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Synthesis and Reaction of 2,2′-Biquinolyl

Shoji Wakabayashi,* Yukihiro Kubo, Takashi Takeda, Jun-ichi Uenishi, and Shigeru Oae*
Department of Chemistry, Faculty of Science, Okayama University of Science, Ridai-cho, Okayama 700
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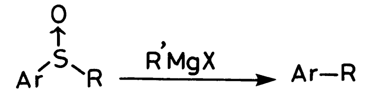
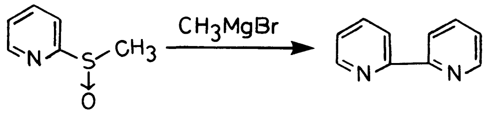
A title compound is readily prepared from methyl 2-quinolyl sulfoxide (**3**) with methylmagnesium bromide in excellent yield and an ipso addition of alkylmagnesium halides to 2,2′-biquinolyl (**4**) is also described.

Ligand coupling reaction of aryl sulfoxides with Grignard reagents has been developed by S. Oae and co-workers.[1] This reaction is interesting in not only mechanistic aspects[2] but also synthetic applicabilities for various types of benzyl-, allyl-, or aryl-substituted aromatic compounds.[3] Recently a formation of bi(heteroaryl) compounds has been reported in the reaction of alkyl pyridyl sulfoxides with alkyl Grignard reagents.[4] This homolytic coupling reaction was found by treating of methyl 2-pyridyl sulfoxide (**1**) with a primary alkyl Grignard reagent in ether or THF and resulted 2,2′-bipyridyl (**2**) in moderate yields.



Ar:Heteroaryl, Aryl
R :Benzyl, Allyl, Aryl
R':Alkyl

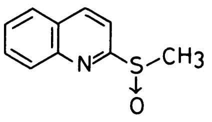


1 **2**

In an extension of this study to obtain bi(heteroaryl) compounds, we would like to describe herein a facile preparation of 2,2′-biquinolyl (**4**) under very mild conditions and also the first example of an alkyl Grignard addition to **4**.

When methyl 2-quinolyl sulfoxide (**3**)[5] was treated with one equivalent of methylmagnesium bromide at room temperature in THF, the reaction completed instantaneously giving **4** exclusively in 90 to 98% yields. This reaction takes place even at lower temperatures. The reaction appears to complete in less than 20 s at −78 °C affording **4** in more than 90% yield. This remarkably high reaction rate is in contrast to that of the formation of **2**, which required about 10 hours to complete the reaction of **1** with methylmagnesium bromide at −78 °C. Approximately the formation of **4** is at least 10^3 faster than that of **2**. The compound **4** is currently used for a wide poupose of coating materials, chelating reagents and catalysts as a copper complex in the modern technological fields.[6]

Among the recent reports for the preparation of **4**, i.e., palladium-catalyzed coupling reaction,[7] nickel-catalyzed coupling reaction[8] or electrochemical reaction,[9] this preparative method offers several advantages such as the mildest reaction conditions, the shortest reaction time, the simple operation and also the high yield.



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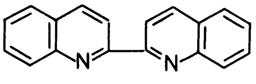

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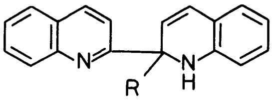
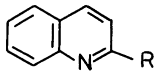


5a-g



6a-g

R; a, CH_3-
b, CH_3CH_2-
c, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CHCH_2-$
d, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH-$
e, Ph-
f, $CH_2{=}CHCH_2-$
g, $\begin{matrix}CH_2{=}CH\\CH_3\end{matrix}\!>CH-$

Another interesting aspect is that the reaction of the same substrate **3** with two equivalents of methylmagnesium bromide did not stop at the same stage of **4** but proceeded further. Eventualy 2-methyl-1,2-dihydro-2,2′-biquinolyl (**5a**) was isolated in 79% yield. This compound was identified by spectroscopic analysis. A mass spectrum has shown the molecular ion peak at 272 (*m/z*), which has lost a methyl group to give a base peak appearing at 257 (*m/z*). In a ^{1}H NMR spectrum a singlet peak at δ 1.83 for 3 protons indicates quaternary methyl group and a broad singlet of secondary amine proton appears at δ 5.01. A ^{13}C NMR spectrum has also supported this structure. Thus the spectrum shows the C-2 substituted methyl carbon at δ 30.84 and C-2 methine carbon at δ 59.15. These carbons appear as a quartet and a singlet

Table 1. Reaction of **3** with Grignard Reagents

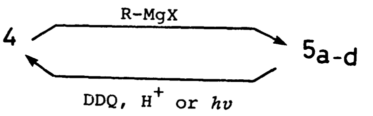
Grignard reagent	(equiv)	Products (yield/%)	
CH_3MgBr	1.1	**4** (98)	
	2.1	**5a** (79)	
CH_3CH_2MgBr	2.1	**5b** (61)	
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHCH_2MgCl$	2.1	**5c** (77)	
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHMgCl$	2.1	**5d** (26)[a]	
PhMgBr	2.1	**6e** (20)	**4** (50)
$CH_2{=}CHCH_2MgCl$	2.1	**6f** (80)	
$\begin{matrix}CH_2{=}CH\\CH_3\end{matrix}\!\!>CHMgCl$	2.1	**6g** (74)	

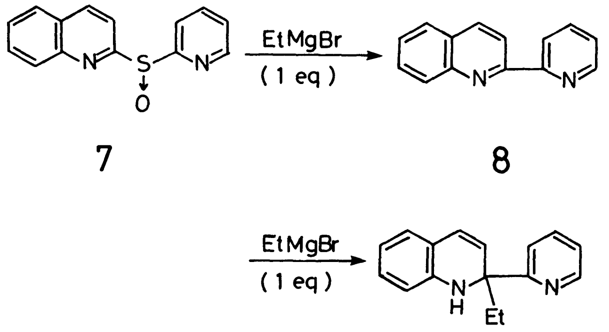
a) The major product was isopropyl 2-quinolyl sulfoxide in 61% yield.

respectively by a off-resonance experiment. In a IR spectrum an absorption of the secondary amine is observed at 3390 cm^{-1}.

Table 1 lists the results in the reactions with several Grignard reagents. Ethyl-, isobutyl-, and isopropylmagnesium halides provided the corresponding C-2 alkyl-substituted products **5b**, **5c**, and **5d** in 61%, 77%, and 26% yields, respectively. In the case of isopropylmagnesium chloride the ligand-exchange product, isopropyl 2-quinolyl sulfoxide was obtained in 61% yield along with the desired product. The reaction of phenylmagnesium bromide gave none of **5e** but **4** as a major product and 2-phenylquinoline (**6e**)[10] as a minor product. Normal ligand-coupling reaction is predominant in the reaction of allyl- and (1-methyl-2-propenyl)magnesium chloride affording 2-allyl- and 2-(1-methyl-2-propenyl)quinolines **6f** and **6g**[11] along with unseparable isomeric α,β-unsaturated compounds in 80% and 74% yields.

The compound **5** have been confirmed to be formed from 2,2′-biquinolyl intermediate. In fact the reaction of **4** with one equivalent of alkylmagnesium halides such as methyl-, ethyl-, isobutyl-, and isopropylmagnesium halides, afforded exclusively the corresponding C-2 alkyl-substituted products, **5a**, **5b**, **5c**, and **5d** in 59%, 68%, 90%, and 39% yields, respectively. However the reaction with phenylmagnesium bromide and allylmagnesium chloride have shown to be totally unreacted. The products **5a**—**d** are considerably stable in frozen benzene at −20 °C for a month but are oxidized spontaneously at room temperature to **4** within a couple of days. Particularly, in the case of **5d** the transformation to **4** takes within a half day in $CDCl_3$ which is much faster than the others. Meanwhile, oxidation of **5a** with DDQ in benzene afforded **4** instantaneously at 0 °C. The half life time of **5a** in acidic ethanol containing 5% of *dl*-10-camphorsulfonic acid was 4 hours and that under the sunlight or ultraviolet irradiation was about a half hour in the same solvent. But no transformation was observed in a day in basic ethanol containing 5% of triethylamine.





7

8

9

Investigations of this addition[12] were carried out in other substrates. None of the corresponding C-2 alkyl-substituted pyridine and/or 1,2-dihydro-2,2′-bipyridyl has been detected in the reaction of **1** with methyl- or ethylmagnesium bromide even when the Grignard reagent has been used in a large excess. Meanwhile treatment of one equivalent of ethylmagnesium bromide with 2-pyridyl 2-quinolyl sulfoxide (**7**) has been found to give ligand-coupling product, 2-(2-pyridyl)quinoline (**8**) in 54% yield as a sole product, which upon treatment with another equivalent of ethylmagnesium bromide gave successively 2-ethyl-2-(2-pyridyl)-1,2-dihydroquinoline (**9**) in 35% yield. In the addition of ethylmagnesium bromide to 2-substituted quinolines **6e** or **6f**, only the starting materials were recovered quantitatively. All these observations reveal clearly that this Grignard addition is a substrate specific reaction to 2-(2-pyridyl and/or 2-quinolyl)-quinolines. The produced compound **9** as well as **5a**—**d** are structurally unique and are fairly stable at low temperature under inert atmosphere, but oxidized easily in certain conditions to give back to **8** and/or **4** quantitatively.

Experimental

Melting points were taken on Yanaco melting point apparatus and were uncorrected. Spectra were measured with the following instruments; ^1H and ^{13}C NMR: JEOL-GX400 (400 MHz and 100 MHz), low- and high-resolution MS: JEOL-JMS-303HF and IR: JASCO IRA-1. NMR spectra were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. Mass spectra were obtained with a direct inlet method at 70 eV by the Analytical Center of Okayama University of Science. Only strong and/or structurally important peaks are reported here for MS and IR. All reactions were carried out under Argon atmosphere. Solvents (THF and ether) for the reactions were freshly distilled over sodium benzophenone ketyl before the use. Methyl- and ethylmagnesium bromide were purchased from the Kanto Chemical Co. Other Grignard reagents were freshly prepared in dry ether or THF by the procedure in literatures.[13] Thin-layer chromatography (TLC) was carried out on 0.25 mm E. Merck precoated silica-gel plates (60F-254) and for silica-gel column chromatography Wako gel (C-200) was used.

Reactions of 3 with Grignard Reagents. To a stirred THF (3 ml) solution of **3** (1 mmol) was added Grignard reagent (1.1 mmol or 2.1 mmol) in THF or ether solution dropwise at room temperature. After 30 min reaction mixture was quenched with a saturated ammonium chloride solution (3 ml) and extracted with ether (50 ml). The ethereal layer was washed with water (2 ml) and brine (2 ml) and dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography on silica gel.

5a: Colorless oil, R_f=0.22 (10% ether in hexane); ^{1}H NMR δ=1.83 (3H, s), 5.01 (1H, bs), 5.89 (1H, d, J=9.9 Hz), 6.47 (1H, d, J=9.9 Hz), 6.56 (1H, d, J=8.1 Hz), 6.58 (1H, td, J=7.4, 0.3 Hz), 6.90 (1H, dd, J=7.5, 1.7 Hz), 6.99 (1H, td, J=7.7, 1.7 Hz), 7.49 (1H, td, J=7.2, 1.1 Hz), 7.68 (1H, d, J=8.6 Hz), 7.69 (1H, td, J=7.2, 2.3 Hz), 7.76 (1H, dd, J=8.2, 2.3 Hz), 8.07 (1H, d, J=9.8 Hz), 8.09 (1H, d, J=8.6 Hz); ^{13}C NMR δ=30.84 (q), 59.15 (s), 113.18 (d), 117.41 (d), 118.77 (d), 119.53 (s), 125.27 (d), 126.19 (d), 126.84 (d), 126.87 (d), 127.40 (d), 127.95 (s), 128.99 (d), 129.38 (d), 129.42 (d), 136.62 (d), 143.06 (s), 147.25 (s), 165.74 (s); MS m/z (rel intensity, %) 272 (M$^+$, 17), 257 (base), 128 (30); IR ($CHCl_3$) 1460, 1600, 2960, 3390 cm^{-1}. HRMS Found: m/z 272.1307. Calcd for $C_{19}H_{16}N_2$: M, 272.1313.

5b: Colorless oil, R_f=0.29 (10% ether in hexane); ^{1}H NMR δ=0.96 (3H, t, J=7.6 Hz), 2.02 (1H, dq, J=14.1, 7.6 Hz), 2.12 (1H, dq, J=14.1, 7.6 Hz), 5.08 (1H, bs), 5.88 (1H, d, J=9.9 Hz), 6.52 (1H, d, J=9.9 Hz), 6.55 (1H, td, J=7.8, 0.8 Hz), 6.61 (1H, d, J=7.9 Hz), 6.88 (1H, dd, J=7.4, 1.6 Hz), 6.99 (1H, td, J=7.8, 1.9 Hz), 7.49 (1H, td, J=7.5, 1.5 Hz), 7.61 (1H, d, J=8.8 Hz), 7.68 (1H, td, J=7.7, 2.1 Hz), 7.76 (1H, dd, J=8.3, 1.5 Hz), 8.06 (1H, d, J=9.2 Hz), 8.09 (1H, d, J=8.8 Hz); ^{13}C NMR δ=8.48 (q), 36.13 (t), 62.36 (s), 113.05 (d), 117.02 (d), 118.71 (d), 119.46 (s), 126.07 (d), 126.26 (d), 126.29 (d), 126.78 (s), 127.37 (d), 128.29 (d), 128.93 (d), 129.29 (d), 129.40 (d), 136.46 (d), 143.64 (s), 147.29 (s), 165.48 (s); MS m/z (rel intensity, %) 286 (M$^+$, 3), 257 (base), 158 (15), 128 (22); IR ($CHCl_3$) 1460, 1600, 2950, 3400 cm^{-1}. HRMS Found: m/z 286.1478. Calcd for $C_{20}H_{18}N_2$: M, 286.1469.

5c: Colorless oil, R_f=0.31 (10% ether in hexane); ^{1}H NMR δ=0.87 (3H, d, J=6.6 Hz), 0.94 (3H, d, J=6.2 Hz), 1.90 (1H, dd, J=13.2, 6.6 Hz), 1.99 (1H, m), 2.04 (1H, dd, J=13.2, 6.2 Hz), 5.07 (1H, bs), 5.91 (1H, d, J=9.6 Hz), 6.46 (1H, d, J=9.6 Hz), 6.54 (1H, td, J=7.3, 1.1 Hz), 6.58 (1H, d, J=8.1 Hz), 6.86 (1H, dd, J=7.3, 1.7 Hz), 6.89 (1H, td, J=7.7, 1.5 Hz), 7.46 (1H, td, J=7.0, 1.1 Hz), 7.59 (1H, d, J=9.2 Hz), 7.66 (1H, td, J=7.0, 1.5 Hz), 7.73 (1H, dd, J=8.1, 1.8 Hz), 8.06 (1H, d, J=8.8 Hz), 8.06 (1H, d, J=9.2 Hz); ^{13}C NMR δ=24.41 (t), 24.44 (q), 24.52 (q), 51.74 (d), 62.38 (s), 113.05 (d), 116.98 (d), 118.54 (d), 119.36 (d), 125.69 (d), 126.06 (d), 126.74 (s), 126.80 (d), 127.27 (d), 127.35 (d), 128.94 (d), 129.29 (d), 129.38 (d), 136.51 (d), 143.42 (s), 147.72 (s), 165.88 (s); MS m/z (rel intensity, %) 314 (M$^+$, 8), 258 (base), 186 (57), 143 (18), 128 (58); IR ($CHCl_3$) 1480, 1600, 2940, 3380 cm^{-1}. HRMS Found: m/z 314.1782. Calcd for $C_{22}H_{22}N_2$: M, 314.1795.

5d: Colorless oil, R_f=0.37 (10% ether in hexane); ^{1}H NMR δ=0.85 (1H, d, J=6.6 Hz), 0.98 (1H, d, J=6.6 Hz), 2.48 (1H, m), 5.16 (1H, bs), 5.91 (1H, d, J=9.8 Hz), 6.50 (1H, d, J=9.8 Hz), 6.51 (1H, td, J=7.5, 0.7 Hz), 6.61 (1H, d, J=7.7 Hz), 6.83 (1H, dd, J=7.3, 1.5 Hz), 6.97 (1H, td, J=7.3, 1.7 Hz), 7.48 (1H, td, J=7.0, 1.1 Hz), 7.53 (1H, d, J=8.6 Hz), 7.67 (1H, td, J=7.3, 2.0 Hz), 7.75 (1H, dd, J=8.1, 1.7 Hz), 8.05 (1H, d, J=9.5 Hz), 8.07 (1H, d, J=8.6 Hz); ^{13}C NMR δ=17.64 (q), 39.04 (d), 65.05 (s), 112.92 (d), 116.77 (d), 118.95 (d), 119.95 (s), 126.70 (d), 126.78 (d), 126.93 (d), 127.38 (d), 127.63 (d), 128.42 (s), 128.93 (d), 129.54 (d), 136.74 (d), 144.02 (s), 147.89 (s), 165.70 (s); MS m/z (rel intensity, %) 300 (M$^+$, 2), 257 (base), 128 (20); IR ($CHCl_3$) 1465, 1600, 2960, 3360 cm^{-1}. HRMS Found: m/z 300.1658. Calcd for $C_{21}H_{20}N_2$: M, 300.1625.

6e:[10] Mp 80 °C (from hexane); R_f=0.25 (10% ether in hexane); ^{1}H NMR δ=7.47—7.56 (5H, m), 7.73 (1H, td, J=6.8, 1.4 Hz), 7.84 (1H, dd, J=7.5, 0.4 Hz), 7.89 (1H, d, J=8.6 Hz), 8.17 (1H, d, J=7.2 Hz), 8.18 (1H, td, J=5.1, 0.8 Hz), 8.23 (1H, d, J=8.6 Hz).

6f:[11] Colorless oil, R_f=0.25 (10% ether in hexane); ^{1}H NMR δ=3.77 (2H, d, J=7.0 Hz), 5.18 (1H, d, J=10.9 Hz), 5.22 (1H, d, J=17.8 Hz), 6.14 (1H, ddt, J=17.8, 10.9, 7.0 Hz), 7.31 (1H, d, J=8.2 Hz), 7.49 (1H, td, J=7.9, 1.5 Hz), 7.68 (1H, td, J=7.7, 1.8 Hz), 7.77 (1H, dd, J=8.5, 1.5 Hz), 8.05 (1H, d, J=8.4 Hz), 8.06 (1H, d, J=8.4 Hz).

6g:[11] Colorless oil, R_f=0.38 (10% ether in hexane); ^{1}H NMR δ=1.54 (3H, d, J=7.2 Hz), 3.85 (1H, m), 5.14 (1H, ddd, J=10.3, 1.6, 1.3 Hz), 5.19 (1H, ddd, J=17.4, 1.6, 1.3 Hz), 6.18 (1H, ddd, J=17.4, 10.3, 6.5 Hz), 7.32 (1H, d, J=8.5 Hz), 7.49 (1H, td, J=7.8, 1.0 Hz), 7.69 (1H, td, J=7.7, 1.8 Hz), 7.78 (1H, dd, J=7.9, 1.1 Hz), 8.07 (1H, d, J=8.0 Hz), 8.08 (1H, d, J=8.0 Hz).

2-Pyridyl 2-Quinolyl Sulfoxide (7). To a mixture of 2-chloroquinoline (2.945 g, 18 mmol) and 2-pyridinethiol (2.0 g, 18 mmol) in hexamethylphosphoric triamide (HMPA, 20 ml) was added pieced of sodium metal (414 mg, 18 mmol) by several portions and the mixture was heated at 80 °C with stirring. After 2 days it was quenched with water (20 ml) and extracted with ether (200 ml). The ethereal layer was washed with water (3 ml×5) and brine (3 ml) and dried over $MgSO_4$. The solvent was removed and the crude sulfide, R_f=0.23 (20% ether in hexane), was used for the next reaction without any purification. To a chloroform solution (15 ml) of the crude sulfide was added carefully *m*-chloroperbenzoic acid portionwise at room temperature and the reaction was monitored by TLC to check the starting material consumed. It was diluted with chloroform (100 ml) and washed with aq. sodium thiosulfate (6 ml×2), aq. sodium hydrogencarbonate (6 ml×2), water (6 ml), and brine (6 ml) and dried over $MgSO_4$. After removal of the solvent under reduced pressure the residue was purified by column chromatography on silica gel eluted with 60% ethyl acetate in hexane to give **7** (1.5 g) in 35% yield. Mp 86—87 °C (from benzene); ^{1}H NMR δ=7.30 (1H, m), 7.59 (1H, td, J=8.3, 1.6 Hz), 7.76 (1H, td, J=7.9, 0.7 Hz), 7.83 (1H, d, J=8.5 Hz), 7.86 (1H, td, J=7.7, 1.4 Hz), 8.04 (1H, dd, J=8.6, 1.1 Hz), 8.11 (1H, d, J=8.1 Hz), 8.21 (1H, d, J=8.8 Hz), 8.30 (1H, d, J=8.8 Hz), 8.58 (1H, d, J=5.3 Hz); ^{13}C NMR δ=115.53 (d), 119.52 (d), 124.96 (d), 127.85 (d), 128.04 (d), 128.43 (s), 129.78 (d), 130.59 (d), 137.98 (d), 138.45 (d), 147.57 (s), 150.06 (d), 163.68 (s), 163.87 (s); IR ($CHCl_3$) 1060, 1580, 1590, 2960 cm^{-1}. Found: C, 66.18; H, 3.80; N, 11.00; S, 12.59%. Calcd for $C_{14}H_{10}N_2OS$: C, 66.12; H, 3.96; N, 11.02; S, 12.61%.

2-(2-Pyridyl)quinoline (8).[14] Methylmagnesium bromide (0.8 ml, 0.5 M solution in THF; 1 M=1 mol dm^{-3}) was dropped into **7** (94 mg, 0.36 mmol) in THF (4 ml) at room temperature. The mixture was stirred for 15 min at the same temperature. Then it was quenched with a saturated ammonium chloride solution (8 ml) and extracted with chloroform (40 ml). The organic layer was washed with water (2 ml×2) and brine (2 ml) and dried over $MgSO_4$. The solvent was removed and the residual oil was chromatographed on silica gel eluted with 25% ether in hexane to afford **8** (40 mg) in 54% yield. Mp 98 °C (from ethanol); R_f=0.20 (30% ether in hexane); ^{1}H NMR δ=7.36 (1H, td, J=6.4, 1.4 Hz), 7.56 (1H, td, J=7.1, 1.5 Hz), 7.74 (1H, dt, J=7.9, 1.5 Hz), 7.85 (1H, d, J=8.5 Hz), 7.88 (1H, td, J=7.3, 1.9 Hz), 8.19 (1H, d, J=8.7 Hz), 8.29 (1H, d, J=8.2 Hz), 8.56 (1H, d, J=8.2 Hz), 8.66 (1H, dd, J=8.1, 1.1 Hz), 8.75 (1H, ddd, J=4.7, 1.9, 1.1 Hz).

2-Ethyl-2-(2-pyridyl)-1,2-dihydroquinoline (9). To a stirred THF solution (3 ml) of **8** (58 mg, 0.28 mmol) was dropped ethylmagnesium bromide (0.34 ml, 1 M solution in THF) at room temperature. After 3 min it was quenched with a saturated ammonium chloride solution (3 ml) and extracted with chloroform (20 ml). The organic layer was washed with water (5 ml) and brine (5 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography eluted with 15% ether in hexane to give **9** as colorless oil (23 mg) in 35% yield. R_f=0.32 (30% ether in hexane); ^{1}H NMR δ=0.91 (3H, t, J=7.3 Hz), 1.98 (2H, qd, J=7.3, 0.7 Hz), 4.77 (1H, bs), 5.82 (1H, dd, J=9.9, 1.4 Hz), 6.50 (1H, d, J=9.9 Hz), 6.53 (1H, d, J=8.4 Hz), 6.55 (1H, td, J=7.3, 1.1 Hz), 6.87 (1H, dd, J=7.3, 1.1 Hz), 6.97 (1H, td, J=7.7, 1.5 Hz), 7.09 (1H, ddd, J=7.3, 4.8, 1.1 Hz), 7.42 (1H, ddd, J=7.0, 1.1, 0.7 Hz), 7.61 (1H, td, J=7.8, 1.8 Hz), 8.56 (1H, ddd, J=4.8, 1.8, 1.1 Hz); ^{13}C NMR δ=8.56 (q), 35.99 (t), 61.70 (s), 112.82 (d), 117.06 (d), 119.54 (s), 120.61 (d), 121.44 (d), 126.10 (d), 126.36 (d), 126.81 (d), 128.86 (d), 136.46 (d), 143.44 (s), 149.01 (d), 165.83 (s); MS m/z (rel intensity, %) 236 (M^+, 45), 208 (base), 158 (70), 143 (30), 128 (33), 104 (40), 77 (20); IR ($CHCl_3$) 1450, 1580, 1630, 2950, 3400 cm^{-1}. HRMS Found: m/z 236.1313. Calcd for $C_{16}H_{16}N_2$: M, 236.1313.

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