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A General Protocol for Radical Anion [3+2] Cycloaddition Enabled by Tandem Lewis Acid Photoredox Catalysis

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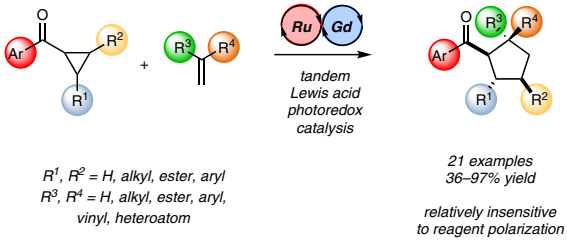

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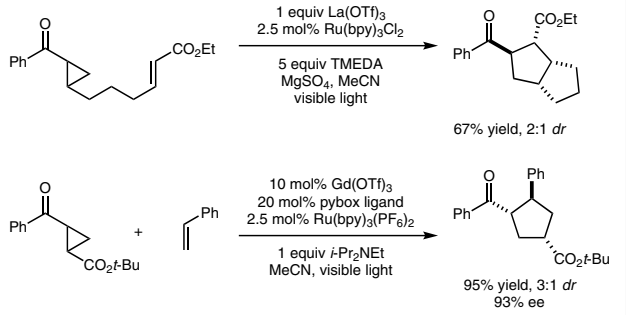
Abstract A method for intermolecular [3+2] cycloaddition between aryl cyclopropyl ketones and alkenes involving the combination of Lewis acid and photoredox catalysis is reported. In contrast to other more common methods for [3+2] cycloaddition, these conditions operate using a broad range of both electron-rich and electron-deficient reaction partners. The critical factors predicting the success of these reactions is the redox potential of the cyclopropyl ketone and the ability of the alkene to stabilize a key radical intermediate.

Key words cycloaddition, photoredox, photocatalysis, cyclopropane, cyclopentane

Five-membered carbocycles feature prominently in a variety of complex natural products and many other small-molecule compounds of biological interest. As a result, significant research efforts have been directed towards the discovery of selective and flexible methods to synthesize cyclopentanes.[1] While numerous successful strategies have been developed (cyclizations,[2] ring expansions,[3] etc.), [3+2] cycloaddition reactions are particularly appealing because they provide a direct means to access a diverse array of cyclopentanoid frameworks from relatively simple building blocks. The most common strategies for [3+2] cycloadditions involve 1,3-dipolar and zwitterionic reagents,[4] vinyl carbenoids,[5] or reductive cycloadditions.[6] While the existence of these various methods offers flexibility in the synthesis of complex cyclopentane-containing compounds, they are generally sensitive to the polarity of the coupling partners and are often incompatible with polar functional groups.

Organoradical intermediates can be synthetically attractive because they often react with both electron-rich and electron-poor partners and are generally tolerant of a range of common functional groups. Our group has been interested in the development of cycloaddition methods that take advantage of radical anion intermediates generated using visible light photocatalysis.[7] We recently reported two photocatalytic methods that result in the formal [3+2] cycloaddition of aryl cyclopropyl ketones with alkenes (Scheme 1).[8–10] In these reactions, a Lewis acid co-catalyst is used to activate the cyclopropyl ketone towards one-electron reduction by a photogenerated Ru^{I} catalyst; the resulting ketyl radical reacts with an alkene coupling partner to afford a new five-membered carbocycle. The correct choice of Lewis acid and careful tuning of the coordination sphere of the Lewis acid proved to be critical for the success of these reactions. Unfortunately, the scope of these reactions has proven to be somewhat limited: the optimal conditions for intramolecular [3+2] cycloadditions did not translate smoothly to intermolecular reactions, and the optimal conditions for enantioselective intermolecular cycloadditions unfortunately required the use of relatively reactive cyclopropanes and electron-rich alkene partners to achieve reasonable yields. In order to perform a more comprehensive survey of the synthetic capabilities and limitations of this unique strategy for [3+2] cycloaddition, we became interested in developing robust conditions that allow for efficient racemic [3+2] cycloadditions with a relatively broad substrate scope. The results of these investigations are described herein.

Our initial optimization studies focused on the reaction of simple unsubstituted cyclopropyl phenyl ketone (**1**) with a relatively unpolarized styrene partner. We first assessed this reaction under conditions previously reported for the intramolecular version of this reaction, employing 1 equivalent of the Lewis acid $La(OTf)_3$, 2.5 mol% of the photocatalyst $Ru(bpy)_3Cl_2$, and 5 equivalents of TMEDA as reductive quencher. An initial experiment provided the desired cycloadduct in 44% yield after 24 hours (Table 1, entry 1). Al-



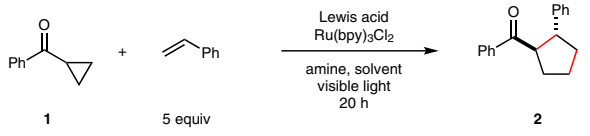
Scheme 1 Top: Racemic photocatalytic intramolecular [3+2] cycloadditions. Bottom: Enantioselective photocatalytic intermolecular [3+2] cycloadditions.

ternative solvents showed no improvements in the overall efficiency of the reaction (entries 2–4). The identity of the Lewis acid co-catalyst had a more positive effect. A screen of Lewis acids revealed that lanthanide triflates are uniquely competent in this transformation and that $Gd(OTf)_3$ offers the greatest yield among those screened (entries 5–7). Alternate tertiary amine additives proved to be less effective than TMEDA, consistent with its proposed dual role as a chelating ligand and a reductive quencher in this reaction (entries 8 and 9). The loading of $Gd(OTf)_3$ could be decreased to 50 mol% with a modest decrease in yield (entry 10), which could be restored by lowering the concentration of TMEDA (entry 11). Lowering the loading of the photocatalyst to 1 mol% did not appear to have an appreciable influence on the effectiveness of the reaction. These optimal conditions provided the desired cycloadduct in 71% yield after 20 hours (entry 12). Control reactions verified that the photocatalyst, Lewis acid, quencher, and light source are all required for any product formation, validating the photocatalytic nature of this reaction.

Having identified optimized reaction conditions, the generality of this transformation was next explored. The scope with respect to the cyclopropane substrate proved to be relatively broad (Scheme 2). A heteroaryl cyclopropyl ketone was well tolerated (**3**).[11] In general, aryl and alkyl substituents on the cyclopropane provided superior reactivity compared to the unsubstituted cyclopropyl phenyl ketone, presumably due to the increased stability of the radical resulting from homolytic opening of the cyclopropane ring (**4** and **5**). Multiple alkyl substitutions were also well tolerated, allowing for the construction of quaternary centers (**6** and **7**). Interestingly this cycloaddition also tolerated electron-withdrawing substituents (e.g., ester and ketone, **8** and **9**). This is in stark contrast to the majority of methodologies available for [3+2] cycloadditions which tend to be very sensitive to the polarity of each coupling partner. Cyclopropanes substituted on all three carbons react smoothly (**10**). When ring-opening of an unsymmetrically substituted cyclopropane can result in the formation of two different radical intermediates, the major product is formed with excellent regioselectivity consistent with reaction through the more stable radical (**11**).

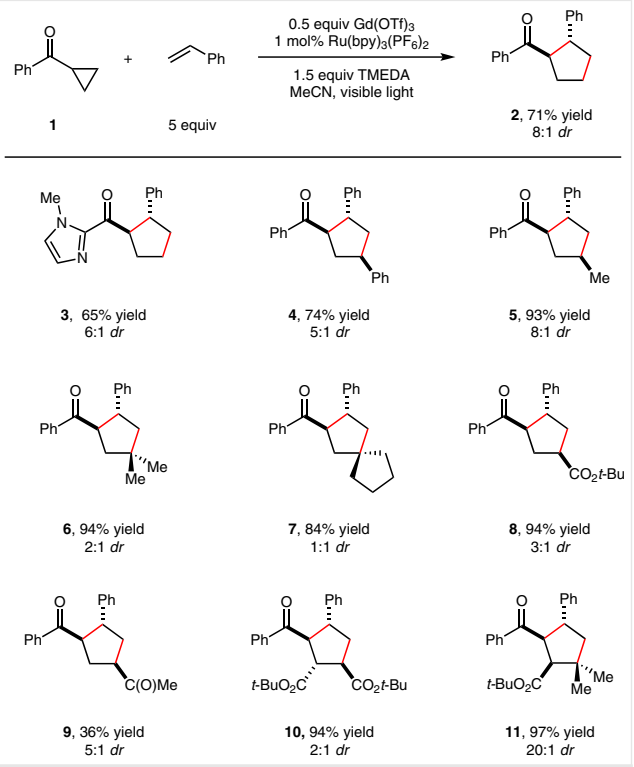
The scope with respect to the alkene reaction partner is summarized in Figure 1. A variety of alkenes participate in this reaction, with the limitation that the olefin must bear a radical-stabilizing substituent. Thus, styrenes are good coupling partners for this transformation: both electron-rich and electron-poor styrenes react smoothly (**12** and **13**). Neither reactive halides nor the introduction of steric bulk on the aryl ring of the styrene adversely impact the transformation (**14** and **15**). Substitutions at the α-position of styrenes were also well tolerated (**16**–**18**). In line with our design plan, a range of alkene reaction partners with quite varied polarities are readily tolerated. Very electron-rich heteroatom-substituted coupling partners such as a vinylcarbazole (**19**) and a silyl enol ether (**20**) readily undergo [3+2] cycloaddition. Electron-deficient alkenes such as acrylates (**21**) also worked well under these conditions. Interestingly 1,3-butadiene was also an efficient coupling partner (**22**). The broad scope of the olefin coupling partner thus represents a complementary feature to many of the existing [3+2] cycloaddition methodologies. However, 1,2-

Table 1 Optimization of Reaction Conditions[a]



Entry	Solvent	Lewis acid	Base[b]	Yield (%)[c]
1	MeCN	$La(OTf)_3$ (1 equiv)	TMEDA (5 equiv)	44
2	EtOAc	$La(OTf)_3$ (1 equiv)	TMEDA (5 equiv)	32
3	DMF	$La(OTf)_3$ (1 equiv)	TMEDA (5 equiv)	0
4	CH_2Cl_2	$La(OTf)_3$ (1 equiv)	TMEDA (5 equiv)	0
5	MeCN	$Zn(OTf)_3$ (1 equiv)	TMEDA (5 equiv)	0
6	MeCN	$Er(OTf)_3$ (1 equiv)	TMEDA (5 equiv)	55
7	MeCN	$Gd(OTf)_3$ (1 equiv)	TMEDA (5 equiv)	69
8	MeCN	$Gd(OTf)_3$ (1 equiv)	*i*-Pr_2NEt (5 equiv)	9
9	MeCN	$Gd(OTf)_3$ (1 equiv)	PMP (5 equiv)	7
10	MeCN	$Gd(OTf)_3$ (0.5 equiv)	TMEDA (5 equiv)	49
11	MeCN	$Gd(OTf)_3$ (0.5 equiv)	TMEDA (1.5 equiv)	69
12[d]	MeCN	$Gd(OTf)_3$ (0.5 equiv)	TMEDA (1.5 equiv)	71

[a] Reaction conditions: 0.2 M in indicated solvent, 0.04 mmol cyclopropane, 2.5% [Ru].
[b] PMP: 1,2,2,6,6-Pentamethylpiperidine.
[c] Yields determined by ^{1}H NMR spectroscopy using phenanthrene as an internal standard.
[d] Using 1% $Ru(bpy)_3(PF_6)_2$.



Scheme 2 *Reagents and conditions*: Cyclopropane **1** (1 equiv), alkene partner (5 equiv), $Ru(bpy)_3(PF_6)_2$ (1 mol%), $Gd(OTf)_3$ (0.5 equiv), and TMEDA (1.5 equiv) in MeCN (0.2 M). Reactions were irradiated with a 23 W compact fluorescent bulb. Yields are of isolated cyclopentane derivatives. Diasteromer ratios were determined by ^1H NMR analysis of the unpurified products.

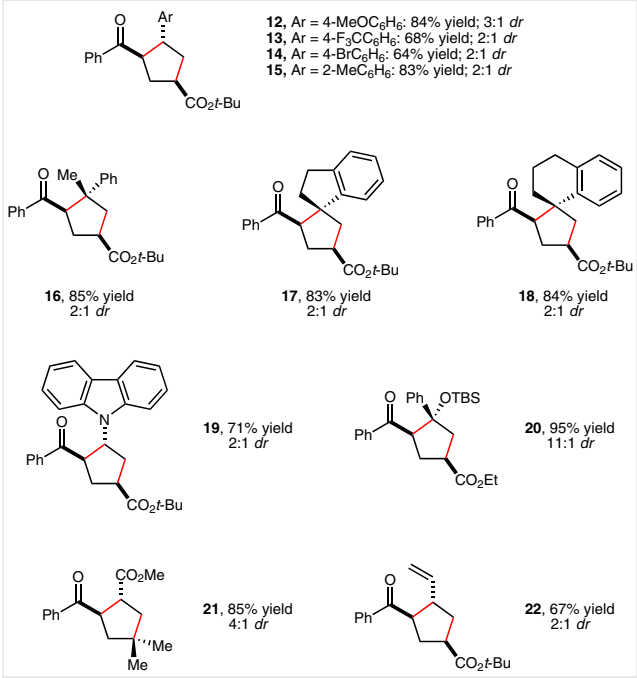
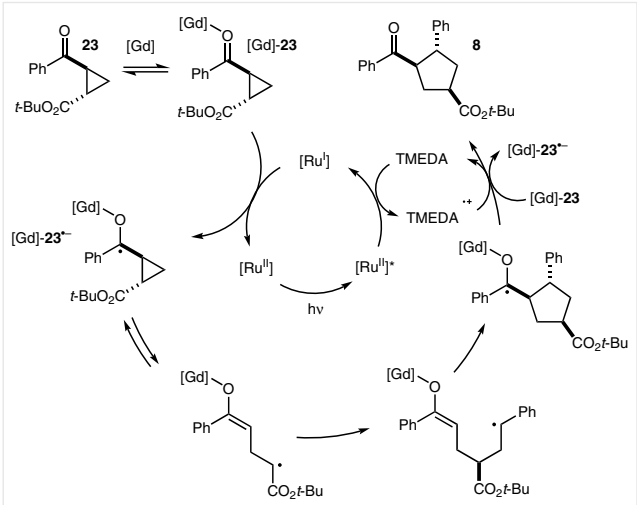


Figure 1 For a general equation, see Scheme 2. *Reagents and conditions*: Cyclopropane **1** (1 equiv), alkene partner (5 equiv), $Ru(bpy)_3(PF_6)_2$ (1 mol%), $Gd(OTf)_3$ (0.5 equiv), and TMEDA (1.5 equiv) in MeCN (0.2 M). Reactions were irradiated with a 23 W compact fluorescent bulb. Yields are of isolated cyclopentane derivatives. Diasteromer ratios were determined by ^1H NMR analysis of the unpurified products.

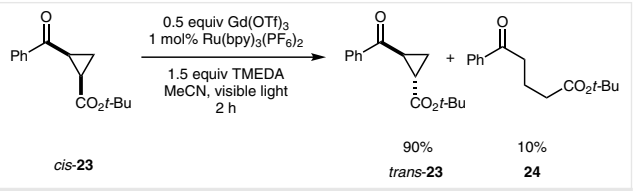
disubstituted alkenes such as β-methylstyrene failed to produce identifiable quantities of cycloadduct and represent a limitation of this method.

Scheme 3 outlines a mechanism for this intermolecular [3+2] cycloaddition analogous to that previously proposed for the intramolecular method. Photoexcitation of $Ru(bpy)_3^{2+}$ with visible light and subsequent reductive quenching by TMEDA results in the generation of $Ru(bpy)_3^{1+}$, which can then reduce the [Gd]-cyclopropane complex ([Gd]-**23**). The ketyl radical anion then undergoes reversible ring opening to a distonic radical anion. This reactive intermediate then undergoes stepwise [3+2] cycloaddition with an olefin reaction partner to produce the ketyl radical of the product. Oxidation to produce the neutral cycloadduct occurs either through reduction of the radical cation of TMEDA or through a radical chain process[12] to produce another equivalent of the radical anion of [Gd]-**23**. The rapid reversibility of the ring-opening of ketyl radical anions has been studied extensively by Tanko and co-workers.[13] To support the relevance of this process in this transformation, diastereomerically pure *cis*-**23** was observed to undergo isomerization to *trans*-**23** within 2 hours upon exposure to the reaction conditions (Scheme 4). This isomerization only occurs in the presence of photocatalyst, Lewis acid, and TMEDA, which suggests that the isomerization is occurring through an electron-transfer process. Additional-



Scheme 3 Proposed mechanism for intermolecular [3+2] cycloaddition

ly, we observed the formation of 10% yield of reductive ring cleavage product **24**, which constitutes a significant by-product in many of the lower-yielding cycloadditions.



Scheme 4 Isomerization of *cis*-cyclopropane under photocatalytic conditions

In conclusion, we have identified conditions for an efficient intermolecular [3+2] cycloaddition between a range of simple aryl cyclopropyl ketones and olefins. The choice of Lewis acid and loading of the reductive quencher proved critical in attaining efficient reactivity. This [3+2] cycloaddition provides a valuable complement to the existing methodologies in the literature for the construction of five-membered carbocycles. Particularly notable is the relative insensitivity of this cycloaddition to the polarity of the substrates. The critical constraints are the reduction potential of the cyclopropane and the ability of the olefin coupling partner to stabilize a key radical intermediate in the stepwise cycloaddition. This method should thus prove to be a valuable tool for the synthesis of a variety of structurally complex five-membered-ring compounds.

All glassware were oven-dried at 130 °C overnight or flame-dried immediately prior to use. MeCN, THF, and CH_2Cl_2 were purified by elution through alumina as described by Grubbs.[14] A 23 W (1200 lumens) SLI Lighting Mini-Lynx compact fluorescent light bulb was used for all photochemical reactions. $Gd(OTf)_3$, $La(OTf)_3$, and other Lewis acids were purchased from Strem, stored in a glove box, and used without further purification. Flash column chromatography was performed with Silicycle 40–63Å silica gel (230–400 mesh). Styrene, *i*-Pr_2NEt, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, Et_3N, 1,2,2,6,6-pentamethylpiperidine, and DABCO were purchased from Sigma Aldrich and subsequently purified either by distillation or recrystallization. Cyclopropyl phenyl ketone, cyclopropyl 4-chlorophenyl ketone, and cyclopropyl 4-methoxyphenyl ketone was purchased from Sigma Aldrich and purified by short-path distillation prior to use. Sodium oxalate was purchased from Sigma Aldrich and used without further purification. ^1H and $^{13}C\{H\}$ NMR data for all previously uncharacterized compounds were obtained using a Bruker Avance-400 spectrometer and are referenced to TMS (0.0 ppm) and $CDCl_3$ (77.0 ppm), respectively. IR spectral data were obtained using a Bruker Vector 22 spectrometer. Mass spectrometry was performed with a Micromass LCT (electrospray ionization, time-of-flight analyzer or electron impact). Melting points were obtained using a Mel-Temp II (Laboratory Devices, Inc., USA) melting point apparatus.

For details on the preparation and characterization of starting materials, see the Supporting Information.

Intermolecular [3+2] Cycloadditions of Aryl Cyclopropyl Ketones with Alkenes; General Procedure

An oven-dried Schlenk tube equipped with a magnetic stir-bar was charged with $Gd(OTf)_3$ (0.5 equiv). A flame-dried vial was charged with the appropriate aryl cyclopropyl ketone (1 equiv), the corresponding alkene (5 equiv), $Ru(bpy)_3(PF_6)_2$ (1 mol%), TMEDA (1.5 equiv), and MeCN (0.2 M concentration). The contents of the vial were then transferred to the Schlenk tube. The reaction mixture was then thoroughly degassed through three freeze-pump-thaw cycles, then backfilled with N_2. The reaction flask was then placed in front of a 23 W (1380 lumen) compact fluorescent lamp and stirred at r.t. Upon consumption of the starting materials, the reaction mixture was diluted with 1:1 Et_2O/pentanes and passed through a short plug of silica gel. The filtrate was concentrated and the residue purified by column chromatography.

Phenyl(*trans* 2-phenylcyclopentyl)methanone (2)

Colorless oil; yield: 71.1 mg (71%, 8:1 *dr*); R_f = 0.3 (Et_2O/pentanes, 1:9).

^1H and ^{13}C NMR data were consistent with the literature.[15]

(1-Methyl-1*H*-imidazol-2-yl)(2-phenylcyclopentyl)methanone (3)

Colorless oil; yield: 66.1 mg (65%, 6:1 *dr*); R_f = 0.3 (acetone/pentanes, 1:3).

IR (ATR): 2983, 1705, 1274, 1080 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.31–7.27 (m, 2 H), 7.23 (dd, *J* = 8.5, 6.9 Hz, 2 H), 7.16–7.09 (m, 2 H), 7.09 (d, *J* = 0.9 Hz, 1 H), 6.96 (d, *J* = 0.9 Hz, 1 H), 4.32 (td, *J* = 9.6, 8.0 Hz, 1 H), 3.95 (s, 3 H), 3.61 (td, *J* = 9.7, 7.8 Hz, 1 H), 2.45–2.33 (m, 1 H), 2.30–2.18 (m, 1 H), 2.01–1.88 (m, 1 H), 1.91–1.77 (m, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 194.72, 144.32, 143.19, 129.05, 128.29, 127.48, 126.89, 126.01, 54.54, 47.78, 36.19, 35.55, 32.66, 25.21.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $[C_{16}H_{19}N_2O]^+$: 255.1492; found: 255.1492.

2,4-Diphenylcyclopentyl(phenyl)methanone (4)

Colorless oil; yield: 111.1 mg (74%, 5:1 *dr*); R_f = 0.3 (Et_2O/pentanes, 1:9).

IR (ATR): 2978, 1718, 1305, 1272, 1150 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (d, *J* = 7.3 Hz, 2 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.42–7.13 (m, 12 H), 4.16–3.82 (m, 2 H), 3.58 (dt, *J* = 17.9, 9.0 Hz, 1 H), 2.69–2.52 (m, 1 H), 2.48–2.28 (m, 2 H), 2.26–2.04 (m, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.51, 143.26, 136.96, 136.34, 132.98, 132.90, 128.63, 128.54, 128.47, 128.36, 127.45, 127.33, 126.49, 54.72, 47.44, 45.57, 37.52, 34.81.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $[C_{24}H_{22}O]^+$: 326.1671; found: 326.1670.

(4-Methyl-2-phenylcyclopentyl)(phenyl)methanone (5)

White solid; yield: 49.1 mg (93%, 11:1 *dr*); mp 44.9–51 °C; R_f = 0.3 (Et_2O/pentanes, 1:10).

IR (ATR): 2957, 2868, 1681, 1602, 1451, 1266, 1012 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.74 (d, *J* = 7.4 Hz, 2 H), 7.42 (t, *J* = 7.4 Hz, 1 H), 7.30 (t, *J* = 7.7 Hz, 2 H), 7.24–7.11 (m, 4 H), 7.13–7.00 (m, 1 H), 3.90–3.69 (m, 2 H), 2.48–2.22 (m, 2 H), 2.02 (dt, *J* = 15.2, 7.8 Hz, 1 H), 1.82 (ddd, *J* = 13.0, 8.8, 7.2 Hz, 1 H), 1.55–1.43 (m, 1 H), 1.03 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.90, 145.50, 132.80, 128.55, 128.44, 128.41, 127.37, 127.30, 126.07, 55.96, 46.89, 42.50, 41.01, 34.44, 20.78.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for [$C_{19}H_{24}NO$]$^+$: 282.1852; found: 282.1853.

(4,4-Dimethyl-2-phenylcyclopentyl)(phenyl)methanone (6)

Yield: 52.3 mg (94%, 2:1 *dr*); R_f = 0.3 (Et_2O/pentanes, 1:10).

Major Diastereomer

White solid; mp 105.3–107.8 °C.

IR (ATR): 2941, 2863, 1678, 1448, 1283, 1015 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (d, *J* = 8.4 Hz, 2 H), 7.48 (t, *J* = 7.4 Hz, 1 H), 7.37 (t, *J* = 8.0 Hz, 2 H), 7.29–7.18 (m, 4 H), 7.12 (t, *J* = 7.0 Hz, 1 H), 4.04–3.84 (m, 2 H), 2.12 (dd, *J* = 13.0, 9.2 Hz, 1 H), 2.04 (dd, *J* = 12.7, 6.8 Hz, 1 H), 1.86 (t, *J* = 11.9 Hz, 1 H), 1.73 (dd, *J* = 13.1, 7.8 Hz, 1 H), 1.21 (s, 3 H), 1.13 (s, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.72, 144.08, 137.00, 132.80, 128.43, 128.43, 128.38, 127.39, 126.15, 54.88, 49.42, 46.79, 46.76, 39.02, 30.59, 29.55.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for [$C_{20}H_{23}O$]$^+$: 279.1743; found: 279.1743.

Minor Diastereomer

White solid; mp 71.6–73.4 °C.

IR (ATR): 2953, 1927, 2866, 1679, 1463, 1448, 1367, 1221 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88 (d, *J* = 8.2 Hz, 2 H), 7.62 (d, *J* = 8.3 Hz, 2 H), 7.33–7.06 (m, 5 H), 3.98 (q, *J* = 9.3 Hz, 1 H), 3.62 (ddd, *J* = 11.3, 9.4, 7.6 Hz, 1 H), 3.02 (ddd, *J* = 16.5, 9.2, 7.3 Hz, 1 H), 2.63–2.38 (m, 2 H), 2.25–2.00 (m, 2 H), 1.49 (s, 6 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 202.23, 142.11, 136.99, 132.03, 128.46, 127.96, 127.93, 127.71, 125.98, 50.97, 48.93, 48.45, 43.26, 38.47, 29.40, 28.53.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for [$C_{20}H_{23}O$]$^+$: 279.1743; found: 279.1741.

Phenyl(3-phenylspiro[4.4]nonan-2-yl)methanone (7)

Yield: 51.1 mg (84%, 1:1 *dr*); R_f = 0.3 (Et_2O/pentanes, 1:30).

Major Diastereomer

Colorless oil.

IR (ATR): 2945, 2858, 1680, 1448, 1216 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (d, *J* = 7.1 Hz, 2 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.38 (t, *J* = 7.6 Hz, 2 H), 7.32–7.18 (m, 4 H), 7.13 (t, *J* = 6.9 Hz, 1 H), 3.97–3.82 (m, 2 H), 2.21 (dd, *J* = 12.9, 9.6 Hz, 1 H), 2.12 (dd, *J* = 12.6, 6.5 Hz, 1 H), 2.02–1.88 (m, 1 H), 1.83 (dd, *J* = 12.9, 6.9 Hz, 1 H), 1.77–1.49 (m, 8 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.76, 144.22, 136.98, 132.77, 128.44, 128.42, 128.36, 127.38, 126.13, 54.64, 50.57, 47.52, 46.91, 44.98, 40.28, 39.78, 24.40, 24.34.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for [$C_{22}H_{25}O$]$^+$: 305.1900; found: 305.1899.

Minor Diastereomer

Colorless oil.

IR (ATR): 2950, 2863, 1679, 1448, 1220, 1023 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.56 (d, *J* = 7.2 Hz, 2 H), 7.36 (t, *J* = 7.3 Hz, 1 H), 7.29–7.18 (m, 2 H), 6.97 (7.02–6.90 (m, 5 H), 4.34–4.21 (m, 1 H), 3.71 (td, *J* = 10.4, 7.6 Hz, 1 H), 2.39 (dd, *J* = 13.0, 9.0 Hz, 1 H), 2.16–1.97 (m, 2 H), 1.90–1.47 (m, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 202.33, 142.17, 138.18, 132.06, 128.39, 127.97, 127.96, 127.72, 125.97, 50.89, 49.81, 48.59, 46.82, 41.52, 39.26, 38.89, 24.81, 24.66.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for [$C_{22}H_{25}O$]$^+$: 305.1900; found: 305.1900.

***tert*-Butyl 3-Benzoyl-4-phenylcyclopentanecarboxylate (8)**

Yield: 131.8 mg (94%, 3:1 *dr*); R_f = 0.3 (Et_2O/pentanes, 1:5).

Major Diastereomer

White solid; mp 97.1–98.5 °C.

IR (ATR): 2980, 1722, 1682, 1368, 1265, 1151cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 7.9 Hz, 2 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.37 (t, *J* = 7.7 Hz, 2 H), 7.28–7.22 (m, 4 H), 7.16 (dq, *J* = 9.1, 4.3 Hz, 1 H), 3.94–3.73 (m, 2 H), 3.17–3.00 (m, 1 H), 2.58–2.44 (m, 2 H), 2.22 (dt, *J* = 13.3, 9.0 Hz, 1 H), 2.13 (dt, *J* = 13.1, 9.0 Hz, 1 H), 1.46 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.56, 174.21, 143.74, 136.85, 132.92, 128.52, 128.47, 128.39, 127.31, 126.42, 80.52, 54.75, 47.14, 44.46, 37.31, 35.36, 28.08.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for [$C_{23}H_{27}O_3$]$^+$: 351.1955; found: 351.1955.

Minor Diastereomer

White solid; mp 111.5–113.0 °C.

IR (ATR): 2981, 1719, 1684, 1365, 1262, 1150 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (d, *J* = 7.6 Hz, 2 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.37 (t, *J* = 7.7 Hz, 2 H), 7.28–7.22 (m, 4 H), 7.15 (t, *J* = 6.8 Hz, 1 H), 3.99 (q, *J* = 9.3 Hz, 1 H), 3.68 (dt, *J* = 11.0, 8.4 Hz, 1 H), 3.00 (ddd, *J* = 16.6, 9.2, 7.5 Hz, 1 H), 2.62–2.43 (m, 2 H), 2.14 (dt, *J* = 13.2, 8.9 Hz, 2 H), 1.48 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.32, 174.92, 142.96, 136.62, 133.04, 128.51, 128.50, 128.50, 127.42, 126.53, 80.49, 53.70, 48.34, 44.20, 38.84, 34.83, 28.13.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for [$C_{23}H_{30}NO_3$]$^+$: 368.2220; found: 368.2220.

1-(3-Benzoyl-4-phenylcyclopentyl)ethanone (9)

Colorless oil; yield: 21.1 mg (36%, 5:1 *dr*); R_f = 0.3 (Et_2O/pentanes, 1:15).

IR (ATR): 2966, 1708, 1683, 1262, 1114 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.72 (d, *J* = 8.6 Hz, 2 H), 7.45–7.38 (m, 1 H), 7.30 (dd, *J* = 8.4, 7.1 Hz, 2 H), 7.23–7.04 (m, 4 H), 6.97–6.84 (m, 1 H), 3.85 (q, *J* = 8.7 Hz, 1 H), 3.60 (q, *J* = 8.7 Hz, 1 H), 3.19 (qd, *J* = 8.5, 5.9 Hz, 1 H), 2.55–2.32 (m, 2 H), 2.23–2.18 (m, 1 H), 2.15 (s, 3 H), 2.04 (dt, *J* = 13.3, 9.4 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 208.91, 200.61, 143.46, 136.73, 133.00, 128.59, 128.49, 128.40, 127.27, 126.55, 54.47, 51.45, 47.51, 36.23, 33.80, 28.41.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for [$C_{20}H_{21}O_2$]$^+$: 293.1536; found: 293.1535.

Di-*tert*-butyl 3-Benzoyl-4-phenylcyclopentane-1,2-dicarboxylate (10)

Yield: 84.7 mg (94%, 2:1 *dr*); R_f = 0.3 (Et_2O/pentanes, 1:5).

Major Diastereomer

White solid; mp 96–97 °C.

IR (ATR): 2977, 1724, 1681, 1393, 1368, 1257, 1158 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.70 (d, *J* = 7.7 Hz, 2 H), 7.43 (t, *J* = 7.3 Hz, 1 H), 7.29 (t, *J* = 7.7 Hz, 2 H), 7.24–7.2 (m, 4 H), 7.14 (dq, *J* = 8.2, 5.5, 4.8 Hz, 1 H), 4.17 (t, *J* = 9.5 Hz, 1 H), 3.64 (dt, *J* = 25.1, 8.8 Hz, 2 H), 3.36 (dq, *J* = 9.3, 5.5 Hz, 1 H), 2.51 (ddd, *J* = 13.4, 8.1, 5.5 Hz, 1 H), 2.27 (dt, *J* = 13.2, 9.8 Hz, 1 H), 1.49 (s, 9 H), 1.25 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.49, 173.03, 172.54, 141.91, 137.22, 132.93, 128.59, 128.40, 128.29, 127.20, 126.81, 81.21, 80.89, 57.00, 53.04, 49.76, 47.34, 37.16, 28.05, 27.78.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $[C_{28}H_{35}O_5]^+$: 451.2479; found: 451.2479.

Minor Diastereomer

White solid; mp 83.7–85.1 °C.

IR (ATR): 2978, 2936, 1725, 1680, 1367, 1257, 1154 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.57 (d, *J* = 7.0 Hz, 2 H), 7.46–7.33 (m, 1 H), 7.27–7.23 (m, 2 H), 7.07–6.91 (m, 5 H), 4.50 (dd, *J* = 10.0, 7.7 Hz, 1 H), 3.93 (dd, *J* = 10.3, 7.7 Hz, 1 H), 3.70 (td, *J* = 10.0, 7.3 Hz, 1 H), 3.10 (td, *J* = 10.5, 7.9 Hz, 1 H), 2.57–2.36 (m, 2 H), 1.53 (s, 9 H), 1.43 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 172.61, 132.42, 128.32, 128.07, 128.05, 127.94, 126.59, 53.83, 48.52, 48.27, 36.85, 28.15, 28.08.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $[C_{28}H_{35}O_5]^+$: 451.2479; found: 451.2478.

***tert*-Butyl 5-Benzoyl-2,2-dimethyl-4-phenylcyclopentanecarboxylate (11)**

White solid; yield: 74.2 mg (97%, 20:1 *dr*); mp 134.7–138.5 °C; R_f = 0.3 (Et_2O/pentanes, 1:10).

IR (ATR): 2960, 1722, 1667, 1369, 1153 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.70 (d, *J* = 7.1 Hz, 2 H), 7.42 (t, *J* = 7.4 Hz, 1 H), 7.28 (t, *J* = 8.1 Hz, 4 H), 7.20 (t, *J* = 7.6 Hz, 2 H), 7.11 (t, *J* = 7.3 Hz, 1 H), 4.37 (dd, *J* = 10.2, 8.1 Hz, 1 H), 3.68 (td, *J* = 10.5, 8.4 Hz, 1 H), 2.86 (d, *J* = 8.1 Hz, 1 H), 2.15–1.94 (m, 2 H), 1.40 (s, 9 H), 1.28 (s, 3 H), 1.18 (s, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.86, 173.23, 142.94, 137.18, 132.79, 128.47 (d, *J* = 6.8 Hz), 128.22, 127.58, 126.46, 80.96, 59.98, 57.17, 49.51, 47.24, 42.31, 30.24, 28.09, 26.41.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $[C_{25}H_{31}O_3]^+$: 379.2268; found: 379.2268.

***tert*-Butyl 3-Benzoyl-4-(4-methoxyphenyl)cyclopentanecarboxylate (12)**

Yield: 64.2 mg (84%, 3:1 *dr*); R_f = 0.3 (acetone/pentanes, 1:29).

Major Diastereomer

White solid; mp 95.5–98.5 °C.

IR (ATR): 2975, 1721, 1679, 1612, 1513, 1366, 1246, 1012, cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 6.9 Hz, 2 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.37 (t, *J* = 7.8 Hz, 2 H), 7.15 (d, *J* = 8.7 Hz, 2 H), 6.78 (d, *J* = 8.6 Hz, 2 H), 3.82 (td, *J* = 9.5, 8.0 Hz, 1 H), 3.77–3.71 (m, 1 H), 3.75 (s, 3 H), 3.07 (qd, *J* = 8.4, 5.7 Hz, 1 H), 2.54–2.43 (m, 2 H), 2.21 (ddd, *J* = 13.2, 9.8, 8.3 Hz, 1 H), 2.08 (dt, *J* = 13.3, 9.1 Hz, 1 H), 1.46 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.72, 174.30, 158.12, 136.92, 135.69, 132.90, 128.47, 128.39, 128.23, 113.90, 80.46, 55.24, 54.88, 46.54, 44.30, 37.40, 35.27, 28.08.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $[C_{24}H_{29}O_4]^+$: 381.2060; found: 381.2053.

Minor Diastereomer

White solid; mp 110.5–113.5 °C.

IR (ATR): 2975, 1723, 1680, 1514, 1448, 1367, 1249, 1220, 1152, 1036, 830, 701 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (d, *J* = 7.2 Hz, 2 H), 7.50 (t, *J* = 7.4 Hz, 1 H), 7.37 (t, *J* = 7.7 Hz, 2 H), 7.18 (d, *J* = 8.6 Hz, 2 H), 6.78 (d, *J* = 8.7 Hz, 2 H), 3.93 (q, *J* = 9.4 Hz, 1 H), 3.74 (s, 3 H), 3.69–3.54 (m, 1 H), 2.99 (ddd, *J* = 16.6, 9.3, 7.3 Hz, 1 H), 2.54–2.41 (m, 2 H), 2.18–2.01 (m, 2 H), 1.48 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.51, 175.01, 158.20, 136.69, 134.93, 133.01, 128.49, 128.49, 128.34, 113.89, 80.46, 55.24, 53.85, 47.74, 44.11, 38.92, 34.76, 28.14.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $[C_{24}H_{32}NO_4]^+$: 398.2326; found: 398.2322.

***tert*-Butyl 3-Benzoyl-4-(4-trifluoromethylphenyl)cyclopentanecarboxylate (13)**

Yield: 57.6 mg (68%, 2:1 *dr*); R_f = 0.3 (acetone/pentanes, 1:49).

Major Diastereomer

White solid; mp 106.9–108.4 °C.

IR (ATR): 2978, 1724, 1682, 1619, 1449, 1368, 1326, 1258, 1156, 1124, 1069, 1017, 842, 701 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (d, *J* = 7.1 Hz, 2 H), 7.55–7.47 (m, 3 H), 7.40 (t, *J* = 7.8 Hz, 2 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 3.93–3.81 (m, 2 H), 3.15–3.07 (m, 1 H), 2.55 (qd, *J* = 8.2, 4.1 Hz, 2 H), 2.19 (ddd, *J* = 13.1, 9.5, 8.0 Hz, 1 H), 2.12 (dt, *J* = 13.5, 9.2 Hz, 1 H), 1.46 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 199.89, 173.95, 147.72, 136.59, 133.17, 128.75 (q, *J* = 32.5 Hz), 128.59, 128.35, 127.70, 125.45 (q, *J* = 3.9 Hz), 124.47 (q, *J* = 272.9 Hz), 80.73, 54.76, 46.57, 44.28, 37.02, 35.45, 28.05.

^{19}F NMR ($CDCl_3$, 377 MHz): δ = –62.46.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $[C_{24}H_{26}F_3O_3]^+$: 419.1829; found: 419.1826.

Minor Diastereomer

White solid; mp 122.8–125.9 °C.

IR (ATR): 2974, 1722, 1677, 1369, 1327, 1281, 1247, 1225, 1164, 1138, 1170, 1018, 842, 699 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (d, *J* = 7.1 Hz, 2 H), 7.57–7.46 (m, 3 H), 7.40 (t, *J* = 7.5 Hz, 4 H), 3.98 (q, *J* = 9.4 Hz, 1 H), 3.83–3.71 (m, 1 H), 3.01 (ddd, *J* = 16.4, 9.2, 7.3 Hz, 1 H), 2.60–2.48 (m, 2 H), 2.20–2.06 (m, 2 H), 1.49 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.62, 174.73, 147.10, 136.36, 133.29, 128.80 (q, *J* = 31.1 Hz), 128.62, 128.45, 127.82, 125.44 (q, *J* = 3.7 Hz), 124.16 (q, *J* = 271.3), 80.72, 53.75, 47.67, 44.03, 38.34, 34.99, 28.11.

^{19}F NMR ($CDCl_3$, 377 MHz): δ = –62.47.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for [$C_{24}H_{29}F_3NO_3$]$^+$: 436.2095; found: 436.2093.

tert-Butyl 3-Benzoyl-4-(4-bromophenyl)cyclopentanecarboxylate (14)

Yield: 55.3 mg (64%, 2:1 *dr*); R_f = 0.3 (acetone/pentanes, 1:29).

Major Diastereomer

White solid; mp 103.1–104.4 °C.

IR (ATR): 2976, 1722, 1681, 1490, 1448, 1366, 1257, 1150, 1074, 1010, 848, 821, 701 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (d, *J* = 7.3 Hz, 2 H), 7.52 (t, *J* = 7.4 Hz, 1 H), 7.42–7.34 (m, 4 H), 7.12 (d, *J* = 8.4 Hz, 2 H), 3.83–3.74 (m, 2 H), 3.08 (qd, *J* = 8.2, 5.7 Hz, 1 H), 2.57–2.45 (m, 2 H), 2.23–2.13 (m, 1 H), 2.07 (dt, *J* = 13.4, 9.2 Hz, 1 H), 1.45 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.16, 174.05, 142.62, 136.69, 133.11, 131.56, 129.10, 128.57, 128.35, 120.13, 80.65, 54.77, 46.40, 44.26, 37.09, 35.41, 28.06.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for [$C_{23}H_{26}BrO_3$]$^+$: 429.1060; found: 429.1074.

Minor Diastereomer

White solid; mp 129.1–132.8 °C.

IR (ATR): 2975, 1722, 1680, 1490, 1448, 1367, 1284, 1246, 1220, 1152, 1074, 1011, 823, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83 (d, *J* = 7.3 Hz, 2 H), 7.52 (t, *J* = 7.4 Hz, 1 H), 7.44–7.32 (m, 4 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 3.92 (q, *J* = 9.4 Hz, 1 H), 3.65 (ddd, *J* = 11.3, 9.5, 7.6 Hz, 1 H), 2.99 (ddd, *J* = 16.5, 9.3, 7.3 Hz, 1 H), 2.50 (ddd, *J* = 13.3, 9.8, 6.8 Hz, 2 H), 2.17–2.02 (m, 2 H), 1.48 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.92, 174.82, 141.95, 136.47, 133.23, 131.56, 129.20, 128.60, 128.46, 120.25, 80.64, 53.74, 47.56, 44.03, 38.46, 34.93, 28.12.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for [$C_{23}H_{29}BrNO_3$]$^+$: 446.1326; found: 446.1313.

tert-Butyl 3-Benzoyl-4-(2-methylphenyl)cyclopentanecarboxylate (15)

Yield: 60.5 mg (83%, 2:1 *dr*); R_f = 0.3 (Et_2O/pentanes, 1:49).

Major Diastereomer

White solid; mp 70.7–74.1 °C.

IR (ATR): 2975, 1723, 1681, 1448, 1367, 1218, 1149, 1101, 848, 753, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 7.3 Hz, 2 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.37 (t, *J* = 7.7 Hz, 2 H), 7.26 (d, *J* = 7.7 Hz, 1 H), 7.16 (dt, *J* = 7.9, 4.3 Hz, 1 H), 7.10–7.01 (m, 2 H), 4.08–3.92 (m, 2 H), 3.09 (td, *J* = 8.5, 6.5 Hz, 1 H), 2.59–2.45 (m, 2 H), 2.31 (s, 3 H), 2.24 (dt, *J* = 13.1, 8.8 Hz, 1 H), 1.96 (dt, *J* = 13.3, 8.5 Hz, 1 H), 1.46 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.83, 174.40, 142.30, 136.88, 136.65, 133.05, 130.57, 128.60, 128.49, 126.38, 126.28, 125.49, 80.60, 54.16, 44.80, 43.00, 37.70, 35.29, 28.21, 20.00.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for [$C_{24}H_{29}O_3$]$^+$: 365.2111; found: 365.2105.

Minor Diastereomer

Colorless oil.

IR (ATR): 2976, 1723, 1680, 1448, 1367, 1290, 1216, 1151, 848, 575, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 7.4 Hz, 2 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.41–7.31 (m, 3 H), 7.23–7.12 (m, 1 H), 7.10–7.01 (m, 2 H), 4.09 (q, *J* = 9.0 Hz, 1 H), 3.88 (dt, *J* = 11.0, 8.3 Hz, 1 H), 3.01 (p, *J* = 8.9 Hz, 1 H), 2.51 (dq, *J* = 13.5, 7.3 Hz, 2 H), 2.28 (s, 3 H), 2.23–2.12 (m, 1 H), 2.05–1.91 (m, 1 H), 1.48 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.48, 174.93, 141.45, 136.53, 136.33, 133.01, 130.31, 128.46, 128.46, 126.42, 126.20, 125.81, 80.45, 53.47, 44.43, 43.81, 39.39, 34.61, 28.13, 19.83.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for [$C_{24}H_{32}NO_3$]$^+$: 382.2377; found: 382.2372.

tert-Butyl 4-Benzoyl-3-methyl-3-phenylcyclopentanecarboxylate (16)

Yield: 63.0 mg (85%, 2.0:1 *dr*); R_f = 0.3 (acetone/toluene, 0:100 to 10:90).

Major Diastereomer

White solid; mp 74.2–79.5 °C.

IR (ATR): 2977, 1675, 1597, 1447, 1367, 1285, 1253, 848, 732, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.52 (d, *J* = 7.0 Hz, 2 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.31–7.16 (m, 7 H), 4.09 (dd, *J* = 9.8, 6.7 Hz, 1 H), 3.08 (dt, *J* = 18.3, 9.3 Hz, 1 H), 2.63 (dt, *J* = 13.3, 10.0 Hz, 1 H), 2.53 (dd, *J* = 13.7, 9.2 Hz, 1 H), 2.29–2.14 (m, 2 H), 1.49 (s, 9 H), 1.26 (s, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.35, 174.34, 148.87, 137.78, 132.57, 128.39, 128.38, 128.15, 126.15, 125.88, 80.38, 57.65, 49.53, 45.42, 43.63, 32.71, 28.14, 24.30.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for [$C_{24}H_{29}O_3$]$^+$: 365.2112; found: 365.2115.

Minor Diastereomer

Colorless oil.

IR (ATR): 2977, 1724, 1676, 1449, 1369, 1258, 1222, 1154, 1086, 1026, 803, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49 (d, *J* = 7.1 Hz, 2 H), 7.37 (t, *J* = 7.4 Hz, 1 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 7.25–7.09 (m, 5 H), 4.17 (t, *J* = 8.7 Hz, 1 H), 3.17 (qd, *J* = 9.0, 5.6 Hz, 1 H), 2.68–2.57 (m, 2 H), 2.28 (ddd, *J* = 13.9, 8.6, 5.6 Hz, 1 H), 2.17 (dd, *J* = 13.1, 8.2 Hz, 1 H), 1.49 (s, 9 H), 1.30 (s, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.56, 175.76, 147.07, 137.78, 132.47, 128.29, 128.23, 128.05, 126.21, 126.19, 80.42, 56.74, 50.65, 46.99, 42.29, 32.17, 28.15, 22.14.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for [$C_{24}H_{32}NO_3$]$^+$: 382.2377; found: 382.2376.

tert-Butyl 2-Benzoyl-2′,3′-dihydrospiro[cyclopentane-1,1′-indene]-4-carboxylate (17)

Yield: 61.7 mg (83%, 2:1 *dr*); R_f = 0.3 (acetone/pentanes, 1:49).

Major Diastereomer

Colorless oil.

IR (ATR): 2975, 2935, 1724, 1672, 1478, 1448, 1392, 1367, 1225, 1151, 1002, 849, 756, 732, 691 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.49 (d, *J* = 7.0 Hz, 2 H), 7.40–7.32 (m, 2 H), 7.26 (m, 1 H), 7.17 (t, *J* = 7.8 Hz, 2 H), 7.09 (t, *J* = 7.3 Hz, 1 H), 6.93 (d, *J* = 6.9 Hz, 1 H), 3.91 (dd, *J* = 10.4, 6.9 Hz, 1 H), 3.06 (dt, *J* = 17.3, 8.3 Hz, 1 H), 2.73–2.60 (m, 2 H), 2.44 (dd, *J* = 13.3, 9.1 Hz, 1 H), 2.38–2.22 (m, 4 H), 1.93–1.83 (m, 1 H), 1.48 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.23, 174.36, 149.28, 143.69, 137.38, 132.57, 128.16, 128.02, 127.08, 126.62, 124.69, 122.27, 80.35, 59.06, 56.04, 44.49, 43.23, 36.75, 33.47, 30.97, 28.12.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $[C_{25}H_{29}O_3]^+$: 377.2111; found: 377.2107.

Minor Diastereomer

Colorless oil.

IR (ATR): 2976, 2932, 1720, 1671, 1448, 1367, 1220, 1150, 908, 846, 729, 690 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.49–7.41 (m, 3 H), 7.31 (t, *J* = 7.4 Hz, 1 H), 7.26–7.18 (m, 1 H), 7.11 (t, *J* = 7.8 Hz, 2 H), 7.03 (t, *J* = 7.6 Hz, 1 H), 6.84 (d, *J* = 7.5 Hz, 1 H), 4.05 (t, *J* = 8.7 Hz, 1 H), 3.11 (tdd, *J* = 9.9, 7.6, 6.1 Hz, 1 H), 2.71 (dt, *J* = 13.6, 9.7 Hz, 1 H), 2.67–2.57 (m, 1 H), 2.54 (dd, *J* = 12.8, 9.8 Hz, 1 H), 2.47–2.25 (m, 2 H), 2.27–2.09 (m, 2 H), 1.76 (dt, *J* = 12.4, 8.9 Hz, 1 H), 1.50 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.42, 175.61, 147.06, 143.90, 137.16, 132.45, 128.14, 127.82, 127.19, 126.54, 124.57, 122.60, 80.39, 60.28, 55.35, 46.18, 42.58, 34.90, 31.96, 30.78, 28.17.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $[C_{25}H_{32}NO_3]^+$: 394.2377; found: 394.2374.

***tert*-Butyl 2-Benzoyl-3′,4′-dihydro-2′*H*-spiro[cyclopentane-1,1′-naphthalene]-4-carboxylate (18)**

Yield: 66.6 mg (84%, 2:1 *dr*); R_f = 0.3 (acetone/pentanes, 1:49).

Major Diastereomer

White solid; mp 104.0–106.8 °C.

IR (ATR): 2974, 2936, 1724, 1673, 1447, 1366, 1254, 1230, 1152, 754, 720, 691 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.52 (d, *J* = 7.9 Hz, 1 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.35 (t, *J* = 7.4 Hz, 1 H), 7.27 (d, *J* = 6.2 Hz, 1 H), 7.14 (t, *J* = 7.8 Hz, 2 H), 7.10 (t, *J* = 7.7 Hz, 1 H), 6.90 (d, *J* = 7.6 Hz, 1 H), 4.16 (dd, *J* = 11.6, 6.4 Hz, 1 H), 3.10 (dtd, *J* = 11.6, 9.3, 7.2 Hz, 1 H), 2.72 (q, *J* = 11.8 Hz, 1 H), 2.57 (dt, *J* = 16.5, 5.5 Hz, 1 H), 2.36 (qd, *J* = 11.7, 10.4, 4.5 Hz, 2 H), 2.23 (ddd, *J* = 13.5, 7.9, 5.5 Hz, 2 H), 1.81–1.64 (m, 2 H), 1.66–1.50 (m, 2 H), 1.47 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.38, 174.27, 143.94, 137.78, 137.47, 132.45, 129.28, 128.34, 128.08, 126.70, 126.46, 125.88, 80.39, 58.96, 49.24, 48.71, 43.93, 34.36, 33.26, 29.98, 28.13, 20.23.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $[C_{26}H_{31}O_3]^+$: 391.2273; found: 391.2263.

Minor Diastereomer

Colorless oil.

IR (ATR): 2976, 2937, 1723, 1674, 1447, 1366, 1218, 1151, 733 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.67 (d, *J* = 8.0 Hz, 1 H), 7.46 (d, *J* = 8.2 Hz, 2 H), 7.32 (t, *J* = 7.4 Hz, 1 H), 7.30–7.21 (m, 1 H), 7.13 (t, *J* = 7.8 Hz, 2 H), 7.04 (t, *J* = 7.3 Hz, 1 H), 6.85 (d, *J* = 7.6 Hz, 1 H), 4.32 (t, *J* = 8.3 Hz, 1 H), 3.17–3.04 (m, 1 H), 2.73 (dt, *J* = 13.7, 8.7 Hz, 1 H), 2.52 (dt, *J* = 16.1, 5.0 Hz, 1 H), 2.40–2.22 (m, 4 H), 1.73 (ddd, *J* = 13.1, 9.4, 3.4 Hz, 1 H), 1.67–1.49 (m, 3 H), 1.49 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 202.08, 175.59, 141.75, 138.18, 137.82, 132.34, 129.00, 128.31, 127.96, 127.36, 126.41, 125.88, 80.36, 58.12, 50.62, 49.53, 42.83, 32.01, 31.97, 30.32, 28.16, 20.50.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $[C_{26}H_{34}NO_3]^+$: 408.2533; found: 408.2529.

***tert*-Butyl 3-Benzoyl-4-(9*H*-carbazol-9-yl)cyclopentanecarboxylate (19)**

Yield: 63.5 mg (71%, 2:1 *dr*); R_f = 0.3 (acetone/pentanes, 1:29).

Major Diastereomer

Colorless oil.

IR (ATR): 2976, 1724, 1682, 1597, 1484, 1453, 1367, 1337, 1227, 1154, 847, 750, 724, 698 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 8.04 (d, *J* = 7.7 Hz, 2 H), 7.62 (d, *J* = 7.2 Hz, 2 H), 7.57 (d, *J* = 8.3 Hz, 2 H), 7.44 (t, *J* = 7.8 Hz, 2 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.27–7.14 (m, 4 H), 5.94 (q, *J* = 9.1 Hz, 1 H), 4.66 (q, *J* = 9.1 Hz, 1 H), 3.40 (p, *J* = 8.1 Hz, 1 H), 2.85–2.57 (m, 3 H), 2.38 (dt, *J* = 13.3, 9.1 Hz, 1 H), 1.50 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 199.53, 173.42, 139.31, 136.18, 133.14, 128.39, 128.26, 125.66, 123.41, 120.39, 119.08, 109.76, 81.12, 56.17, 49.49, 44.09, 34.36, 31.36, 28.10.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $[C_{29}H_{30}NO_3]^+$: 440.2220; found: 440.2217.

Minor Diastereomer

Colorless oil.

IR (ATR): 2977, 1722, 1681, 1597, 1484, 1453, 1367, 1337, 1221, 1151, 750, 724, 699 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 8.05 (d, *J* = 7.7 Hz, 2 H), 7.71 (d, *J* = 7.2 Hz, 2 H), 7.64 (d, *J* = 7.0 Hz, 2 Hz), 7.49–7.35 (m, 3 H), 7.28–7.17 (m, 5 H), 5.81 (dt, *J* = 11.0, 8.5 Hz, 1 H), 4.85–4.74 (m, 1 H), 3.09 (dt, *J* = 15.9, 7.8 Hz, 1 H), 2.97–2.84 (m, 1 H), 2.76 (ddd, *J* = 13.5, 9.9, 7.7 Hz, 1 H), 2.51 (dt, *J* = 13.3, 8.1 Hz, 1 H), 2.30 (dt, *J* = 14.0, 7.6 Hz, 1 H), 1.52 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.20, 174.24, 139.40, 135.75, 133.31, 128.49, 128.47, 125.71, 123.40, 120.34, 119.11, 109.90, 81.07, 56.75, 47.76, 42.78, 33.31, 32.53, 28.15.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $[C_{29}H_{30}NO_3]^+$: 440.2220; found: 440.2217.

Ethyl 4-Benzoyl-3-[(*tert*-butyldimethylsilyl)oxy]-3-phenylcyclopentanecarboxylate (20)

Colorless oil; yield: 80.8 mg (94%, 11:1 *dr*); R_f = 0.3 (Et_2O/pentanes, 1:5).

IR (ATR): 2960, 1722, 1667, 1369, 1153 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.76 (d, *J* = 7.76 Hz, 2 H), 7.5 (t, *J* = 7.8 Hz, 1 H), 7.4 (t, *J* = 7.8 Hz, 2 H), 7.35–7.3 (m, 2 H), 7.2–7.1 (m, 3 H), 4.4 (ddd, *J* = 8.6, 3.6, 1.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2 H), 3.43 (tt, *J* = 10.8, 7.4 Hz, 1 H), 3.15 (dd, *J* = 13.1, 10.9 Hz, 1 H), 2.7 (dt, *J* = 13.1, 9.8 Hz, 1 H), 2.57 (dd, *J* = 13.1, 7.4 Hz, 1 H), 2.41 (ddd, *J* = 13.1, 6.7, 4.1 Hz, 1 H), 1.34 (t, *J* = 7.1 H, 3 H), 0.97 (s, 9 H), –0.07 (s, 3 H), –0.45 (s, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 201.33, 175.22, 142.04, 137.67, 132.49, 128.21, 127.65, 127.43, 127.05, 88.15, 60.63, 58.64, 41.92, 40.43, 31.81, 25.96, 18.30, 14.28, –2.76, –3.47.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $[C_{27}H_{37}O_4Si]^+$: 453.2456; found: 453.2456.

Methyl 2-Benzoyl-4,4-dimethylcyclopentanecarboxylate (21)

Colorless oil; yield: 44.3 mg (85%, 4:1 *dr*); R_f = 0.3 (Et_2O/pentanes, 1:19).

IR (ATR): 2960, 1722, 1667, 1369, 1153 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.03–7.92 (m, 2 H), 7.60–7.52 (m, 1 H), 7.47 (t, *J* = 7.5 Hz, 2 H), 4.24 (dt, *J* = 10.0, 8.6 Hz, 1 H), 3.71 (q, *J* = 9.0 Hz, 1 H), 3.63 (s, 3 H), 2.04 (dd, *J* = 12.8, 10.0 Hz, 1 H), 1.97 (dd, *J* = 12.7, 8.9 Hz, 1 H), 1.82 (dd, *J* = 12.7, 9.4 Hz, 1 H), 1.59 (ddd, *J* = 12.9, 8.6, 0.8 Hz, 1 H), 1.11 (s, 3 H), 1.03 (s, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.88, 175.88, 136.51, 133.06, 128.62, 128.57, 51.86, 49.43, 46.00, 44.94, 44.52, 39.99, 29.15, 28.71.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $[C_{16}H_{21}O_3]^+$: 260.14; found: 260.15.

***tert*-Butyl 3-Benzoyl-4-vinylcyclopentanecarboxylate (22)**

Yield: 124.7 mg (67%, 3:1 *dr*); R_f = 0.3 (Et_2O/pentanes, 1:9).

Major Diastereomer

Colorless oil.

IR (ATR): 2977, 2933, 1725, 1681, 1449, 1367, 1258, 1152 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87 (d, *J* = 7.3 Hz, 2 H), 7.48 (t, *J* = 7.4 Hz, 1 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 5.71 (ddd, *J* = 17.4, 10.2, 7.4 Hz, 1 H), 4.95 (d, *J* = 17.1 Hz, 1 H), 4.87 (d, *J* = 10.3 Hz, 1 H), 3.49 (q, *J* = 8.3 Hz, 1 H), 3.10 (p, *J* = 7.9 Hz, 1 H), 2.95–2.73 (m, 1 H), 2.28 (dt, *J* = 13.1, 8.2 Hz, 1 H), 2.17 (ddd, *J* = 14.0, 8.0, 6.4 Hz, 1 H), 2.07 (dt, *J* = 13.1, 9.1 Hz, 1 H), 1.76 (dt, *J* = 13.1, 8.6 Hz, 1 H), 1.37 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.70, 174.32, 140.11, 137.02, 132.99, 128.56, 128.46, 114.72, 80.39, 52.21, 45.98, 43.86, 35.09, 34.47, 28.06.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $[C_{19}H_{25}O_3]^+$: 301.1804; found: 301.1803.

Minor Diastereomer

Colorless oil.

IR (ATR): 2981, 2934, 1719, 1678, 1368, 1155 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.90 (d, *J* = 7.3 Hz, 2 H), 7.54 (t, *J* = 7.4 Hz, 1 H), 7.44 (t, *J* = 7.6 Hz, 2 H), 5.61 (dt, *J* = 16.9, 9.7 Hz, 1 H), 4.81–4.71 (m, 2 H), 3.92 (q, *J* = 9.0 Hz, 1 H), 3.05 (p, *J* = 8.0 Hz, 1 H), 2.83 (dt, *J* = 17.3, 8.7 Hz, 1 H), 2.48 (dt, *J* = 13.2, 10.0 Hz, 1 H), 2.22 (dt, *J* = 13.4, 8.0 Hz, 1 H), 2.12 (dt, *J* = 13.9, 7.4 Hz, 1 H), 1.99 (ddd, *J* = 13.3, 8.9, 7.4 Hz, 1 H), 1.47 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.46, 174.29, 138.13, 137.62, 132.81, 128.48, 128.31, 115.40, 80.30, 50.58, 47.40, 44.08, 35.63, 31.60, 28.10.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $[C_{19}H_{28}NO_3]^+$: 318.2069; found: 318.2067.

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Supporting Information

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