Diethyl Azodicarboxylate-promoted Oxidative Coupling Reaction of *N*-Phenyl Tetrahydroisoquinoline with β-Keto Acids

Yong Hwan Kim, Min Gyun Gil, and Dae Young Kim*

Department of Chemistry, Soonchunhyang University, Chungnam 31538, Korea.
**E-mail: dyoung@sch.ac.kr*
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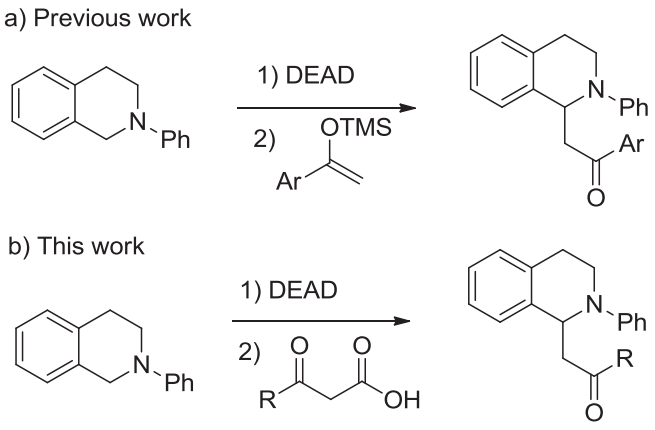
The direct oxidative cross-dehydrogenative coupling (CDC) of two C─H bonds can be an atom-economic and environmentally benign strategy the field of organic synthesis.[1] Since the pioneering work on CDC demonstrated by Murahashi and Li groups on oxidative iminium ions formation from tetrahydroisoquinoline (THIQ) derivatives,[2] various nucleophiles have been utilized to combine the iminium intermediates to form new C─C bonds using numerous oxidation methods.[3] Several groups reported the efficient CDC of C(sp^3)─H with fluorinated active methins, Grignard reagents, and allyl silanes by using diethyl azodicarboxylate (DEAD) as the oxidant.[4] Recently, Akiyama and coworkers have reported DEAD-promoted phenacylmethylation to form C1-phenacylmethylated THIQ derivatives from the reaction of silyl enol ethers with *N*-phenyl terahydroisoquinolines (Scheme 1(a)).[3g] The decarboxylative additions of β-keto acids as ketones or ketone enolate equivalents have received much attention.[5] We envisioned the decarboxylative Mannich-type reaction of the β-keto acids to the C1-acylmethylated THIQs through DEAD-promoted oxidation (Scheme 1(b)).

As part of a research program related to the development of internal redox reaction, we recently reported the intramolecular redox reactions via C─H bond activation.[6] Herein, we report C1-phenacylmethylation of THIQs with β-keto acids using DEAD as the oxidant.



Scheme 1. C1-phenacylmethylation of THIQs.

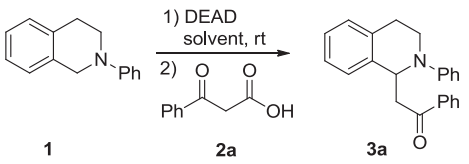
To determine optimum conditions for the DEAD-promoted oxidative coupling reaction of THIQs, we examined the CDC reaction of *N*-phenyl tetrahydroisoquinoline (**1**) with 3-oxo-3-phenylpropanoic acid (**2a**). This reaction was initiated with *N*-phenyl tetrahydroisoquinoline (**1**) with DEAD in toluene at room temperature for 0.5 h, subsequent addition of 3-oxo-3-phenylpropanoic acid (**2a**) at room temperature gave the corresponding coupling product **3a** in 43% yield (Table 1, entry 1). A survey of the reaction media indicated that common solvents (Table 1, entries 1–10), such as toluene, benzene, dichloromethane, chloroform, THF, ethyl acetate, acetonitrile, DMF, DMSO, and ethanol, were well tolerated in this conjugate addition. Among the solvents probed, the best result was achieved when the reaction was conducted in acetonitrile (Table 1, entry 7, 77% yield).

With the optimal reaction conditions in hand, we investigated the scope of this DEAD-promoted oxidative coupling reaction of *N*-phenyl tetrahydroisoquinoline (**1**) with 3-oxoalkanoic acid **2** in acetonitrile at room temperature. As shown in Table 2, various 3-oxoalkanoic acids **2** with electron-donating or electron-withdrawing aryl groups furnished the corresponding coupling products with moderate to high yields (60–80%, Table 2, entries 1–10). The naphthyl- and heteroaryl-substituted β-keto acids provided the desired products with high yields (71–80%, Table 2, entries 11, 12). In addition, alkyl-substituted β-keto acid **2m** also afforded the corresponding product, but with relatively lower yield (55%, Table 2, entry 13).

In order to check the synthetic viability of this oxidative coupling system, we performed the DEAD-promoted coupling reaction at the gram scale. As shown in Scheme 2, when *N*-phenyl tetrahydroisoquinoline (**1**) was treated with 3-oxo-3-phenylpropanoic acid (**2a**) the optimal reaction conditions, the reaction proceeded smoothly to afford the desired 1-phenyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (**3a**) with 75% yield.

In conclusion, we have presented a mild and efficient process for the oxidative coupling reaction of *N*-phenyl

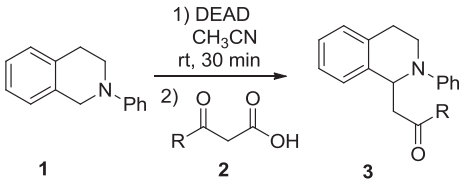
Table 1. Optimization of the reaction conditions.[a]



Entry	Solvent	Time (h)	Yield[b] (%)
1	PhMe	20	43
2	PhH	20	38
3	CH_2Cl_2	20	65
4	$CHCl_3$	20	61
5	THF	20	40
6	EtOAc	20	47
7	CH_3CN	6	77
8	DMF	10	63
9	DMSO	20	43
10	EtOH	20	42

[a] Reactions were carried out *N*-phenyl tetrahydroisoquinoline (**1**, 0.3 mmol), DEAD (0.33 mmol) in solvent (3 mL) at room temperature for 0.5 h, then, 3-oxo-3-phenylpropanoic acid (**2a**, 0.45 mmol) was added.
[b] Isolated yield.

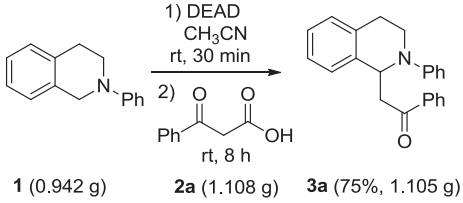
Table 2. Variation of substrates **2**.[a]



Entry	**2**, R	Time (h)	Yield[b] (%)
1	Ph	6	**3a**, 77
2	4-F,C_6H_4	8	**3b**, 71
3	4-Cl,C_6H_4	3	**3c**, 63
4	4-Br,C_6H_4	3	**3d**, 75
5	4-OMe,C_6H_4	7	**3e**, 68
6	4-Me,C_6H_4	8	**3f**, 64
7	4-NO_2,C_6H_4	9	**3g**, 75
8	3-Me,C_6H_4	9	**3h**, 60
9	3-Br,C_6H_4	10	**3i**, 65
10	2-Me,C_6H_4	13	**3j**, 67
11	2-Naphthyl	10	**3k**, 80
12	2-Thienyl	6	**3l**, 71
13	Benzyl	15	**3m**, 55

[a] Reactions were carried out *N*-phenyl tetrahydroisoquinoline (**1**, 0.3 mmol), DEAD (0.33 mmol) in acetonitrile (3 mL) at room temperature for 0.5 h, then, 3-oxo-alkanoic acids **2** (0.45 mmol) was added.
[b] Isolated yield.

tetrahydroisoquinoline (**1**) with 3-oxoalkanoic acids **2** using DEAD as the oxidant. This process represents a robust approach for the syntheses of diverse C1-acylmethylated



Scheme 2. Gram-scale oxidative coupling reaction of *N*-phenyl tetrahydroisoquinoline (**1**) with 3-oxo-3-phenylpropanoic acid (**2a**).

THIQ compounds. Further studies on oxidative coupling reaction of other nucleophiles and on the more detailed investigation of the reaction mechanisms are currently underway in our laboratories.

Experimental

General Procedure for the DEAD-promoted Oxidative Coupling Reaction of *N*-Phenyl Tetrahydroisoquinoline with β-Keto Acids. To a stirred solution of *N*-phenyl tetrahydroisoquinoline (**1**, 63 mg, 0.3 mmol), in acetonitrile (3 mL) was added DEAD (0.33 mmol) under N_2 atmosphere. The reaction mixture was stirred at room temperature for 0.5 h. Then, 3-oxoalkanoic acid **2** (0.45 mmol) was added and the mixture was further stirred for 3–15 h at room temperature. After the reaction was completed, the mixture was directed purified by column chromatography on silica gel (ethyl acetate:*n*-hexane = 1:20) to afford the C1-acylmethylated THIQs **3**.

1-Phenyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) ethanone (3a). Pale yellow solid; yield = 77%; mp 106–107 °C (lit.3 mp 104–106°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.29–7.10 (m, 6H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 7.5 Hz, 1H), 5.68 (dd, *J* = 6.8 Hz, 5.1 Hz, 1H), 3.70–3.60 (m, 2H), 3.60 (dd, *J* = 16.4, 5.1 Hz, 1H), 3.40 (dd, *J* = 16.8, 7.2 Hz, 1H), 3.13 (m, 1H), 2.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 148.7, 138.3, 137.3, 134.4, 133.0, 129.3, 128.5, 128.1, 127.1, 126.7, 126.2, 117.9, 114.3, 55.0, 45.4, 42.2, 27.5; EI-MS: *m/z* = 327.2 $[M]^+$.

1-(4-Fluorophenyl)-2-(2-phenyl-1,2,3,4-tetrahydroiso-quinolin-1-yl)ethanone (3b). Pale yellow solid; yield = 71%; mp 78–79°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 9.0, 5.2 Hz, 2H), 7.25–7.04 (m, 8H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 5.63 (dd, *J* = 7.4, 5.0 Hz, 1H), 3.69–3.57 (m, 2H), 3.54 (dd, *J* = 16.4, 4.8 Hz, 1H), 3.34 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.15–3.07 (m, 1H), 2.95–2.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 167.0, 164.4, 148.7, 138.4, 134.5, 133.7, 130.8, 130.7 (d, *J* = 9.6 Hz), 129.4, 128.6, 127.1, 127.0 (d, *J* = 20.0 Hz), 126.3, 118.0, 115.7, 115.6 (d, *J* = 21.9 Hz), 114.3, 55.2, 45.2, 42.1, 27.5; ^{19}F NMR (376 MHz, $CDCl_3$) : *δ* −106; EI-MS: *m/z* = 345.2 $[M]^+$.

1-(4-Chlorophenyl)-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3c). Pale yellow solid; Yield = 63%; mp 76–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.29–7.14 (m, 6H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.79 (t, *J* = 7.6 Hz, 1H), 5.65 (dd, *J* = 6.8, 5.2 Hz, 1H), 3.70–3.60 (m, 2H), 3.57 (dd, *J* = 16.4, 4.8 Hz, 1H), 3.37 (dd, *J* = 16.4, 7.2 Hz, 1H), 3.14 (m, 1H), 2.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 148.5, 139.6, 138.2, 135.5, 134.5, 129.5, 129.4, 128.9, 128.6, 127.1, 126.9, 126.3, 118.1, 114.5, 55.3, 45.3, 42.2, 27.5; EI-MS: m/z = 361.1 $[M]^+$.

1-(4-Bromophenyl)-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3d). Pale yellow solid; yield = 75%; mp 80–81°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.23–7.02 (m, 6H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 5.61 (dd, *J* = 7.2, 6.2 Hz, 1H), 3.68–3.56 (m, 2H), 3.53 (dd, *J* = 16.4, 4.8 Hz, 1H), 3.31 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.17–3.06 (m, 1H), 2.94–2.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 148.6, 138.2, 135.9, 134.4, 131.8, 129.6, 129.3, 128.6, 128.2, 127.0, 126.9, 126.3, 118.1, 114.3, 55.3, 45.2, 42.1, 27.5; EI-MS: *m/z* = 405.1 $[M]^+$.

1-(4-Methoxyphenyl)-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3e). Pale yellow solid; yield = 68%; mp 99–100°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.23–7.09 (m, 6H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 6.8 Hz, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 5.64 (dd, *J* = 7.4, 5.2 Hz, 1H), 3.83 (s, 3H), 3.69–3.56 (m, 2H), 3.50 (dd, *J* = 16.2, 5.2 Hz, 1H), 3.33 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.14–3.06 (m, 1H), 2.94–2.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 163.4, 148.7, 138.6, 134.4, 130.4, 130.3, 129.3, 128.4, 127.1, 126.7, 126.2, 117.7, 114.1, 113.6, 55.4, 55.0, 44.8, 42.0, 27.5; EI-MS: *m/z* = 357.2 $[M]^+$.

2-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-(p-tolyl) ethanone (3f). Pale yellow solid; yield = 64%; mp 102–103°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.25–7.06 (m, 8H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 7.2 Hz, 1H), 5.64 (dd, *J* = 7.4, 4.8 Hz, 1H), 3.68–3.50 (m, 2H), 3.53 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.34 (dd, *J* = 16.8, 7.2 Hz, 1H), 3.14–3.07 (m, 1H), 2.95–2.88 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 143.9, 138.6, 134.8, 134.5, 129.3, 129.2, 128.5, 128.2, 127.1, 126.8, 126.2, 117.8, 114.2, 55.0, 45.2, 42.1, 27.6, 21.6; EI-MS: *m/z* = 341.2 $[M]^+$.

1-(4-Nitrophenyl)-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3g). Pale yellow solid; yield = 75%; mp 81–83°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.24–7.01 (m, 8H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 5.8 Hz, 1H), 5.63 (dd, *J* = 9.8, 5.2 Hz, 1H), 3.68–3.57 (m, 2H), 3.54 (dd, *J* = 16.4, 4.8 Hz, 1H), 3.34 (dd, *J* = 16.6, 7.2 Hz, 1H), 3.15–3.07 (m, 1H), 2.95–2.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5 148.9, 139.6, 138.0, 135.2, 134.6, 131.7, 130.3, 129.4, 129.3, 128.8, 128.5, 127.0, 126.9, 126.3, 118.0, 114.3, 55.1, 49.7, 42.0, 27.0; EI-MS: *m/z* = 372.1 $[M]^+$.

2-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-(m-tolyl) ethanone (3h). Pale yellow solid; yield = 60%; mp 103–105°C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.63 (m, 2H), 7.34–7.08 (m, 8H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 5.66 (dd, *J* = 6.8, 4.8 Hz, 1H), 3.68–3.60 (m, 2H), 3.56 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.37 (dd, *J* = 16.6, 7.4 Hz, 1H), 3.15–3.08 (m, 1H), 2.96–2.89 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 148.7, 138.6, 138.3, 137.2, 134.5, 133.8, 129.3, 128.7, 128.5, 128.4, 127.1, 126.8, 126.2, 125.3, 117.3, 114.2, 54.9, 45.4, 42.1, 27.6, 21.3; HRMS *m/z* calcd for $C_{24}H_{24}NO$ $[M + H]^+$: 342.1858; found 342.1855.

1-(3-Bromophenyl)-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3i). Pale yellow solid; yield = 65%; mp 85–87°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.29–7.09 (m, 7H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 5.63 (dd, *J* = 6.8, 4.8 Hz, 1H), 3.69–3.3.59 (m, 2H), 3.55 (dd, *J* = 16.4, 5.2 Hz, 1H), 3.33 (dd, *J* = 16.8, 7.2 Hz, 1H), 3.15–3.07 (m, 1H), 2.95–2.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 148.7, 138.9, 138.2, 135.9, 134.5, 131.2, 130.1, 129.4, 128.6, 127.0, 126.9, 126.6, 126.3, 122.9, 118.2, 114.5, 55.1, 45.4, 42.1, 27.5; HRMS *m/z* calcd for $C_{23}H_{21}BrNO$ $[M + H]^+$: 406.0807; found 406.0810.

2-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-(o-tolyl) ethanone (3j). Pale yellow solid; yield = 67%; mp 99–101°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.25–7.11 (m, 8H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 5.60 (t, *J* = 6.4 Hz, 1H), 3.67–3.54 (m, 2H), 3.48 (dd, *J* = 16.2, 5.8 Hz, 1H), 3.30 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.11–3.03 (m, 1H), 2.88–2.82 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.7, 148.8, 138.4, 138.4, 138.0, 134.5, 131.8, 131.5, 131.1, 129.3, 129.0, 128.7, 128.2, 126.9, 126.8, 126.4, 126.2, 125.5, 118.0, 114.4, 55.3, 48.4, 42.0, 27.2, 20.9; HRMS *m/z* calcd for $C_{24}H_{24}NO$ $[M + H]^+$: 342.1858; found 342.1855.

1-(Naphthalen-2-yl)-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone (3k). Pale yellow solid; yield = 80%; mp 76–78°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.95 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.90–7.79 (m, 3H), 7.62–7.45 (m, 2H), 7.25–7.08 (m, 6H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 5.71 (dd, *J* = 7.2, 5.6 Hz, 1H), 3.72–3.64 (m, 3H), 3.50 (dd, *J* = 16.6, 7.6 Hz, 1H), 3.16–3.08 (m, 1H), 2.97–2.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 148.7, 138.4, 135.5, 134.5, 132.3, 129.8, 129.5, 129.3, 128.5, 128.4, 127.7, 127.1, 126.8, 126.7, 126.2, 123.8, 117.9, 114.3, 55.1, 45.3, 42.1, 27.5; EI-MS : *m/z* = 377.2 $[M]^+$.

2-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-(thiophen-2-yl)ethanone (3l). Pale yellow solid; yield = 71%; mp 81–82°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 5.2 Hz, 1H), 7.54 (d, *J* = 3.2 Hz, 1H), 7.25–7.08 (m,

6H), 7.04 (t, J = 4.4 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 6.75 (t, J = 7.4 Hz, 1H), 5.61 (dd, J = 7.2, 6.4 Hz, 1H), 3.69–3.59 (m, 2H), 3.53 (dd, J = 16.0, 5.2 Hz, 1H), 3.28 (dd, J = 15.8, 7.2 Hz, 1H), 3.15–3.08 (m, 1H), 2.94–2.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 148.6, 144.6, 138.1, 134.4, 133.9, 132.0, 129.3, 128.5, 128.0, 127.1, 126.8, 126.2, 117.9, 114.3, 55.5, 45.9, 41.9, 29.7, 27.4; EI-MS: m/z = 333.1 $[M]^+$.

1-Phenyl-3-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) propan-2-one (3m). Pale yellow solid; yield = 55%; mp 70–72°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.21 (m, 5H), 7.15–7.09 (m, 4H), 7.05–7.03 (m, 2H), 6.92–6.90 (d, J = 8.4 Hz, 2H), 6.78–6.75 (t, J = 7.2 Hz, 1H), 5.41–5.37 (t, J = 6.4 Hz, 1H) 3.61–3.54 (m, 3H), 3.45–3.39 (m, 1H), 3.11–2.98 (m, 2H), 2.80–2.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.76, 148.81, 138.02, 134.51, 133.62, 129.48, 129.30, 128.64, 126.98, 126.90, 126.78, 126.21, 118.20, 114.70, 55.23, 51.17, 48.27, 41.84, 27.02; EI-MS: m/z = 341.2 $[M]^+$.

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