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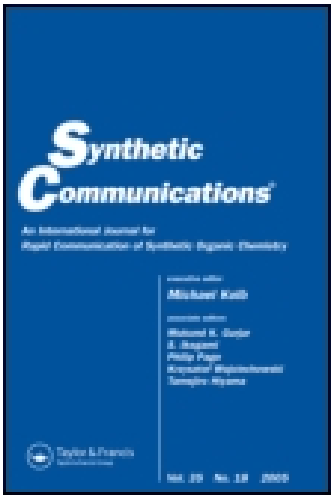

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Mild and Efficient Allylation of Indoles and Amides Using Amberlyst-15 as a Recyclable Heterogeneous Catalyst

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MILD AND EFFICIENT ALLYLATION OF INDOLES AND AMIDES USING AMBERLYST-15 AS A RECYCLABLE HETEROGENEOUS CATALYST

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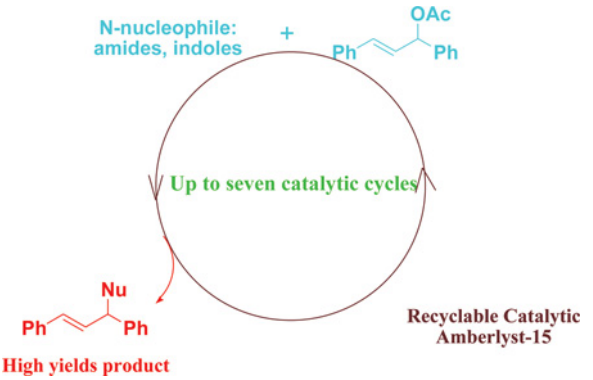
GRAPHICAL ABSTRACT



Abstract *A mild and efficient allylation of indoles and amides in the presence of a catalytic amount of Amberlyst-15 has been described in this context. The recyclable heterogeneous catalytic system is practical and facile for the synthesis of C- and N-allylated derivatives and would be of importance for the development of the accordingly functional complex molecules.*

Keywords Allylation; Amberlyst-15; heterogeneous catalysis; recyclable

INTRODUCTION

Allylation of C- and heteroatom-nucleophiles have attracted much attention in modern organic chemistry. Indole and its derivatives are important and reactive nucleophiles, existing in a number of pharmaceutical molecules and naturally occurring products that show significant bioactivities and broad applications in pharmaceutical, material, industrial, and agrochemical fields.[1] Recently, allylation[2–8] of

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indole derivatives, in both intermolecular and intramolecular manners, has attracted much attention and has been applied to elegant synthesis of indolic alkaloids.

The Friedel–Crafts allylation of indoles and amides with allylic alcohols or esters usually employed precious transition metals such as Pd,[9–13] Mo,[14] or Co[15] as catalysts. However, poor regioselectivity[10,13,14] or harsh reaction conditions (high temperature) limited their practical applications. Although allylation of aromatic compounds with allylic or benzyl alcohols can be promoted by some Lewis acids,[16–22] such as $Sc(OTf)_3$,[17,18] $Hf(OTf)_4$, $Cl_2Si(OTf)_2$,[19] or $Ce(SO_4)_3$,[20] stoichiometric amounts of Lewis acids were often required. Recently, Qin et al. reported an efficient protocol of N-allylation catalyzed by $Bi(OTf)_3$,[22] but additives and bases were indispensable for this transformation. All this encourages us to develop more efficient, highly regioselective, operationally simple, and general allylation protocols.

In recent years, economical, environmentally benign, and green chemistry[23,24] has prevailed in modern organic chemistry, and this gives rise to developments of various heterogeneous catalytic transformations. These novel methodologies make the synthetic process safe, clean, efficient, and inexpensive. The purification process can be simplified, and the employment of toxic organic solvents is always decreased. Amberlyst-15 has been emerged as an efficient heterogeneous catalyst because many organic reactions[25–30] can been catalyzed or promoted by this powerful ion-exchange resin. It is a cheap and nonhazardous solid acid catalyst and can be easily handled and removed from the reaction mixtures by simple filtration. The recovered catalyst can be recycled consecutively several times without an obvious decrease of catalytic efficiency. In this contribution, we describe an efficient allylation of indoles and amides using Amberlyst-15 as heterogeneous catalyst in a recyclable manner.

RESULTS AND DISCUSSION

As an extension of our previous work, various reaction conditions were initially screened in both organic and aqueous media, and the results are summarized in Table 1. The experimental data indicated that in organic solvents this Amberlyst-15-catalyzed allylation could be achieved to exclusively give the desired product of 3-allylated indole without any by-products (entries 1–4). However, trace yield was afforded in pure water at room temperature (entry 5). To our delight, acetonitrile was found to be the best solvent in which indole could be mildly transformed into an allylated product with an isolated chemical yield of 86% at room temperature

Table 1. Amberlyst-15-catalyzed allylation of indole in different solvents

Entry	Solvent	Temperature	Yield[a] (%)
1	CH_2Cl_2	Rt	72
2	CH_2Cl_2	Reflux	69
3	CH_3CN	Rt	86
4	THF	Rt	61
5	Water	Rt	Trace

[a]Isolated yield.

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by utilizing catalytic Amberlyst-15 (30 mg/1 mmol). See Fig. 1. As for the regioselectivity, no N-allylated or bisallylated[10,13,14] by-products were observed (entry 3).

Encouraged by these results, we then reacted various indoles with allylic acetates to explore the generality of this protocol under the optimized conditions. As shown in Table 2 and Fig. 2, various indoles could be transformed to produce good yields and good purity of the desired products after flash chromatograph or simple filtration without further purifications (entries 1–7 and 9). However, 5-methoxy indole and 7-azaindole were not reactive in the model reaction (entries 8 and 11). 2-Methyl furan could also be converted into the corresponding product in good yield (81%, entry 10). All products are characterized by NMR, infrared (IR), and mass spectrometry.

To further extend the substrate scope for this catalytic approach, other nucleophiles besides indoles, such as sulfonamides, carbamates, and carboxamides, were also employed to explore the generality (Table 3 and Fig. 3). Under the optimized conditions, these N-nucleophiles could be easily transformed into desired C-N linked allylated products in excellent yields (entries 1–5), except that because low nucleophilicity resulted from a strong electron-withdrawing functional group, 4-nitrobenzenesulfonamide showed decreased reactivity to giving product in a reasonable yield (entry 6). To the best of our knowledge, this is the first report that C- and N-nucleophiles could be readily converted into corresponding allylated products just with catalytic Amberlyst-15 under solid-acid and heterogeneous catalysis, in which involvement of metals, additives, and complex conditions were avoided.[22]

With these satisfactory results, we next investigated recyclable allylation by simply recycling and reusing the catalyst Amberlyst-15. Four indoles were employed in a four-cycle allylation reaction, and excellent yields were observed without any obvious decrease of catalytic efficiency (Table 4 and Figs. 4 and 5), which further proved high efficacy of this catalytic strategy. The allylation could be achieved with acceptable yields to afford the corresponding products after Amberlyst-15 were reused up to seven cycles within 12 hours, which indicated the availability to perform this transformation in such an efficient and recyclable manner.

Considering the simplicity, this heterogeneous catalytic strategy might be easily applied to parallel (multichannel) synthetic chemistry with high through-put of allylated products in a readily operational way. The product can be isolated with common filtration, and recovered Amberlyst-15 can be used for a couple of cycles. Because efficient, high-yielding, environmentally benign, and catalyst-recyclable syntheses are of great importance for both academic and industrial organic synthesis, our protocol would give possible access to the rapid and efficient allylation of indoles

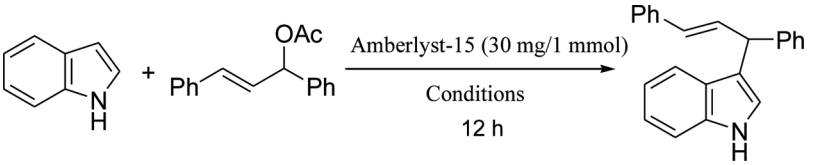

Figure 1. Screening of reaction conditions of Amberlyst-15–catalyzed allylation of indole.

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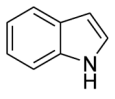
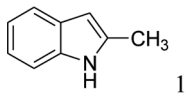
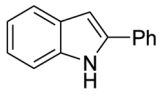
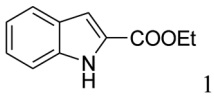
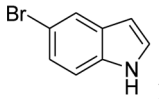
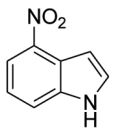
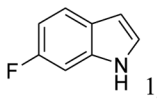
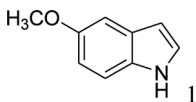
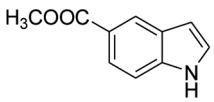
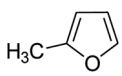
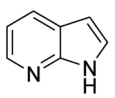
Table 2. Allylation of indoles catalyzed by Amberlyst-15

Entry	Indole	Time (h)	Product	Yield[a] (%)
1	 1a	12	3a	86
2	 1b	10	3b	98
3	 1c	8	3c	97
4	 1d	8	3d	89
5	 1e	10	3e	98
6	 1f	8	3f	97
7	 1g	10	3g	91
8	 1h	12	3h	Trace
9	 1i	8	3i	98
10	 1j	8	3j	81
11	 1k	15	—	Nr[b]

[a]Isolated yield.
[b]Nr = no reaction.

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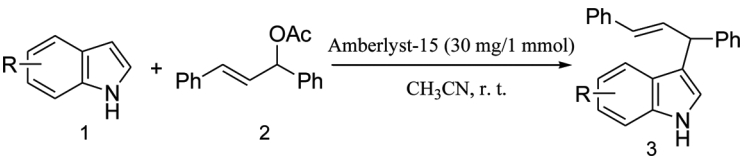

Figure 2. Broad scope of Amberlyst-15–catalyzed allylation of indoles.

and amides, as well as other suitable electrophiles in heterogeneous catalytic synthetic chemistry.

CONCLUSION

In summary, a mild, efficient and regioselective allylation of indoles and amides has been described in this contribution, which were accomplished in the presence of commercially available solid-acid catalyst Amberlyst-15 in a heterogeneous catalytic system and the catalyst could be reused for seven times without obvious diminished efficiency. Applications of this practical protocol to the synthesis of functional complex molecules are being investigated in our laboratory.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Brucker 300 (300-MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) from tetramethylsilane (TMS) with solvent resonance as the internal standard (deuterochloroform: $\delta = 7.27$ ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Brucker 300 (75-MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: $\delta = 77.0$ ppm). Electron impact (EI) and high-resolution mass spectrometry (HRMS) were performed on GCT-MS Micromass UK. Infrared (IR) analyses were obtained with a Brucker Fourier transform (FT)–IR spectrophotometer. IR spectra are expressed by wavenumber (cm^{-1}). Elemental analyses were carried out using a Flash EA 1112 analyzer. Melting points were uncorrected. Chromatographic purification was done with 200- to 300-mesh silica gel, eluting with ethyl acetate and petroleum ether. Thin-layer chromatography (TLC) was performed on glass-backed silica plates precoated with silica. The dispatched reaction components were then visualized under ultraviolet light to be separated.

Representative Procedure for the Preparation of 3-Allylated Indoles

Indole **1a** (117 mg, 1 mmol) and 1,3-diphenylprop-2-enyl acetate **2** (252 mg, 1 mmol) were added into a flask at room temperature. Acetonitrile (8 ml) was then poured, and the resulting mixture was vigorously stirred. Amberlyst-15 (30 mg) was added, and the mixture was stirred for 12 h, monitored by TLC. After the

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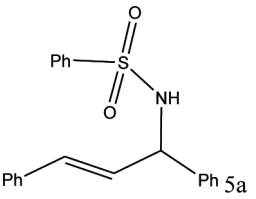
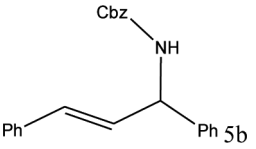
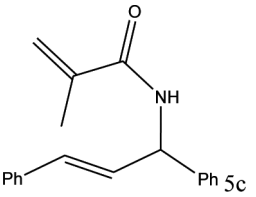
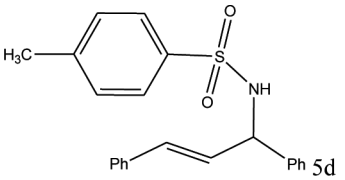
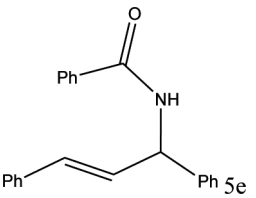
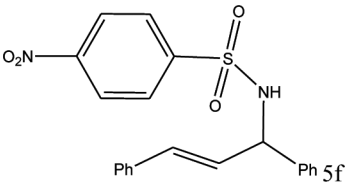
Table 3. Allylation of N-nucleophiles catalyzed by Amberlyst-15

Entry	N-Nuclephile	Time (h)	Product	Yield[a] (%)
1	$PhSO_2NH_2$(4a)	24	 5a	91
2	$CbzNH_2$(4b)	18	 5b	97
3	Methacrylamide(4c)	20	 5c	81
4	p-Toluenesulfonamide(4d)	20	 5d	90
5	$PhCONH_2$(4e)	16	 5e	93
6	4-Nitrobenzenesulfonamide(4f)	16	 5f	34

[a]Isolated yield.

completion of reactions, the solvent was evaporated and the clean product was afforded after simple flash chromatography (266 mg, 86%). The spectral (NMR and MS) and analytical data of the unknown compounds are given. The spectral

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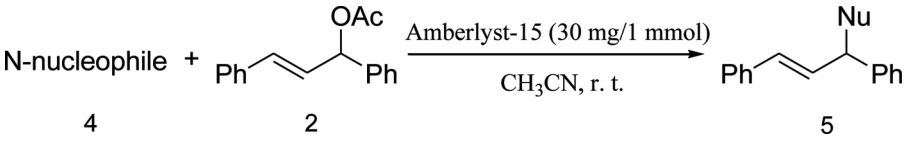


Figure 3. Amberlyst-15–catalyzed allylation of various N-nucleophiles.

properties of the remaining known compounds matched well with and can be referred to those reported earlier.

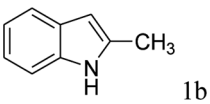
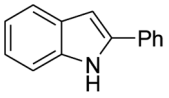
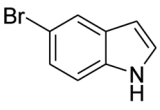
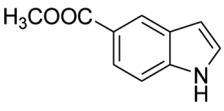
Ethyl 3-[(E)-1,3-Diphenyl-allyl]-*1H*-indole-2-carboxylate (3d)

White solid. Mp 60–62 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.42$ (t, $J = 7.1$ Hz, 3H), 4.42 (q, $J = 5.3$ Hz, 2H), 6.14 (d, $J = 7.4$ Hz, 1H), 6.49 (d, $J = 15.9$ Hz, 1H), 6.89 (m, $J = 15.9$ Hz, 1H), 6.95–7.53 (m, 14H), 8.83 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.5$, 44.6, 60.9, 111.9, 120.2, 122.9, 123.4, 125.0, 125.4, 126.2, 126.3, 126.9, 127.2, 128.2, 128.2, 128.5, 131.5, 131.6, 136.2, 137.4, 143.2, 162.2. IR (film): 3422, 3058, 3027, 1692, 1246, 968, 746, 697 cm^{-1}. HRMS (EI): m/z calcd. for $C_{26}H_{23}NO_2$: 381.1729; found: 381.1730. Elemental analylsis: calcd for $C_{26}H_{23}NO_2$: C, 81.86; H, 6.08; N, 3.67. Found: C, 81.19; H, 6.21; N, 3.67.

3-[(E)-1,3-Diphenyl-allyl]-6-fluoro-*1H*-indole (3g)

Green oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.04$ (d, $J = 7.2$ Hz, 1H), 6.4 (d, $J = 15.8$ Hz, 1H), 6.67 (m, $J = 15.8$ Hz, 1H), 6.76–7.34 (m, 14H), 7.74 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 46.3$, 97.3, 97.7, 108.1, 108.5, 118.9, 120.6, 120.7,

Table 4. Recyclable allylation of indoles catalyzed by Amberlyst-15

Entry	Indole	Product	Yield[a] (%) (Cycles 1, 2, 3, 4, 7)
1	 1b	3b	98, 97, 93, 91, 83
2	 1c	3c	97, 97, 96, 94, 79
3	 1e	3e	98, 97, 97, 95, 82
4	 1i	3i	98, 96, 92, 91, 80

[a]Isolated yield.

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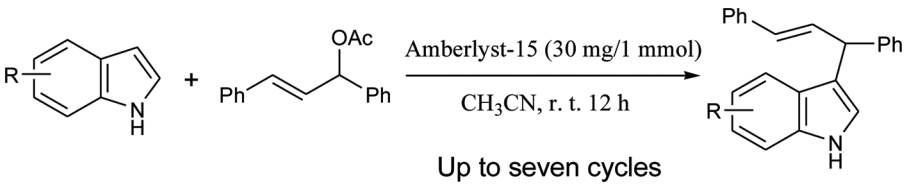

Figure 4. Amberlyst-15–catalyzed allylation of indoles in a recyclable manner.

122.9, 123.0, 123.5, 126.4, 126.6, 127.4, 128.5, 128.6, 128.6, 130.8, 132.4, 136.6, 136.7, 137.5, 143.2, 158.5, 161.6. IR ($CDCl_3$): 3430, 3059, 3025, 1625, 1138, 967, 745, 699 cm^{-1}. HRMS (EI): m/z calcd. for $C_{23}H_{18}FN$: 327.1423; found: 327.1413.

Methyl 3-[(E)-1,3-Diphenyl-allyl]-*1H*-indole-5-carboxylate (3i)

Yellow powder. Mp 125–127 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.85$ (s, 3H), 5.14 (d, $J = 7.1$ Hz, 1H), 6.39 (d, $J = 15.8$ Hz, 1H), 6.69 (m, $J = 15.8$ Hz, 1H), 6.91 (d, $J = 1.5$ Hz, 1H), 7.15–8.21 (m, 13H), 8.37 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 45.8$, 51.9, 110.9, 120.1, 121.5, 122.7, 123.6, 124.1, 126.4, 126.5, 126.6, 127.3, 128.5, 128.5, 130.9, 132.3, 137.4, 139.3, 143.1. IR (film): 3419, 3026, 1694, 1110, 970, 750, 699 cm^{-1}. HRMS (EI): m/z calcd. for $C_{25}H_{21}NO_2$: 367.1572; found: 367.1577. Elemental analylsis: calcd. for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.11; H, 6.00; N, 3.72.

2-[(E)-1,3-Diphenyl-allyl]-2-methyl-furan (3j)

Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.34$ (s, 3H), 4.93 (d, $J = 7.3$ Hz, 1H), 5.98 (d, $J = 2.1$ Hz, 1H), 6.05 (d, $J = 2.1$ Hz, 1H), 6.48 (d, $J = 15.9$ Hz, 1H), 6.65

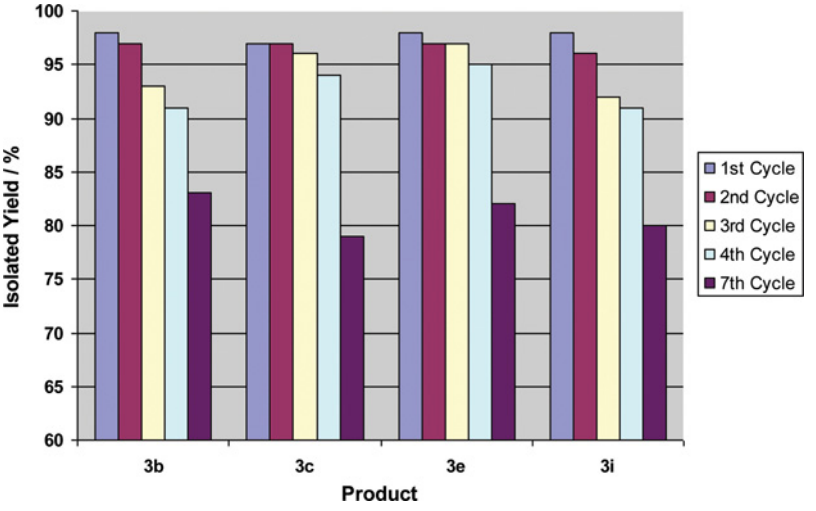

Figure 5. Efficient allylation in the presence of Amberlyst-15 in a recyclable manner. (Figure is provided in color online.)

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(m, $J = 15.9$ Hz, 1H), 7.28–7.46 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.7$, 48.5, 106.1, 107.6, 126.5, 126.8, 127.5, 128.4, 128.6, 128.6, 130.2, 131.4, 137.2, 141.5, 151.5, 154.3. IR ($CDCl_3$): 3059, 3027, 1599, 1218, 965, 745, 697 cm^{-1}. HRMS (EI): m/z calcd. for $C_{20}H_{18}O$: 274.1400; found: 274.1355.

N-[(E)-1,3-Diphenyl-allyl]-methacrylamide (5c)

Pale yellow solid. Mp 119–121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.96$ (s, 3H), 5.33 (s, 1H), 5.73 (s, 1H), 5.84 (t, $J = 7.1$ Hz, 1H), 6.35 (m, $J = 15.9$ Hz, 1H), 6.42 (d, $J = 7.9$ Hz, 1H), 6.52 (d, $J = 15.9$ Hz, 1H), 7.18–7.35 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.8$, 54.9, 119.8, 126.6, 127.2, 127.7, 127.8, 128.6, 128.8, 128.9, 131.7, 136.5, 140.1, 140.9, 167.5. IR ($CDCl_3$): 3304, 3060, 3028, 1654, 1616, 1522, 1210, 967, 746, 696 cm^{-1}. HRMS (EI): m/z calcd. for $C_{19}H_{19}NO$: 277.1467; found: 277.1469.

N-[(E)-1,3-Diphenyl-allyl]-4-nitro-phenylsulfonamide (5f)

White solid. Mp 169–171 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.19$–5.29 (m, 2H), 6.08 (m, $J = 15.9$ Hz, 1H), 6.41 (d, $J = 15.9$ Hz, 1H), 7.16–7.27 (m, 10H), 7.85 (d, $J = 8.7$ Hz, 2H), 8.10 (d, $J = 8.7$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 60.3$, 123.9, 126.5, 127.1, 127.3, 128.3, 128.4, 128.7, 128.9, 133.1, 135.5, 138.7, 146.7. IR ($CDCl_3$): 3278, 1528, 1344, 1157, 736, 695 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{21}H_{18}N_2O_4S$: 394.1000; found: 393.0915 ($M^+ - H$).

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