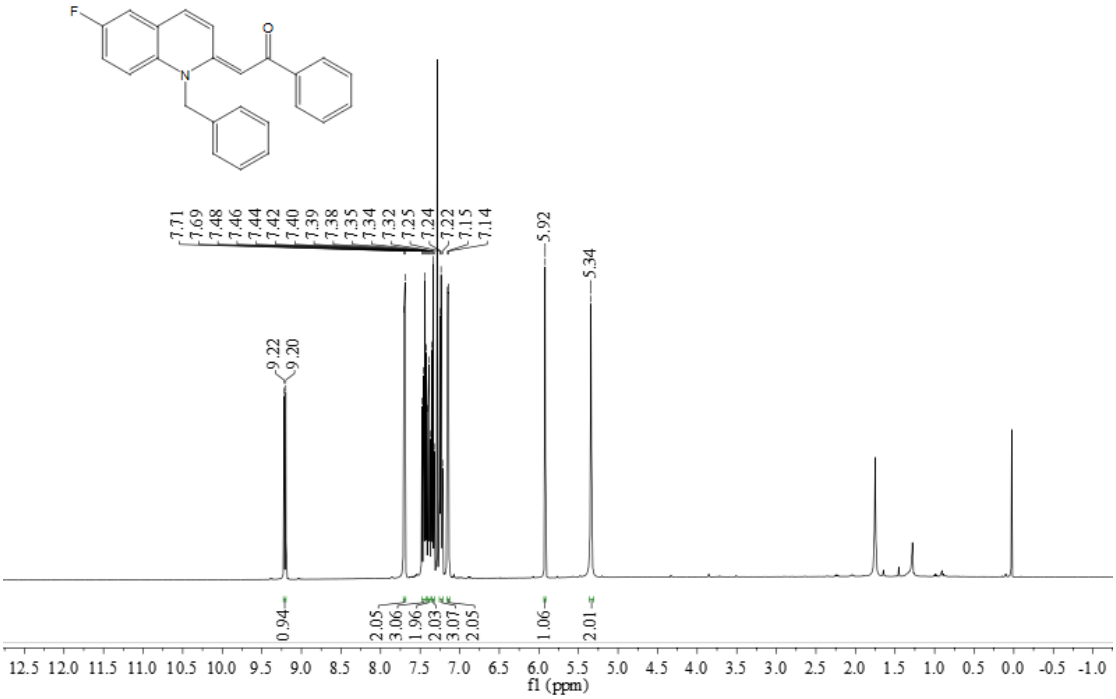
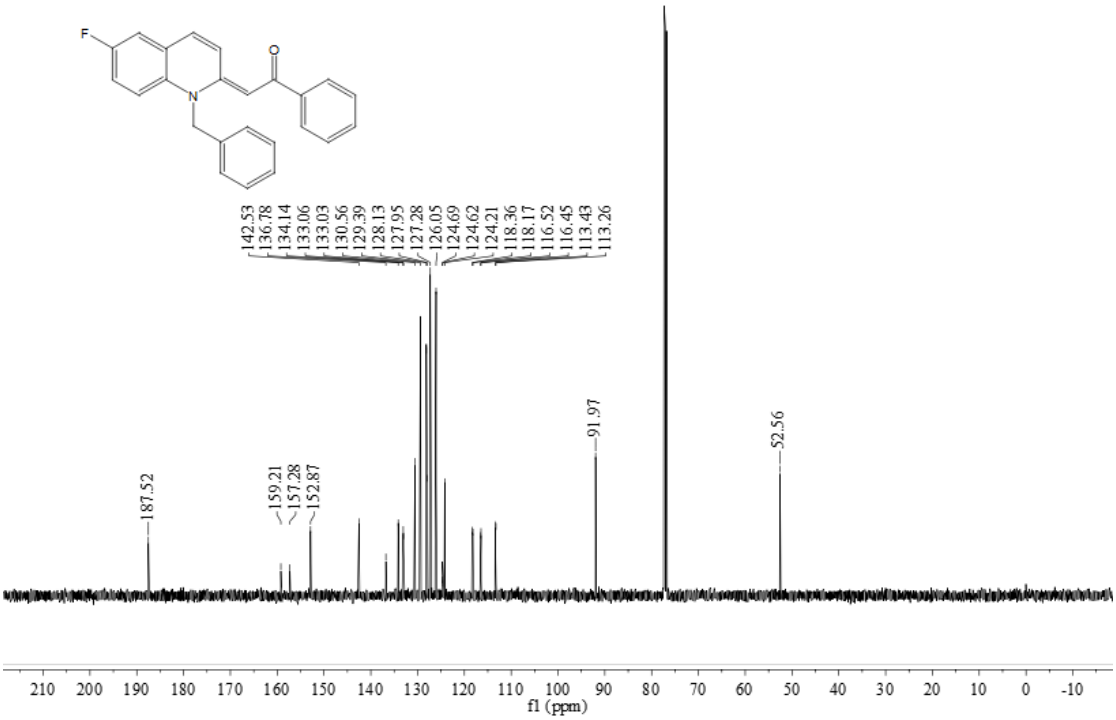


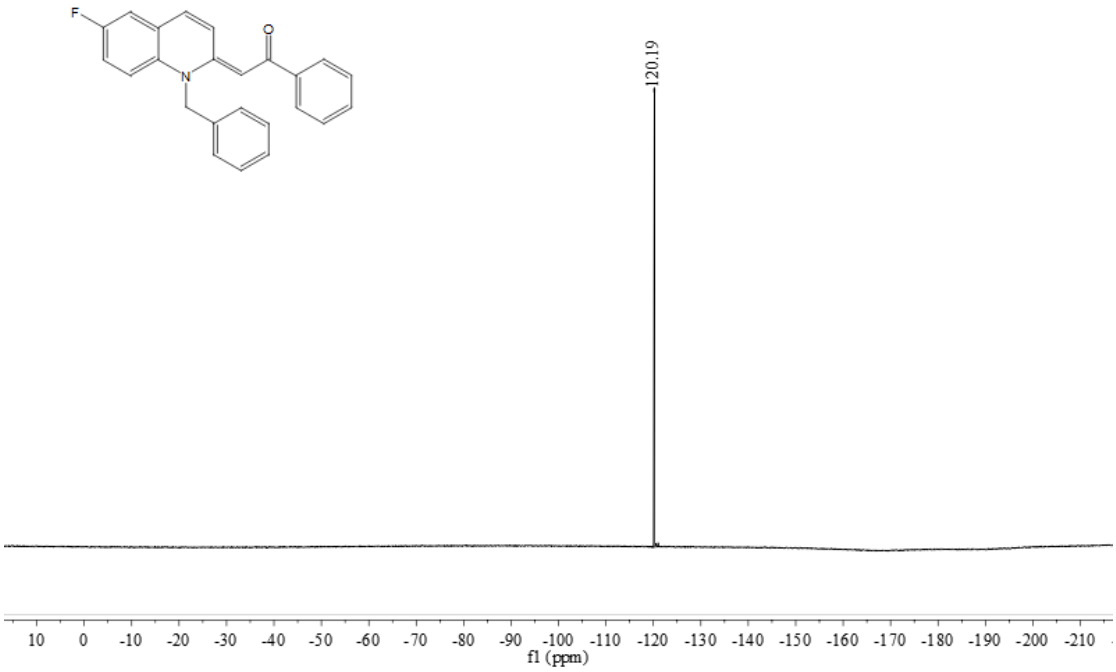
^{1}H NMR spectra of 5c (500 MHz, $CDCl_3$)



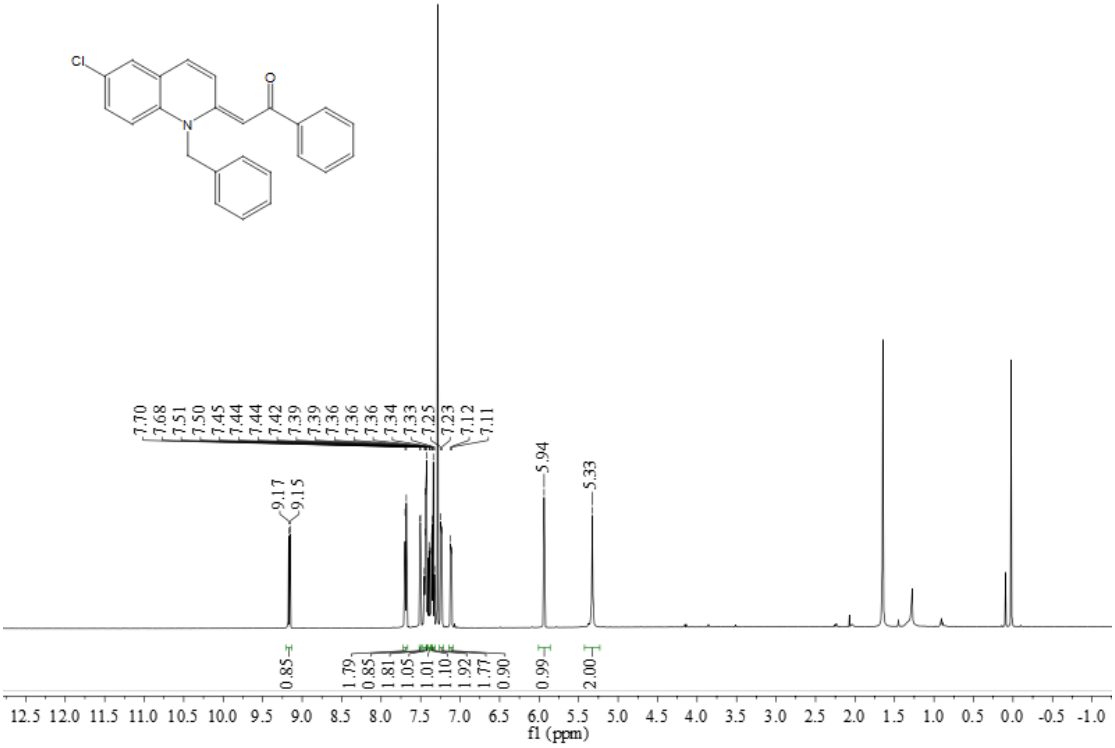
^{13}C NMR spectra of 5c (126 MHz, $CDCl_3$)



^{19}F NMR spectra of 5c (471 MHz, $CDCl_3$)



^{1}H NMR spectra of 5d (500 MHz, $CDCl_3$)



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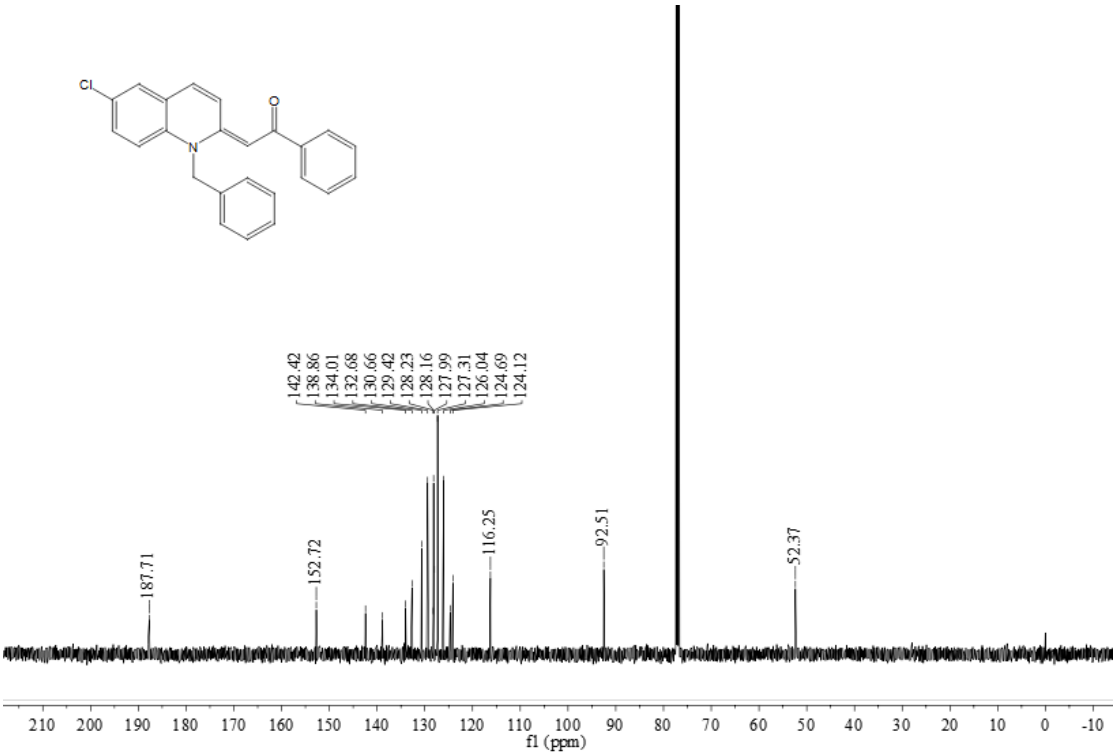
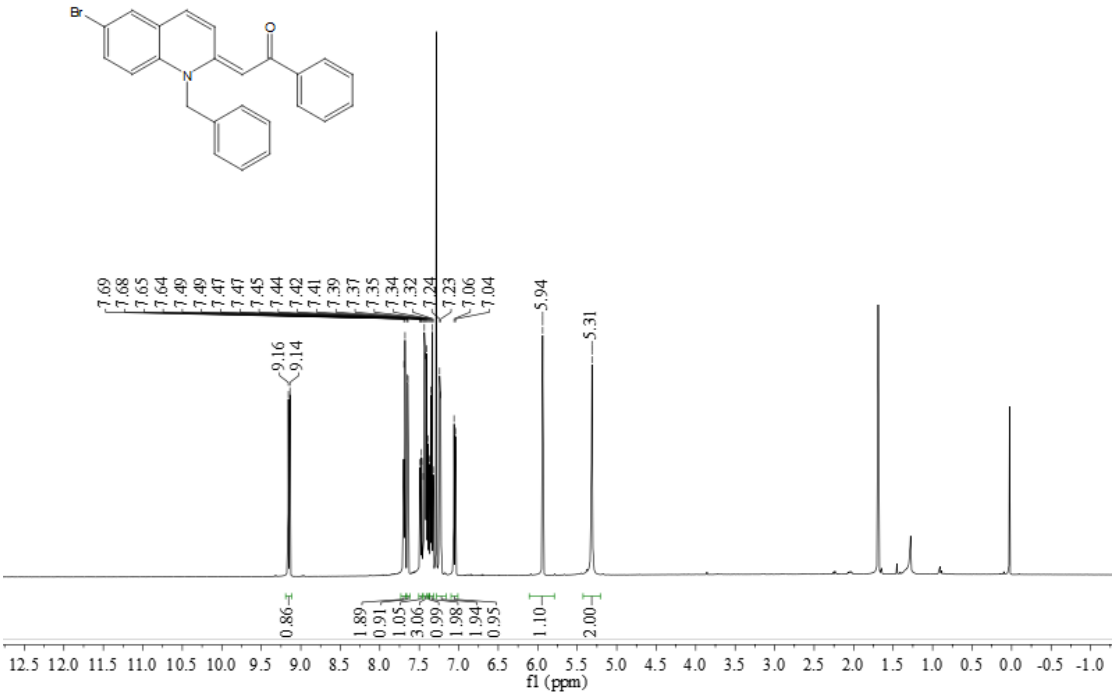
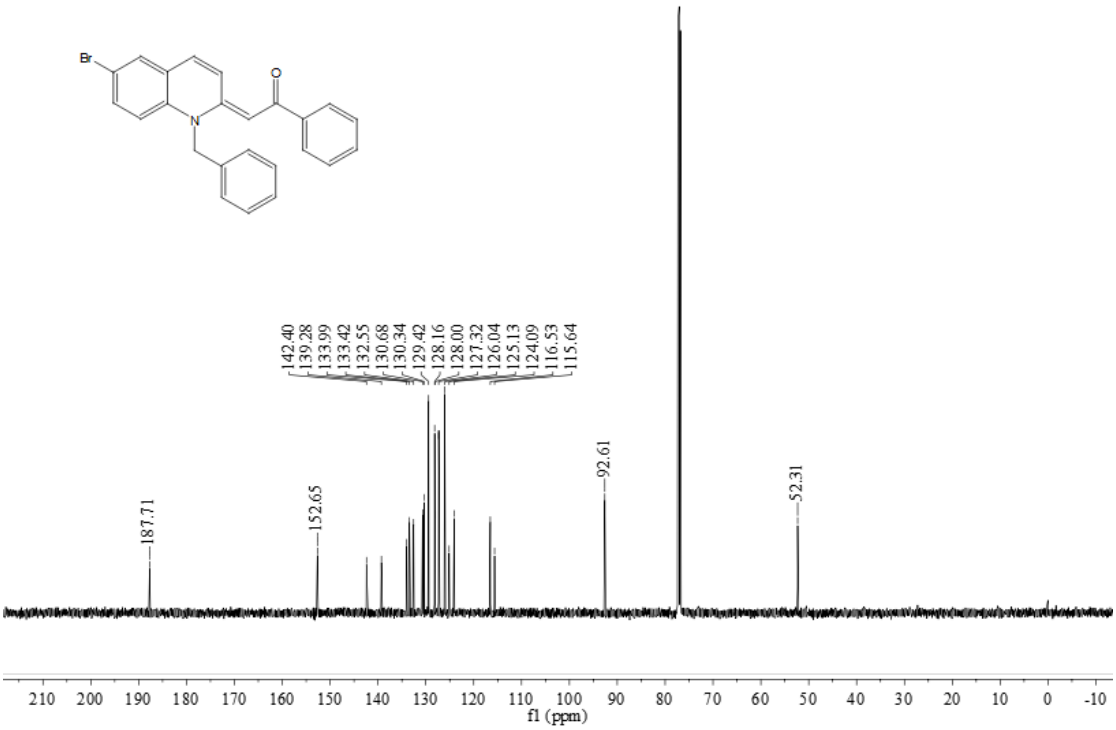


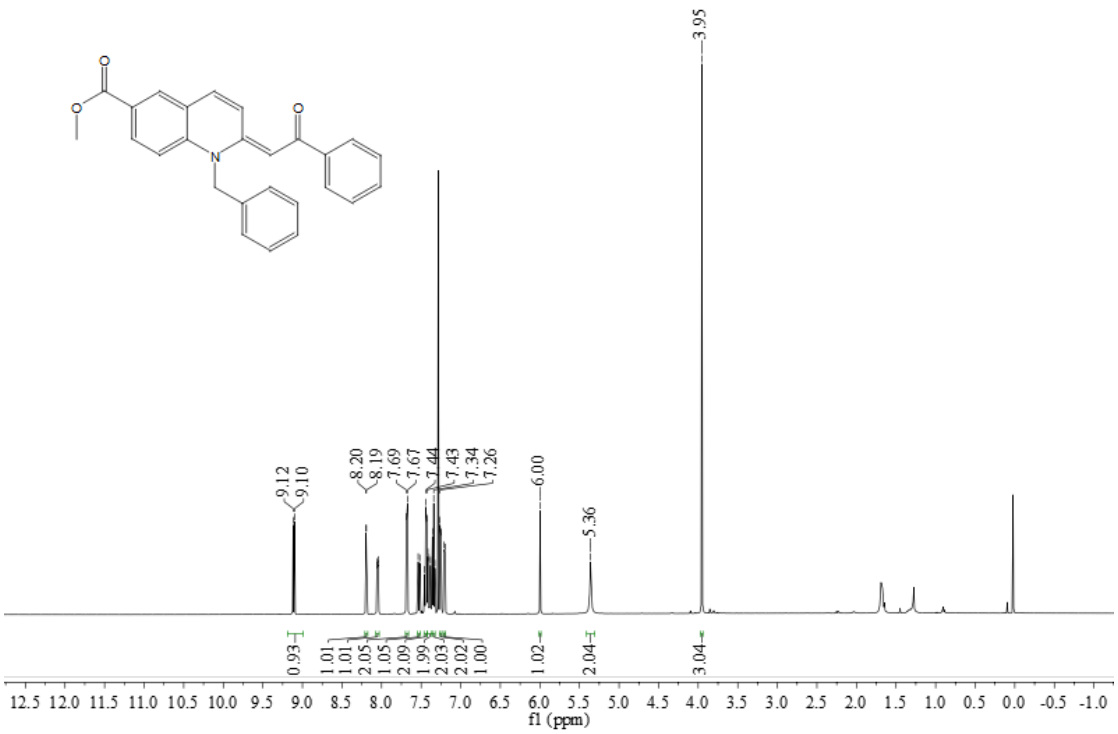
^{1}H NMR spectra of 5e (500 MHz, $CDCl_3$)



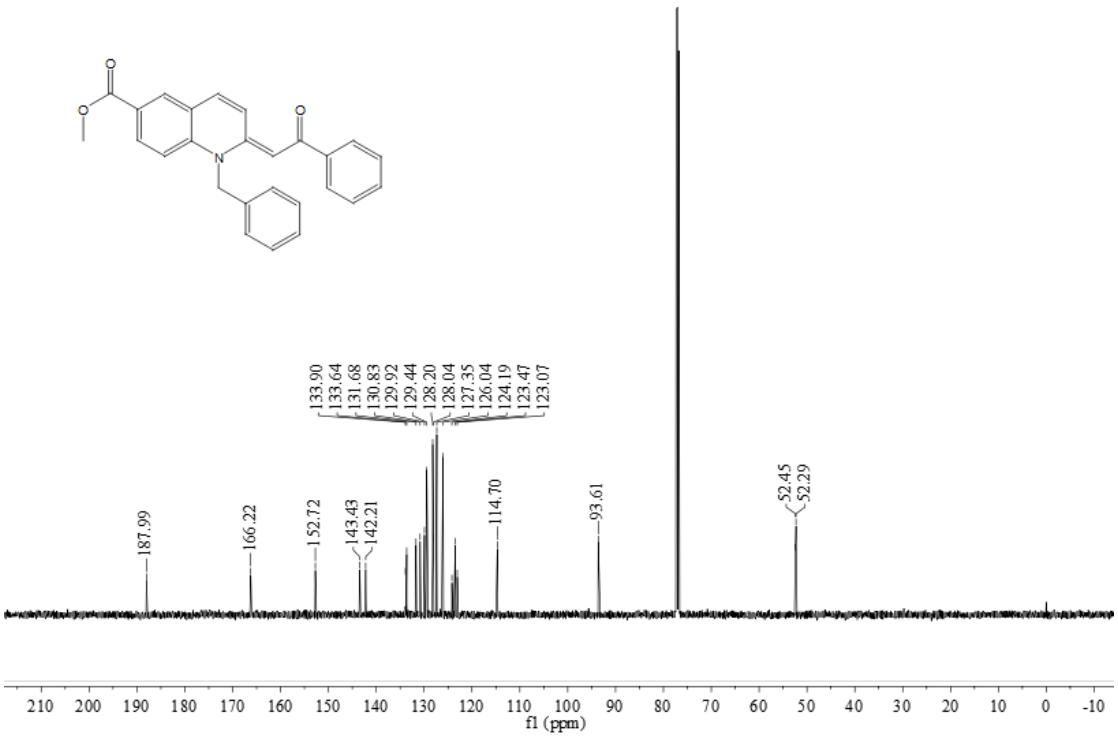
^{13}C NMR spectra of 5e (126 MHz, $CDCl_3$)



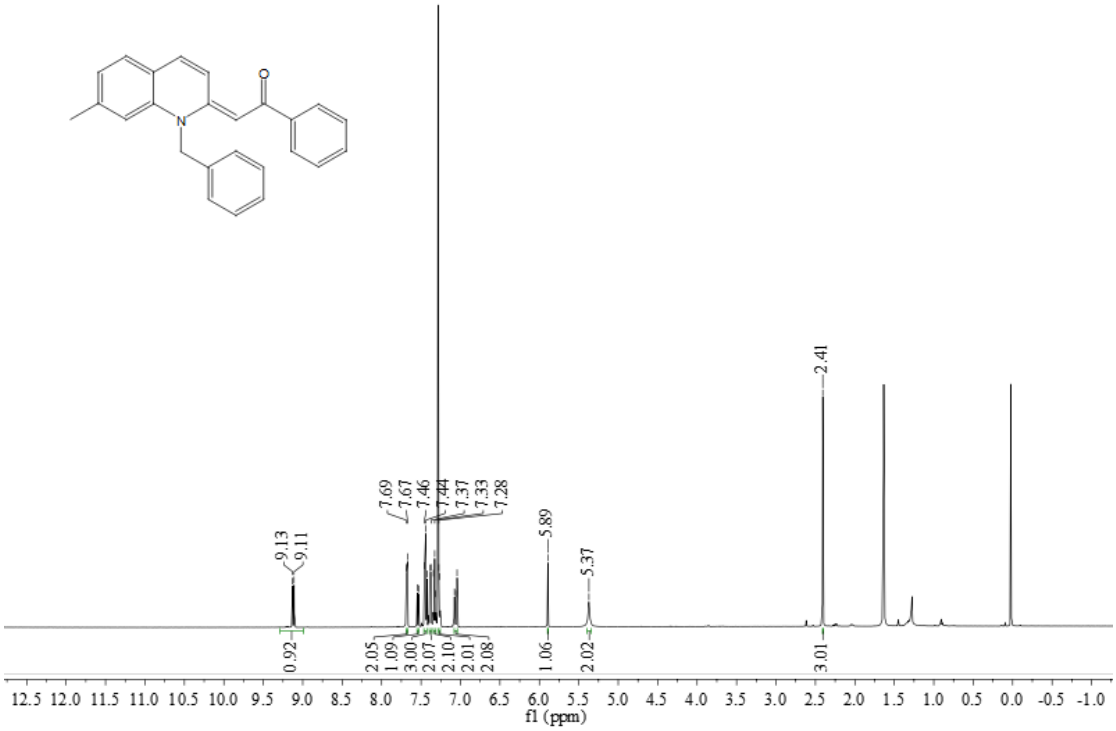
^{1}H NMR spectra of 5f (500 MHz, $CDCl_3$)



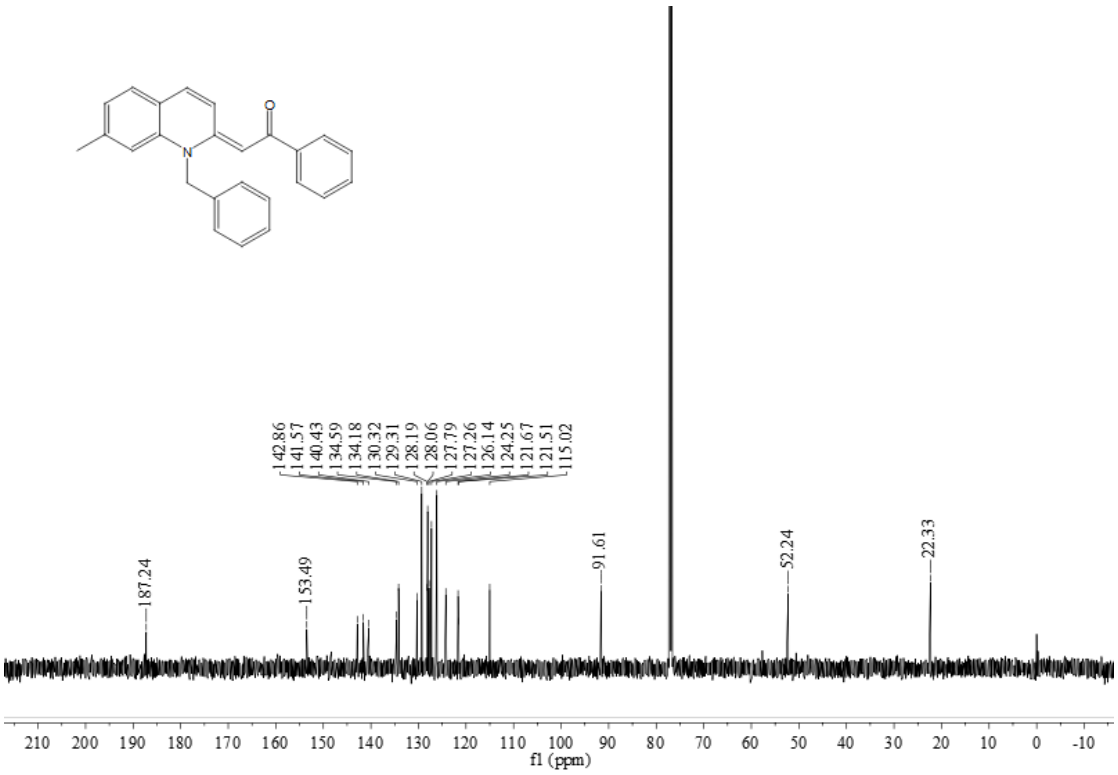
^{13}C NMR spectra of 5f (126 MHz, $CDCl_3$)



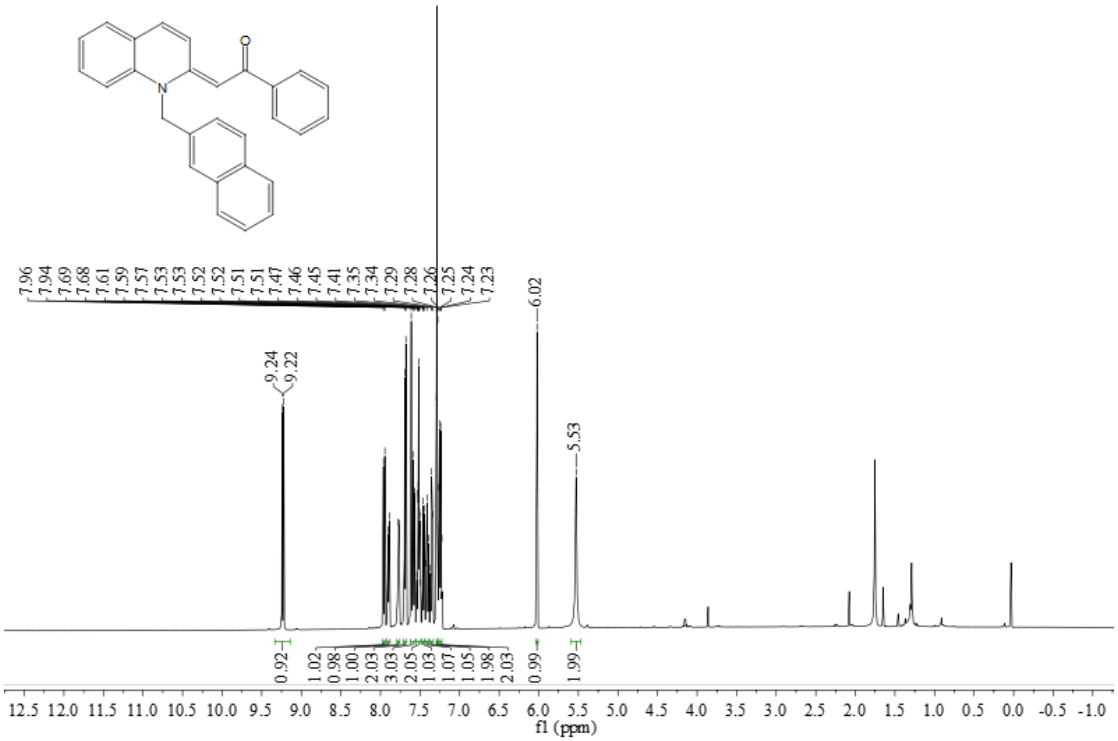
^{1}H NMR spectra of 5g (500 MHz, $CDCl_3$)



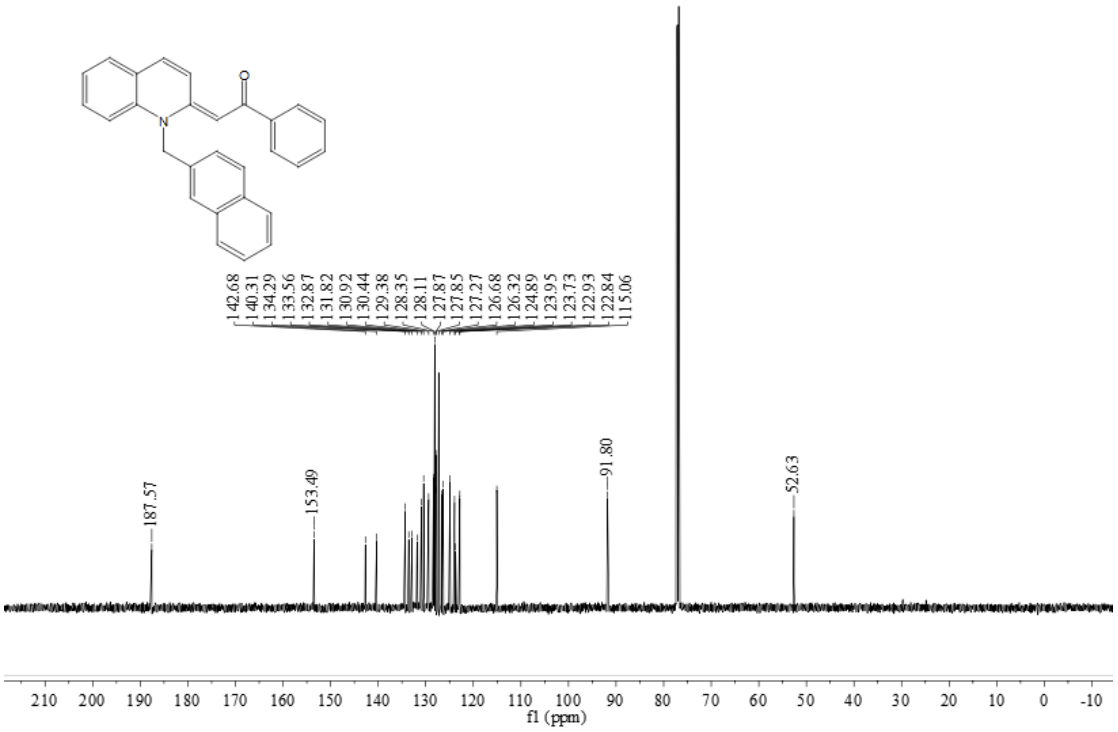
^{13}C NMR spectra of 5g (126 MHz, $CDCl_3$)



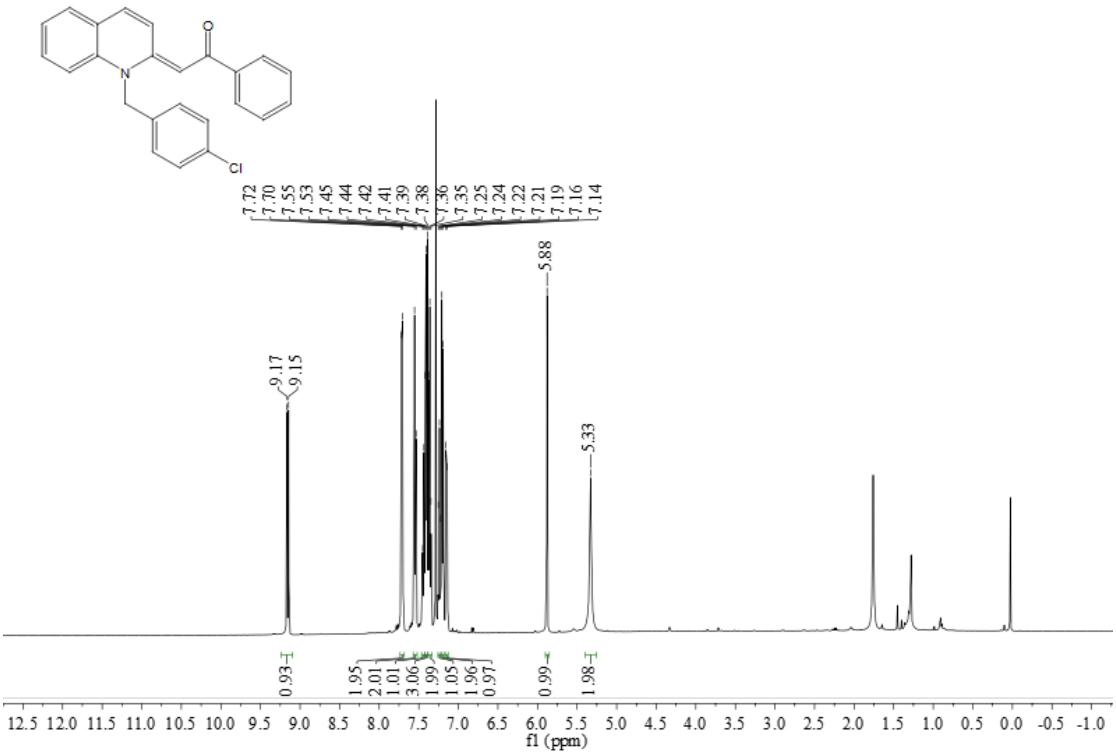
^{1}H NMR spectra of 5h (500 MHz, $CDCl_3$)



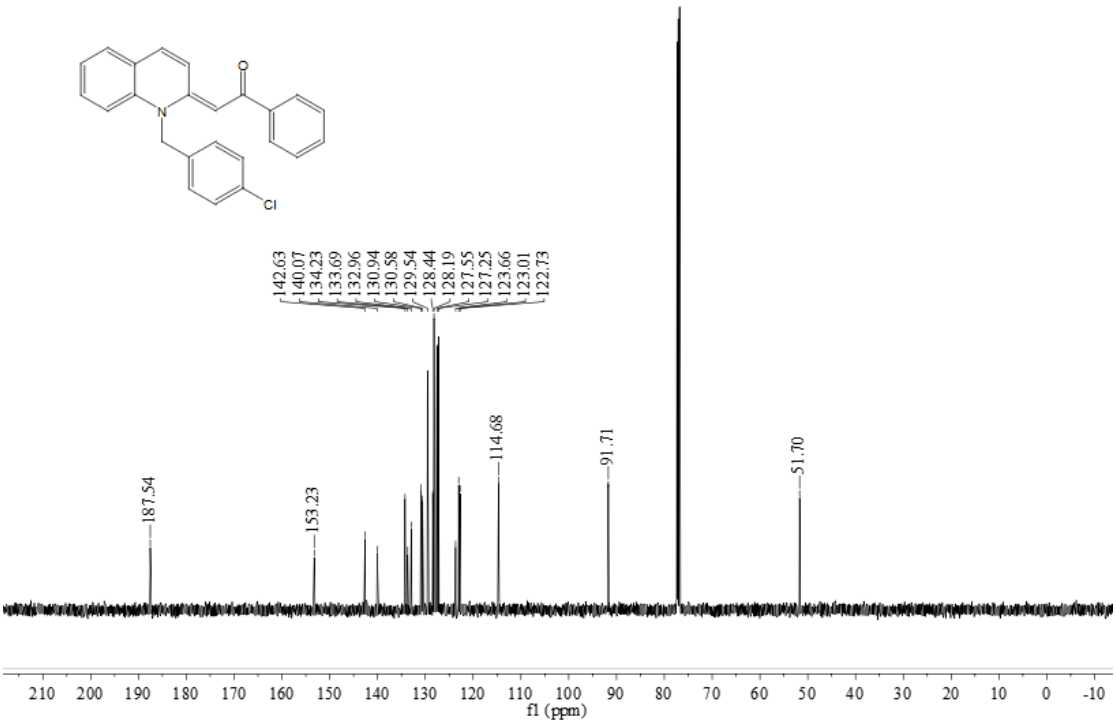
^{13}C NMR spectra of 5h (126 MHz, $CDCl_3$)



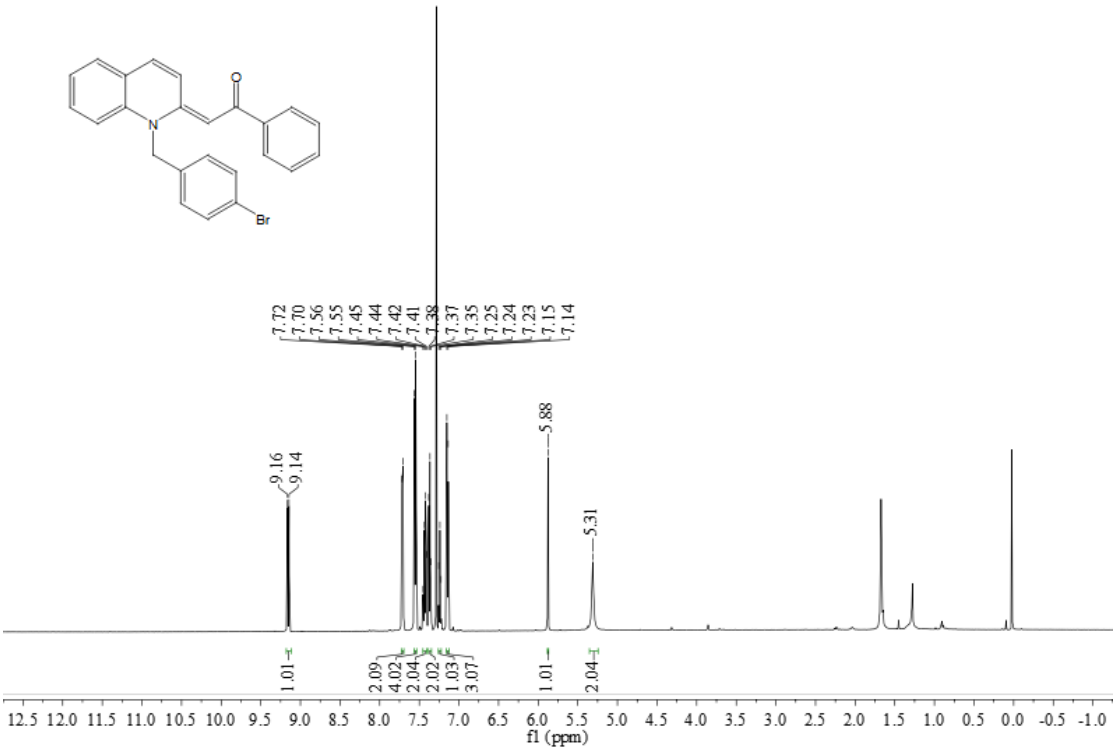
^{1}H NMR spectra of 5i (500 MHz, $CDCl_3$)



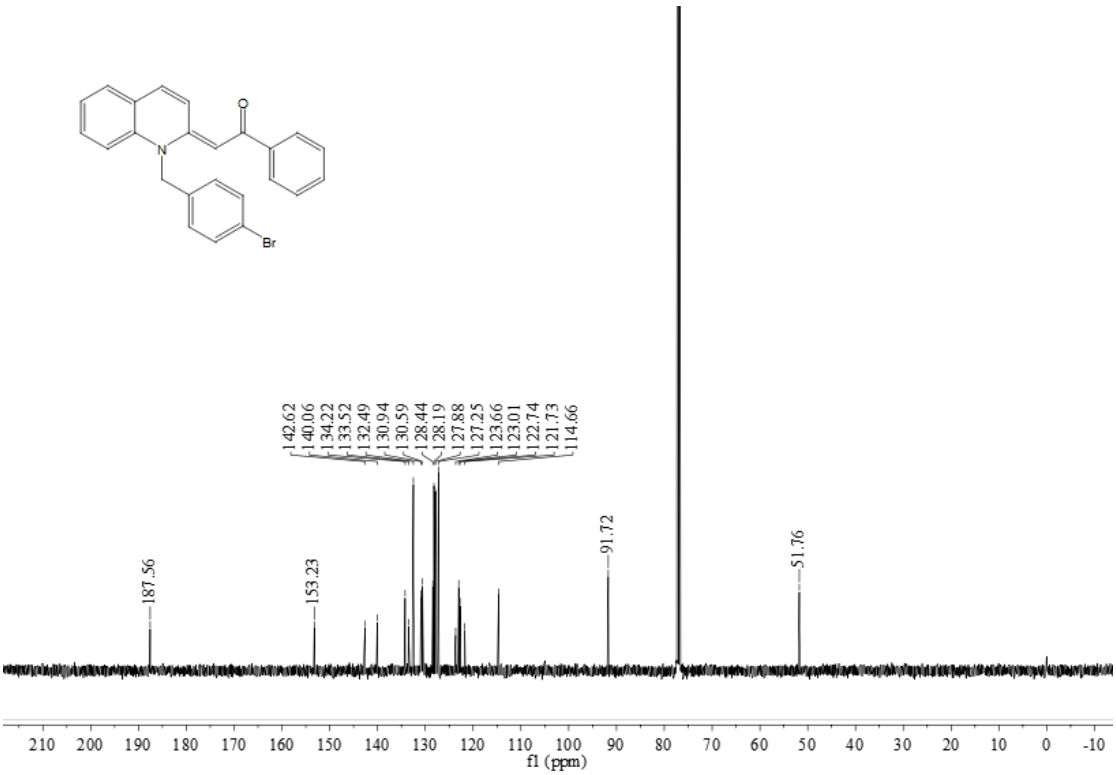
^{13}C NMR spectra of 5i (126 MHz, $CDCl_3$)



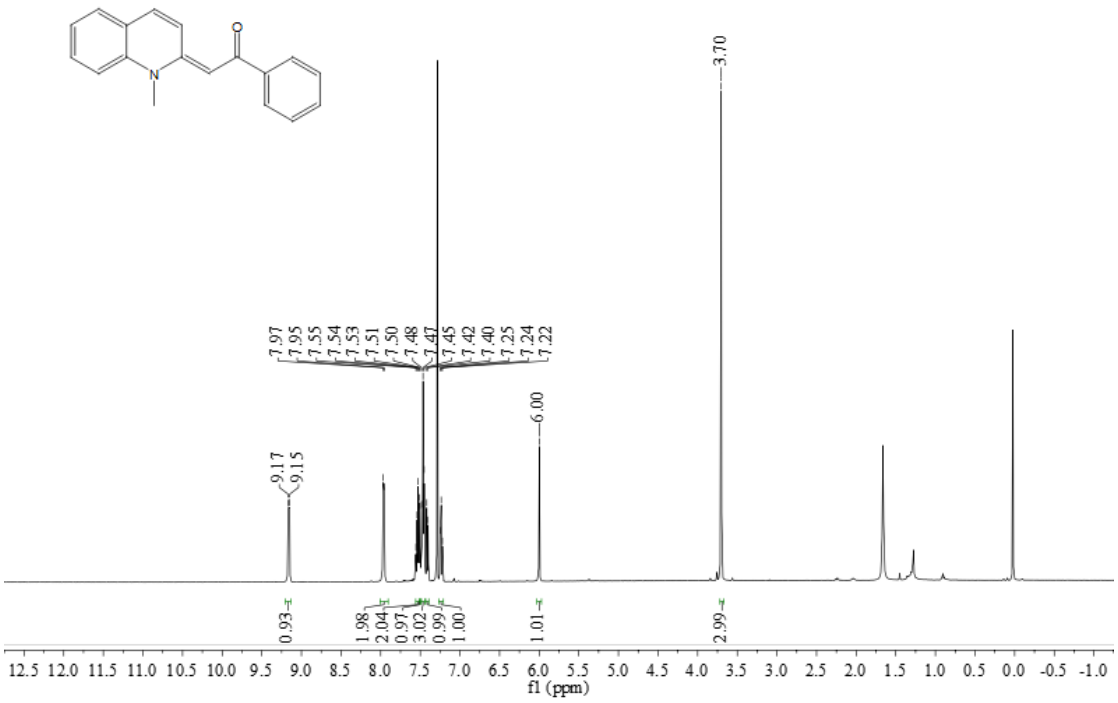
^{1}H NMR spectra of 5j (500 MHz, $CDCl_3$)



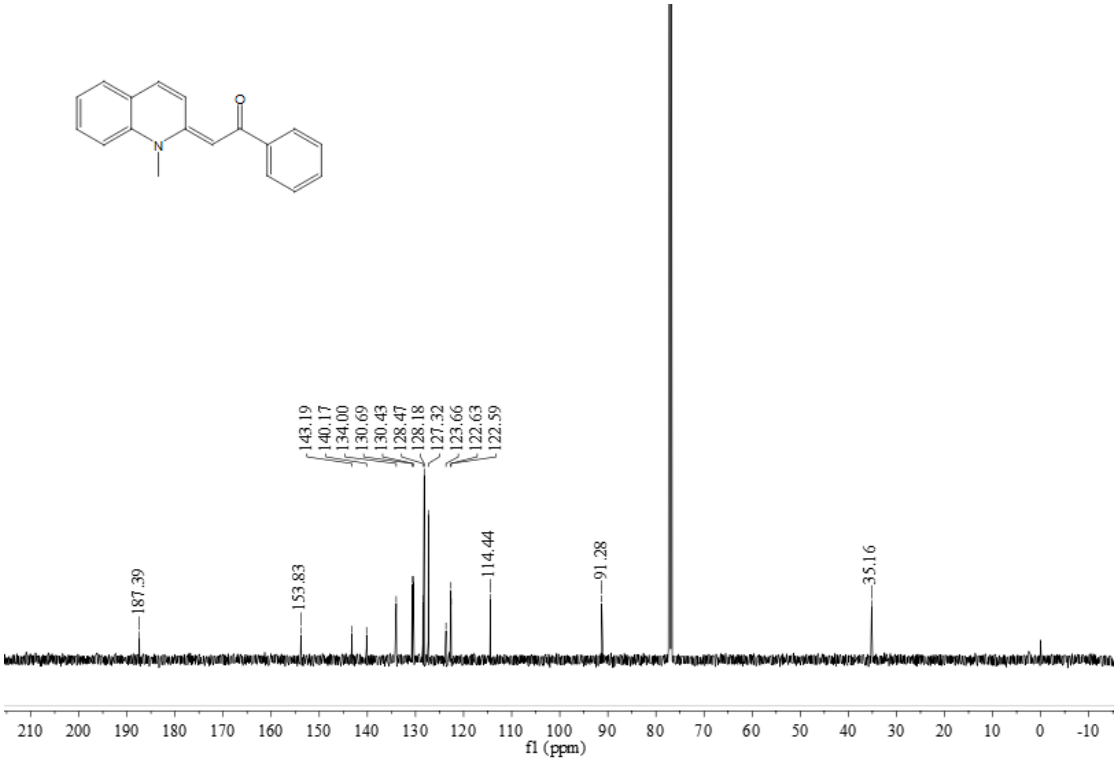
^{13}C NMR spectra of 5j (126 MHz, $CDCl_3$)



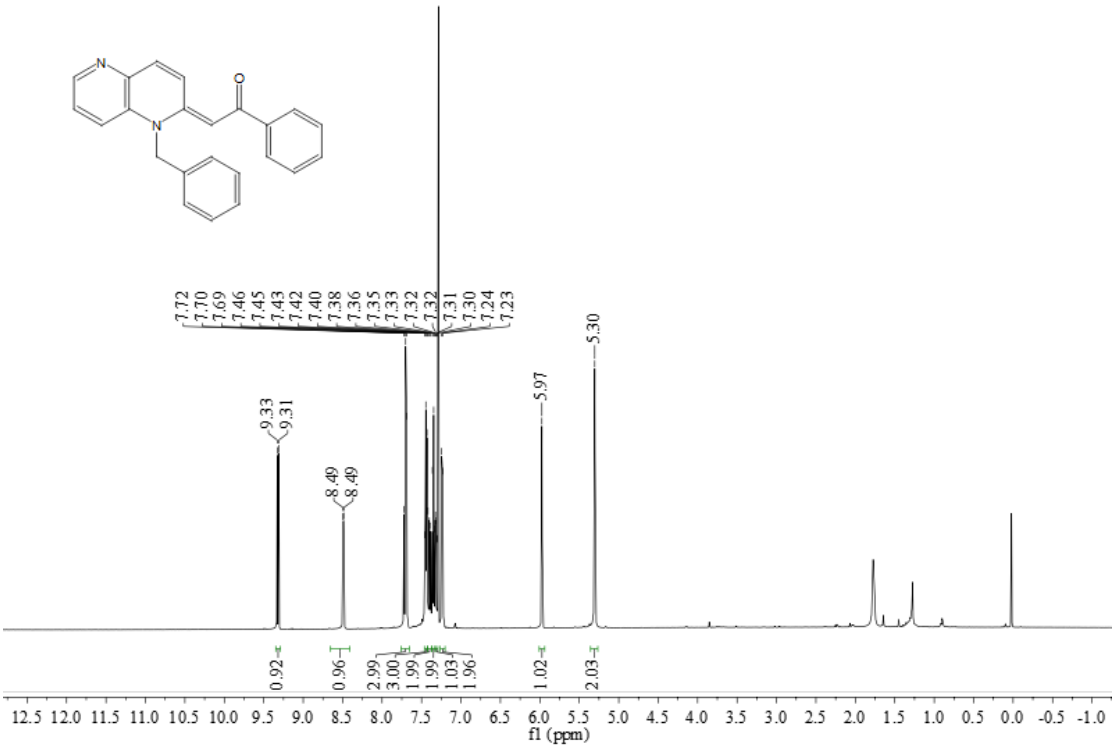
^{1}H NMR spectra of 5k (500 MHz, $CDCl_3$)



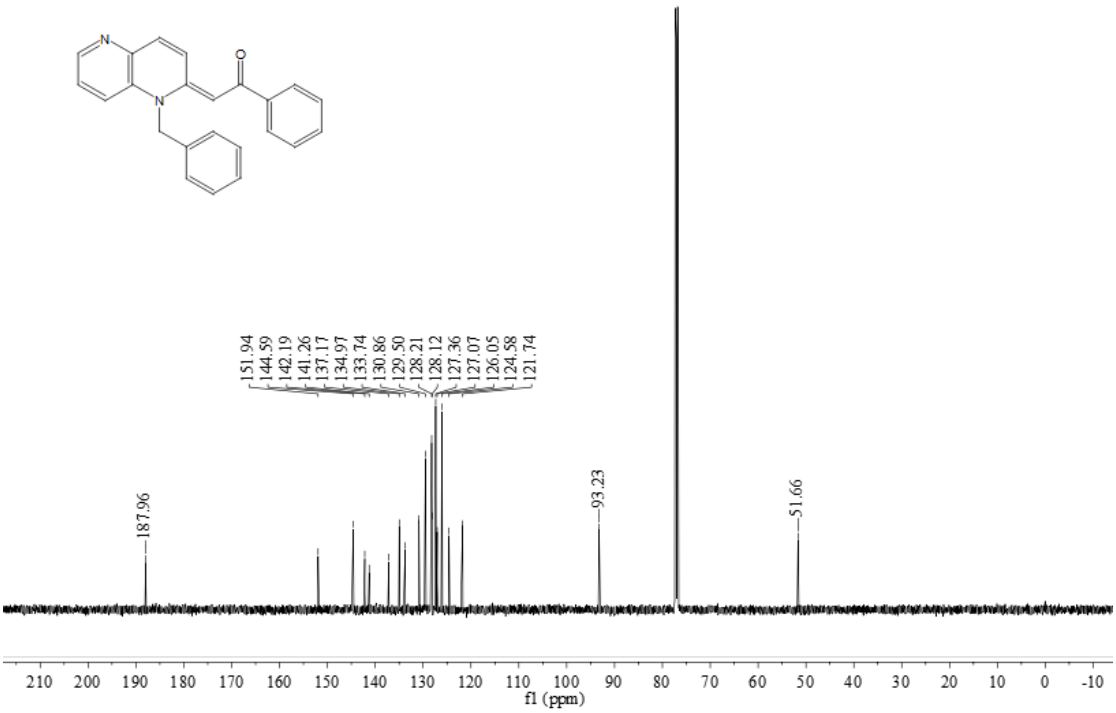
^{13}C NMR spectra of 5k (126 MHz, $CDCl_3$)



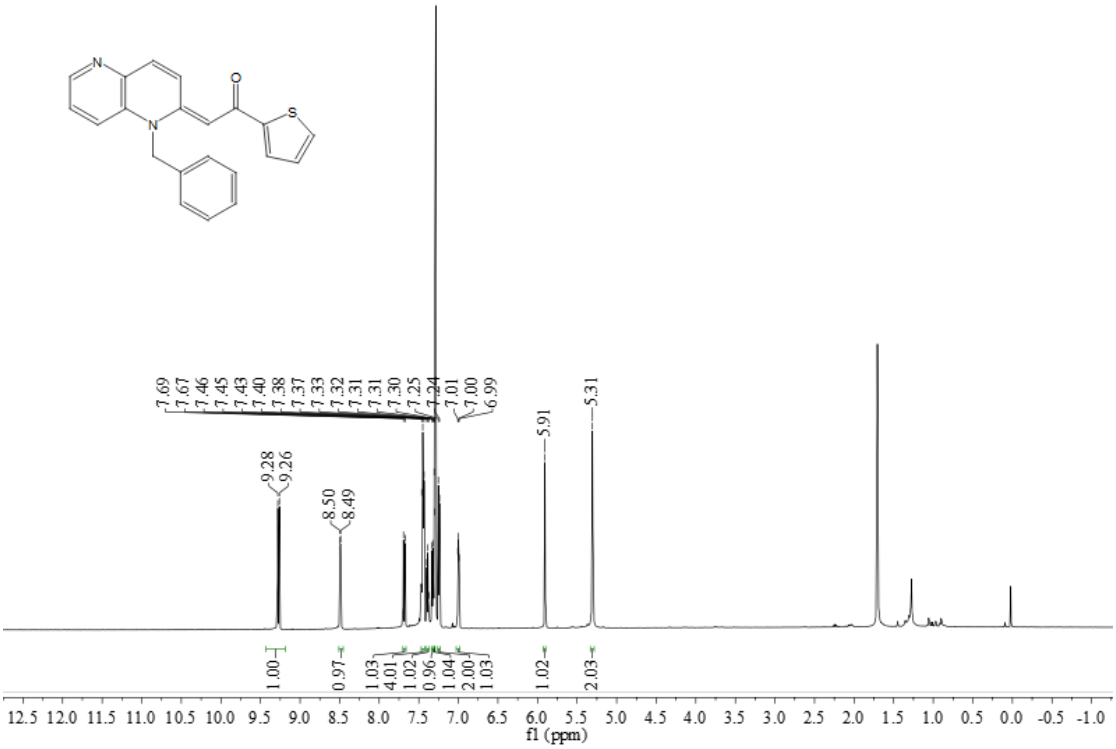
^{1}H NMR spectra of 5l (500 MHz, $CDCl_3$)



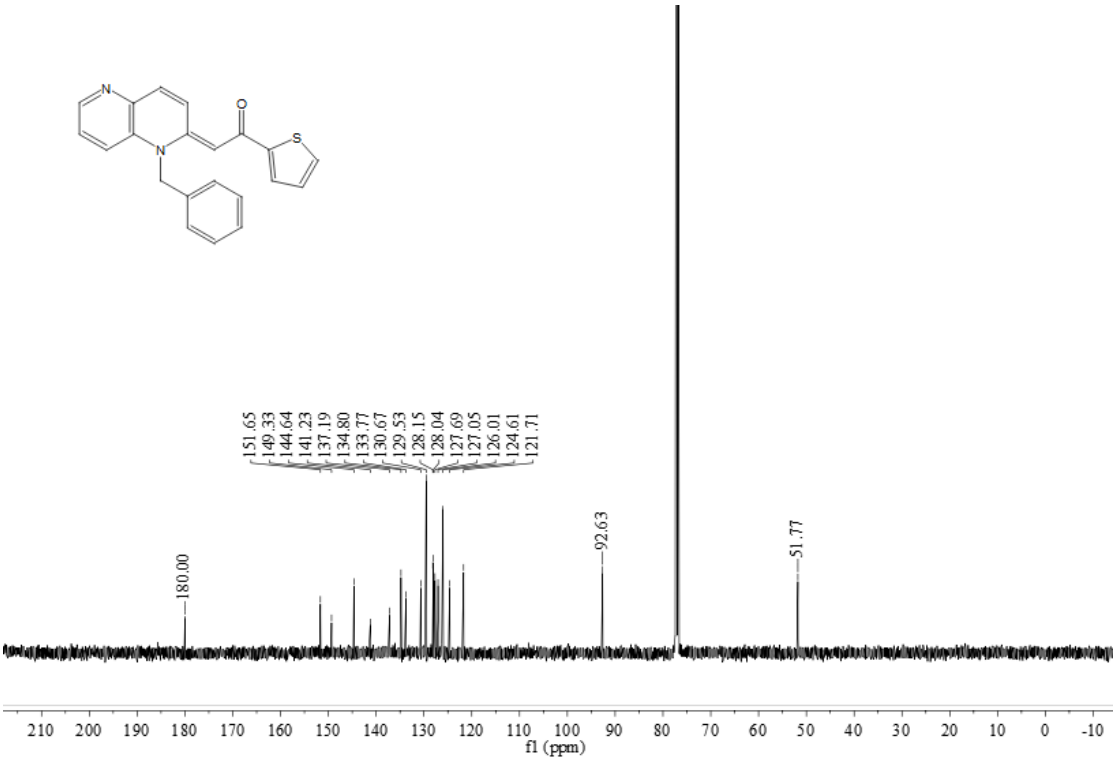
^{13}C NMR spectra of 5l (126 MHz, $CDCl_3$)



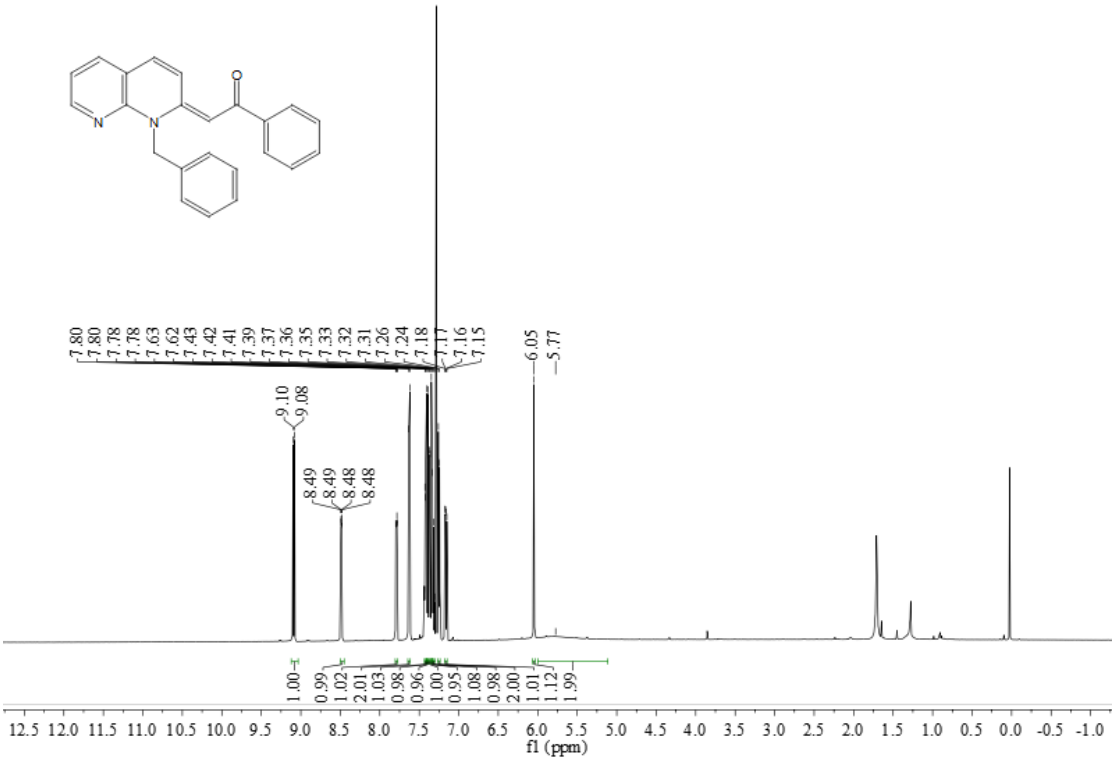
^{1}H NMR spectra of 5m (500 MHz, $CDCl_3$)



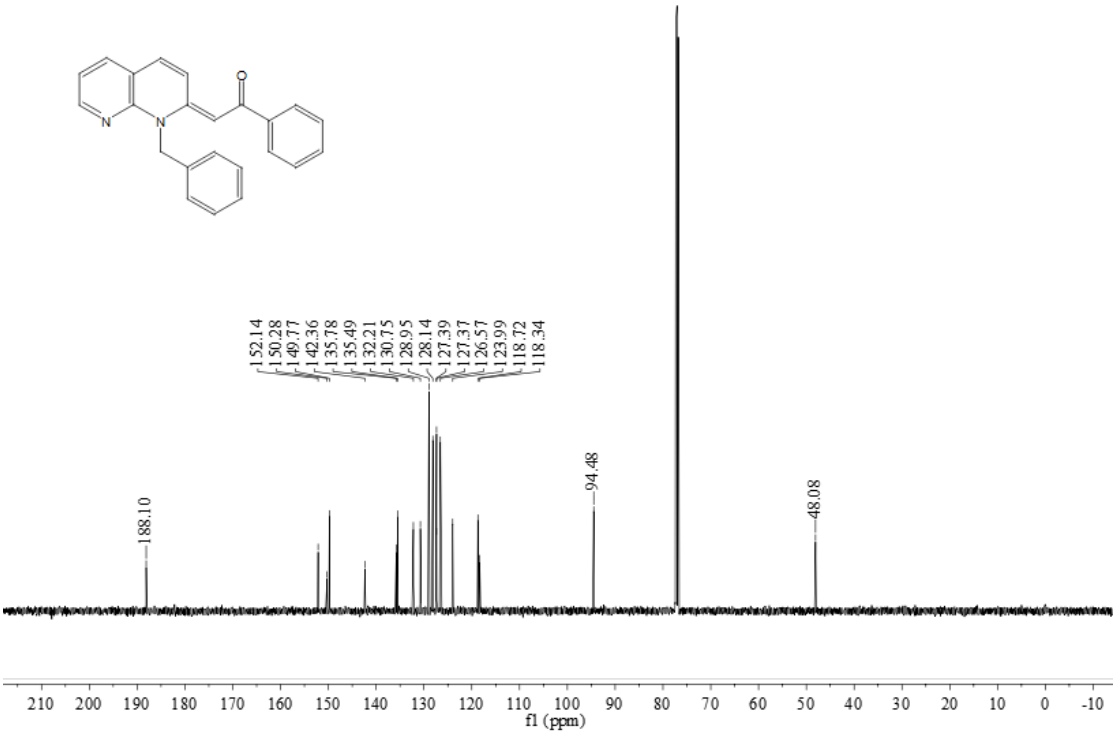
^{13}C NMR spectra of 5m (126 MHz, $CDCl_3$)



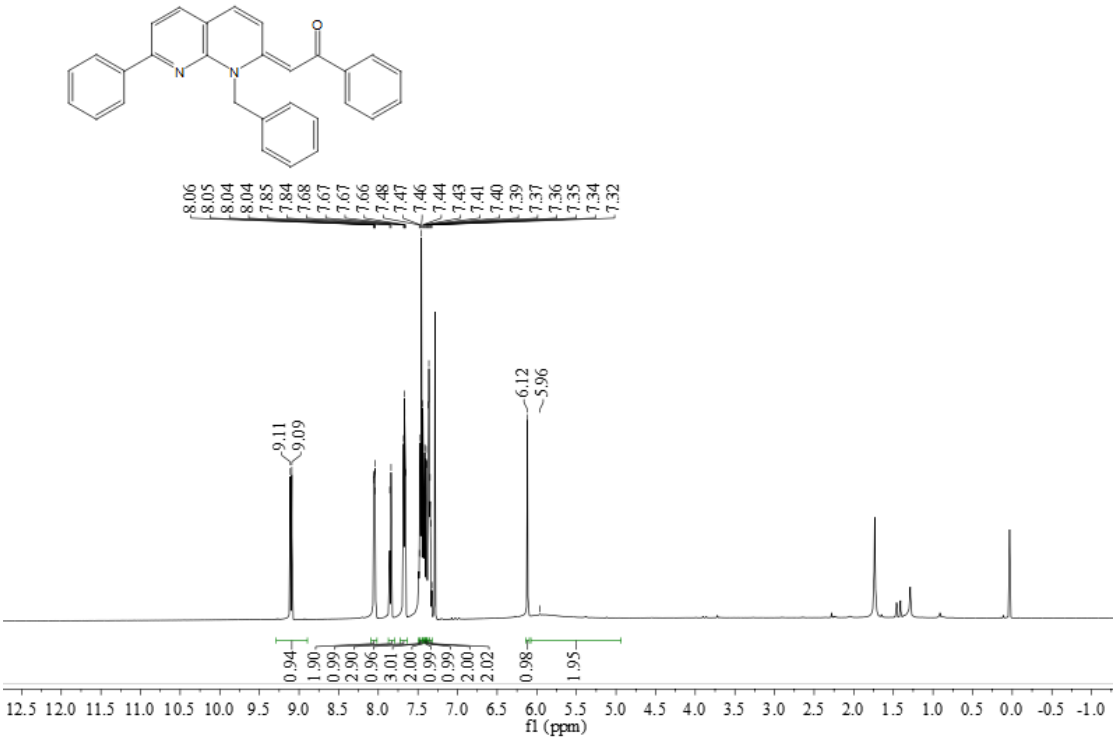
^{1}H NMR spectra of 5n (500 MHz, $CDCl_3$)



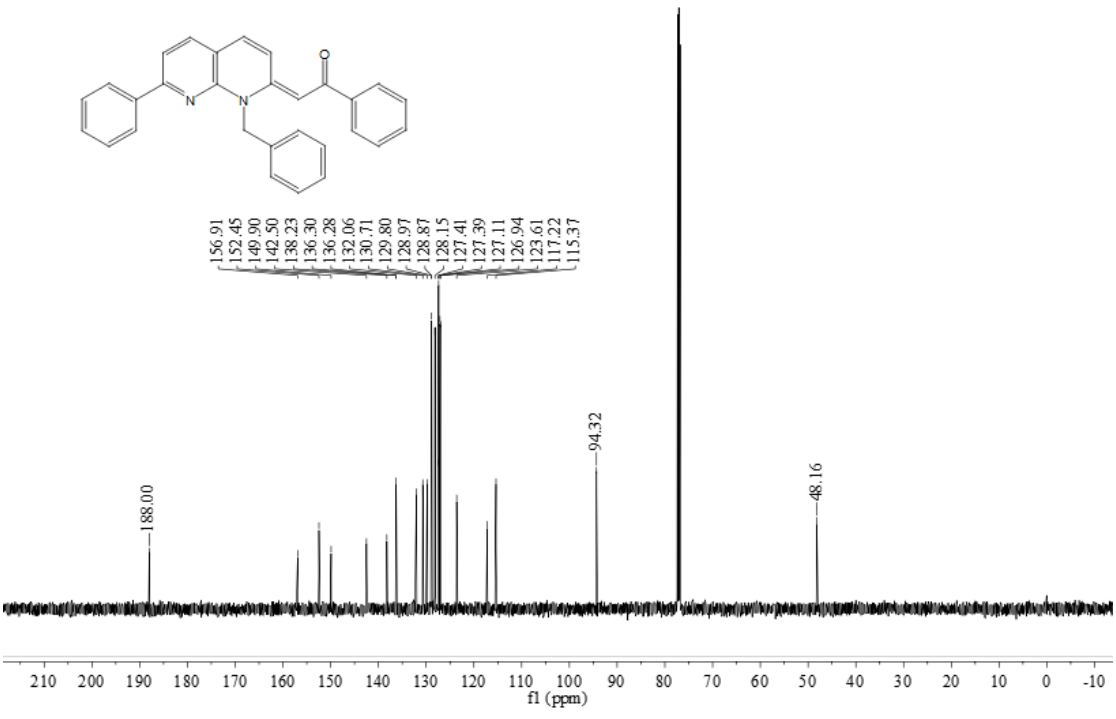
^{13}C NMR spectra of 5n (126 MHz, $CDCl_3$)



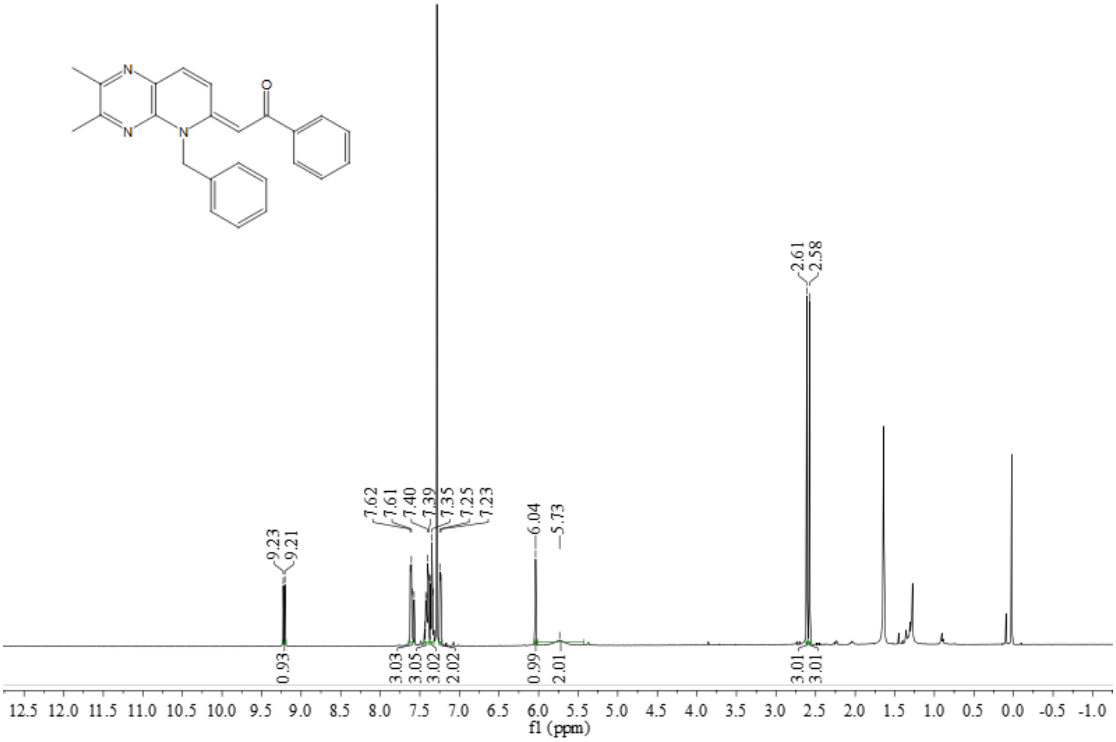
^{1}H NMR spectra of 5o (500 MHz, $CDCl_3$)



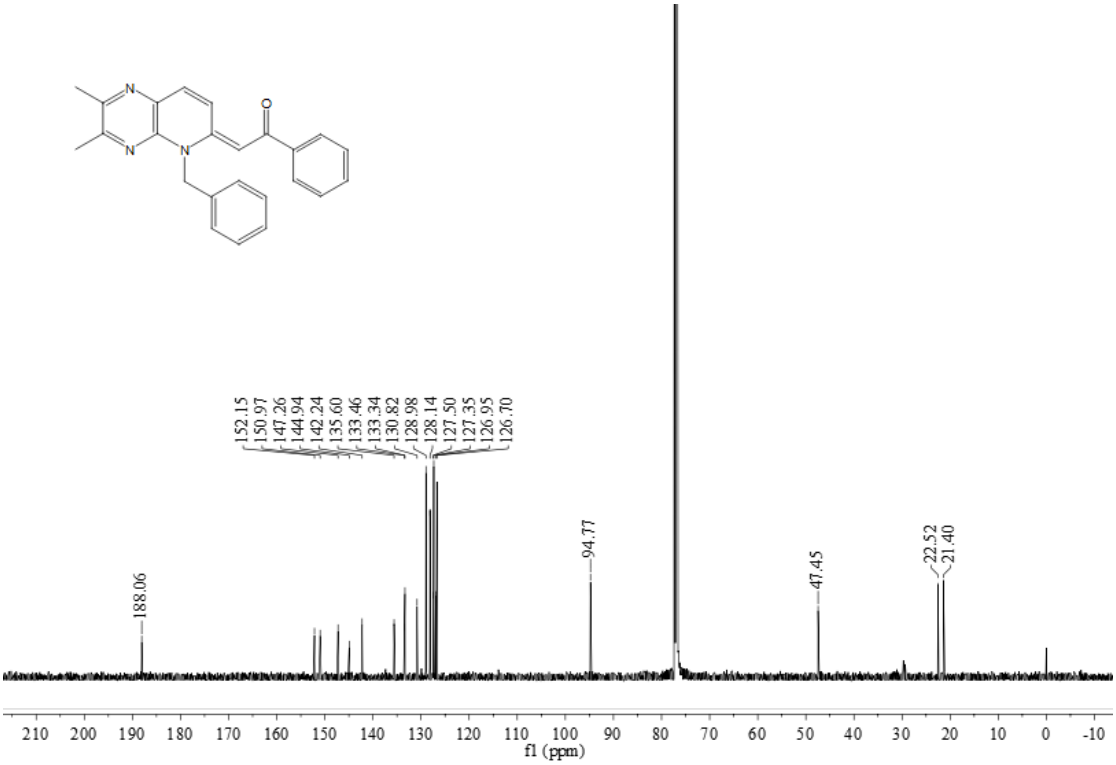
^{13}C NMR spectra of 5o (126 MHz, $CDCl_3$)



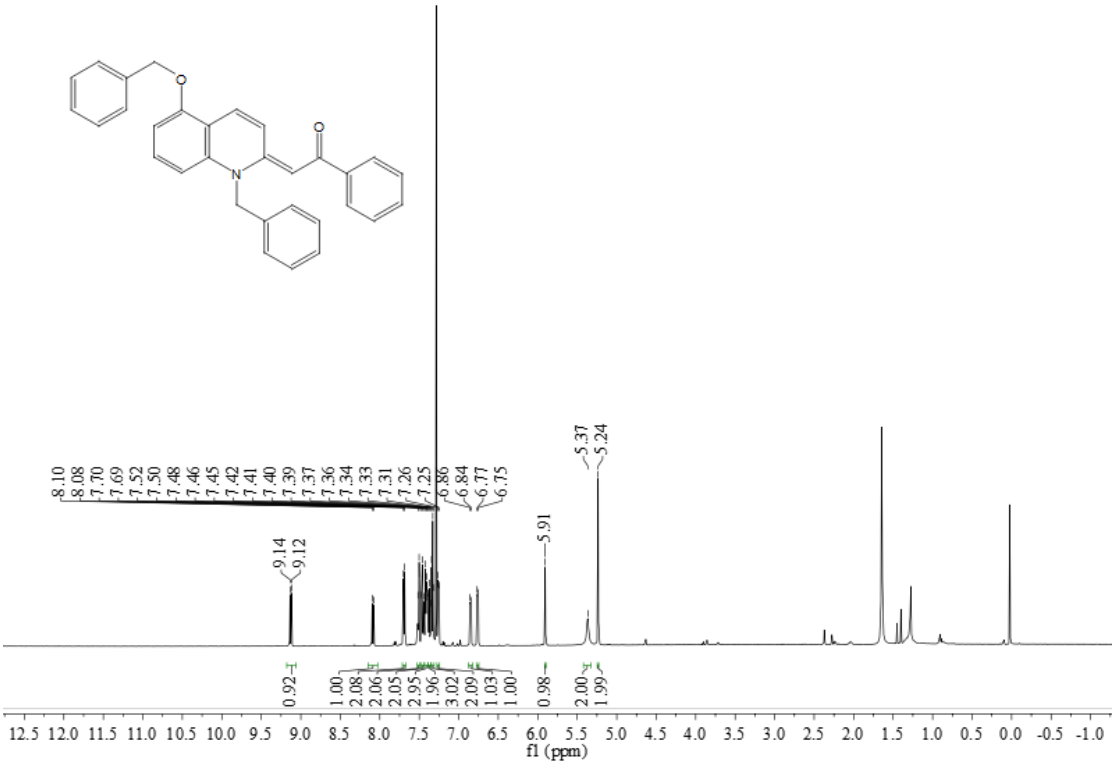
^{1}H NMR spectra of 5p (500 MHz, $CDCl_3$)



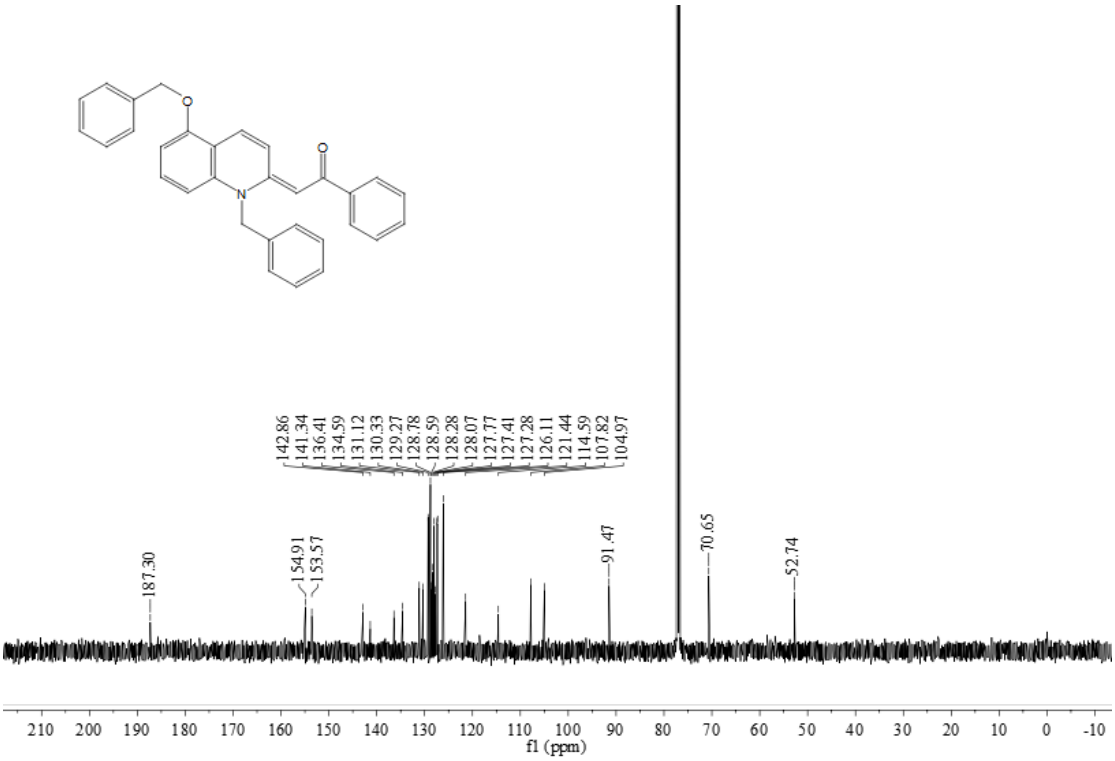
^{13}C NMR spectra of 5p (126 MHz, $CDCl_3$)



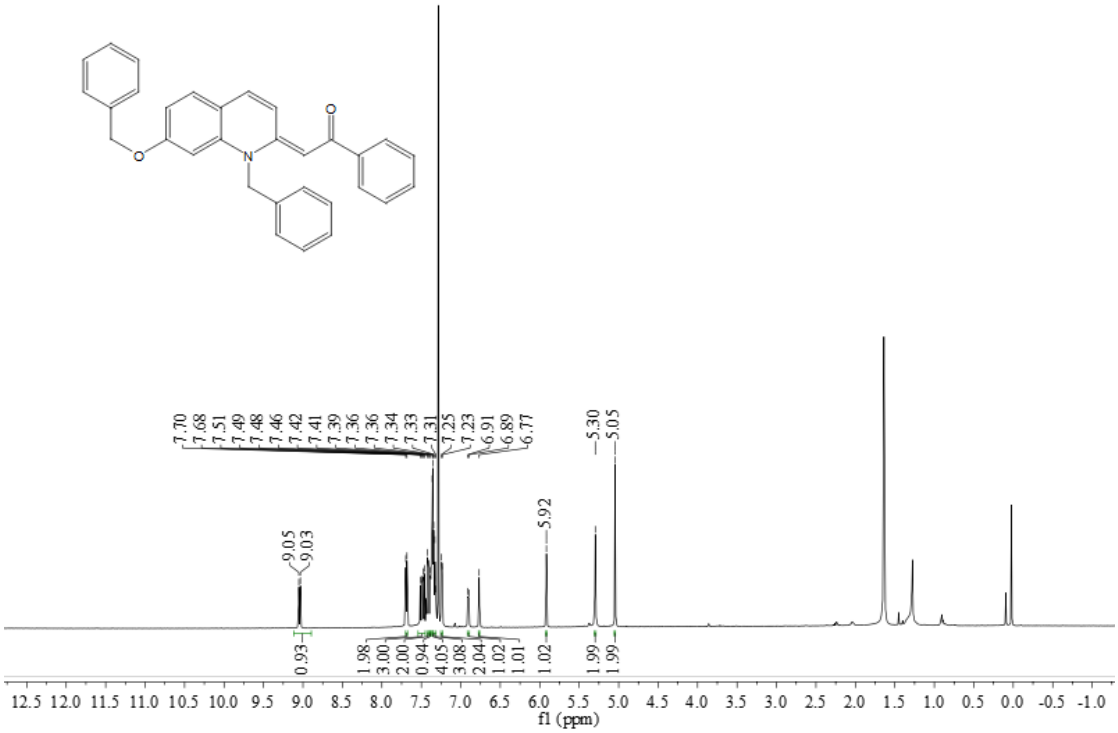
^{1}H NMR spectra of 5q (500 MHz, $CDCl_3$)



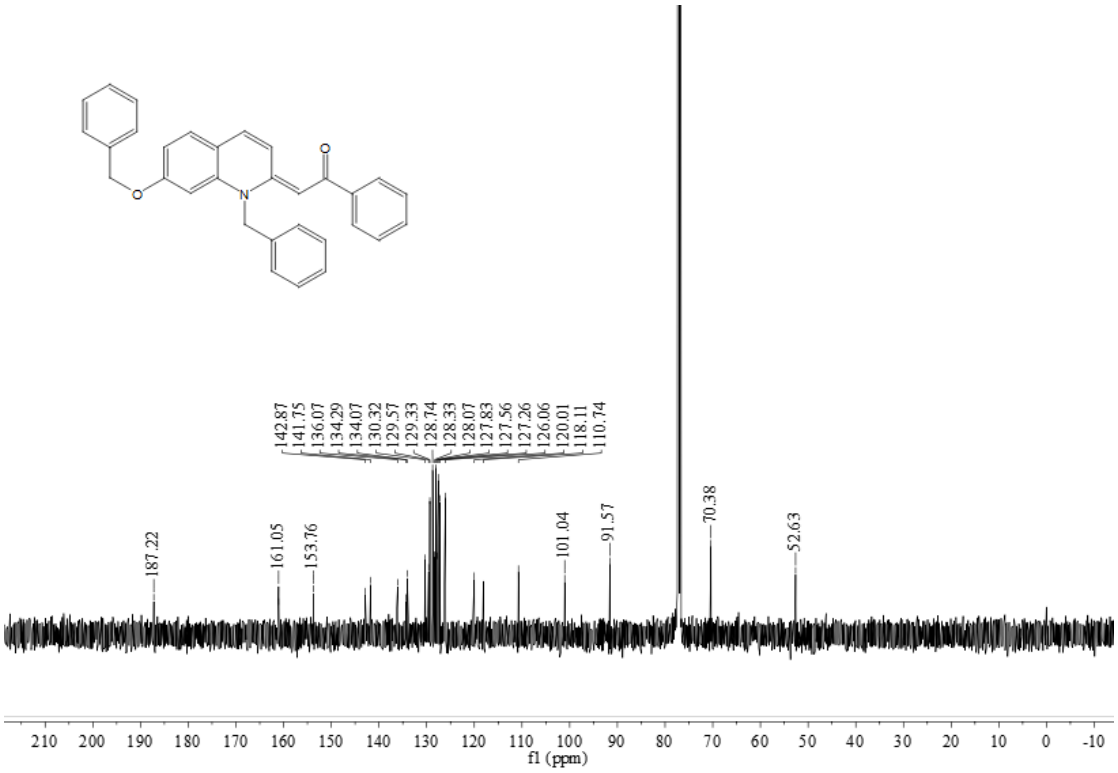
^{13}C NMR spectra of 5q (126 MHz, $CDCl_3$)



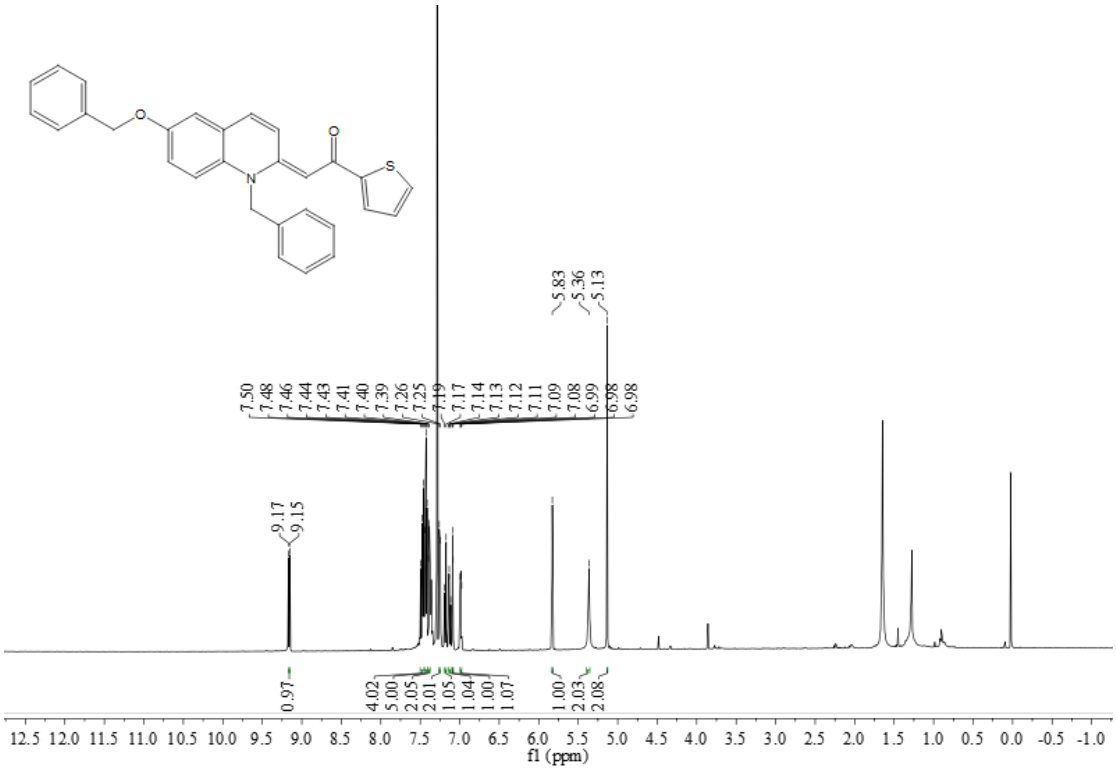
^{1}H NMR spectra of 5r (500 MHz, $CDCl_3$)



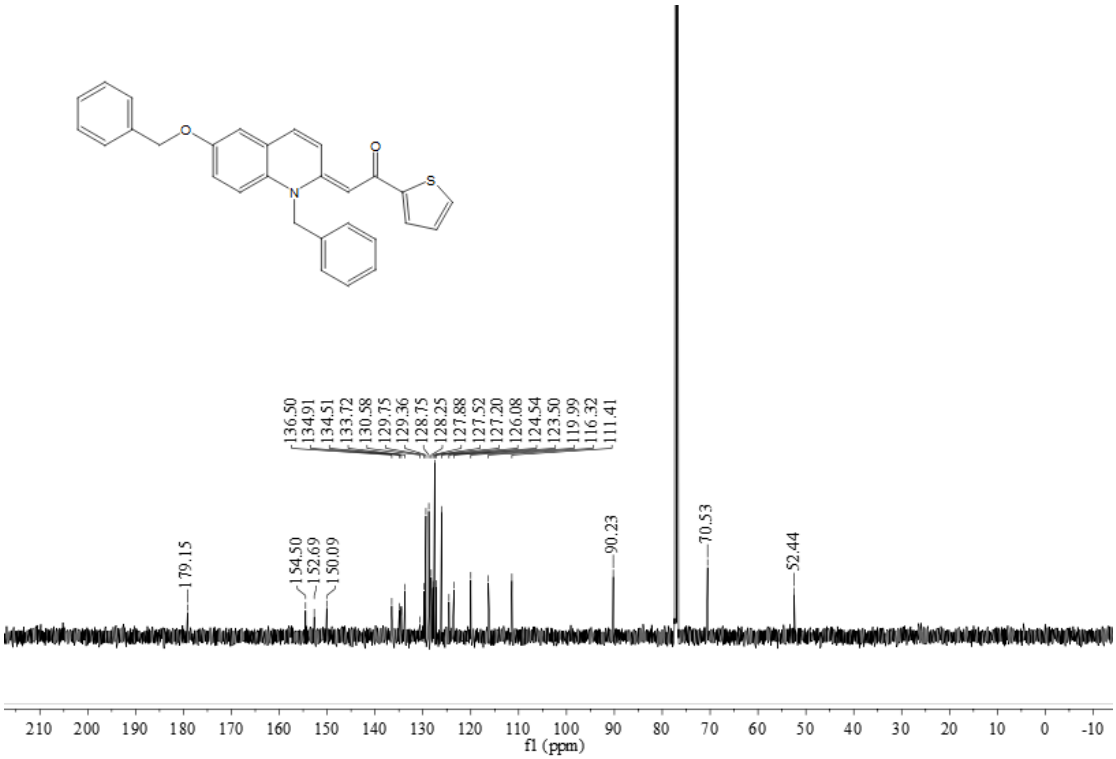
^{13}C NMR spectra of 5r (126 MHz, $CDCl_3$)



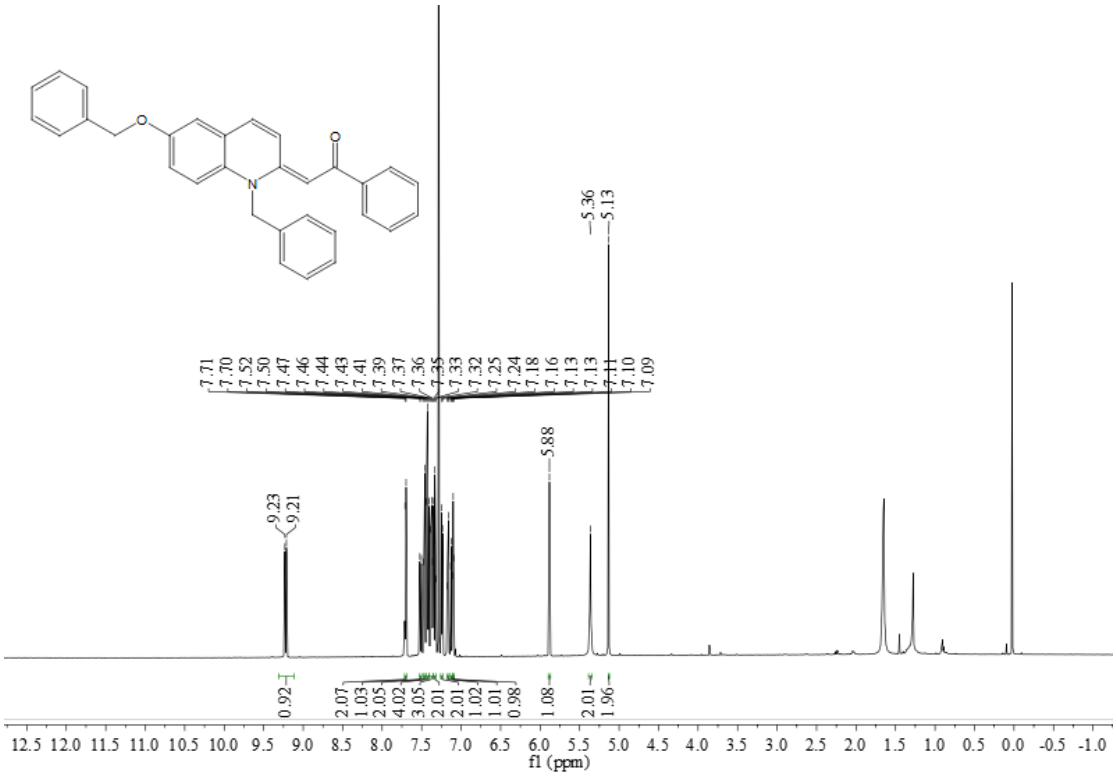
^{1}H NMR spectra of 5s (500 MHz, $CDCl_3$)



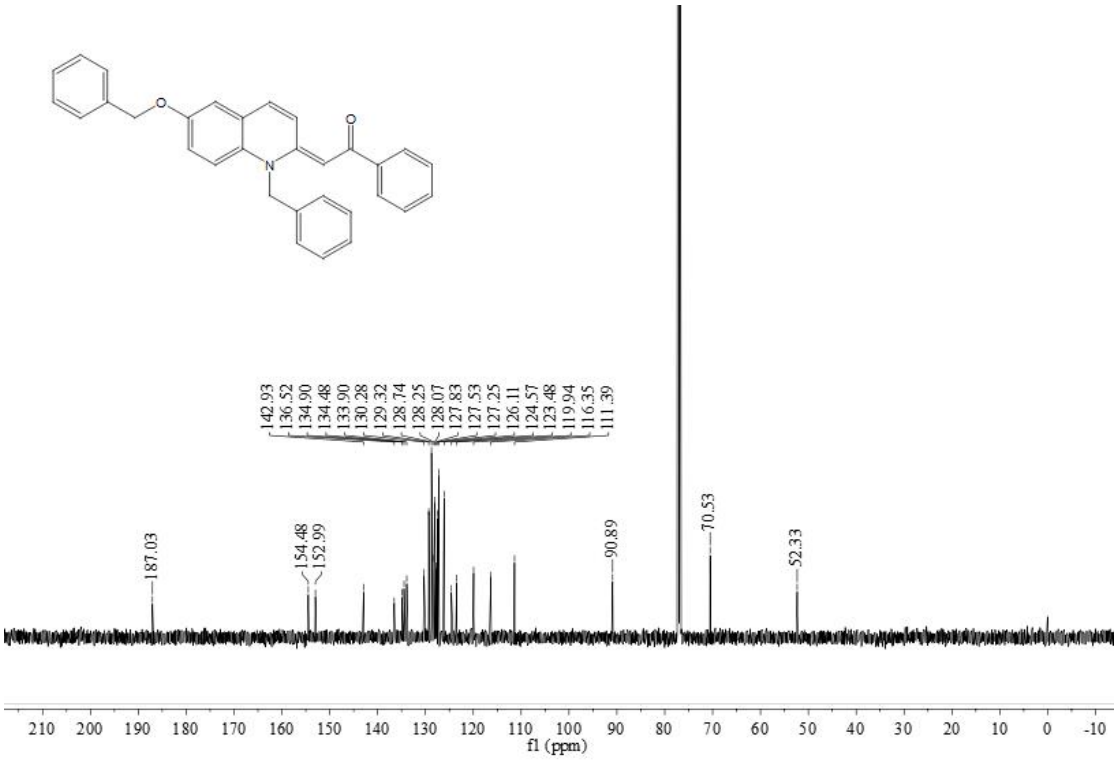
^{13}C NMR spectra of 5s (126 MHz, $CDCl_3$)



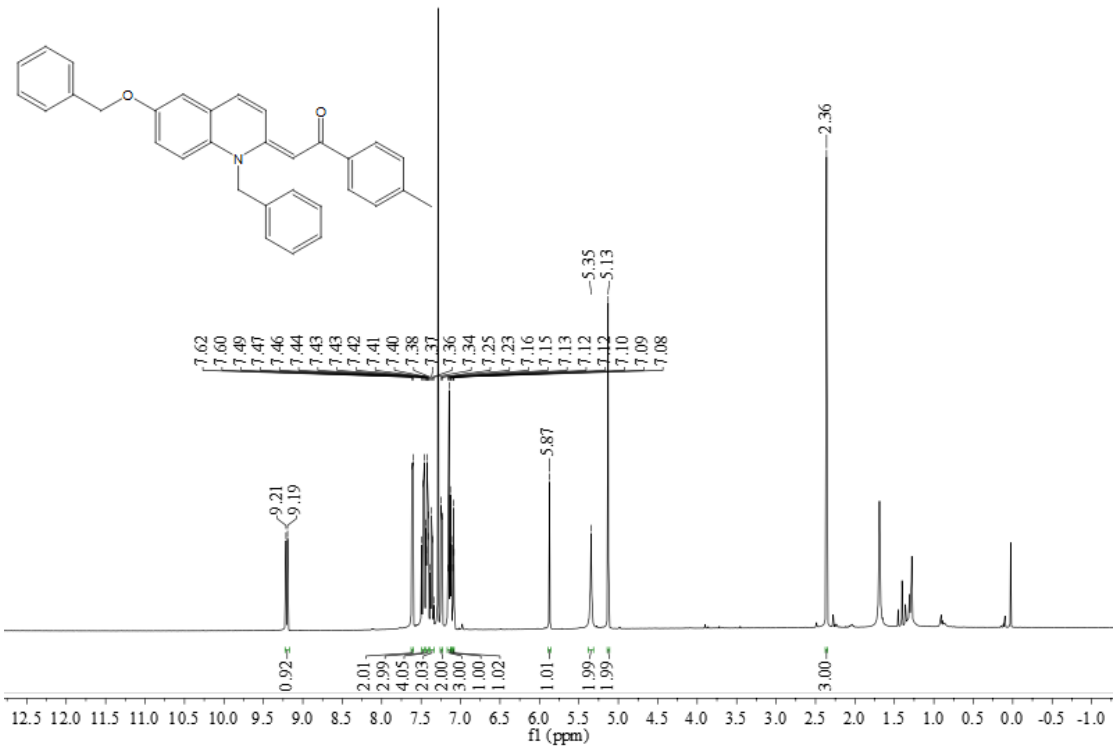
^{1}H NMR spectra of 5t (500 MHz, $CDCl_3$)



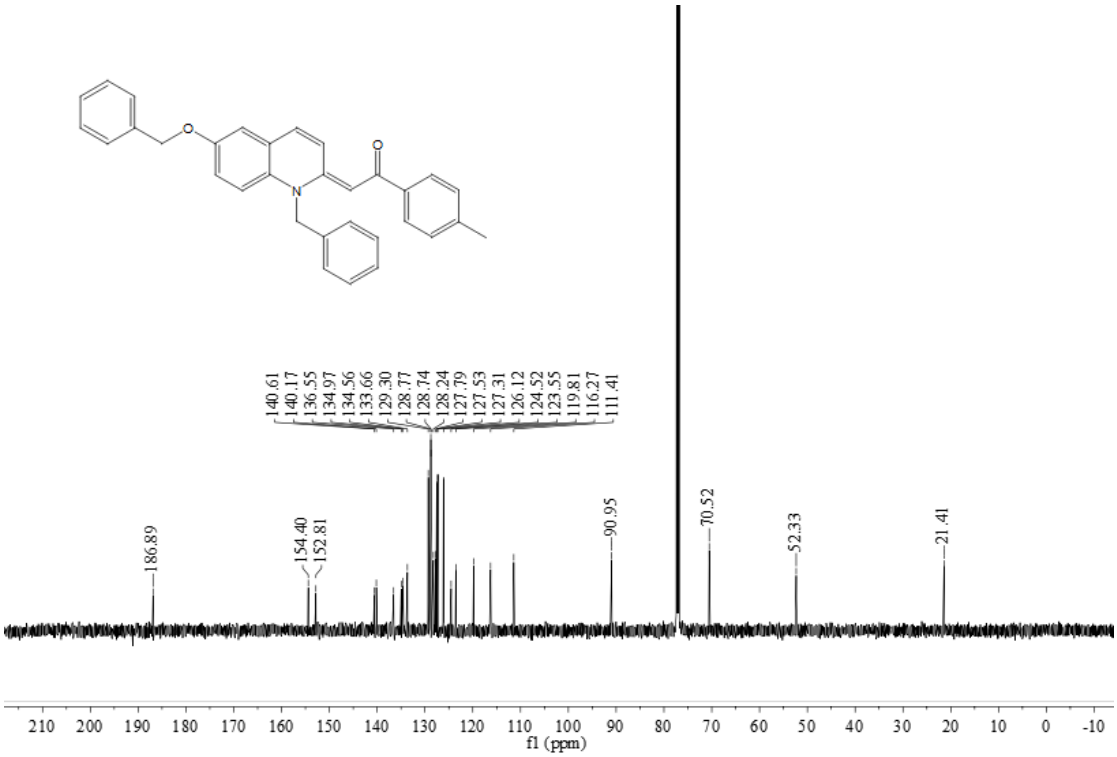
^{13}C NMR spectra of 5t (126 MHz, $CDCl_3$)



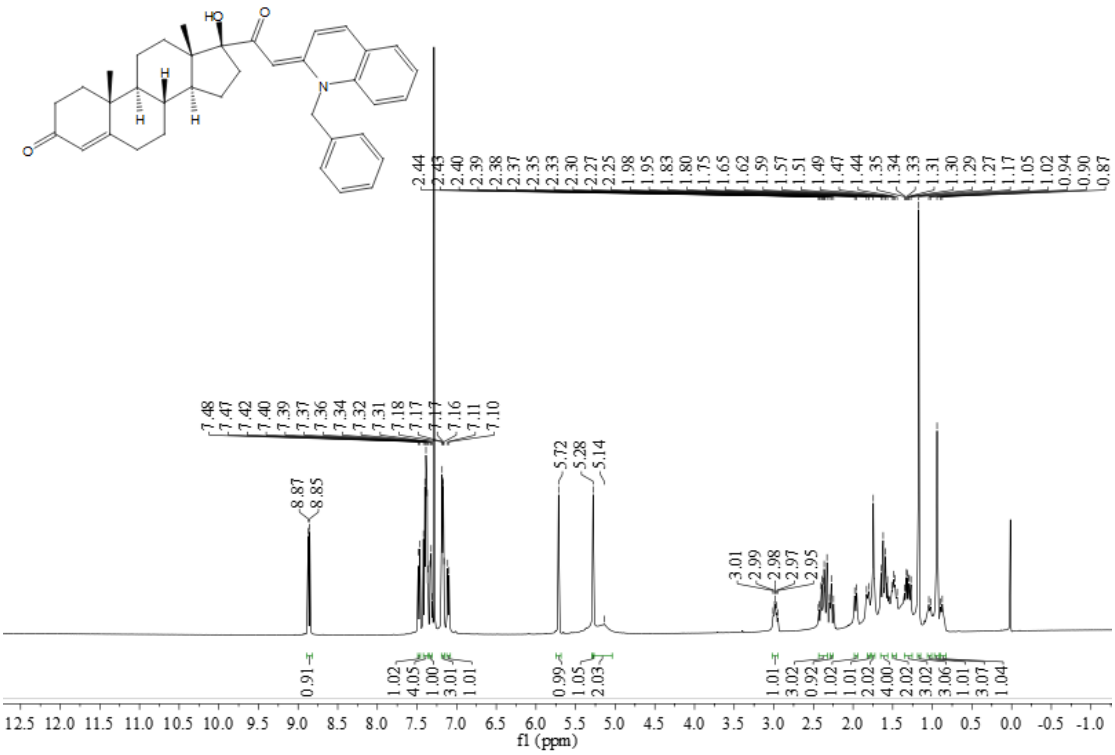
^{1}H NMR spectra of 5u (500 MHz, $CDCl_3$)



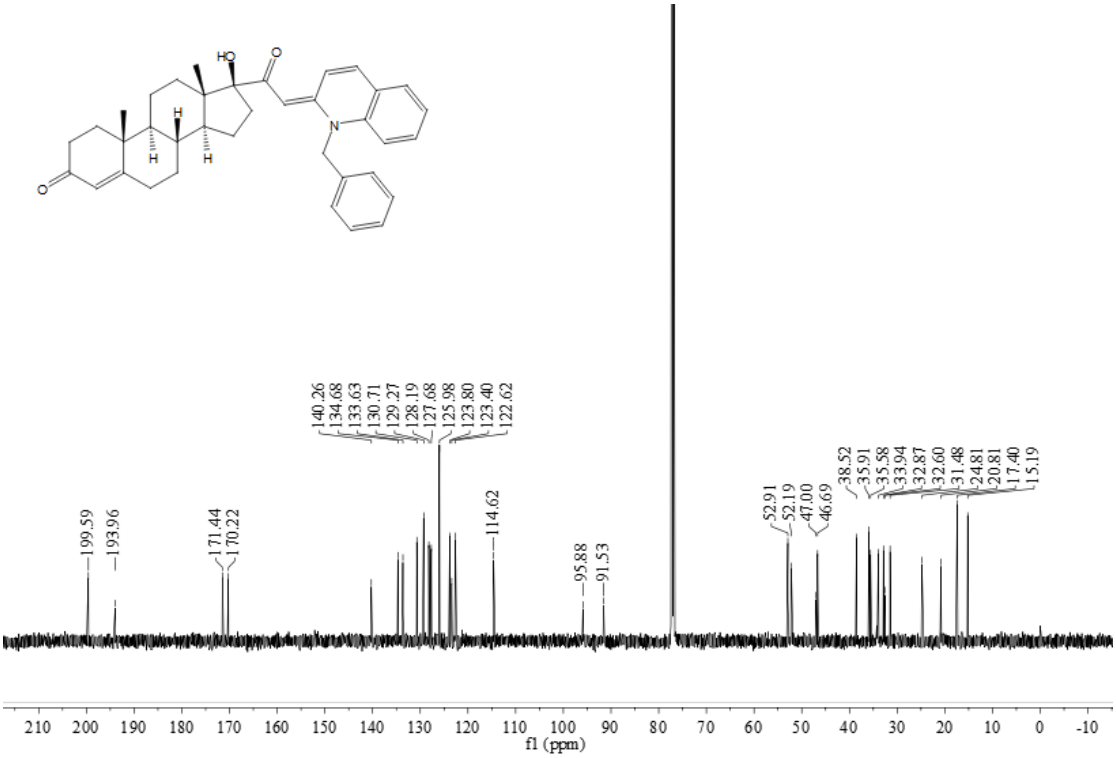
^{13}C NMR spectra of 5u (126 MHz, $CDCl_3$)



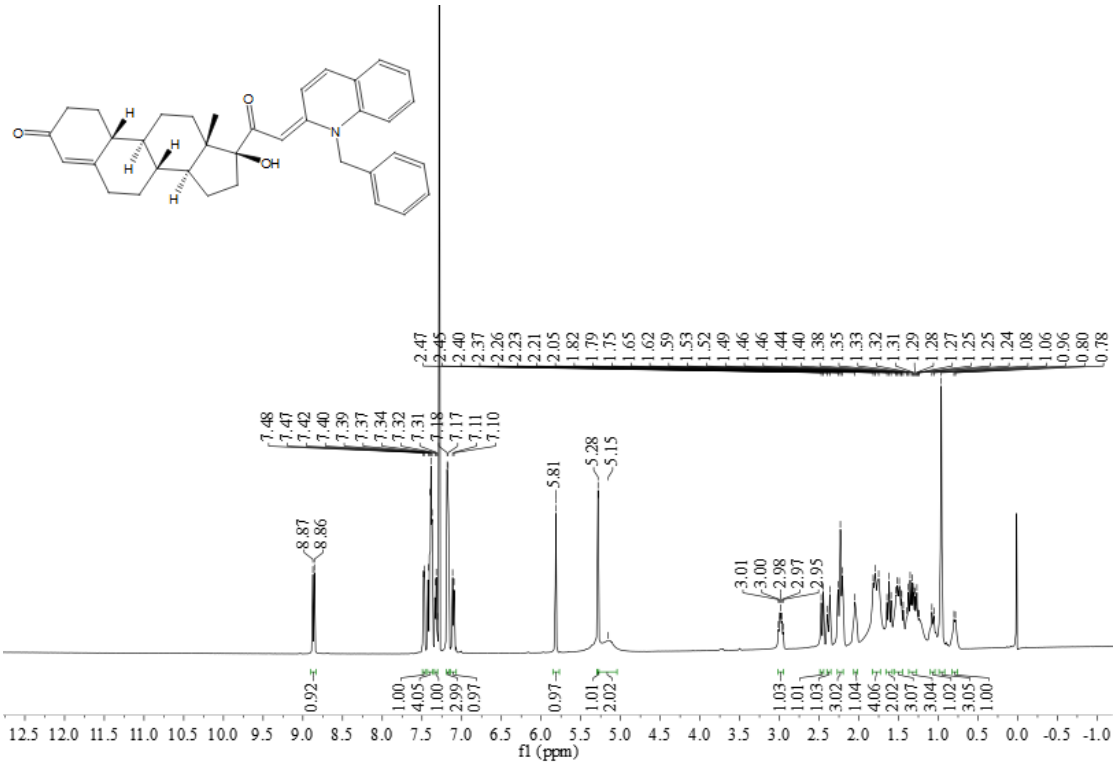
^{1}H NMR spectra of 6a (500 MHz, $CDCl_3$)



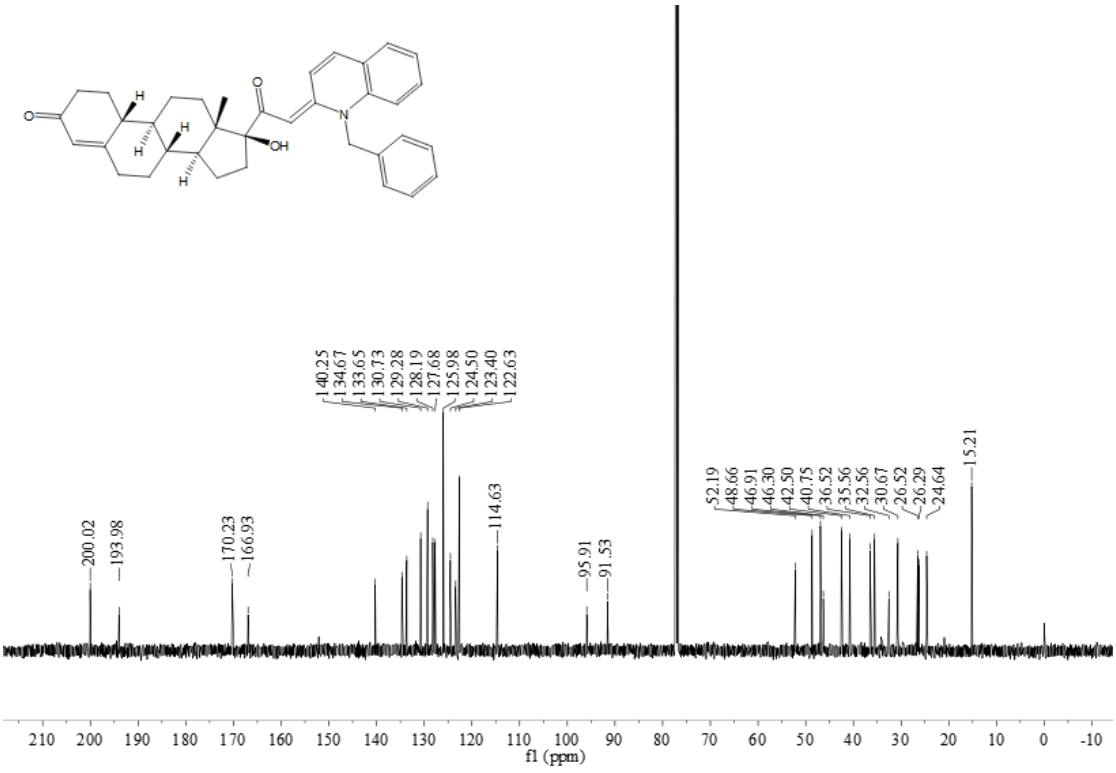
^{13}C NMR spectra of 6a (126 MHz, $CDCl_3$)



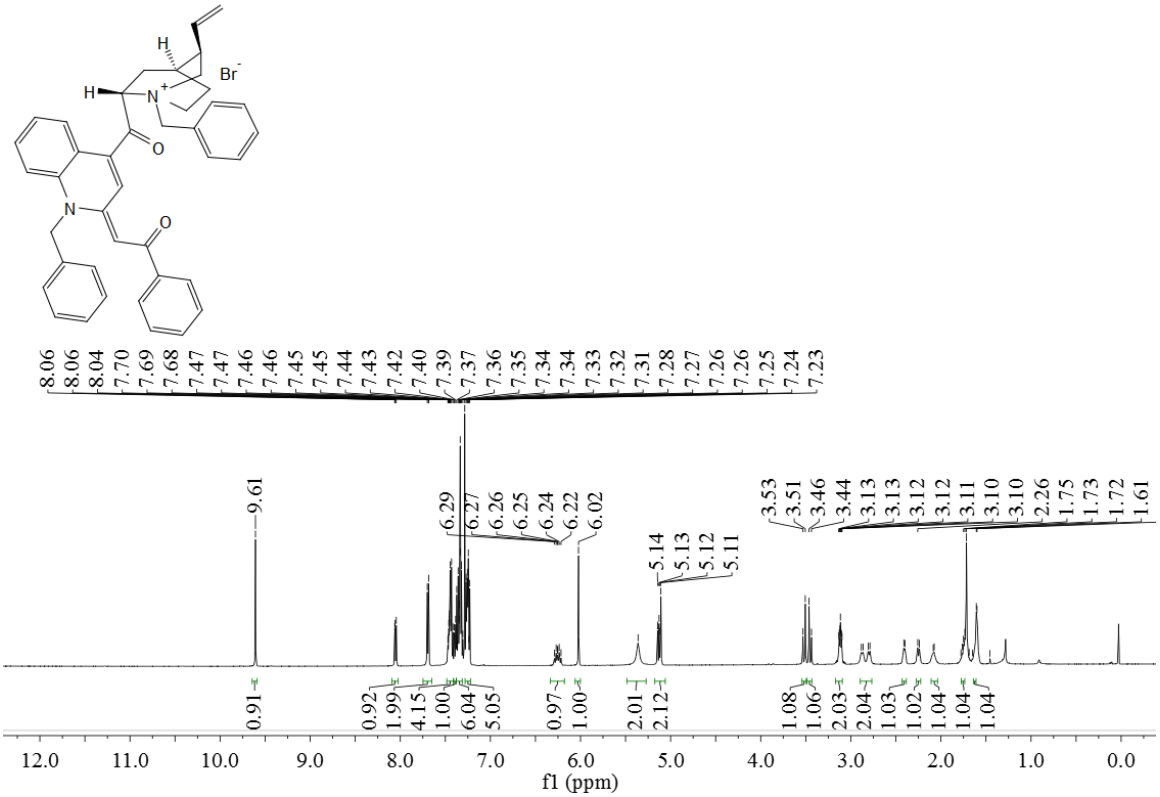
^{1}H NMR spectra of 6b (500 MHz, $CDCl_3$)



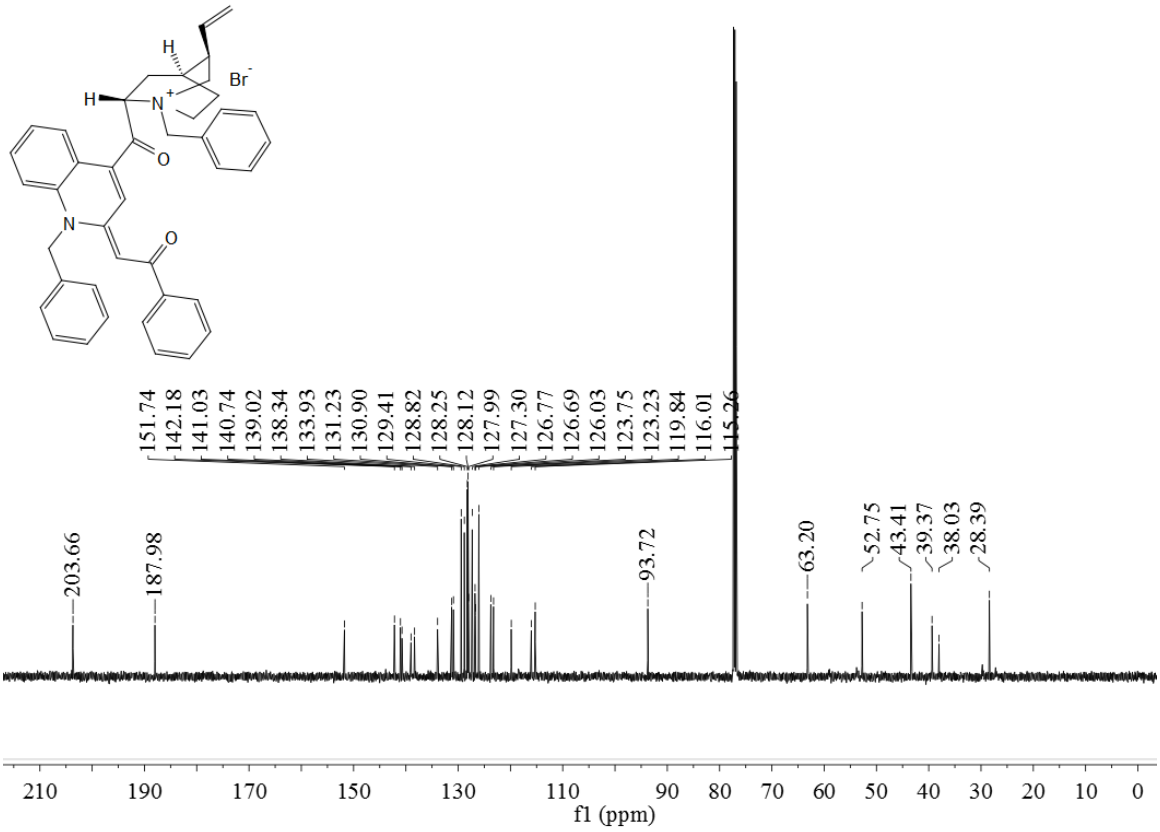
^{13}C NMR spectra of 6b (126 MHz, $CDCl_3$)



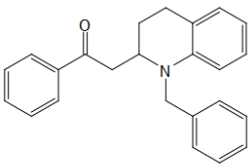
^{1}H NMR spectra of 6c (500 MHz, $CDCl_3$)

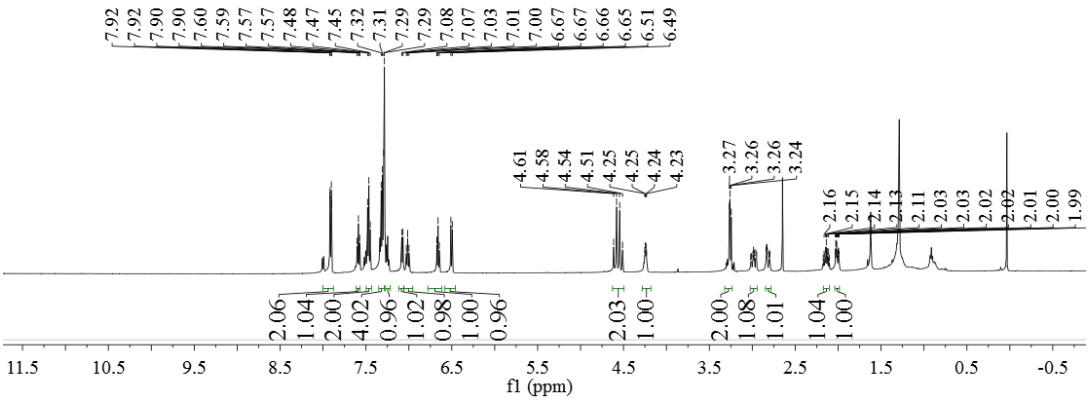


^{13}C NMR spectra of 6c (126 MHz, $CDCl_3$)



^{1}H NMR spectra of 4a' (500 MHz, $CDCl_3$)





^{13}C NMR spectra of 4a' (126 MHz, $CDCl_3$)