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Quinolines from Morita–Baylis–Hillman acetates of 2-azidobenzaldehydes

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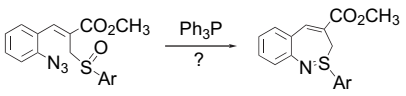
ABSTRACT

A simple method for synthesizing several 2-alkoxy-3-arylsulfinylmethylquinolines using an aza-Wittig type reaction of 3-(2-azidophenyl)-2-(arylsulfinylmethyl)propenoates, which were readily obtained from the Morita–Baylis–Hillman acetates of 2-azidobenzaldehydes, has been developed.

1. Introduction

The Morita–Baylis–Hillman reaction is a versatile carbon–carbon bond forming reaction, which provides multi functionalized adducts, α-methylene-β-hydroxy carbonyl compounds.[1] These adducts and their derivatives have widely been explored for the nucleophilic displacement with various nucleophiles[2] including sulfur nucleophiles.[3] Recently, the cyclization of 3-(aryliminophosphoranyl)-4-sulfoxyarylisoxazoles via an intramolecular aza-Wittig type reaction resulted in the formation of cyclic sulfimides (N=S), giving the isoxazolo[4,3-*c*][2,1]benzothiazine.[4] In a continuation studies in the area of the Morita–Baylis–Hillman chemistry,[5] we desired to have the sulfoxy group at the allylic position of 3-(2-azidophenyl)-2-propenoates. In principle, the latter might be extended further toward the building of 2,1-benzothiazepine derivatives via an intramolecular aza-Wittig reaction as shown in Scheme 1.



Scheme 1.

Herein, we describe the synthesis of allyl sulfoxides from the Morita–Baylis–Hillman acetates of 2-azidobenzaldehydes and their conversion to the unexpected quinoline derivatives involving an intramolecular aza-Wittig type ring closure process between an ester carbonyl and an iminophosphorane.

2. Results and discussion

The readily available Morita–Baylis–Hillman acetates **4**[6] provide a convenient starting point for the synthesis of allyl sulfoxides **7**. Treatment of the acetates **4** with benzenethiols **5** in the presence of triethylamine in dichloromethane at room temperature gave the allyl aryl sulfides **6** solely with (*Z*)-stereoselectivity in good to excellent yields as shown in Table 1. The stereochemistry of the

Table 1
Preparation of sulfides **6**, sulfoxides **7**, and quinolines **10**

Entry	**6** (Yield/time)	**7** (Yield/time)	**10** (Yield/time)
1	**6a** (89%/15 min)	**7a** (81%/10 min)	**10a** (73%/1 h 50 min)
2	**6b** (79%/20 min)	**7b** (79%/20 min)	**10b** (84%/2 h)
3	**6c** (85%/10 min)	**7c** (82%/20 min)	**10c** (73%/1 h 40 min)
4	**6d** (65%/10 min)	**7d** (82%/30 min)	**10d** (61%/2 h 30 min)
5	**6e** (73%/15 min)	**7e** (75%/10 min)	**10e** (85%/3 h)
6	**6f** (66%/20 min)	**7f** (93%/15 min)	**10f** (62%/2 h)
7	**6g** (69%/10 min)	**7g** (99%/5 min)	**10g** (69%/1 h 30 min)
8	**6h** (67%/10 min)	**7h** (93%/5 min)	**10h** (73%/1 h 10 min)
9	**6i** (78%/10 min)	**7i** (86%/5 min)	**10i** (78%/2 h)
10	**6j** (67%/10 min)	**7j** (77%/5 min)	**10j** (81%/2 h)
11	**6k** (71%/20 min)	**7k** (75%/10 min)	**10k** (62%/1 h 40 min)
12	**6l** (96%/10 min)	**7l** (72%/5 min)	**10l** (61%/2 h 20 min)
13	**6m** (80%/10 min)	**7m** (79%/5 min)	**10m** (75%/3 h)
14	**6n**(70%/10 min)	**7n** (72%/10 min)	**10n** (64%/2 h)

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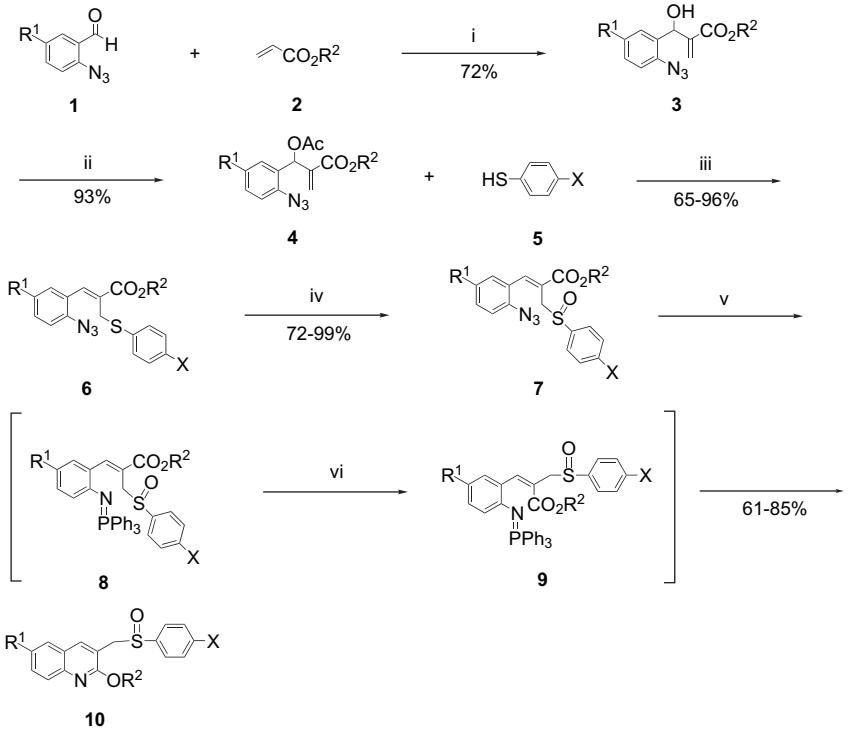
products was established by comparing ^{1}H NMR values of olefinic proton (δ 7.54–7.74) with literature values of similar compounds.[7] It is reported that β-vinylic proton cis and trans to the ester group appears at ca. δ 7.50–7.90 and 6.50–6.85, respectively. Oxidation of the sulfides **3** with 1 equiv of *m*-chloroperoxybenzoic acid in dichloromethane at 0 °C gave allyl aryl sulfoxides **7** in high yields (Table 1). Again, the (*Z*)-stereochemistry of the sulfoxides **7** was determined by comparing ^{1}H NMR values of vinylic proton, which appeared at δ 7.93–8.07.

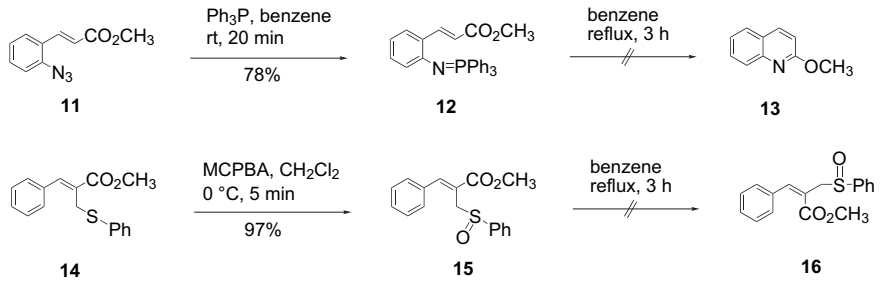
The Staudinger reaction between methyl 3-(2-azidophenyl)-2-(phenylsulfinylmethyl)propenoate (**7a**) and triphenylphosphine in anhydrous benzene at room temperature for 30 min gave the corresponding iminophosphorane **8a** in 85% yield. Treatment of iminophosphorane **8a** in benzene at reflux for 1.5 h gave, after column chromatography, 90% yield of 2-methoxy-3-phenylsulfinylmethylquinoline (**10a**) together with triphenylphosphine oxide (90%). The possible expected seven-membered ring closure product 2,1-benzothiazepine was not produced at all. Only product resulting from cyclization at the ester carbonyl function was formed. In situ generation of iminophosphoranes **8** and subsequent aza-Wittig type ring closure of other 3-(2-azidophenyl)-2-(phenylsulfinylmethyl)-propenoates **7** were successful giving the corresponding quinoline derivatives **7** in 61–85% yields (Scheme 2, Table 1).

In the literature, the phosphorous–nitrogen bond of the ethyl 3-(2-triphenylphosphoranylidenaminocyclopent-1-enyl)propenoate being strongly polarized, a negative charge located on α-carbon of ester group enables cyclization via the cis isomer has been noted.[8] Also, it was reported that triethyl phosphite reacts with methyl 2-azidocinnamate to give phosphorimidate, which can be cyclized photolytically (not thermally) to 2-methoxyquinoline via the *E*/*Z* isomerization.[9] In order to explain for the transformation of **7** into **10** more accurately we examined two additional experiments as shown in Scheme 3. First, we synthesized methyl 2-(triphenylphosphoranylidenamino)cinnamate (**12**) from the reaction of known methyl 2-azidocinnamate (**11**)[9] with triphenylphosphine in benzene at room temperature. Attempted cyclization of the iminophosphorane **12** was unsuccessful in refluxing benzene for 3 h, only unchanged iminophosphorane **12** was recovered quantitatively.



1	R^1	**2**	R^2	**3**, **4**	R^1	R^2	**5**	X	**6**, **7**, **8**, **10**	R^1	R^2	X
a	H	**a**	Me	**a**	H	Me	**a**	H	**a**	H	Me	H
b	Cl	**b**	Et	**b**	Cl	Me	**b**	Cl	**b**	Cl	Me	H
c	NO_2	**c**	Bu	**c**	NO_2	Me	**c**	Me	**c**	NO_2	Me	H
d	MeO			**d**	MeO	Me			**d**	MeO	Me	H
				e	H	Et			**e**	H	Me	Cl
				f	H	Bu			**f**	Cl	Me	Cl
									g	NO_2	Me	Cl
									h	MeO	Me	Cl
									i	H	Me	Me
									j	Cl	Me	Me
									k	NO_2	Me	Me
									l	MeO	Me	Me
									m	H	Et	H
									n	H	Bu	H

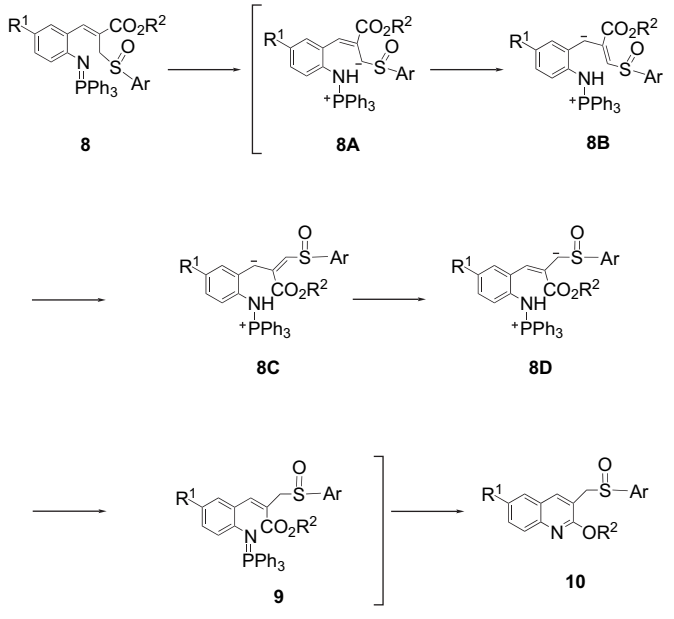
Scheme 2. Reagents and conditions: (i) DABCO, $N(CH_2CH_2OH)_3$, neat, rt, 24 h; (ii) Ac_2O, DMAP, CH_2Cl_2, rt, 5 min; (iii) Et_3N, CH_2Cl_2, rt, 10–20 min; (iv) MCPBA, CH_2Cl_2, 0 °C, 5–30 min; (v) Ph_3P, benzene, rt, 30 min; (vi) benzene, reflux, 1–3 h.



Scheme 3.

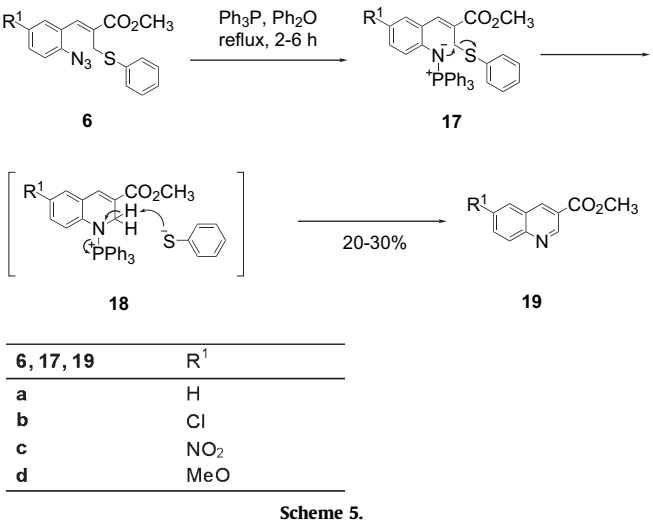
Second, we prepared (*Z*)-methyl 3-phenyl-2-(phenylsulfinylmethyl)propenoate (**15**) from the reaction of known (*Z*)-methyl 3-phenyl-2-(phenylthiomethyl)propenoate (**14**)[7c] with *m*-chloroperoxybenzoic acid. Attempted *E*/*Z* isomerization of **15** was unsuccessful in refluxing benzene for 3 h. Again, unchanged allyl sulfoxide **15** was recovered quantitatively. These observations gave us direct information that an iminophosphorane **12** or an allyl sulfoxide **15** each alone could not isomerize thermally.

The proposed mechanism for the transformation of **7** into **10** is shown in Scheme 4 based on additional experimental results. Although the isolation of (*E*)-iminophosphorane **9** was unsuccessful under reaction conditions, we recognize that the mechanistic sequence may involve an abstraction of acidic α-hydrogen of sulfoxide by the nitrogen anion of (*Z*)-iminophosphorane **8** to give several zwitter ionic intermediates (**8A**–**8D**). Thus, the formula **8B** corresponding to a negative charge located on C-3 enables rotation about C-2 and C-3 bond, and subsequent proton migration through the zwitter ionic intermediates to give (*E*)-iminophosphorane **9**, followed by aza-Wittig reaction at ester carbonyl group to produce quinoline **10**.



Scheme 4.

Attempts to prepare arylthiomethyl-substituted quinolines using azidosulfides **6** with triphenylphosphine by the present protocol led only to the formation of iminophosphoranes **17** in refluxing benzene, toluene or xylene. However, in refluxing diphenyl ether only 3-carbomethoxyquinolines **19** were produced in poor yields (20–30%).[10] This product presumably arose by initial nucleophilic displacement of thiophenoxide by nitrogen anion followed by proton abstraction by thiophenoxide and subsequent extrusion of triphenylphosphine (Scheme 5). Obviously *E*/*Z* isomerization of iminophosphoranes **17** did not occur because of decrease of acidity of the α-hydrogen of sulfenyl group. So, aza-Wittig reaction could not proceed.



6, 17, 19	R^1
a	H
b	Cl
c	NO_2
d	MeO

Scheme 5.

Quinolines and their derivatives occur in numerous natural products,[11] and display interesting physiological activities and have found attractive applications as pharmaceuticals and agrochemicals.[12] Many synthetic methods have been developed for the preparation of quinolines,[13] but the synthetic methods of 3-arylsulfinylmethylquinolines are rare.[14]

3. Conclusions

In summary, we have prepared several 2-alkoxyquinoline derivatives having an arylsulfinylmethyl group via an intramolecular aza-Wittig type reaction of 3-(2-azidophenyl)-2-(phenylsulfinylmethyl)propenoates, which were readily obtained from the Morita–Baylis–Hillman acetates of 2-azidobenzaldehydes.

4. Experimental

4.1. Synthesis general

The melting points were measured on an Electrothermal melting point apparatus and are uncorrected. TLC analyses were carried out on Merck silica gel $60F_{254}$ and spots were visualized under UV light. Chromatography on silica gel was carried out on Merck silica (70–230 mesh ASTM). IR spectra were determined on a Nicolet Magna 550 FTIR spectrometer using KBr discs. The ^{1}H NMR spectra were recorded on a Varian 300 spectrometer in $CDCl_3$ at 300 MHz. All

chemical shifts are given in parts per million (ppm) using δ_H Me_4Si=0 ppm as reference and J values are given in hertz. The ^{13}C NMR spectra were run in the same instrument at 75.4 MHz using the solvent peak as internal reference. The ^{31}P NMR spectra were measured in the same instrument at 121 MHz using $(PhO)_3PO$=0 as reference. Low resolution mass spectra were recorded on a ThermoQuest Polaris Q mass spectrometer operating at 70 eV. Elemental analyses were carried out on a Thermo Electron Corporation Flash EA 1112 instrument. The known Morita–Baylis–Hillman acetates, methyl 3-acetoxy-3-(2-azidophenyl)-2-methylenepropanoates **4a**–**4d**,[6] ethyl 3-acetoxy-3-(2-azidophenyl)-2-methylenepropanoate (**4e**),[6] methyl 2-azidocinnamate (**11**),[9] and (*Z*)-methyl 3-phenyl-2-(phenylthiomethyl)propenoate (**14**)[7c] were prepared according to the reported procedures.

4.2. Synthesis of Morita–Baylis–Hillman adduct: butyl 3-(2-azidophenyl)-3-hydroxy-2-methylenepropanoate (3f)

A mixture of 2-azidobenzaldehyde **1a** (1.47 g, 10 mmol), butyl acrylate **2c** (3.84 g, 30 mmol), DABCO (1.23 g, 10 mmol), and triethanolamine (1.19 g, 8 mmol) without solvent was stirred at room temperature for 30 h. The reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (3×10 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated in vacuo. The resulting mixture was chromatographed on silica gel eluting with hexane and ethyl acetate (4:1) to produce 1.98 g (72%) of **3f** as a yellow oil; IR (neat) 3388, 2128, 1722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, J=7.4 Hz, 3H, CH_3), 1.27–1.39 (m, 2H, CH_2), 1.56–1.65 (m, 2H, CH_2), 3.32 (d, J=5.5 Hz, 1H, OH), 4.13 (m, 2H, CH_2), 5.70 (s, 1H, CH), 5.81 (d, J=5.5 Hz, 1H, CH), 6.33 (s, 1H, CH), 7.12–7.17 (m, 2H, aromatic), 7.31–7.37 (m, 1H, aromatic), 7.43–7.46 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 13.6, 19.1, 30.5, 64.9, 67.9, 118.0, 125.0, 126.2, 128.0, 129.1, 132.0, 137.3, 141.2, 166.5; EIMS: *m*/*z* (%) 247 (12), 218 (17), 174 (5), 162 (15), 146 (17), 118 (100). Anal. Calcd for $C_{14}H_{17}N_3O_3$: C, 61.08; H, 6.22; N, 15.26. Found: C, 60.85; H, 6.03; N, 15.07.

4.3. Synthesis of Morita–Baylis–Hillman acetate: butyl 3-acetoxy-3-(2-azidophenyl)-2-methylenepropanoate (4f)

Acetic anhydride (1.22 g, 7.5 mmol) was added to a stirred solution of **3f** (1.38 g, 5 mmol) and DMAP (0.12 g, 1 mmol) in 15 mL of dichloromethane at room temperature. After stirring for 5 min, the mixture was neutralized with 10% aqueous $NaHCO_3$ solution and extracted with dichloromethane (3×10 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography with silica gel by elution with hexane and ethyl acetate (4:1) to produce 1.48 g (93%) of **4f** as a yellow oil; IR (neat) 2128, 1746, 1723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J=7.3 Hz, 3H, CH_3), 1.24–1.36 (m, 2H, CH_2), 1.54–1.63 (m, 2H, CH_2), 2.11 (s, 3H, CH_3), 4.13 (t, J=6.6 Hz, 2H, CH_2), 5.63 (s, 1H, CH), 6.44 (s, 1H, CH), 6.91 (s, 1H, CH), 7.11–7.19 (m, 2H, aromatic), 7.27–7.40 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 13.6, 19.0, 20.9, 30.5, 64.9, 68.2, 118.3, 124.7, 127.1, 128.3, 128.8, 129.7, 138.1, 138.8, 165.0, 169.2; EIMS: *m*/*z* (%) 289 (1), 229 (14), 173 (100), 156 (53), 146 (60), 128 (60), 118 (39). Anal. Calcd for $C_{16}H_{19}N_3O_4$: C, 60.56; H, 6.03; N, 13.24. Found: C, 60.39; H, 5.85; N, 13.07.

4.4. General procedure for the synthesis of alkyl 3-(2-azidophenyl)-2-(arylthiomethyl)propenoates 6

An aryl thiol **5** (2.2 mmol) and Et_3N (2.4 mmol) were added to a well-stirred solution of Morita–Baylis–Hillman acetates **4** (2 mmol) in 5 mL of dichloromethane at room temperature. After stirring for 10–20 min, the mixture was diluted with 5 mL of water and extracted with dichloromethane (2×20 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was subjected to column chromatography with silica gel by elution with hexane and ethyl acetate (10:1). The fractions containing the pure compound were combined and evaporated under reduced pressure to afford **6**.

*4.4.1. (Z)-Methyl 3-(2-azidophenyl)-2-(phenylthiomethyl)propenoate (**6a**).* Reaction time: 15 min; yield: 89%; yellow oil; IR (neat) 2127, 2094, 1716 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.83 (s, 3H, CH_3), 3.93 (s, 2H, CH_2), 7.04–7.41 (m, 9H, aromatic), 7.72 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 32.4, 52.3, 118.2, 124.6, 126.3, 126.8, 128.7, 129.7, 130.0, 130.1, 131.3, 135.3, 136.5, 138.9, 167.2; EIMS: *m*/*z* (%) 297 (15), 188 (100), 156 (56), 128 (34). Anal. Calcd for $C_{17}H_{15}N_3O_2S$: C, 62.75; H, 4.65; N, 12.91. Found: C, 62.58; H, 4.88; N, 12.70.

*4.4.2. (Z)-Methyl 3-(2-azido-5-chlorophenyl)-2-(phenylthiomethyl)-propenoate (**6b**).* Reaction time: 20 min; yield: 79%; light yellow solid: mp 72–73 °C (hexane–EtOAc); IR (KBr) 2130, 2092, 1711 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.84 (s, 3H, CH_3), 3.88 (s, 2H, CH_2), 7.02 (d, J=8.2 Hz, 1H, aromatic), 7.21–7.37 (m, 8H, aromatic), 7.58 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 32.8, 52.4, 119.4, 127.3, 127.7, 128.8, 129.7, 129.8, 129.9, 131.0, 132.4, 134.6, 134.7, 137.3, 166.9; EIMS: *m*/*z* (%) 333 (5), 331 (14), 224 (33), 222 (100), 192 (27), 190 (63). Anal. Calcd for $C_{17}H_{14}ClN_3O_2S$: C, 56.74; H, 3.92; N, 11.68. Found: C, 56.53; H, 3.78; N, 11.42.

*4.4.3. (Z)-Methyl 3-(2-azido-5-nitrophenyl)-2-(phenylthiomethyl)-propenoate (**6c**).* Reaction time: 10 min; yield: 85%; yellow solid: mp 74–75 °C (hexane–EtOAc); IR (KBr) 2129, 2090, 1707, 1515, 1342 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.87 (s, 3H, CH_3), 3.90 (s, 2H, CH_2), 7.17–7.22 (m, 4H, aromatic), 7.33–7.36 (m, 2H, aromatic), 7.58 (s, 1H, CH), 8.17–8.26 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 32.9, 52.6, 118.6, 125.0, 125.5, 127.1, 127.5, 128.8, 132.2, 132.9, 133.5, 134.1, 144.1, 145.1, 166.6; EIMS: *m*/*z* (%) 342 (12), 233 (100), 201 (53), 173 (19). Anal. Calcd for $C_{17}H_{14}N_4O_4S$: C, 55.13; H, 3.81; N, 15.13. Found: C, 55.02; H, 3.63; N, 14.98.

*4.4.4. (Z)-Methyl 3-(2-azido-5-methoxyphenyl)-2-(phenylthiomethyl)-propenoate (**6d**).* Reaction time: 10 min; yield: 65%; yellow solid: mp 89–90 °C (hexane–EtOAc); IR (KBr) 2127, 2094, 1719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.71 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 3.98 (s, 2H, CH_2), 6.90–6.94 (m, 1H, aromatic), 7.04–7.34 (m, 7H, aromatic), 7.74 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 32.3, 52.4, 55.6, 114.4, 116.8, 119.3, 126.6, 127.1, 128.8, 129.4, 130.6, 131.3, 135.5, 136.7, 156.4, 167.1; EIMS: *m*/*z* (%) 327 (13), 218 (100), 186 (67). Anal. Calcd for $C_{18}H_{17}N_3O_3S$: C, 60.83; H, 4.82; N, 11.82. Found: C, 60.64; H, 4.64; N, 11.63.

*4.4.5. (Z)-Methyl 3-(2-azidophenyl)-2-[(4-chlorophenyl)thiomethyl]-propenoate (**6e**).* Reaction time: 15 min; yield: 73%; yellow oil; IR (neat) 2127, 2093, 1716 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.84 (s, 3H, CH_3), 3.91 (s, 2H, CH_2), 7.07–7.39 (m, 8H, aromatic), 7.70 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 32.6, 52.4, 118.3, 124.5, 126.2, 128.8, 129.5, 129.9, 130.1, 133.0, 133.1, 133.6, 136.6, 138.8, 167.1; EIMS: *m*/*z* (%) 333 (3), 331 (7), 188 (100), 156 (61). Anal. Calcd for $C_{17}H_{14}ClN_3O_2S$: C, 56.74; H, 3.92; N, 11.68. Found: C, 56.52; H, 3.73; N, 11.43.

*4.4.6. (Z)-Methyl 3-(2-azido-5-chlorophenyl)-2-[(4-chlorophenyl)-thiomethyl]propenoate (**6f**).* Reaction time: 20 min; yield: 66%; yellow solid: mp 69–70 °C (hexane–EtOAc); IR (KBr) 2123, 2081, 1712 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.85 (s, 3H, CH_3), 3.87 (s, 2H, CH_2), 7.04 (d, J=8.5 Hz, 1H, aromatic), 7.15–7.19 (m, 2H, aromatic), 7.23 (d, J=2.5 Hz, 1H, aromatic), 7.25–7.28 (m, 2H, aromatic), 7.32 (dd, J=8.5 and 2.5 Hz, 1H, aromatic), 7.58 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 33.0, 52.5, 119.4, 127.6, 129.0, 129.6, 129.9 (two), 130.8, 133.0, 133.7, 133.9,

134.9, 137.4, 166.8; EIMS: *m*/*z* (%) 367 (7), 365 (10), 224 (34), 222 (100), 192 (28), 190 (61). Anal. Calcd for $C_{17}H_{13}Cl_2N_3O_2S$: C, 51.79; H, 3.32; N, 10.66. Found: C, 51.54; H, 3.15; N, 10.72.

*4.4.7. (Z)-Methyl 3-(2-azido-5-nitrophenyl)-2-[(4-chlorophenyl)-thiomethyl]propenoate (**6g**).* Reaction time: 10 min; yield: 69%; light yellow solid:mp 114–115 °C (hexane–EtOAc); IR (KBr) 2126, 2084, 1714, 1526, 1351 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.87 (s, 3H, CH_3), 3.91 (s, 2H, CH_2), 7.12–7.16 (m, 2H, aromatic), 7.22 (d, *J*=8.8 Hz, 1H, aromatic), 7.26–7.30 (m, 2H, aromatic), 7.60 (s, 1H, CH), 8.23 (dd, *J*=8.8 and 2.5 Hz, 1H, aromatic), 8.28 (d, *J*=2.5 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 33.1, 52.7, 118.6, 125.1, 125.4, 126.9, 128.9, 131.8, 132.6, 133.7, 133.9, 134.4, 144.0, 145.2, 166.5; EIMS: *m*/*z* (%) 378 (2), 376 (5), 233 (100), 201 (54). Anal. Calcd for $C_{17}H_{13}ClN_4O_4S$: C, 50.44; H, 3.24; N, 13.84. Found: C, 50.60; H, 3.02; N, 13.63.

*4.4.8. (Z)-Methyl 3-(2-azido-5-methoxyphenyl)-2-[(4-chlorophenyl)-thiomethyl]propenoate (**6h**).* Reaction time: 10 min; yield: 67%; light yellow solid: mp 66–67 °C (hexane–EtOAc); IR (KBr) 2120, 2090, 1704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.74 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 3.94 (s, 2H, CH_2), 6.90–6.97 (m, 2H, aromatic), 7.06 (d, *J*=8.5 Hz, 1H, aromatic), 7.14–7.26 (m, 4H, aromatic), 7.70 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 32.7, 52.4, 55.6, 114.6, 116.4, 119.4, 127.0, 128.9, 129.5, 131.3, 132.5, 133.0, 133.8, 136.7, 156.4, 167.0; EIMS: *m*/*z* (%) 363 (3), 361 (7), 218 (100), 186 (62). Anal. Calcd for $C_{18}H_{16}ClN_3O_3S$: C, 55.45; H, 4.14; N, 10.78. Found: C, 55.21; H, 4.36; N, 10.57.

*4.4.9. (Z)-Methyl 3-(2-azidophenyl)-2-(p-tolylthiomethyl)propenoate (**6i**).* Reaction time: 10 min; yield: 78%; yellow oil; IR (neat) 2126, 2093, 1716 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 3.89 (s, 2H, CH_2), 6.99–7.11 (m, 4H, aromatic), 7.20–7.26 (m, 2H, aromatic), 7.30–7.37 (m, 2H, aromatic), 7.69 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 21.1, 32.9, 52.3, 118.1, 124.5, 126.4, 129.5, 130.0 (two), 130.1, 131.5, 132.2, 136.2, 137.1, 138.8, 167.3; EIMS: *m*/*z* (%) 311 (16), 188 (100), 156 (65). Anal. Calcd for $C_{18}H_{17}N_3O_2S$: C, 63.70; H, 5.05; N, 12.38. Found: C, 63.48; H, 5.19; N, 12.15.

*4.4.10. (Z)-Methyl 3-(2-azido-5-chlorophenyl)-2-(p-tolylthiomethyl)-propenoate (**6j**).* Reaction time: 10 min; yield: 67%; light yellow solid: mp 65–66 °C (hexane–EtOAc); IR (KBr) 2129, 2093, 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.32 (s, 3H, CH_3), 3.82 (s, 2H, CH_2), 3.84 (s, 3H, CH_3), 6.99–7.04 (m, 3H, aromatic), 7.16–7.17 (m, 1H, aromatic), 7.24–7.30 (m, 3H, aromatic), 7.54 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 21.2, 33.3, 52.4, 119.3, 127.8, 129.7 (two), 129.8, 130.7, 131.3, 133.2, 134.4, 137.2, 137.7, 167.0; EIMS: *m*/*z* (%) 347 (6), 345 (18) 224 (33), 222 (100), 192 (29), 190 (67). Anal. Calcd for $C_{18}H_{16}ClN_3O_2S$: C, 57.83; H, 4.31; N, 11.24. Found: C, 57.64; H, 4.09; N, 11.10.

*4.4.11. (Z)-Methyl 3-(2-azido-5-nitrophenyl)-2-(p-tolylthiomethyl)-propenoate (**6k**).* Reaction time: 20 min; yield: 71%; yellow solid: mp 67–68 °C (hexane–EtOAc); IR (KBr) 2124, 2087, 1705, 1518, 1347 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.29 (s, 3H, CH_3), 3.85 (s, 2H, CH_2), 3.87 (s, 3H, CH_3), 6.97–7.00 (m, 2H, aromatic), 7.15–7.29 (m, 3H, aromatic), 7.55 (s, 1H, CH), 8.17–8.20 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.1, 33.3, 52.6, 118.4, 124.8, 125.5, 127.2, 129.6, 130.4, 132.4, 133.2, 133.5, 137.9, 144.1, 145.0, 166.7; EIMS: *m*/*z* (%) 356 (1), 232 (72), 201 (100), 173 (66), 127 (50). Anal. Calcd for $C_{18}H_{16}N_4O_4S$: C, 56.24; H, 4.20; N, 14.57. Found: C, 56.48; H, 4.07; N, 14.35.

*4.4.12. (Z)-Methyl 3-(2-azido-5-methoxyphenyl)-2-(p-tolylthiomethyl)-propenoate (**6l**).* Reaction time: 10 min; yield: 96%; yellow oil; IR (neat) 2122, 2096, 1716 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H, CH_3), 3.74 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 3.93 (s, 2H, CH_2), 6.89–6.93 (m, 1H, aromatic), 7.01–7.06 (m, 4H, aromatic), 7.21–7.25 (m, 2H, aromatic), 7.70 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 21.0, 32.9, 52.3, 55.6, 114.5, 116.6, 119.2, 127.2, 129.6, 129.8, 131.3, 131.5, 131.6, 136.4, 137.0, 156.4, 167.2; EIMS: *m*/*z* (%) 341 (15), 218 (100), 186 (68). Anal. Calcd for $C_{19}H_{19}N_3O_3S$: C, 61.77; H, 5.18; N, 11.37. Found: C, 61.52; H, 4.90; N, 11.52.

*4.4.13. (Z)-Ethyl 3-(2-azidophenyl)-2-(phenylthiomethyl)propenoate (**6m**).* Reaction time: 10 min; yield: 80%; yellow oil; IR (neat) 2126, 2091, 1711 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (t, *J*=7.2 Hz, 3H, CH_3), 3.93 (s, 2H, CH_2), 4.29 (q, *J*=7.2 Hz, 2H, CH_2), 7.05–7.22 (m, 5H, aromatic), 7.28–7.38 (m, 4H, aromatic), 7.71 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 14.2, 32.4, 61.3, 118.2, 124.6, 126.5, 126.7, 128.7, 130.0, 130.1 (two), 131.3, 135.5, 136.2, 138.8, 166.7; EIMS: *m*/*z* (%) 311 (22), 202 (100), 174 (88), 156 (27), 128 (31). Anal. Calcd for $C_{18}H_{17}N_3O_2S$: C, 63.70; H, 5.05; N, 12.38. Found: C, 63.51; H, 5.19; N, 12.15.

*4.4.14. (Z)-Butyl 3-(2-azidophenyl)-2-(phenylthiomethyl)propenoate (**6n**).* Reaction time: 10 min; yield: 70%; yellow oil; IR (neat) 2125, 2093, 1712 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, *J*=7.3 Hz, 3H, CH_3), 1.38–1.51 (m, 2H, CH_2), 1.69–1.72 (m, 2H, CH_2), 3.93 (s, 2H, CH_2), 4.24 (t, *J*=6.6 Hz, 2H, CH_2), 7.08–7.13 (m, 2H, aromatic), 7.19–7.26 (m, 3H, aromatic), 7.30–7.38 (m, 4H, aromatic), 7.72 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 13.7, 19.2, 30.6, 32.4, 65.1, 118.2, 124.6, 126.5, 126.7, 128.7, 128.9, 130.0, 130.1, 131.3, 135.5, 136.2, 138.9, 166.8; EIMS: *m*/*z* (%) 339 (12), 230 (34), 174 (100), 156 (15), 128 (18). Anal. Calcd for $C_{20}H_{21}N_3O_2S$: C, 65.37; H, 5.76; N, 11.44. Found: C, 65.25; H, 5.64; N, 11.62.

4.5. General procedure for the synthesis of (*Z*)-alkyl 3-(2-azidophenyl)-2-(arlysulfinylmethyl)propenoates 7

MCPBA (1.1 mmol) was added to a stirred solution of allyl aryl sulfide **6** (1 mmol) in 5 mL of dichloromethane at 0 °C. After stirring for 5–30 min, the mixture was neutralized with 10% aqueous $NaHCO_3$ solution and extracted with dichloromethane (3×10 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography with silica gel by elution with hexane and ethyl acetate (4:1) to produce sulfoxide **7**.

*4.5.1. (Z)-Methyl 3-(2-azidophenyl)-2-(phenylsulfinylmethyl)propenoate (**7a**).* Reaction time: 10 min; yield: 81%; light yellow solid: mp 58–59 °C (hexane–EtOAc); IR (KBr) 2127, 2094, 1712, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.81 (s, 3H, CH_3), 3.98 and 4.06 (AB quartet, *J*=12.4 Hz, 2H, CH_2), 7.12–7.20 (m, 2H, aromatic), 7.37–7.53 (m, 4H, aromatic), 7.62–7.66 (m, 2H, aromatic), 7.75–7.77 (m, 1H, aromatic), 8.04 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 52.5, 56.7, 118.2, 123.4, 124.2, 124.8, 125.4, 129.0, 130.6, 130.7, 131.1, 138.8, 141.8, 143.6, 166.8; EIMS: *m*/*z* (%) 341 (1) [M^+], 187 (45), 156 (64), 128 (100). Anal. Calcd for $C_{17}H_{15}N_3O_3S$: C, 59.81; H, 4.43; N, 12.31. Found: C, 59.63; H, 4.25; N, 12.46.

*4.5.2. (Z)-Methyl 3-(2-azido-5-chlorophenyl)-2-(phenylsulfinylmethyl)-propenoate (**7b**).* Reaction time: 20 min; yield: 79%; yellow solid: mp 72–73 °C (hexane–EtOAc); IR (KBr) 2128, 2095, 1715, 1046 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.84 (s, 3H, CH_3), 3.86 and 4.00 (AB quartet, *J*=12.2 Hz, 2H, CH_2), 7.03–7.07 (m, 1H, aromatic), 7.33–7.37 (m, 1H, aromatic), 7.48–7.50 (m, 3H, aromatic), 7.61–7.69 (m, 2H, aromatic), 7.80–7.87 (m, 1H, aromatic), 7.96 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 52.7, 56.5, 119.3, 124.0, 124.6, 126.8, 128.5, 129.2, 130.1, 130.5, 131.2, 137.3, 140.6, 143.7, 166.4; EIMS: *m*/*z* (%) 223 (26), 221 (76), 192 (33), 190 (100), 164 (30), 162 (90), 127 (50). Anal. Calcd for $C_{17}H_{14}ClN_3O_3S$: C, 54.33; H, 3.75; N, 11.18. Found: C, 54.11; H, 4.02; N, 11.03.

*4.5.3. (Z)-Methyl 3-(2-azido-5-nitrophenyl)-2-(phenylsulfinylmethyl)-propenoate (**7c**).* Reaction time: 20 min; yield: 82%; yellow solid: mp 116–117 °C (hexane–EtOAc); IR (KBr) 2129, 2094, 1701, 1520, 1344,

1047 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.87 (s, 3H, CH_3), 3.87 and 3.99 (AB quartet, J=12.2 Hz, 2H, CH_2), 7.27 (d, J=8.9 Hz, 1H, aromatic), 7.49–7.53 (m, 3H, aromatic), 7.72–7.75 (m, 2H, aromatic), 8.03 (s, 1H, CH), 8.28 (dd, J=8.9 and 2.7 Hz, 1H, aromatic), 8.96 (d, J=2.4 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.8, 56.2, 118.5, 123.9, 125.6, 125.7, 126.1, 126.3, 129.2, 131.2, 139.5, 143.6, 144.2, 145.3, 166.1; EIMS: m/z (%) 232 (80), 201 (100), 173 (60), 127 (50). Anal. Calcd for $C_{17}H_{14}N_4O_5S$: C, 52.84; H, 3.65; N, 14.50. Found: C, 52.62; H, 3.41; N, 14.28.

*4.5.4. (Z)-Methyl 3-(2-azido-5-methoxyphenyl)-2-(phenylsulfinylmethyl)propenoate (**7d**).* Reaction time: 30 min; yield: 82%; brown solid: mp 104–105 °C (hexane–EtOAc); IR (KBr) 2122, 2096, 1710, 1044 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.83 (s, 3H, CH_3), 3.90 and 4.05 (AB quartet, J=13.1 Hz, 2H, CH_2), 3.92 (s, 3H, CH_3), 6.97 (dd, J=8.5 and 2.7 Hz, 1H, aromatic), 7.06 (d, J=8.5 Hz, 1H, aromatic), 7.47–7.54 (m, 3H, aromatic), 7.59 (d, J=2.7 Hz, 1H, aromatic), 7.64–7.69 (m, 2H, aromatic), 8.07 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 52.6, 56.2, 57.2, 115.0, 117.9, 119.2, 123.6, 124.0, 126.1, 129.1, 131.0, 131.1, 142.0, 143.8, 156.7, 166.8; EIMS: m/z (%) 217 (100), 186 (85), 158 (87). Anal. Calcd for $C_{18}H_{17}N_3O_4S$: C, 58.21; H, 4.61; N, 11.31. Found: C, 58.03; H, 4.39; N, 11.15.

*4.5.5. (Z)-Methyl 3-(2-azidophenyl)-2-[(4-chlorophenyl)sulfinylmethyl]propenoate (**7e**).* Reaction time: 10 min; yield: 75%; light yellow solid: mp 98–99 °C (hexane–EtOAc); IR (KBr) 2127, 2094, 1712, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.83 (s, 3H, CH_3), 3.97 and 4.06 (AB quartet, J=12.3 Hz, 2H, CH_2), 7.13–7.19 (m, 2H, aromatic), 7.37–7.44 (m, 3H, aromatic), 7.51–7.56 (m, 2H, aromatic), 7.63–7.66 (m, 1H, aromatic), 8.00 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 52.6, 56.8, 118.3, 123.0, 124.7, 125.3, 125.6, 129.2, 130.4, 130.8, 137.4, 138.8, 141.8, 142.1, 166.7; EIMS: m/z (%) 187 (49), 156 (84), 128 (100). Anal. Calcd for $C_{17}H_{14}ClN_3O_3S$: C, 54.33; H, 3.75; N, 11.18. Found: C, 54.12; H, 3.49; N, 11.42.

*4.5.6. (Z)-Methyl 3-(2-azido-5-chlorophenyl)-2-[(4-chlorophenyl)sulfinylmethyl]propenoate (**7f**).* Reaction time: 15 min; yield: 93%; light yellow solid: mp 96–97 °C (hexane–EtOAc); IR (KBr) 2124, 2089, 1708, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.85 (s, 3H, CH_3), 3.89 and 4.00 (AB quartet, J=12.4 Hz, 2H, CH_2), 7.07 (d, J=8.8 Hz, 1H, aromatic), 7.36 (dd, J=8.8 and 2.5 Hz, 1H, aromatic), 7.42–7.47 (m, 2H, aromatic), 7.57–7.61 (m, 2H, aromatic), 7.79 (d, J=2.5 Hz, 1H, aromatic), 7.95 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 52.7, 56.5, 119.4, 124.1, 125.5, 126.7, 129.4, 130.1, 130.3, 130.6, 137.4, 137.5, 140.7, 142.2, 166.4; EIMS: m/z (%) 223 (23), 221 (70), 192 (35), 190 (100), 164 (32), 162 (99), 127 (53). Anal. Calcd for $C_{17}H_{13}Cl_2N_3O_3S$: C, 49.77; H, 3.19; N, 10.24. Found: C, 49.53; H, 3.41; N, 10.09.

*4.5.7. (Z)-Methyl 3-(2-azido-5-nitrophenyl)-2-[(4-chlorophenyl)sulfinylmethyl]propenoate (**7g**).* Reaction time: 5 min; yield: 99%; white solid: mp 87–88 °C (hexane–EtOAc); IR (KBr) 2126, 2090, 1706, 1519, 1349, 1047 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.88 (s, 3H, CH_3), 3.90 and 3.97 (AB quartet, J=12.4 Hz, 2H, CH_2), 7.28 (d, J=8.8 Hz, 1H, aromatic), 7.45–7.49 (m, 2H, aromatic), 7.64–7.69 (m, 2H, aromatic), 8.03 (s, 1H, CH), 8.29 (dd, J=8.8 and 2.5 Hz, 1H, aromatic), 8.92 (d, J=2.5 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.9, 56.3, 118.6, 125.3, 125.4, 125.8, 126.0, 126.1, 129.5, 137.5, 139.7, 142.1, 144.2, 145.4, 166.1; EIMS: m/z (%) 232 (77), 201 (100), 173 (62), 127 (50). Anal. Calcd for $C_{17}H_{13}ClN_4O_5S$: C, 48.52; H, 3.11; N, 13.31. Found: C, 48.34; H, 3.35; N, 13.12.

*4.5.8. (Z)-Methyl 3-(2-azido-5-methoxyphenyl)-2-[(4-chlorophenyl)sulfinylmethyl]propenoate (**7h**).* Reaction time: 5 min; yield: 93%; yellow solid: mp 120–121 °C (hexane–EtOAc); IR (KBr) 2123, 2093, 1704, 1049 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.84 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 3.93 and 4.04 (AB quartet, J=12.4 Hz, 2H, CH_2), 6.97 (dd, J=8.8 and 2.8 Hz, 1H, aromatic), 7.07 (d, J=8.8 Hz, 1H aromatic), 7.43–7.46 (m, 3H, aromatic), 7.56–7.60 (m, 2H, aromatic), 8.04 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 52.6, 56.1, 57.2, 115.1, 117.6, 119.3, 123.3, 125.5, 126.0, 129.3, 131.2, 137.4, 142.0, 142.3, 156.6, 166.8; EIMS: m/z (%) 217 (91), 186 (84), 158 (100), 143 (21). Anal. Calcd for $C_{18}H_{16}ClN_3O_4S$: C, 53.27; H, 3.97; N, 10.35. Found: C, 53.03; H, 3.71; N, 10.17.

*4.5.9. (Z)-Methyl 3-(2-azidophenyl)-2-(p-tolylsulfinylmethyl)propenoate (**7i**).* Reaction time: 5 min; yield: 86%; yellow oil; IR (neat) 2127, 2094, 1713, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.39 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 3.92 and 4.04 (AB quartet, J=12.4 Hz, 2H, CH_2), 7.11–7.19 (m, 2H, aromatic), 7.23–7.26 (m, 2H, aromatic), 7.37–7.43 (m, 1H, aromatic), 7.49–7.52 (m, 2H, aromatic), 7.73–7.76 (m, 1H, aromatic), 8.01 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 21.4, 52.5, 56.7, 118.1, 123.5, 124.2, 124.7, 125.5, 128.5, 129.7, 130.7, 138.8, 140.4, 141.5, 141.6, 166.8; EIMS: m/z (%) 355 (2) [M^+], 188 (100), 156 (66), 128 (33). Anal. Calcd for $C_{18}H_{17}N_3O_3S$: C, 60.83; H, 4.82; N, 11.82. Found: C, 60.68; H, 4.92; N, 11.61.

*4.5.10. (Z)-Methyl 3-(2-azido-5-chlorophenyl)-2-(p-tolylsulfinylmethyl)propenoate (**7j**).* Reaction time: 5 min; yield: 77%; light yellow solid: mp 97–98 °C (hexane–EtOAc); IR (KBr) 2133, 2098, 1692, 1044 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.41 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 3.85 and 3.99 (AB quartet, J=12.4 Hz, 2H, CH_2), 7.05 (d, J=8.5 Hz, 1H, aromatic), 7.28 (d, J=8.0 Hz, 2H, aromatic), 7.35 (dd, J=8.5 and 2.5 Hz, 1H, aromatic), 7.54 (d, J=8.0 Hz, 2H, aromatic), 7.82 (d, J=2.5 Hz, 1H, aromatic), 7.93 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 21.4, 52.6, 56.5, 119.2, 124.1, 124.7, 126.8, 129.8, 130.0, 130.4, 130.5, 137.3, 140.4, 140.5, 141.7, 166.4; EIMS: m/z (%) 223 (24), 221 (68), 192 (34), 190 (100), 164 (35), 162 (100). Anal. Calcd for $C_{18}H_{16}ClN_3O_3S$: C, 55.45; H, 4.14; N, 10.78. Found: C, 55.23; H, 3.98; N, 10.55.

*4.5.11. (Z)-Methyl 3-(2-azido-5-nitrophenyl)-2-(p-tolylsulfinylmethyl)propenoate (**7k**).* Reaction time: 10 min; yield: 75%; white solid: mp 92–93 °C (hexane–EtOAc); IR (KBr) 2129, 2097, 1716, 1521, 1344, 1047 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.39 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 3.85 and 3.97 (AB quartet, J=12.8 Hz, 2H, CH_2), 7.26 (d, J=8.9 Hz, 1H, aromatic), 7.29 (d, J=8.2 Hz, 2H, aromatic), 7.59 (d, J=8.2 Hz, 2H, aromatic), 8.00 (s, 1H, CH), 8.27 (dd, J=8.9 and 2.1 Hz, 1H, aromatic), 8.90 (d, J=2.1 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.4, 52.8, 56.4, 118.5, 124.0, 125.6, 125.9, 126.2, 126.3, 129.9, 139.3, 140.4, 141.9, 144.3, 145.2, 166.2; EIMS: m/z (%) 232 (71), 201 (100), 173 (71), 127 (56). Anal. Calcd for $C_{18}H_{16}N_4O_5S$: C, 53.99; H, 4.03; N, 13.99. Found: C, 54.26; H, 4.30; N, 13.76.

*4.5.12. (Z)-Methyl 3-(2-azido-5-methoxyphenyl)-2-(p-tolylsulfinylmethyl)propenoate (**7l**).* Reaction time: 5 min; yield: 72%; yellow solid: mp 116–117 °C (hexane–EtOAc); IR (KBr) 2119, 2091, 1701, 1051 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 3.88 and 4.04 (AB quartet, J=12.4 Hz, 2H, CH_2), 3.91 (s, 3H, CH_3), 6.97 (dd, J=8.8 and 2.8 Hz, 1H, CH), 7.05 (d, J=8.8 Hz, 1H, aromatic), 7.28 (d, J=8.3 Hz, 2H, aromatic), 7.54 (d, J=8.3 Hz, 2H, aromatic), 7.57 (d, J=2.8 Hz, 1H, aromatic), 8.05 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 21.4, 52.5, 56.2, 57.2, 115.1, 117.8, 119.1, 123.7, 124.0, 126.1, 129.8, 131.1, 140.6, 141.6, 141.8, 156.6, 166.8; EIMS: m/z (%) 217 (97), 186 (85), 158 (100), 143 (21). Anal. Calcd for $C_{19}H_{19}N_3O_4S$: C, 59.21; H, 4.97; N, 10.90. Found: C, 59.05; H, 4.73; N, 10.68.

*4.5.13. (Z)-Ethyl 3-(2-azidophenyl)-2-(phenylsulfinylmethyl)propenoate (**7m**).* Reaction time: 5 min; yield: 79%; white solid: mp 69–70 °C (hexane–EtOAc); IR (KBr) 2124, 2083, 1697, 1052 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (t, J=6.9 Hz, 3H, CH_3), 3.92 and 4.05 (AB quartet, J=12.6 Hz, 2H, CH_2), 4.20–4.32 (m, 2H, CH_2),[15] 7.12–7.15 (m, 1H, aromatic), 7.17–7.20 (m, 1H, aromatic), 7.37–7.40 (m, 1H, aromatic), 7.42–7.48 (m, 3H, aromatic), 7.60–7.66 (m, 2H, aromatic), 7.74–7.76 (m, 1H,

aromatic), 8.03 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 14.2, 56.9, 61.6, 118.2, 123.8, 124.2, 124.8, 125.6, 129.0, 130.6, 130.7, 131.1, 138.8, 141.5, 143.8, 166.3; EIMS: *m*/*z* (%) 201 (56), 173 (39), 156 (100), 128 (78). Anal. Calcd for $C_{18}H_{17}N_3O_3S$: C, 60.83; H, 4.82; N, 11.82. Found: C, 60.72; H, 4.93; N, 11.61.

*4.5.14. (Z)-Butyl 3-(2-azidophenyl)-2-(phenylsulfinylmethyl)-propenoate (**7n**).* Reaction time: 10 min; yield: 72%; white solid: mp 64–65 °C (hexane–EtOAc); IR (KBr) 2135, 2094, 1696, 1045 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, *J*=7.3 Hz, 3H, CH_3), 1.40–1.53 (m,2H, CH_2), 1.67–1.77 (m, 2H, CH_2), 3.97 and 4.05 (AB quartet, *J*=12.4 Hz, 2H, CH_2), 4.14–4.28 (m, 2H, CH_2),[15] 7.12–7.20 (m, 2H, aromatic), 7.37–7.49 (m, 4H, aromatic), 7.61–7.64 (m, 2H, aromatic), 7.74–7.76 (m, 1H, CH), 8.03 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 13.7, 19.2, 30.6, 56.9, 65.5, 118.2, 123.8, 124.2, 124.8, 125.6, 129.0, 130.6, 130.7, 131.0, 138.8, 141.6, 143.8, 166.3; EIMS: *m*/*z* (%) 229 (18), 173 (100), 156 (60), 128 (61). Anal. Calcd for $C_{20}H_{21}N_3O_3S$: C, 62.64; H, 5.52; N, 10.96. Found: C, 62.43; H, 5.64; N, 10.73.

4.6. Two-step synthesis of 2-methoxy-3-(phenylsulfinylmethyl)quinoline (10a)

*4.6.1. (Z)-Methyl 3-[2-N-(triphenylphosphoranylidene)phenyl]-2-(phenylsulfinylmethyl)propenoate (**8a**).* A mixture of azidosulfoxide **7a** (0.33 g, 1 mmol) and Ph_3P (0.29 g, 1.1 mmol) in 5 mL of anhydrous benzene was stirred at room temperature for 30 min. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography with silica gel by elution with hexane and ethyl acetate (3:1) providing 0.49 g (85%) of **7a** as a yellow solid: mp 82–83 °C (hexane–EtOAc); IR (KBr) 1701, 1589, 1044 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 3H, CH_3), 3.97 and 4.32 (AB quartet, *J*=12.5 Hz, 2H, CH_2), 6.46–6.49 (m, 1H, aromatic), 6.67–6.72 (m, 1H, aromatic), 6.91–6.96 (m, 1H, aromatic), 7.40–7.55 (m, 13H, aromatic), 7.70–7.76 (m, 8H, aromatic), 8.91 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 51.9, 57.2, 117.3, 118.0, 121.6, 124.4, 128.5, 128.7, 128.8, 129.7, 130.0, 130.3, 130.8, 131.4, 131.8, 131.9, 132.4, 132.5, 144.2, 146.1, 147.7, 151.2, 168.0; ^{31}P NMR [$CDCl_3$/$(PhO)_3PO$] δ 19.77. Anal. Calcd for $C_{35}H_{30}NO_3PS$: C, 73.03; H, 5.25; N, 2.43. Found: C, 72.74; H, 5.53; N, 2.29.

*4.6.2. 2-Methoxy-3-(phenylsulfinylmethyl)quinoline (**10a**).* Iminophosphorane **8a** (0.57 g, 1 mmol) in 10 mL of anhydrous benzene was stirred at reflux temperature for 1 h 30 min. The mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel eluting with hexane and ethyl acetate (3:1) providing 0.27 g (90%) of **10a** and 0.25 g (90%) of triphenylphosphine oxide in the order of elution: mp 116–117 °C (hexane–EtOAc); IR (KBr) 1624, 1042 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 3H, CH_3), 4.14 and 4.22 (AB quartet, *J*=12.5 Hz, 2H, CH_2), 7.35–7.44 (m, 6H, aromatic), 7.59–7.68 (m, 2H, aromatic), 7.76 (s, 1H, aromatic), 7.79–7.82 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 53.6, 58.0, 113.9, 124.2, 124.3, 124.8, 126.9, 127.5, 128.8, 129.8, 131.1, 140.5, 142.9, 146.3, 159.9; EIMS: *m*/*z* (%) 297 (1) [M$^+$], 281 (6), 172 (78), 142 (100), 115 (43). Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.08; N, 4.71. Found: C, 68.39; H, 4.91; N, 4.48.

4.7. General procedure for one-pot synthesis of 2-alkoxy-3-(arylsulfinylmethyl)quinolines 10

A mixture of azidosulfoxide **7** (1 mmol) and Ph_3P (1.1 mmol) in 5 mL of benzene was stirred at reflux temperature for 70 min–3 h. The mixture was cooled to room temperature and concentrated under reduced pressure. The resulting mixture was chromatographed on silica gel eluting with hexane and ethyl acetate (2:1) to produce pure quinoline **10**.

*4.7.1. 2-Methoxy-3-(phenylsulfinylmethyl)quinoline (**10a**).* Reaction time: 1 h 50 min; yield: 73%; white solid: mp 116–117 °C (hexane–EtOAc). The spectral data were the same as described previously.

*4.7.2. 6-Chloro-2-methoxy-3-(phenylsulfinylmethyl)quinoline (**10b**).* Reaction time: 2 h; yield: 84%; light yellow solid: mp 147–148 °C (hexane–EtOAc); IR (KBr) 1620, 1042 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3H, CH_3), 4.13 and 4.21 (AB quartet, *J*=12.5 Hz, 2H, CH_2), 7.42–7.48 (m, 5H, aromatic), 7.54 (dd, *J*=9.2 and 2.4 Hz, 1H, aromatic), 7.64 (d, *J*=2.4 Hz, 1H, aromatic), 7.68 (s, 1H, aromatic), 7.73 (d, *J*=8.9 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 53.7, 57.6, 115.0, 124.2, 125.4, 126.2, 128.5, 128.8, 129.6, 130.4, 131.2, 139.4, 142.8, 144.7, 160.1; EIMS: *m*/*z* (%) 331 (1) [M$^+$], 208 (35), 206 (100), 178 (28), 176 (77), 140 (39). Anal. Calcd for $C_{17}H_{14}ClNO_2S$: C, 61.53; H, 4.25; N, 4.22. Found: C, 61.29; H, 4.48; N, 4.04.

*4.7.3. 2-Methoxy-6-nitro-3-(phenylsulfinylmethyl)quinoline (**10c**).* Reaction time: 1 h 40 min; yield: 73%; yellow solid: mp 114–115 °C (hexane–EtOAc); IR (KBr) 1618, 1526, 1337, 1039 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H, CH_3), 4.18 and 4.23 (AB quartet, *J*=12.5 Hz, 2H, CH_2), 7.43–7.53 (m, 5H, aromatic), 7.87 (d, *J*=9.2 Hz, 1H, CH), 7.93 (s, 1H, aromatic), 8.39 (dd, *J*=9.2 and 2.4 Hz, 1H, aromatic), 8.64 (d, *J*=2.4 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 54.2, 56.9, 116.4, 123.5, 124.1 (two), 128.3, 128.9, 131.4, 141.3, 142.5 (two), 143.9, 149.4, 162.3; EIMS: *m*/*z* (%) 342 (1) [M$^+$], 326 (33), 217 (100), 187 (57), 141 (34). Anal. Calcd for $C_{17}H_{14}N_2O_4S$: C, 59.64; H, 4.12; N, 8.18. Found: C, 59.42; H, 4.35; N, 7.98.

*4.7.4. 2,6-Dimethoxy-3-(phenylsulfinylmethyl)quinoline (**10d**).* Reaction time: 2 h 30 min; yield: 61%; yellow solid: mp 92–93 °C (hexane–EtOAc); IR (KBr) 1605, 1043 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 4.13 and 4.20 (AB quartet, *J*=12.5 Hz, 2H, CH_2), 6.99 (d, *J*=2.7 Hz, 1H, aromatic), 7.27 (dd, *J*=9.2 and 2.7 Hz, 1H, aromatic), 7.39–7.52 (m, 5H, aromatic), 7.71 (d, *J*=9.2 Hz, 1H, aromatic), 7.72 (s, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 53.4, 55.5, 57.9, 106.0, 114.0, 121.5, 124.2, 125.3, 128.2, 128.7, 131.1, 139.5, 141.8, 143.0, 156.2, 158.6; EIMS: *m*/*z* (%) 327 (1) [M$^+$], 202 (100), 172 (69), 116 (33). Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.23; N, 4.28. Found: C, 65.89; H, 5.04; N, 4.09.

*4.7.5. 3-[(4-Chlorophenyl)sulfinylmethyl]-2-methoxyquinoline (**10e**).* Reaction time: 3 h; yield: 85%; light yellow solid: mp 133–134 °C (hexane–EtOAc); IR (KBr) 1621, 1053 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3H, CH_3), 4.13 and 4.21 (AB quartet, *J*=12.7 Hz, 2H, CH_2), 7.33–7.41 (m, 5H, aromatic), 7.60–7.70 (m, 2H, aromatic), 7.80 (s, 1H, aromatic), 7.82–7.83 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 53.5, 57.7, 113.3, 124.4, 124.7, 125.7, 127.0, 127.5, 129.0, 129.9, 137.3, 140.6, 141.4, 146.4, 159.8; EIMS: *m*/*z* (%) 331 (1) [M$^+$], 315 (8), 172 (100), 142 (88), 115 (30). Anal. Calcd for $C_{17}H_{14}ClNO_2S$: C, 61.53; H, 4.25; N, 4.22. Found: C, 61.38; H, 4.06; N, 4.01.

*4.7.6. 6-Chloro-3-[(4-chlorophenyl)sulfinylmethyl]-2-methoxyquinoline (**10f**).* Reaction time: 2 h; yield: 62%; light yellow solid: mp 136–137 °C (hexane–EtOAc); IR (KBr) 1619, 1043 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3H, CH_3), 4.12 and 4.19 (AB quartet, *J*=12.4 Hz, 2H, CH_2), 7.32–7.42 (m, 4H, aromatic), 7.55 (dd, *J*=9.1 and 2.2 Hz, 1H, aromatic), 7.67 (d, *J*=2.2 Hz, 1H, aromatic), 7.73 (s, 1H, aromatic), 7.74 (d, *J*=9.1 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 53.7, 57.3, 114.4, 125.3, 125.6, 126.2, 128.5, 129.0, 129.8, 130.6, 137.4, 139.6, 141.2, 144.8, 160.0; EIMS: *m*/*z* (%) 351 (11), 349 (15), 208 (32), 206 (100), 178 (24), 176 (70), 140 (38). Anal. Calcd for $C_{17}H_{13}Cl_2NO_2S$: C, 55.75; H, 3.58; N, 3.82. Found: C, 55.53; H, 3.74; N, 3.68.

*4.7.7. 3-[(4-Chlorophenyl)sulfinylmethyl]-2-methoxy-6-nitroquinoline (**10g**).* Reaction time: 1 h 30 min; yield: 69%; yellow solid: mp 148–149 °C (hexane–EtOAc); IR (KBr) 1616, 1526, 1336, 1043 cm^{-1}; ^{1}H

NMR ($CDCl_3$) δ 3.87 (s, 3H, CH_3), 4.16 and 4.21 (AB quartet, J=12.9 Hz, 2H, CH_2), 7.34–7.44 (m, 4H, aromatic), 7.89 (d, J=9.2 Hz, 1H, aromatic), 8.01 (s, 1H, aromatic), 8.41 (dd, J=9.2 and 2.5, 1H, aromatic), 8.67 (d, J=2.5 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 54.2, 56.6, 115.8, 123.4, 123.6, 124.2, 125.5, 128.3, 129.1, 137.6, 141.0, 141.5, 144.0, 149.4, 162.1; EIMS: m/z (%) 360 (21), 217 (100), 187 (54), 141 (37) 140 (21). Anal. Calcd for $C_{17}H_{13}ClN_2O_4S$: C, 54.19; H, 3.48; N, 7.43. Found: C, 54.03; H, 3.71; N, 7.24.

*4.7.8. 3-[(4-Chlorophenyl)sulfinylmethyl]-2,6-dimethoxyquinoline (**10h**).* Reaction time: 1 h 10 min; yield: 73%; yellow solid: mp 95–96 °C (hexane–EtOAc); IR (KBr) 1612, 1036 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 4.11 and 4.20 (AB quartet, J=12.7 Hz, 2H, CH_2), 7.01 (d, J=2.8 Hz, 1H, aromatic), 7.28 (dd, J=9.0 and 2.8 Hz, 1H, aromatic), 7.32–7.41 (m, 4H, aromatic), 7.72 (d, J=9.0 Hz, 1H, aromatic), 7.72 (s, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 53.4, 55.5, 57.7, 106.0, 113.4, 121.7, 125.3, 125.7, 128.3, 129.0, 137.3, 139.6, 141.4, 141.9, 156.2, 158.5; EIMS: m/z (%) 345 (16), 202 (100), 172 (67), 116 (28). Anal. Calcd for $C_{18}H_{16}ClNO_3S$: C, 59.75; H, 4.46; N, 3.87. Found: C, 59.53; H, 4.23; N, 3.63.

*4.7.9. 2-Methoxy-3-(p-tolylsulfinylmethyl)quinoline (**10i**).* Reaction time: 2 h; yield: 78%; light yellow solid: mp 130–131 °C (hexane–EtOAc); IR (KBr) 1623, 1039 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 4.12 and 4.19 (AB quartet, J=12.4 Hz, 2H, CH_2), 7.23 (d, J=8.3 Hz, 2H, aromatic), 7.33–7.40 (m, 3H, aromatic), 7.58–7.68 (m, 2H, aromatic), 7.76 (s, 1H, aromatic), 7.81 (d, J=8.3 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.4, 53.5, 58.2, 114.2, 124.2 (two), 124.8, 126.9, 127.5, 129.5, 129.7, 139.9, 140.4, 141.6, 146.3, 160.0; EIMS: m/z (%) 311 (2) [M$^+$], 172 (64), 142 (100), 115 (33). Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.43; H, 5.50; N, 4.50. Found: C, 69.59; H, 5.78; N, 4.26.

*4.7.10. 6-Chloro-2-methoxy-3-(p-tolylsulfinylmethyl)quinoline (**10j**).* Reaction time: 2 h; yield: 81%; light yellow solid: mp 128–129 °C (hexane–EtOAc); IR (KBr) 1622, 1045 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H, CH_3), 3.86 (s, 3H, CH_3), 4.10 and 4.17 (AB quartet, J=12.4 Hz, 2H, CH_2), 7.23 (d, J=8.3 Hz, 2H, aromatic), 7.33 (d, J=8.3 Hz, 2H, aromatic), 7.54 (dd, J=8.8 and 2.4 Hz, 1H, aromatic), 7.63 (d, J=2.4 Hz, 1H, aromatic), 7.67 (s, 1H, aromatic), 7.73 (d, J=8.8 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.4, 53.7, 57.8, 115.3, 124.2, 125.4, 126.2, 128.5, 129.5, 129.6, 130.4, 139.3, 139.7, 141.7, 144.7, 160.2; EIMS: m/z (%) 345 (1) [M$^+$], 331 (16), 329 (39), 208 (33), 206 (100), 178 (26), 176 (74), 140 (36). Anal. Calcd for $C_{18}H_{16}ClNO_2S$: C, 62.51; H, 4.66; N, 4.05. Found: C, 62.38; H, 4.39; N, 4.28.

*4.7.11. 2-Methoxy-6-nitro-3-(p-tolylsulfinylmethyl)quinoline (**10k**).* Reaction time: 1 h 40 min; yield: 62%; yellow solid: mp 155–156 °C (hexane–EtOAc); IR (KBr) 1623, 1538, 1340, 1042 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 4.15 and 4.19 (AB quartet, J=12.7 Hz, 2H, CH_2), 7.23–7.27 (m, 2H, aromatic), 7.31–7.34 (m, 2H, aromatic), 7.88 (d, J=7.2 Hz, 1H, aromatic), 7.92 (s, 1H, aromatic), 8.40 (dd, J=9.1 and 2.5 Hz, 1H, aromatic), 8.64 (d, J=2.5 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.4, 54.2, 57.2, 116.7, 123.4, 123.5, 124.2, 128.3, 129.6, 132.5, 139.4, 141.3, 141.9, 143.9, 149.4, 162.4; EIMS: m/z (%) 356 (1) [M$^+$], 340 (58), 217 (100), 187 (68), 141 (39). Anal. Calcd for $C_{18}H_{16}N_2O_4S$: C, 60.66; H, 4.53; N, 7.86. Found: C, 60.43; H, 4.31; N, 7.63.

*4.7.12. 2,6-Dimethoxy-3-(p-tolylsulfinylmethyl)quinoline (**10l**).* Reaction time: 2 h 20 min; yield: 61%; light yellow solid: mp 109–110 °C (hexane–EtOAc); IR (KBr) 1613, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 4.11 and 4.17 (AB quartet, J=12.4 Hz, 2H, CH_2), 6.99 (d, J=2.8 Hz, 1H, aromatic), 7.23 (d, J=8.0 Hz, 2H, aromatic), 7.27 (dd, J=8.8 and 2.8 Hz, 1H, aromatic), 7.34 (d, J=8.0 Hz, 2H, aromatic), 7.71 (s, 1H, aromatic), 7.72 (d, J=8.8 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.4, 53.4, 55.5, 58.1, 106.1, 114.3, 121.5, 124.2, 125.4, 128.2, 129.4, 139.5, 139.9, 141.5, 141.8, 156.2, 158.7; EIMS: m/z (%) 341 (1) [M$^+$], 325 (28), 202 (100), 172 (67), 116 (28). Anal. Calcd for $C_{19}H_{19}NO_3S$: C, 66.84; H, 5.61; N, 4.10. Found: C, 66.61; H, 5.39; N, 3.96.

*4.7.13. 2-Ethoxy-3-(phenylsulfinylmethyl)quinoline (**10m**).* Reaction time: 3 h; yield: 75%; white solid: mp 82–83 °C (hexane–EtOAc); IR (KBr) 1621, 1603, 1042 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J=7.2 Hz, 3H, CH_3), 4.15 and 4.23 (AB quartet, J=12.4 Hz, 2H, CH_2), 4.26–4.46 (m, 2H, CH_2),[15] 7.33–7.46 (m, 6H, aromatic), 7.57–7.66 (m, 2H, aromatic), 7.75 (s, 1H, aromatic), 7.76–7.79 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 14.4, 58.3, 62.0, 114.1, 124.1, 124.2, 124.7, 126.9, 127.5, 128.8, 129.7, 131.1, 140.3, 143.2, 146.5, 159.7; EIMS: m/z (%) 311 (1) [M$^+$], 295 (20), 186 (100), 158 (17), 142 (67), 130 (27). Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.12; H, 5.88; N, 4.30. Found: C, 69.87; H, 5.60; N, 4.18.

*4.7.14. 2-Butoxy-3-(phenylsulfinylmethyl)quinoline (**10n**).* Reaction time: 2 h; yield: 64%; white solid: mp 64–65 °C (hexane–EtOAc); IR (KBr) 1621, 1604, 1041 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.01 (t, J=7.4 Hz, 3H, CH_3), 1.44–1.57 (m, 2H, CH_2), 1.70–1.80 (m, 2H, CH_2), 4.14 and 4.22 (AB quartet, J=12.4 Hz, 2H, CH_2), 4.23–4.44 (m, 2H, CH_2),[15] 7.33–7.49 (m, 6H, aromatic), 7.58–7.66 (m, 2H, aromatic), 7.74 (s, 1H, aromatic), 7.78–7.81 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 13.9, 19.4, 30.9, 58.7, 66.0, 114.4, 124.1, 124.2, 124.7, 126.9, 127.5, 128.9, 129.8, 131.1, 140.3, 143.4, 146.5, 159.8; EIMS: m/z (%) 339 (1) [M$^+$], 323 (16), 214 (100), 172 (13), 158 (66), 142 (22), 130 (44). Anal. Calcd for $C_{21}H_{23}NO_2S$: C, 71.36; H, 6.56; N, 3.96. Found: C, 71.22; H, 6.70; N, 3.82.

4.8. Additional experiments to examine mechanistic pathway

*4.8.1. (E)-Methyl 3-[2-(triphenylphosphoranylidenamino)phenyl]-propenoate (**12**).* A mixture of 2-azidocinnamate **11** (0.42 g, 2.1 mmol) and Ph_3P (0.60 g, 2.3 mmol) in 5 mL of anhydrous benzene was stirred at room temperature for 20 min. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography with silica gel by elution with hexane and ethyl acetate (3:1) to produce 0.72 g (78%) of **12** as a yellow solid: mp 58–59 °C (hexane–EtOAc); IR (KBr) 1708, 1618, 1590, 1471 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 3H, CH_3), 6.43–6.47 (m, 1H, aromatic), 6.51 (d, J=16.2 Hz, 1H, CH), 6.60–6.65 (m, 1H, aromatic), 6.84–6.90 (m, 1H, aromatic), 7.42–7.57 (m, 10H, aromatic), 7.72–7.80 (m, 6H, aromatic), 8.77 (d, J=16.2 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 51.3, 114.4, 117.3, 122.2, 127.6, 128.2, 128.6, 128.7, 130.1, 130.4, 131.4, 131.7, 131.8, 132.4, 132.6, 144.6, 151.5, 168.7; ^{31}P NMR [$CDCl_3$/$(PhO)_3PO$] δ 20.70. Anal. Calcd for $C_{28}H_{24}NO_2P$: C, 76.87; H, 5.53; N, 3.20. Found: C, 76.74; H, 5.40; N, 3.29.

Attempted cyclization of **12**: a stirred solution of **12** (0.44 g, 1 mmol) in 5 mL of anhydrous benzene was heated at reflux temperature for 3 h. The solvent was evaporated and the crude solid obtained was crystallized with hexane and diethyl ether to give unchanged iminophosphorane **12** in quantitative yield.

*4.8.2. (Z)-Methyl 3-phenyl-2-(phenylsulfinylmethyl)propenoate (**15**).* MCPBA (1.87 g, 8.3 mmol) was added to a stirred solution of known (*Z*)-methyl 3-phenyl-2-(phenylthiomethyl)propenoate **14** (2.15 g, 7.6 mmol) in 20 mL of dichloromethane at 0 °C. After stirring for 5 min, the mixture was neutralized with 10% aqueous $NaHCO_3$ solution and extracted with dichloromethane (3×10 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography with silica gel by elution with hexane and ethyl acetate (4:1) to produce 2.20 g (97%) of **15** as a colorless oil; IR (neat) 1710, 1046 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.76 (s,

3H, CH_3), 3.98 and 4.19 (AB quartet, J=12.7 Hz, 2H, CH_2), 7.35–7.40 (m, 3H, aromatic), 7.42–7.49 (m, 3H, aromatic), 7.53–7.57 (m, 2H, aromatic), 7.64–7.69 (m, 2H, aromatic), 8.04 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 52.4, 56.6, 122.1, 124.2, 128.6, 129.0, 129.3, 129.5, 131.2, 133.9, 143.7, 146.2, 167.2; EIMS: m/z (%) 284 (23), 175 (32), 143 (6), 131 (10), 115 (100). Anal. Calcd for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37. Found: C, 67.85; H, 5.25.

Attempted E/Z isomerization of **15**: a stirred solution of **15** (0.30 g, 1 mmol) in 5 mL of anhydrous benzene was heated at reflux temperature for 3 h. The solvent was evaporated and the unchanged allyl sulfoxide **15** was recovered in quantitative yield.

4.9. Two-step synthesis of methyl quinoline-3-carboxylate (19a)

*4.9.1. (Z)-Methyl 3-[2-N-(triphenylphosphoranylidene)phenyl]-2-(phenylthiomethyl)propenoate (**17a**).* A mixture of azidosulfide **6a** (0.36 g, 1.1 mmol) and Ph_3P (0.31 g, 1.2 mmol) in 5 mL of anhydrous benzene was stirred at room temperature for 40 min. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography with silica gel by elution with hexane and ethyl acetate (3:1) providing 0.48 g (77%) of **17a** as a yellow solid: mp 124–125 °C (hexane–EtOAc); IR (KBr) 1703, 1619, 1585 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 3H, CH_3), 4.09 (s, 2H, CH_2), 6.48–6.51 (m, 1H, aromatic), 6.61–6.66 (m, 1H, aromatic), 6.87–6.93 (m, 1H, aromatic), 7.12–7.26 (m, 3H, aromatic), 7.40–7.58 (m, 12H, aromatic), 7.71–7.77 (m, 6H, aromatic), 8.72 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 32.7, 51.9, 117.3, 121.6, 121.7, 123.7, 126.0, 128.5, 128.6, 128.7, 129.2, 129.5, 129.7, 129.8, 130.2, 131.5, 131.7, 131.8, 132.4, 132.6, 137.2, 143.3, 151.3, 168.5; ^{31}P NMR [$CDCl_3$/$(PhO)_3PO$] δ 19.52. Anal. Calcd for $C_{35}H_{30}NO_2PS$: C, 75.11; H, 5.40; N, 2.50. Found: C, 74.82; H, 5.64; N, 2.36.

*4.9.2. Methyl quinoline-3-carboxylate (**19a**)*[16,17]. Iminophosphorane **17a** (1.83 g, 3.2 mmol) in 20 mL of diphenyl ether was stirred at reflux temperature for 4 h. After cooling to room temperature, the mixture was chromatographed on silica gel eluting with hexane and ethyl acetate (3:1) providing 0.19 g (32%) of **19a** as a white solid: mp 76–77 °C (hexane–EtOAc); IR (KBr) 1722, 1621 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.02 (s, 3H, CH_3), 7.59–7.64 (m, 1H, aromatic), 7.80–7.85 (m, 1H, aromatic), 7.92 (d, J=8.0 Hz, 1H, aromatic), 8.16 (d, J=8.2 Hz, 1H, aromatic), 8.84 (d, J=1.7 Hz, 1H, aromatic), 9.44 (d, J=1.9 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.4, 122.9, 126.8, 127.4, 129.0, 129.4, 131.8, 138.7, 149.7, 149.9, 165.8; EIMS: m/z (%) 187 (55) [M$^+$], 156 (81), 128 (100).

4.10. General procedure for one-pot synthesis of methyl quinoline-3-carboxylates 19

A mixture of azidosulfide **6** (2 mmol) and Ph_3P (2.2 mmol) in 6 mL of diphenyl ether was stirred at reflux temperature for 2–6 h. After cooling to room temperature, the mixture was chromatographed on silica gel eluting with hexane and ethyl acetate (3:1) to produce pure 3-carbomethoxyquinoline **19**.

*4.10.1. Methyl quinoline-3-carboxylate (**19a**)*[16,17]. Reaction time: 4 h 30 min; yield: 25%; white solid: mp 76–77 °C (hexane–EtOAc). The spectral data were the same as described previously.

*4.10.2. Methyl 6-chloroquinoline-3-carboxylate (**19b**)*[17]. Reaction time: 2 h; yield: 20%; light yellow solid: mp 169–170 °C (hexane–EtOAc); IR (KBr) 1615, 1724 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.03 (s, 3H, CH_3), 7.76 (dd, J=9.1 and 2.4 Hz, 1H, aromatic), 7.91 (d, J=2.2 Hz, 1H, aromatic), 8.10 (d, J=9.1 Hz, 1H, aromatic), 8.75 (d, J=1.9 Hz, 1H, aromatic), 9.43 (d, J=2.2 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.6, 123.8, 127.4, 127.5, 131.1, 132.7, 133.3, 137.7, 148.2, 150.2, 165.5; EIMS: m/z (%) 223 (40), 221 (95) [M$^+$], 192 (32), 190 (100), 164 (20), 162 (58), 127 (46).

*4.10.3. Methyl 6-nitroquinoline-3-carboxylate (**19c**).* Reaction time: 6 h; yield: 24%; light yellow solid: mp 212–213 °C (hexane–EtOAc); IR (KBr) 1716, 1625, 1523, 1343 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.07 (s, 3H, CH_3), 8.32 (d, J=9.4 Hz, 1H), 8.60 (dd, J=9.4 and 2.5 Hz, 1H, aromatic), 8.91 (d, J=2.5 Hz, 1H, aromatic), 9.03 (d, J=1.9 Hz, 1H, aromatic), 9.61 (d, J=2.2 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.9, 124.8, 125.0, 125.6, 125.8, 131.5, 140.2, 146.1, 151.6, 153.3, 164.8; EIMS: m/z (%) 232 (69) [M$^+$], 201 (100), 173 (70), 127 (52). Anal. Calcd for $C_{11}H_8N_2O_4$: C, 56.90; H, 3.47; N, 12.06. Found: C, 56.68; H, 3.31; N, 11.85.

*4.10.4. Methyl 6-methoxyquinoline-3-carboxylate (**19d**).* Reaction time: 2 h; yield: 30%; brown solid: mp 107–108 °C (hexane–EtOAc); IR (KBr) 1711, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.94 (s, 3H, CH_3), 4.01 (s, 3H, CH_3), 7.15 (d, J=2.8 Hz, 1H, aromatic), 7.20 (dd, J=9.1 and 1.9 Hz, 1H, aromatic), 8.04 (d, J=9.4 Hz, 1H, aromatic), 8.73 (s, 1H, aromatic), 9.29 (d, J=1.9 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.4, 55.6, 106.0, 123.2, 124.8, 128.0, 130.8, 137.3, 146.0, 147.5, 158.3, 166.0; EIMS: m/z (%) 217 (100) [M$^+$], 186 (68), 158 (67). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.12; H, 4.88; N, 6.33.

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