Supporting Information

Metal and acid-free synthesis of acenaphthenone-2-ylidene ketones in PEG 400 and their radical nitration by TBN in water.

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General information of materials and instruments :

All commercially available chemicals were purchased from Aldrich, USA or Spectrochem, India, and used without further purification. All solvents were used as received. The progress of the reaction was checked by glass sheets pre-coated TLC with silica gel (with binder, 300 mesh, Spectrochem) and column chromatography was performed using silica gel (100-200 mesh). Bruker 300 MHz and 400 MHz instruments were used for ^{1}H and ^{13}C NMR spectra at 300 MHz, 400 MHz and 75 MHz, 100 MHz respectively. Chemical shifts are reported in parts per million (ppm) downfield from an internal TMS (tetramethylsilane) reference. Coupling constants (*J*) are reported in hertz (Hz), and spin multiplicities are represented by the symbols s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). HRMS with an ESI resource were acquired using a Waters XEVO-G2S Q TOF mass specrtrometer. 2400 Series II CHNS Analyzer, Perkin Elmer USA was used for elemental analyses. For all four compounds, the ground state geometries were optimized using the hybrid density functional B3LYP method, i.e., Becke's three parameter nonlocal-exchange functional [1] with the nonlocal correlation functional of Lee, Yang and Parr [2], with high angular momentum basis set 6-31G (d, p) [3]. Optimization is followed by frequency calculation using the same basis set to obtain the appropriate stationary point for each compound. All the calculations have been performed starting from a Molecular Mechanics [4] optimized geometry of the compounds using Gaussian'09.

Procedure for synthesis of compound (E)-3aa :

Acenaphthylene 1,2 dione **1** (1 mmol) , Acetophenone **2aa** (1 mmol) were added with 1 ml of PEG 400 in a dry 10 ml round bottom flask with a magnetic stirrer bar . Then the reaction mixture was allowed to run at 110 ^{o}C for 2.5 hour . After reaching the completion, which was further monitored by TLC the reaction mixture was cooled to room temperature and diluted with 10 ml of ice cooled water and extracted with EtOAc (3 × 5 ml) . The organic layer was combined and washed with brine and dried over anhydrous Na_2SO_4 .After the solvent was removed under reduced pressure, the crude product was purified by column chromatography using 100-200 mesh silica gel and petroleum ether-ethyl acetate mixture as the eluent to afford the desired product **(E)-3aa**.

Procedure for synthesis of compound (E)-3ba :

Acenaphthylene 1,2 dione **1** (1 mmol) ,Methyl 2-(triphenylphosphoranylidene)acetate **2ba** (1 mmol) were added with 1 ml of PEG 400 in a dry 10 ml round bottom flask with a magnetic stirrer bar . Then the reaction mixture was allowed to run at 110 ^{o}C for 2.5 hour . After reaching the completion, which was further monitored by TLC the reaction mixture was cooled to room temperature and diluted with 10 ml of ice cooled water and extracted with EtOAc (3 × 5 ml). The organic layer was combined and washed with brine and dried over anhydrous Na_2SO_4 .After the solvent was removed under reduced pressure, the crude product was purified by column chromatography using 100-200 mesh silica gel and petroleum ether-ethyl acetate mixture as the eluent to afford the desired product **(E)-3ba** .

Procedure for synthesis of compound (Z)-5aa :

(E)-2-(2-oxo-2-phenylethylidene)acenaphthylen-1(2H)-one **(3aa)** (1mmol) , **4** (1.2 mmol) were added with 1 ml of H_2O in a dry 10 ml round bottom flask with a magnetic stirrer bar . Then the reaction mixture was allowed to run at 80 ^{o}C for 2 hour . After reaching the completion, which was further monitored by TLC the reaction mixture was cooled to room temperature and diluted with 10 ml of ice cooled water and extracted with EtOAc (3 × 5 ml). The organic layer was combined and washed with brine and dried over anhydrous Na_2SO_4 .After the solvent was removed under reduced pressure, the crude product was purified by column chromatography using 100-200 mesh silica gel and petroleum ether-ethyl acetate mixture as the eluent to afford the desired product **(Z)-5aa**.

Gram scale synthesis of (Z)- 5aa :

(E)-2-(2-oxo-2-phenylethylidene)acenaphthylen-1(2H)-one **(3aa)** (1.57 gm, 6 mmol, 1.0 equiv) , **4** (7.2 mmol, 1.2 equiv) were added with 5 ml of H_2O in a dry 10 ml round bottom flask with a magnetic stirrer bar . Then the reaction mixture was allowed to run at 80 ^{o}C for 2 hour . After reaching the completion, which was further monitored by TLC the reaction mixture was cooled to room temperature and diluted with 20 ml of ice cooled water and extracted with EtOAc (3 × 10 ml). The organic layer was combined and washed with brine and dried over anhydrous Na_2SO_4 .After the solvent was removed under reduced pressure, the crude product was purified by column chromatography using 100-200 mesh silica gel and petroleum ether-ethyl acetate mixture as the eluent to afford the desired product **(Z)-5aa**.

Procedure for synthesis of compound (Z)- 5ba :

Methyl (E)-2-(2-oxoacenaphthylen-1(2H)-ylidene)acetate **(3ba)** (1 mmol) , **4** (1.2 mmol) were added with 1 ml of H_2O in a dry 10 ml round bottom flask with a magnetic stirrer bar . Then the reaction mixture was allowed to run at 80 ^oC for 2 hour. After reaching the completion, which was further monitored by TLC the reaction mixture was cooled to room temperature and diluted with 10 ml of ice cooled water and extracted with EtOAc (3 × 5 ml). The organic layer was combined and washed with brine and dried over anhydrous Na_2SO_4 .After the solvent was removed under reduced pressure, the crude product was purified by column chromatography using 100-200 mesh silica gel and petroleum ether-ethyl acetate mixture as the eluent to afford the desired product **(Z)-5ba** .

Gram scale synthesis of (Z)-5ba :

Methyl (E)-2-(2-oxoacenaphthylen-1(2H)-ylidene)acetate **(3ba)** (1.35gm , 6 mmol, 1.0 equiv) , **4** (7.2 mmol, 1.2 equiv) were added with 5 ml of H_2O in a dry 10 mL round bottom flask with a magnetic stirrer bar . Then the reaction mixture was allowed to run at 80 ^oC for 2 hour . After reaching the completion, which was further monitored by TLC the reaction mixture was cooled to room temperature and diluted with 20 ml of ice cooled water and extracted with EtOAc (3 × 10 ml). The organic layer was combined and washed with brine and dried over anhydrous Na_2SO_4 .After the solvent was removed under reduced pressure, the crude product was purified by column chromatography using 100-200 mesh silica gel and petroleum ether-ethyl acetate mixture as the eluent to afford the desired product **(Z)-5ba**.

(E)-2-(2-oxo-2-phenylethylidene)acenaphthylen-1(2H)-one (Table 2, entry 1, **3aa**)

Yellow solid, Yield: 90% ; Rf : 0.2 (8% Ethyl Acetate in Petroleum Ether) ; M.P. = 126-128 ^0C ; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.73 (d, J = 9 Hz , 1H), 8.18 (t, 3H) ,8.11 (d, J = 6 Hz, 2H), 8.02 (d, J = 6 Hz, 1H), 8.01 (d, J = 8 Hz, 1H), 7.99 (s, 1H) , 7.81- 7.70 (m, 2H) , 7.66 (d, J = 9 Hz , 1H) , 7.58 (t ,2H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 190.6 , 186.4 ,143.5 , 135.2 , 134.6 , 132.6 , 130.8 , 130.4 , 130.0 , 129.9 , 129.6 , 129.2 , 129.1 , 129.0 , 128.5 , 127.0 , 125.9 , 123.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{12}O_2]$: 284.0837 ; Found : 284.0830 .

(E)-2-(2-oxo-2-(p-tolyl)ethylidene)acenaphthylen-1(2H)-one(Table 2, entry 2, **3ab**)

Yellow solid, Yield: 93% ; Rf : 0.2 (10% Ethyl Acetate in Petroleum Ether) ; M.P. = 132-134 ^{0}C ;^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.68 (d, J = 9 Hz, 1H), 8.13 (d, J = 6 Hz, 1H), 8.09 (d, J = 9 Hz, 3H) , 7.99 (d, J = 9 Hz, 1H) , 7.96 (s, 1H) , 7.78- 7.67 (m, 2H), 7.36 (d, J = 9 Hz, 2H) , 2.47 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 192.8 , 191.4 , 144.8 , 142.8 , 142.0 , 135.5 , 131.8 , 131.4 , 130.8 , 130.6 , 129.6 , 129.0 , 128.8 , 128.0 , 127.8 , 125.2 , 124.2 , 121.9 , 21.8 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{21}H_{14}O_2]$: 298.0994 ; Found : 298.0992 .

(E)-2-(2-(4-methoxyphenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 3, **3ac**)

Yellow solid, Yield: 92% ; Rf : 0.25 (8% Ethyl Acetate in Petroleum Ether) ; M.P. = 130-132 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.64 (d, J = 8 Hz , 1H), 8.19 (d, J= 8 Hz, 2H) ,8.16 (d, J = 8 Hz, 1H), 8.11 (d, J = 8 Hz, 1H), 8.01 (d, J = 8 Hz, 1H), 7.97 (s, 1H) , 7.81- 7.69 (m, 2H) , 7.04 (d, J = 8 Hz , 2H) , 3.93 (s,3H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 192.9 , 190.4 , 164.2, 142.7 , 141.7 , 131.8 , 131.5 , 131.3 , 131.0 , 130.9 , 130.7 , 128.8 , 127.9 , 127.8 , 125.1 , 124.6 , 121.9 , 114.2 , 55.6 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{21}H_{14}O_3]$: 314.0943 ; Found : 314.0949 .

(E)-2-(2-(2-methoxyphenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 4, **3ad**)

Yellow solid, Yield: 89% ; Rf : 0.3 (10% Ethyl Acetate in Petroleum Ether) ; M.P. = 131-133 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.82 (d, J = 8 Hz , 1H), 8.14 (d, J = 8 Hz , 1H) ,8.08 (d, J = 4 Hz , 1H), 8.00 (d , J = 12 Hz, 1H) , 7.91 (s, 1H), 7.89 (d, J = 8Hz, 1H), 7.78-7.70 (m , 2H), 7.56 (t, 1H) , 7.12 (t, 1H), 7.05 (t, 1H), 3.95 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 193.5 , 192.8 , 159.2 , 142.6 , 139.9 , 134.5 , 131.7 , 131.6 , 131.2 , 130.9 , 130.6 , 128.9 , 128.8 , 128.7 , 127.8 , 127.7 , 125.0 , 121.7 , 120.9 , 111.9 , 55.9 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{21}H_{14}O_3]$: 314.0943 ; Found : 314.0948 .

(E)-2-(2-(4-ethoxyphenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 5, **3ae**)

Yellow solid, Yield: 91% ; Rf : 0.25 (10% Ethyl Acetate in Petroleum Ether) ; M.P. = 138-140 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.62 (d, J = 6 Hz ,

1H), 8.15 (t, 3H) ,8.09 (d, J = 6 Hz , 1H), 7.99 (d , J = 6 Hz, 1H) , 7.94 (s, 1H), 7.76 (t, 1H), 7.69 (t, 1H) , 7.01 (d, J = 9 Hz , 2H), 4.19- 4.12 (m, 2H), 1.48 (t, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 192.8 , 190.3 , 163.6 , 141.6 , 132.6 , 131.8 , 131.4 , 131.3 , 131.0 , 130.8 , 130.6 , 128.8 , 128.5 , 127.8 , 127.8 , 125.1 , 124.6 , 122.1 , 121.9 , 114.6 , 63.9 , 14.7 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{22}H_{16}O_3]$: 328.1099 ; Found : 328.1090.

(E)-2-(2-oxo-2-(4-propoxyphenyl)ethylidene)acenaphthylen-1(2H)-one (Table 2, entry 6, **3af**)

Yellow solid, Yield: 90% ; Rf : 0.2 (12% Ethyl Acetate in Petroleum Ether) ; M.P. = 143-145 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.63 (d, J = 6 Hz , 1H), 8.18- 8.10 (m, 4H) , 8.00 (d, J = 9 Hz , 1H), 7.96 (s, 1H), 7.80 – 7.68 (m, 2H), 7.02 (d, J = 6Hz, 1H), 4.04 (t, 2H), 1.91 – 1.84 (m, 2H) , 1.08 (t, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 192.9 , 190.4 , 163.8 , 141.6 , 131.8 , 131.5 , 131.3 , 130.9 , 130.8 , 130.7 , 130.6 , 128.8 , 127.8 , 127.8 , 125.1 , 124.7 , 121.9 , 114.6 , 114.1 , 69.9 , 22.5 , 10.4 ppm ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{23}H_{18}O_3]$: 342.1256 ; Found : 342.1258.

(E)-2-(2-(4-hydroxyphenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 7, **3ag**)

Yellow solid, Yield: 90% ; Rf : 0.2 (8% Ethyl Acetate in Petroleum Ether) ; M.P. = 152-154 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.81 (s, 1H) , 8.62 (d, J = 8 Hz , 1H), 8.17 (d, J= 8 Hz, 2H) ,8.14 (d, J = 8 Hz, 1H), 8.09 (d, J = 8 Hz, 1H), 8.01 (d, J = 8 Hz, 1H), 7.96 (s, 1H) , 7.79 - 7.69 (m, 2H) , 7.03 (d, J = 8 Hz , 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 192.8 , 190.3 , 157.1 , 141.5 , 131.7 , 131.4 , 131.3 , 130.8 , 130.8 , 130.6 , 130.6 , 128.7 , 127.8 , 127.8 , 125.0 , 124.7 , 121.9 , 114.6 ,114.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{12}O_3]$: 300.0786 ; Found : 300.0780 .

(E)-2-(2-(3-hydroxyphenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 8, **3ah**)

Yellow solid, Yield: 91% ; Rf : 0.2 (10% Ethyl Acetate in Petroleum Ether) ; M.P. = 150-152 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.71 (d, J = 6 Hz , 1H), 8.17 (d, J = 6 Hz , 1H) ,8.13 (d, J = 3 Hz, 1H), 8.03 (d, J = 6 Hz, 1H), 7.97 (s, 1H), 7.81- 7.73 (m , 2H) , 7.70 (d, J = 6 Hz, 2H), 7.45 (t, 1H) , 7.17 (d, J = 6 Hz , 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 192.6 , 190.3 , 156.3 , 132.0 , 130.7 , 130.3 , 128.8 , 128.2 , 127.9 , 125.3 , 123.9 , 122.1 , 121.5 , 121.1 , 115.0 ;

HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{12}O_3]$: 300.0786 ; Found : 300.0789 .

(E)-2-(2-(4-chlorophenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 9, **3ai**)

Yellow solid, Yield: 93% ; Rf : 0.2 (8% Ethyl Acetate in Petroleum Ether) ; M.P. = 151-153 ^{0}C ;^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.76 (d, J = 9 Hz , 1H), 8.17 (d, J= 12 Hz, 2H) ,8.12 (d, J = 6 Hz, 2H), 8.05 (d, J = 6 Hz, 1H), 7.94 (s, 1H) , 7.83- 7.72 (m, 2H) , 7.55 (d, J = 6 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 192.6 , 190.5 , 143.1 , 142.9 , 140.3 , 136.3 , 131.9 , 131.2 , 130.7 , 130.6 , 130.2 , 129.3 , 128.8 , 128.4 , 128.0 , 125.5 , 123.0 , 121.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{11}ClO_2]$: 318.0448 ; Found : 318.0448.

(E)-2-(2-(2-chlorophenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one(Table 2, entry 10, **3aj**)

White solid, Yield: 91% ; Rf : 0.25 (10% Ethyl Acetate in Petroleum Ether) ; M.P. = 150-152 ^{0}C ;^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.98 (d, J = 8 Hz , 1H), 8.16 (d, J = 8 Hz , 1H) ,8.09 (d, J = 8 Hz , 1H), 8.05 (d , J = 8 Hz, 1H) , 7.79-7.75 (m , 3H), 7.73 (s , 1H) ,7.51 (d, J = 4 Hz , 2H) , 7.45- 7.41 (m, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 192.9 , 191.0 , 150.0 , 143.2 , 142.2 , 139.2 , 132.7 , 132.2 , 131.9 , 131.2 , 130.8 , 130.7 , 130.2 , 128.9 , 128.6 , 127.9 , 127.2 , 125.9 , 125.6 , 122.0 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{11}ClO_2]$: 318.0448 ; Found : 318.0443.

(E)-2-(2-(2,4-dichlorophenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 11, **3ak**)

Yellow solid, Yield: 93% ; Rf : 0.3 (12% Ethyl Acetate in Petroleum Ether) ; M.P. = 155-157 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.99 (d, J = 9 Hz , 1H), 8.19 (d, J = 6 Hz , 1H) ,8.10 (t , 2H), 7.83-7.77 (m , 2H), 7.73 (d, J = 9 Hz, 1H) ,7.70 (s,1H) , 7.55 (d, J = 3 Hz, 1H) , 7.43 (d, J = 6 Hz , 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 192.7 , 191.7 , 143.4 , 142.7 , 138.4 , 137.5 , 131.9 , 131.3 , 131.2 , 130.7 , 128.9 , 128.8 , 128.0 , 127.6 , 126.0 , 125.0 , 122.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{10}Cl_2O_2]$: 352.0058 ; Found : 352.0055.

(E)-2-(2-(4-bromophenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one(Table 2, entry 12, **3al**)

Yellow solid, Yield: 90% ; Rf : 0.2 (10% Ethyl Acetate in Petroleum Ether) ; M.P. = 158-160 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.76 (d, J = 8 Hz , 1H), 8.19 (d, J = 8 Hz , 1H), 8.13 (d, J = 8 Hz , 1H), 8.08-8.04 (m , 3H), 7.94 (s, 1H), 7.83-7.74 (m, 2H), 7.72 (d, J = 8Hz , 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 190.7 , 188.1 145.9 , 143.7 , 134.2 , 132.7 , 132.7 , 132.5 , 131.9 , 131.7 , 130.8 , 130.5 , 130.2 , 129.0 , 128.5 , 128.5 , 126.8 , 126.1 , 123.3 , 122.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{11}BrO_2]$: 361.9942 ; Found : 361.9949 .

(E)-2-(2-(3-bromophenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 13, **3am**)

Yellow solid, Yield: 89% ; Rf : 0.3 (12% Ethyl Acetate in Petroleum Ether) ; M.P. = 155-157 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.79 (d, J = 4 Hz , 1H), 8.33 (d, J= 4 Hz, 1H) ,8.18 (d, J = 8 Hz, 1H), 8.13 (d, J = 8 Hz, 2H), 8.06 (d, J = 8 Hz, 1H), 7.93 (s, 1H) , 7.83- 7.74 (m, 3H) , 7.46 (t , 1H) , ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 192.6 , 190.3 , 143.3 , 143.2 , 139.7 , 136.5 , 132.0 , 131.7 , 131.2 , 130.7 , 130.6 , 130.5 , 128.8 , 128.5 , 128.0 , 127.4 , 125.6 , 123.3 , 122.7 , 122.2 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{11}BrO_2]$: 361.9942 ; Found : 361.9940 .

(E)-2-(2-(2-bromophenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 14, **3an**)

Yellow solid, Yield: 87% ; Rf : 0.2 (12% Ethyl Acetate in Petroleum Ether) ; M.P. = 159-161 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.03 (d, J = 4 Hz , 1H), 8.18 (d, J = 8 Hz , 1H), 8.11 (d, J = 4 Hz , 1H), 8.08 (d, J = 8 Hz , 1H), 7.79 (t, 2H), 7.73 – 7.69 (m, 3H), 7.48 (t, 1H), 7.41 (t, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 193.7 , 192.8 , 143.3 , 142.4 , 141.3 , 133.9 , 132.6 , 131.9 , 131.2 , 130.8 , 130.7 , 130.0 , 128.9 , 128.7 , 127.9 , 127.7 , 126.1 , 125.3 , 122.1 , 120.2 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{11}BrO_2]$: 361.9942 ; Found : 361.9948 .

(E)-2-(2-(4-iodophenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 15, **3ao**)

Yellow solid, Yield: 88% ; Rf : 0.3 (10% Ethyl Acetate in Petroleum Ether) ; M.P. = 163-165 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.76 (d, J = 9 Hz , 1H), 8.17 (d, J = 9 Hz , 1H), 8.11 (d, J = 6 Hz , 1H), 8.04 (d, J = 9 Hz , 1H), 7.94 (d, J = 9 Hz , 1H), 7.90 (s, 1H), 7.88 (d, J = 6 Hz , 2H), 7.81 – 7.71 (m, 2H) ; ^{13}C NMR

(75 MHz, $CDCl_3$), δ(ppm) = 192.6 , 190.9 , 143.1 , 143.0 , 138.2 , 137.3 , 131.9 , 131.2 , 130.7 , 130.1 , 128.8 , 128.4 , 127.9 , 125.5 , 122.8 , 122.1 , 102.0 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{11}IO_2]$: 409.9804 ; Found : 409.9805.

(E)-2-(2-(4-fluorophenyl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 16, **3ap**)

Yellow solid, Yield: 96% ; Rf : 0.2 (12% Ethyl Acetate in Petroleum Ether) ; M.P. = 139-141 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.72 (d, J = 8 Hz , 1H), 8.25 (d, J= 4 Hz, 1H) ,8.22 (d, J = 8 Hz, 1H), 8.17 (d, J = 8 Hz, 1H), 7.94 (s, 1H) , 7.82- 7.72 (m, 2H) , 7.25 (t , 2H) , ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 190.6 , 185.0 , 145.6 , 143.6 , 132.7 , 132.0 , 131.9 , 131.9 , 131.8 , 130.8 , 130.1 , 129.9 , 129.0 , 128.5 , 126.8 , 125.9 , 123.2 , 116.6 , 116.4 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{11}FO_2]$: 302.0743 ; Found : 302.0748.

(E)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)acenaphthylen-1(2H)-one (Table 2, entry 17, **3aq**)

White solid, Yield: 95% ; Rf : 0.25 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 163-165 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.23 (d, J = 8 Hz , 1H), 8.07 (d, J = 8 Hz , 1H) ,8.01 (d, J = 8 Hz , 1H), 7.95-7.88 (m , 2H), 7.80 (d, J = 8 Hz, 1H) ,7.76 (t ,1H) , 7.69- 7.65 (m, 3H) , 7.62 (t , 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 204.2 , 196.8 , 142.1 , 133.5 , 131.2 , 129.5 , 128.2 , 128.0 , 127.9 , 126.7 , 126.6 , 125.2 , 125.0 , 124.5 , 124.1 , 124.0 , 124.0 , 123.1 , 123.0 , 121.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{21}H_{11}F_3O_2]$:352.0711 ; Found : 352.0710.

(E)-2-(2-(naphthalen-2-yl)-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 2, entry 18, **3ar**)

Yellow solid, Yield: 94% ; Rf : 0.3 (10% Ethyl Acetate in Petroleum Ether) ; M.P. = 146-148 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.89 (d, J = 9 Hz , 1H), 8.81 (d, J = 9 Hz , 1H) ,8.19 (d, J = 9 Hz , 1H), 8.13 (d , J = 6 Hz, 2H) , 8.09-7.96 (m, 3H), 7.91 (s, 1H), 7.80 (t, 1H) , 7.76-7.68 (m , 2H), 7.65-7.56 (m, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 194.9 , 192.8 , 143.0 , 142.0 , 135.7 , 134.0 , 133.9 , 131.9 , 131.4 , 130.8 , 130.7 , 130.5 , 130.0 , 128.8 , 128.7 , 128.5 , 128.2 , 127.9 , 12.1 , 126.8 , 125.8 , 125.4 , 124.6 , 122.0 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{24}H_{14}O_2]$: 334.0994 ; Found : 334.0999.

(E)-2-(2-oxo-2-(thiophen-3-yl)ethylidene)acenaphthylen-1(2H)-one (Table 2, entry 19, **3as**)

Yellow solid, Yield: 88% ; Rf : 0.2 (10% Ethyl Acetate in Petroleum Ether) ; M.P. = 121-123 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.91 (d, J = 9 Hz , 1H), 8.38 (s,1H), 8.17 (d, J = 9 Hz , 1H) , 8.11 (d, J = 9 Hz , 1H), 8.04 (d , J = 9 Hz, 1H) , 7.88 (s, 1H), 7.80 – 7.73 (m, 3H), 7.44 (d, J = 3 Hz, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 192.9 , 185.1 , 143.6 , 143.1 , 142.4 , 133.7 , 131.9 , 131.3 , 130.8 , 130.7 , 128.8 , 128.3 , 127.9 , 127.3 , 127.0 , 125.9 , 123.9 , 122.0 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{18}H_{10}O_2S]$: 290.0402 ; Found : 290.0408.

methyl (E)-2-(2-oxoacenaphthylen-1(2H)-ylidene)acetate(Table 4, entry 1, **3ba**)

Yellow solid, Yield: 92% ; Rf : 0.25 (10% Ethyl Acetate in Petroleum Ether) ; M.P. = 122-124 ^{0}C ;^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.93 (d, J = 9 Hz , 1H), 8.16 (d, J = 9 Hz , 1H) , 8.07 (d, J = 6 Hz , 1H), 8.02 (d , J = 9 Hz, 1H) , 7.79- 7.73 (m, 2H), 6.99 (s, 1H), 3.94 (s,3H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 192.1 , 166.8 , 143.9 , 143.0 , 131.8 , 131.1 , 130.6 , 130.4 , 128.8 , 128.0 , 127.9 , 126.3 , 122.0 , 119.7 , 52.2 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{15}H_{10}O_3]$: 238.0630 ; Found : 238.0637.

ethyl (E)-2-(2-oxoacenaphthylen-1(2H)-ylidene)acetate(Table 4, entry 2, **3bb**)

Yellow solid, Yield: 90% ; Rf : 0.2 (10% Ethyl Acetate in Petroleum Ether) ; M.P. = 127-129 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.86 (d, J = 6 Hz , 1H), 8.08 (d, J = 3 Hz , 1H), 8.00- 7.9(m , 2H), 7.74- 7.66 (m, 2H), 6.94 (d, J = 6Hz , 1H), 4.42-4.35 (m, 2H), 1.42 (t, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 192.0 , 166.3 , 143.6 , 142.8 , 131.7 , 131.1 , 130.5 , 130.4 , 128.8 , 127.9 , 127.8 , 126.3 , 121.9 , 120.2 , 61.2 , 14.3 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{16}H_{12}O_3]$: 252.0786 ; Found : 252.0789.

tert-butyl (E)-2-(2-oxoacenaphthylen-1(2H)-ylidene)acetate (Table 4, entry 3, **3bc**)

Yellow solid, Yield: 89% ; Rf : 0.2 (8% Ethyl Acetate in Petroleum Ether) ; M.P. = 133-135 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.66 (d, J = 8 Hz , 1H), 8.13 (d, J = 8 Hz , 1H), 7.96 (d, J = 8 Hz , 1H), 7.92 (d, J = 4 Hz , 1H), 7.83 (d, J = 8 Hz , 1H), 7.68 (t,1H), 7.57 (t, 1H) 7.73 – 7.69 (m, 3H), 7.48 (t, 1H), 7.41 (t, 1H) , 1.42 (s, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 188.0 , 165.3 , 145.6 142.4 , 132.7 , 131.7 , 128.7 , 128.4 , 127.7 , 127.6 , 125.9 , 122.3 , 121.9 , 121.7 , 81.7 , 28.0 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{18}H_{16}O_3]$: 280.1099 ; Found : 280.1095.

benzyl (E)-2-(2-oxoacenaphthylen-1(2H)-ylidene)acetate (Table 4, entry 4 , **3bd**)

Yellow solid, Yield: 91% ; Rf : 0.3 (12% Ethyl Acetate in Petroleum Ether) ; M.P. = 142-144 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.92 (d, J = 6 Hz, 1H), 8.16 (d, J = 9 Hz, 1H) , 8.08-8.01 (m , 2H) , 7.80- 7.72 (m, 2H) , 7.48 (t, 2H) , 7.45-7.38 (m, 3H) , 7.05 (s, 1H) , 5.38 (s, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) =192.0 , 166.1 , 144.1 , 143.0 , 135.6 , 131.8 , 131.1 , 130.6 , 130.4 , 128.8 , 128.7 , 128.5 , 128.4 , 128.1 , 127.9 , 126.4 , 122.0 , 119.8 , 66.9 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{21}H_{14}O_3]$: 314.0943 ; Found : 314.0949.

(Z)-2-(1-nitro-2-oxo-2-phenylethylidene)acenaphthylen-1(2H)-one (Table 6, entry 1, **5aa**)

Orange solid, Yield: 86% ; Rf : 0.2 (12% Ethyl Acetate in Petroleum Ether) ; M.P. = 198-200 ^{0}C ;^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.40 (d, J = 6 Hz, 1H) , 8.23 (d, J = 6 Hz, 1H), 8.21- 8.09 (m, 3H) , 7.98 (d, J = 6Hz , 1H), 7.86-7.77 (m, 2H), 7.67 (t, 1H), 7.54 (t, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 190.6 , 186.4 , 143.5 , 135.2 , 134.6 , 132.6 , 130.8 , 130.4 , 130.0 , 130.0 , 129.6 , 129.2 , 129.1 , 129.0 , 128.5 , 127.0 , 125.8 , 123.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{11}NO_4]$: 329.0688 ; Found : 329.0681.

(Z)-2-(1-nitro-2-oxo-2-(p-tolyl)ethylidene)acenaphthylen-1(2H)-one (Table 6, entry 2, **5ab**)

Orange solid, Yield: 90% ; Rf : 0.3 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 204-206 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.36 (d, J= 8 Hz , 1H) , 8.23 (d, J= 12 Hz , 1H) , 8.15 (d, J= 8 Hz , 1H) , 7.99 (t , J= 8 Hz , 3H) , 7.85-7.78 (m , 2H) , 7.34 (d, J= 8 Hz , 2H) , 2.46 (s , 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 190.6 , 185.9 , 145.9 , 143.4, 132.8 , 132.5 , 132.1 , 130.8 , 130.7 , 130.3 , 130.0 , 129.9 , 129.9 , 129.4 , 129.0 , 128.5 , 127.0 , 125.6 , 123.0 , 21.9 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{23}H_{11}NO_4]$: 343.0845 ; Found : 343.0847.

(Z)-2-(2-(4-methoxyphenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one(Table 6, entry 3, **5ac**)

Orange solid, Yield: 87% ; Rf : 0.2 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 207-209 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.30 (d, J= 4 Hz , 1H), 8.22 (d , J= 8 Hz , 1H) , 8.14 (d, J = 8 Hz , 1H), 8.08 (d , J= 8 Hz, 2H) , 7.99 (d, J= 4Hz, 1H), 7.83- 7.78 (m, 2H), 7.01 (d, J = 12 Hz, 2H), 3.90 (s, 3H) ;

^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 190.5 , 184.6 , 164.8 , 146.6 , 143.1 , 135.2 , 132.5 , 131.8 , 131.7 , 130.8 , 130.1 , 129.7 , 128.9 , 128.5 , 128.3 , 127.5 , 127.0 , 125.2 , 125.0 , 123.0 , 55.6 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{21}H_{13}NO_5]$: 359.0794 ; Found : 359.0790.

(Z)-2-(2-(2-methoxyphenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 6, entry 4, **5ad**)

Orange solid, Yield: 86% ; Rf : 0.25 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 206-208 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.63 (d, J = 6 Hz, 1H) , 8.31 (d, J = 6 Hz, 1H), 8.19 (d, J = 6 Hz, 1H), 8.12 (d, J = 6 Hz, 1H), 7.95(d, J = 6 Hz, 1H) , 7.84-7.73 (m, 2H), 7.60 (t, 1H) 7.20 (t,1H) , 6.96 (d, J = 6 Hz, 1H), 3.74 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 191.5 , 184.2 , 159.8 , 143.5 , 135.9 , 132.4 , 131.5 , 130.7 , 130.6 , 130.1 , 129.6 , 129.0 , 128.2 , 128.0 , 126.8 , 124.6 , 122.7 , 121.6 , 112.0 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{21}H_{13}NO_5]$: 359.0794 ; Found : 359.0798.

(Z)-2-(2-(4-ethoxyphenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one(Table 6, entry 5, **5ae**)

Orange solid, Yield: 87% ; Rf : 0.2 (12% Ethyl Acetate in Petroleum Ether) ; M.P. = 210-212 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.29 (d, J = 9 Hz ,1H), 8.21 (d, J = 3 Hz ,1H), 8.13 (d, J = 6 Hz, 1H), 8.06 (d, J = 9 Hz ,4H), 7.98 (d, J = 6 Hz ,1H), 7.83- 7.77 (m ,2H) , 4.18-4.09 (m, 2H) , 1.47 (t, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 190.4 , 184.7 , 164.3 , 143.1 , 133.3 , 132.4 , 132.3 , 132.1 , 132.0 , 131.8 , 129.7 , 129.0 , 128.4 , 125.1 , 124.6 , 123.2 , 123.0 , 115.0 , 114.9 , 114.1 , 64.0 , 14.6 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{22}H_{15}NO_5]$: 373.0950 ; Found : 373.0958.

(Z)-2-(1-nitro-2-oxo-2-(4-propoxyphenyl)ethylidene)acenaphthylen-1(2H)-one(Table 6, entry 6, **5af**)

Orange solid, Yield: 89% ; Rf : 0.3 (20% Ethyl Acetate in Petroleum Ether) ; M.P. =215-217 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.28 (d, J = 8 Hz, 1H), 8.22 (d, J = 8 Hz, 1H), 8.14 (d, J = 8 Hz, 1H), 8.06 (d, J = 8 Hz, 1H), 7.98 (d, J = 8 Hz, 1H), 7.80 (d, J = 8 Hz, 2H), 6.99 (d, J= 4 Hz, 2H), 4.02 (t, 2H), 1.88-1.82 (m 2H), 1.06 (t, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 190.4 , 184.5 , 164.5 , 143.1 , 133.2 , 132.4 , 131.8 , 130.8 , 130.2 , 129.7 , 128.9 , 128.4 , 128.0 , 127.0 ,

125.1 , 123.0 , 114.9 , 69.9 , 22.4 , 10.5 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{23}H_{17}NO_5]$: 387.1107 ; Found : 387.1109.

(Z)-2-(2-(4-hydroxyphenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 6, entry 7, **5ag**)

Orange solid, Yield: 86% ; Rf : 0.25 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 207-209 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 11.04 (s, 1H), 8.77 (d, J = 4 Hz, 1H), 8.47 (d, J = 8 Hz, 1H) , 8.34 (d, J = 8 Hz , 1H), 8.25 (d, J = 8 Hz, 1H), 8.19 (d , J = 8 Hz, 1H), 7.98 (d, J = 8 Hz, 1H), 7.87-7.79 (m, 2H) , 7.34 (d, J = 8Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) =.190.8 , 183.8 , 159.2 , 143.9 , 137.0 , 133.5 , 133.3 , 132.9 , 130.8 , 130.5 , 129.6 , 129.1 , 128.6 , 128.5 , 128.5 , 127.7 , 127.1 , 126.6 , 123.3 , 121.3 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{11}NO_5]$: 345.0637 ; Found : 345.0630.

(Z)-2-(2-(3-hydroxyphenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 6, entry 8, **5ah**)

Orange solid, Yield: 85% ; Rf : 0.3 (20% Ethyl Acetate in Petroleum Ether) ; M.P. = 203-205 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.61 (s, 1H), 8.92 (d, J = 12 Hz , 1H), 8.32 (d, J = 12 Hz , 1H), 8.21 (d, J = 12 Hz , 1H), 8.16-8.09 (m , 2H), 7.96 (d, J = 4Hz , 1H), 7.91 (s, 1H) , 7.5-7.74 (m, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 192.4 , 186.2 , 155.1 , 144.4 , 143.6 , 132.0 , 130.7 , 129.1 , 128.8 , 128.0 , 126.0 , 125.9 , 122.3 , 121.4 , 120.6 , 119.5 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{11}NO_5]$: 345.0637 ; Found : 345.0635.

(Z)-2-(2-(4-chlorophenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 6, entry 9, **5ai**)

Orange solid, Yield: 88% ; Rf : 0.25 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 208-210 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.43(d, J= 9 Hz , 1H) , 8.24 (d, J= 6 Hz , 1H) , 8.18 (d , J= 9 Hz , 1H), 8.04-7.98 (m, 3H) , 7.87-7.79 (m , 2H) , 7.52 (d, J = 9 Hz , 2H) ;^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 190.7 , 185.5 , 143.7 , 141.1, 133.8 , 132.8 , 132.7 , 130.8 , 130.5 , 130.2 , 129.8, 129.5 , 129.0 , 128.5 , 126.8 , 126.1 , 123.2 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{10}ClNO_4]$: 363.0298 ; Found : 363.0299.

(Z)-2-(2-(2-chlorophenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 6, entry 10, **5aj**)

Orange solid, Yield: 87% ; Rf : 0.3 (20% Ethyl Acetate in Petroleum Ether) ; M.P. = 205-207 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.09 (d, J = 8 Hz, 1H), 8.70 (d, J = 8 Hz, 1H), 8.58 (d, J = 8 Hz, 1H), 8.53 (d, J = 8 Hz, 2H), 8.20 (t, 3H), 7.79 (t, 2H), 7.51 (d, J = 8 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm) = 191.1 , 184.8 , 143.8 , 134.9 , 134.3 , 132.6 , 132.5 , 132.4 , 131.7 , 131.7 , 130.7 , 130.3 , 129.1 , 128.4 , 127.3 127.3 , 126.9 , 125.3 , 124.7 , 123.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{10}ClNO_4]$: 363.0298 ; Found : 363.0291.

(Z)-2-(2-(2,4-dichlorophenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one(Table 6, entry 11, **5ak**)

Orange solid, Yield: 88% ; Rf : 0.2 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 214-216 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.62 (d, J = 8 Hz, 1H), 8.24 (d, J = 8 Hz, 1H), 8.17 (t, 2 H), 8.00 (d, J = 8 Hz, 1H), 7.87- 7.79 (m, 2H) , 7.53 (d, J = 4 Hz, 1H), 7.45 (d, J = 8 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 191.2 , 183.9 , 144.1 , 140.2 , 135.1 , 133.2 , 132.7 , 132.2 , 131.4 , 130.8 , 130.5 , 129.6 , 129.1 , 128.5 ,127.8 , 127.2 , 125.6 , 124.8 , 123.3 , 122.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_9Cl_2NO_4]$: 396.9909 ; Found : 396.9905.

(Z)-2-(2-(4-bromophenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 6, entry 12, **5al**)

Orange solid, Yield: 89% ; Rf : 0.3 (20% Ethyl Acetate in Petroleum Ether) ; M.P. = 220-222 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.44 (d, J= 12 Hz , 1H) , 8.25 (d, J= 12 Hz , 1H) , 8.18 (d , J = 12 Hz , 1H) , 8.00 (d, J = 8 Hz , 1H), 7.96 (d, J= 12 Hz, 2H) , 7.87-7.79 (m, 2H) , 7.69 (d, J = 12 Hz , 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 190.7 , 188.1, 145.9 , 143.7 , 134.2 , 132.7 , 132.7 , 132.5 , 131.9 , 131.7, 130.8 , 130.5 , 130.2 , 129.0 , 128.5 , 128.5 , 126.8 , 126.1 , 123.3 , 122.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{10}BrNO_4]$: 406.9793 ; Found : 406.9790.

(Z)-2-(2-(3-bromophenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one(Table 6, entry 13, **5am**)

Orange solid, Yield: 88% ; Rf : 0.25 (20% Ethyl Acetate in Petroleum Ether) ; M.P. = 219-221 ^{0}C ;^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.49 (d, J= 8 Hz , 1H) , 8.26-8.18 (m , 3H) , 8.01 (d , J = 4 Hz , 2H) , 7.88-7.78 (m , 3H) , 7.42 (t ,

1H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 190.7 , 185.5 , 145.1 , 143.9 , 137.3 , 137.1 , 133.2 , 132.8 , 131.8 , 130.8 , 130.6 , 130.4 , 129.7 , 129.1 , 128.5 , 127.7 , 126.8 , 126.5 , 123.4 , 123.3 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{10}BrNO_4]$: 406.9793 ; Found : 406.9799.

(Z)-2-(2-(2-bromophenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one(Table 6, entry 14, **5an**)

Orange solid, Yield: 89% ; Rf : 0.3 (20% Ethyl Acetate in Petroleum Ether) ; M.P. = 217-219 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.05 (d, J = 12 Hz, 1H), 8.66 (d, J = 8 Hz, 1H), 8.45 (d, J = 8 H, 1H), 8.40 (d, J = 8 Hz, 1H), 8.18 (d, J = 8 Hz, 1H), 8.12 (d, J = 8 Hz, 1H), 7.75 (t, 2H), 7.44 (t, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 190.8 , 185.3 , 143.62 , 135.4 , 135.3 , 134.7 , 134.2 , 132.7 , 132.6 , 130.3 , 129.0 , 128.5 , 127.8 , 127.7 , 127.6 , 126.5 , 124.9 , 124.8 , 123.2 , 122.6 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{10}BrNO_4]$: 406.9793 ; Found : 406.9797.

(Z)-2-(2-(4-iodophenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 6, entry 15, **5ao**)

Orange solid, Yield: 84% ; Rf : 0.25 (12% Ethyl Acetate in Petroleum Ether) ; M.P. = 223-225 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.12 (d, J = 9 Hz, 1H) , 8.71(d, J = 9 Hz, 1H), 8.64 (d, J = 6Hz, 1H), 8.37 (d, J = 3 Hz, 1H), 8.34 (d, J = 3 Hz, 1H), 7.90 (d, J= 9 Hz, 3H), 7.81 (d, J = 9 Hz, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 190.6 , 186.1 , 143.6 , 138.7 , 138.5 , 135.4 , 133.5 , 132.7 , 132.2 , 130.4 , 130.3 , 129.0 , 128.5 , 127.5 , 127.2 126.1 , 124.8 , 124.2 , 123.2 , 122.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{10}INO_4]$: 454.9655 ; Found : 454.9652.

(Z)-2-(2-(4-fluorophenyl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one(Table 6, entry 16, **5ap**)

Orange solid, Yield: 86% ; Rf : 0.2 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 207-209 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.30 (d , J= 8 Hz , 1H) , 8.14 (d, J = 8 Hz , 1H) , 8.08-8.02 (m , 3H) , 7.9 (d, J= 8 Hz , 1H), 7.76-7.71 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 190.6 , 185.0 , 165.3 , 143.6 , 132.7 , 132.6 , 132.0 , 131.9 , 131.9 , 131.8 , 130.8 , 130.1 , 129.9 , 129.0 , 128.5 , 126.8 , 125.9 , 123.2 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{20}H_{10}FNO_4]$: 347.0594 ; Found : 347.0599.

(Z)-2-(1-nitro-2-oxo-2-(4-(trifluoromethyl)phenyl)ethylidene)acenaphthylen-1(2H)-one (Table 6, entry 17, **5aq**)

Orange solid, Yield: 88% ; Rf : 0.2 (20% Ethyl Acetate in Petroleum Ether) ; M.P. = 213-215 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.51 (d, J = 8 Hz, 1H), 8.26 (d, J = 8 Hz , 1H) , 8.20 (d, J = 8 Hz, 3H), 8.00 (d, J = 8 Hz, 1H), 7.87 (t, 1H), 7.82 (t, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 190.8 , 185.9 , 144.0 , 138.0 , 133.4 , 132.8 130.8 , 130.5 , 129.6 , 129.5 , 129.3 , 129.1 , 128.6 , 126.7 , 126.6 , 126.3 , 126.2 , 126.2 , 126.1 , 123.4 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{21}H_{10}F_3NO_4]$: 397.0562 ; Found : 397.0560.

(Z)-2-(2-(naphthalen-2-yl)-1-nitro-2-oxoethylidene)acenaphthylen-1(2H)-one (Table 6, entry 18, **5ar**)

Orange solid, Yield: 90% ; Rf : 0.3 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 204-206 ^{0}C ;^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.35 (d, J = 8 Hz, 1H), 8.31 (d, J = 8 Hz, 1H), 8.21-8.10 (m, 4H), 7.97 (d, J = 4 Hz, 1H), 7.92 (d, J = 4 Hz, 1H), 7.82 (t, 2H), 7.76 (t, 1H), 7.67 (t, 1H) , 7.48 (t, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 190.7 , 187.2 , 147.7 , 143.2 , 135.6 , 134.1 , 132.6 , 132.5 , 131.7 , 131.6 , 131.1 , 130.8 , 129.8 , 129.5 , 129.0 , 128.7 , 128.5 , 127.2 , 126.3 , 125.2 , 124.3 , 123.0 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{24}H_{13}NO_4]$: 347.0594 ; Found : 347.0598 .

(Z)-2-(1-nitro-2-oxo-2-(thiophen-2-yl)ethylidene)acenaphthylen-1(2H)-one(Table 6, entry 19, **5as**)

Orange solid, Yield: 87% ; Rf : 0.3 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 199-201 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.31 (d, J = 12 Hz, 2H), 8.27 – 8.20 (m, 2H), 8.12 (d, J = 8 Hz, 2H), 7.87 (t, 2H) , 7.79 (t, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 188.1 , 179.3 , 145.9 , 135.3 , 132.7 , 132.6 , 131.0 , 129.9 , 129.0 , 128.6 , 128.5 , 128.5 , 127.6 , 127.5 , 126.9 , 125.4 , 123.1 ,122.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{18}H_9NO_4S]$: 335.0252 ; Found : 335.0251 .

methyl (Z)-2-nitro-2-(2-oxoacenaphthylen-1(2H)-ylidene)acetate(Table 7, entry 1, **5ba**)

Orange solid, Yield: 88% ; Rf : 0.2 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 195-197 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.89 (d, J = 8 Hz,

1H) , 8.18 (d , J = 8 Hz, 1H) , 8.10 (d , J = 8 Hz, 1H) , 8.04 (d , J = 8 Hz, 1H), 7.79 (d, J = 8 Hz, 2H), 4.04 (s ,3H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 189.7 , 185.0 , 160.0 , 143.0 , 132.6 , 132.4 , 130.0 , 129.0 , 128.5 , 128.5 , 128.4 , 128.0 , 123.1 , 123.0 , 54.0 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{15}H_9NO_5]$: 283.0481 ; Found : 283.0483 .

ethyl (Z)-2-nitro-2-(2-oxoacenaphthylen-1(2H)-ylidene)acetate (Table 7, entry 2, **5bb**)

Orange solid, Yield: 90% ; Rf : 0.25 (15% Ethyl Acetate in Petroleum Ether) ; M.P. = 201-203 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.37 (d, J = 4 Hz, 1H), 8.15 (t, 2H), 8.10-8.04 (m, 2H), 8.00 (d, J = 8 Hz, 1H), 7.73 (d, J = 8 Hz , 2H) 4.62-4.57 (M, 2H), 1.49 (t, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 189.6 , 180.0 , 160.1 , 143.4 , 132.5 , 132.3 , 130.4 , 129.9 , 129.0 , 128.3 , 128.0 , 126.9 , 123.0 , 122.9 , 63.6 , 13.8 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{16}H_{11}NO_5]$: 297.0637 ; Found : 297.0639 .

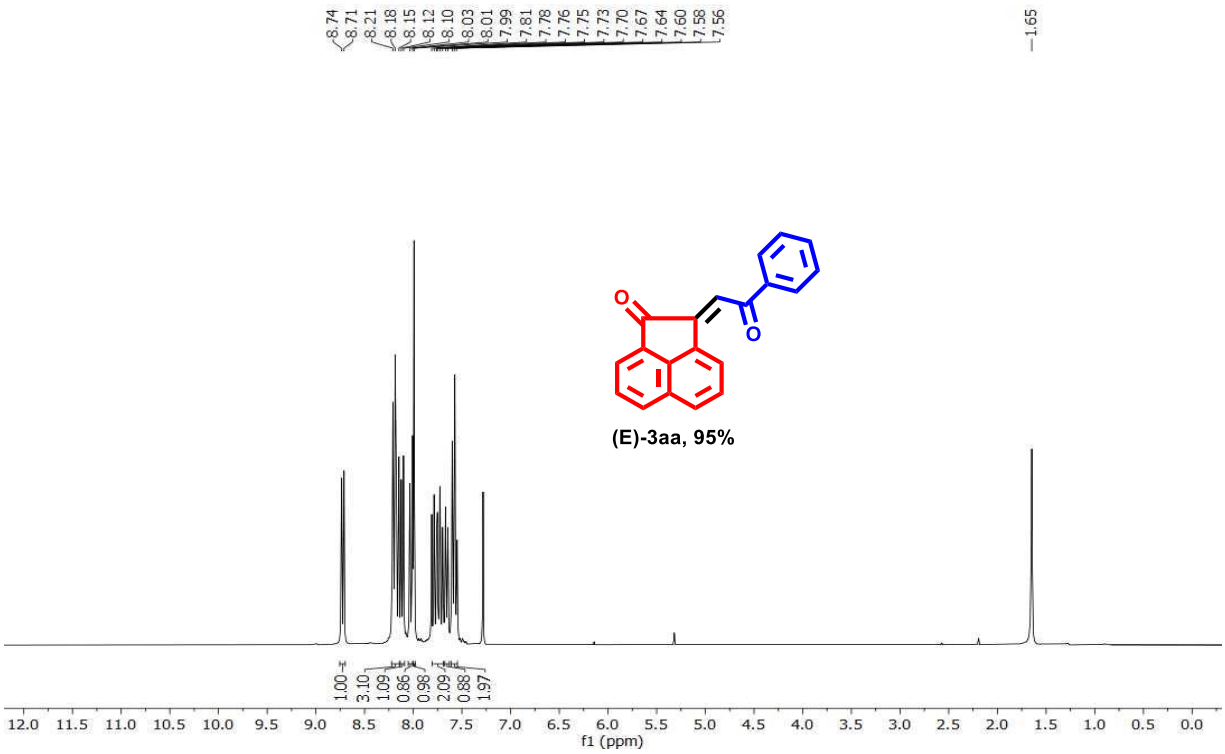
tert-butyl (Z)-2-nitro-2-(2-oxoacenaphthylen-1(2H)-ylidene)acetate(Table 7, entry 3 , **5bc**)

Orange solid, Yield: 89% ; Rf : 0.2 (12% Ethyl Acetate in Petroleum Ether) ; M.P. = 210-212 ^{0}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.38 (d, J = 4 Hz, 1H), 8.17 (t, 2H), 8.12-8.02 (m, 2H) , 8.00 (d, J = 8 Hz, 1H) , 7.74 (d, J = 8 Hz , 2H) , 1.44 (s, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm) = 188.9, 165.4, 145.7, 143.1, 132.7, 131.7, 128.7, 128.4, 127.8, 127.7, 125.9, 122.3, 121.9, 121.7, 81.9, 28.1 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{16}H_{11}NO_5]$: 325.0950 ; Found : 325.0955 .

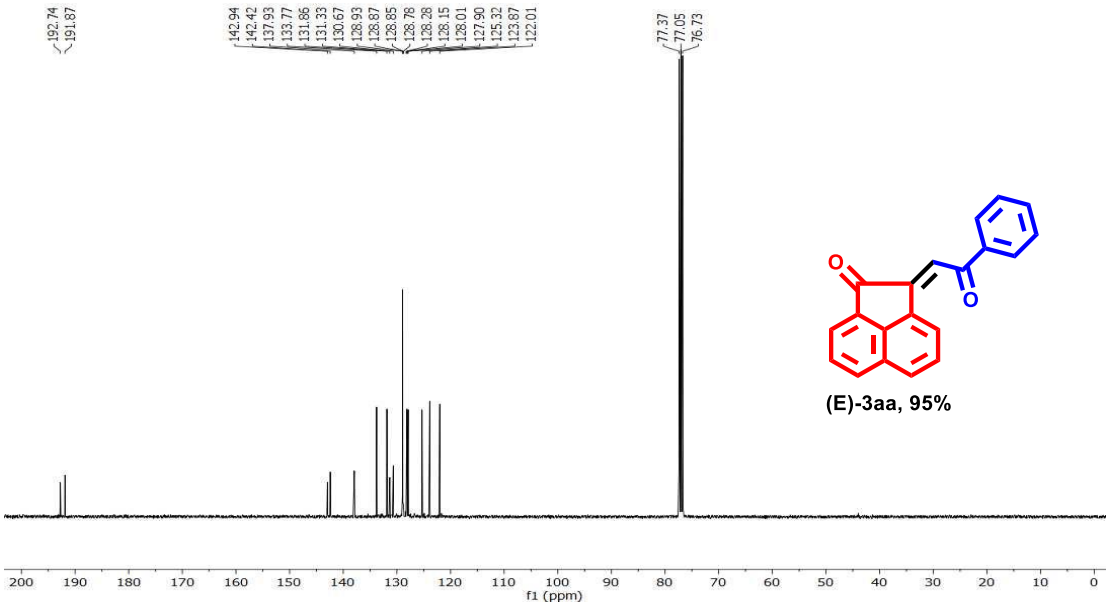
benzyl (Z)-2-nitro-2-(2-oxoacenaphthylen-1(2H)-ylidene)acetate (Table 7, entry 4 , **5bd**)

Orange solid, Yield: 87% ; Rf : 0.3 (20% Ethyl Acetate in Petroleum Ether) ; M.P. = 217-219 ^{0}C ; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.48 (d, J = 9 Hz, 1H) , 8.19 (d, J = 9Hz, 1H) , 8.13- 8.05 (m, 2H) , 7.82- 7.73 (m, 2H) , 7.52 (d, J = 6 Hz , 2H) , 7.42 (d, J = 6 Hz , 3H), 5.56 (s,2H) ; ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm) = 189.7 , 160.2 , 143.6 , 134.4 , 132.5 , 130.6 , 130.6 , 129.7 , 129.1 , 129.0 , 128.8 , 128.8 , 128.7 , 128.7, 128.4 , 128.4 , 127.3 , 126.8 , 123.1 , 69.3 ; HRMS (ESI/TOF-Q) M/Z : $[M+H]^+$ Calcd. for $[C_{21}H_{13}NO_5]$: 359.0794 ; Found : 359.0792.

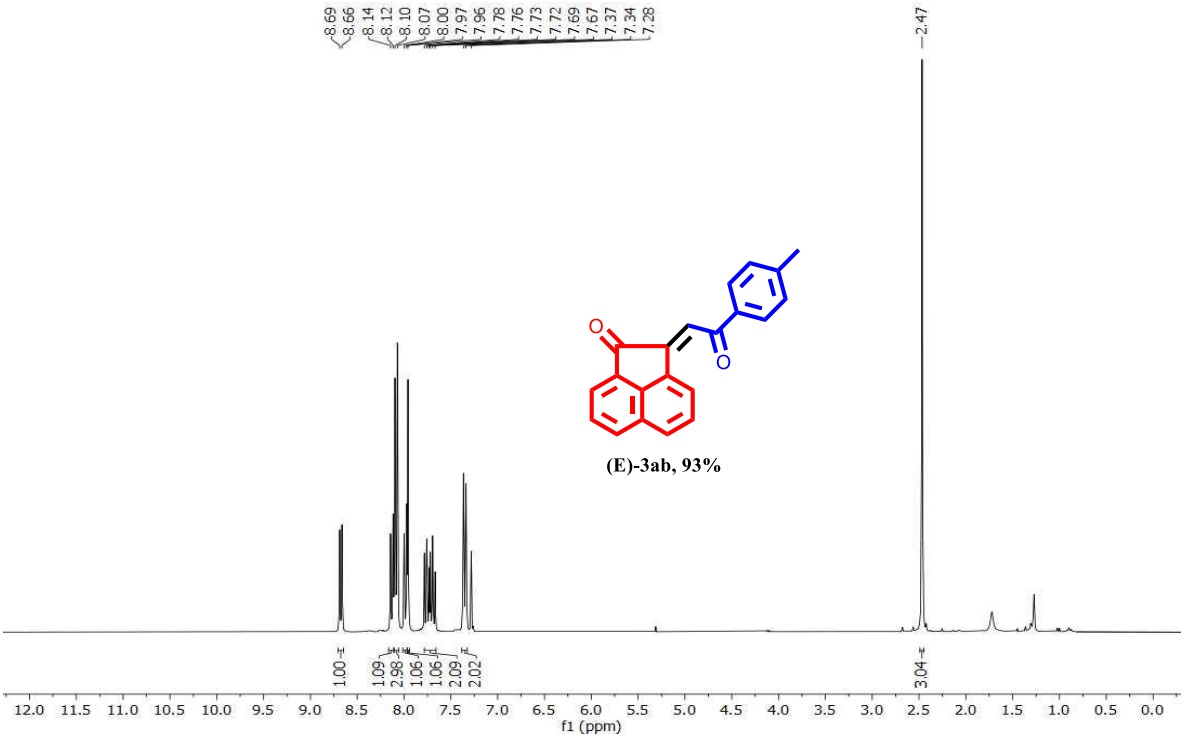
^{1}H and ^{13}C NMR of compounds



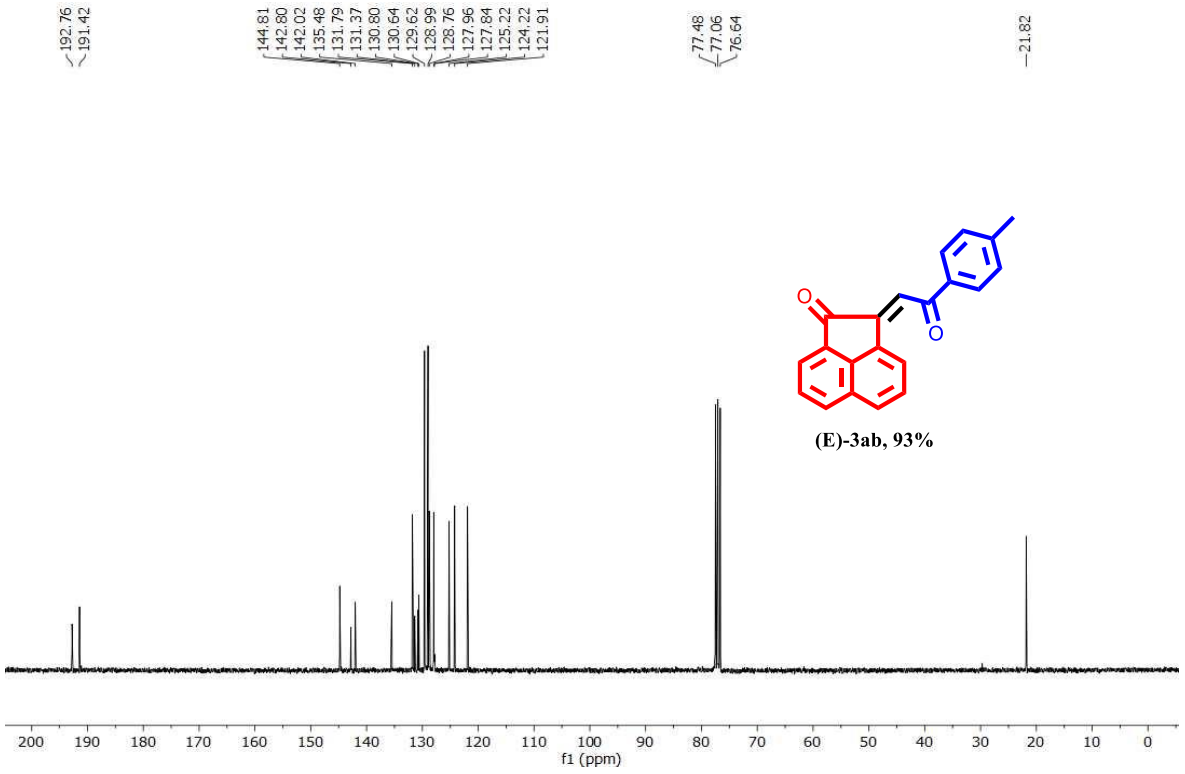
^{1}H NMR Spectrum of (E)-3aa



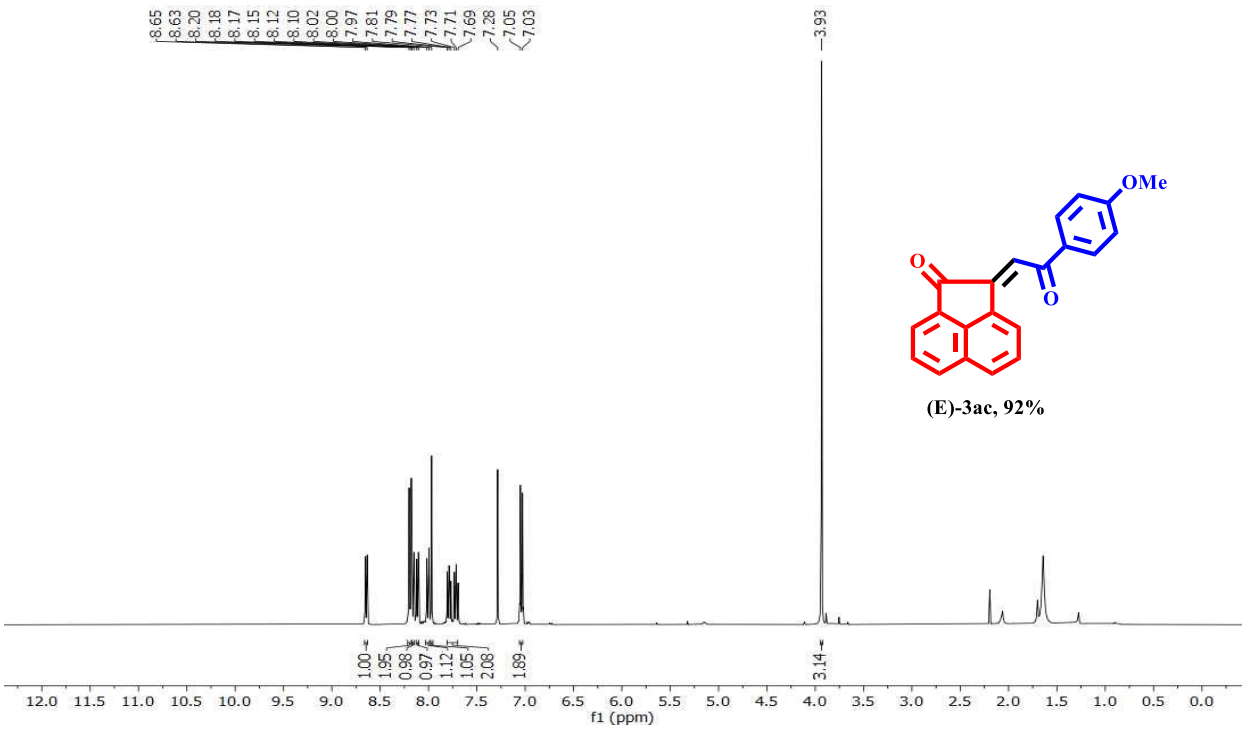
^{13}C NMR Spectrum of (E)-3aa



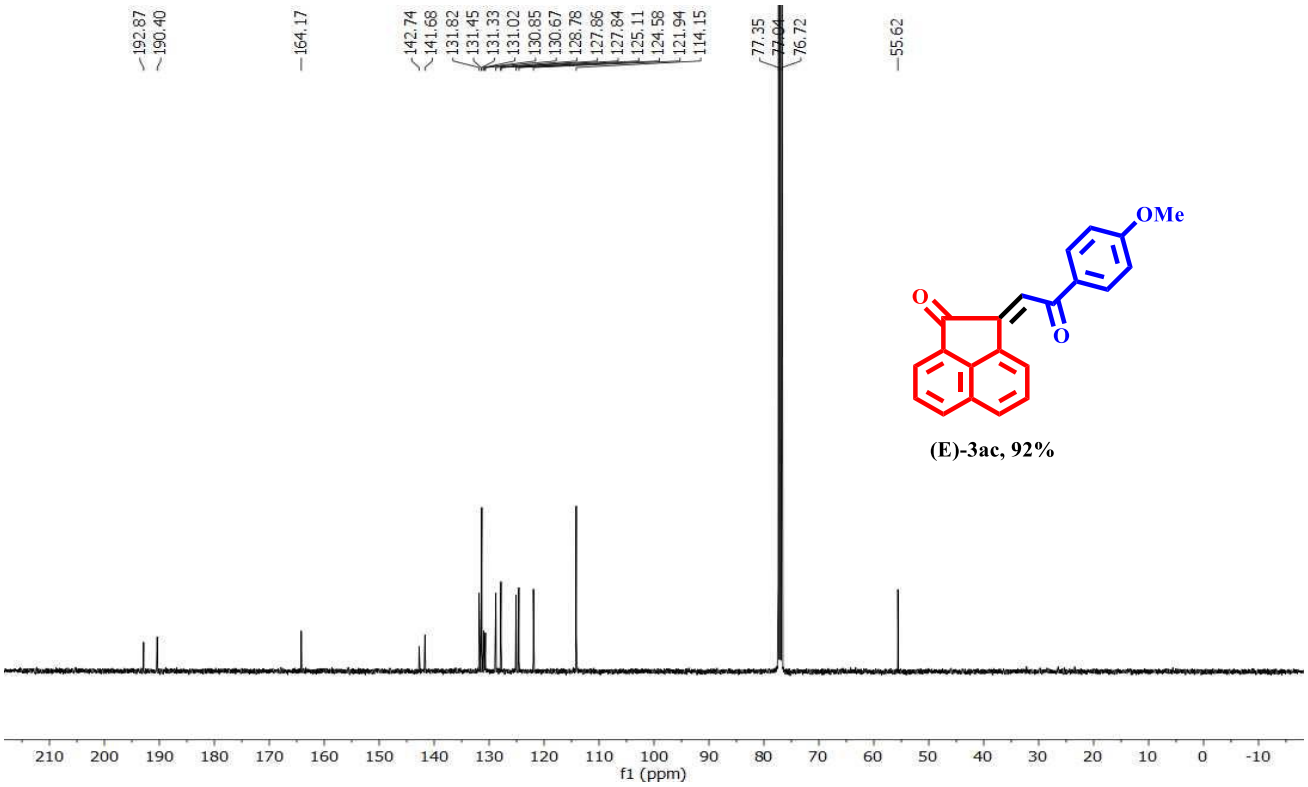
^{1}H NMR Spectrum of (E)-3ab



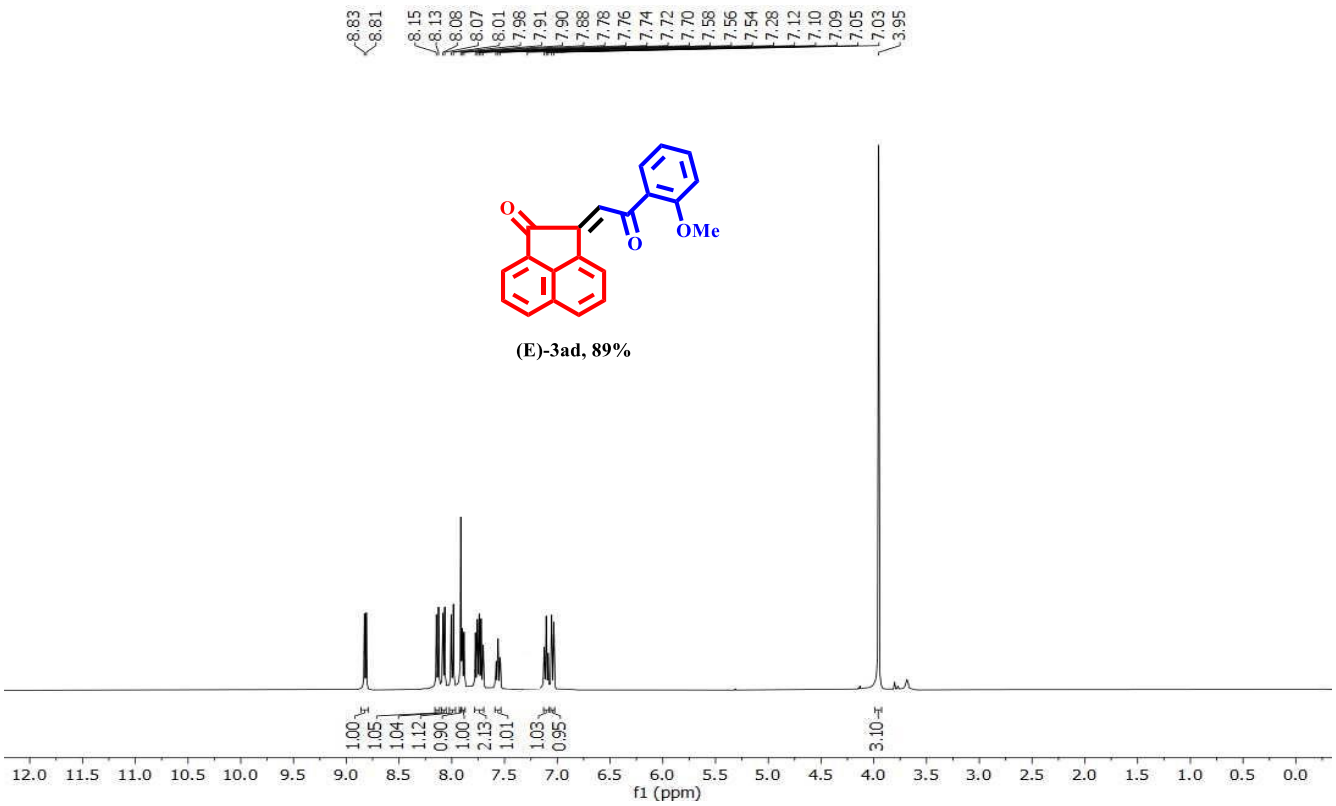
^{13}C NMR Spectrum of (E)-3ab



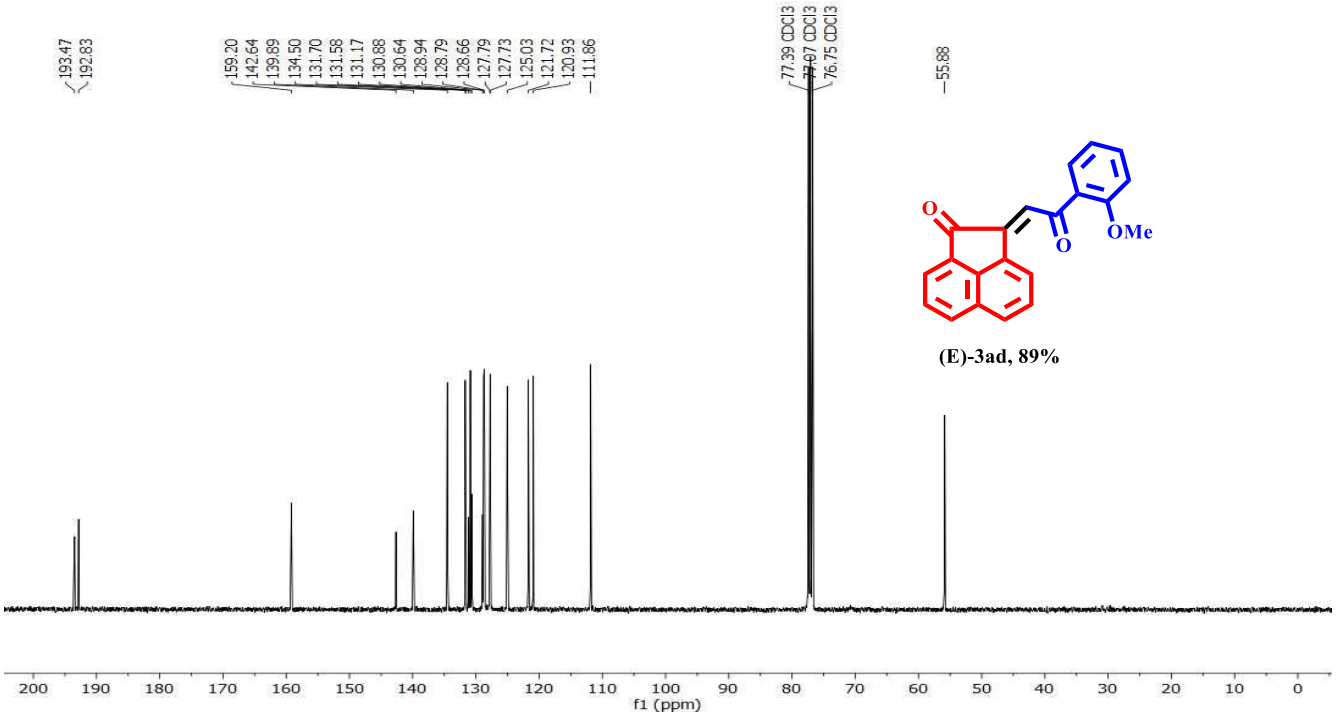
^{1}H NMR Spectrum of (E)-3ac



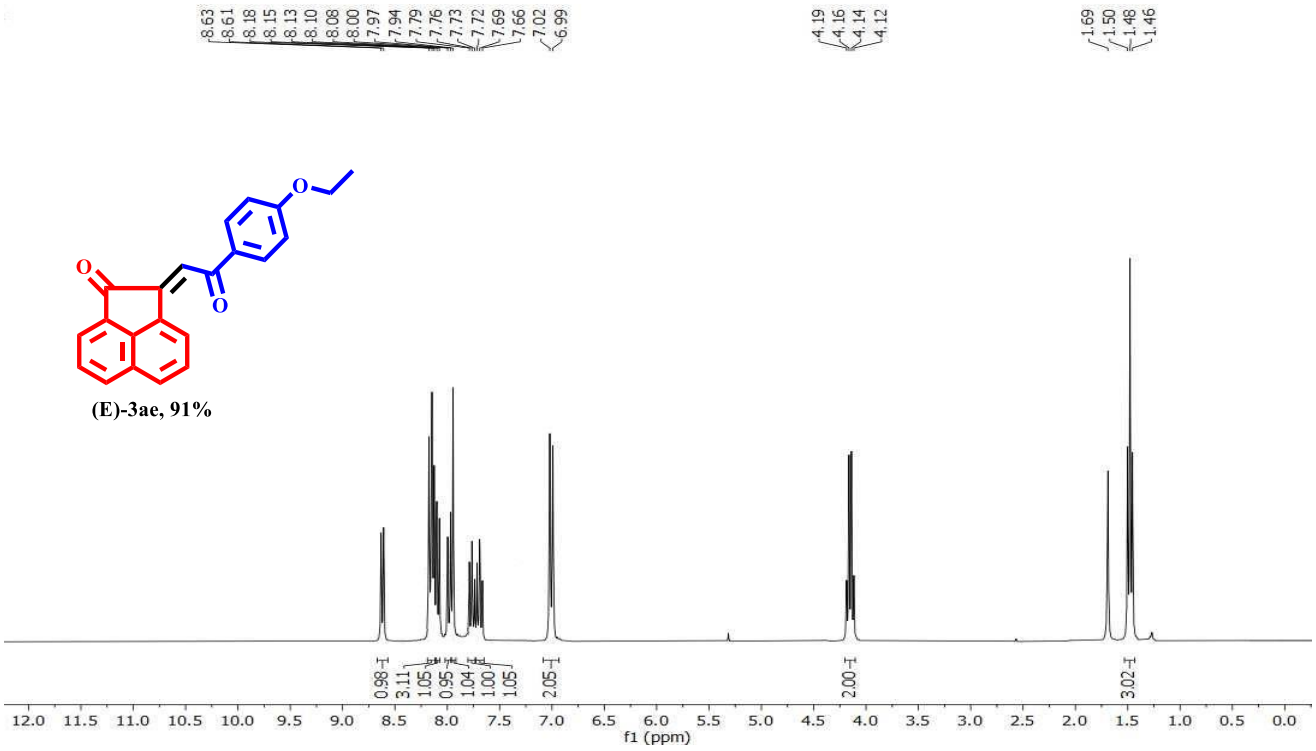
^{13}C NMR Spectrum of (E)-3ac



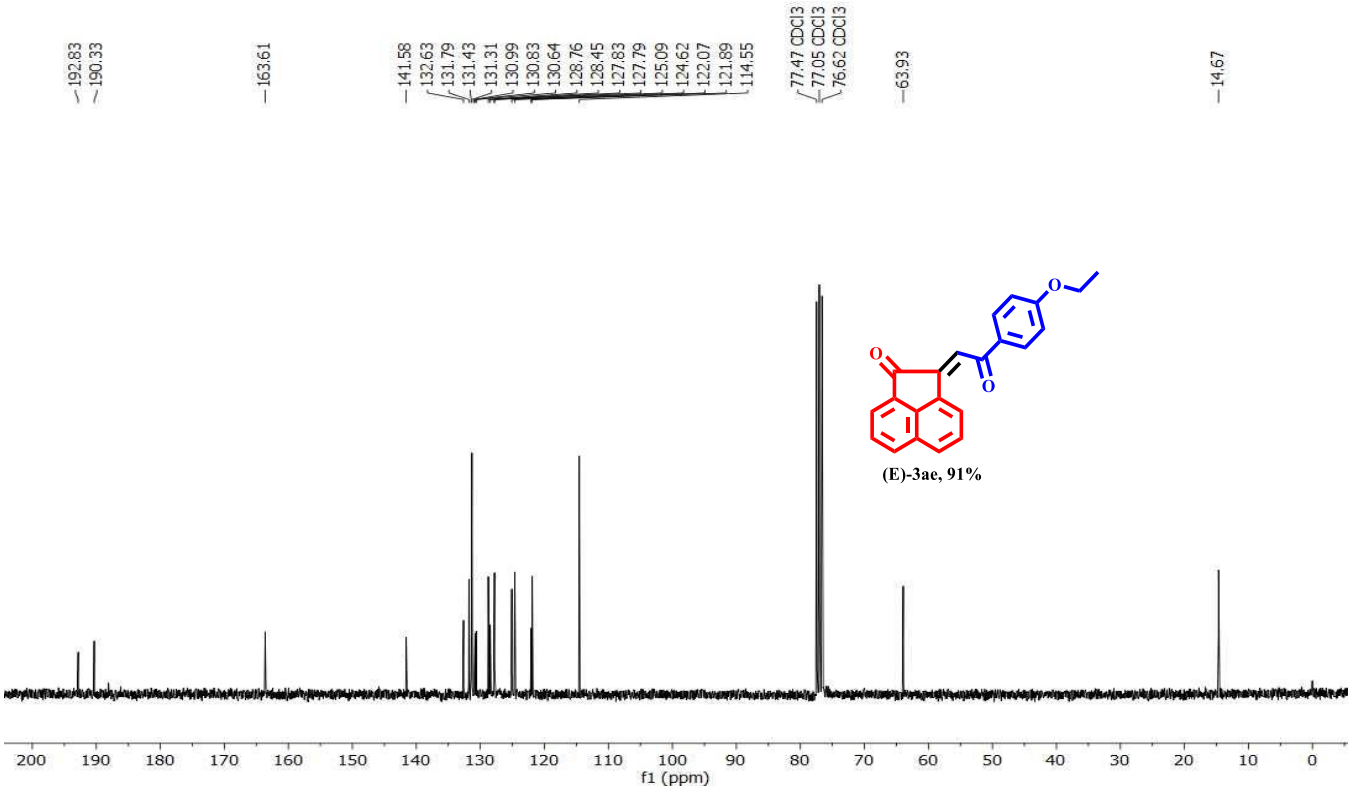
^{1}H NMR Spectrum of (E)-3ad



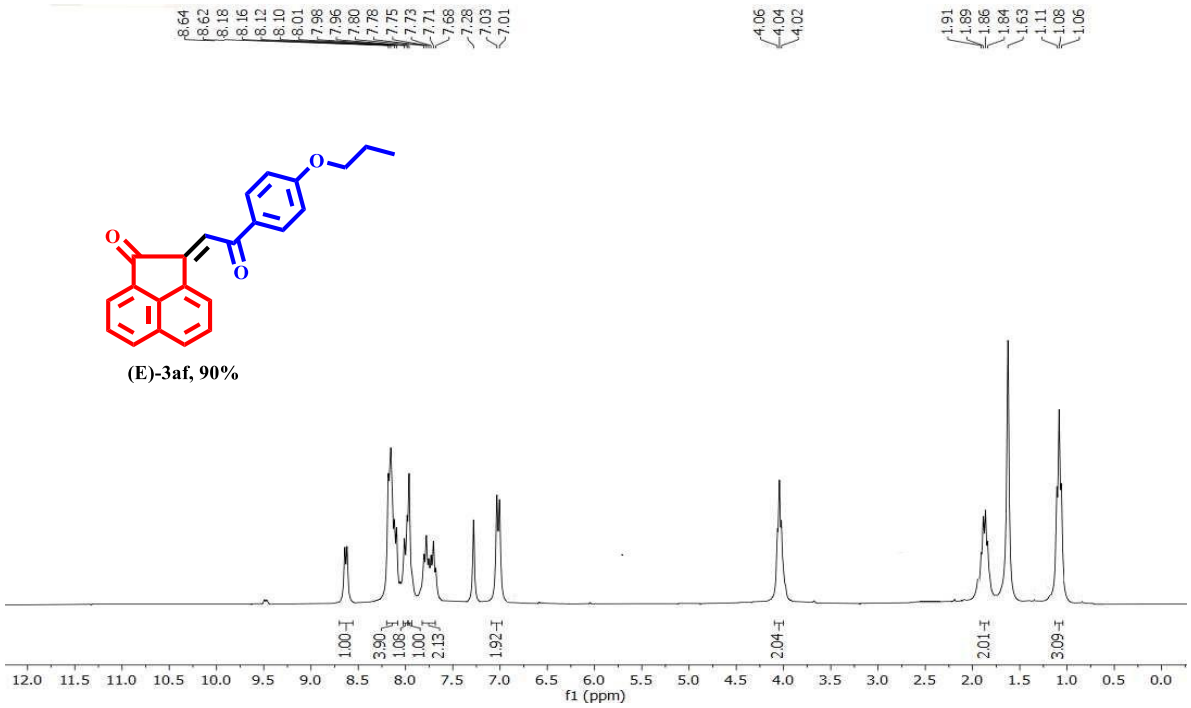
^{13}C NMR Spectrum of (E)-3ad



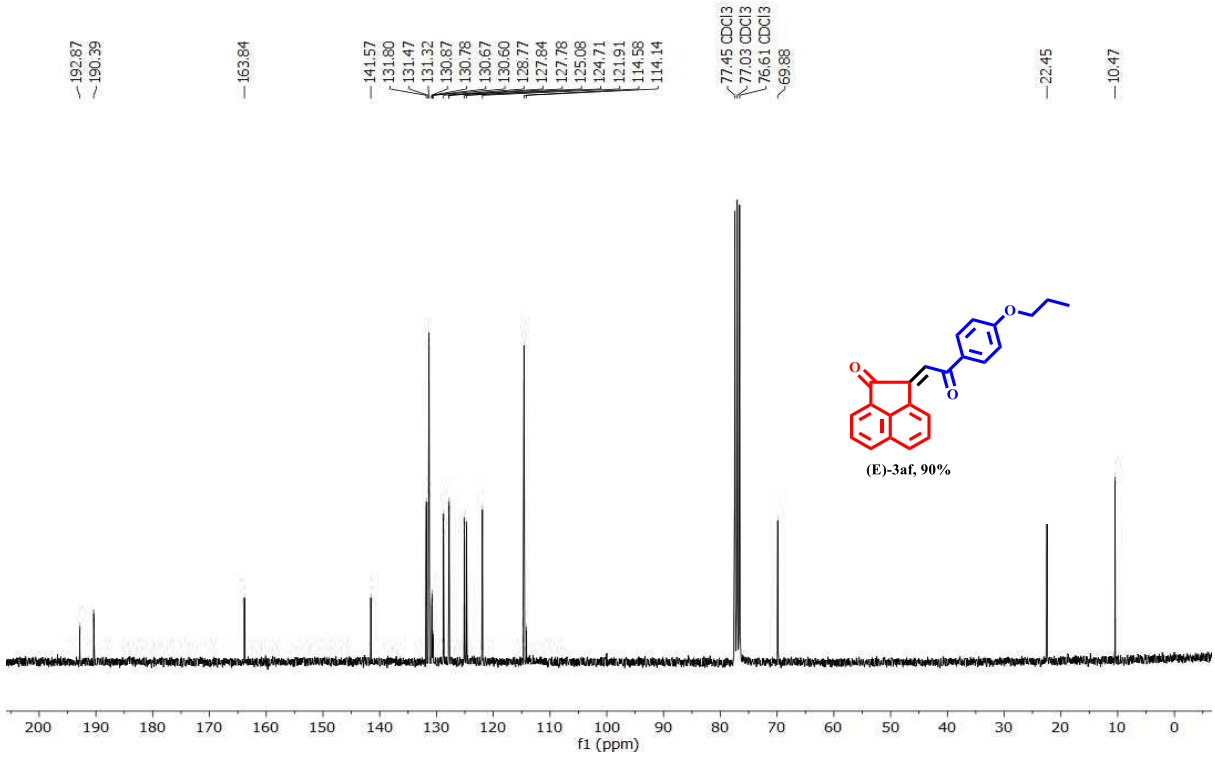
^{1}H NMR Spectrum of (E)-3ae



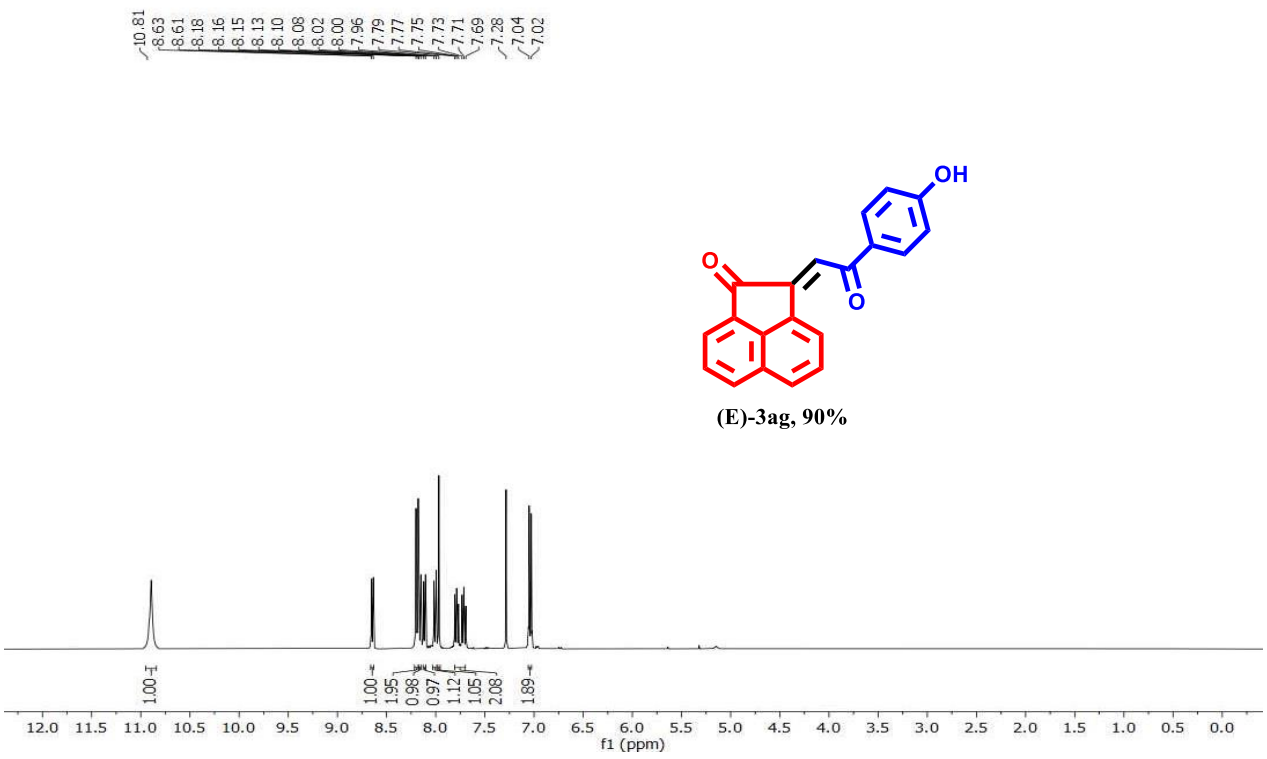
^{13}C NMR Spectrum of (E)-3ae



^{1}H NMR Spectrum of (E)-3af

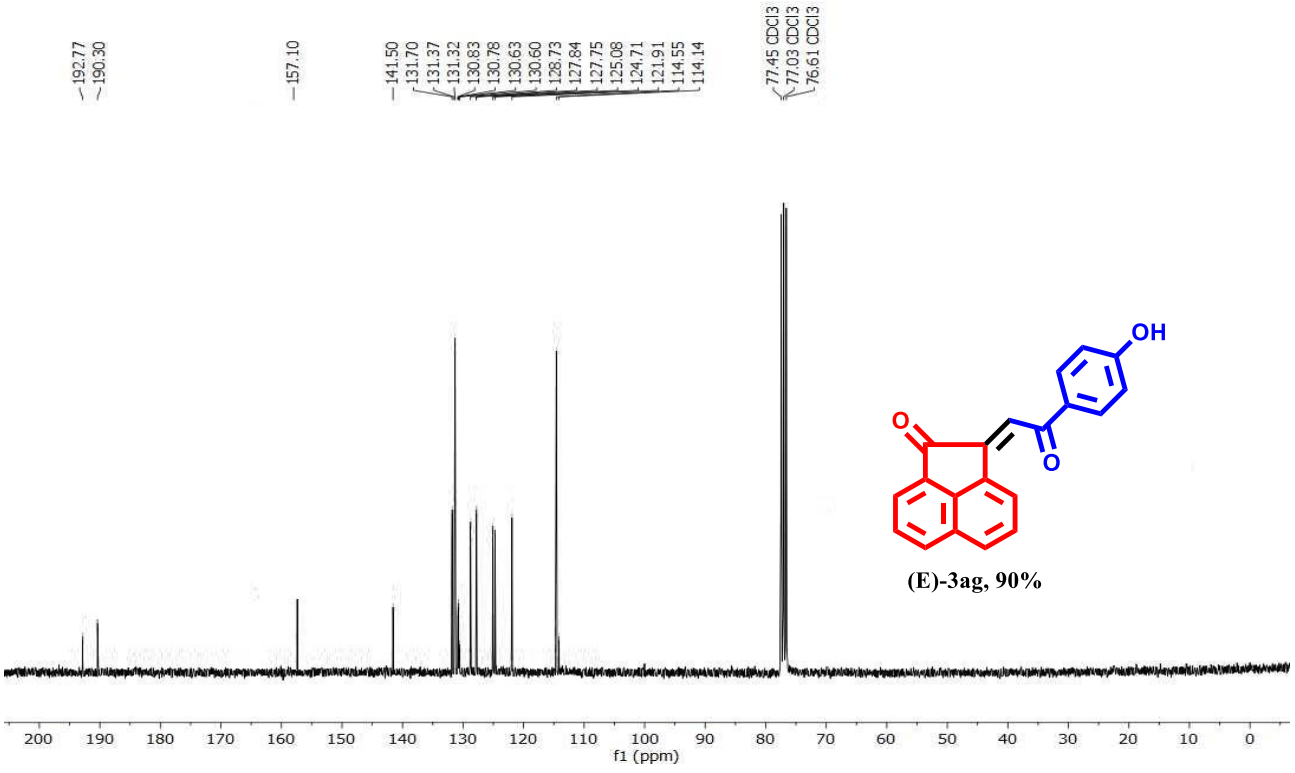


^{13}C NMR Spectrum of (E)-3af



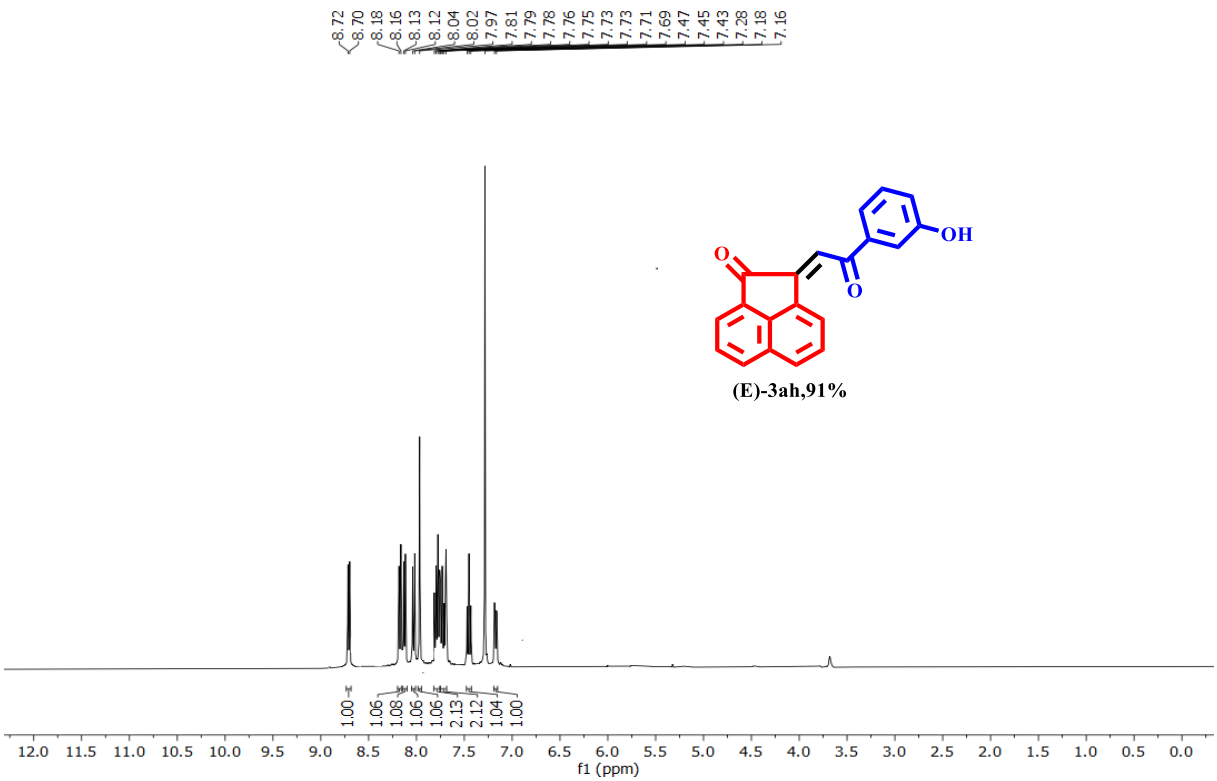
(E)-3ag, 90%

^{1}H NMR Spectrum of (E)-3ag

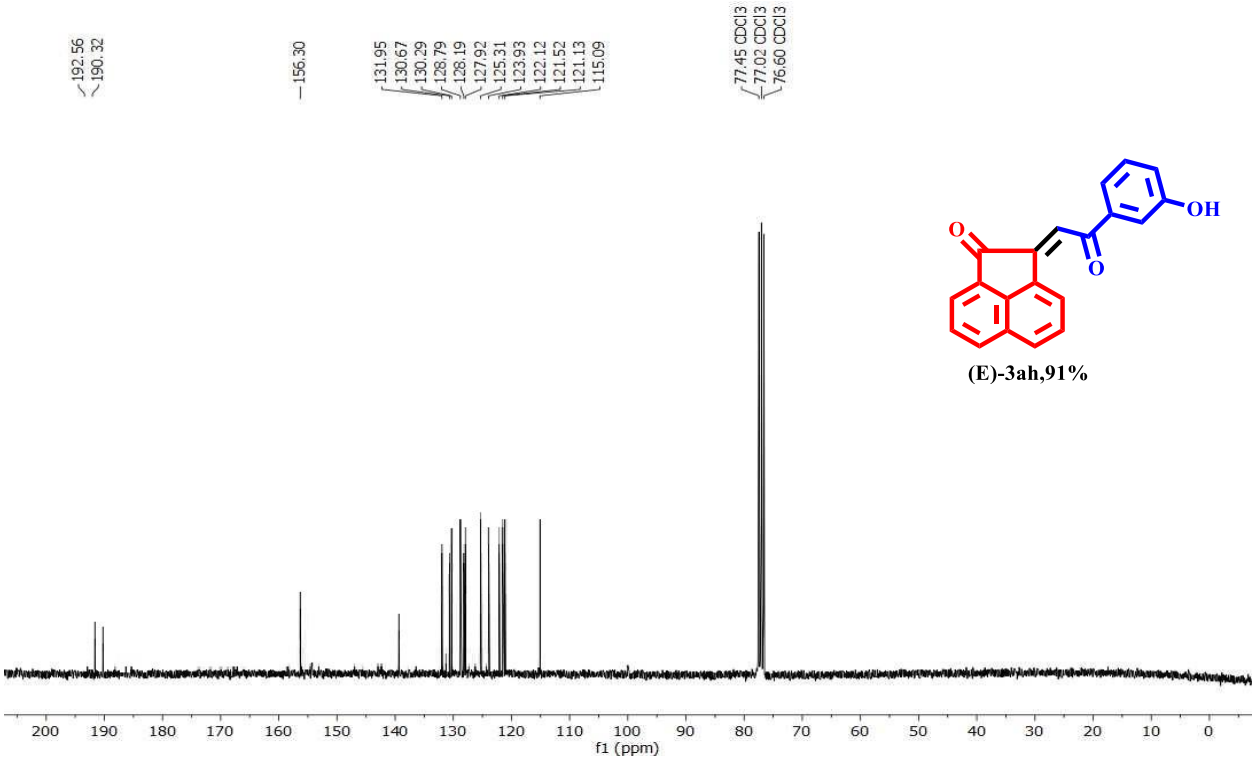


(E)-3ag, 90%

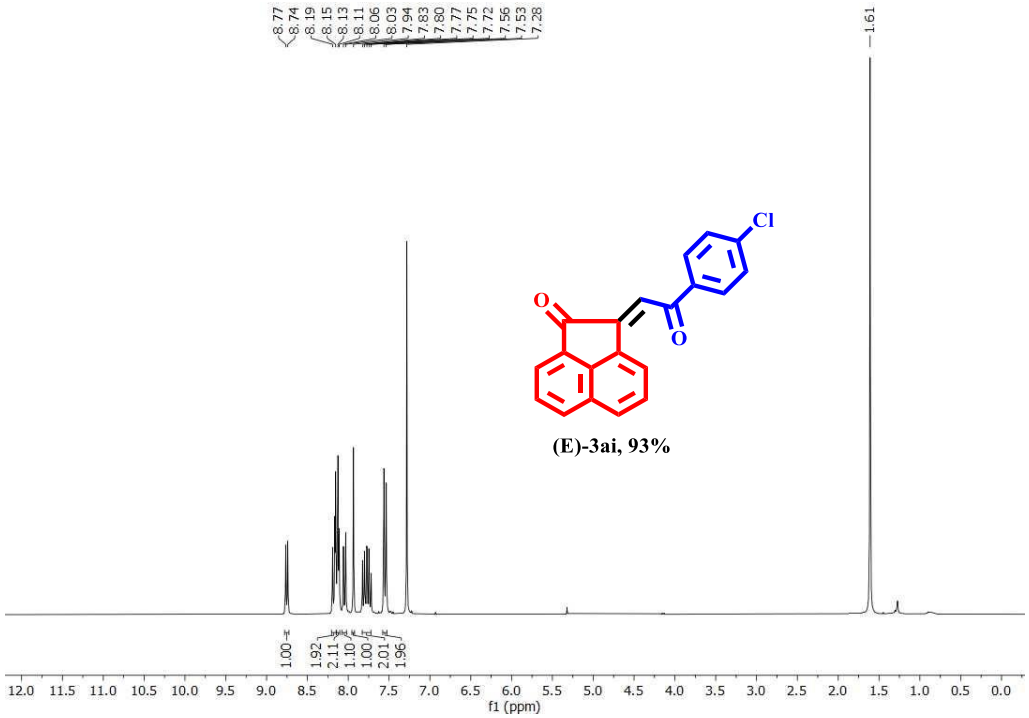
^{13}C NMR Spectrum of (E)-3ag



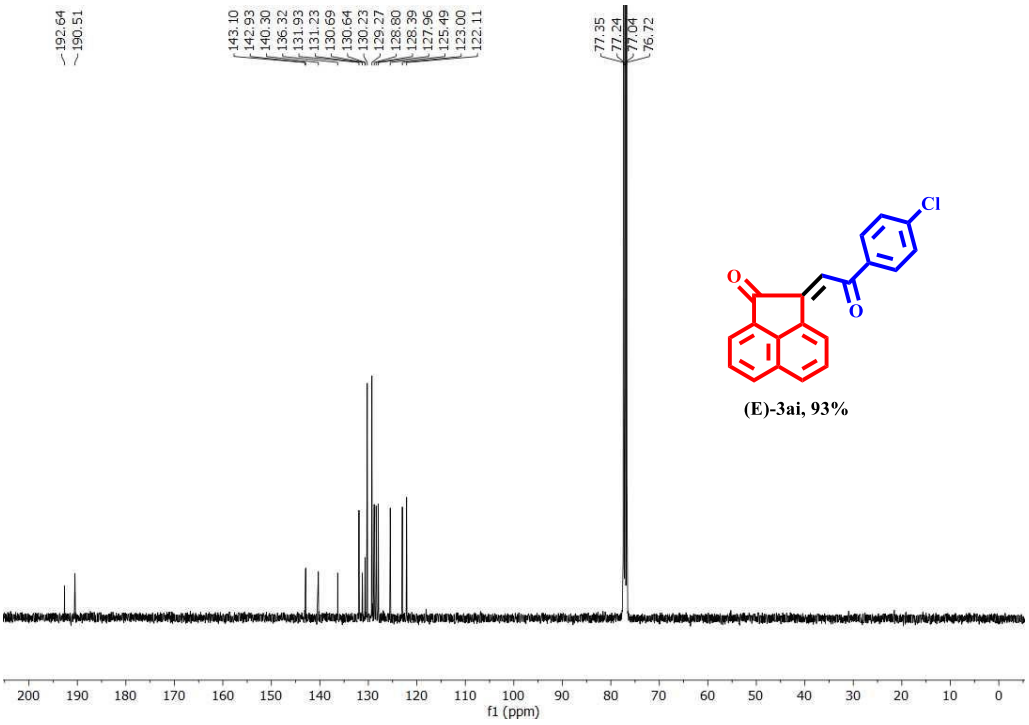
^{1}H NMR Spectrum of (E)-3ah



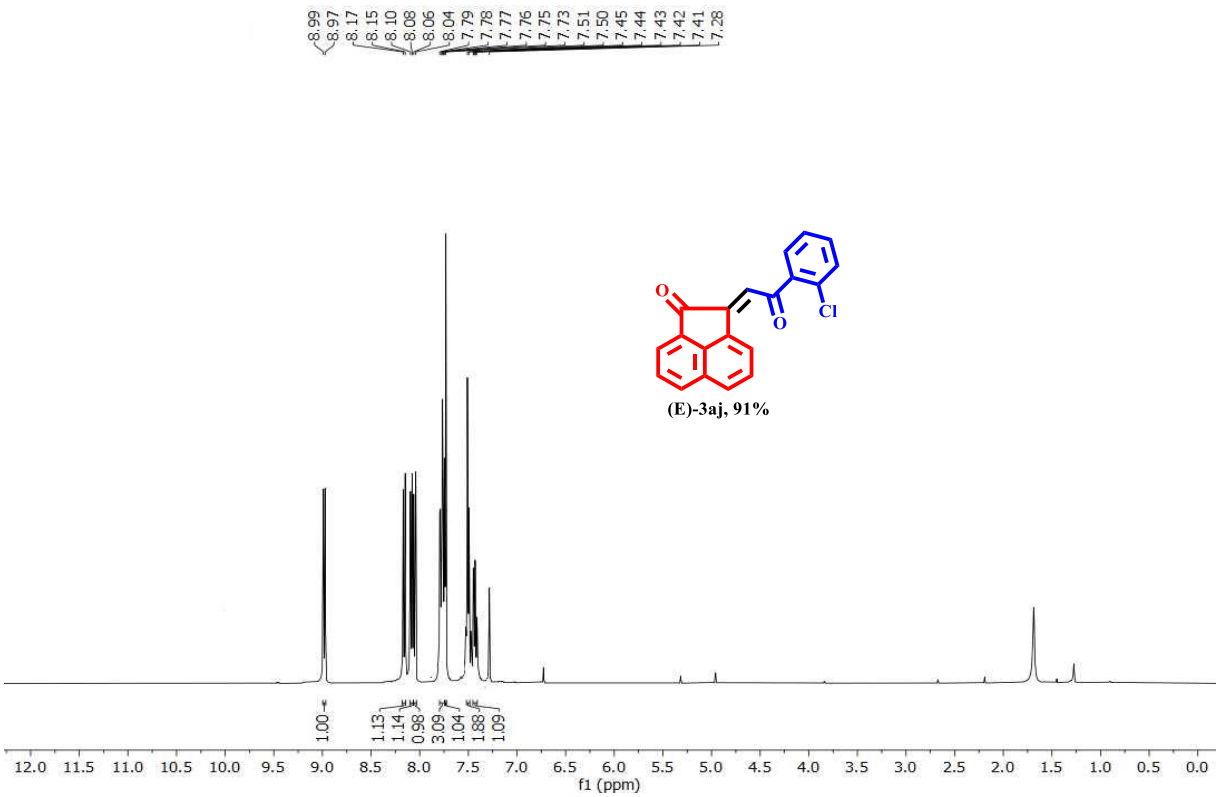
^{13}C NMR Spectrum of (E)-3ah



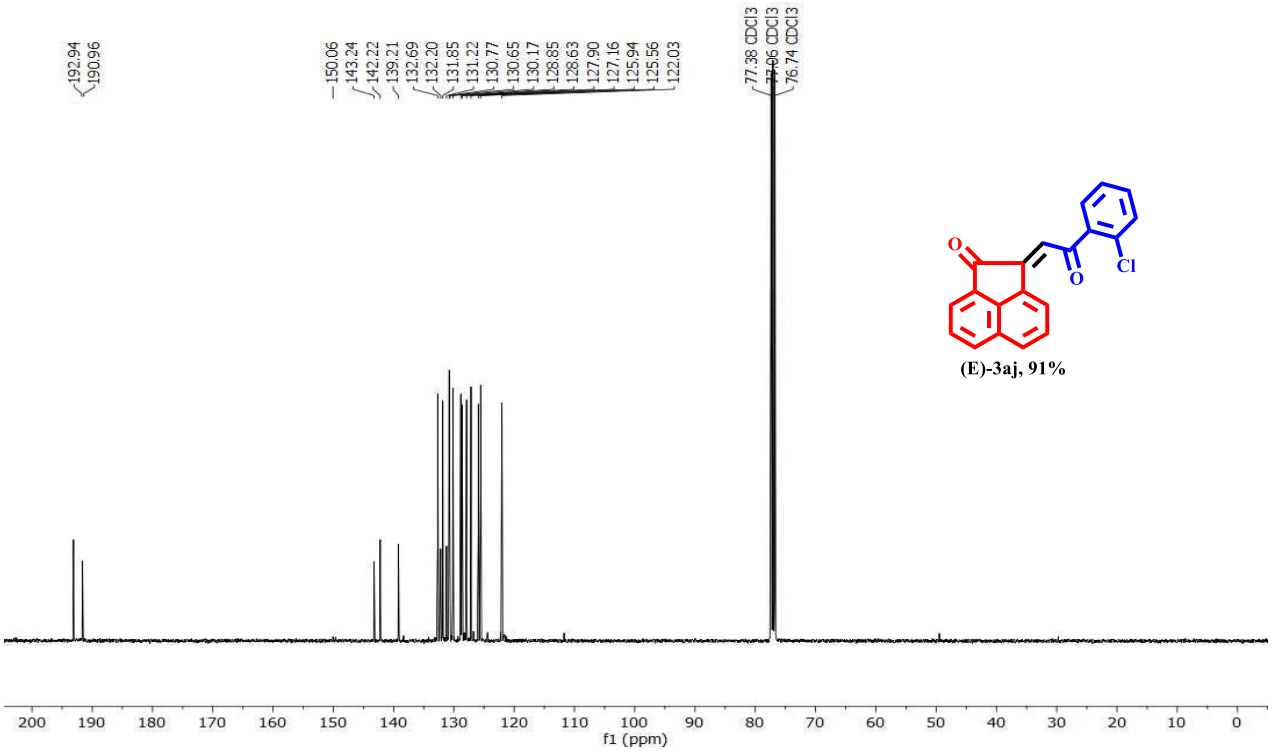
^{1}H NMR Spectrum of (E)-3ai



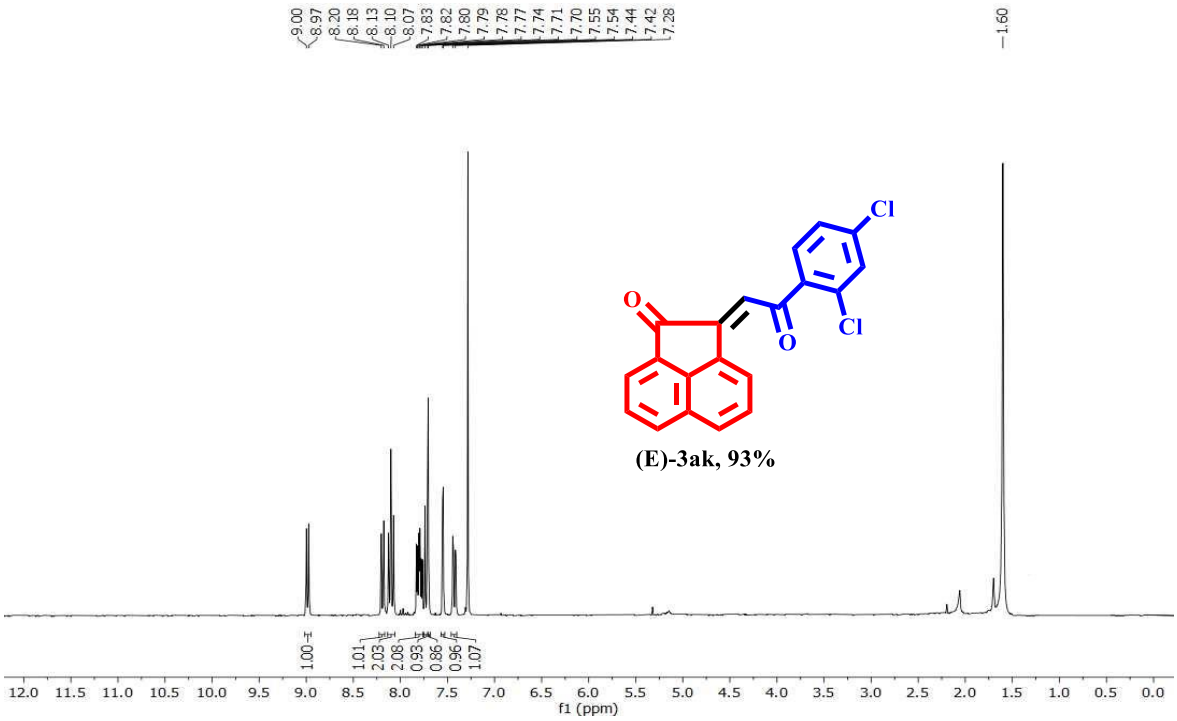
^{13}C NMR Spectrum of (E)-3ai



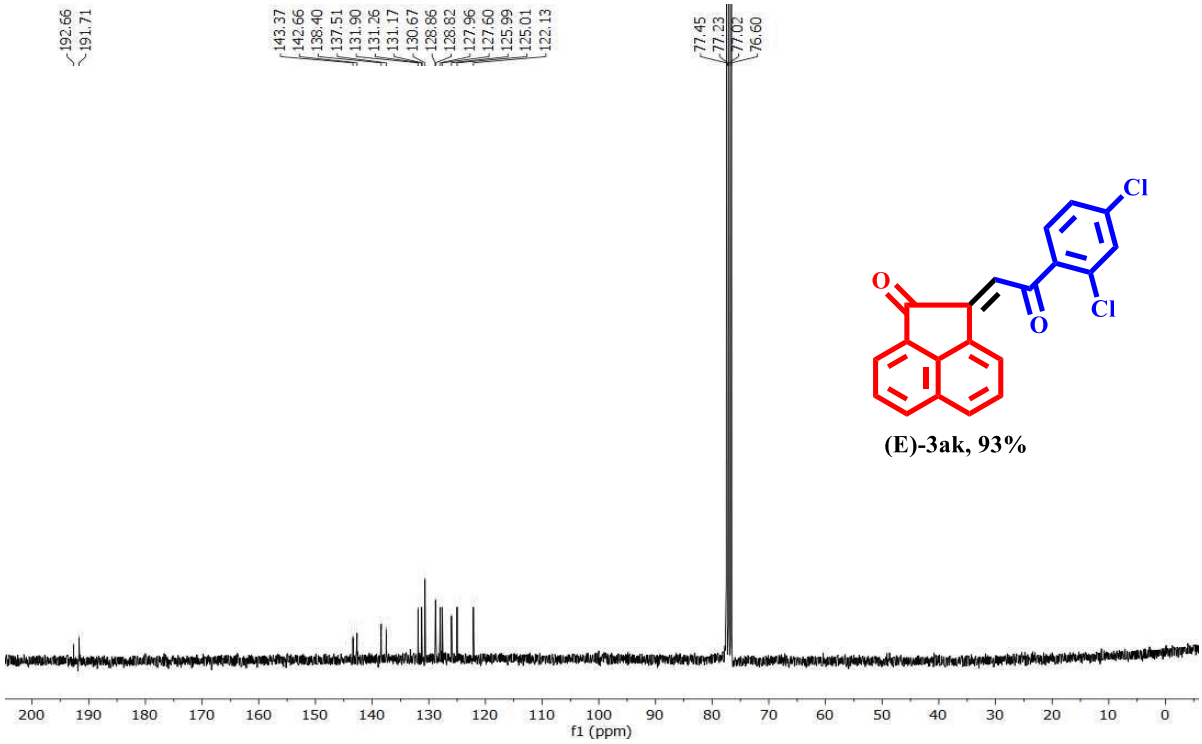
^{1}H NMR Spectrum of (E)-3aj



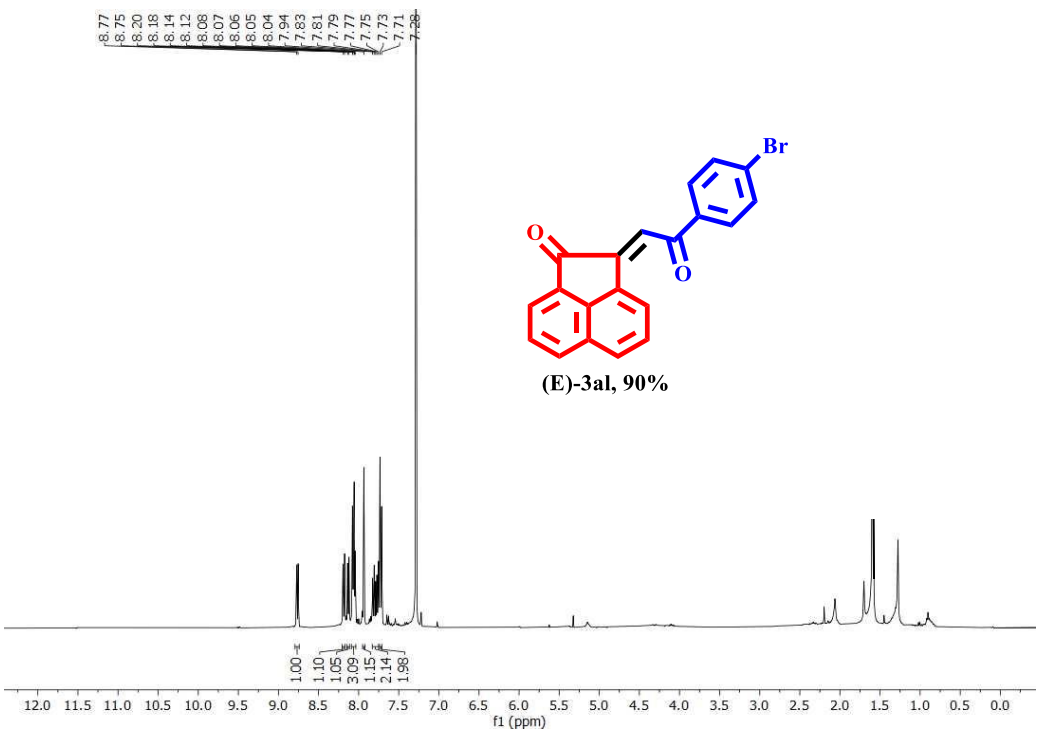
^{13}C NMR Spectrum of (E)-3aj



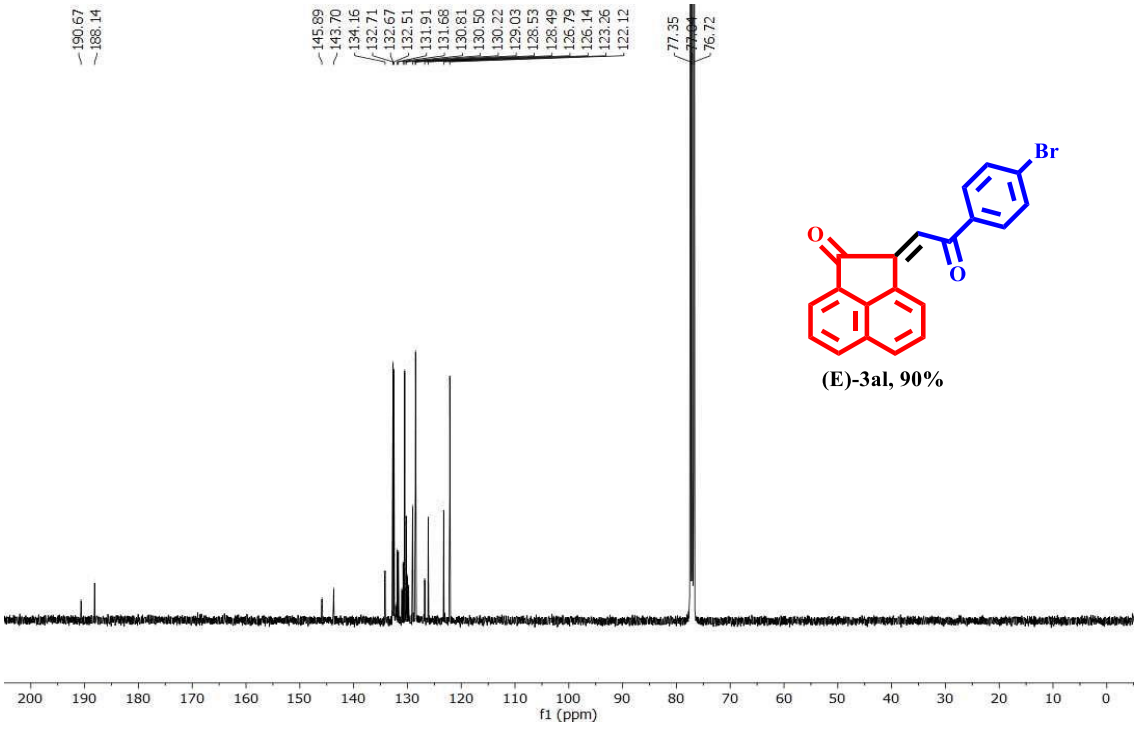
^{1}H NMR Spectrum of (E)-3ak



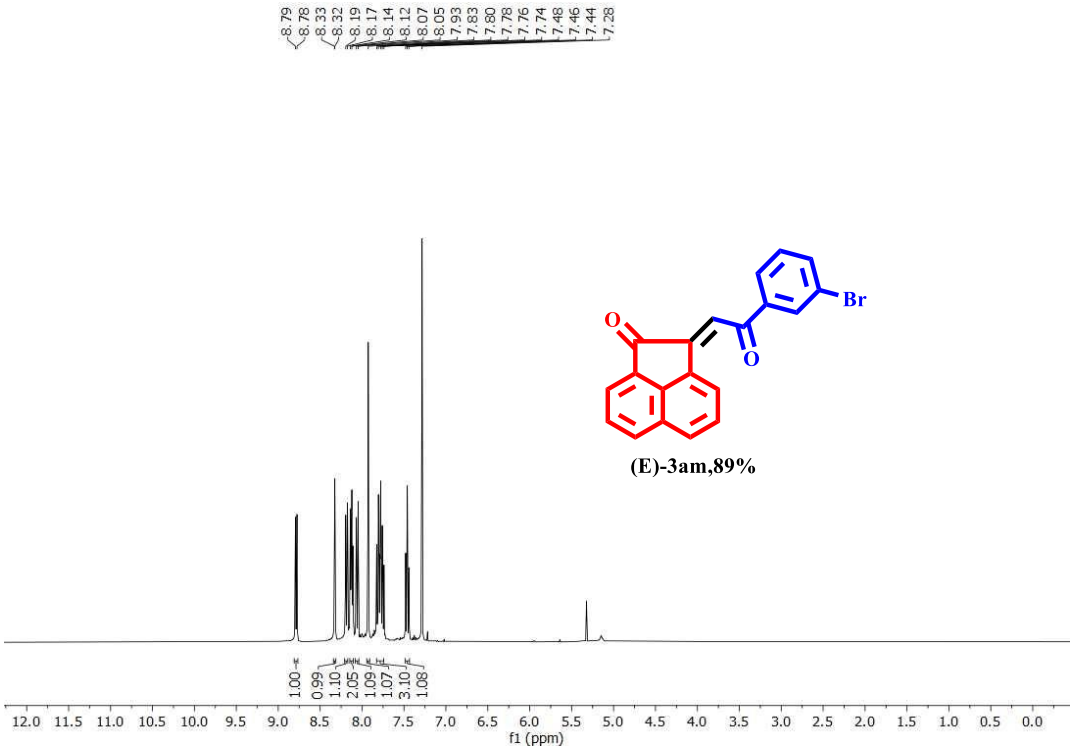
^{13}C NMR Spectrum of (E)-3ak



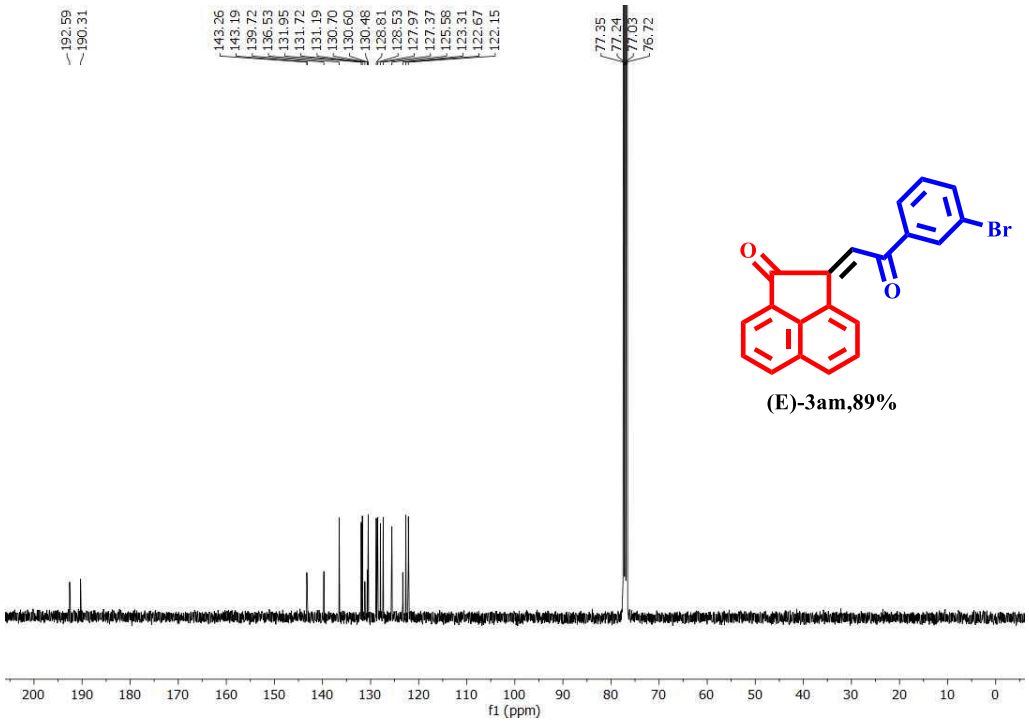
^{1}H NMR Spectrum of (E)-3al



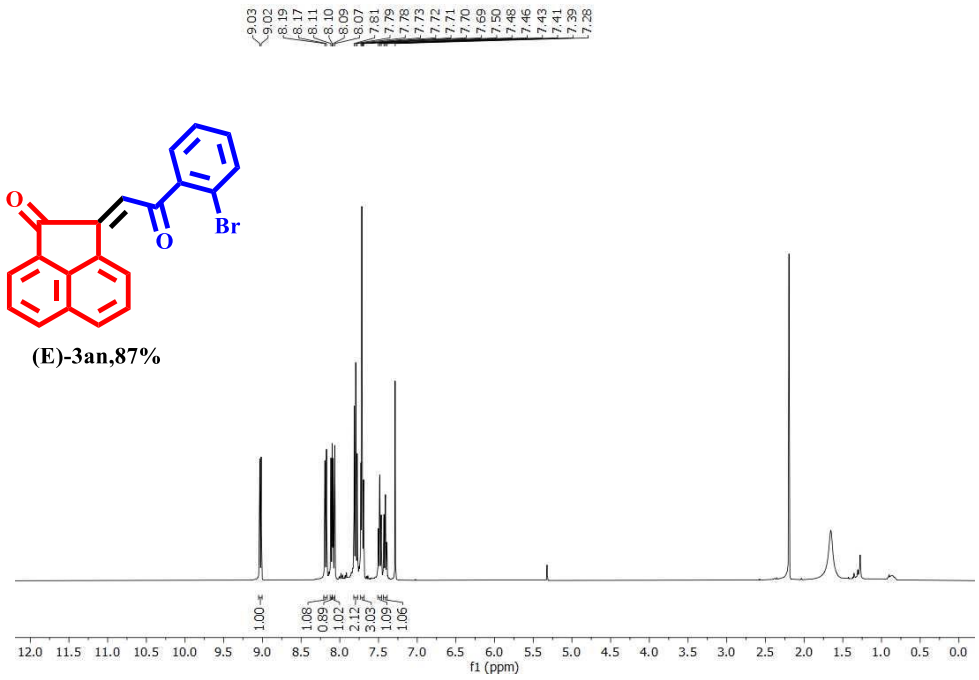
^{13}C NMR Spectrum of (E)-3al



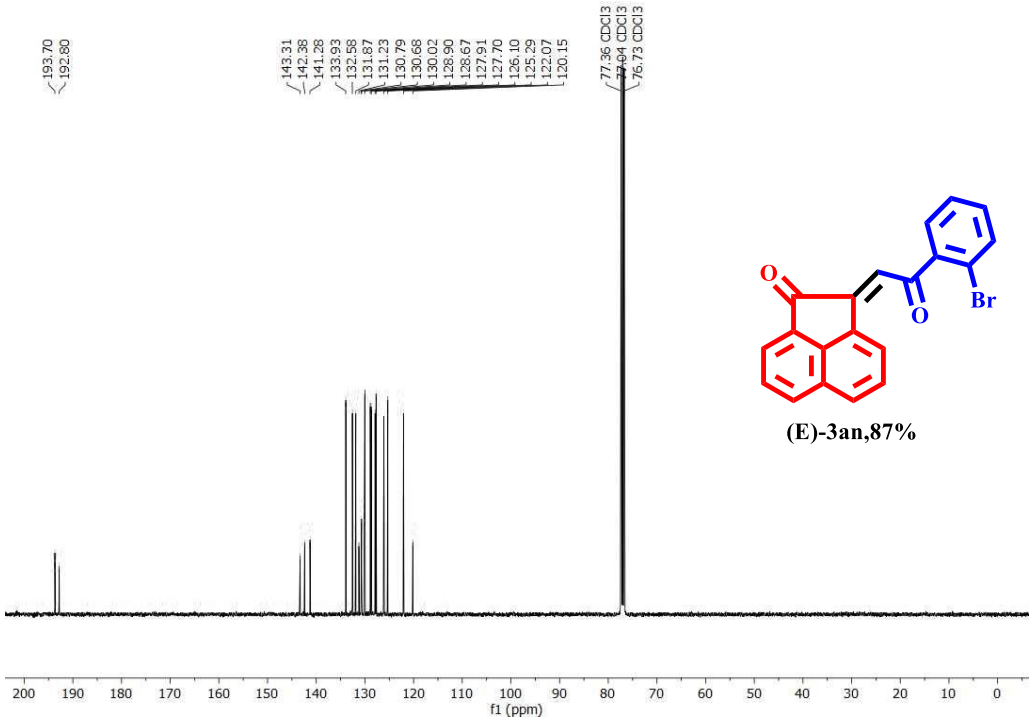
^{1}H NMR Spectrum of (E)-3am



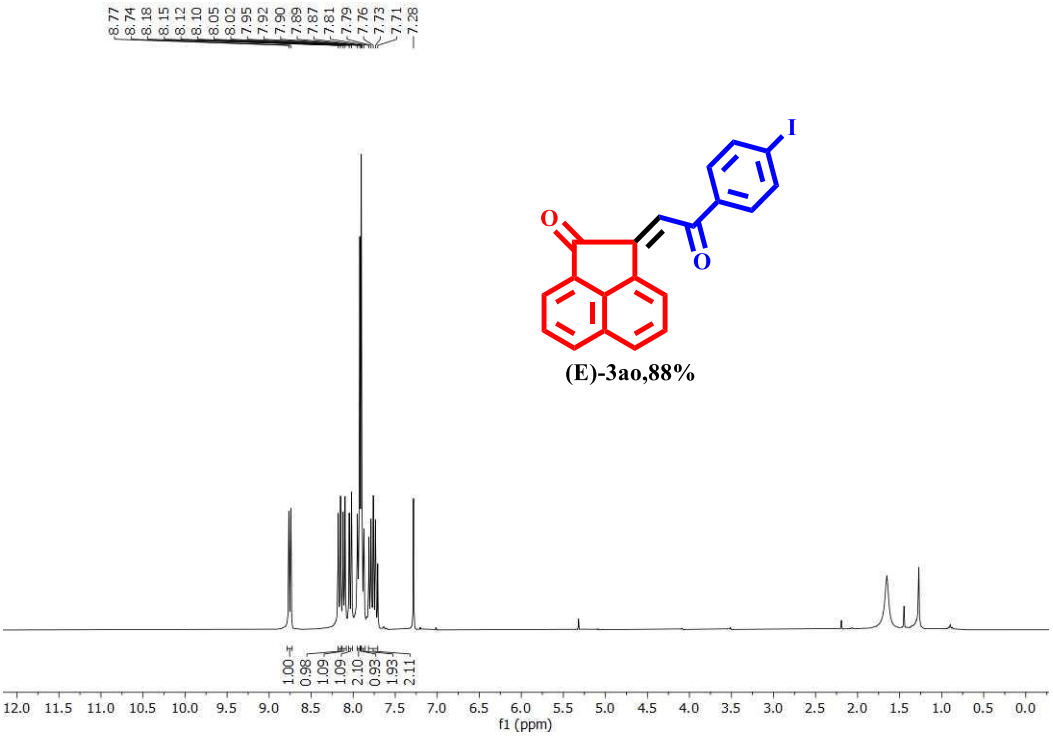
^{13}C NMR Spectrum of (E)-3am



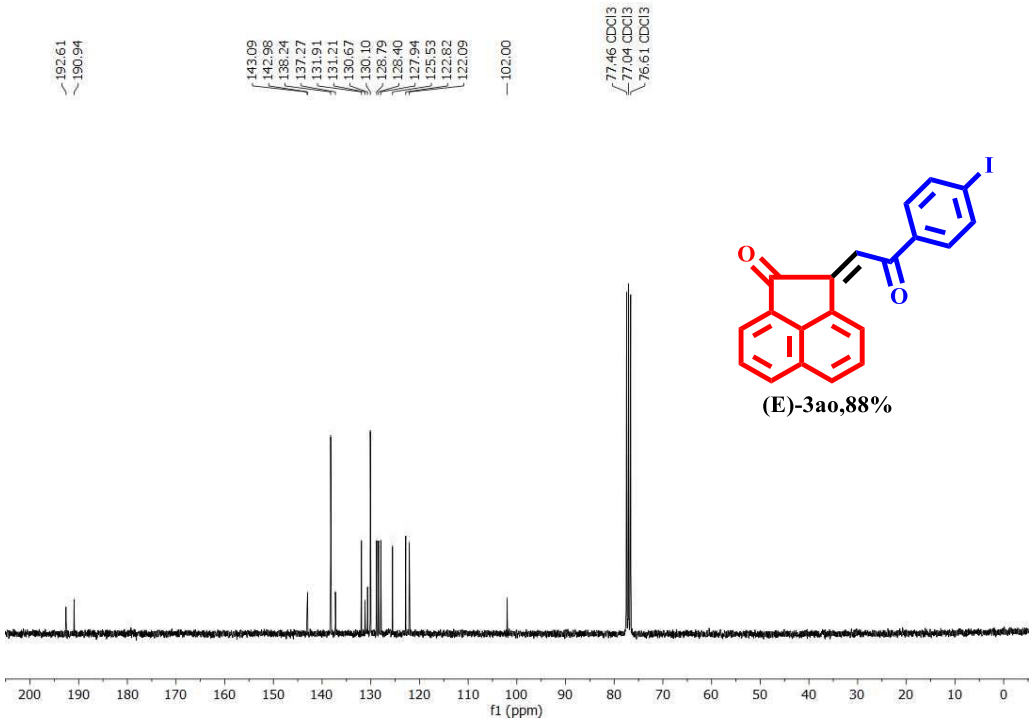
^{1}H NMR Spectrum of (E)-3an



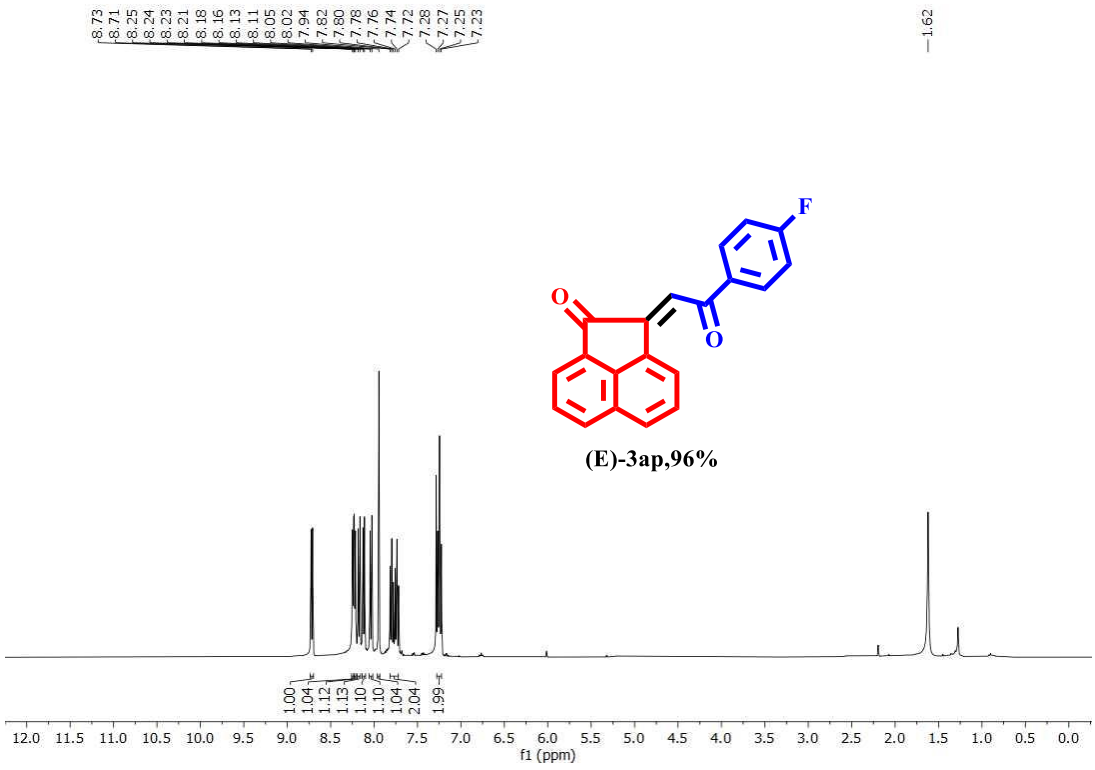
^{13}C NMR Spectrum of (E)-3an



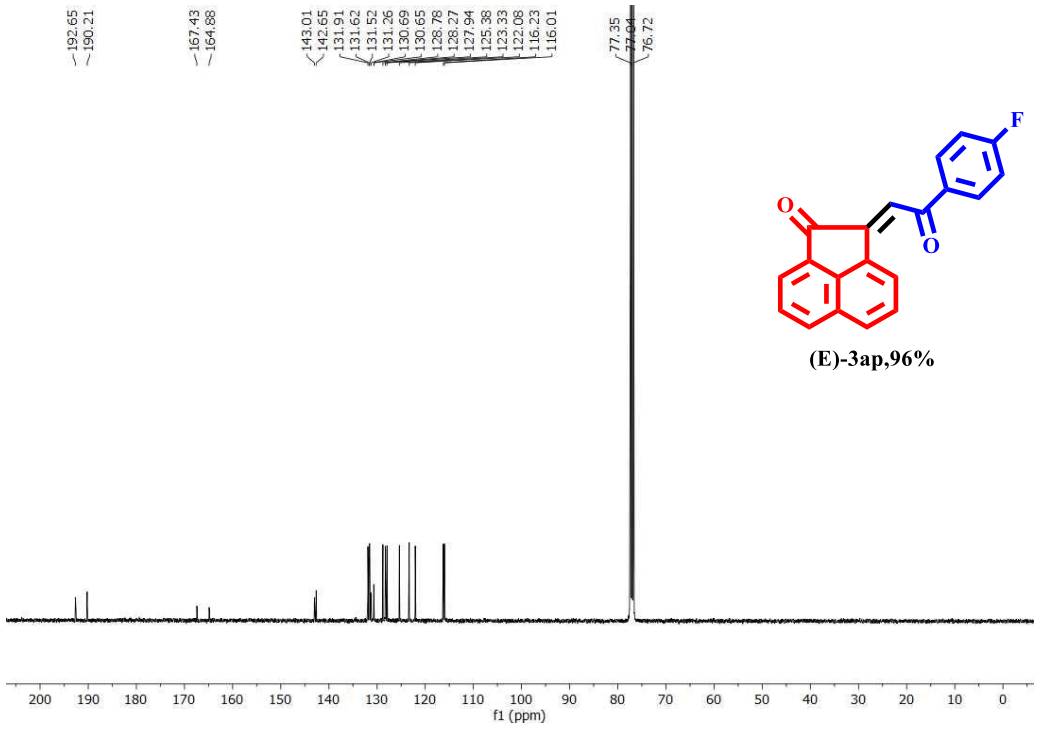
^{1}H NMR Spectrum of (E)-3ao



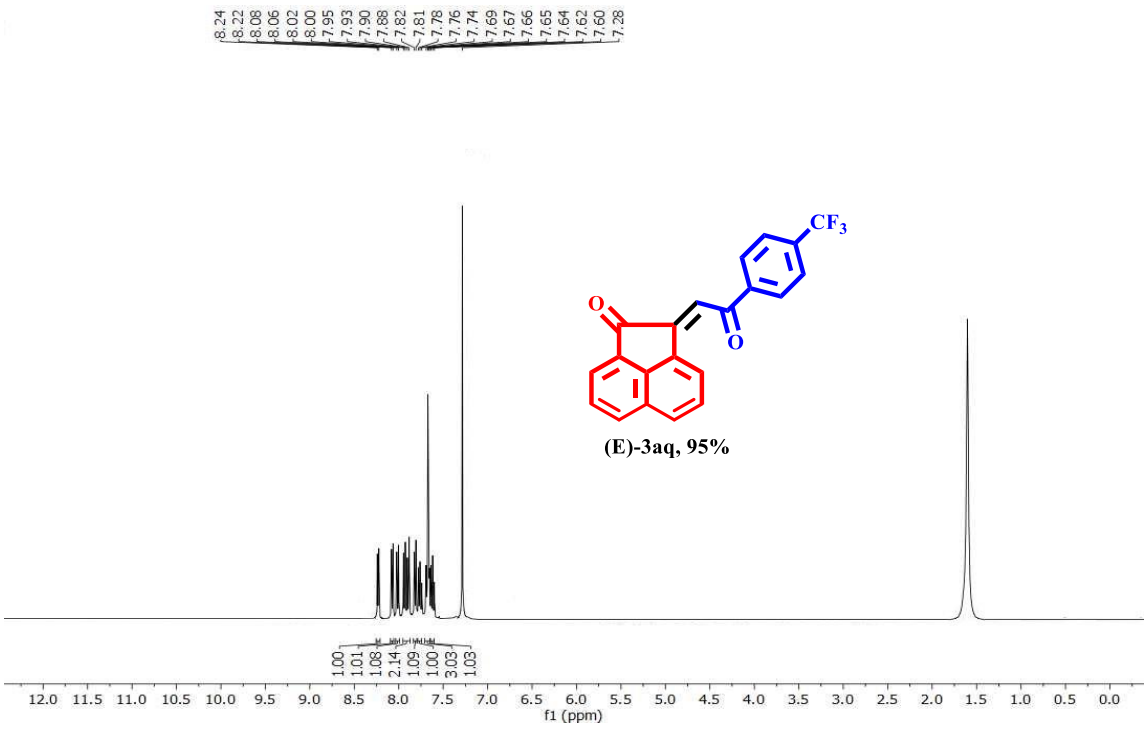
^{13}C NMR Spectrum of (E)-3ao



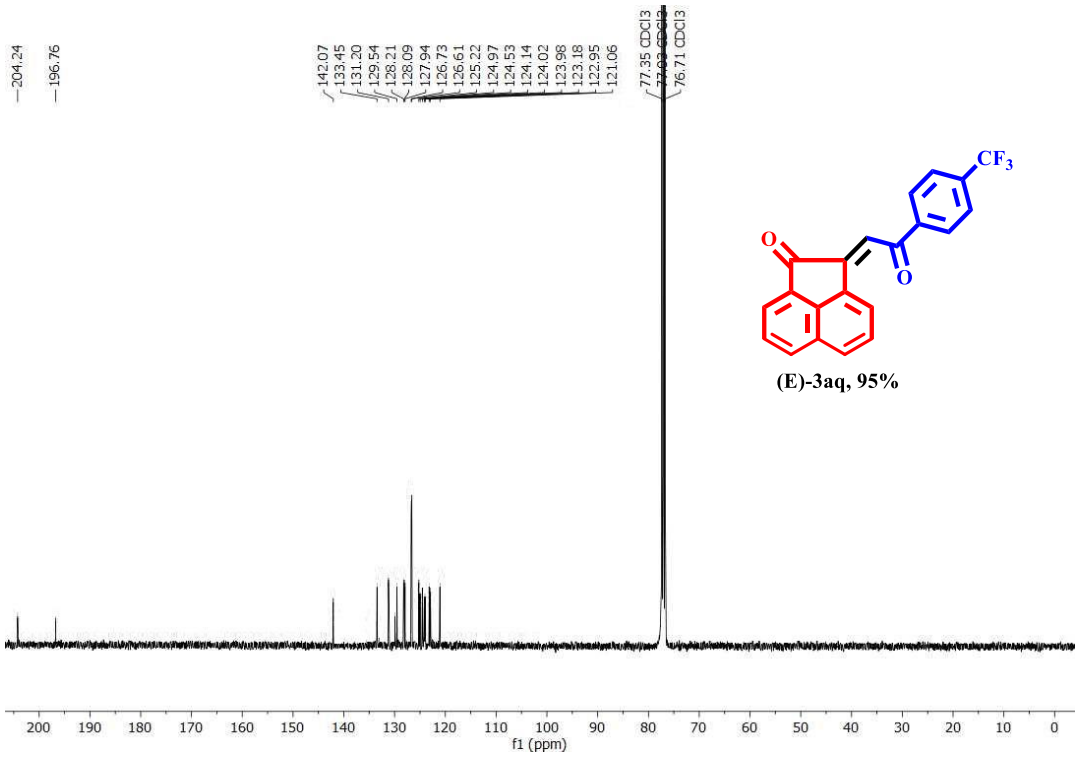
^{1}H NMR Spectrum of (E)-3ap



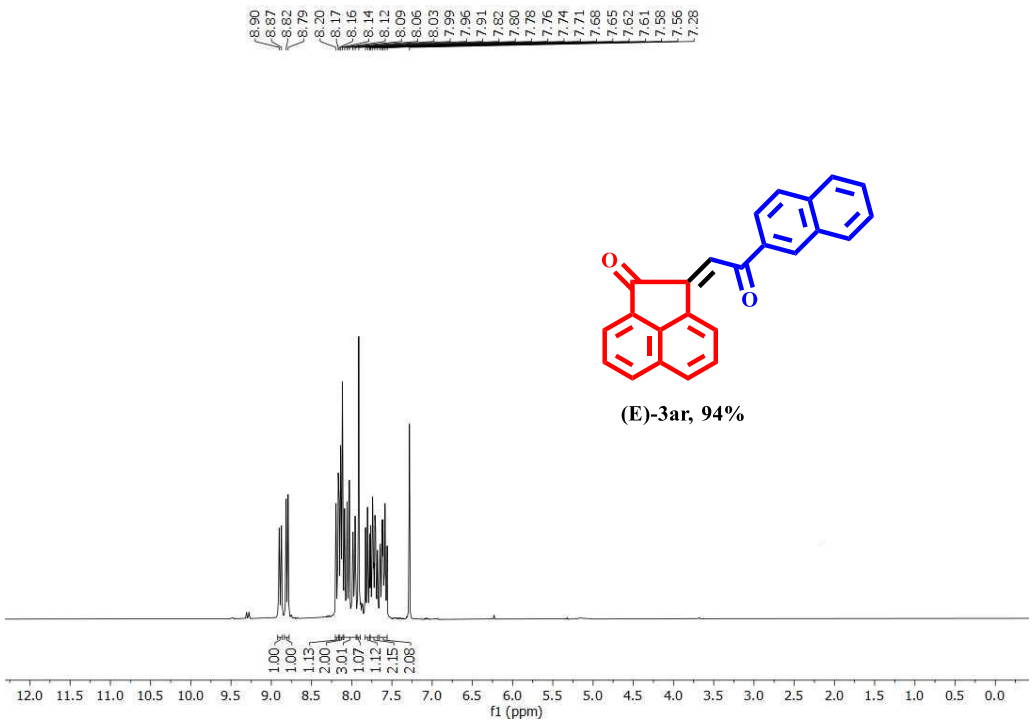
^{13}C NMR Spectrum of (E)-3ap



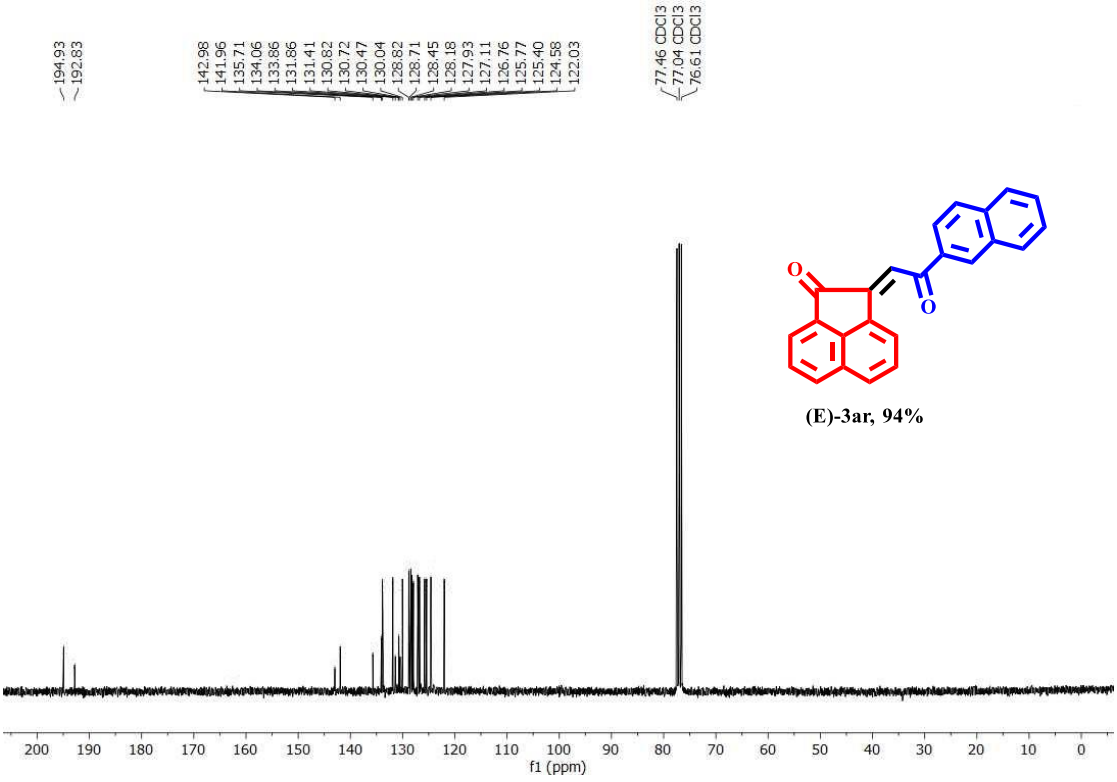
^{1}H NMR Spectrum of (E)-3aq



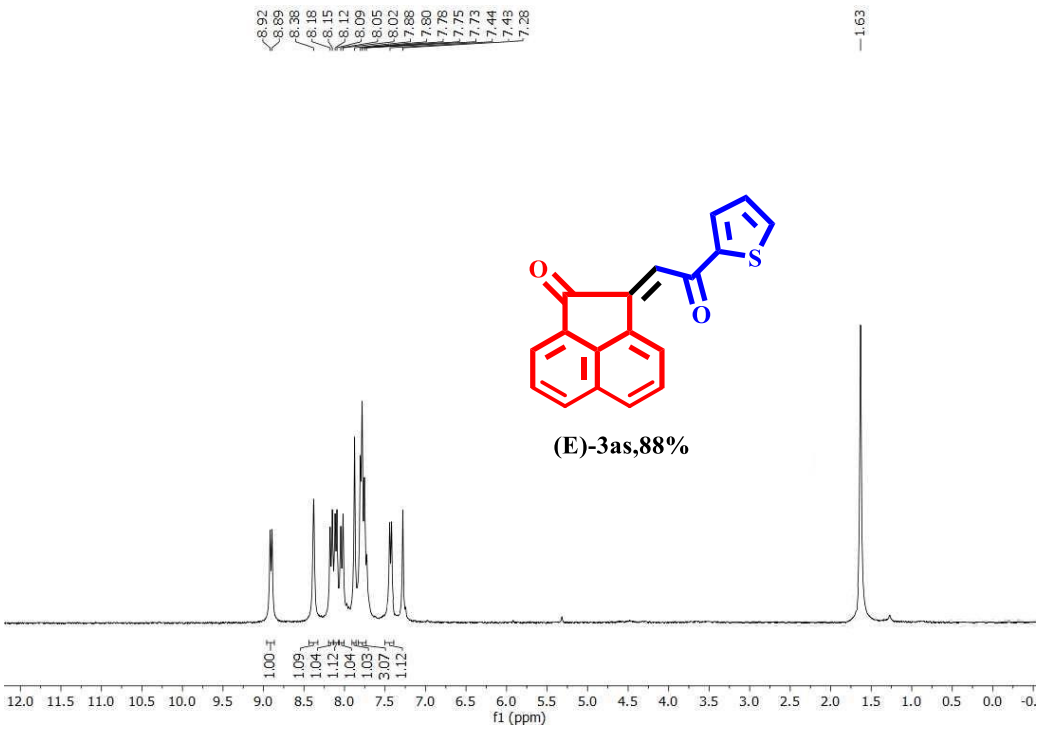
^{13}C NMR Spectrum of (E)-3aq



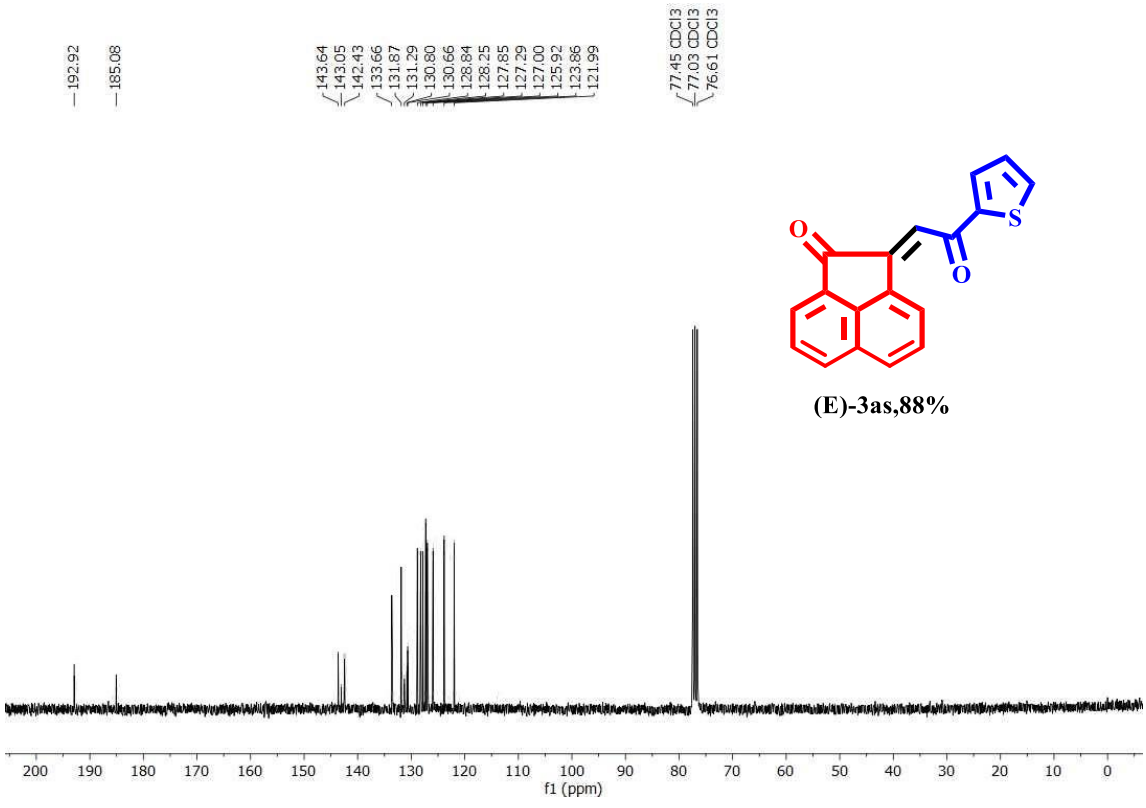
^{1}H NMR Spectrum of (E)-3ar



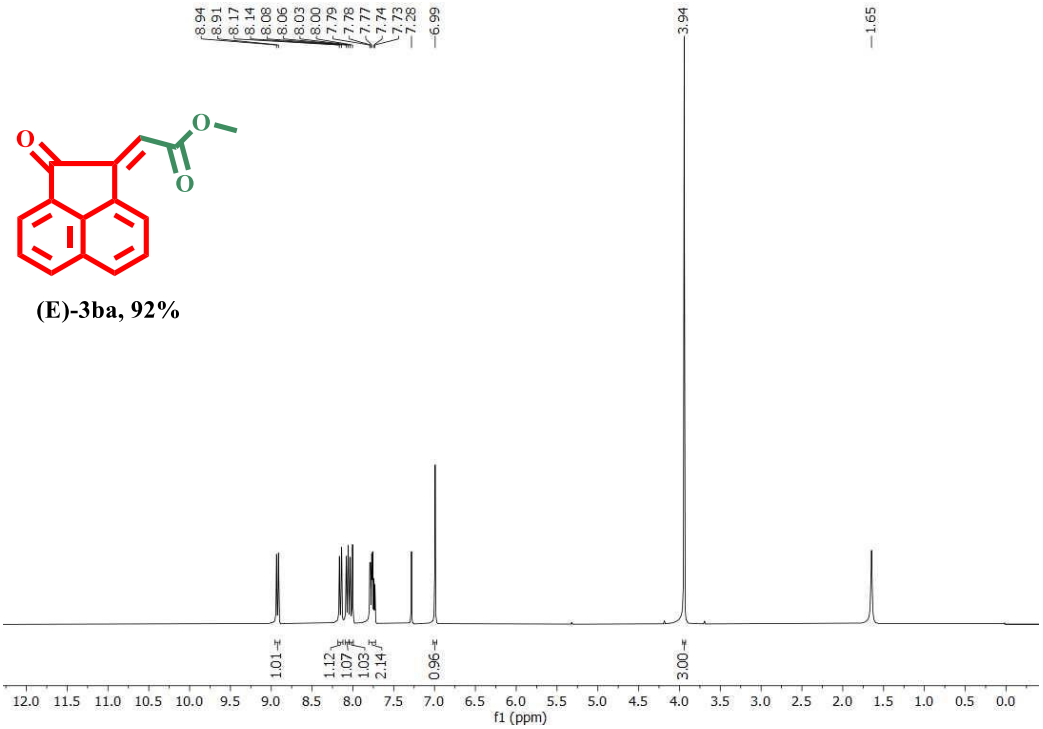
^{13}C NMR Spectrum of (E)-3ar



^{1}H NMR Spectrum of (E)-3as

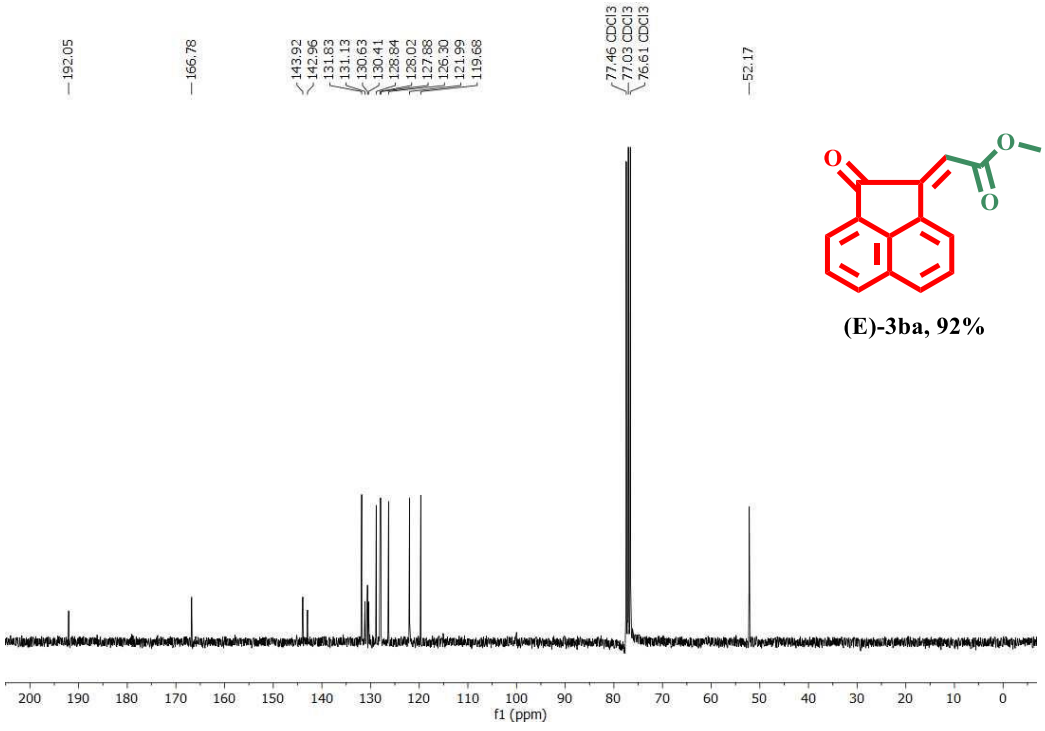


^{13}C NMR Spectrum of (E)-3as



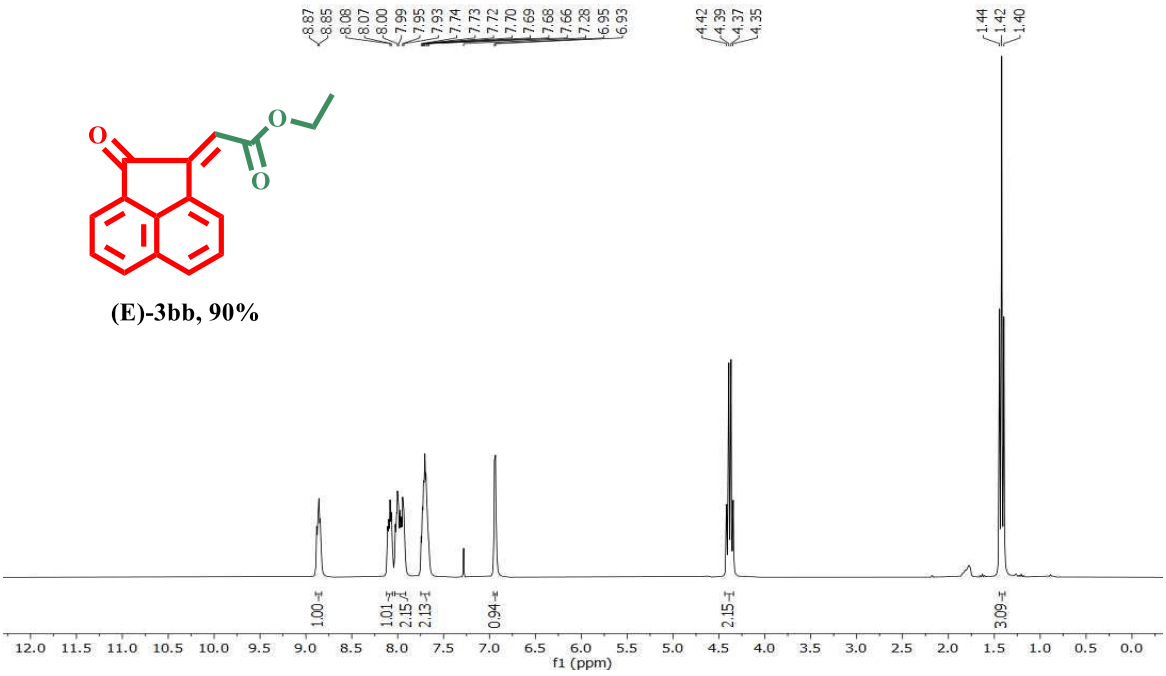
(E)-3ba, 92%

^{1}H NMR Spectrum of (E)-3ba



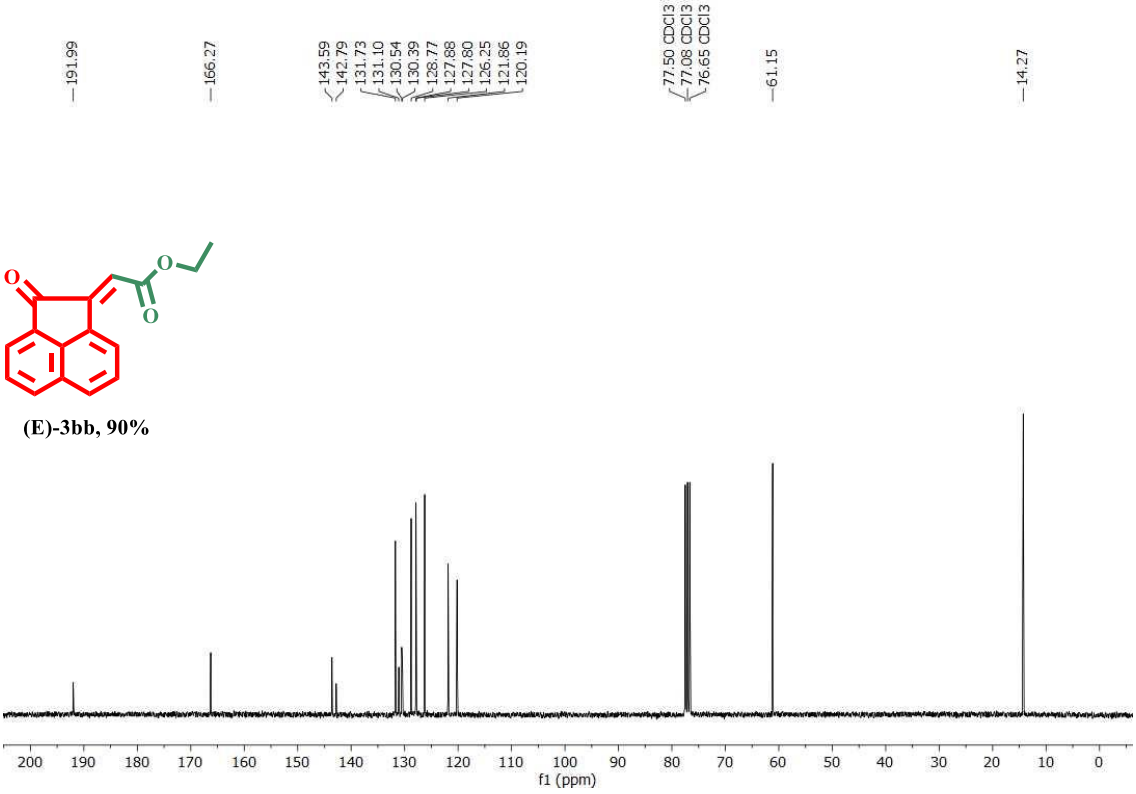
(E)-3ba, 92%

^{13}C NMR Spectrum of (E)-3ba



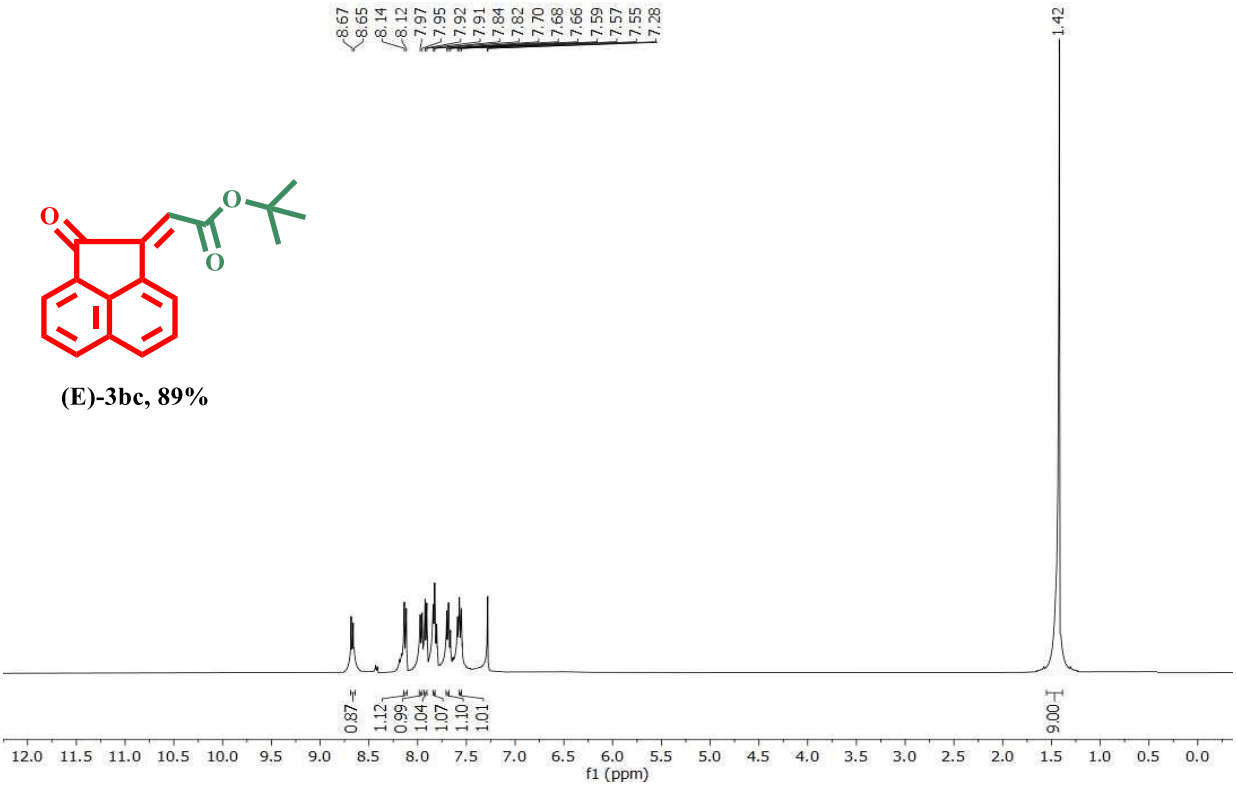
(E)-3bb, 90%

^{1}H NMR Spectrum of (E)-3bb



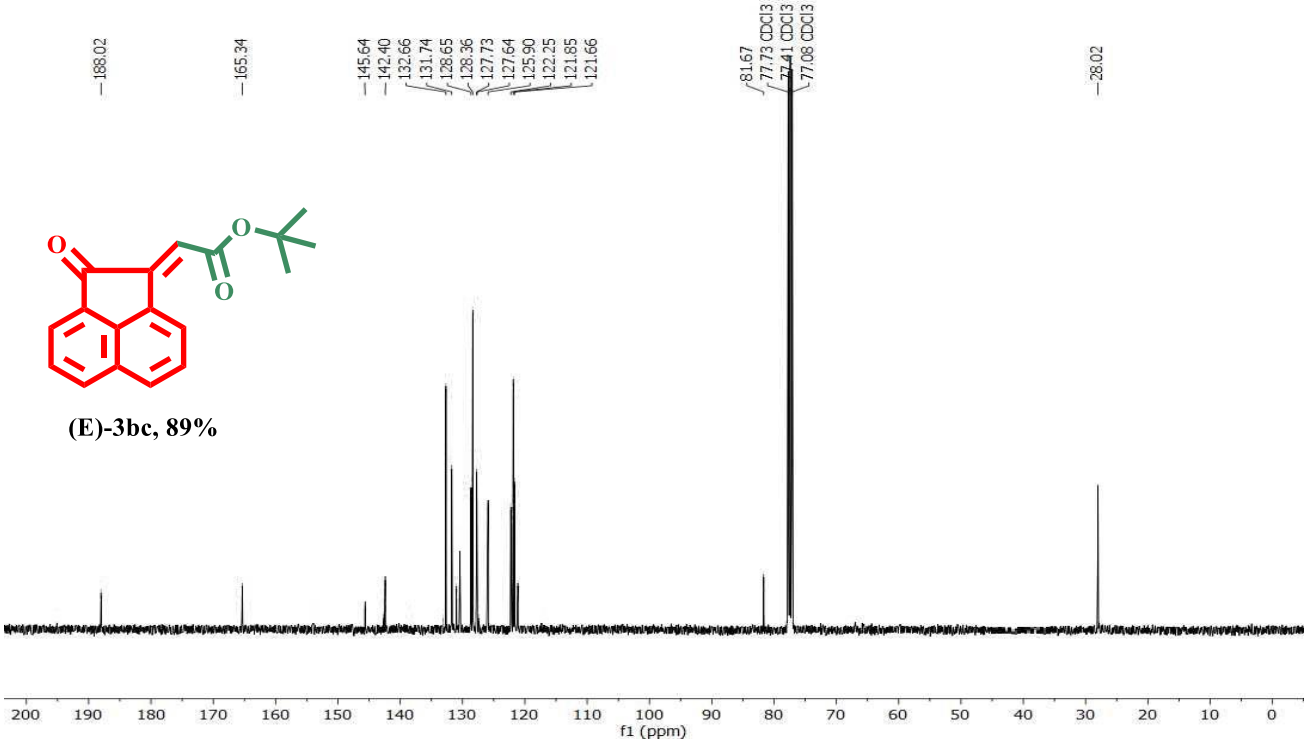
(E)-3bb, 90%

^{13}C NMR Spectrum of (E)-3bb



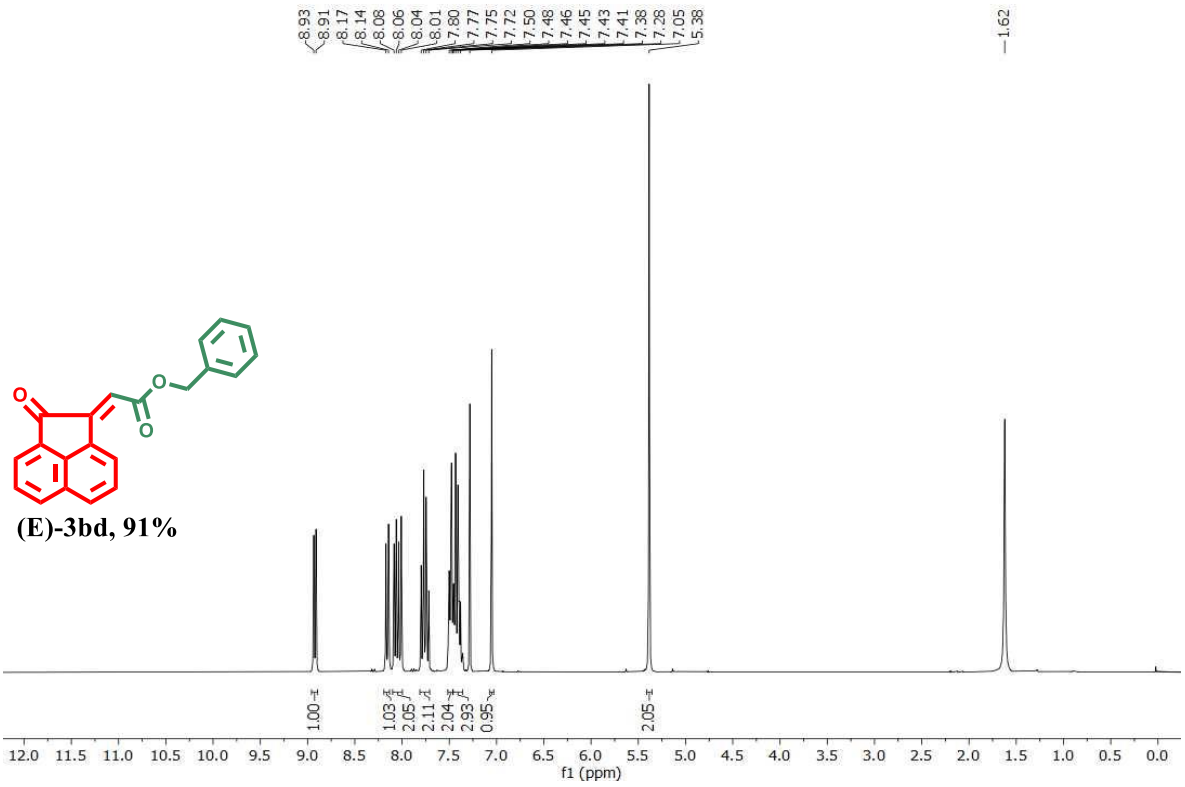
(E)-3bc, 89%

^{1}H NMR Spectrum of (E)-3bc



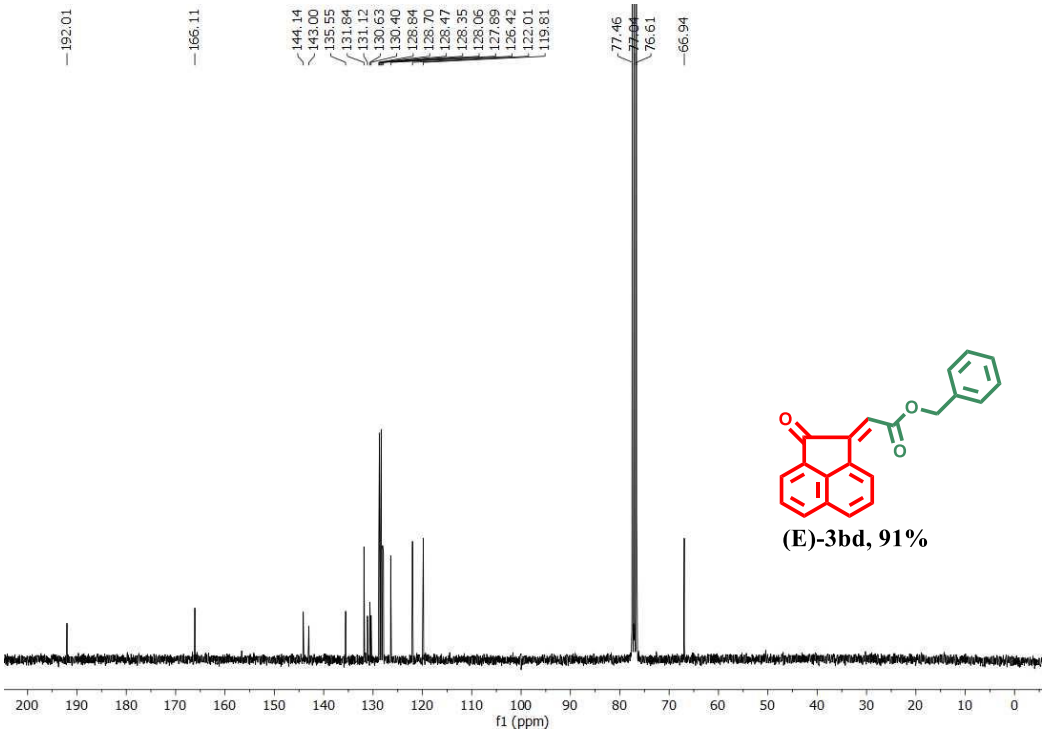
(E)-3bc, 89%

^{13}C NMR Spectrum of (E)-3bc



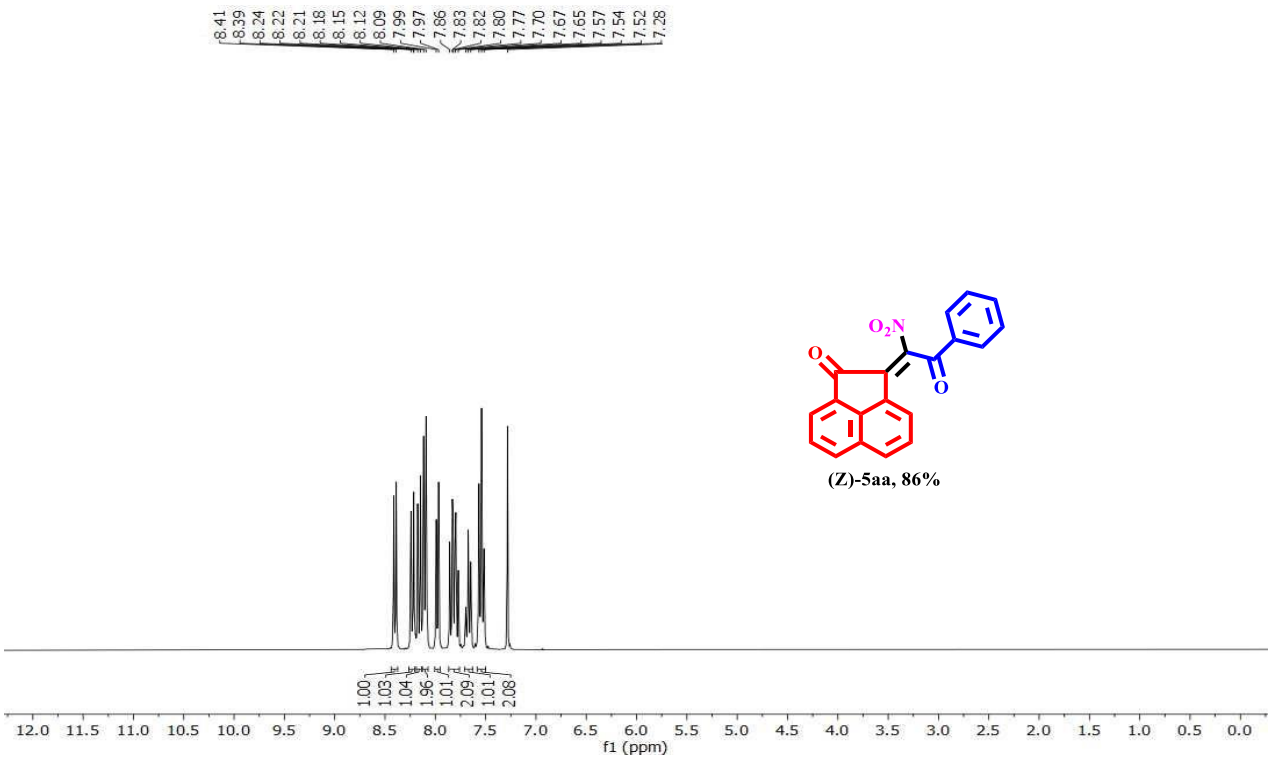
(E)-3bd, 91%

^{1}H NMR Spectrum of (E)-3bd

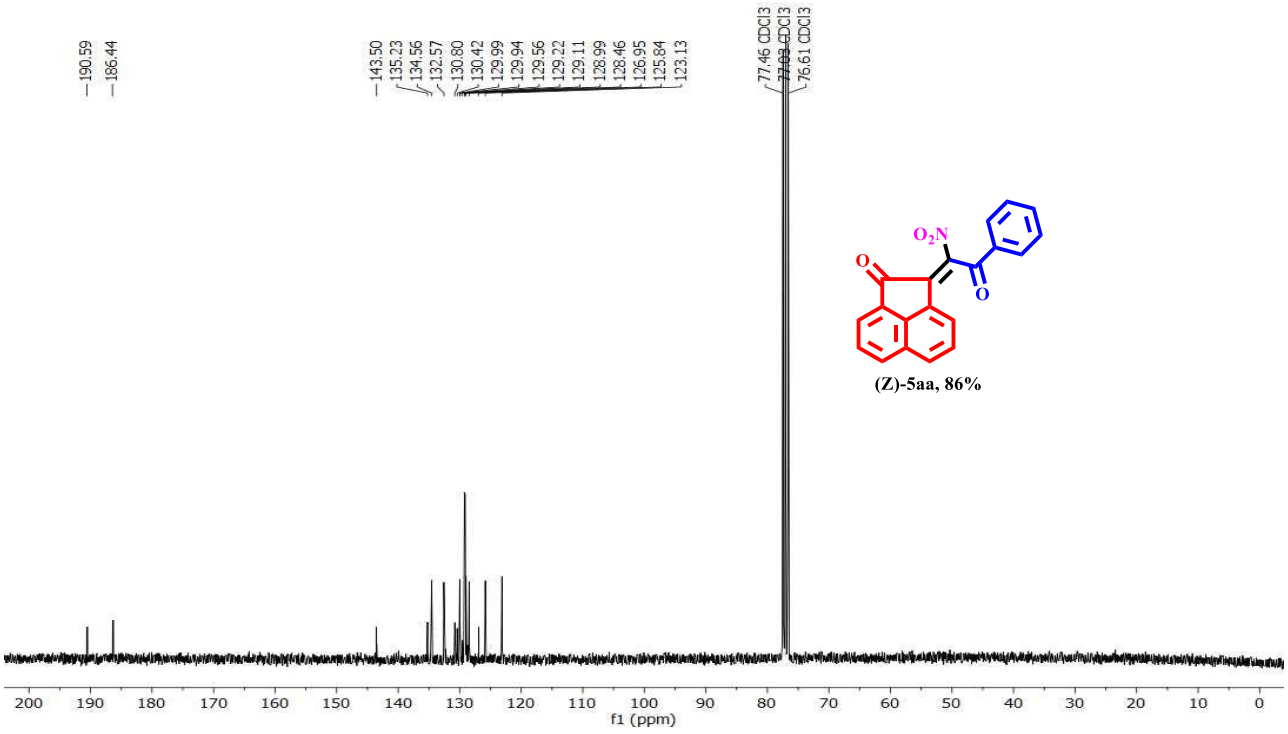


(E)-3bd, 91%

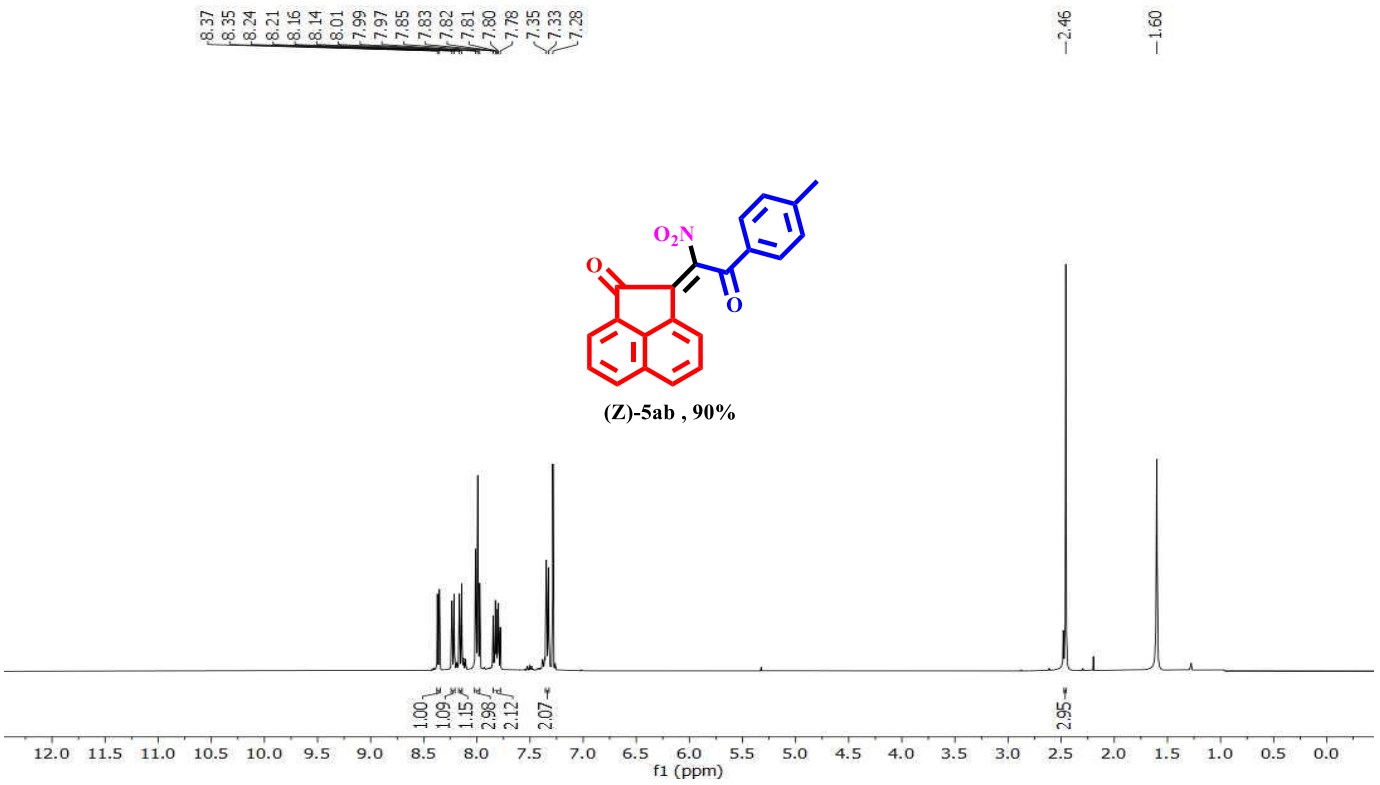
^{13}C NMR Spectrum of (E)-3bd



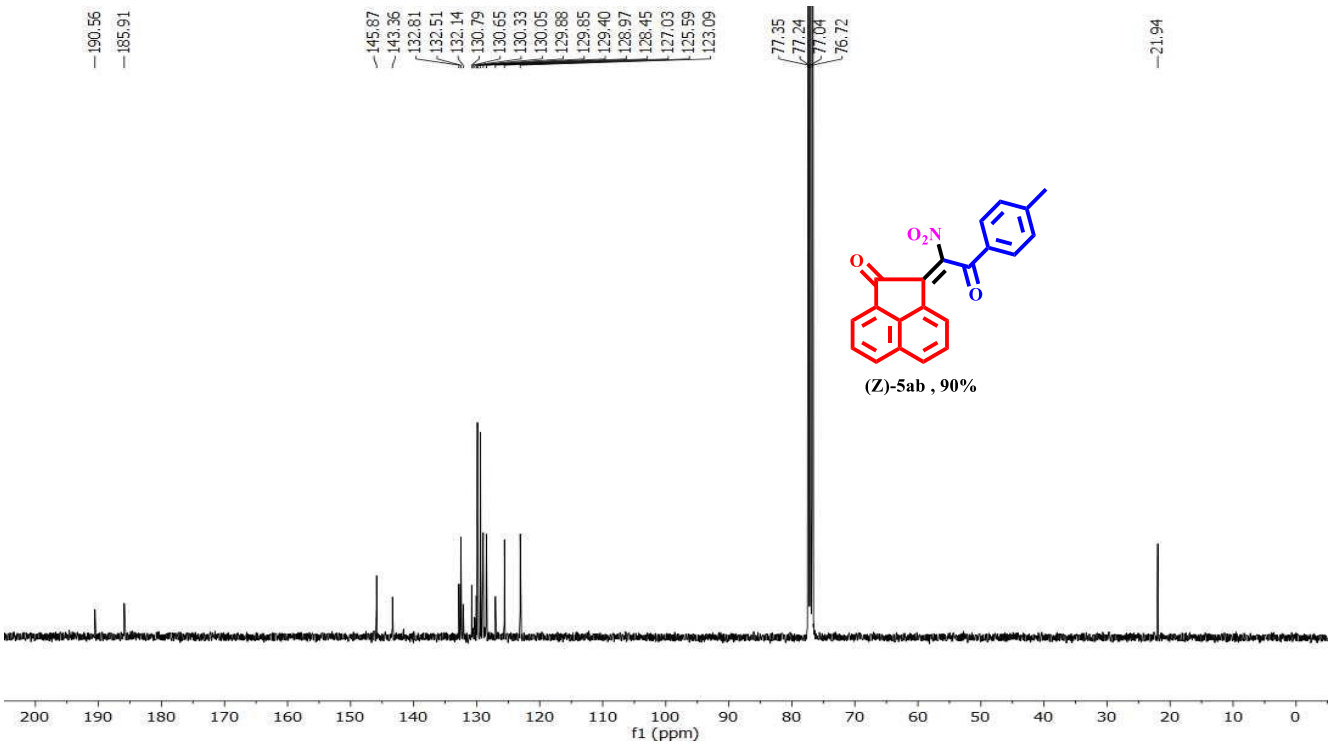
^{1}H NMR Spectrum of (Z)-5aa



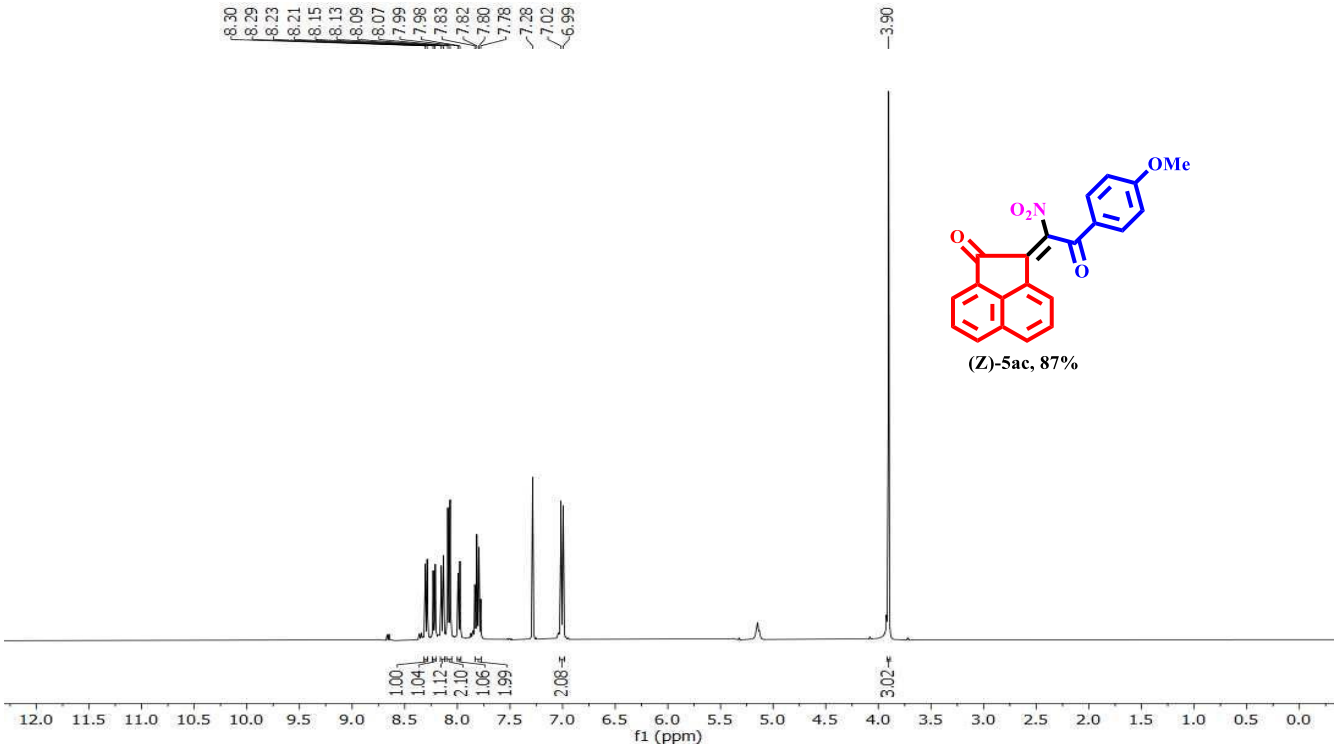
^{13}C NMR Spectrum of (Z)-5aa



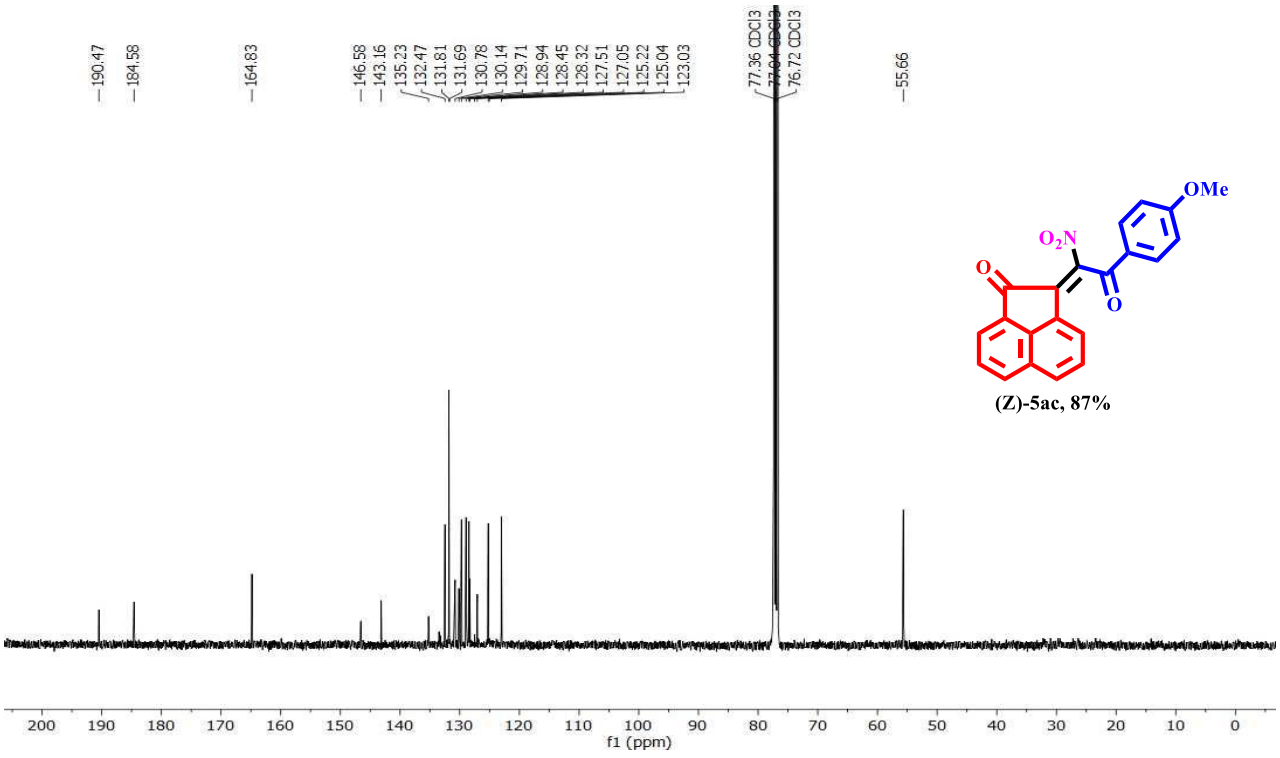
^{1}H NMR Spectrum of (Z)-5ab



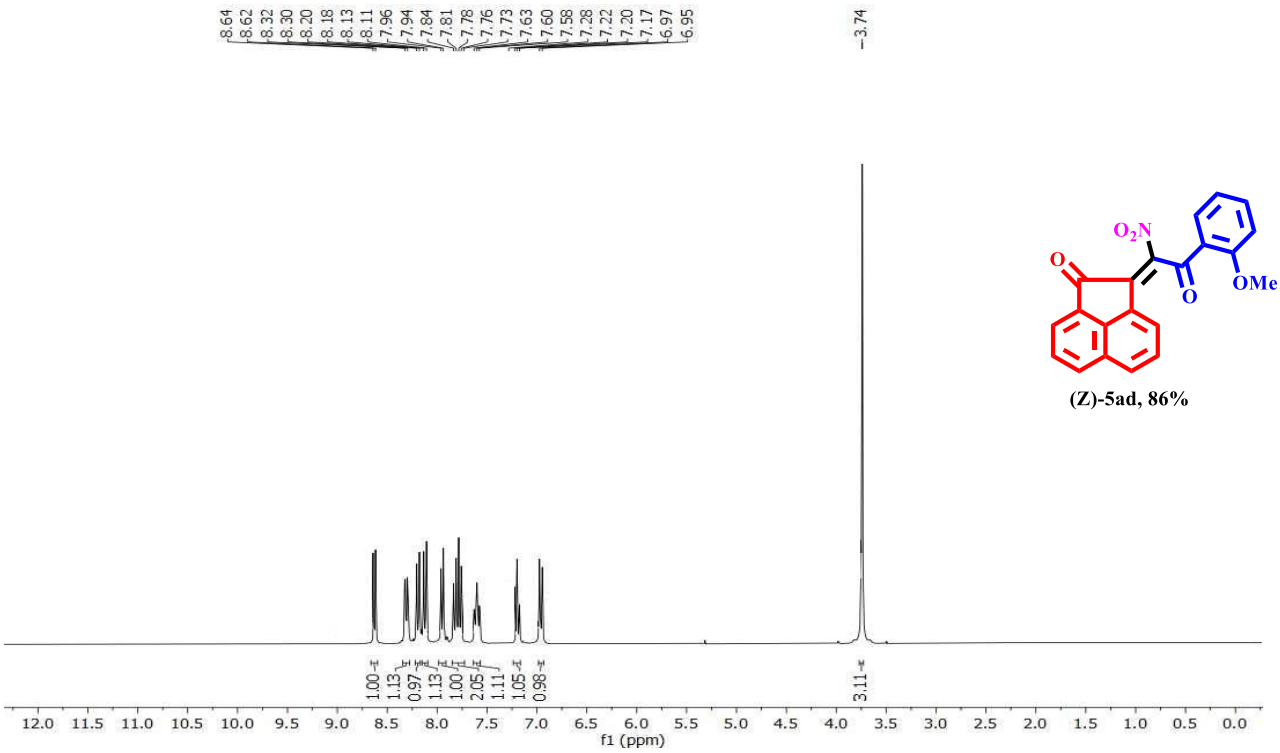
^{13}C NMR Spectrum of (Z)-5ab



^{1}H NMR Spectrum of (Z)-5ac

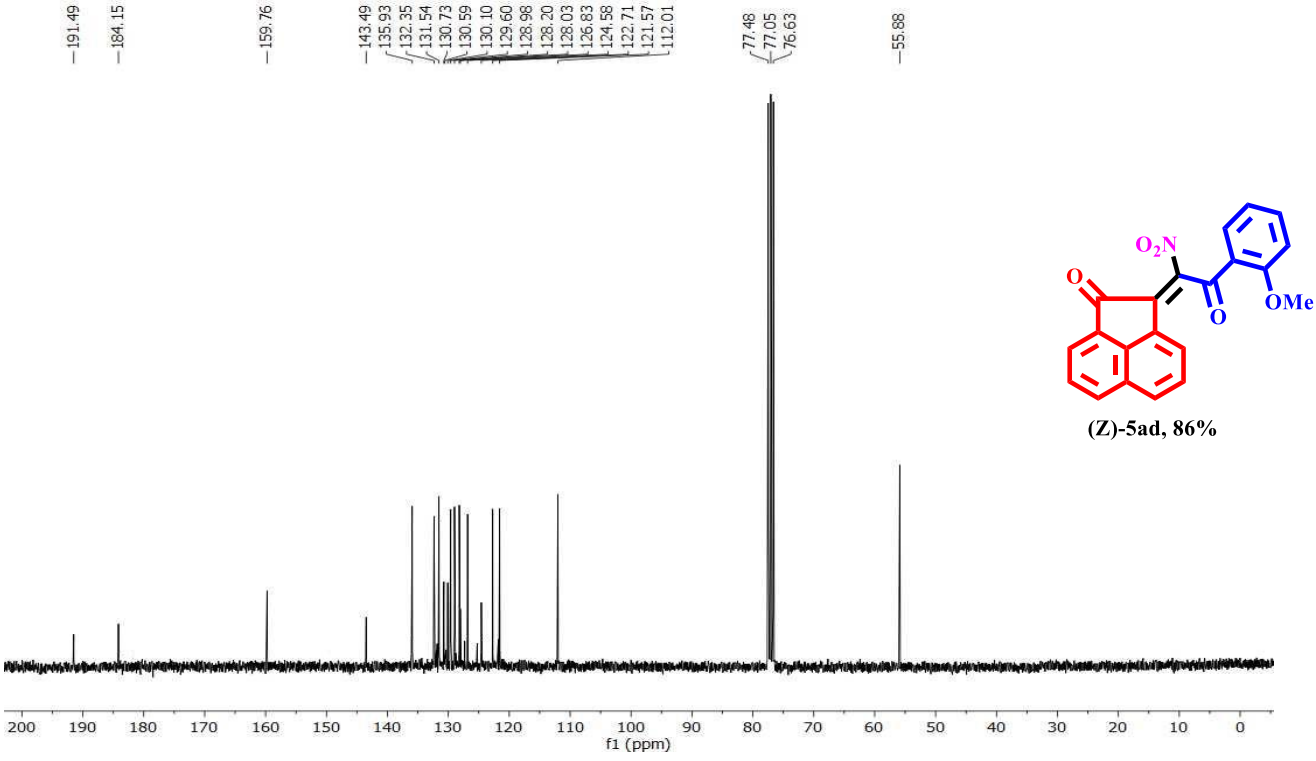


^{13}C NMR Spectrum of (Z)-5ac



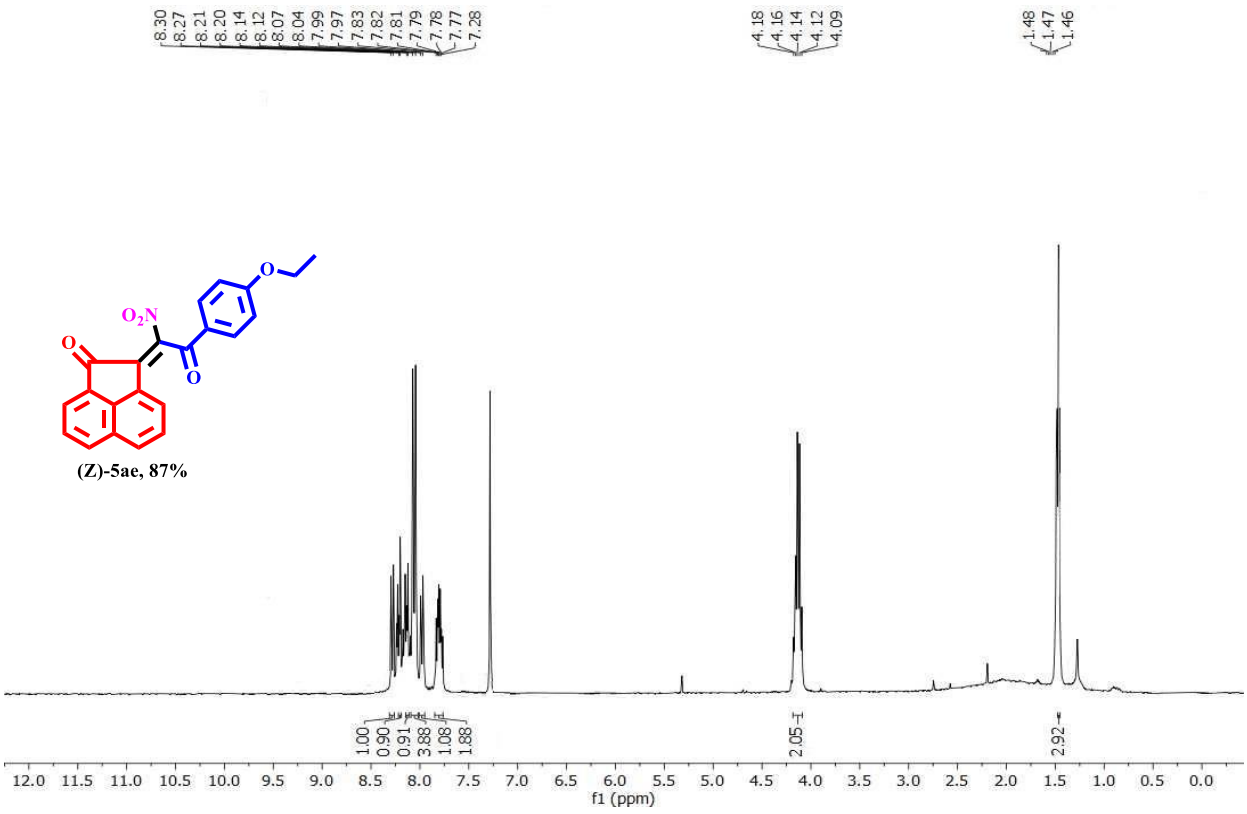
(Z)-5ad, 86%

^{1}H NMR Spectrum of (Z)-5ad

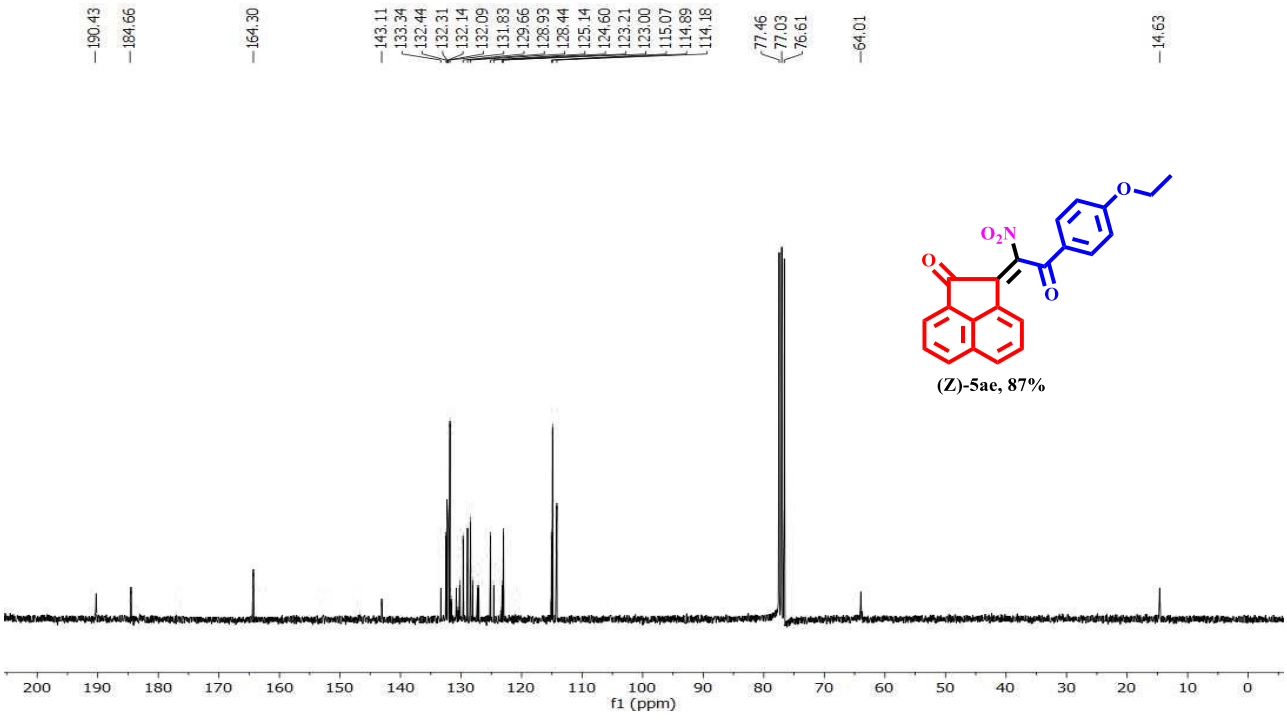


(Z)-5ad, 86%

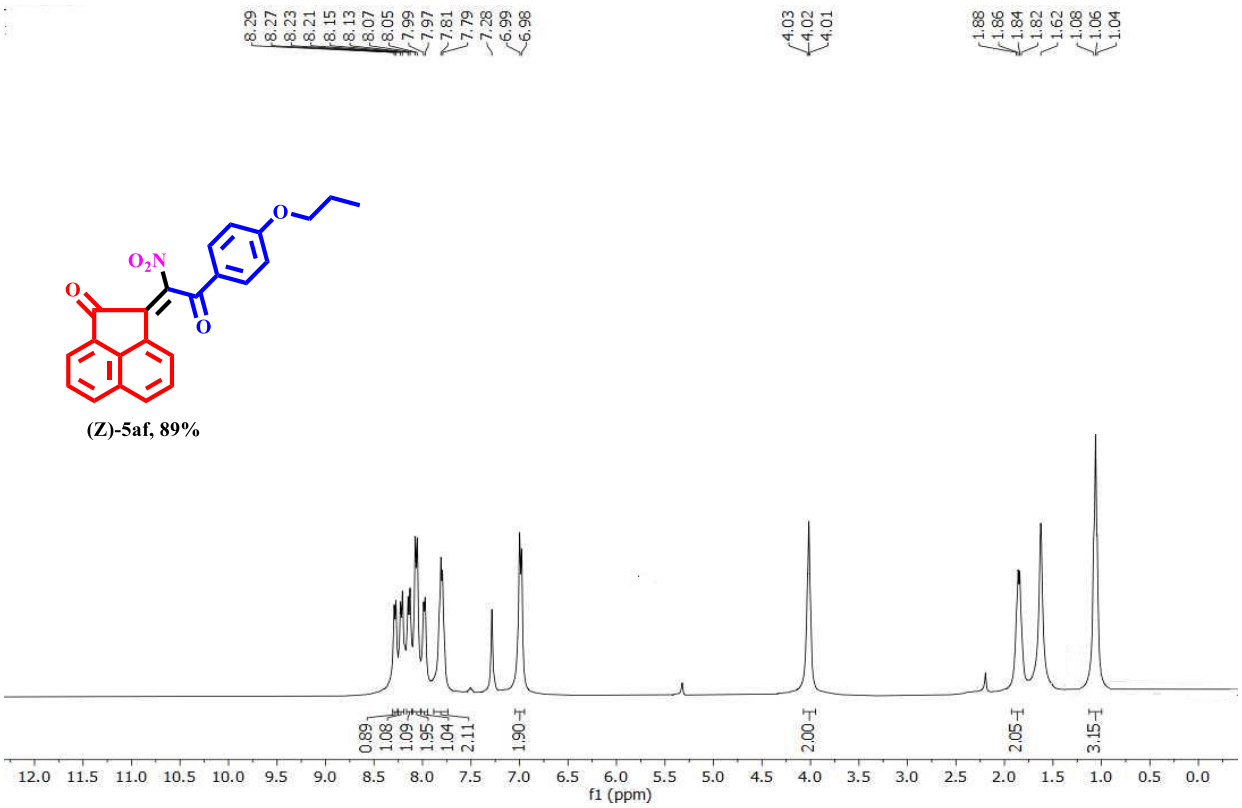
^{13}C NMR Spectrum of (Z)-5ad



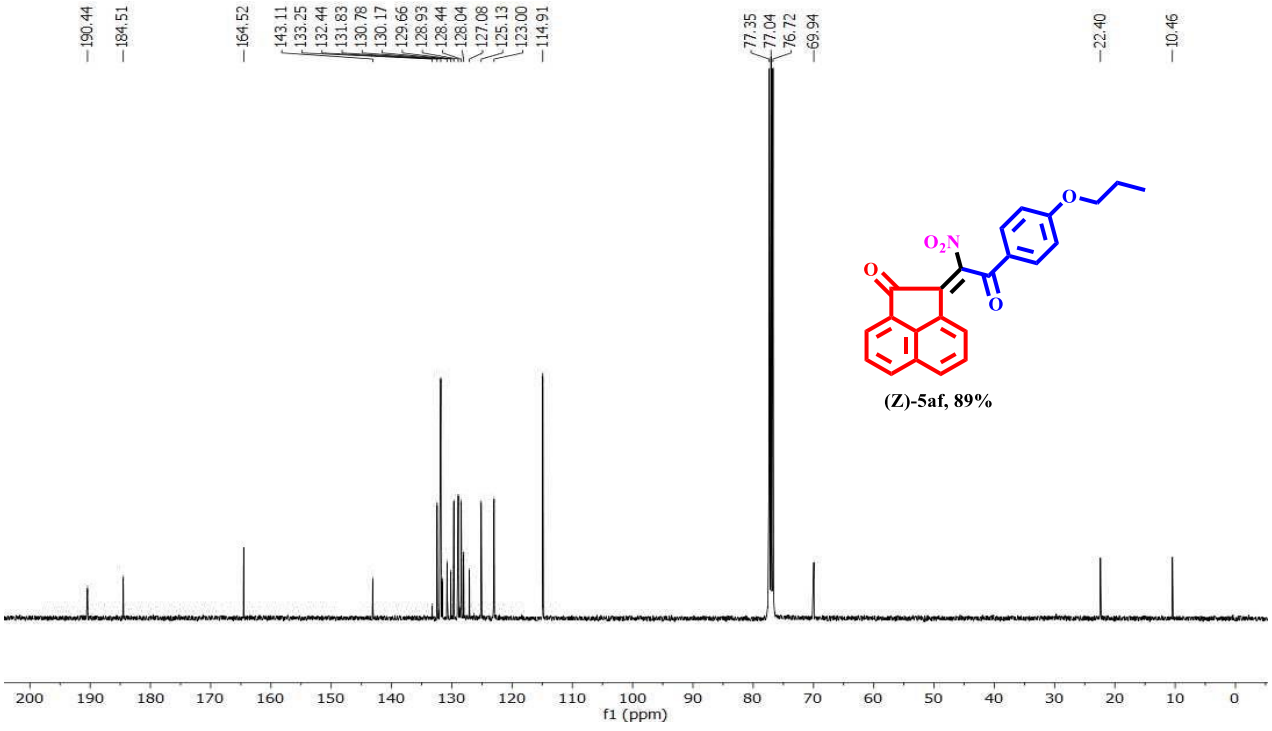
^{1}H NMR Spectrum of (Z)-5ae



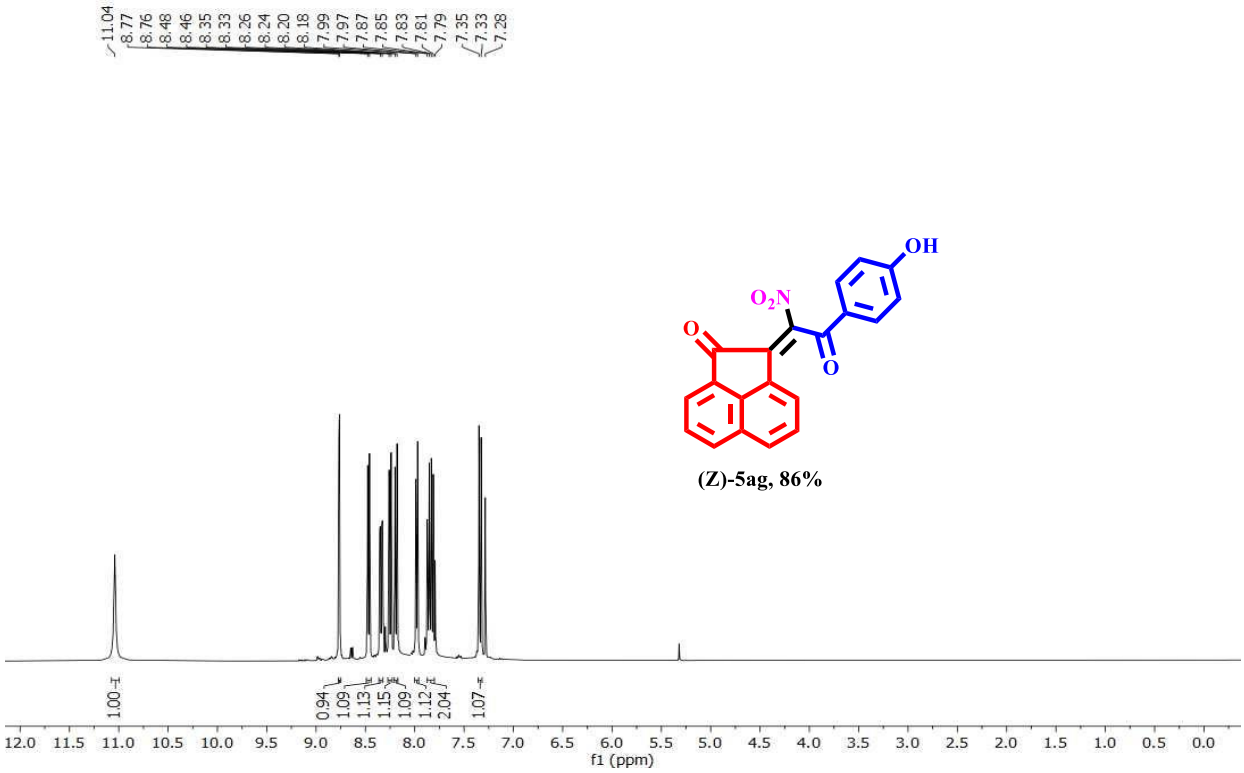
^{13}C NMR Spectrum of (Z)-5ae



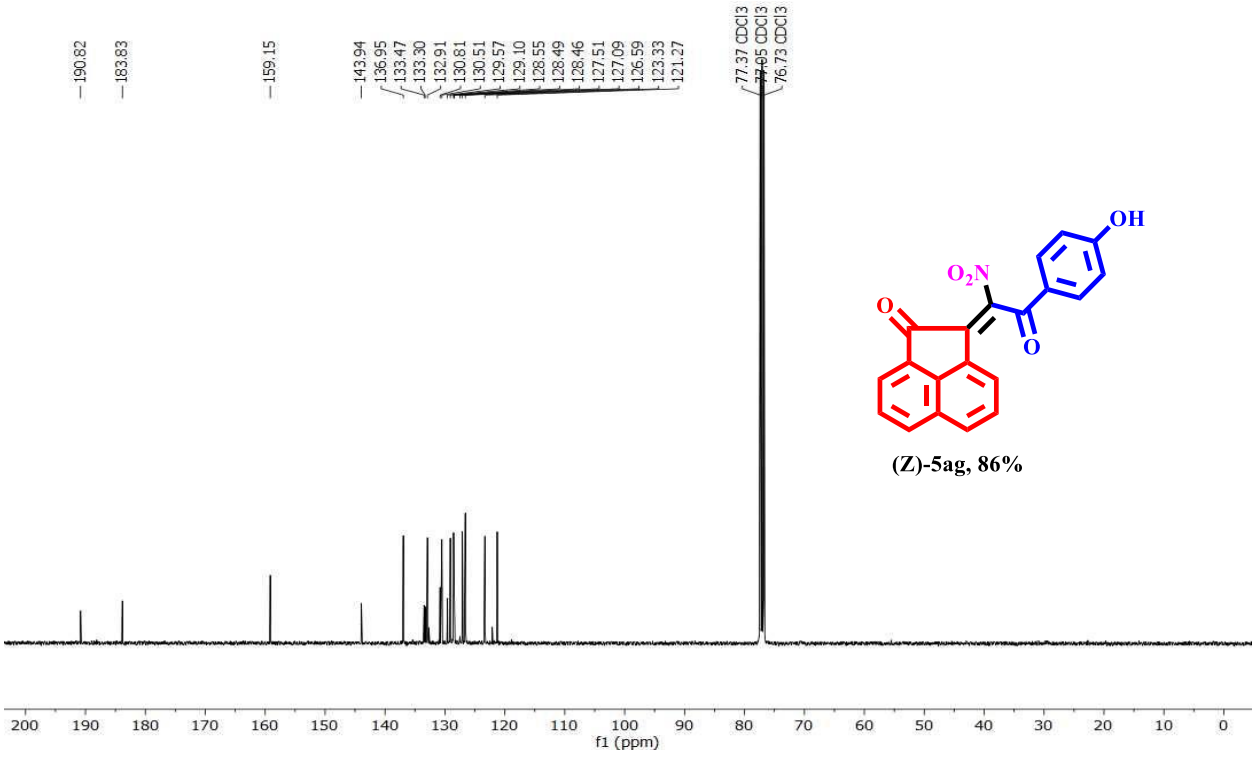
^{1}H NMR Spectrum of (Z)-5af



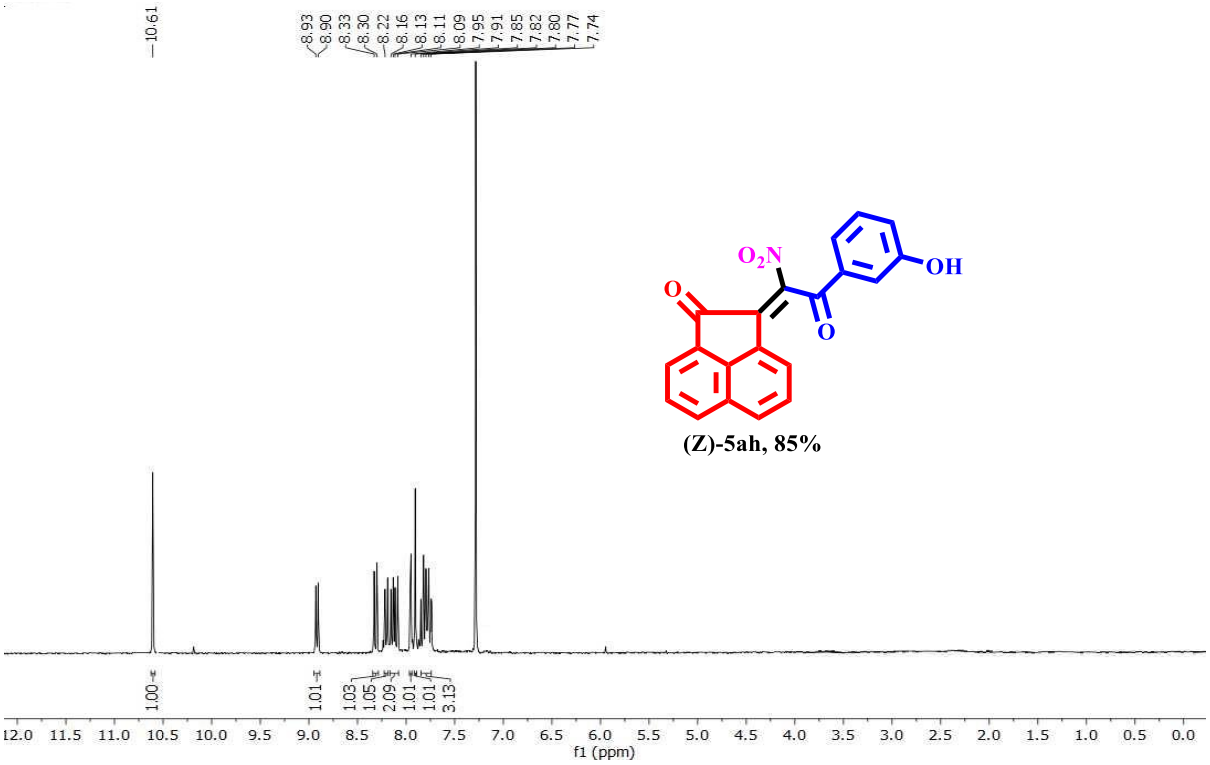
^{13}C NMR Spectrum of (Z)-5af



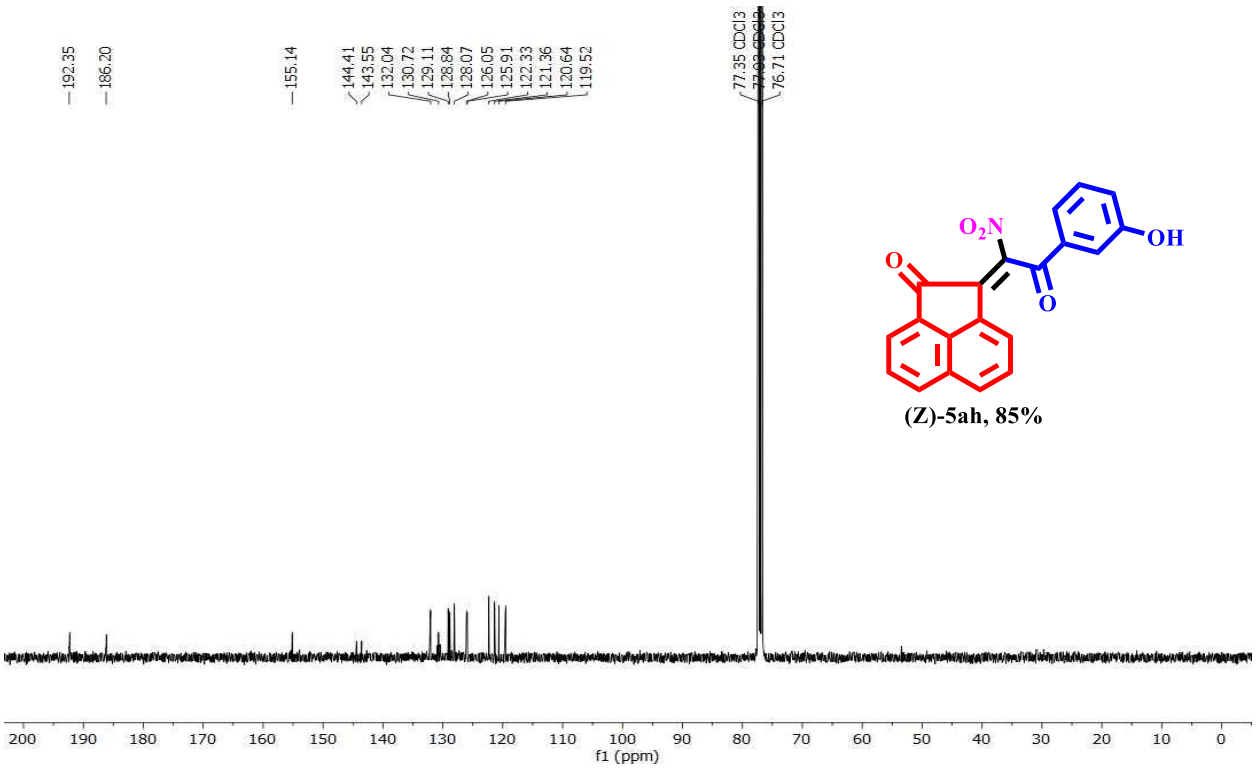
^{1}H NMR Spectrum of (Z)-5ag



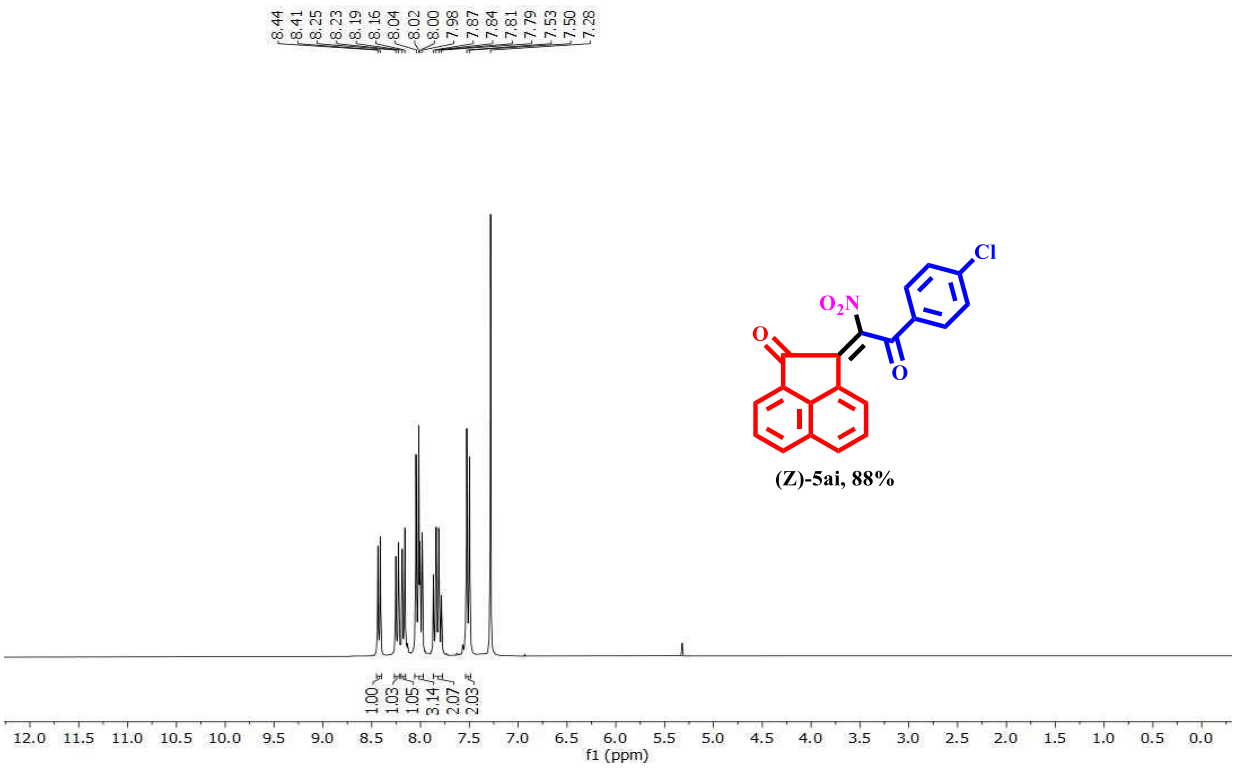
^{13}C NMR Spectrum of (Z)-5ag



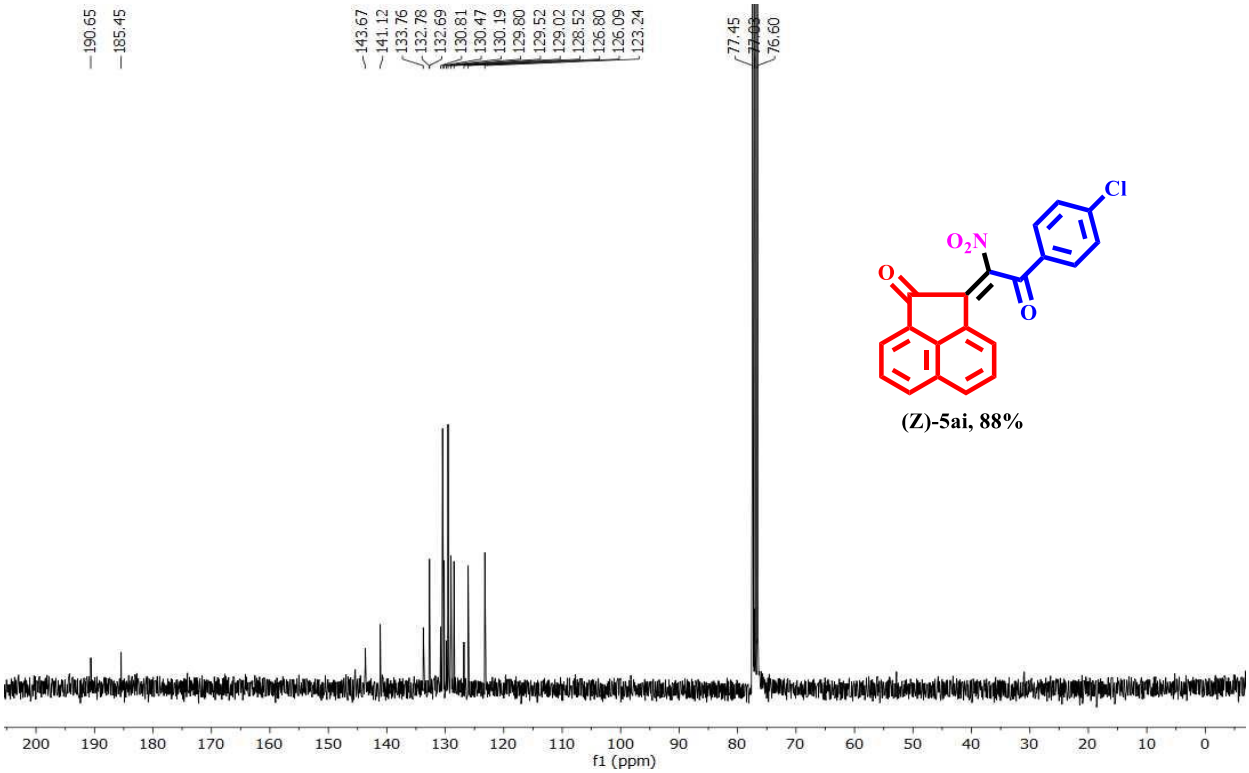
^{1}H NMR Spectrum of (Z)-5ah



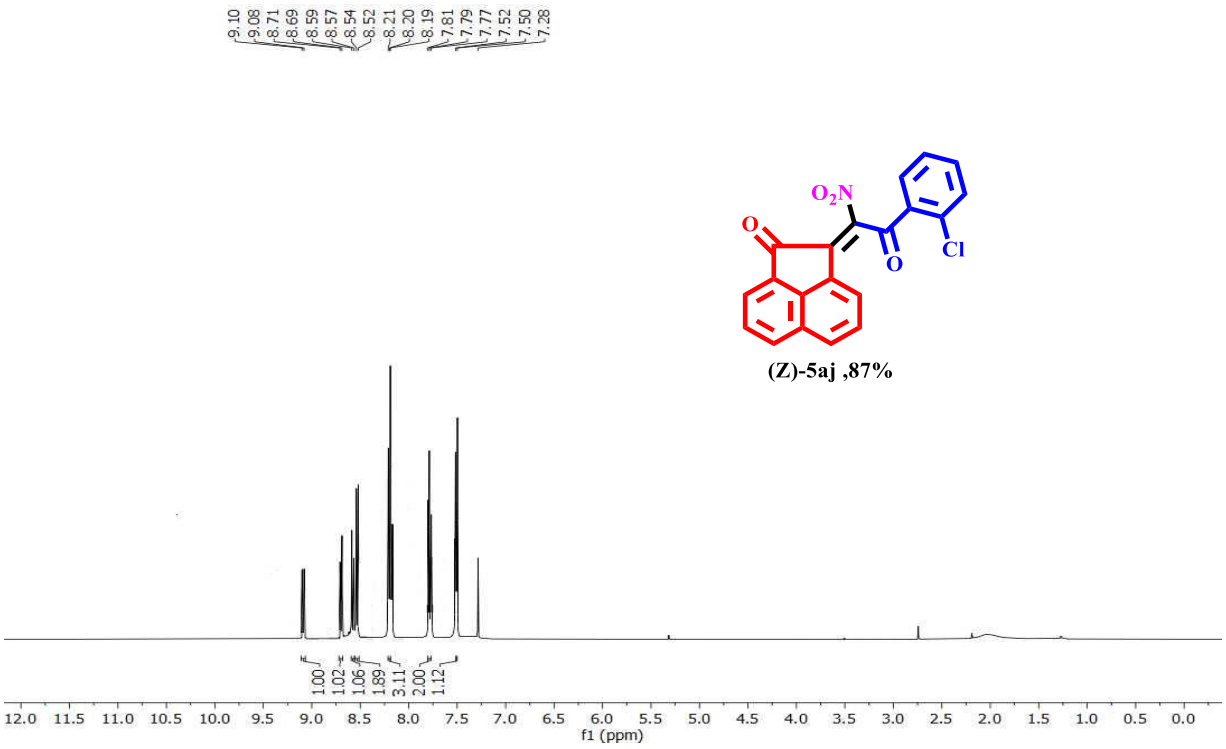
^{13}C NMR Spectrum of (Z)-5ah



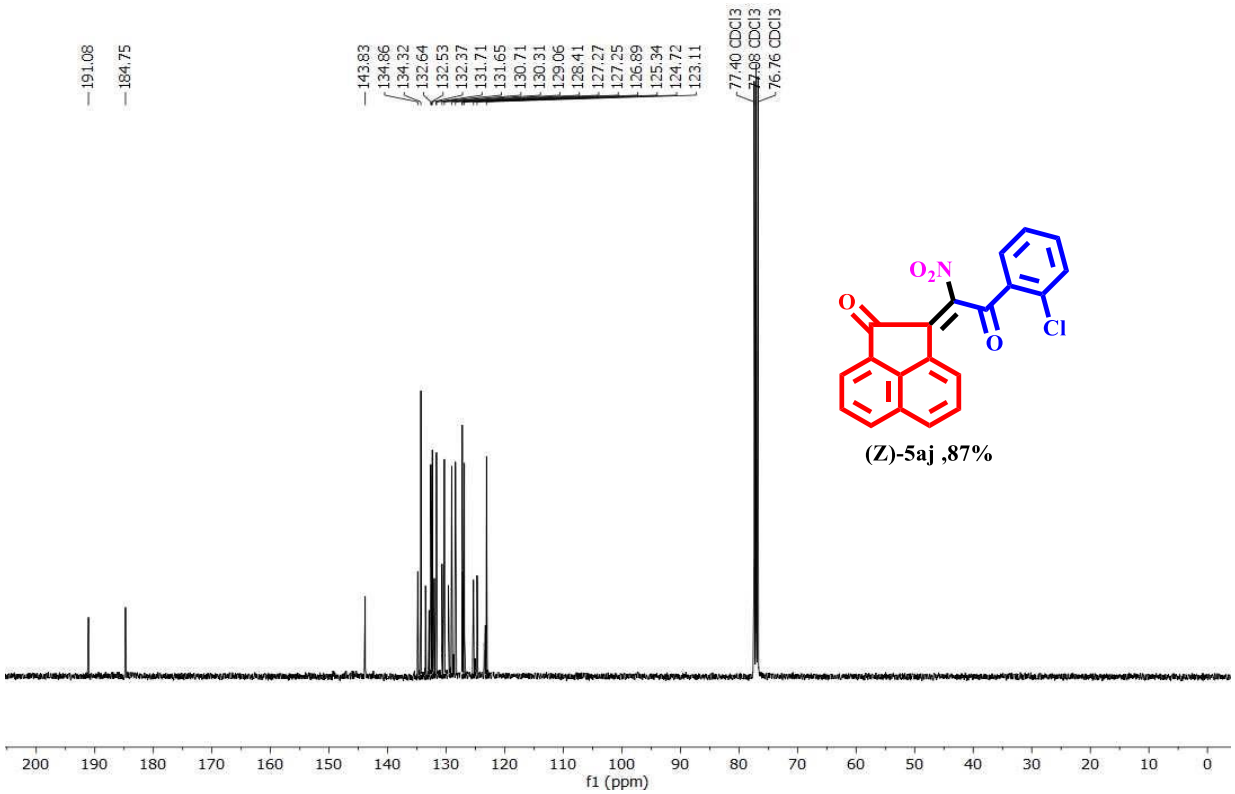
^{1}H NMR Spectrum of (Z)-5ai



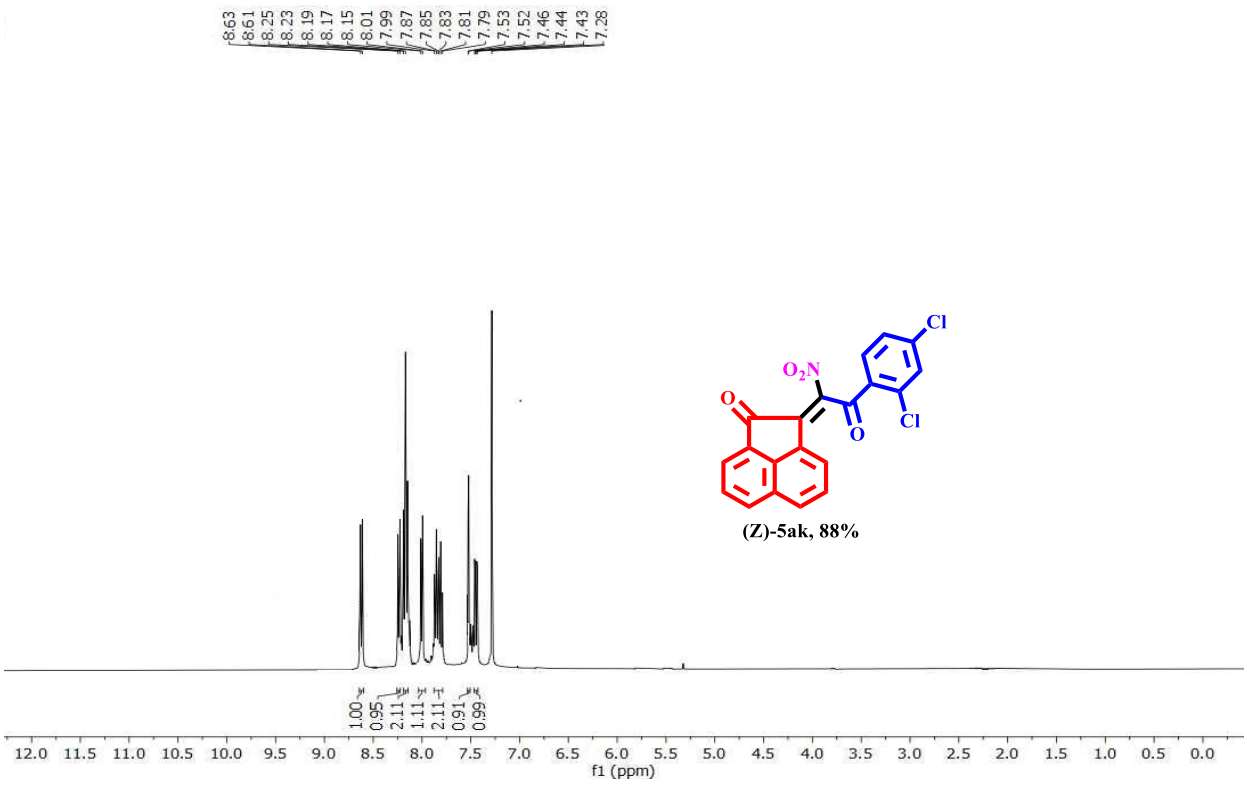
^{13}C NMR Spectrum of (Z)-5ai



^{1}H NMR Spectrum of (Z)-5aj

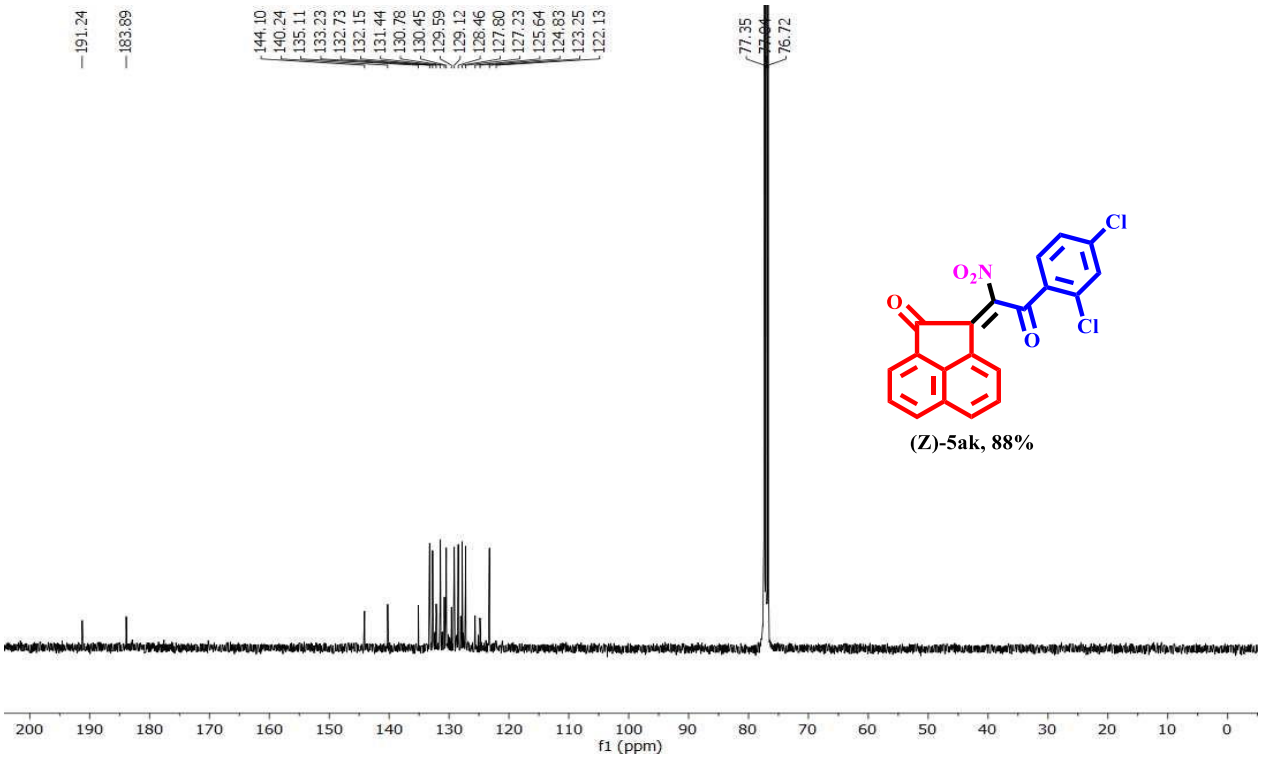


^{13}C NMR Spectrum of (Z)-5aj



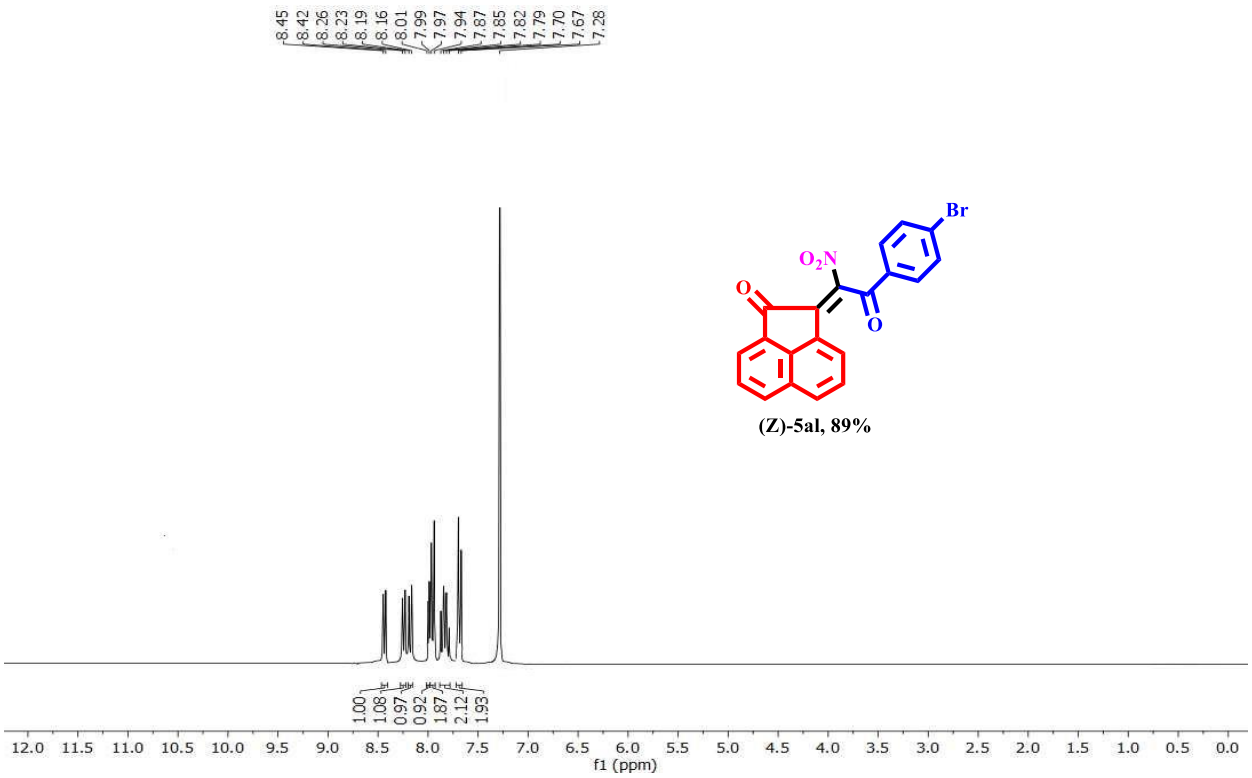
(Z)-5ak, 88%

^{1}H NMR Spectrum of (Z)-5ak

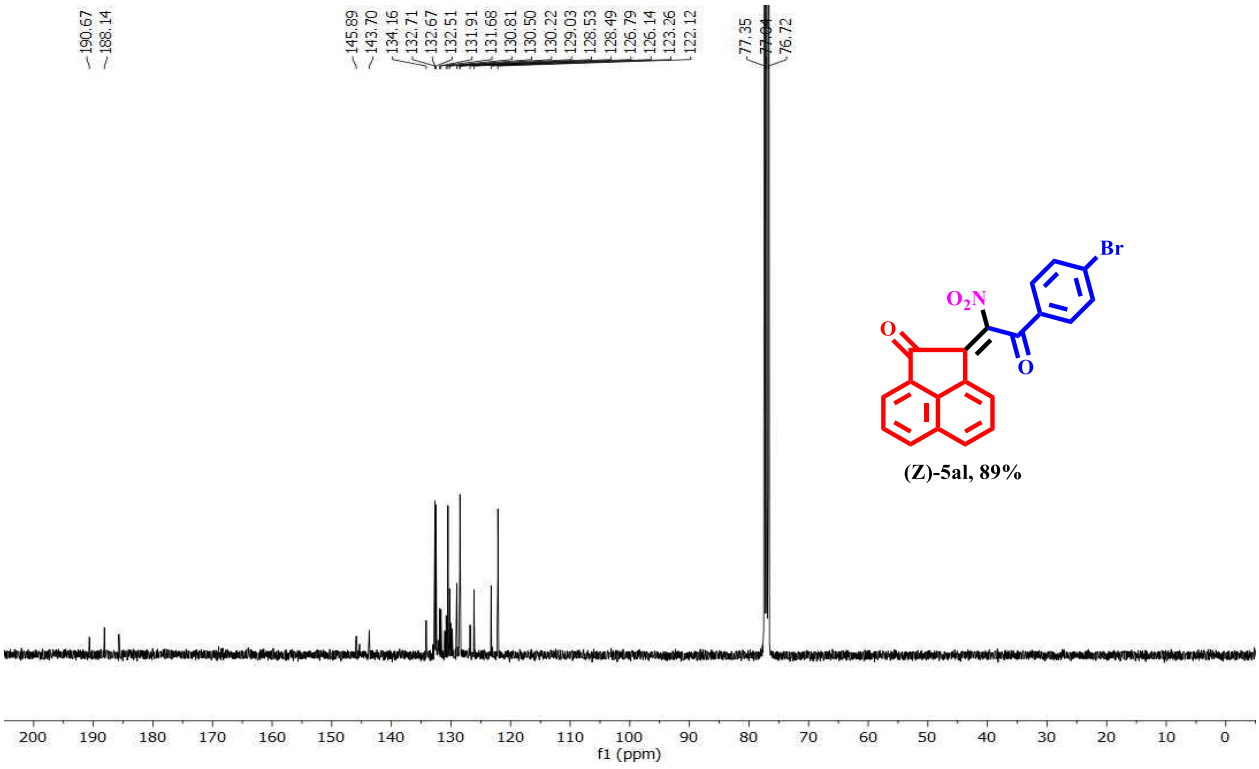


(Z)-5ak, 88%

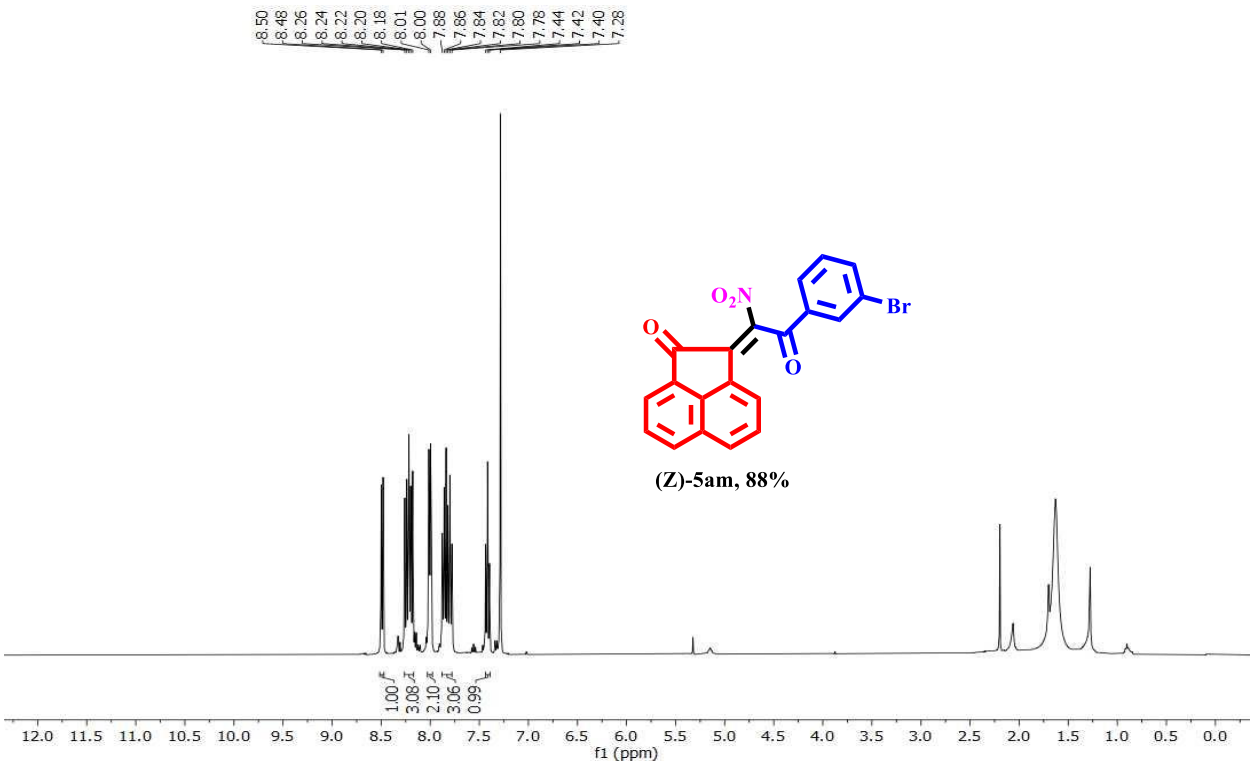
^{13}C NMR Spectrum of (Z)-5ak



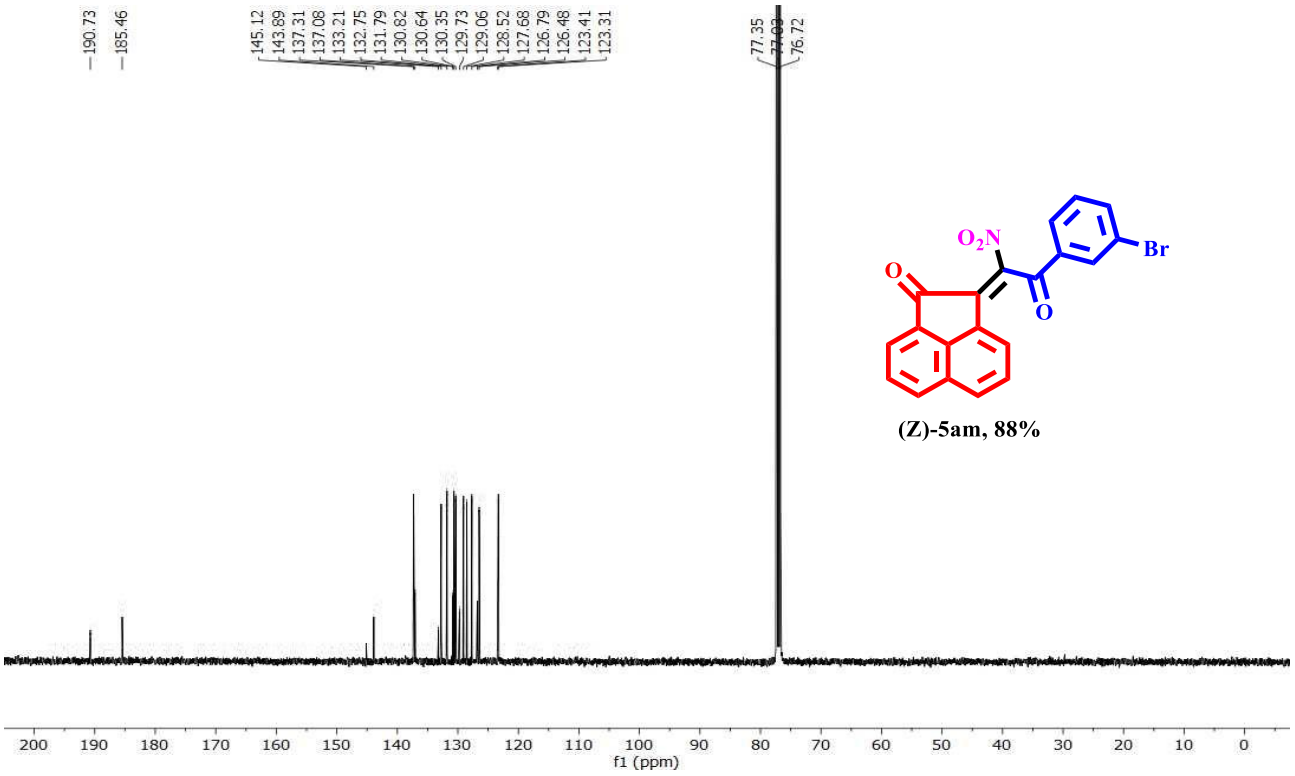
^{1}H NMR Spectrum of (Z)-5al



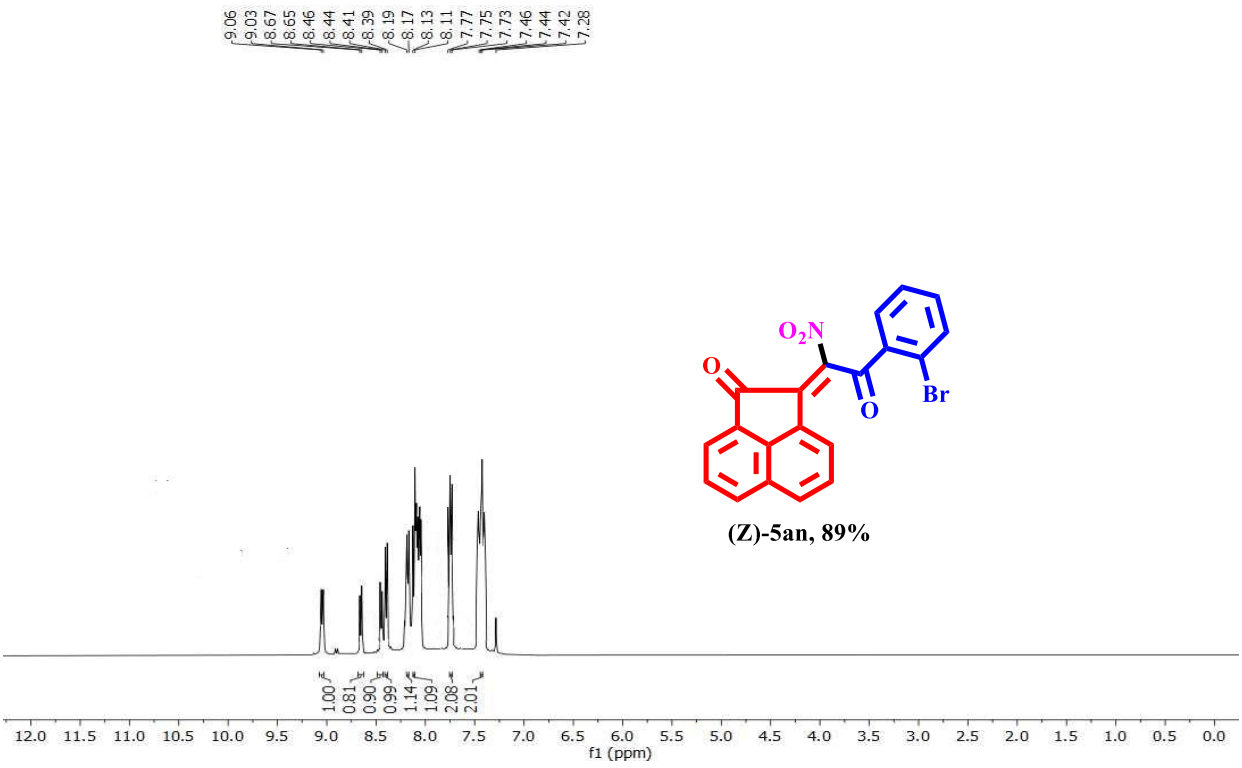
^{13}C NMR Spectrum of (Z)-5al



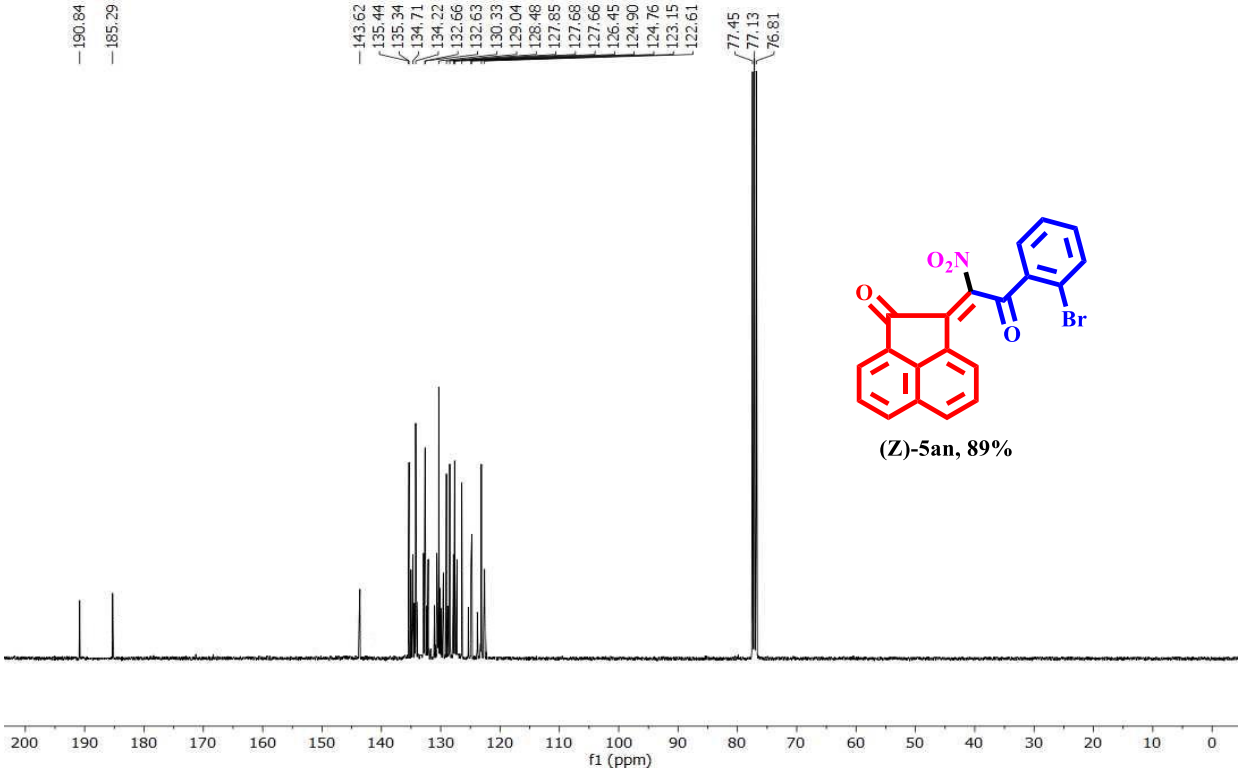
^{1}H NMR Spectrum of (Z)-5am



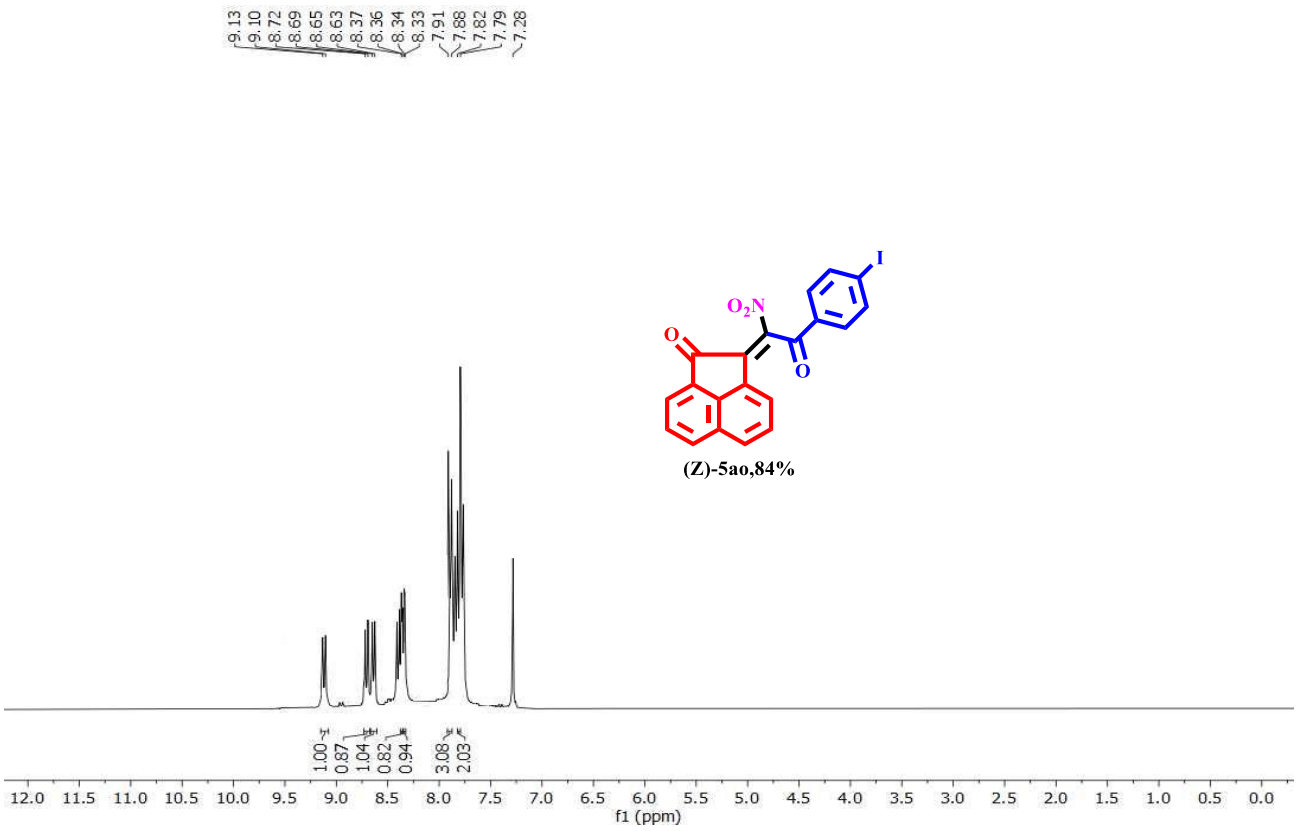
^{13}C NMR Spectrum of (Z)-5am



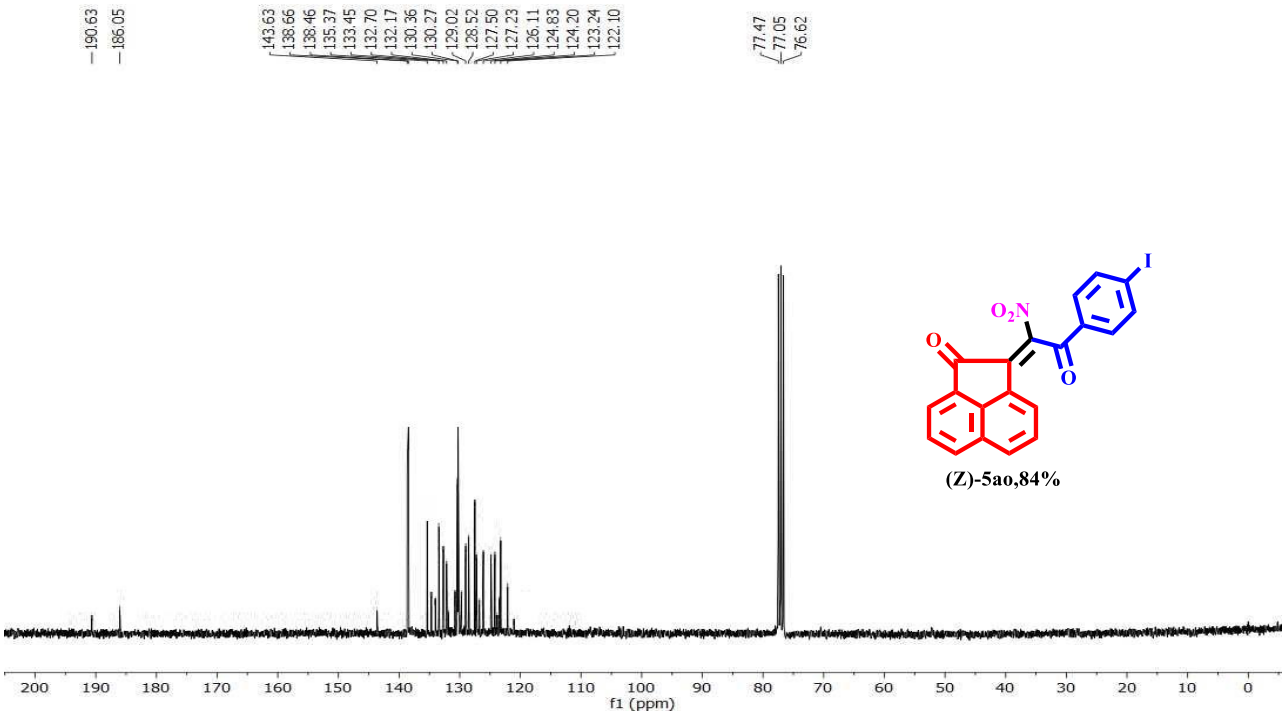
^{1}H NMR Spectrum of (Z)-5an



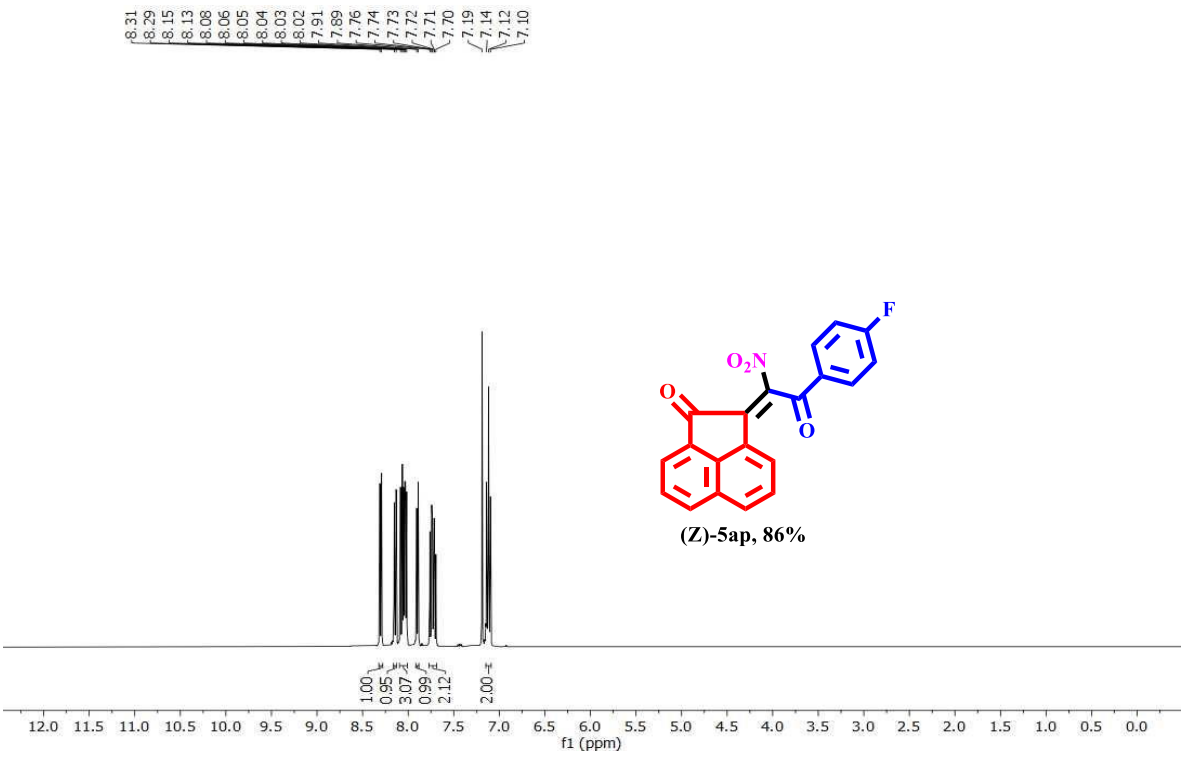
^{13}C NMR Spectrum of (Z)-5an



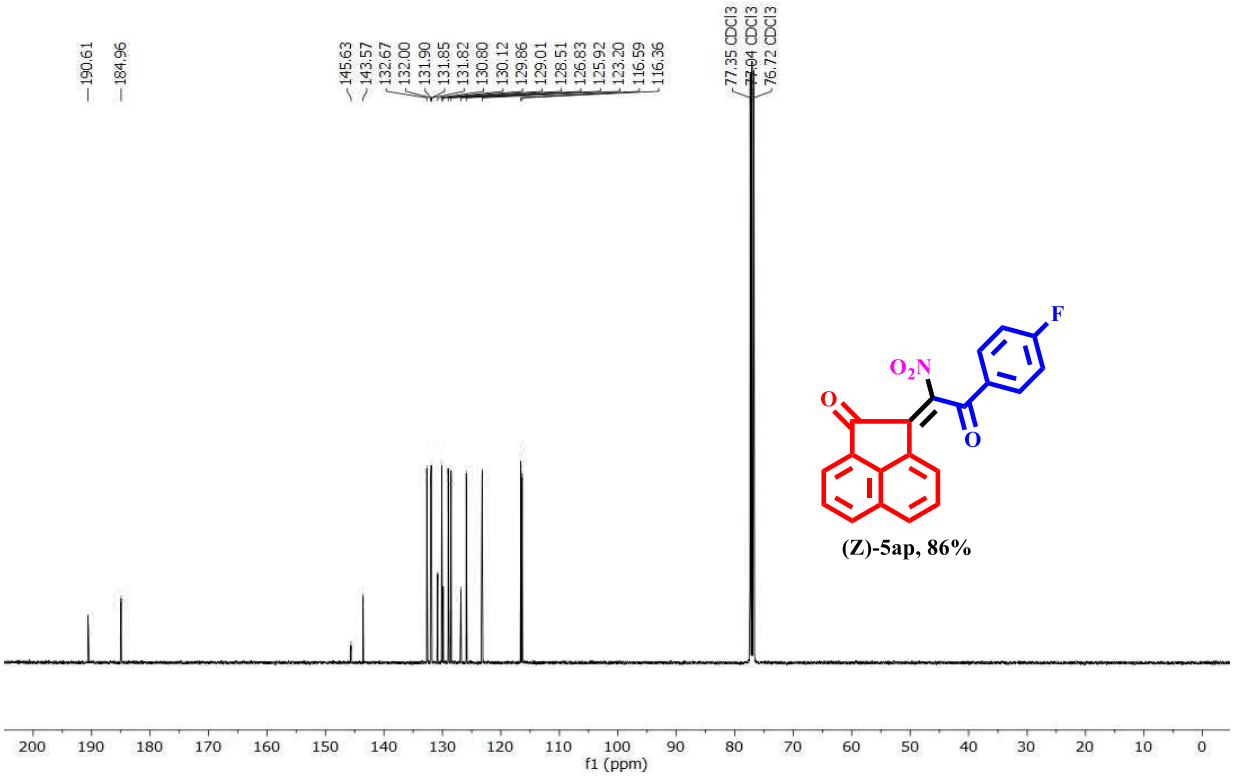
^{1}H NMR Spectrum of (Z)-5ao



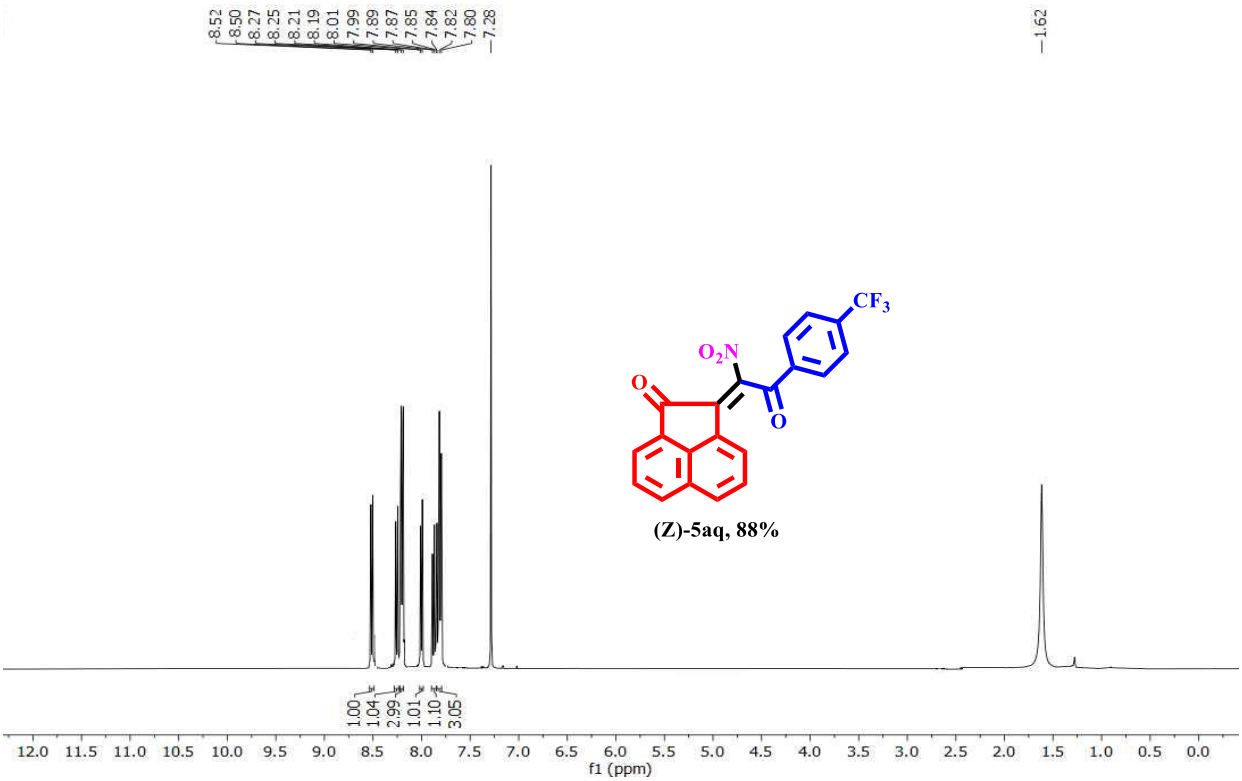
^{13}C NMR Spectrum of (Z)-5ao



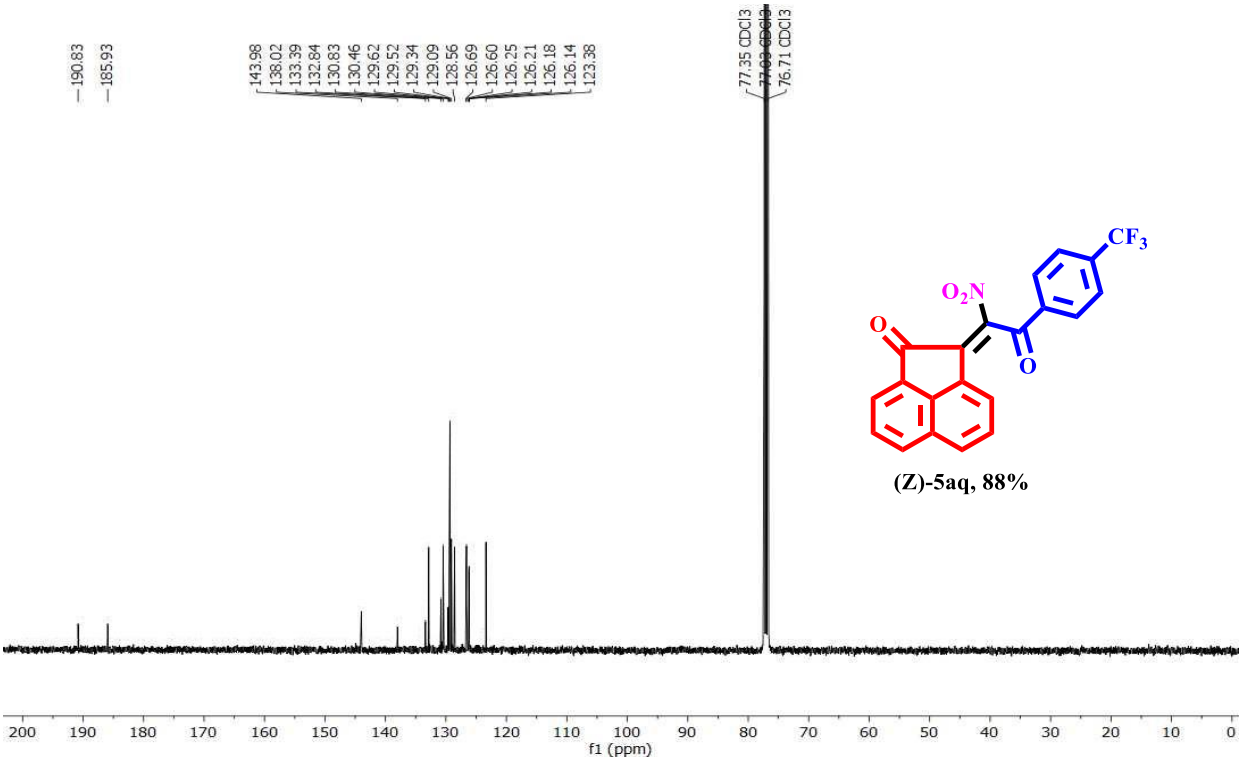
^{1}H NMR Spectrum of (Z)-5ap



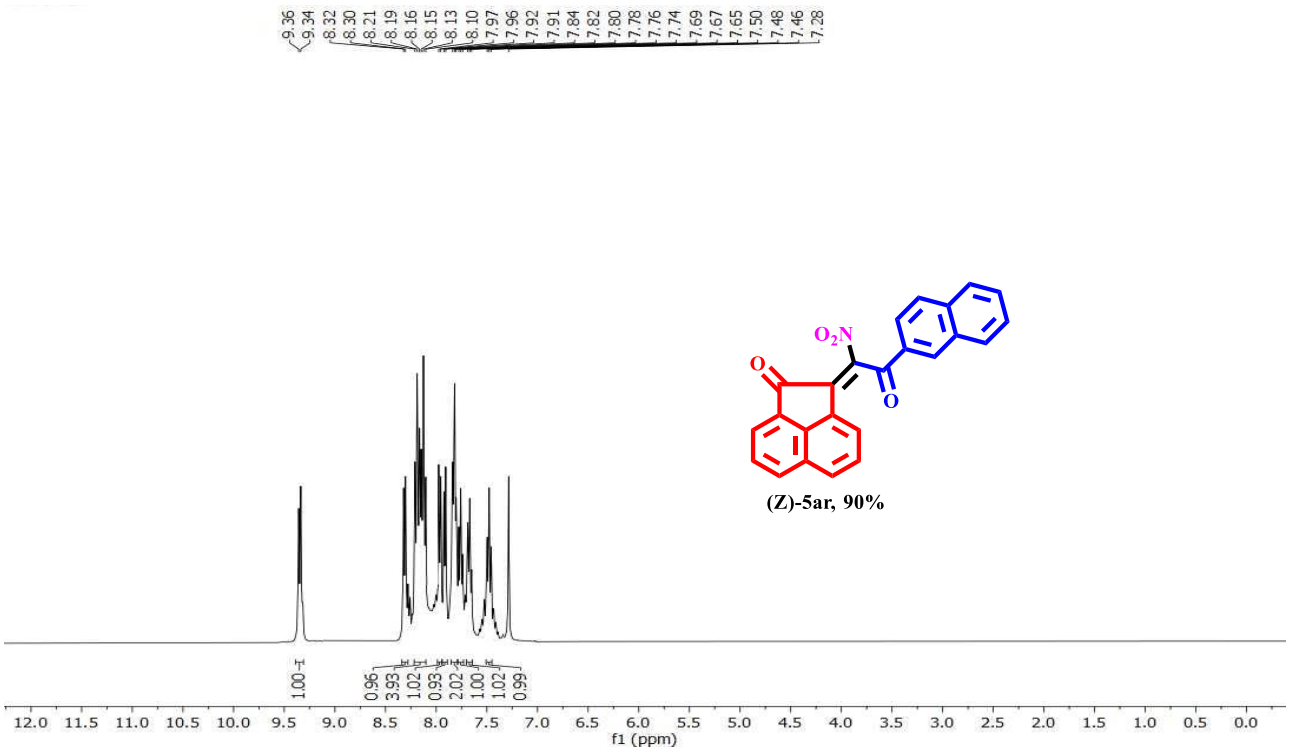
^{13}C NMR Spectrum of (Z)-5ap



^{1}H NMR Spectrum of (Z)-5aq

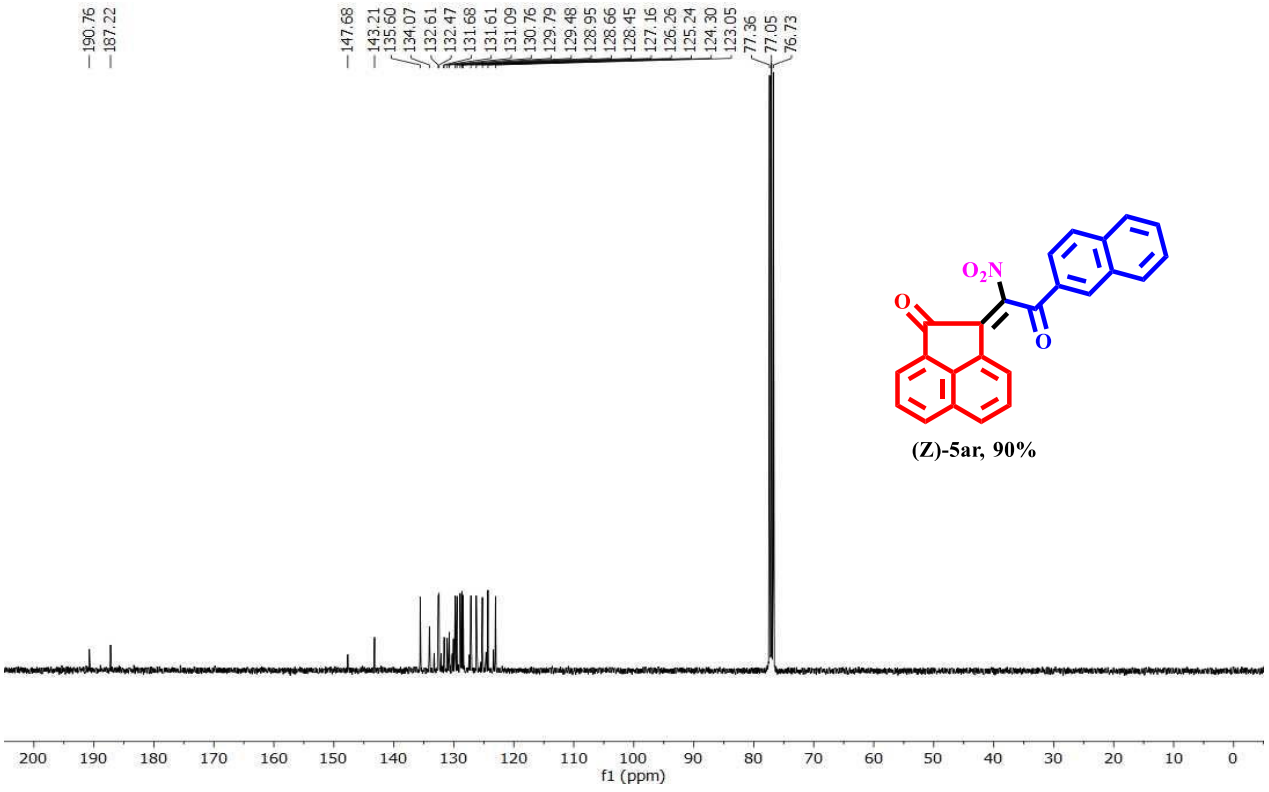


^{13}C NMR Spectrum of (Z)-5aq



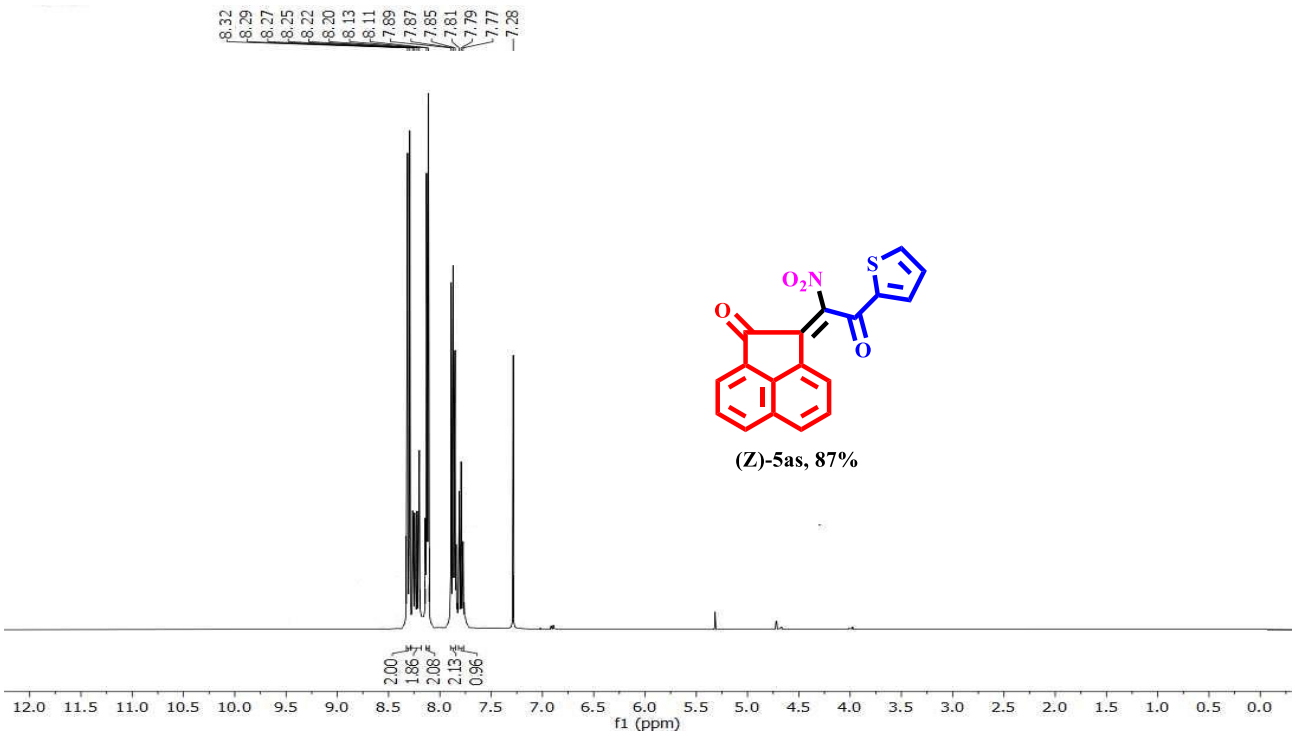
(Z)-5ar, 90%

^{1}H NMR Spectrum of (Z)-5ar



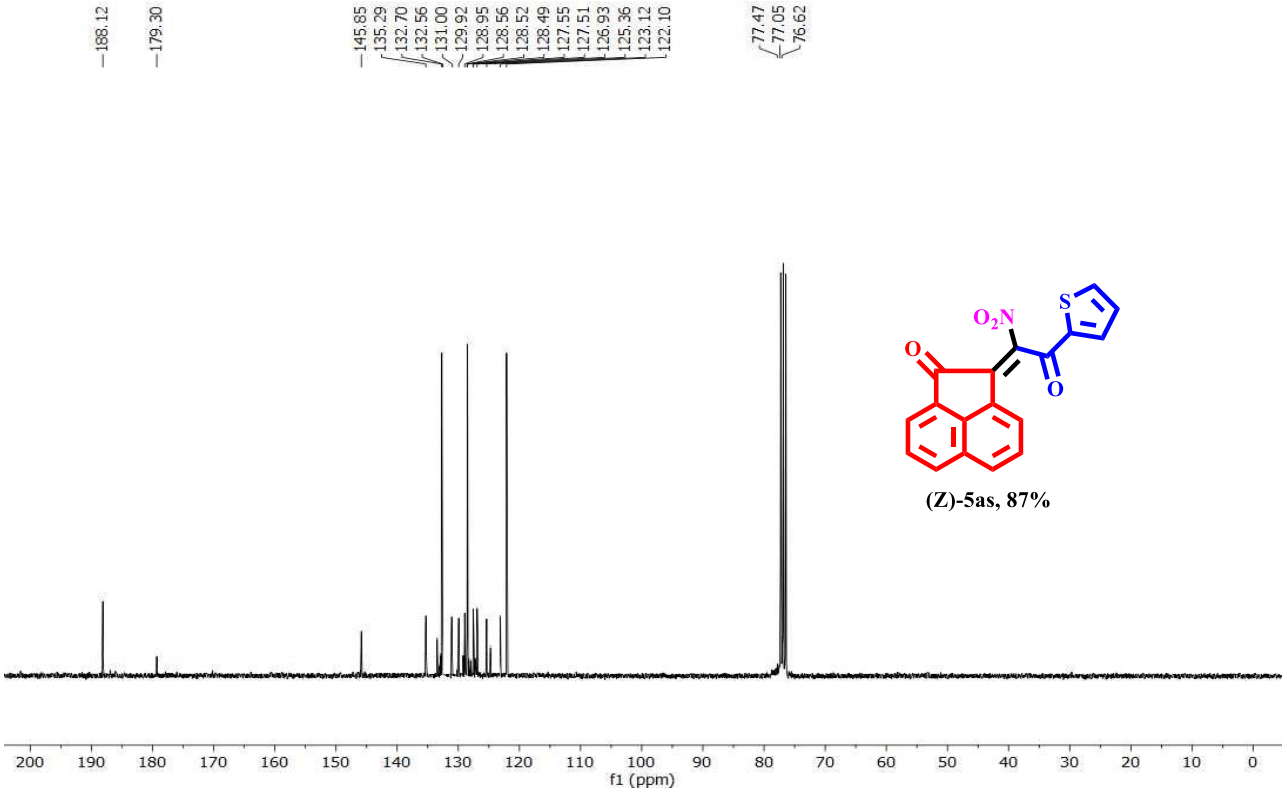
(Z)-5ar, 90%

^{13}C NMR Spectrum of (Z)-5ar



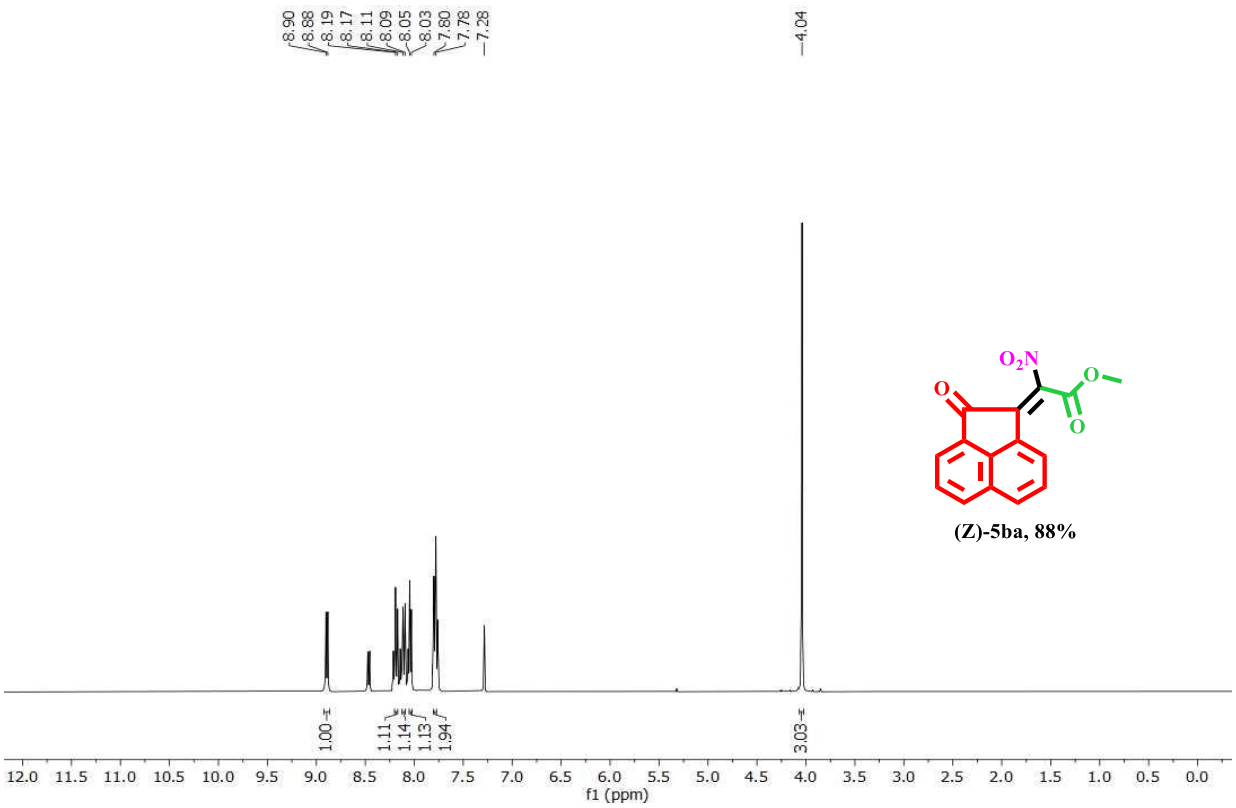
(Z)-5as, 87%

^{1}H NMR Spectrum of (Z)-5as

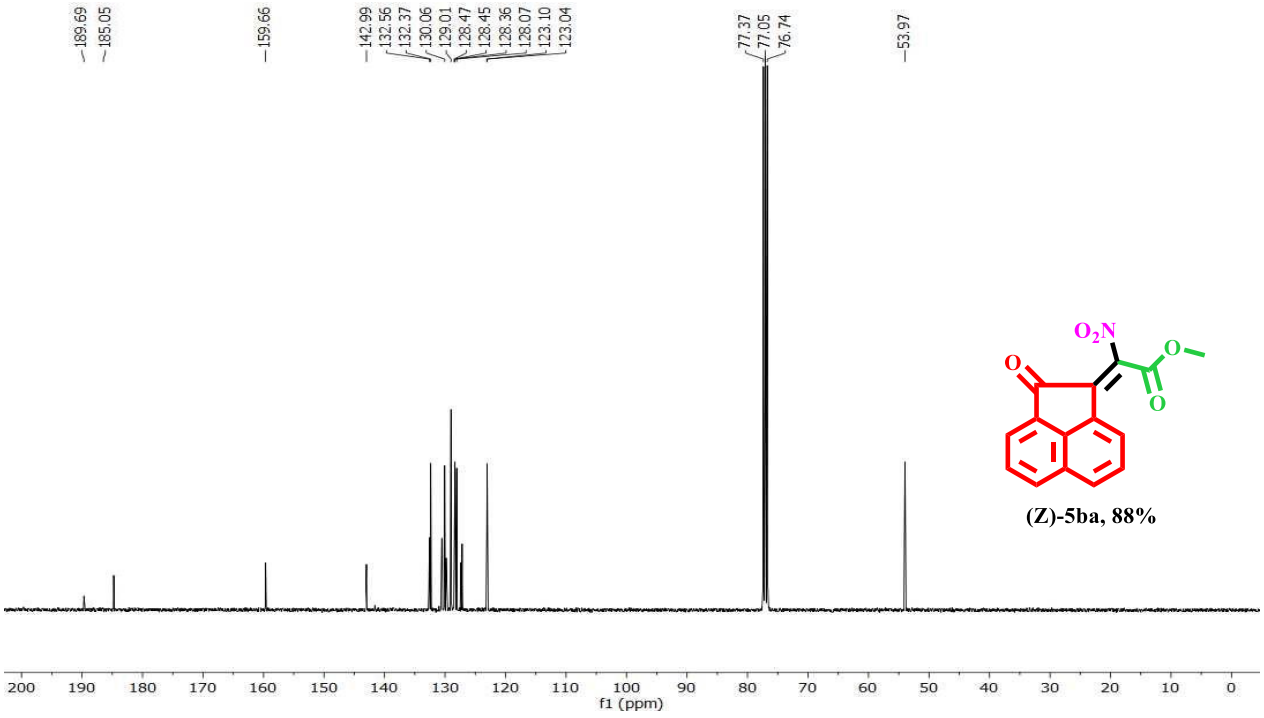


(Z)-5as, 87%

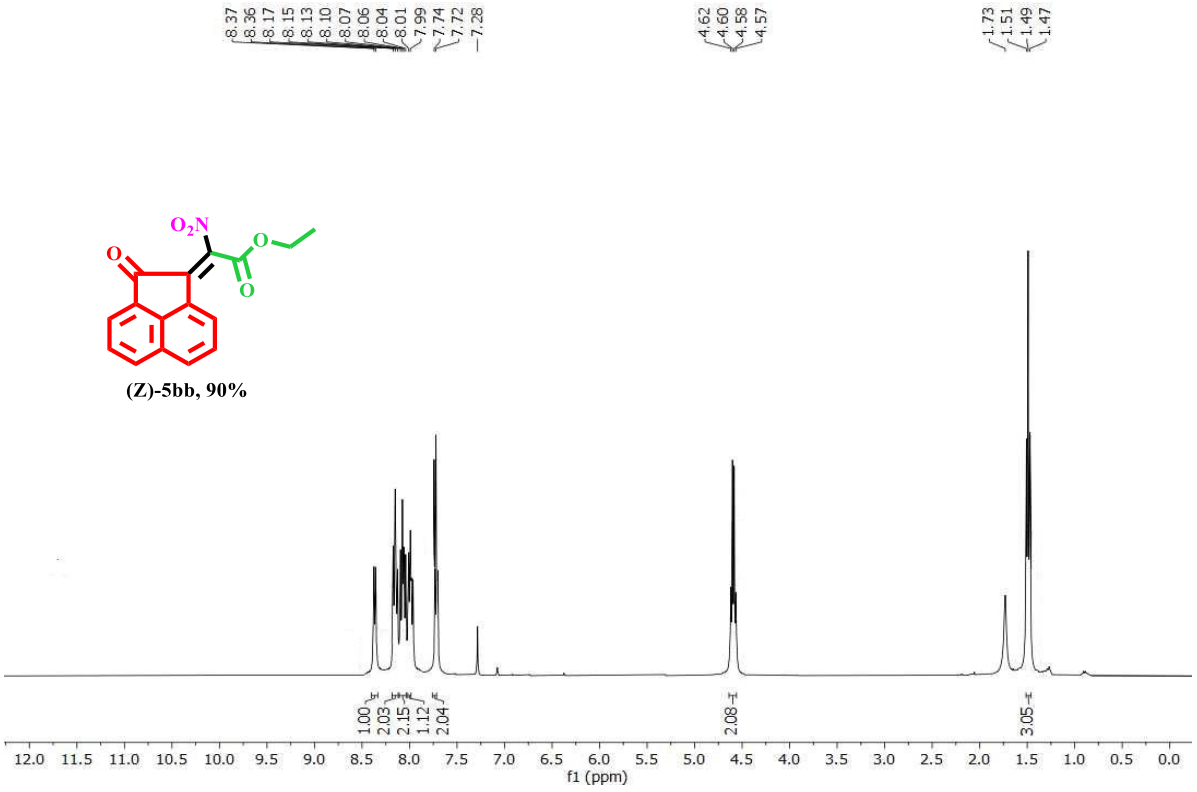
^{13}C NMR Spectrum of (Z)-5as



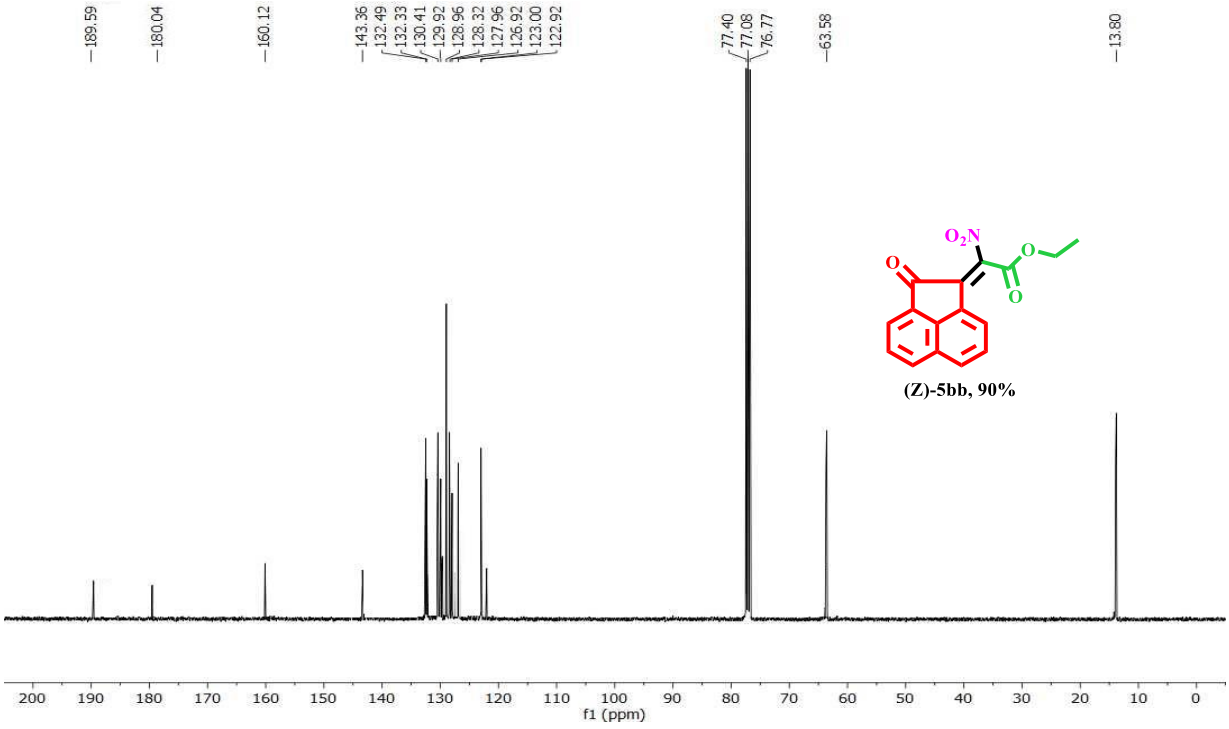
^{1}H NMR Spectrum of (Z)-5ba



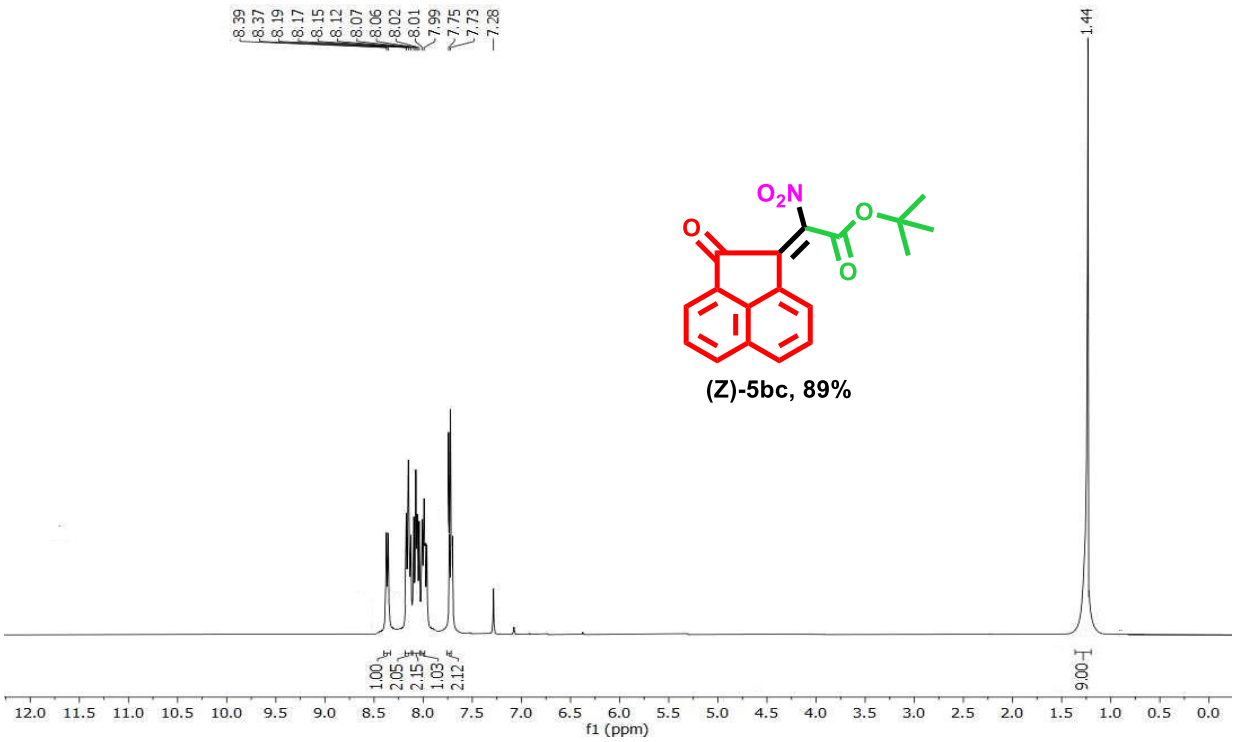
^{13}C NMR Spectrum of (Z)-5ba



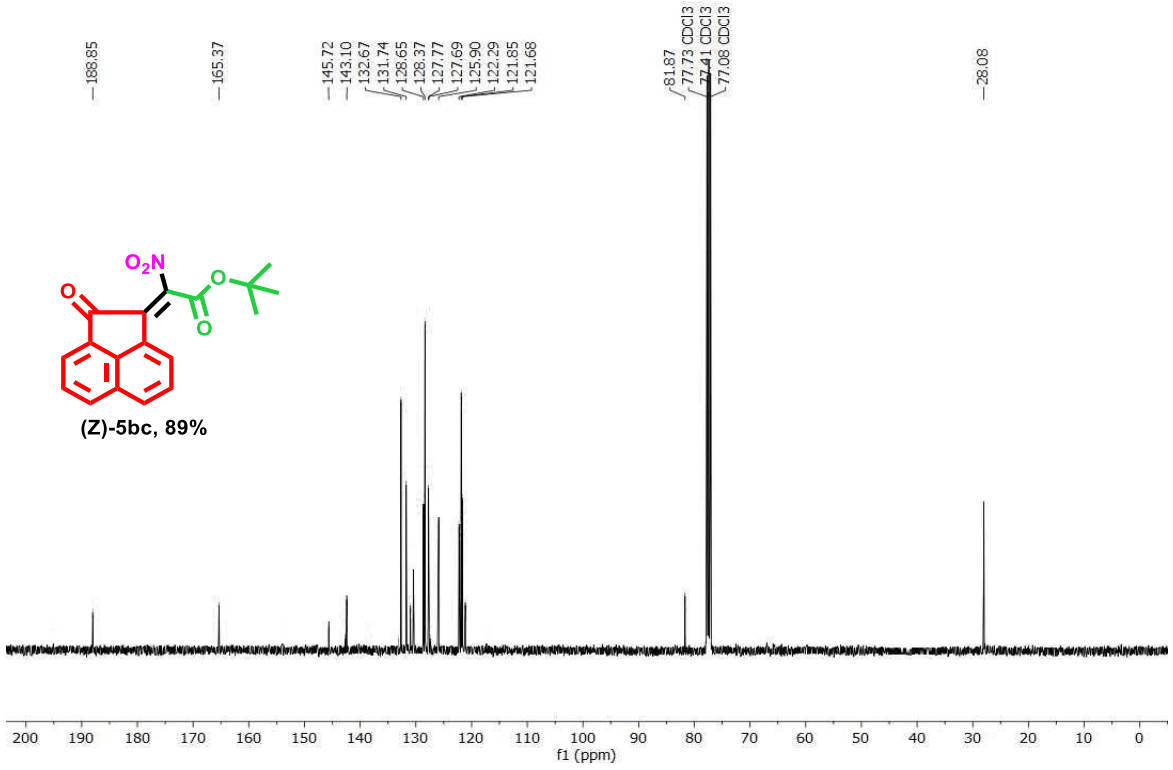
^{1}H NMR Spectrum of (Z)-5bb



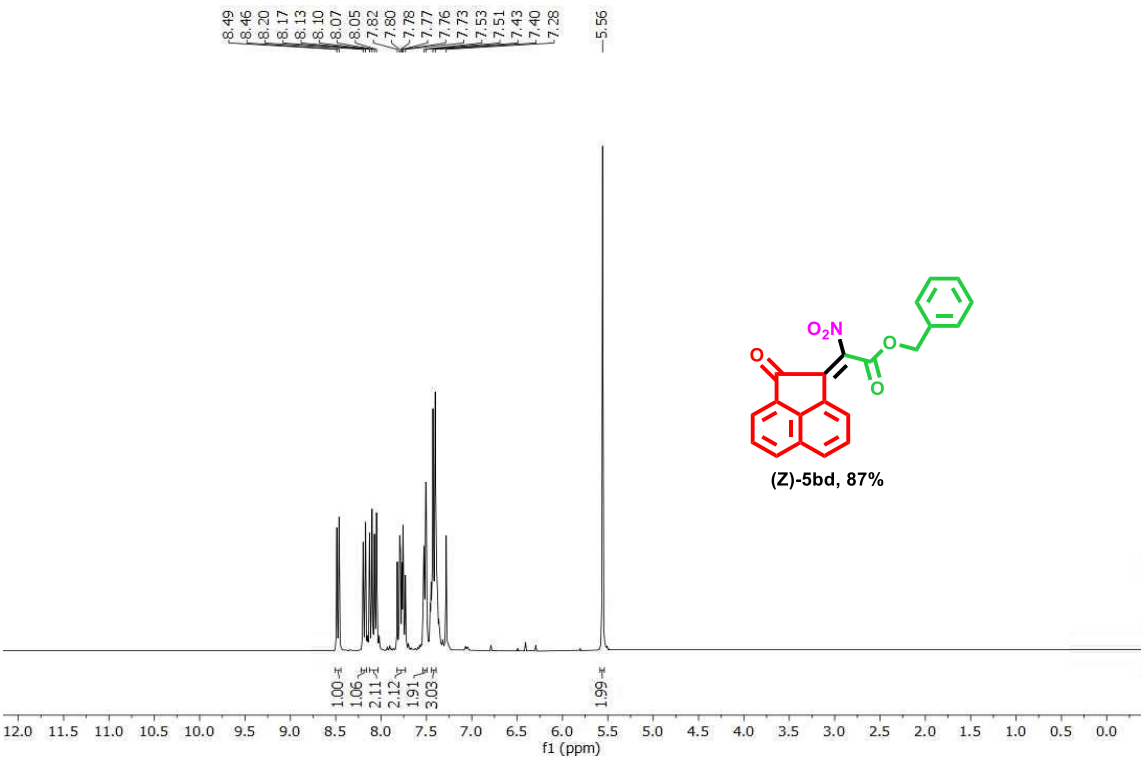
^{13}C NMR Spectrum of (Z)-5bb



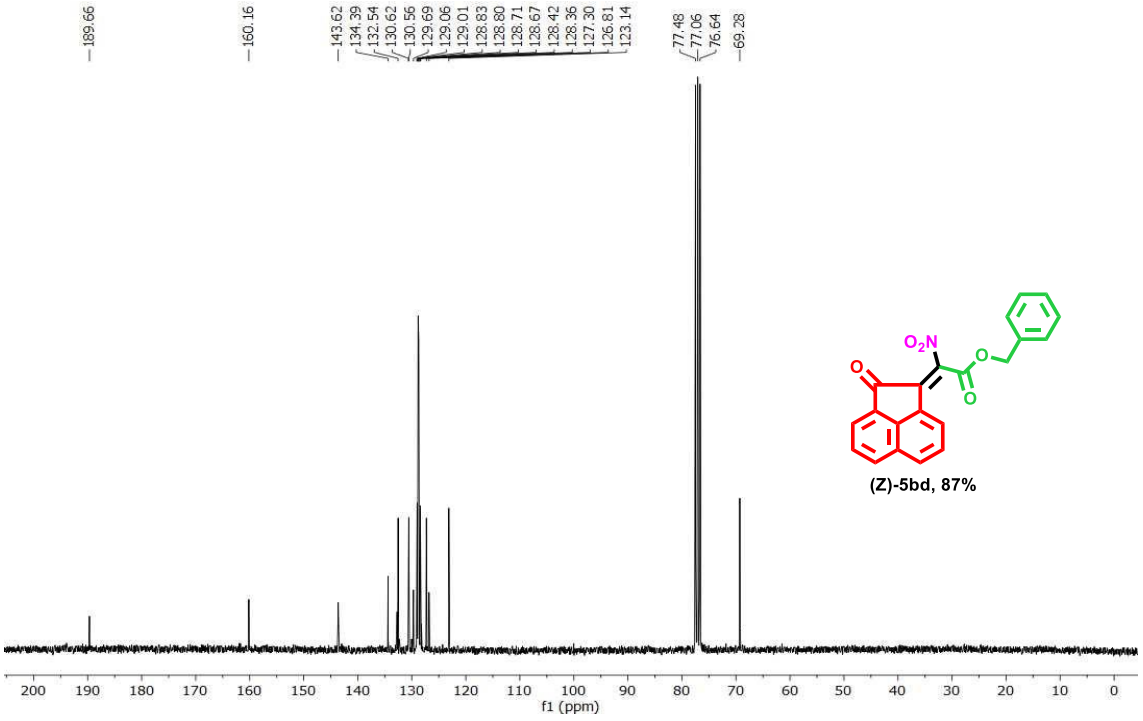
^{1}H NMR Spectrum of (Z)-5bc



^{13}C NMR Spectrum of (Z)-5bc

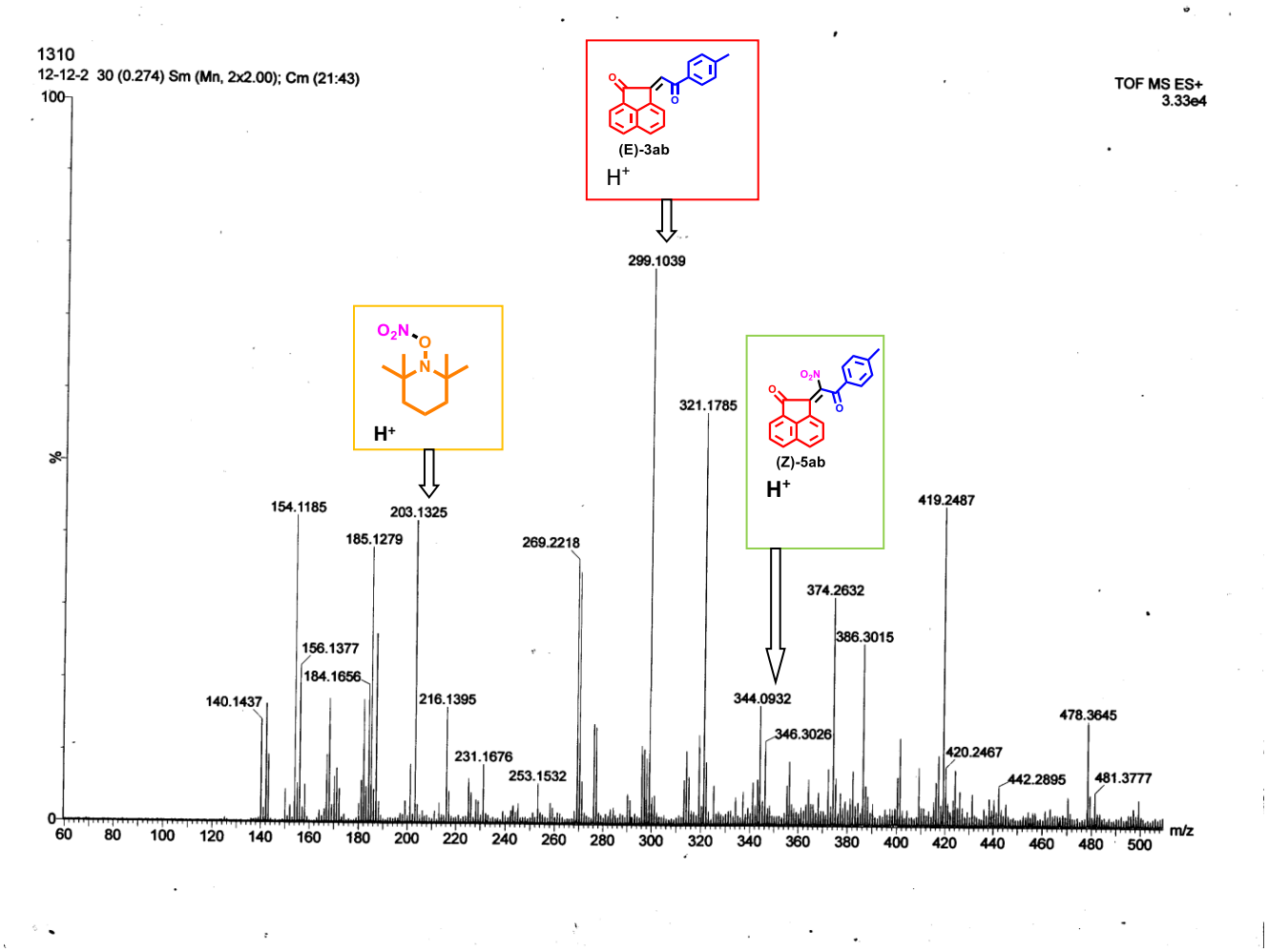


^{1}H NMR Spectrum of (Z)-5bd



^{13}C NMR Spectrum of (Z)-5bd

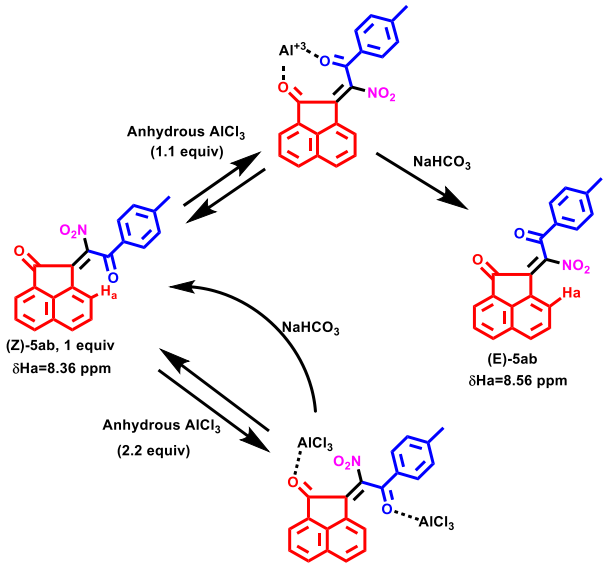
Mass spectrum of the crude reaction mixture



Experiment to prove the geometry of the synthesized compound (Z)-5ab :

Initially we took 1.1 equiv. of **(Z)-5ab** in a dry 10 ml round bottomed flask in dry CH_2Cl_2 (5 ml) in presence of 1 equiv. of anhydrous $AlCl_3$. After 48 hours the reaction was quenched in an aqueous solution of saturated $NaHCO_3$, extracted with CH_2Cl_2 and the column chromatography was performed to obtain both the diastereomer of **5ab** in the ratio of 80:20 yield. This is due to the fact that the 2 carbonyl group must have to lie in the same side in order to form chelation with 1.1 equiv. of $AlCl_3$. From the ^1H NMR spectrum of both the diastereomer we have found out that the NMR spectrum of major diastereomer is different from the ^1H NMR spectrum of pre-$AlCl_3$ addition compound i,e; **(Z)-5ab**.The H_a proton of the major diastereomer (δ 8.56 ppm) is more deshielded than **(Z)-5ab**. This fact indicates that the major diastereomer is in **(E)** configuration. The H_a proton of **(E)** diastereomer is more deshielded compare to the **(Z)** diastereomer because the higher paramagnetic deshielding effect of NO_2 group.

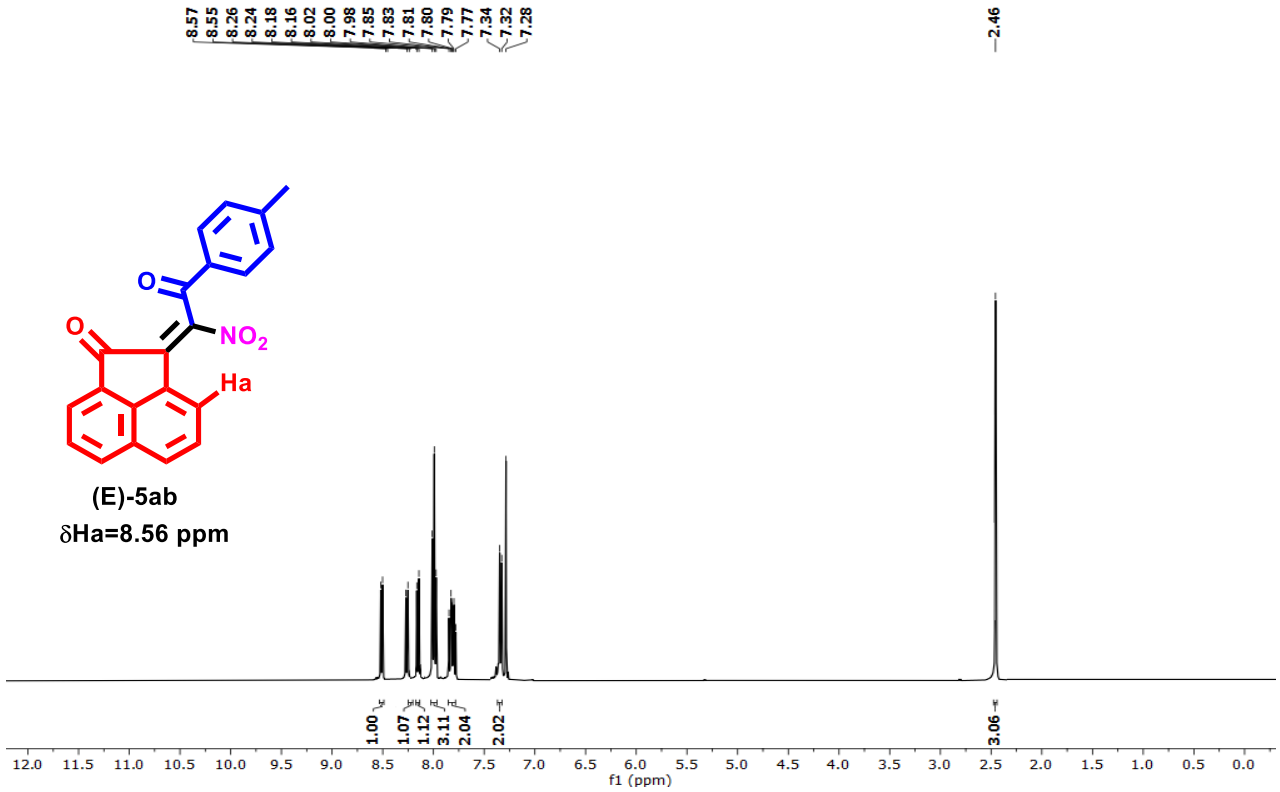
On the other hand the minor one has exactly the same ^1H NMR spectrum as **(Z)-5ab** which implies the minor diastereomer is in **(Z)** configuration. Therefore the starting **5ab** has the **(Z)** configuration.



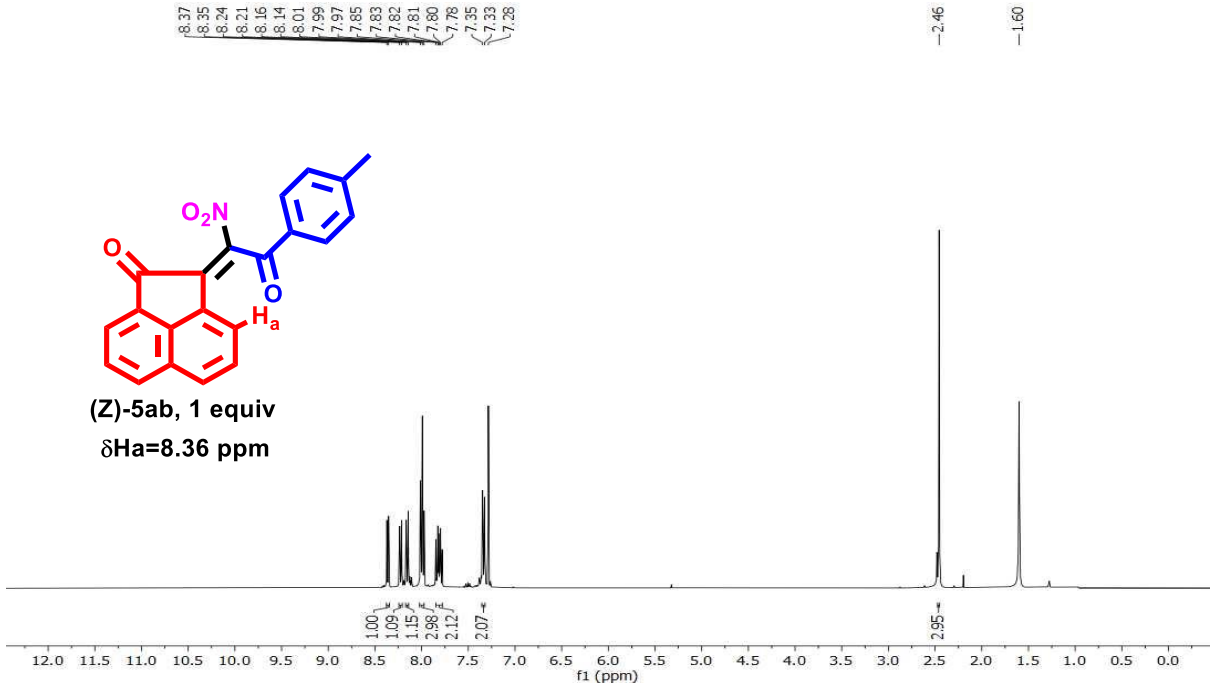
[a]**Reaction conditions: 1) (Z)-5ab** (1 equiv.) and anhydrous **$AlCl_3$** (1.1equiv.) in dry CH_2Cl_2 (5 ml) at room temperature (25-30 ^oC) for 48 hours**. 2) (Z)-5ab** (1 equiv.) and anhydrous **$AlCl_3$** (2.2 equiv.) in dry CH_2Cl_2 (5 ml) at room temperature (25-30 ^oC) for 48 hours**.**

If the same reaction was performed in presence of 2.2 equiv. of anhydrous $AlCl_3$ instead of 1.1 equiv. of $AlCl_3$, we obtained (Z)-5ab as the major diastereomer which was concluded from the ^1H NMR spectrum of the final compound. From

this experiment we can conclude that the geometry of our final product 5ab is (Z).

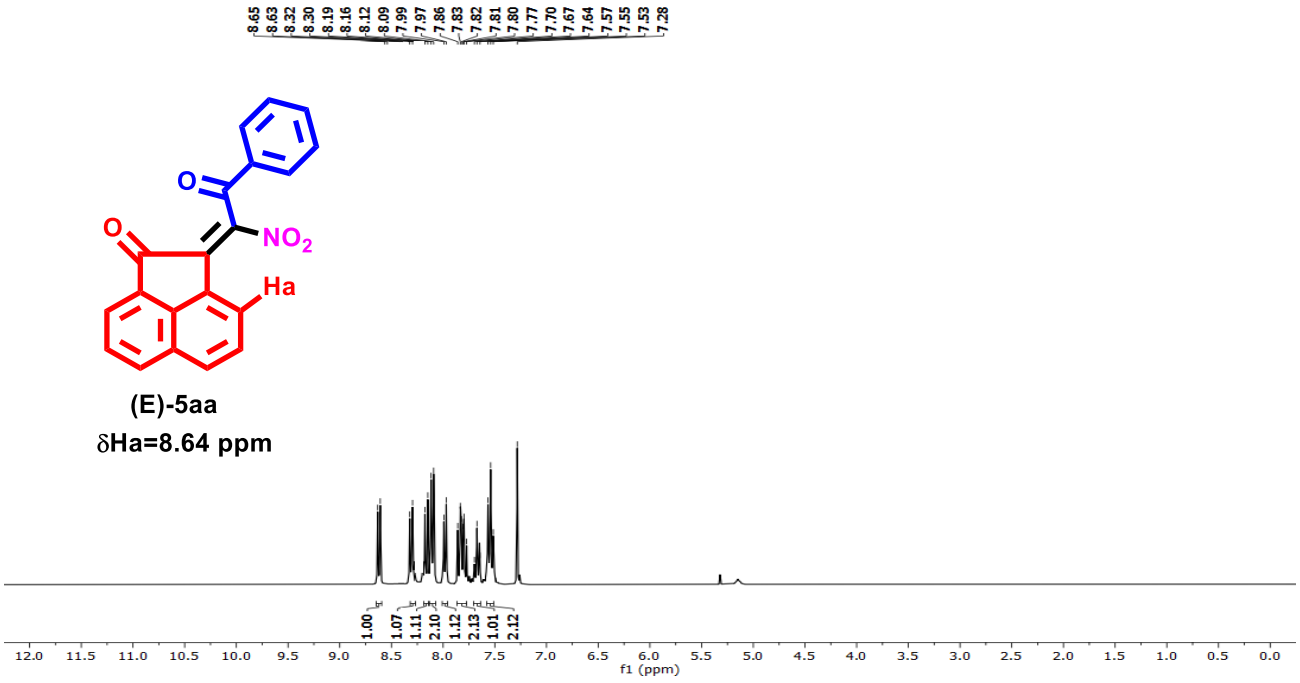


^{1}H NMR spectrum of (E)-5ab

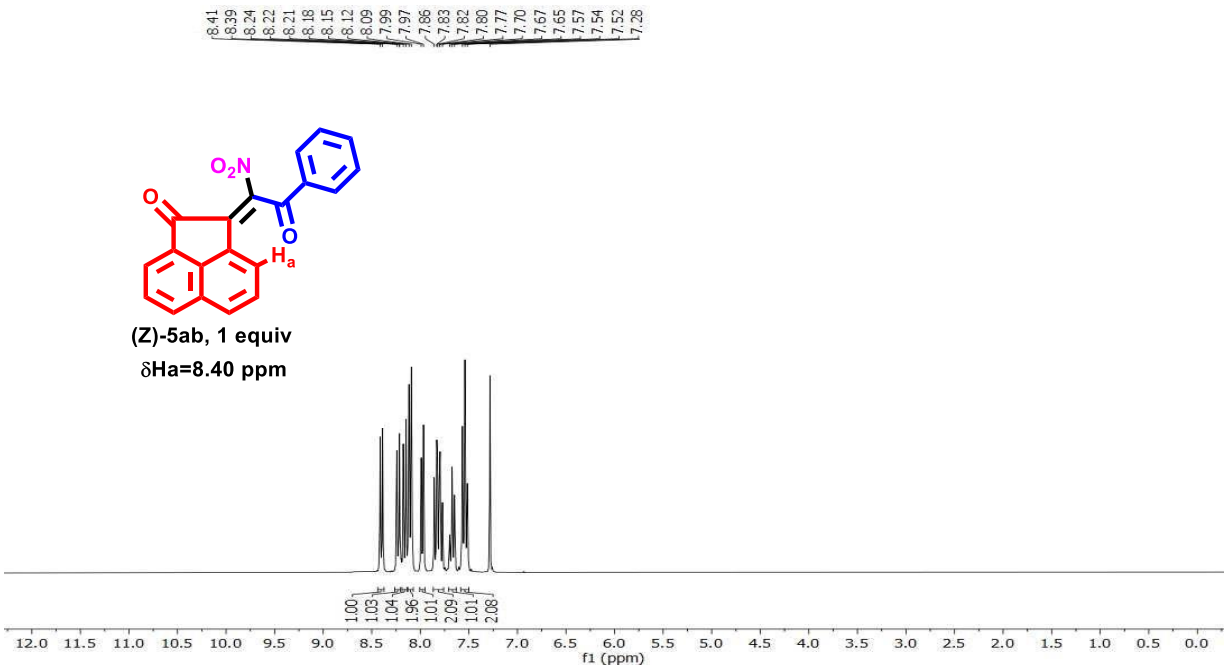


^{1}H NMR spectrum of (Z)-5ab

Also we have done same experiment with (Z)-5aa and we have observed the changes in δ value of H_a proton of final product (E)-5aa and the experimental ^1H NMR data has been given in.

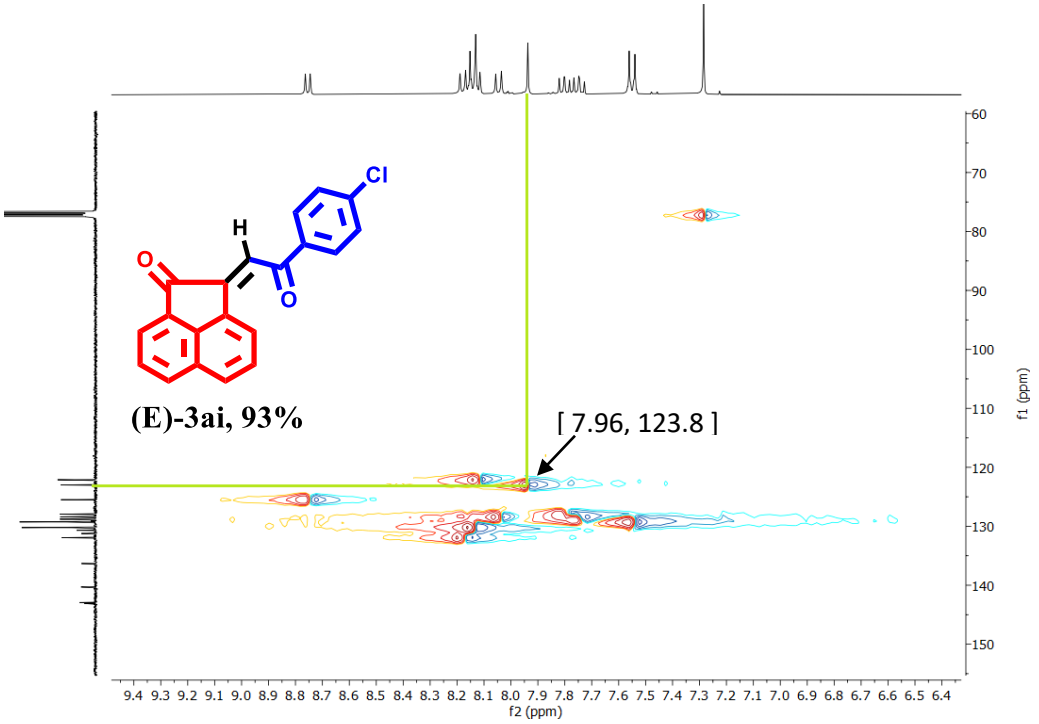


^1H NMR spectrum of (E)-5aa

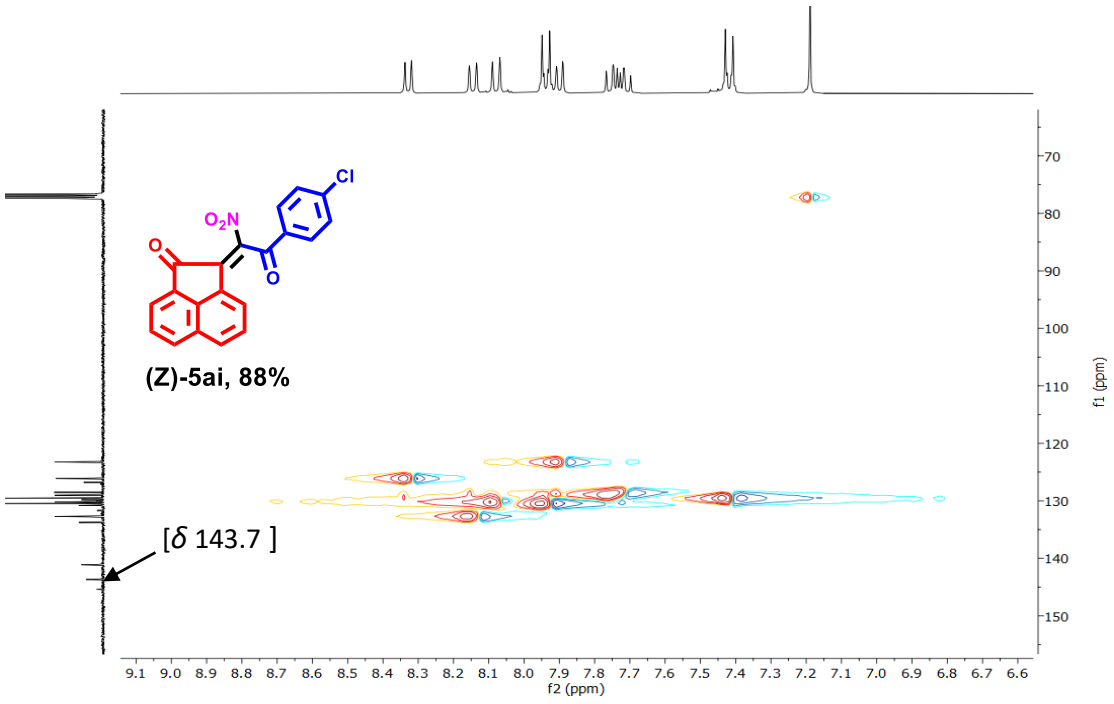


^1H NMR spectrum of (Z)-5aa

HSQC of compound 3ai and 5ai



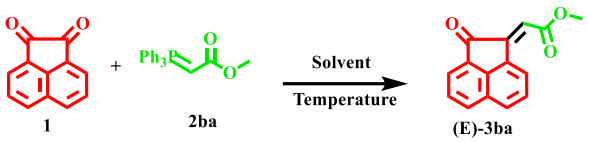
HSQC of compound 3ai



HSQC of compound 5ai

Figure 3 represents the 400 MHz HSQC spectra of (E)-3ai and (E)-5ai.The molecule (E)-3ai exhibits a two-bond correlation between its proton and carbon (shown in oval shape) and indicated by the peak (δ 7.96, 123.8). However, in (E)-5ai, this bond correlation is absent, indicating that the proton that was present in the preceding compound has disappeared. On the other hand, the ipso carbon containing the NO_2 has appeared at δ 143.7.

Table 1 : Optimization of reaction condition



1 2ba (E)-3ba

Entry	Solvent	Temperature (°C)	Yield(%)[b]
1.	Neat	r.t (25)	nr
2.	PEG 400	r.t (25)	nr
3.	PEG 400	80	70
4.	**PEG 400**	**110**	**92**
5.	PEG 400	110	92[c]
6.	H_2O	110	nr
7.	EtOH	110	20
8.	MeOH	110	18
9.	THF	110	22
10.	1,4 dioxane	110	25
11.	DCM	110	14
12.	DMSO	110	21

[a]**Reaction condition** : A mixture of acenaphthylene 1,2-dione **1**(1mmol) and **2ba** (1 mmol) was reacted in various solvent (1 ml) at different temperature for 2.5 hour. [b] Yield after column purification. [c]Reaction mixture was run for 5 hours.

We examined the following reaction with different solvent at different temperature but it seems that PEG 400 at 110 °C is best suitable to obtain the desired products **(Table 1).**

Analysis of green chemistry metrics

The following equations have been used for calculating Effective Mass Yield (EMY), Atom Economy (AE), Carbon Efficiency (CE), Reaction Mass Efficiency (RME) and E-factor. Calculated data for compound 3aa ,3ba ,5aa and 5ba have been shown in **Table X.**

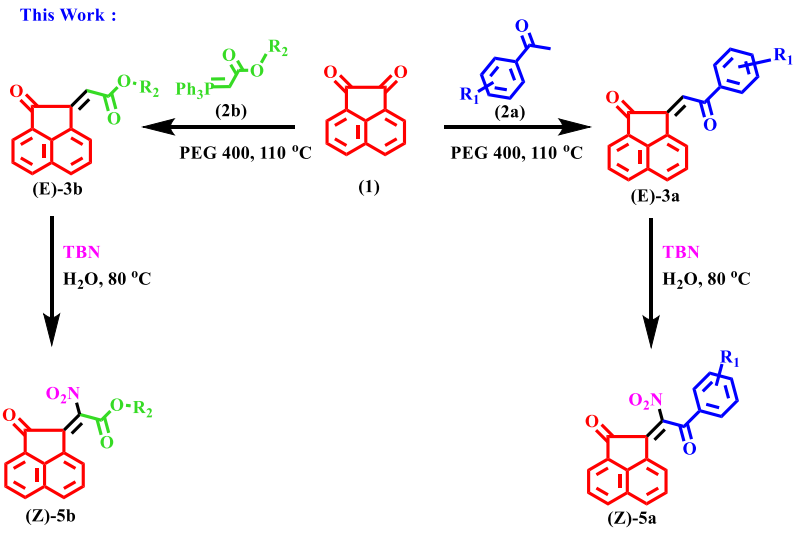
$$\text{EMY (\%)} = \frac{\text{Mass of the product}}{\text{Mass of the nonbenign reagents}} \times 100$$

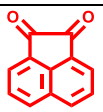
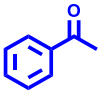
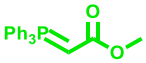
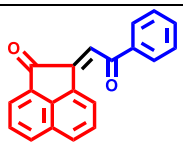
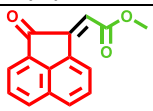
$$\text{AE (\%)} = \frac{\text{Molecular weight of the product}}{\text{Total molecular weight of the reactants}} \times 100$$

$$\text{CE (\%)} = \frac{\text{Amount of carbon in the product}}{\text{Total carbon present in the reactants}} \times 100$$

$$\text{RME (\%)} = \frac{\text{Mass of the isolated product}}{\text{Total mass of the reactants}} \times 100$$

$$\text{E-factor (g/g)} = \frac{\text{Total mass of wastes}}{\text{Mass of the product}} = \frac{\text{(Mass of raw materials-mass of product)}}{\text{Mass of the the product}}$$



Reactants	Amount used for reaction (g) (1.00 mmol)	Molecular weight (MW)	No of C-atom present in reactant
 (1)	0.182	182.0368	12
 (2aa)	0.120	120.0575	8
 (2ba)	0.348	348.1279	22
t-BuONO (4)	0.103	103.0633	4
 (E)-3aa	0.284	284.0837	20
 (E)-3ba	0.238	238.0630	15

Materials and their respective amount used for metrics calculations :

Product	Molecular weight (MW)	Yield (%)	Amount of product (g)	No of C-atom present in product	Mole no of product
3aa	284.0837	95	0.270	20	0.0009504241179
3ba	238.0630	92	0.219	15	0.0009199245577
5aa	329.0688	86	0.283	20	0.0008600025283
5ba	283.0481	88	0.249	15	0.0008797091377

Representative calculations of green metrics for (E)-2-(2-oxo-2-phenylethylidene)acenaphthylen-1(2H)-one derivative (**3aa**):

$$\text{EMY (\%)} = \frac{\text{Mass of the product}}{\text{Mass of the nonbenign reagents}} \times 100 = \frac{0.270}{0.182 + 0.120} \times 100 = 89.40\%$$

$$\text{AE (\%)} = \frac{\text{Molecular weight of the product}}{\text{Total molecular weight of the reactants}} \times 100 = \frac{284.0837}{182.0368 + 120.0575} \times 100 = 94.03\%$$

$$\text{CE (\%)} = \frac{\text{Amount of carbon in the product}}{\text{Total carbon present in the reactants}} \times 100 = \frac{(0.0009504241179 \times 20)}{(0.001 \times 12) + (0.001 \times 8)} \times 100 = 95.04\%$$

$$\text{RME(\%)} = \frac{\text{Mass of the isolated product}}{\text{Total mass of the reactants}} \times 100 = \frac{284.0837}{182.0368 + 120.0575} \times 100 = 94.03\%$$

$$\text{E-factor (g/g)} = \frac{\text{Total mass of wastes}}{\text{Mass of the product}} = \frac{\text{(Mass of raw materials-mass of product)}}{\text{Mass of the the product}} = \frac{(0.302\text{-}0.270)}{0.302} = 0.11$$

Table X. Green Metrics (EMY, AE, CE, RME and E-factor) for 3aa, 3ba , 5aa and 5ba compound :

Product	Yield (%)	EMY (%)	AE (%)	CE (%)	RME (%)	E-factor (g/g)
3aa	95	89.40	94.03	95.04	94.03	0.11
3ba	92	41.32	44.90	40.58	44.90	0.59
5aa	86	73.13	85.00	71.67	85.00	0.27
5ba	88	73.02	67.38	69.45	67.38	0.27