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Redox-Neutral 1,3-Dipolar Cycloaddition of 2*H*-Azirines with 2,4,6-Triarylpyrylium Salts under Visible Light Irradiation

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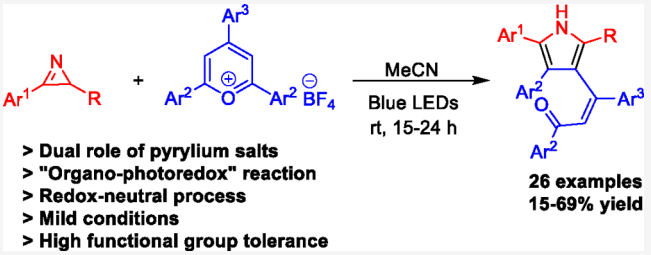
ABSTRACT: A novel visible light mediated redox-neutral 1,3-dipolar cycloaddition of 2*H*-azirines with 2,4,6-triarylpyrylium tetrafluoroborate salts providing tetrasubstituted pyrroles has been developed. The 2,4,6-triarylpyrylium salt acts as dipolarophile as well as photosensitizer in the reaction, under blue light irradiation. The control experiments indicated single electron oxidation of 2*H*-azirines by photoexcited pyrylium salts, followed by coupling between an azaallenyl radical cation and triarylpyranyl radical as the key mechanistic feature. The mild conditions, wide substrate scope, and complete regioselectivity are the noticeable attributes of the reaction.



INTRODUCTION

After Ciamiacin suggested the prospects of utilizing sunlight for driving chemical reactions a century ago,[1] the field of visible light photoredox catalysis has seen unprecedented refinement, innovation, and application.[2] This brilliant approach of employing visible light "active" molecules called photocatalysts/photosensitizers to harness the energy of sunlight for subsequent activation of photo-inactive substrates *via* either energy transfer or single electron transfer processes has provided direct access to numerous valuable heterocyclic scaffolds.[3] Among these, one particular heterocycle of interest is pyrrole owing to its ubiquitous presence in the natural products as well as in synthetic pharmaceuticals, agrochemicals, dyes, photographic chemicals, optoelectronic materials, etc.[4] Although, for accessing the pyrrole motif, several recent methods in addition to the classical name reactions such as Paal−Knorr, Hantzsch, Barton−Zard, and Piloty−Robinson reactions, have been reported in the literature,[5,6] there are only a few scattered reports of visible light mediated pyrrole synthesis. For instance, Wu and co-workers reported visible light mediated Hantzsch synthesis of 2,5-diaryl substituted pyrroles.[7] The reaction employed an Ir photocatalyst for the photocatalytic reduction of α-bromo ketones, generating alkyl radicals which reacted with enamines in Hantzsch fashion to provide disubstituted pyrroles. Recently, Protti, Bandini, and co-workers developed a visible light photoredox catalyzed synthesis of 1,3,4-trisubstituted pyrroles *via* condensation of aryl azides with aldehydes.[8] The reaction employed a Ru photocatalyst and involved in situ generation of aryl amines and 1,4-dialdehydes which undergo Paal−Knorr-type condensation to afford the final product. Another method developed by Maurya and co-workers utilized Ru-polypyridyl complexes to photocatalyze the coupling of 1/2-naphthols and 2-hydroxy-1,4-naphthoquinones with 2*H*-azirines obtained by photodecomposition of azidochalcones to prepare a 2,3-fused pyrrole motif.[9] Unlike all the above-mentioned reports employing Ir or Ru containing photocatalysts, Xiao's group developed organo-photoredox formal [3 + 2]-cycloaddition of 2*H*-azirines with alkynes to access tetrasubstituted pyrroles, employing acridinium salts as photocatalysts.[10a] Recently, our group also successfully applied the same approach for the regioselective synthesis of trisubstituted pyrroles employing nitroalkenes as dipolarophiles.[10b] Evidently, in both the reactions, the high oxidation potential of 2*H*-azirines warrants the usage of a strongly oxidizing acridinium photocatalyst for the photocatalytic cleavage of the azirine ring, generating an azaallenyl radical cation intermediate (Scheme 1a).[10,11]

We envisaged that strongly oxidizing photoexcited 2,4,6-triphenyl pyrylium tetrafluoroborate (TPT) (E_{red} = +2.55 V vs SCE)[12,13] will not only oxidize 2*H*-azirines but also may serve as dipolarophile in [3 + 2]-cycloaddition with the resulting 2-azaallenyl intermediate (Scheme 1b).[14] The pyrylium salts have been classically employed as photosensitizers in the photoinduced electron transfer (PET) mediated cycloadditions.[15] Further, pyrylium salts or pyrylium intermediates have also found use as dienes in the hetero-Diels−Alder reactions and as dipolarophiles in cycloaddition reactions.[16] However, to the best of our knowledge, there is no report suggesting the dual role of

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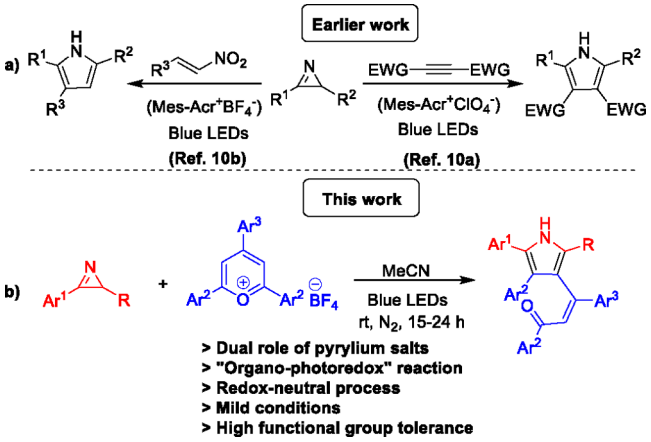
Scheme 1. Visible Light Mediated Synthesis of Pyrroles from 2*H*-Azirines

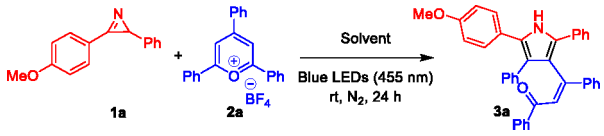


pyrylium salts as photosensitizer and dipolarophile in a 1,3-dipolar cycloaddition sequence.

RESULTS AND DISCUSSION

To validate our hypothesis, we irradiated a 1:1 mixture of 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine **1a** and TPT **2a** in anhydrous CH_3CN with blue LEDs (Table 1). To our delight,

Table 1. Optimization of Reaction Conditions[a]



entry	ratio of **1a**:**2a**	solvent	yield (%)[b]
1	1:1	MeCN	60 (51)[c]
2	1:1.5	MeCN	25
3	1.5:1	MeCN	75 (68)[c]
4	2:1	MeCN	26
5	1.5:1	DMSO	40
6	1.5:1	DCM	40
7	1.5:1	THF	33
8	1.5:1	$CHCl_3$	36
9	1.5:1	MeOH	23

[a]Unless otherwise mentioned, all reactions were carried out at 0.15 mmol scale of **1a** in 2 mL of solvent irradiated with blue LEDs (455 nm) under a N_2 atmosphere for 24 h. [b]NMR yields. [c]Isolated yield in parentheses.

the 1,3-dipolar cycloadduct **3a** was isolated in 51% yield (entry 1). The yield of **3a** was significantly reduced upon increasing the amount of **2a** to 1.5 equiv; however, changing the substrate ratio to 1.5:1 for **1a**:**2a** resulted in yield enhancement (entries 2 and 3). Since a further increase in the amount of azirine **1a** led to lower yield (entry 4), a 1.5:1 ratio of substrates **1a**:**2a** was used for further optimizations. Additionally, screening of solvents such as DMSO, DCM, THF, $CHCl_3$, and MeOH in the reaction revealed that MeCN is the best choice as reaction medium since all other solvents afforded product **3a** in lower yield.

After establishing optimum conditions for the reaction, we proceeded to test the scope and limitations of the reaction in terms of both substrates. In order to prove the general nature of the protocol, reactions of TPT **2a** with various 2*H*-azirines **1**, reactions of nonsubstituted 2*H*-azirine **1b** with several substituted 2,4,6-triarylpyrylium tetrafluoroborate salts **2**, and also reactions of substituted 2*H*-azirines **1** with substituted 2,4,6-triarylpyrylium tetrafluoroborate salts **2** were carried out (Table 2).

While all the substituents with electron withdrawing as well as electron donating tendencies on both the substrates were accommodated well to provide the desired products, the yields in most of the cases were in the range of 50−65%. Notably, the heteroaryl rings were also tolerated well in both the substrates *viz*. azirines (**3f**, **3x**, **3y**) and pyrylium salts (**3m**). The alkyl-aryl azirine also reacted smoothly with nonsubstituted/substituted pyrylium salts under the optimized reaction conditions to afford the products **3g** and **3z**, albeit in low yield. Notably, the gram-scale reaction between **1a** and **2a** under optimized conditions proceeded efficiently and afforded product **3a** in comparable yield.

The structure assigned to the products was based on the spectroscopic investigations and single crystal X-ray analysis of the representative compound **3k**.[17] Further, the complete regioselectivity of the reaction between two nonsymmetric substrates was established by single crystal X-ray analysis of the product **3q**.[17] After establishing the wide scope of the reaction, several control experiments were carried out to gain insight into the reaction mechanism (Scheme 2).

The reaction between **1a** and **2a** under standard conditions, but in the absence of visible light, failed to afford product (Scheme 2a). This observation indicates photoinduced single electron oxidation of **1a** by photoexcited TPT **2a** upon irradiation with blue LEDs.[18] Although, the fluorescence quenching experiments revealed only moderate quenching of TPT fluorescence by **1a** at 460 nm (36.14% at 355 nm and 44.51% at 405 nm excitation wavelength; Scheme 2b), the expected azaallenyl radical cation generated upon single electron oxidation of **1a** by TPT **2a** could be successfully trapped with allyltributyltin, furnishing *N*-benzyl-1-phenylbut-3-en-1-imine **4** (Scheme 2c; confirmed by HRMS; please see Figure S2 in SI). Moreover, the formation of an electron donor-acceptor complex between 2*H*-azirine **1a** and TPT **2a** was also ruled out since practically no change or bathochromic shift in the absorption spectra of TPT **2a** was noticed upon addition of **1a** (Scheme 2d).[19]

While more detailed investigations are required to determine the reaction mechanism, a plausible mechanism concurrent with literature reports and control experiments is illustrated in Scheme 3, exemplified by the reaction between **1b** and TPT **2a**. The TPT **2a**, upon visible light excitation, generates the strongly oxidizing TPT* species (E_{red} = +2.55 V vs SCE in CH_3CN). The ensuing thermodynamically favorable oxidation of 2*H*-azirine **1b** (E_{red} = +1.65 V vs SCE in CH_3CN)[18] by TPT* leads to azirine radical cation **A** and 2,4,6-triphenylpyranyl radical (TP$^{\cdot}$) . The radical cation **A** undergoes ring opening through homolytic C−C bond cleavage, affording 2-azaallenyl radical cation **B**/**B′**. The radical-radical coupling between (TP$^{\cdot}$) and the 2-azaallenyl radical cation leads to the 2-azaallenyl cation **C**. The subsequent pyranyl ring opening and 1,5-cyclization afford dihydropyrrolylium cation **D**, which, upon dehydration, affords the formal [3 + 2]-cycloaddition product **3b**.

CONCLUSION

In conclusion, the tetrasubstituted pyrroles were synthesized through a redox-neutral visible light mediated formal [3 + 2]-cycloaddition between 2*H*-azirines and 2,4,6-triarylpyrylium salts. The pyrylium salts also act as photosensitizer in the

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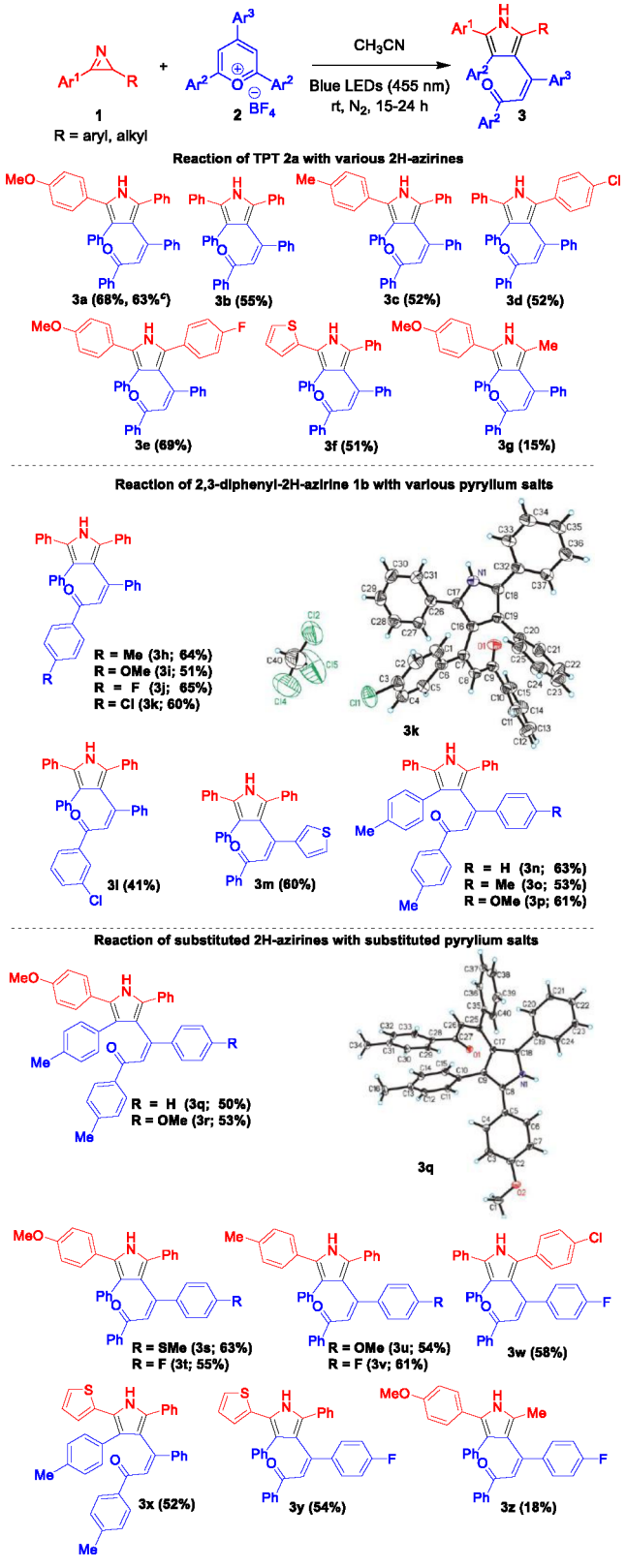
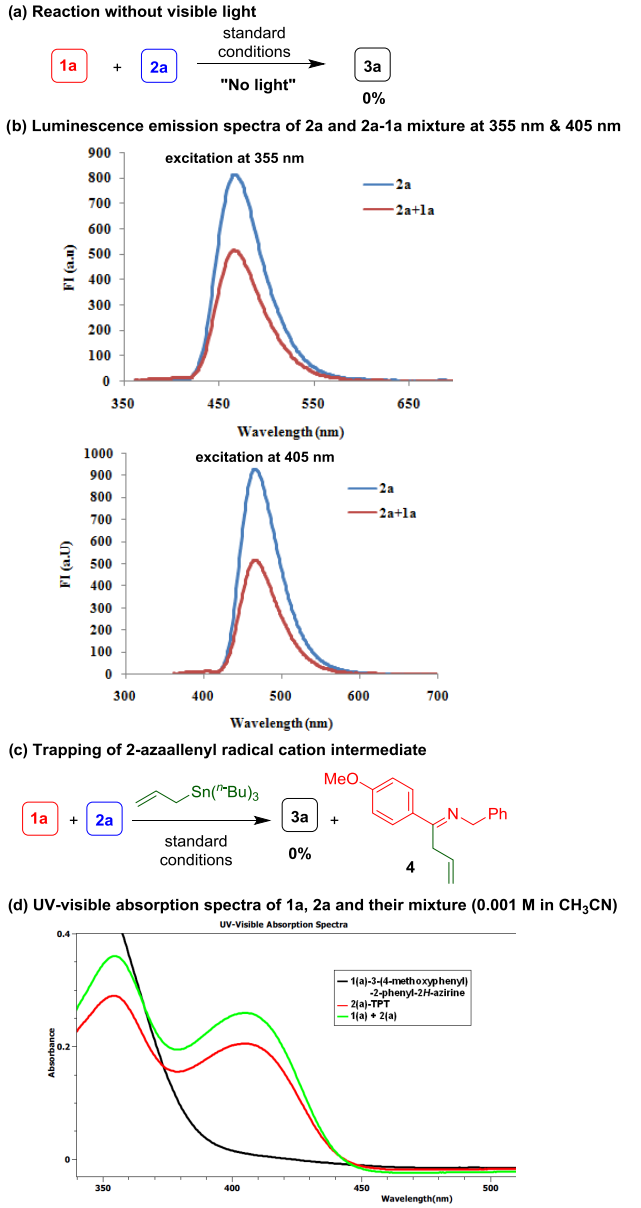
Table 2. Substrate Scope[a,b]

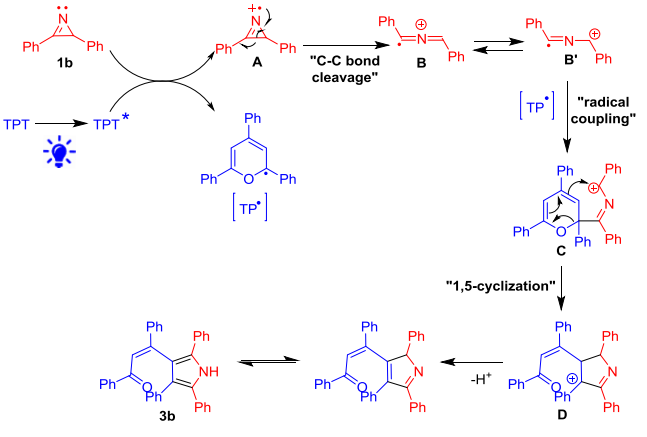


[a]All reactions were performed with **1** (0.3 mmol) and **2** (0.2 mmol) dissolved in MeCN (4 mL) and irradiated with blue LED (455 nm) under a N_2 atmosphere for 15−24 h. [b]Isolated yields in parentheses. [c]Yield of gram-scale reaction.

Scheme 2. Control Experiments



Scheme 3. Plausible Mechanism



reaction. This experimentally simple reaction exhibits a fairly general scope and complete regioselectivity.

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EXPERIMENTAL SECTION

Until mentioned otherwise, all reactions were carried out under a nitrogen atmosphere in flame-dried glassware. All reactions were monitored by Thin Layer Chromatography (TLC); visualization was effected with UV and/or by developing in iodine. Melting points were recorded on a Precision melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker Avance spectrometer at 300/400/500 MHz (^{1}H), 75/100/125 MHz (^{13}C), and 282/376 MHz (^{19}F). Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard. To describe spin multiplicity, standard abbreviations such as s, d, t, q, m, and dd referring to singlet, doublet, triplet, quartet, multiplet, and doublet of doublet, respectively, are used. The ESI-HRMS spectra were recorded on an Agilent 6520-Q-TofLC/MS system. The UV−vis absorption spectroscopy was performed using a Jasco V-750 spectrophotometer, equipped with a temperature control unit. The luminescence quenching experiments were carried out using a Cary Eclipse spectrofluorometer fitted with a Xe light source. The visible light irradiation was performed using high power blue LEDs (make: Original Opulant America, power = 3 W, λ_{max} = 455 nm, luminous flux/radiant flux = 687 mW at 700 mA). The LEDs fitted in an aluminum block (with 6 holes to hold vials and fitted with water inlet-outlet nozzle) irradiated the vials from the bottom at a distance of approximately 2 cm. The vials were cooled to 25 °C by circulating water through the aluminum block holding the vials (please see Figure S1 of SI for a picture of the instrument).

The diarylazirines **1a**−**1f** were synthesized from corresponding ketones by following the procedure reported by Yan and Wang.[20a] On the other hand, the alkyl-arylazirine **1g** was synthesized from the corresponding vinyl azide following the procedure adopted by Tang and co-workers.[20b] The 2,4,6-triarylpyrylium tetrafluoroborate salts **2a**−**2k** were synthesized by following the protocol reported by Sasidhar and co-workers.[21a] All other chemicals and catalysts were purchased from commercial sources and used as received. The solvents were purified by distillation over standard drying agents and used fresh or stored over molecular sieves. The characterization data for the new substrate **1e** have been provided in the relevant section below, whereas all the known starting substrates, i.e., azirines **1a**−**1d**, **1f**−**1g**, and pyrylium salts **2a**−**2k**, were characterized by comparing their spectroscopic data with the reported authentic compounds. The details of substitutions in starting substrates **1** and **2** and the references for corresponding spectroscopic data are provided in Table 3.

General Procedure for the Photocatalytic Cycloaddition between 1 and 2. In an oven-dried 5 mL crimp-seal vial equipped with a magnetic stirring bar, the 2*H*-azirine **1** (0.3 mmol) and 2,4,6-triarylpyrylium tetrafluoroborate salt **2** (0.2 mmol) were dissolved in anhydrous CH_3CN (4.0 mL). The resulting reaction mixture was degassed by three "freeze-pump-thaw" cycles *via* a syringe needle. The vial was irradiated using 455 nm blue LEDs with a cooling device maintaining the temperature around 25 °C. After 15−24 h of irradiation (TLC monitoring), the reaction mixture was concentrated under reduced pressure. The residue was dissolved in ethyl acetate and washed with water (10 mL × 3) and brine (10 mL × 3). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (100−200 mesh) using hexane/ethyl acetate as eluent to afford the pure product **3**.

General Procedure for the Radical Trapping Experiment. In an oven-dried 5 mL crimp-seal vial equipped with a magnetic stirring bar, the 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine **1a** (67 mg, 0.3 mmol), 2,4,6-triphenylpyrylium tetrafluoroborate salt **2a** (79 mg, 0.2 mmol), and allyltributyltin (0.3 mL, 1.0 mmol) were dissolved in anhydrous CH_3CN (4.0 mL). The resulting reaction mixture was degassed by three "freeze-pump-thaw" cycles *via* a syringe needle. The vial was irradiated using 455 nm blue LEDs with a cooling device maintaining the temperature around 25 °C. After 24 h of irradiation (TLC monitoring), the reaction mixture was concentrated under reduced pressure. The residue was dissolved in ethyl acetate and washed with water (10 mL × 3) and brine (10 mL × 3). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product **4** was analyzed by high resolution mass spectrometry (Figure S2 of SI).

Gram-Scale Synthesis of 3a. In an oven-dried 20 mL crimp-seal vial equipped with a magnetic stirring bar, the 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine **1a** (1.0 g, 4.5 mmol) and 2,4,6-triphenylpyrylium tetrafluoroborate salt **2a** (1.2 g, 3.0 mmol) were dissolved in anhydrous CH_3CN (12.0 mL). The resulting reaction mixture was degassed by three "freeze-pump-thaw" cycles *via* a syringe needle. The vial was irradiated using 455 nm blue LEDs with a cooling device maintaining the temperature around 25 °C. After 24 h of irradiation (TLC monitoring), the reaction mixture was concentrated under reduced pressure. The residue was dissolved in ethyl acetate and washed with water (25 mL × 3) and brine (25 mL × 3). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (100−200 mesh) using hexane/ethyl acetate as eluent to afford the pure product **3a** (63% yield, 1.0 g).

2-(4-Fluorophenyl)-3-(4-methoxyphenyl)-2*H*-azirine (1e). White solid; isolated yield 54%. Mp 59−60 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.6 Hz, 2H), 6.95−7.04 (m, 4H), 6.88 (t, J = 8.6 Hz, 2H), 3.80 (s, 3H), 3.17 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.6, 162.2, 162.1 (d, $^1J_{C-F}$ = 243.2 Hz), 136.9 (d, $^4J_{C-F}$ = 2.9 Hz), 131.8, 127.4 (d, $^3J_{C-F}$ = 8.0 Hz), 116.2, 115.1 (d, $^2J_{C-F}$ = 21.4 Hz), 114.8, 55.5, 33.4; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{15}H_{13}FNO$: 242.0976, found: 242.0974.

(*Z*)-3-(5-(4-Methoxyphenyl)-2,4-diphenyl-1*H*-pyrrol-3-yl)-1,3-diphenylprop-2-en-1-one (3a). Following the general procedure, reaction between 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine **1a** (67 mg, 0.3 mmol) and 2,4,6-triphenylpyrylium tetrafluoroborate salt **2a** (79 mg, 0.2 mmol) afforded the product **3a** (72 mg, 68%) as a red solid (R_f 0.50 with 25% EtOAc/hexane; Mp 109−111 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.49 (m appearing as d, J = 6.5 Hz, 4H), 7.35−7.38 (m, 3H), 7.20−7.25 (m, 5H), 7.12−7.17 (m, 4H), 7.00−7.08 (m, 4H), 6.94 (m appearing as d, J = 2.8 Hz, 3H), 6.75 (d, J = 8.6 Hz, 2H), 3.75 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 191.8, 158.3, 148.8, 141.4, 138.4, 135.3, 132.3, 131.7, 130.5, 129.9, 129.1, 128.9, 128.4, 128.2, 127.9, 127.7, 127.6, 126.5, 126.3, 126.3, 125.8, 125.3, 123.1, 120.2, 113.9, 55.2; IR (Film, cm^{-1}): 3373, 1662, 1383, 697; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{38}H_{30}NO_2$: 532.2271, found: 532.2266.

(*Z*)-1,3-Diphenyl-3-(2,4,5-triphenyl-1*H*-pyrrol-3-yl)prop-2-en-1-one (3b). Following the general procedure, reaction between 2,3-diphenyl-2*H*-azirine **1b** (58 mg, 0.3 mmol) and 2,4,6-triphenylpyrylium tetrafluoroborate salt **2a** (79 mg, 0.2 mmol) afforded the product **3b** (55 mg, 55%) as an orange solid (R_f 0.50 with 20% EtOAc/hexane; Mp 98−100 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H),

Table 3. Substrates with Their Literature References

substrate	substituents	reference
1a	Ar^1 = 4-OMe-Ph; R = Ph	20a
1b	Ar^1 = R = Ph	20a
1c	Ar^1 = 4-Me-Ph; R = Ph	20a
1d	Ar^1 = Ph; R = 4-Cl-Ph	20a
1e	Ar^1 = 4-OMe-Ph; R = 4-F-Ph	new
1f	Ar^1 = 2-thienyl; R = Ph	20a
1g	Ar^1 = 4-OMe-Ph; R = Me	20b
2a	Ar^2 = Ar^3 = Ph	21a
2b	Ar^2 = Ph; Ar^3 = 4-Me-Ph	21a
2c	Ar^2 = Ph; Ar^3 = 4-OMe-Ph	21a
2d	Ar^2 = Ph; Ar^3 = 4-F-Ph	21a
2e	Ar^2 = Ph; Ar^3 = 4-Cl-Ph	21a
2f	Ar^2 = Ph; Ar^3 = 3-Cl-Ph	21b
2g	Ar^2 = Ph; Ar^3 = 3-thienyl	21a
2h	Ar^2 = 4-Me-Ph; Ar^3 = Ph	21c
2i	Ar^2 = Ar^3 = 4-Me-Ph	21a
2j	Ar^2 = 4-Me-Ph; Ar^3 = 4-OMe-Ph	21c
2k	Ar^2 = Ph; Ar^3 = 4-SMe-Ph	21d

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7.49 (m appearing as d, J = 6.7 Hz, 4H), 7.36−7.38 (m, 3H), 7.21−7.26 (m merged with solvent peak, 9H), 7.13−7.18 (m, 3H), 7.02−7.10 (m, 4H), 6.95−6.96 (m, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 191.7, 148.7, 141.4, 138.4, 135.2, 132.6, 132.3, 131.8, 130.5, 130.4, 129.1, 128.9, 128.5, 128.5, 128.2, 128.2, 127.9, 127.8, 127.7, 126.8, 126.7, 126.4, 126.3, 126.0, 124.0, 120.5; IR (Film, cm^{-1}): 3361, 1383, 1051, 695; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{37}H_{28}NO$: 502.2165, found: 502.2166.

(*Z*)-3-(2,4-Diphenyl-5-(*p*-tolyl)-1*H*-pyrrol-3-yl)-1,3-diphenylprop-2-en-1-one (3c). Following the general procedure, reaction between 2-phenyl-3-(*p*-tolyl)-2*H*-azirine **1c** (62 mg, 0.3 mmol) and 2,4,6-triphenylpyrylium tetrafluoroborate salt **2a** (79 mg, 0.2 mmol) afforded the product **3c** (54 mg, 52%) as a yellow solid (R_f 0.50 with 20% EtOAc/hexane; Mp 125−127 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.48−7.51 (m, 4H), 7.35−7.37 (m, 3H), 7.14−7.24 (m, 7H), 7.07−7.11 (m, 4H), 7.01−7.03 (m, 4H), 6.94−6.96 (m, 3H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.8, 148.7, 141.5, 138.4, 136.2, 135.3, 132.3, 131.8, 130.6, 130.1, 129.7, 129.2, 129.2, 128.9, 128.5, 128.2, 128.2, 128.0, 127.8, 127.7, 126.7, 126.6, 126.4, 126.3, 125.9, 123.6, 120.4, 21.1; IR (Film, cm^{-1}): 3355, 1383, 1050, 768; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{38}H_{30}NO$: 516.2322, found: 516.2322.

(*Z*)-3-(2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-pyrrol-3-yl)-1,3-diphenylprop-2-en-1-one (3d). Following the general procedure, reaction between 2-(4-chlorophenyl)-3-phenyl-2*H*-azirine **1d** (68 mg, 0.3 mmol) and 2,4,6-triphenylpyrylium tetrafluoroborate salt **2a** (79 mg, 0.2 mmol) afforded the product **3d** (56 mg, 52%) as an orange solid (R_f 0.50 with 15% EtOAc/hexane; Mp 169−171 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.51 (d, J = 7.5 Hz, 2H), 7.45−7.46 (m, 4H), 7.41 (d, J = 7.3 Hz, 1H), 7.26−7.30 (m, 5H), 7.15−7.22 (m, 6H), 7.09 (d, J = 8.3 Hz, 2H), 6.95−6.99 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.7, 148.9, 141.0, 138.3, 135.1, 132.3, 132.2, 132.1, 130.8, 130.5, 129.5, 129.1, 129.0, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.5, 126.8, 126.4, 126.3, 126.0, 124.0, 121.0; IR (Film, cm^{-1}): 3386, 1383, 1060; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{37}H_{27}ClNO$: 536.1776, found: 536.1776.

(*Z*)-3-(2-(4-Fluorophenyl)-5-(4-methoxyphenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1,3-diphenylprop-2-en-1-one (3e). Following the general procedure, reaction between 2-(4-fluorophenyl)-3-(4-methoxyphenyl)-2*H*-azirine **1e** (72 mg, 0.3 mmol) and 2,4,6-triphenylpyrylium tetrafluoroborate salt **2a** (79 mg, 0.2 mmol) afforded the product **3e** (76 mg, 69%) as a red solid (R_f 0.50 with 25% EtOAc/hexane; Mp 115−117 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.50 (d, J = 7.3 Hz, 2H), 7.45−7.47 (m, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.28−7.32 (m, 2H), 7.23−7.26 (m, 5H), 7.12 (d, J = 8.7 Hz, 2H), 7.10 (s, 1H), 6.92−6.98 (m, 5H), 6.81 (t, J = 8.7 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 3.74 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.7, 161.6 (d, $^1J_{C\text{-}F}$ = 244.7 Hz), 158.3, 148.7, 141.3, 138.3, 135.3, 131.9, 130.5, 129.1, 129.0, 128.9, 128.7 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 128.2, 128.2, 128.2, 128.1, 127.9, 127.8, 127.7, 126.3, 125.8, 125.2, 123.0, 120.3, 115.4 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 113.9, 55.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −115.57 (s); IR (Film, cm^{-1}): 3314, 1502, 1035, 835; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{38}H_{29}FNO_2$: 550.2177, found: 550.2172.

(*Z*)-3-(2,4-Diphenyl-5-(thiophen-2-yl)-1*H*-pyrrol-3-yl)-1,3-diphenylprop-2-en-1-one (3f). Following the general procedure, reaction between 2-phenyl-3-(thiophen-2-yl)-2*H*-azirine **1f** (60 mg, 0.3 mmol) and 2,4,6-triphenylpyrylium tetrafluoroborate salt **2a** (79 mg, 0.2 mmol) afforded the product **3f** (52 mg, 51%) as a red solid (R_f 0.50 with 15% EtOAc/hexane; Mp 173−175 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.50−7.52 (m, 2H), 7.46−7.48 (m, 2H), 7.38−7.41 (m, 3H), 7.22−7.26 (m, 5H), 7.16−7.19 (m, 2H), 7.03−7.09 (m, 5H), 6.97−7.02 (m, 3H), 6.87−6.90 (m, 1H), 6.83−6.84 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.5, 148.5, 141.3, 138.4, 134.9, 134.6, 132.0, 131.9, 130.9, 130.4, 129.0, 128.5, 128.2, 127.9, 127.9, 126.7, 127.1, 126.8, 126.5, 126.5, 126.1, 124.6, 124.0, 123.4, 123.0, 120.7; IR (Film, cm^{-1}): 3348, 1645, 1383, 693; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{35}H_{26}NOS$: 508.1730, found: 508.1728.

(*Z*)-3-(5-(4-Methoxyphenyl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)-1,3-diphenylprop-2-en-1-one (3g). Following the general procedure, reaction between 3-(4-methoxyphenyl)-2-methyl-2*H*-azirine **1g** (48 mg, 0.3 mmol) and 2,4,6-triphenylpyrylium tetrafluoroborate salt **2a** (79 mg, 0.2 mmol) afforded the product **3g** (14 mg, 15%) as a red solid (R_f 0.50 with 25% EtOAc/hexane; Mp 248−250 °C). ^1H NMR (400 MHz, DMSO-d_6) δ 10.92 (s, 1H), 7.73 (d, J = 7.5 Hz, 2H), 7.49−7.53 (m, 1H), 7.38−7.42 (m, 4H), 7.25−7.26 (m appearing as br s, 3H), 7.12 (s, 1H), 7.06 (d, J = 8.5 Hz, 2H), 6.87−6.96 (m, 5H), 6.77 (d, J = 8.6 Hz, 2H), 3.70 (s, 3H), 1.93 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 191.7, 157.8, 149.4, 142.0, 138.7, 136.8, 132.5, 130.2, 129.2, 128.6, 128.6, 128.4, 128.2, 128.2, 127.9, 127.5, 126.7, 126.1, 125.6, 124.8, 121.1, 119.4, 114.1, 55.5, 12.2; IR (Film, cm^{-1}): 3412, 1647, 1383, 770; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{33}H_{28}NO_2$: 470.2115, found: 470.2113.

(*Z*)-1-Phenyl-3-*p*-tolyl-3-(2,4,5-triphenyl-1*H*-pyrrol-3-yl)-prop-2-en-1-one (3h). Following the general procedure, reaction between 2,3-diphenyl-2*H*-azirine **1b** (58 mg, 0.3 mmol) and 2,6-diphenyl-4-(*p*-tolyl)pyrylium tetrafluoroborate salt **2b** (82 mg, 0.2 mmol) afforded the product **3h** (66 mg, 64%) as a brown red solid (R_f 0.50 with 15% EtOAc/hexane; Mp 192−194 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.45 (d, J = 7.1 Hz, 2H), 7.31−7.38 (m, 5H), 7.21 (d, J = 2.8 Hz, 1H), 7.05−7.18 (m, 9H), 6.98−7.03 (m, 5H), 6.91−6.93 (m, 3H), 2.26 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 191.7, 148.8, 139.2, 138.7, 138.5, 135.3, 132.7, 132.4, 131.7, 130.5, 130.2, 129.0, 128.5, 128.4, 128.1, 127.8, 127.8, 127.7, 126.8, 126.6, 126.4, 126.3, 125.9, 125.5, 124.0, 120.7, 21.3; IR (Film, cm^{-1}): 3350, 1598, 1383, 1044, 695; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{38}H_{30}NO$: 516.2322, found: 516.2318.

(*Z*)-3-(4-Methoxyphenyl)-1-phenyl-3-(2,4,5-triphenyl-1*H*-pyrrol-3-yl)prop-2-en-1-one (3i). Following the general procedure, reaction between 2,3-diphenyl-2*H*-azirine **1b** (58 mg, 0.3 mmol) and 4-(4-methoxyphenyl)-2,6-diphenylpyrylium tetrafluoroborate salt **2c** (85 mg, 0.2 mmol) afforded the product **3i** (54 mg, 51%) as a red solid (R_f 0.50 with 15% EtOAc/hexane; Mp 129−131 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.40−7.45 (m, 4H), 7.30−7.34 (m, 3H), 7.09−7.19 (m, 9H), 7.03−7.05 (m, 2H), 6.97−6.99 (m, 2H), 6.91−6.93 (m, 3H), 6.72 (d, J = 8.8 Hz, 2H), 3.73 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.6, 160.5, 148.6, 138.8, 135.3, 133.7, 132.6, 132.3, 131.7, 130.5, 130.1, 129.3, 129.0, 128.5, 128.4, 128.1, 127.8, 127.7, 126.8, 126.6, 126.4, 126.3, 125.9, 124.3, 124.0, 120.7, 113.7, 55.3; IR (Fim, cm^{-1}): 3365, 1600, 1033; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{38}H_{30}NO_2$: 532.2271, found: 532.2269.

(*Z*)-3-(4-Fluorophenyl)-1-phenyl-3-(2,4,5-triphenyl-1*H*-pyrrol-3-yl)prop-2-en-1-one (3j). Following the general procedure, reaction between 2,3-diphenyl-2*H*-azirine **1b** (58 mg, 0.3 mmol) and 4-(4-fluorophenyl)-2,6-diphenylpyrylium tetrafluoroborate salt **2d** (83 mg, 0.2 mmol) afforded the product **3j** (68 mg, 65%) as a red solid (R_f 0.50 with 15% EtOAc/hexane; Mp 162−164 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.44−7.50 (m, 4H), 7.35−7.40 (m, 3H), 7.21−7.25 (m, 6H), 7.14−7.19 (m, 3H), 7.08−7.11 (m, 1H), 7.05 (s, 1H), 7.01−7.03 (m, 2H), 6.96−6.98 (m, 3H), 6.89−6.93 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.5, 163.2 (d, $^1J_{C\text{-}F}$ = 247.6 Hz), 147.6, 138.3, 137.5 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 135.1, 132.5, 132.2, 131.9, 130.5, 130.4, 129.7 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 129.1, 128.5, 128.5, 128.1, 127.8, 127.8, 126.8, 126.8, 126.5, 126.4, 126.0, 125.9, 123.9, 120.4, 115.2 (d, $^2J_{C\text{-}F}$ = 21.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −112.42 (s); IR (Film, cm^{-1}): 3381, 1383, 1056, 770; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{37}H_{27}FNO$: 520.2071, found: 520.2066.

(*Z*)-3-(4-Chlorophenyl)-1-phenyl-3-(2,4,5-triphenyl-1*H*-pyrrol-3-yl)prop-2-en-1-one (3k). Following the general procedure, reaction between 2,3-diphenyl-2*H*-azirine **1b** (58 mg, 0.3 mmol) and 4-(4-chlorophenyl)-2,6-diphenylpyrylium tetrafluoroborate salt **2e** (86 mg, 0.2 mmol) afforded the product **3k** (64 mg, 60%) as a red solid (R_f 0.50 with 20% EtOAc/hexane; Mp 81−83 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.46 (d, J = 7.4 Hz, 2H), 7.31−7.39 (m, 5H), 7.21 (d, J = 8.2 Hz, 2H), 7.12−7.18 (m, 9H), 7.06 (d, J = 7.4 Hz, 1H), 7.04 (s, 1H), 6.93−6.99 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.5, 147.4, 139.8, 138.2, 135.1, 134.8, 132.4, 132.1, 132.0, 130.5, 129.1, 129.1, 128.6, 128.5, 128.4, 128.1, 127.8, 127.8, 126.8, 126.8, 126.5, 126.5, 126.4, 126.1, 123.8, 120.0; IR (Film, cm^{-1}): 3375, 1383, 1061, 697; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{37}H_{27}ClNO$: 536.1776, found: 536.1772.

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Selected X-ray Crystallographic Data for ***3k.*** $C_{37}H_{26}ClNO_4 \cdot CHCl_3$, M = 655.41, Monoclinic, $P2_1/n$, a = 12.89128(16) Å, b = 15.15807(17) Å, c = 17.2023(2) Å, V = 3281.88(7) Å^3, β = 102.49° (12), Z = 4, D_c = 1.326 g cm^{-3}, μ (Mo−Kα) = 3.519 mm^{-1}, $F(000)$ = 1352, reflections collected/unique = 5126/6453, [R(int) = 0.1810]. Final R indices [$I > 2\sigma(I)$], R = 0.1246, wR = 0.4009.

(*Z*)-3-(3-Chlorophenyl)-1-phenyl-3-(2,4,5-triphenyl-1*H*-pyrrol-3-yl)prop-2-en-1-one (3l). Following the general procedure, reaction between 2,3-diphenyl-2*H*-azirine **1b** (58 mg, 0.3 mmol) and 4-(3-chlorophenyl)-2,6-diphenylpyrylium tetrafluoroborate salt **2f** (86 mg, 0.2 mmol) afforded the product **3l** (44 mg, 41%) as a red solid (R_f 0.50 with 20% EtOAc/hexane; Mp 91−93 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.47−7.49 (m, 2H), 7.44−7.45 (m, 1H), 7.34−7.40 (m, 4H), 7.21−7.25 (m, 6H), 7.14−7.19 (m, 4H), 7.10−7.13 (m, 1H), 7.07 (br s, 1H), 7.00−7.4 (m, 2H), 6.96−6.98 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.5, 147.0, 143.3, 138.0, 135.0, 134.2, 132.4, 132.1, 132.0, 130.7, 130.5, 129.4, 129.1, 128.8, 128.6, 128.5, 128.2, 127.8, 127.8, 127.1, 126.9, 126.8, 126.5, 126.1, 126.1, 123.9, 119.8; IR (Film, cm^{-1}): 3382, 1382, 1069, 771; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{37}H_{27}ClNO$: 536.1776, found: 536.1771.

(*E*)-1-Phenyl-3-(thiophen-3-yl)-3-(2,4,5-triphenyl-1*H*-pyrrol-3-yl)prop-2-en-1-one (3m). Following the general procedure, reaction between 2,3-diphenyl-2*H*-azirine **1b** (58 mg, 0.3 mmol) and 2,6-diphenyl-4-(thiophen-3-yl)pyrylium tetrafluoroborate salt **2g** (80 mg, 0.2 mmol) afforded the product **3m** (61 mg, 60%) as a red solid (R_f 0.50 with 20% EtOAc/hexane; Mp 196−198 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.40 (d, J = 7.4 Hz, 2H), 7.32−7.38 (m, 2H), 7.16−7.28 (m, 10H), 7.09−7.15 (m, 3H), 6.99−7.06 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.6, 143.5, 143.2, 138.7, 135.2, 132.6, 132.4, 131.8, 130.4, 129.7, 128.9, 128.6, 128.5, 128.1, 127.8, 127.8, 127.2, 126.8, 126.6, 126.4, 126.2, 126.0, 125.9, 125.8, 124.5, 123.7, 120.6; IR (Film, cm^{-1}): 3361, 1382, 1055, 695; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{35}H_{26}NOS$: 508.1730, found: 508.1728.

(*Z*)-3-(2,5-Diphenyl-4-*p*-tolyl-1*H*-pyrrol-3-yl)-3-phenyl-1-*p*-tolylprop-2-en-1-one (3n). Following the general procedure, reaction between 2,3-diphenyl-2*H*-azirine **1b** (58 mg, 0.3 mmol) and 4-phenyl-2,6-di-*p*-tolylpyrylium tetrafluoroborate salt **2h** (85 mg, 0.2 mmol) afforded the product **3n** (67 mg, 63%) as a yellow solid (R_f 0.50 with 15% EtOAc/hexane; Mp 113−115 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.48−7.49 (m, 2H), 7.37−7.41 (m, 4H), 7.21−7.24 m, 6H), 7.15−7.19 (m, 3H), 7.07−7.13 (m, 3H), 7.02 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 7.9 Hz, 2H), 6.72 (d, J = 7.7 Hz, 2H), 2.34 (s, 3H), 2.13 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.3, 148.1, 142.3, 141.6, 135.8, 135.3, 132.7, 132.4, 132.1, 130.4, 130.2, 128.8, 128.8, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 127.9, 126.7, 126.6, 126.4, 126.3, 124.0, 120.8, 21.6, 21.1; IR (Film, cm^{-1}): 3286, 1602, 1383, 1038, 695; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{39}H_{32}NO$: 530.2478, found: 530.2481.

(*Z*)-3-(2,5-Diphenyl-4-*p*-tolyl-1*H*-pyrrol-3-yl)-1,3-di-*p*-tolylprop-2-en-1-one (3o). Following the general procedure, reaction between 32,3-diphenyl-2*H*-azirine **1b** (58 mg, 0.3 mmol) and 2,4,6-tri-*p*-tolylpyrylium tetrafluoroborate salt **2i** (88 mg, 0.2 mmol) afforded the product **3o** (58 mg, 53%) as a orange solid (R_f 0.50 with 15% EtOAc/hexane; Mp 224−226 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.37−7.41 (m, 6H), 7.08−7.25 (m, 9H), 7.00−7.06 (m, 4H), 6.88 (m appearing as br d, J = 8.0 Hz, 2H), 6.72 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 2.29 (s, 3H), 2.13 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.3, 148.2, 142.2, 138.9, 138.6, 136.0, 135.2, 132.8, 132.4, 132.1, 130.4, 130.0, 129.0, 128.8, 128.5, 128.4, 128.4, 128.3, 127.8, 126.7, 126.4, 126.2, 125.7, 123.9, 120.8, 21.6, 21.2, 21.1; IR (Film, cm^{-1}): 3340, 1603, 1383, 1037, 763; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{40}H_{34}NO$: 544.2635, found: 544.2632.

(*Z*)-3-(2,5-Diphenyl-4-*p*-tolyl-1*H*-pyrrol-3-yl)-3-(4-methoxyphenyl)-1-*p*-tolylprop-2-en-1-one (3p). Following the general procedure, reaction between 2,3-diphenyl-2*H*-azirine **1b** (58 mg, 0.3 mmol) and 4-(4-methoxyphenyl)-2,6-di-*p*-tolylpyrylium tetrafluoroborate salt **2j** (91 mg, 0.2 mmol) afforded the product **3p** (68 mg, 61%) as a yellow solid (R_f 0.50 with 25% EtOAc/hexane; Mp 225−227 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.38−7.45 (m, 6H), 7.14−7.25 (m, 8H), 7.02−7.07 (m, 4H), 6.88 (d, J = 6.9 Hz, 2H), 6.72−6.76 (m, 3H), 3.76 (s, 3H), 2.34 (s, 3H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 191.1, 160.3, 148.0, 142.1, 136.2, 135.2, 133.9, 132.8, 132.4, 132.2, 130.3, 129.9, 129.3, 128.8, 128.4, 128.4, 128.4, 128.3, 126.7, 126.4, 126.2, 124.5, 123.9, 120.9, 113.6, 55.2, 21.6, 21.1; IR (Film, cm^{-1}): 3323, 1646, 1383; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{40}H_{34}NO_2$: 560.2584, found: 560.2585.

(*Z*)-3-(5-(4-Methoxyphenyl)-2-phenyl-4-*p*-tolyl-1*H*-pyrrol-3-yl)-3-phenyl-1-*p*-tolylprop-2-en-1-one (3q). Following the general procedure, reaction between 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine **1a** (67 mg, 0.3 mmol) and 4-phenyl-2,6-di-*p*-tolylpyrylium tetrafluoroborate salt **2h** (85 mg, 0.2 mmol) afforded the product **3q** (56 mg, 50%) as a red solid (R_f 0.50 with 25% EtOAc/hexane; Mp 236−238 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.45−7.47 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.19−7.22 (m, 3H), 7.11−7.14 (m, 4H), 7.06 (s, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 7.9 Hz, 2H), 6.72 (d, J = 8.7 Hz, 2H), 6.69 (d, J = 7.9 Hz, 2H), 3.73 (s, 3H), 2.31 (s, 3H), 2.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.3, 158.2, 148.3, 142.2, 141.7, 135.9, 135.1, 132.5, 132.2, 130.4, 129.7, 128.9, 128.7, 128.4, 128.4, 128.4, 128.1, 127.9, 126.5, 126.4, 126.3, 124.5, 123.1, 120.5, 113.9, 55.2, 21.6, 21.0; IR (Film, cm^{-1}): 3379, 1383, 1052; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{40}H_{34}NO_2$: 560.2584, found: 560.2589.

Selected X-ray Crystallographic Data for ***3q.*** $C_{40}H_{33}NO_2$, M = 559.67, Monoclinic, $P2_1/c$, a = 12.8156(9) Å, b = 13.8872(11) Å, c = 18.6299(12) Å, V = 3007.1(4) Å^3, β = 114.914 (4)°, Z = 4, D_c = 1.236 g cm^{-3}, μ (Mo−Kα) = 0.075 mm^{-1}, $F(000)$ = 1184, reflections collected/unique = 47188/7519, [R(int) = 0.1145]. Final R indices [$I > 2\sigma(I)$], R = 0.0636, wR = 0.2049.

(*Z*)-3-(4-Methoxyphenyl)-3-(5-(4-methoxyphenyl)-2-phenyl-4-*p*-tolyl-1*H*-pyrrol-3-yl)-1-*p*-tolylprop-2-en-1-one (3r). Following the general procedure, reaction between 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine **1a** (67 mg, 0.3 mmol) and 4-(4-methoxyphenyl)-2,6-di-*p*-tolylpyrylium tetrafluoroborate salt **2j** (91 mg, 0.2 mmol) afforded the product **3r** (63 mg, 53%) as a yellow solid (R_f 0.50 with 25% EtOAc/hexane; Mp 241−243 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.35−7.41 (m, 4H), 7.32 (d, J = 7.5 Hz, 2H), 7.07−7.11 (m, 4H), 6.96−7.01 (m, 4H), 6.82 (d, J = 7.8 Hz, 2H), 6.68−6.71 (m, 6H), 3.71 (s, 3H), 3.70 (s, 3H), 2.29 (s, 3H), 2.09 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 191.2, 160.3, 158.1, 148.2, 142.1, 136.3, 135.0, 134.0, 132.5, 132.3, 130.4, 129.3, 129.3, 128.8, 128.4, 128.4, 128.3, 128.1, 126.2, 126.1, 125.6, 124.5, 123.0, 120.6, 113.8, 113.6, 55.2, 55.2, 21.5, 21.0; IR (Film, cm^{-1}): 3335, 1648, 1383, 828; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{41}H_{36}NO_3$: 590.2690, found: 590.2692.

(*Z*)-3-(5-(4-Methoxyphenyl)-2,4-diphenyl-1*H*-pyrrol-3-yl)-3-(4-(methylthio)phenyl)-1-phenylprop-2-en-1-one (3s). Following the general procedure, reaction between 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine **1a** (67 mg, 0.3 mmol) and 4-(4-(methylthio)-phenyl)-2,6-di-*p*-tolylpyrylium tetrafluoroborate salt **2k** (94 mg, 0.2 mmol) afforded the product **3s** (73 mg, 63%) as a red solid (R_f 0.50 with 25% EtOAc/hexane; Mp 84−86 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.46 (d, J = 7.3 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.34 (m appearing as d, J = 7.0 Hz, 3H), 7.18−7.23 (m, 2H), 7.04−7.15 (m, 8H), 6.94−6.98 (m, 5H), 6.72 (d, J = 8.4 Hz, 2H), 3.73 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 191.7, 158.3, 148.4, 140.0, 139.5, 138.6, 137.9, 135.4, 132.4, 131.7, 130.5, 129.6, 129.1, 128.5, 128.2, 128.1, 127.8, 127.7, 126.5, 126.2, 125.9, 125.8, 125.4, 125.3, 123.1, 120.1, 113.9, 55.2, 15.4; IR (Film, cm^{-1}): 3368, 1604, 697; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{39}H_{32}NO_2S$: 578.2148, found: 578.2149.

(*Z*)-3-(4-Fluorophenyl)-3-(5-(4-methoxyphenyl)-2,4-diphenyl-1*H*-pyrrol-3-yl)-1-phenylprop-2-en-1-one (3t). Following the general procedure, reaction between 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine **1a** (67 mg, 0.3 mmol) and 4-(4-fluorophenyl)-2,6-diphenylpyrylium tetrafluoroborate salt **2d** (83 mg, 0.2 mmol) afforded the product **3t** (60 mg, 55%) as a red solid (R_f 0.50 with 25% EtOAc/hexane; Mp 150−152 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.44−7.50 (m, 4H), 7.33−7.40 (m, 3H), 7.12−7.25 (m, 6H), 7.05−7.11 (m, 1H), 7.03 (s, 1H), 6.95−7.02 (m, 5H), 6.88−6.93 (m, 2H), 6.74−6.79 (m, 2H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz,

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$CDCl_3$) δ 191.6, 163.2 (d, $^1J_{C\text{-}F}$ = 247.7 Hz), 158.4, 147.8, 138.4, 137.5 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 135.3, 132.3, 131.8, 130.5, 129.9, 129.7 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 129.2, 128.5, 128.2, 128.2, 127.8, 127.7, 126.7, 126.4, 125.9, 125.2, 123.0, 120.1, 115.2 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 114.0, 55.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ −112.48 (s); IR (Film, cm^{-1}): 3372, 1383, 1050; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{38}H_{29}FNO_2$: 550.2177, found: 550.2173.

(*Z*)-3-(2,4-Diphenyl-5-*p*-tolyl-1*H*-pyrrol-3-yl)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (3u). Following the general procedure, reaction between 2-phenyl-3-(*p*-tolyl)-2*H*-azirine **1c** (62 mg, 0.3 mmol) and 4-(4-methoxyphenyl)-2,6-diphenylpyrylium tetrafluoroborate salt **2c** (85 mg, 0.2 mmol) afforded the product **3u** (59 mg, 54%) as a red solid (R_f 0.50 with 20% EtOAc/hexane; Mp 150−152 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 9.2 Hz, 1H), 7.43 (d, J = 7.7 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.29−7.32 (m, 3H), 7.09−7.19 (m, 4H), 7.00−7.05 (m, 4H), 6.91−6.96 (m, 7H), 6.70 (d, J = 8.6 Hz, 2H), 3.71 (s, 3H), 2.22 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.61, 160.46, 148.68, 138.88, 136.10, 135.43, 133.81, 132.43, 131.60, 130.51, 129.80, 129.78, 129.36, 129.22, 129.15, 128.48, 128.10, 127.75, 127.65, 126.75, 126.47, 126.22, 125.84, 124.32, 123.55, 120.59, 113.69, 55.27, 21.14; IR (Film, cm^{-1}): 3382, 1383, 1055, 771; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{39}H_{32}NO_2$: 546.2428, found: 546.2428.

(*Z*)-3-(2,4-Diphenyl-5-(*p*-tolyl)-1*H*-pyrrol-3-yl)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (3v). Following the general procedure, reaction between 2-phenyl-3-(*p*-tolyl)-2*H*-azirine **1c** (62 mg, 0.3 mmol) and 4-(4-fluorophenyl)-2,6-diphenylpyrylium tetrafluoroborate salt **2d** (83 mg, 0.2 mmol) afforded the product **3v** (65 mg, 61%) as a yellow solid (R_f 0.50 with 15% EtOAc/hexane; Mp 156−158 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.43−7.50 (m, 4H), 7.33−7.40 (m, 3H), 7.16−7.25 (m, 4H), 7.06−7.11 (m, 3H), 6.95−7.03 (m, 8H), 6.88−6.94 (m, 2H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.6, 163.2 (d, $^1J_{C\text{-}F}$ = 247.6 Hz), 147.7, 138.3, 137.5 (d, $^4J_{C\text{-}F}$ = 2.7 Hz), 136.3, 135.2, 132.2, 131.9, 130.5, 130.2, 129.7 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 129.6, 129.3, 129.2, 128.5, 128.2, 127.8, 127.7, 126.7, 126.4, 126.0, 123.4, 120.2, 115.2 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 21.14; ^{19}F NMR (282 MHz, $CDCl_3$) δ −112.48 (s); IR (Film, cm^{-1}): 3273, 1639, 1038, 826; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{38}H_{29}FNO$: 534.2228, found: 534.2228.

(*Z*)-3-(2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-pyrrol-3-yl)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (3w). Following the general procedure, reaction between 2-(4-chlorophenyl)-3-phenyl-2*H*-azirine **1d** (68 mg, 0.3 mmol) and 4-(4-fluorophenyl)-2,6-diphenylpyrylium tetrafluoroborate salt **2d** (83 mg, 0.2 mmol) afforded the product **3w** (64 mg, 58%) as a yellow solid (R_f 0.50 with 15% EtOAc/hexane; Mp 201−203 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.54 (d, J = 7.2 Hz, 2H), 7.44−7.46 (m, 1H), 7.37−7.43 (m, 2H), 7.24−7.30 (m, 5H), 7.11−7.20 (m, 5H), 7.10 (s, 1H), 7.04 (d, J = 8.4 Hz, 2H), 6.87−6.96 (m, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 191.5, 163.3 (d, $^1J_{C\text{-}F}$ = 247.9 Hz), 147. 8, 138.2, 137.1, 135.0, 132.4, 132.2, 132.2, 130.7, 130.4, 129.6 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 129.5, 129.0, 128.6, 128.4, 128.2, 128.0, 127.8, 127.5, 126.8, 126.5, 126.1, 125.9, 123.9, 120.8, 115.3 (d, $^2J_{C\text{-}F}$ = 21.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.06 (s); IR (Film, cm^{-1}): 3365, 1383, 1058, 770; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{37}H_{26}ClFNO$: 554.1681, found: 554.1680.

(*Z*)-3-Phenyl-3-(2-phenyl-5-(thiophen-2-yl)-4-*p*-tolyl-1*H*-pyrrol-3-yl)-1-*p*-tolylprop-2-en-1-one (3x). Following the general procedure, reaction between 2-phenyl-3-(thiophen-2-yl)-2*H*-azirine **1f** (60 mg, 0.3 mmol) and 4-phenyl-2,6-di-*p*-tolylpyrylium tetrafluoroborate salt **2h** (85 mg, 0.2 mmol) afforded the product **3x** (56 mg, 52%) as a red solid (R_f 0.50 with 20% EtOAc/hexane; Mp 204−206 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.34−7.38 (m, 4H), 7.30 (d, J = 7.4 Hz, 2H), 7.13−7.17 (m, 3H), 7.06 (t, J = 7.6 Hz, 2H), 6.94−7.00 (m, 5H), 6.85 (d, J = 7.7 Hz, 2H), 6.78 (br s, 2H), 6.68 (d, J = 7.6 Hz, 2H), 2.28 (s, 3H), 2.07 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.1, 147.9, 142.5, 141.5, 135.9, 135.9, 135.1, 132.1, 131.4, 130.8, 130.2, 128.8, 128.5, 128.4, 128.4, 128.1, 127.9, 127.1, 126.7, 126.4, 124.6, 123.9, 123.3, 122.8, 120.9, 21.6, 21.1; IR (Film, cm^{-1}): 3378, 1383, 1055, 771; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{37}H_{30}NOS$: 536.2043, found: 536.2045.

(*Z*)-3-(2,4-Diphenyl-5-(thiophen-2-yl)-1*H*-pyrrol-3-yl)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (3y). Following the general procedure, reaction between 2-phenyl-3-(thiophen-2-yl)-2*H*-azirine **1f** (60 mg, 0.3 mmol) and 4-(4-fluorophenyl)-2,6-diphenylpyrylium tetrafluoroborate salt **2d** (83 mg, 0.2 mmol) afforded the product **3y** (57 mg, 54%) as an orange solid (R_f 0.50 with 20% EtOAc/hexane; Mp 120−122 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.51 (d, J = 7.2 Hz, 2H), 7.35−7.345 (m, 5H), 7.16−7.27 (m, 4H), 7.00−7.11 (m, 8H), 6.83−6.93 (m, 4H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 191.3, 163.2 (d, $^1J_{C\text{-}F}$ = 247.3 Hz), 147.5, 138.3, 137.4 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 134.8, 134.5, 132.0, 131.9, 130.8, 130.4, 129.7 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 128.5, 128.2, 127.9, 127.7, 127.1, 126.9, 126.6, 126.5, 125.8, 124.4, 124.1, 123.5, 123.1, 120.5, 115.2 (d, $^2J_{C\text{-}F}$ = 21.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −112.31 (s); IR (Film, cm^{-1}): 3382, 1383, 1059, 771; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{35}H_{25}FNOS$: 526.1635, found: 526.1636.

(*Z*)-3-(4-Fluorophenyl)-3-(5-(4-methoxyphenyl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)-1-phenylprop-2-en-1-one (3z). Following the general procedure, reaction between 3-(4-methoxyphenyl)-2-methyl-2*H*-azirine **1g** (48 mg, 0.3 mmol) and 4-(4-fluorophenyl)-2,6-diphenylpyrylium tetrafluoroborate salt **2d** (83 mg, 0.2 mmol) afforded the product **3z** (18 mg, 18%) as a red solid (R_f 0.50 with 15% EtOAc/hexane; Mp 197−199 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.52−7.55 (m, 1H), 7.38−7.44 (m, 4H), 7.13 (s, 1H), 7.03−7.09 (m, 4H), 6.88−6.99 (m, 5H), 6.78 (d, J = 8.6 Hz, 2H), 3.70 (s, 3H), 1.95 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 191.6, 162.8 (d, $^1J_{C\text{-}F}$ = 244.2 Hz), 157.8, 148.3, 138.9, 138.4, 136.7, 132.6, 130.4 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 130.1, 128.7, 128.4, 128.2, 128.0, 127.7, 126.7, 126.0, 125.7, 124.6, 121.0, 119.3, 115.3 (d, $^2J_{C\text{-}F}$ = 21.1 Hz), 114.1, 55.4, 12.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −113.16 (s); IR (Film, cm^{-1}): 3370, 1383, 1052, 769; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{33}H_{27}FNO_2$: 488.2020, found: 488.2020.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00082.

Photograph of the visible light photoreactor; HRMS of compound **4**; experimental details of luminescence quenching experiment, UV−visible spectroscopy and X-ray analysis of **3k** and **3q**; ^{1}H, ^{13}C, ^{19}F NMR spectra (PDF)

Accession Codes

CCDC 2011180 and 2054677 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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